

PARTICLE STABILISED THIN FILMS

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DECLARATION

I declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification at this or any other university or institute of learning. All work presented in this thesis is my own except that which is appropriately referenced.

Gareth Morris

ABSTRACT

Froth flotation is widely used by the mining industry to concentrate low grade metal ores. It uses the differences in surface properties between particles of the desired mineral and waste material to separate them using a mineralised froth. The properties of this particle stabilised mineralised froth impact on the efficiency of the separation process. Due to its dynamic and unstable nature it is difficult to study and remains relatively poorly understood.

A deeper insight into the fundamental froth properties can be gained by using computer modelling techniques. Here a series of models are developed using the *Surface Evolver* (Brakke 1992). They are used to investigate the effects of particle shape, hydrophobicity and packing arrangement on the critical capillary pressure of thin films.

Three dimensional simulations of uniformly spaced spherical particles in the film are compared to existing two dimensional (2D) analytical models. It is shown that 2D models over predict the capillary pressure required to rupture the film. The models are developed further to simulate randomly distributed particles in a periodic film. The results are then used to derive an expression for film stability based on particle packing density and contact angle. The different possible failure modes of double layers of particles are also investigated and the conditions under which they occur identified.

A versatile model for simulating non-spherical particles in an interface or film is also derived and used to find the energetically stable orientations of orthorhombic particles at an interface. This information is then used to investigate the effect of particle orientation on the capillary pressure required to rupture the film. It is shown that the combination of contact angle and shape affect the particle orientation. Certain orientations are then shown to reduce the critical capillary pressure of the film by up to 70 %.

TABLE OF CONTENTS

DECLARATION.....	3
ABSTRACT.....	4
TABLE OF CONTENTS	5
ACKNOWLEDGEMENTS.....	11
NOMENCLATURE	12
LIST OF FIGURES.....	17
LIST OF TABLES	24
1. INTRODUCTION.....	25
1.1 Motivation.....	25
1.2 Organisation of thesis	26
2 LITERATURE REVIEW.....	28
2.1 Froth flotation.....	28
2.2 Foams: Formation and structure.....	30
2.3 Film failure.....	32
2.4 Particles at interfaces.....	35
2.4.1 Contact angle	35
2.4.2 Particle characterisation	35
2.4.3 Particles as surfactants.....	36
2.5 Particle stabilisation of films	37
2.5.1 Particle shape and film stability	38
2.6 Experimental investigations	39
2.6.1 Particle coated bubbles.....	40
2.6.2 Particle aggregation behaviour.....	41
2.7 Analytical and computer modelling.....	42
2.7.1 Analytical models of particles in films	42
2.7.2 Porosimetry theory of capillary driven film failure.....	42
2.7.3 Simulating non-spherical particles.....	43
2.8 Summary	44

3	MODELS AND METHODS.....	46
3.1	Introduction.....	46
3.2	Surface Evolver.....	46
3.2.1	Basic model geometry and structure.....	46
3.2.2	Example model - two joined bubbles.....	48
3.2.3	Constraints for boundary conditions and solids.....	50
3.2.4	Defining contact angle.....	52
3.3	Physical assumptions.....	53
3.3.1	Non-dimensionalisation of linear parameters.....	54
3.3.2	Conjoining and disjoining pressures.....	54
3.3.3	Gravity effects.....	54
3.4	2D Models of particles in a film.....	55
3.4.1	Geometric parameters.....	55
3.4.2	Structural description of 2D model.....	55
3.5	3D Models of particles in a film.....	56
3.5.1	Square and hexagonal packing geometry in 3D.....	57
3.5.2	Structural description of regular packing models in 3D.....	58
3.6	Random packing models in 3D.....	60
3.6.1	Boundary conditions.....	60
3.6.2	Particle positioning and constraints.....	61
3.6.3	Particle construction.....	61
3.6.4	Creating periodic models.....	63
3.7	Mesh refinement.....	63
3.8	Double particle layer models.....	65
3.8.1	Structure of a double layer.....	65
3.8.2	Un-bridged double layer model.....	66
3.8.3	Bridged double layer model.....	66
3.9	Non-spherical particle model.....	68
3.9.1	Particle shape.....	68

3.9.2	Particle rotation	70
3.9.3	Describing particle orientation.....	71
3.9.4	Surface Evolver model.....	72
3.9.5	Simulations to identify stable orientations	73
3.10	Summary	75
4	STATIC SINGLE PARTICLE LAYERS.....	76
4.1	Introduction.....	76
4.2	Film failure criteria	77
4.2.1	Capillary pressure driven film failure	77
4.2.2	Particle bridging of the film.....	77
4.2.3	Failure criteria	77
4.3	Modelling procedure	77
4.4	2D Single layer of uniform spherical particles	78
4.4.1	Comparison of 2D and analytical (Ali <i>et al.</i> 2000) data.....	78
4.4.2	Summary of 2D results	81
4.5	3D Single layers of uniform spherical particles	82
4.5.1	Comparison of separation distances in 3D.....	82
4.5.2	Comparison of film area with P^*_{crit}	84
4.5.3	Effect of packing arrangement on TPC position	86
4.5.4	Film distortion.....	87
4.5.5	Summary of regular 3D packing results	87
4.6	Randomly packed uniform spherical particles	88
4.6.1	Introduction.....	88
4.6.2	Random packing model.....	89
4.6.3	Particle packing considerations for periodic cells	90
4.6.4	Packing density and critical capillary pressure.....	91
4.6.5	Statistical analysis	94
4.6.6	Comparison of combined model data	94
4.6.7	Summary for randomly placed particles.....	97

4.7	Summary	97
5	DOUBLE LAYERS OF PARTICLES IN A THIN FILM	99
5.1	Introduction.....	99
5.2	Failure criteria.....	99
5.2.1	Packing geometry and maximum stable contact angle.....	99
5.2.2	Failure modes.....	101
5.3	Identifying failure modes.....	103
5.3.1	Identifying $P^*_{critmax}$	103
5.3.2	Determining film failure mode	108
5.4	Failure criteria for hexagonal double layer	110
5.5	Summary	113
6	NON-SPHERICAL PARTICLES.....	115
6.1	Introduction.....	115
6.2	Cubic particles at an interface.....	115
6.2.1	Introduction.....	115
6.2.2	Model and simulations	116
6.2.3	Results and discussion.....	116
6.2.4	Film stability with cubic particles	119
6.2.5	Summary.....	121
6.3	Oblong and flattened square particles.....	122
6.3.1	Introduction.....	122
6.3.2	Model parameters.....	122
6.3.3	Oblong particles	122
6.3.4	Flat square particles	131
6.4	Conclusions and summary	138
7	CONCLUSIONS	140
7.1	Single layers of particles.....	140
7.2	Double layers of particles.....	141
7.3	Non-spherical particles	142

7.4	Summary	143
8	FUTURE WORK.....	144
9	REFERENCES	146
10	APPENDIX A: DYNAMIC MODELS OF PARTICLES IN FILMS.....	149
10.1	Introduction.....	149
10.2	Dynamic models in 2D.....	150
10.2.1	Physical assumptions	150
10.2.2	Modelling steps	150
10.2.3	Evolving model to minimum energy surface.....	150
10.2.4	Entering or leaving a film.....	151
10.2.5	Calculation of particle forces	151
10.2.6	Particle motion.....	154
10.2.7	Changing film properties.....	155
10.3	Dynamic models in 3D.....	155
10.3.1	Model parameters	155
10.3.2	Surface tension forces.....	156
10.3.3	Pressure forces	157
10.3.4	Particle motion.....	158
10.3.5	Particle interaction forces.....	158
10.4	Dynamic particles in 2D films	159
10.4.1	Particle perturbation.....	159
10.4.2	Particle perturbation.....	160
10.4.3	Particle spreading.....	162
10.4.4	Summary	163
10.5	Dynamic Models of Single Layers	164
10.5.1	Introduction	164
10.5.2	Small scale motion.....	164
10.6	Summary	172
11	APPENDIX B	174

12	APPENDIX C	181
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NOMENCLATURE

GREEK LETTERS

$\alpha_{\max}$	Geometric parameter related to film position (from Horozov <i>et al.</i> 2005)
α, β, γ	Angle of rotation around the x, y and z axis respectively
γ	Surface tension
$\gamma_{\alpha\beta}$	Surface tension between phases α and β (from Binks 2003)
γ_{SL}	Surface tension for solid liquid interface
γ_{LV}	Surface tension for liquid vapour surface
γ_{SV}	Surface tension for solid vapour interface
ϵ_i	Geometric coefficient for defining particle shape
θ	Contact angle
$\theta_{\max \text{ hex}}$	Maximum sustainable contact angle
π	Pi
$\Pi(h)$	Disjoining pressure
Π_{el}	Electrostatic component of disjoining pressure
Π_{vw}	Van der Waals component of disjoining pressure
ϱ	Density
Φ	Geometric coefficient for calculation of film shape
θ_{N_i}	Angle made by N_i and the Z-axis
$\theta_{(n)\gamma}$	Angle of liquid vapour interface to the horizontal at the TPC

LATIN LETTERS

$\mathcal{A}_{pp}^*$	Non-dimensionalised area of film per particle
$area_{hex}$	Area of film per particle for hexagonal packing

$area_{square}$	Area of film per particle for square packing
Bo	Bond number
d	Diameter
ee	Edge id number in <i>Surface Evolver</i>
ee_l	Length of edge ee
$ee_{x,y,z}$	x, y or z component of length of edge ee
ΔE_s	Energy difference between energy ridge and local minima
E	Energy
$f_{overlap}$	Reaction force coefficient
ff	Facet id number in <i>Surface Evolver</i>
ff_{area}	Area of facet ff
$ff_{x,y,z}$	x, y or z component of facet normal
$\hat{F}_{ffphase}$	Pressure force vector of facet in liquid or vapour <i>phase</i>
F_F	Film force
F_{Fmax}	Maximum occurring film force
$\hat{F}_\gamma$	Total force vector due to surface tension
$\hat{F}_{\gamma e}$	Force vector for a single edge
F_{LPx}	Force due to liquid pressure in the x direction
F_{LPy}	Force due to liquid pressure in the y direction
$F_{i,max}^{CP2}$	Interfacial force (from Kaptay 2004)
F^*	Non-dimensionalised force
$F_{(n)\gamma H}$	Horizontal force due to surface tension
$F_{(n)\gamma V}$	Vertical force due to surface tension
$F_{(n)\gamma}$	Magnitude of force due to surface tension

$\hat{F}_{phase}$	Total force vector for liquid or vapour phase
$\hat{F}_{ppnm}$	Reaction force between particles n and m
F_{ppx}	Particle reaction force in x direction
F_{ppy}	Particle reaction force in y direction
$\hat{F}_{res}$	Total particle reaction force vector
F_R	Reaction force
$\hat{F}_{tot}$	Total force vector
F_{totyH}	Total horizontal force due to surface tension
F_{totyV}	Total vertical force due to surface tension
F_{VPx}	Force due to vapour pressure in the x direction
F_{VPy}	Force due to vapour pressure in the y direction
g	Acceleration due to gravity (9.81ms^{-1})
h	Film thickness
H	Vertical distance between equators of two particles
K_I	Dynamic time step for film forces
K	Coefficient related to the calculation of P_{crit}^*
K_{step}	Time step
K_{tot}	Total time passed
K_{touch}	Dynamic time step for particle interaction
l_{max}^*	Vertical distance between the equator and top of two particles
L^*	Non-dimensional length scale
L_p^*	Periodic cell edge length
LS	Liquid-Solid interface
LV	Liquid-Vapour interface

M_{max}	Maximum movement coefficient
n_p	Number of particles in periodic cell
$\hat{n}_{ee}$	Normalised direction vector of edge ee
$\hat{n}_{ff}$	Normalised direction vector of facet ff
N_i	Normals of the faces of an orthorhombic particle
P	Pressure
P^*	Non-dimensional pressure scale
P_C	Critical capillary pressure (from Ali et al 2000)
P^*_{crit}	Non-dimensional critical capillary pressure
$P^*_{critmax}$	Non-dimensional maximum sustainable capillary pressure
ΔP	Pressure difference
P_H	Probability of horizontal orientation
P_L	Pressure in the liquid phase
P_{phase}	Pressure in liquid or vapour phase
PP_{ij}	Particle positions matrix
P^*_{step}	Small increment in P^*
P_V	Pressure in the vapour phase
r	Refine mesh command (<i>Surface Evolver</i>)
R_1	Radius of film curvature
R_2	Secondary radius of film curvature
R_f	Radius of film curvature (from Purcell 1950)
R_L	Radius of curvature for liquid vapour interface
R_M	Radius of cylinder fitting between three closely packed spheres
R_t	Radius of toroidal throat (from Purcell 1950)

R_p	Radius of particle
R_s	Radius of particle (from Kaptay 2004)
s_i	Coefficient controlling particle dimensions
Sep_{ij}	Overlap between particles i and j
Sep_{ijx}	Overlap between particles i and j in the x direction
Sep_{ijy}	Overlap between particles i and j in the y direction
S_P	Particle separation distance
S^*_P	Non-dimensional particle separation distance
S	Solid
SL	Solid-Liquid interface
S_{nm}	Distance between particles n and m
$\hat{S}_{nm}$	Overlap distance vector
S^*_{PF}	Particle-film separation
S^*_{Pmin}	Minimum value of S^*_P
S^*_{PP}	Particle-particle separation
S_{PPC}	Particle-particle separation at which failure mode changes
SV	Solid-Vapour interface
TPC	Three Point Contact
vv	Vertex id in <i>Surface Evolver</i>
$\hat{v}_\gamma$	Direction vector
V	Volume
V^*_{step}	Small increment in volume
$\mathbf{x}, \mathbf{y}, \mathbf{z}$	Expressions for x, y and z in rotational geometry
z_{LP}	z coordinate of the lowest point on the film

LIST OF FIGURES

Figure 2-1. Flow chart detailing the process of extracting, concentrating, smelting and refining an ore.	28
Figure 2-2. Bank of flotation tanks, Western Limb tailings retreatment plant. Ellipse highlights person for scale.	29
Figure 2-3. Cross section of flotation cell, showing the flow of material through it.	30
Figure 2-4. A foam forming from a bubbly liquid.....	31
Figure 2-5. Spherical bubble turning to a polyhedral cell as liquid drains out of a 3D foam.	31
Figure 2-6. The junction of three lamellae at 120° (a) Plateau border at the junction of three lamellae(b).32	
Figure 2-7. (a) A network of Plateau borders in a regular foam generated using <i>Surface Evolver</i> (Brakke 1992) and (b) the vertex formed by four Plateau borders meeting at 109°.....	32
Figure 2-8. The shape of a lamella and its two, orthogonal radii of curvature (after Weire and Hutzler 2005).....	33
Figure 2-9. Showing amphiphilic surfactant molecules attached to the surfaces of thick and thin films after (Exerowa 1997). As the film thins the like charges are brought closer together and a repulsive force arises.....	34
Figure 2-10. A graph representing the disjoining pressure as a function of film thickness, positive values represent an attractive force. Points 1 and 2 represent Newton black and common black films respectively, after (Weire and Hutzler 2005).....	34
Figure 2-11. A particle sitting at a Liquid-Vapour interface, θ (contact angle) and the position of the TPC is labelled. Effect of contact angle on particle position at an interface illustrated on far right.	35
Figure 2-12. Cross section of the toroidal pore used by (Purcell 1950).....	43
Figure 3-1. The vertex, edge and facet geometry of <i>Surface Evolver</i> . The facet normal (<i>ff.normal</i>) direction is governed by the direction in which the edges are linked.....	47
Figure 3-2. Facets before (top) and after (bottom) <i>Surface Evolver</i> has split them into a union of triangles.47	
Figure 3-3. Refinement of an edge in the string model. Each dot represents a vertex.	48
Figure 3-4. The method for refining a triangular facet; first the each edge is split into two next the new vertices are joined up to make 4 smaller triangles where there was originally one.	48
Figure 3-5. The double bubble model, wireframe (top), blank surfaces (bottom).	48
Figure 3-6. Vertices in data file and Cartesian coordinates.	49
Figure 3-7. Edges in the data file and the model's current state.	49
Figure 3-8. Facet list as it appears in the <i>Surface Evolver</i> data file and visual representation of the corresponding model.....	50
Figure 3-9. Showing the evolution of a model of two bubbles with 4 step of refinement.	50
Figure 3-10. An initial model of a square face on a circular constraint adopting the circular boundary over 4 refinement steps.....	51

Figure 3-11. Showing the effect of a non-convex constraint on vertex behaviour at a curved constraint. Before evolution (a), after evolution, with vertices gathering (b).	52
Figure 3-12. Showing the wireframe and surface renders of a spherical particle with a droplet attached. $R_p=0.62$	52
Figure 3-13. Spherical particle with liquid phase contact angle 45° , 90° or 135° (left to right) with a droplet attached.....	53
Figure 3-14. Showing a 2D particle laden film. Particles are bridging both sides of the film. The key parameters for the model are the separation distance S_p , the film thickness at its lowest point h , the particle radius R_p , and the contact angle of the particles θ . The 3 phases are also annotated with the vapour phase corresponding to V , the liquid phase L and the solid particle S . Grey area highlights the <i>Surface Evolver</i> model volume.	55
Figure 3-15. 2D model of a circular particle in a thin film. The initially defined coarse model is on the left, the refined and evolved one on the right.	56
Figure 3-16. Rotation of 2D model to create a 3D model.	57
Figure 3-17. The separation distances and film boundaries for (a) hexagonal and (b) square packing. S_{pp}^* is half the distance between the centre of two adjacent particles. S_{pf}^* is distance from the centre of a particle to the midpoint of the film. The midpoint of the film is the point farthest from any surrounding particles.	58
Figure 3-18. Showing the initial models for square and hexagonal packing of spherical particles.	59
Figure 3-19. Showing the initial periodic cell once loaded into <i>Surface Evolver</i> and details of the vertex and edge description in the datafile. <i>no_refine</i> is a setting in the datafile that prevents <i>Surface Evolver</i> from needlessly refining the edges in the uppermost and lowermost facets. <i>film_thickness</i> is a constant that is used to set the initial film thickness in the model. Vertices 1-4 are highlighted by the small black circles in the lower right corner of each surface. Vertex 1 is at the top, 4 at the bottom, 2 and 3 in the middle.	60
Figure 3-20. The steps involved in defining a particle; (a) Facets are chosen for the solid-vapour interfaces. (b) Edges are constructed. (c) Facets are defined to form a continuous surface. (d) Facets are assigned to particle body to form a coarse representation of the particle. (e) Particle edges are refined to produce a well-defined spherical particle.	62
Figure 3-21. Original square period cell with one particle (a) and more complex irregularly placed particle models (b), (c) and (d)	63
Figure 3-22. Shape of the TPC before (a) and after (b) <i>edgeswap</i> is used to correct the mesh geometry. (c) shows how the TPC can now reform to a straight line after evolution.	64
Figure 3-23. Periodic cell with an edge length of 15, containing 20 particles that has undergone 4 <i>adaptive_mesh</i> iterations.	65
Figure 3-24. Close packed double layer of particles in a film.	65

Figure 3-25. Double layers with different inter particle separation distances. ($S_{pp}^* = 1, 1.2, 1.5$) At larger separation distances particles bridge both sides of the film whilst maintaining a distinct double layer pattern.....	66
Figure 3-26. The unit cell for a double layer of particles. Red hexagon highlights the cell in the bulk double layer (a), from the side (b) and from just the surrounding particles (c).	67
Figure 3-27. Basic bridged double layer mesh in <i>Surface Evolver</i> , viewed from the side (a), on angle (b) and top (c). (d) shows the evolved surface from the top and on angle.	67
Figure 3-28. Equations used to define a cylinder and a sphere.	68
Figure 3-29. Examples of varying s_i and ε_i . Column A $\varepsilon_{1,2,3}=2$, B $\varepsilon_{1,2}=2$, $\varepsilon_3=20$, C $\varepsilon_{1,2,3}=20$, D $\varepsilon_{1,2,3}=1.25$. Rows (1) $s_{1,2,3}=1$, (2) $s_1=2$, $s_{1,3}=1$, (3) $s_{1,2}=2$, $s_3=1$	69
Figure 3-30. Cubic particle generated using $\varepsilon_i=200$	70
Figure 3-31. Examples of particle shapes at various mesh refinements all starting from the initially defined particle volume.	70
Figure 3-32. A cubic and cylindrical particle at orientations of (A) $\alpha=\beta=\gamma=0^\circ$, (B) $\alpha=30^\circ$, $\beta=\gamma=0^\circ$ and (C) $\alpha=\beta=30^\circ$, $\gamma=0^\circ$	71
Figure 3-33. Showing the angles θ_{N1} , θ_{N2} and θ_{N3} , made by the facet normals (N_1 , N_2 and N_3) and the Z-axis.....	72
Figure 3-34. Galena particle bridging both sides of a film (a) and one side of a film (b). S is the solid phase, V the vapour phase and L the liquid phase	73
Figure 3-35. The energy surface landscape of a cubic particle with a contact angle of 45° . Circles highlight stable orientations at the energy minima where visible.	74
Figure 4-1. Comparison between the P_{crit}^* from the analytical solution of Ali <i>et al.</i> , (2000) and simulated results for P_{crit}^* as a function of S_p^* , $\theta=15^\circ$, $P_{step}^*=0.005$	79
Figure 4-2. Percentage difference between simulated and calculated P_{crit}^* as a function of S_p^* for $P_{step}^*=0.005$ and 0.0005 , $\theta=75^\circ$	80
Figure 4-3. P_{crit}^* as a function of S_p^* for analytical solution (Ali <i>et al.</i> 2000) and <i>Surface Evolver</i> models at different contact angles. Range bars for θ of 60° , 75° and 85° of 0.005 are shown to demonstrate the effect of P_{step}^* at low P_{crit}^*	80
Figure 4-4. The effect of θ on P_{crit} whilst keeping the separation distance between particles constant.	81
Figure 4-5. Comparison of square, hexagonal and 2D P_{crit}^* as a function of S_{pp}^* . $\theta=45^\circ$ in all cases.....	82
Figure 4-6. Comparison of square, hexagonal and 2D P_{crit}^* as a function of S_{PF}^* for all cases $\theta=45^\circ$	83
Figure 4-7. Percentage free film area of a square cell taken up by a hexagonal cell as a function of S_{pp}^* ..	84
Figure 4-8. Comparison of square and hexagonal packing P_{crit} as a function of film area for both cases $\theta=45^\circ$	85
Figure 4-9. Comparison of P_{crit} for square and hexagonal packing as a function of film area on log-log axis, $\theta=45^\circ$. The thick dashed line represents the minimum cell area achievable for hexagonal packing and the	

thin dashed line the same for square packing. The dotted line is the point at which P_{crit}^* begins to diverge.	86
Figure 4-10. The z coordinate of the film at the three phase contact plotted against the longitudinal angle around the particle at $S_{pp}^*=1.13$, $\theta=45^\circ$ at the point of failure.	86
Figure 4-11. The Evolved surface for hexagonal packing at $S_{pp}^*=1.13$, $\theta=45^\circ$ and P_{crit}^* . Figure only shows the upper surface of the film.	87
Figure 4-12. Evolved surface for square packing at $S_{pp}^*=1.13$, $\theta=45^\circ$ and P_{crit}^* . Figure only shows the upper surface of the film.	87
Figure 4-13. Periodic cells of edge length 5, 7, 10 and 15 containing 5, 10, 10 and 20 particles respectively.	89
Figure 4-14. Showing the large scale uniformity of smaller periodic boundaries, close particle packing has been exaggerated to illustrate the empty film areas. Shaded area highlights the difference in area of exposed film.	90
Figure 4-15. P_{crit}^* vs A_{pp}^* for various θ and P_{crit}^* vs θ for various A_{pp}^* for a period with edge length of 5 and contact angles of 29° , 38° , 50° , 63° and 76° .	91
Figure 4-16. P_{crit}^* vs A_{pp}^* and P_{crit}^* vs θ for a period with edge length of 7 for contact angles of 29° , 38° , 50° , 63° , 76° .	92
Figure 4-17. P_{crit}^* vs A_{pp}^* and P_{crit}^* vs θ for a period with edge length of 10 for contact angles of 29° , 38° , 50° , 63° , 76° .	92
Figure 4-18. P_{crit}^* vs A_{pp}^* and P_{crit}^* vs θ for a period with edge length of 15 for contact angles of 29° , 38° , 50° , 63° , 76° .	93
Figure 4-19. P_{crit}^* vs A_{pp}^* for contact angles of 29° (left) and 76° (right).	93
Figure 4-20. P_{crit}^* vs A_{pp}^* for randomly packed particles with contact angles of 29° , 38° , 50° , 63° or 76° . Error bars show the 95 % confidence interval.	94
Figure 4-21. $\theta=29$, $K=1.859$.	95
Figure 4-22. $\theta=38$, $K=1.734$.	95
Figure 4-23. $\theta=50^\circ$, $K=1.440$.	95
Figure 4-24. $\theta=63$, $K=1.057$.	95
Figure 4-25. $\theta=76$, $K=0.661$.	96
Figure 4-26. K vs contact angle.	96
Figure 4-27. P_{crit}^* vs A_{pp}^* for square and hexagonal packing, with the predicted values of P_{crit}^* from equation (4-6), $K=1.547$.	97
Figure 5-1. Double layer of particles in a film.	100
Figure 5-2. Showing the geometry of a close packed hexagonal double layer. Coloured dots represent the centre of a particle.	100
Figure 5-3. The maximum θ that does not bridge the opposite layer of particles as a function of the separation distance (S_{pp}^*) between particles in the same layer.	101

Figure 5-4. 2D representation of particle bridging in a double layer. Initially the films are flat at $P^*=0$ but sitting below the particle equator at (a). P^* increases and the film curvature brings the interfaces in contact with the particles in the opposite layer (b). Once the particles bridge the opposite layer the interfaces move to the new "below equator" line which involves them passing through each other (c). Clearly this involve the opposite sides coming into contact with each other resulting in failure of the film.	102
Figure 5-5. The gaps in between double layers of particle where the opposite sides of the film can meet. The figure also shows a bridged double layer of particles.....	102
Figure 5-6. Single unit cell for a double layer at capillary driven failure. Particle and film (left), just film side view (right), point at which the interfaces meet highlighted by circle.....	103
Figure 5-7. Increase in film curvature (exaggerated for illustration) with P^* (left to right) until film inversion occurs (far right).	103
Figure 5-8. P^* as a function volume, $\theta=30^\circ$, $S_{pp}^*=1.13$	104
Figure 5-9. $P_{critmax}^*$ as a function of S_{pp}^* for varying contact angle.	105
Figure 5-10. P_{crit}^* and $P_{critmax}^*$ as functions of S_{pp}^* for contact angles of 15° (left) and 60° (right).	105
Figure 5-11. $P_{critmax}^*$ as a function of θ , comparing toroidal pore model and <i>Surface Evolver</i> model. $S_{pp}^*=1$	106
Figure 5-12 Showing the increase in distortion in film surface from $\theta=15^\circ$ to $\theta=105^\circ$	107
Figure 5-13. ζ_{LP} as a function of θ for various S_{pp}^*	107
Figure 5-14. ζ_{LP} and $-l_{max}^*$ as a function of S_{pp}^* . Red background represents values of S_{pp}^* at which film bridges particles, Blue values at which film fails through <i>film inversion</i>	108
Figure 5-15. ζ_{LP} and $-l_{max}^*$ as a function of S_{pp}^* for contact angle of 15° , 30° , 45° , 60° and 75°	109
Figure 5-16. S_{ppc}^* as a function of θ , showing a peak at $\theta=60^\circ$	109
Figure 5-17. P_{crit}^* as a function of S_{pp}^* , the vertical line represents S_{ppc}^* , $\theta=45^\circ$	110
Figure 5-18. Comparison of P_{crit}^* for double and single layers for contact angles of 15° , 30° , 60° and 75° . Dotted lines highlight transition from one failure mode to another.	111
Figure 5-19. $P_{critmax}^*$ as a fraction of P_{crit}^* plotted as a function of contact angle.	112
Figure 5-20. showing the difference in P_{crit}^* and $P_{critmax}^*$ for varying contact angles.	112
Figure 6-1. Rotated (a), horizontal (b) and diagonal (c) orientations of cubic particles at an interface.	116
Figure 6-2. Energy surface orientations for cubic particles at contact angles of 45° (a), 70° (b) and 85° (c). Circles highlight the rotated orientation, squares the horizontal orientation.....	117
Figure 6-3. The difference in surface energy and the maximum energy orientation for both the horizontal or rotated orientations as it changes with θ	118
Figure 6-4. Critical capillary pressure as a function contact angle for cubic particles bridging a thin film. Dashed lines represent the limiting contact angles at which both orientations are stable.	120
Figure 6-5. P_H against contact angle. Below $\theta=65^\circ$ it is 1, above 80° it is 0.....	121

Figure 6-6. Four stable orientations for an oblong particle horizontal(a), diagonal(b), rotated(c) and vertical(d) , a- $(\theta_{N1}=0^\circ/\theta_{N2}=90^\circ$ or $\theta_{N1}=90^\circ/\theta_{N2}=0^\circ)$, b- $(\theta_{N1}=\theta_{N2}=45^\circ)$, c- $(\theta_{N1}=\theta_{N2}=55^\circ)$, d- $(\theta_{N1}=\theta_{N2}=90^\circ)$	123
Figure 6-7. Surface plot of energy as a function of θ_{N1} and θ_{N2} at $s_3=2$, $s_2=s_3=1.1$, $\theta=65^\circ$ (1, 2) and $\theta=45^\circ$ (3, 4). Orientations (a), (b) and (d) are labelled.	124
Figure 6-8. Energy surfaces for $\theta=45^\circ$, $s_3=1.2$ (a), 1.3(b), 1.5(c), 1.7(d), 1.9(e), 2(f).	125
Figure 6-9. Energy surfaces for $\theta=75^\circ$, $s_3=1.2$ (a), 1.3(b), 1.5(c), 1.7(d), 1.9(e), 2(f).	125
Figure 6-10. Energy surfaces for $\theta=90^\circ$, $s_3=1.2$ (a), 1.3(b), 1.5(c), 1.7(d), 1.9(e), 2(f).	126
Figure 6-11. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_3=1.2$	126
Figure 6-12. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_3=1.5$	127
Figure 6-13. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_3=2$	127
Figure 6-14. ΔE_s for horizontal orientations as a function of contact angle for $1.2 < s_3 < 2$	128
Figure 6-15. P^*_{crit} as a function of contact angle for vertical, horizontal, rotated and diagonal orientations $s_3=1.2$. Black lines highlight contact angles where stable orientations overlap.	129
Figure 6-16. P^*_{crit} as a function of contact angle for vertical, horizontal, rotated and diagonal orientations $s_3=1.5$. Black lines highlight contact angles where stable orientations overlap.	130
Figure 6-17. P^*_{crit} as a function of contact angle for vertical, horizontal, rotated and diagonal orientations $s_3=2$. Black lines highlight contact angles where stable orientations overlap.	131
Figure 6-18. Energy surfaces for ratios of (a) $s_1=1.1$, $s_2=s_3=1.2$, (b) $s_1=1.1$, $s_2=s_3=1.3$, (c) $s_1=1.1$, $s_2=s_3=1.5$, (d) $s_1=1.1$, $s_2=s_3=1.7$, $\theta=45^\circ$, particle shapes for each model are shown above the relevant model.	132
Figure 6-19. Energy surfaces for particle with aspect ratios of $s_1=1.1$, $s_2=s_3=1.2$ and contact angles of (a) $\theta=45^\circ$, (b) $\theta=60^\circ$, (c) $\theta=65^\circ$, (d) $\theta=70^\circ$, (e) $\theta=75^\circ$, (f) $\theta=80^\circ$ and (g) $\theta=90^\circ$	132
Figure 6-20. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1$, $s_2=s_3=1.2$	134
Figure 6-21. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1$, $s_2=s_3=1.3$	134
Figure 6-22. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1$, $s_2=s_3=1.5$	134
Figure 6-23. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1$, $s_2=s_3=1.7$	135
Figure 6-24. P^*_{crit} as a function of contact angle, $s_2=s_3=1.2$	135
Figure 6-25. P^*_{crit} as a function of contact angle, $s_2=s_3=1.5$	136
Figure 6-26. P^*_{crit} as a function of contact angle, $s_2=s_3=1.7$	136

Figure 6-27. Showing the film distortion for rotated (a), horizontal (b) and diagonal orientations (c, d).	137
Figure 10-1 Particle entering the film (1, 2, 3) or being ejected from it (3, 2, 1).	151
Figure 10-2 Surface tension forces acting on a particle in 2D.	151
Figure 10-3 Breakdown of the structure of a 2D model.	152
Figure 10-4 Particle surrounded by a TPC (red edges), highlighting the facet used to calculate the surface tension component of force (coloured blue).	156
Figure 10-5 Vector used to find the direction of tension.	157
Figure 10-6. 2D model of 21 particles in a double layer $S^*=1.1$, central particle perturbed up (a) or down (b) by decreasing or increasing the separation of surrounding particles, $\theta=15^\circ$.	160
Figure 10-7 Particles with an initial perturbation down causing a single layer to form and spread, $\theta=75^\circ$, initial separation is 1.1 (a) and 1.4(b).	160
Figure 10-8 Particle perturbed up in the film acting as a seed for double layers, $\theta=75^\circ$, separations are 1.1 (a), 1.2 (b), 1.4 (c).	161
Figure 10-9 Contact angle of 45° initial separation of 1.4, central particle perturbed up (a) and down (b).	161
Figure 10-10 Contact angle of 30° initial separation of 1.4, central particle perturbed up (a) and down (b).	162
Figure 10-11 Contact angle of 15° initial separation of 1.4, central particle perturbed up (a) and down (b).	162
Figure 10-12 Expanding film containing a double layer of particles, $\theta=45^\circ$.	163
Figure 10-13 Particles attached to a thin film forming rafts.	164
Figure 10-14 Initial particle models.	165
Figure 10-15 Showing particle agglomeration for initial models (a) and (b).	166
Figure 10-16 The evolution of the initial model found in (c).	166
Figure 10-17 Evolution of four particle to a close packed hexagonal arrangement.	167
Figure 10-18 Initial model for three particle set out at the corners of an equilateral triangle of edge length $3R_p^*$ centred around the origin.	168
Figure 10-19 Non-dimensional force as a function of distance from the origin for particle 1 for capillary pressures of 0.05, 0.03 and 0.01.	169
Figure 10-20 Non-dimensional force as a function of distance from the origin for particle 2 for capillary pressures of 0.05, 0.03 and 0.01.	169
Figure 10-21 Non-dimensional force as a function of distance from the origin for particle 2 for capillary pressures of 0.05, 0.03 and 0.01.	170
Figure 10-22 Initial positions of particles before iteration, film radius is $20R_p^*$, all particles in any one model are given the same θ .	171
Figure 10-23 Packing of particles at different contact angles after 73 time steps.	171
Figure 10-24 Packing of particles at different contact angles after 50 time steps.	172

LIST OF TABLES

Table 1. Showing the combination of particle numbers, $\mathcal{A}_{pp}^*$ and L_p^* for periodic models.....	89
Table 2. Values of K and κ for different θ	94
Table 3. Showing the stable orientations for different combinations of s_3 and θ . Orientations are; horizontal (a), diagonal (b), rotated (c) and vertical (d) from Figure 100.	124
Table 4. stable orientations for given values of s_2 , s_3 and θ . Orientations are; horizontal (a), diagonal (b), rotated (c) and vertical (d) from Figure 100. For flat cubic particles in rotated orientations the θ_{N1} and θ_{N2} are between 45° and 60°	133

1. INTRODUCTION

1.1 MOTIVATION

The mining industry is currently under immense pressure to reduce the environmental impact of the processes it uses to extract and refine metals, whilst simultaneously increasing process efficiency. At the same time it is facing an unprecedented increase in demand for those metals as countries such as China and India begin mass development of their infrastructure. For example it is forecast that in the next 50 years our civilisation will require an amount of copper equal to all of the copper already mined in the entirety of human history. It is therefore necessary to develop more efficient methods of processing mineral bodies so that the maximum amount of useful material can be extracted from them. A more efficient production of metals will also allow lower grade deposits to be economically exploited to help satisfy the increasing worldwide demand for raw materials.

The extraction of metals from the earth is an expensive and energy intensive process which produces a large amount of waste. Roughly 6 % of the world's energy is used in the breaking of rocks. The waste material left over after the valuable minerals have been extracted is also often left impregnated with chemicals and heavy metals which cause environmental pollution for years to come. However, the technology used to extract the valuable fraction of minerals from the mined ore is always improving. It is now at the point where the waste (tailings) dumps from older mines in Africa contain a higher concentration of valuable minerals than some of the ore bodies being newly developed.

Once an ore has been mined, the metal needs to be extracted, usually by smelting. This is a process by which the ore is melted and the metal compounds present reduced so that the pure metal can be separated from the waste (gangue). Smelting is an energy intensive process, and many ore bodies that are currently being mined produce ore that is too low a grade to economically smelt in its native form, i.e. the cost of the energy required to smelt the ore is more than the value of the metal extracted. It is therefore necessary to concentrate the ore before it is smelted.

One method to concentrate low grade ore adopted by the mining industry is froth flotation, which has been used for over 100 years. On average more than 90 % of the valuable fraction is recovered from the ore at a much increased grade. The remaining 10 % goes to the tailings dams. This leftover fraction is now too low a concentration to be economically recovered using current technology and is effectively lost. As flotation is the primary concentration step and the only point at which the amount of valuable material entering the tailings dams can be altered, an improvement in flotation performance will allow a greater amount of the valuable fraction to be recovered.

Froth flotation uses the differences in the surface properties of small particles (10-100 μ m, Wills 1997) of milled ore to separate the valuable minerals from a slurry, leaving the gangue (waste material) behind. Air

is injected into the base of a flotation tank containing the slurry. As the bubbles rise through it the valuable, hydrophobic particles attached to their surface. These particle laden bubbles form a mineralised froth on the surface of the slurry which is then collected. The mineralised froth is a key stage in this process and its properties affect both the final grade of concentrated ore and the percentage of valuable minerals recovered. Therefore, a key to improving flotation efficiency is an improved understanding the behaviour of the froth phase. Flotation is huge worldwide industry with plants often processing hundreds if not thousands of tonnes of ore per hour, clearly even a tiny increase in efficiency will have a large impact on profitability.

Whilst froth flotation has been used for a over a 100 years the structure and properties of the froth phase are still relatively poorly understood. The primary reason for this is that the froth is a highly complicated and dynamic system with a huge number of variables affecting its properties and performance. This makes direct experimental observation very difficult especially as the froths are opaque.

One method to gain deeper insight into the froth behaviour is through the use of computer modelling techniques, which can be applied over a range of scales. At the larger scales this includes the modelling of bulk froth properties including the recovery and grade of valuable minerals or foam structure and liquid content. On a smaller scale it includes models looking at the molecular interaction of surfactants at a film interface or the conditions under which attached particles stabilise the liquid films. This thesis is concerned with the last of these, particle stabilised thin films.

The individual films that make up a flotation froth are heavily laden with hydrophobic particles that can stabilise the film to varying degrees depending on their properties. These properties include; surface chemistry, roughness, hydrophobicity, packing arrangement in the film and particle shape. It is the last three of these properties that will be investigated in this thesis. A series of models will be developed and used to simulate both spherical and non-spherical particles with varying contact angles and packing arrangements in a thin liquid film or at an interface. This investigation of some of the fundamental aspects of froth stability will be used to develop a better understanding of the processes through which flotation froths are stabilised or destabilised.

1.2 ORGANISATION OF THESIS

The literature review presented begins with an overview of the flotation process and why it is used. This broad topic is then progressively narrowed down to the area of interest to this thesis; particle stabilised thin films.

The structure of a foam is explained followed by the methods through which it decays and the problems this presents before introducing previous work done on particle stabilised films and particles at interfaces. Previous experimental, analytical and computer modelling approaches are introduced and examined before a summary is presented of research in this area to date.

The models and methods chapter (chapter 3) introduces the *Surface Evolver* (Brakke 1992) program which is used for the majority of the modelling conducted in this thesis. A brief overview is followed by an introduction to the methods used to construct and solve the models used in later chapters.

The static single particle layers chapter (chapter 4) presents results and analysis of spherical particles attached to a film in a single layer. Previous analytical models in 2 dimensions (2D) are compared to numerical simulations in 2D and 3 dimensions (3D). They are used to investigate the effects of contact angle and particle packing on the stability of thin liquid films. Initially, regularly packed spherical particles in hexagonal or square arrangements are used but these are later expanded to large scale models of periodic cells with multiple particles. The periodic models are used to investigate irregular particle packing arrangements and an expression for film stability is derived based on contact angle and particle packing density.

In chapter 5 models of the more complex regime of a film containing a double layer of particles in a thin film are developed from the models of single layers of hexagonally packed particles. These are then used to identify the different failure modes a double layer of spherical particles can experience and the conditions under which they occur. As in chapter 4 the key variables investigated are contact angle and particle packing density.

The non-spherical particles chapter (chapter 6) moves away from multiple particle models and concentrates on the effects of particle shape on the stability of thin films. Once a particle is not spherical its orientation in the film becomes important. The orientation causes changes in the interface shape surrounding the particle and therefore the film stability. The energetically stable orientations of a cubic particle at an interface and how they vary with contact angle are investigated. The shape of the cubic particle is then changed, first to an oblong and then a flattened square to further investigate the stable orientations adopted. The stable orientations are then used in conjunction with models of a particle bridging the film to investigate the effects of shape and orientation on film stability.

Finally, chapter 7 summarises the results from all previous chapters and draws relevant conclusions from them. The relevance of the results to the flotation industry is also described. Chapter 8 describes the future work that can be carried out with the models described in this thesis, either as they are or with further, minor development.

Appendices B and C contain papers based on work in this thesis that have been published in peer reviewed journals (Morris *et al.* 2008, Morris *et al.* 2010a).

2 LITERATURE REVIEW

2.1 FROTH FLOTATION

Froth flotation has been used by the mining industry for over 100 years to achieve specific separations from complex ores. It is the largest tonnage separation operation in the world and is used in the production of many metals such as copper, zinc, lead, platinum and gold as well as coal and the waste treatment of water. It forms only a small part of the long process of extracting metal from the earth (Figure 2-1), but it is the key separation process. Improvements in the efficiency of the flotation stage greatly increase the economic performance of a mining operation.

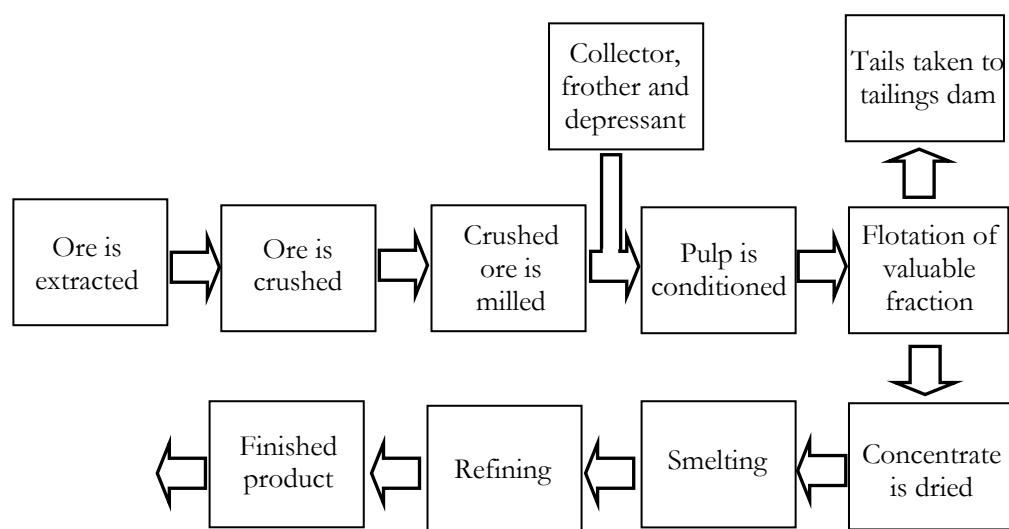


Figure 2-1. Flow chart detailing the process of extracting, concentrating, smelting and refining an ore.

Before flotation can be used, the valuable minerals in the ore must be liberated from the surrounding rock. This is achieved by first crushing and then milling the ore to a size range of 10-300 μ m (Wills 1997). If the particles are any larger than this they are generally too heavy to float, any smaller than 10 μ m and problems arise from the oxidation of their exposed surfaces. Further, at small size ranges the cost of milling increases dramatically.

Whilst the ore is being milled it is mixed with water to form a slurry (or pulp) which is then pumped into the flotation circuit. Before entering the flotation tanks the pulp has chemicals added to it; frother, collector and sometimes a depressant. The frother promotes the formation of froth and helps control bubble size. It is usually a polyglycol and is added in very small quantities (20-100 g/t ore). The collector alters the surface chemistry of the valuable particles, rendering them hydrophobic, so that they are likely to attach to the surfaces of the bubbles and be collected. The collector varies with ore type but for sulphide minerals it is often a member of the xanthate family. Finally, the depressant is used to prevent the flotation of naturally hydrophobic gangue such as talc. The pulp, after a brief conditioning period, is

pumped into the flotation cells which have a volume of between 10 m³ and 300 m³. Modern flotation plants usually have 3 or 4 flotation stages, each with 6-10 tanks (Figure 2-2).



Figure 2-2. Bank of flotation tanks, Western Limb tailings retreatment plant. Ellipse highlights person for scale.

When the pulp enters a flotation cell it is kept moving by an impeller which prevents sedimentation and promotes mixing. Air is injected into the bottom of the cell through the impeller forming bubbles of around 2 mm diameter. These bubbles rise through the pulp and as particles and bubbles collide the hydrophobic particles attach to their surface and are collected. Eventually the particle laden bubbles reach the top of the pulp and there is a transition phase where the bubbly liquid becomes a mineralised froth and particles that are not attached to the bubbles can become entrained in the gaps between the bubbles. As more bubbles continuously arrive at the base of the froth they force the uppermost froth to overflow the lip of the cell carrying the concentrated ore with it. This is then taken away for further processing or dried and transported to the smelter. A cross-section of a flotation tank is shown in Figure 2-3 with the flows of material labelled.

Bubbles generally enter the bottom of the froth with a diameter 2 mm, but are up to 200 mm in diameter by the time they reach the surface indicating large amounts of coalescence occurring within the froth. The surface of the froth is also highly unstable and a large proportion of the bubbles burst before overflowing the lip. Every time a bubble on the surface of the froth bursts, the particles attached to it drain through the froth re-attach or re-enter the pulp, reducing the efficiency and selectivity of the process. Similarly if a film separating two bubbles within the froth ruptures, causing coalescence, there is an associated loss in surface area and some of the particles that were attached to the film may also sink back into the pulp.

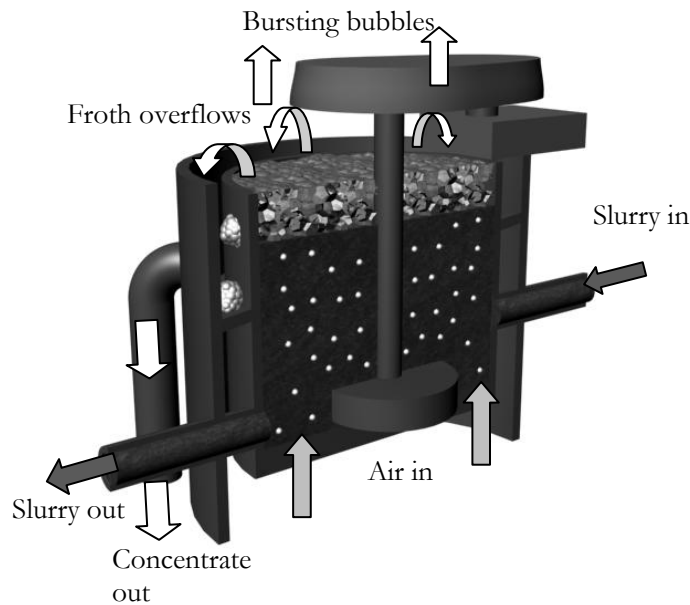


Figure 2-3. Cross section of flotation cell, showing the flow of material through it.

Flotation froths are usually kept between 30 cm and 1 m deep but the height of the froth has an effect on the concentrate that over flows. If the froth is deep there is more time for the liquid to drain out of it, taking the entrained gangue (non-valuable waste material) with it. Therefore, as the froth has less gangue in it when it overflows this produces a higher grade concentrate. However, the increased drainage time before collection of the concentrate also results in increased film thinning. Thinner films rupture more readily, increasing the number of attached, valuable particles which are lost as well. This lowers the total recovery of valuable minerals in the final concentrate. If the froth is shallower the reverse is true, there is less time for drainage so more gangue is collected, reducing the grade, but the films do not rupture as readily resulting a higher recovery of valuable material.

The dynamics and process of coalescence and bursting within the froth is poorly understood but the fact that attached particles affect the stability of froths, foams and emulsions has been known for a long time and reviewed by Aveyard *et al.* (2003) and Hunter *et al.* (2008). The stabilisation of thin films by small particles is affected by a large number of variables including particle size, shape, surface properties and packing density. Clearly the froth phase is a complicated system with many factors affecting its structure and properties, however before these are investigated it is necessary to understand the basic physics of a two phase foam.

2.2 FOAMS: FORMATION AND STRUCTURE

A foam is a cellular structure in which the cell walls are made up of thin liquid films called lamellae and the cells are the vapour phase. It is impossible to make a foam using a pure liquid without the addition of a surfactant. Surfactants are amphiphilic molecules which concentrate at the liquid-vapour interfaces and lower the surface tension of the liquid. When a bubble rises through a liquid and reaches the upper

surface the surfactant molecules act to stabilise the thin film that forms between the bubble and the bulk vapour phase. It is this stabilisation of the thin films against rupture that allows that the formation of foams. Once a surfactant has been added to the liquid a foam can be formed by agitating it or blowing gas through it.

The liquid content in a foam affects its appearance and properties, a foam with a liquid content of around 26 % will exhibit completely spherical bubbles packed tightly together. If the liquid content is increased beyond this, the bubbles are no longer tightly packed and the foam becomes a bubbly liquid. This is known as the wet limit of a foam (Exerowa 1997). If the liquid content is reduced the bubbles will gradually lose their spherical shape and begin to form polyhedral cells with rounded edges. The radius of curvature of the edges decreases with liquid content until the bubbles can be regarded as completely polyhedral this point is taken to be at 1 % liquid content and foam is now termed a dry foam (Figure 2-4).

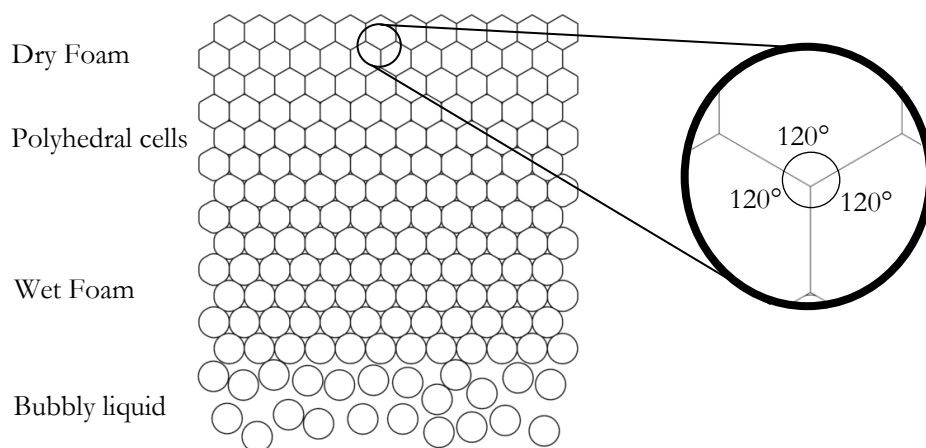


Figure 2-4. A foam forming from a bubbly liquid.

Figure 2-4 shows a foam composed of bubbles of uniform size (monodisperse), coming together to form a bubbly liquid and then a foam. As the bubbles rise, the liquid drains out from between them causing the cells to take on a polyhedral shape. As the foam becomes drier nearer the top it is possible to discern that the lamellae all meet at a junction of three, forming an angle of 120° with each other. This feature is clear enough to be easily identified in a monodisperse 2D foam but is a structural characteristic true of all foams in 2 or 3 dimensions, mono- or poly-disperse. In three dimensions, spherical bubbles turn into polyhedral cells as the liquid drains out from between them (Figure 2-5).

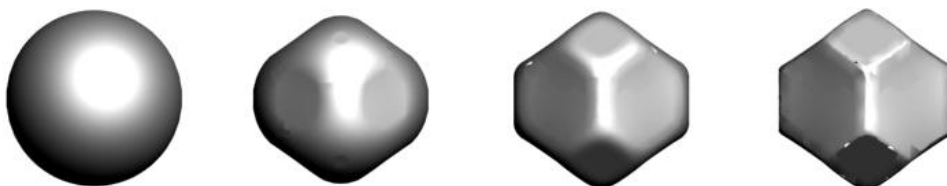


Figure 2-5. Spherical bubble turning to a polyhedral cell as liquid drains out of a 3D foam.

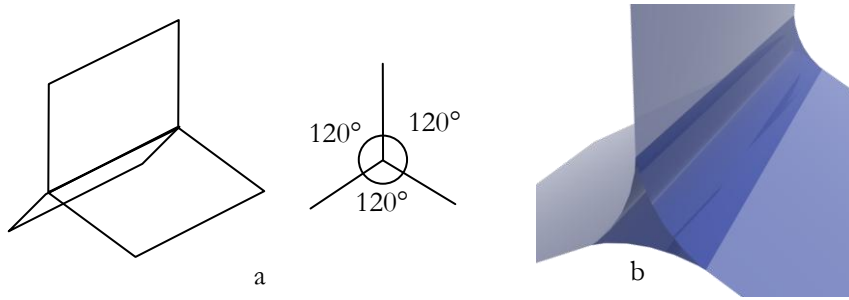


Figure 2-6. The junction of three lamellae at 120° (a) Plateau border at the junction of three lamellae(b).

As in the 2D case, at the edge of each polyhedral cell in 3D three lamellae meet, again at an angle of 120° (Figure 2-6a). At this junction of three lamellae a small channel is formed called a Plateau border (Figure 2-6b). Most of the liquid in a foam is held in the network of Plateau borders and it is through these that liquid drains out of the foam. Figure 2-7a (generated in *Surface Evolver*, Brakke 1992) shows the network of Plateau borders found in a foam. The point at which four Plateau borders meet is called a node and at the node the angle between each border is always 109° , shown in Figure 2-7b.

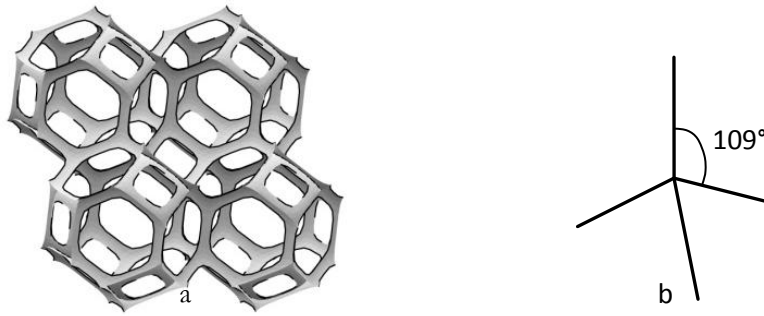


Figure 2-7. (a) A network of Plateau borders in a regular foam generated using *Surface Evolver* (Brakke 1992) and (b) the vertex formed by four Plateau borders meeting at 109° .

2.3 FILM FAILURE

As the liquid in the lamellae is drawn into the Plateau borders by capillary pressure they become thinner and eventually the opposite sides touch, at which point the film fails and the two bubbles it separated coalesce. If the pressure between the two adjacent bubbles is different the lamellae between them will curve in towards the bubble of lower pressure. In three dimensions (3D) this curvature of the lamella can be described using two orthogonal radii of curvature, shown in Figure 2-8. Using the Young Laplace law (equation 2-1) the curvature of the lamella such as the one shown in Figure 2-8 can be related to the pressure difference between the two bubbles.

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad 2-1$$

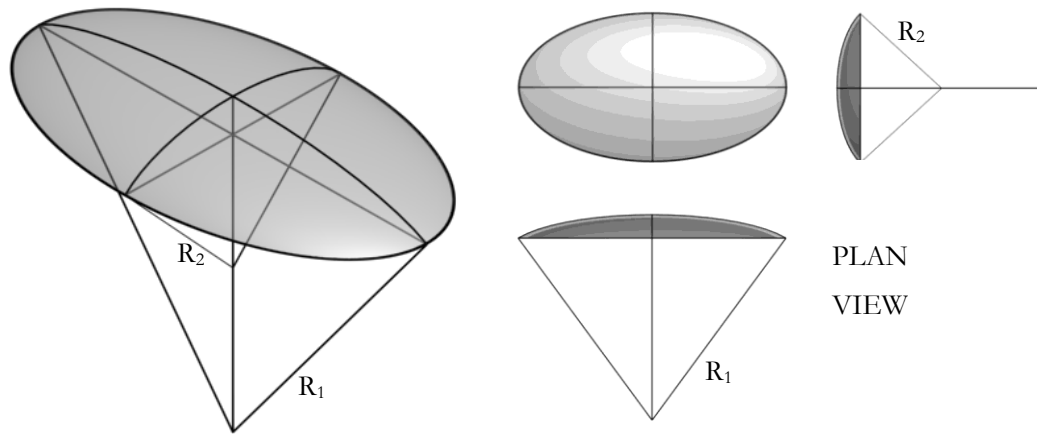


Figure 2-8. The shape of a lamella and its two, orthogonal radii of curvature (after Weire and Hutzler 2005)

Where γ is the surface tension at the Liquid-Vapour (LV) interface, R_1 and R_2 are orthogonal radii of curvature of the interface and ΔP is the difference in pressure between the two bubbles. For a film where $R_1 = R_2$ (i.e. a spherical bubble), the smaller the curvature, the higher the pressure, therefore the smaller the bubble the higher its pressure. Equation 2-1 can also be used to describe the curvature of the liquid-vapour interface. All terms remain the same except ΔP which now refers to the difference in pressure between the liquid and vapour phases. In 2D R_2 tends to ∞ and the $1/R_2$ term becomes zero simplifying equation 2-1 to:

$$\Delta P = \frac{\gamma}{R_1} \quad 2-2$$

When a foam forms, initially the lamellae are relatively thick and contain a comparatively large amount of liquid, however as they drain through the action of capillary pressure they become thinner, drawing the opposite sides together (Figure 2-9).

The initial drainage of liquid from a film is fast, causing it to rapidly thin and this thinning accelerates when the opposite sides are close enough for the van der Waals forces to take effect. However, as the film continues to thin the presence of surfactant at the liquid-vapour interface causes a repulsive force between the opposite sides of the film. This is known as the disjoining pressure and slows the final stages of film thinning, temporarily stabilising it.

There are two types of surfactant, ionic and non-ionic. Ionic surfactants dissolve to form ionic molecules with a positive head and a longer negatively charged alkane tail these molecules concentrate at the liquid vapour interface and produce a charge. Non-ionic surfactants do not dissolve but still produce a charge at the liquid vapour interface. Both types of surfactant concentrate at the liquid vapour interface, creating a diffuse electric layer which stabilises the films. When the opposite sides of the film get close enough the

electric double layer formed by the surfactant molecules exerts a repulsive force on the opposite sides of the film as shown in Figure 2-9.

These forces only become strong enough to affect the film when its thickness is below around 100 nm. A graph of the total potential energy of the film on an arbitrary scale is shown in Figure 2-10. It can be seen that there are two points on the graph (labelled 1 and 2) where the film will be stable until the capillary pressure becomes strong enough to overcome the disjoining pressure. These stable points allow the formation of very thin films, called Newton Black Films (NBF, point 1) and Common Black Films (CBF, point 2), (Exerowa 1997).

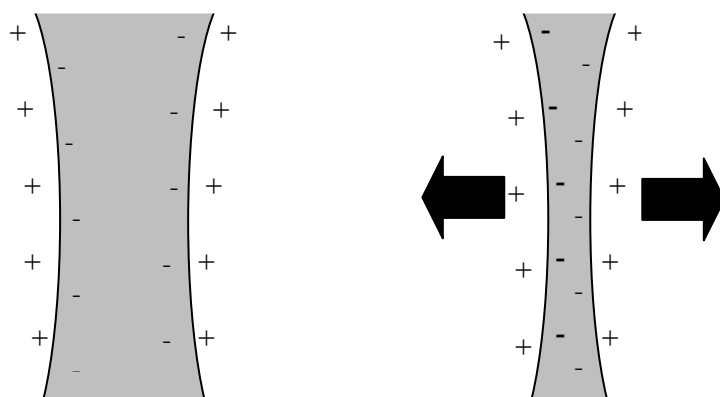


Figure 2-9. Showing amphiphilic surfactant molecules attached to the surfaces of thick and thin films after (Exerowa 1997). As the film thins the like charges are brought closer together and a repulsive force arises.

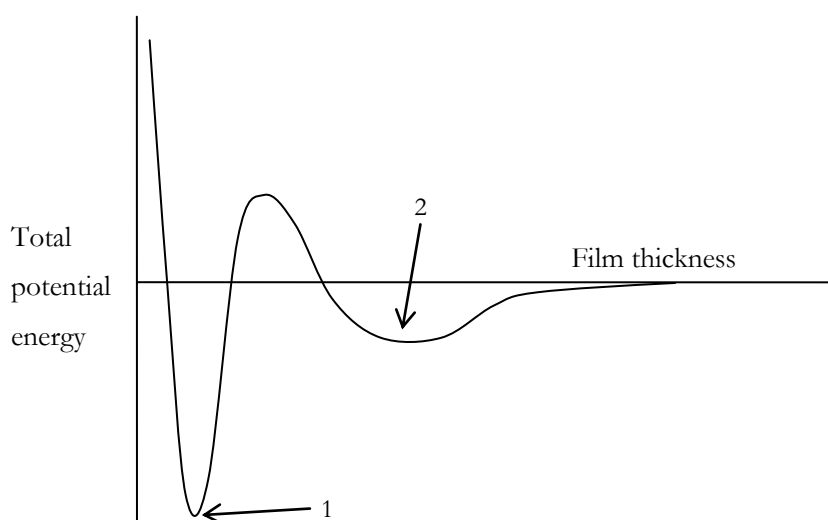


Figure 2-10. A graph representing the disjoining pressure as a function of film thickness, positive values represent an attractive force. Points 1 and 2 represent Newton black and common black films respectively, after (Weire and Hutzler 2005).

DLVO theory, named after Derjaguin, Landau, Verwey and Overbeek, (Exerowa 1997) considers the total disjoining pressure acting in a thick film to be the sum of the van der Waals and electrostatic components and is shown in (equation 2-3).

$$\Pi = \Pi_{el} + \Pi_{vw} \quad 2-3$$

Where Π is the total disjoining pressure, Π_{el} the electrostatic component and Π_{vw} the van der Waals component.

The basic structure and physics of a foam are therefore a delicate balance of opposing forces over a range of scales from the molecular to the macroscopic acting to both stabilise and destroy the foam from the moment it is created. However, it is also possible to stabilise a foam with the addition of surface active particles, which act to slow film thinning and liquid drainage.

2.4 PARTICLES AT INTERFACES

2.4.1 CONTACT ANGLE

When considering the behaviour of a particle at an interface an important characteristic is its hydrophobicity which is measured in terms contact angle (θ). For a particle at a liquid-vapour interface, contact angle is defined as the angle made between the surface of the particle and the interface at the three phase contact (TPC), it is shown in Figure 2-11 as θ below. The TPC is the point at which the liquid-vapour interface meets the particle surface. The higher the contact angle the more hydrophobic the particle.

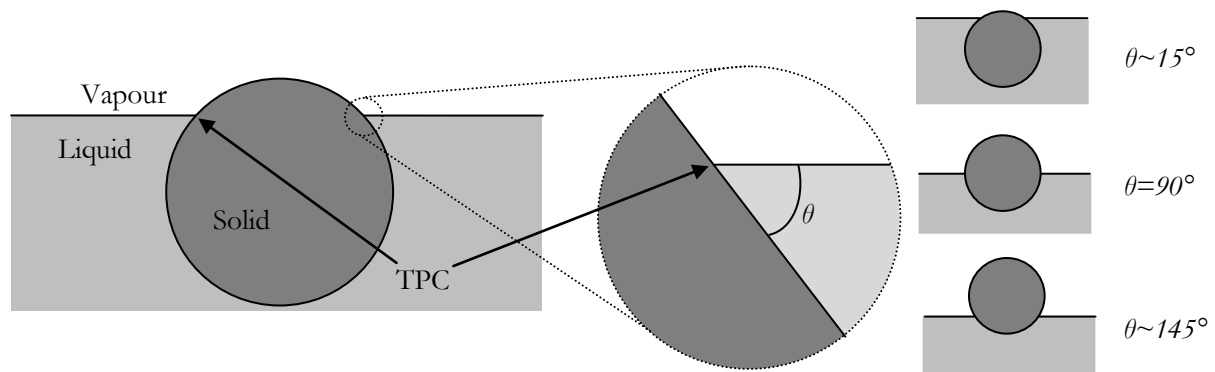


Figure 2-11. A particle sitting at a Liquid-Vapour interface, θ (contact angle) and the position of the TPC is labelled. Effect of contact angle on particle position at an interface illustrated on far right.

2.4.2 PARTICLE CHARACTERISATION

When investigating the effects of hydrophobic particles at an interface, ascertaining the contact angle of the materials being used is imperative. With the fabrication of increasingly small particles this becomes more difficult so it is often assumed that the contact angle formed on a flat plate of the same material is

analogous to that of the particle. Another method widely used is to form a packed bed from particles identical to those to be used and to measure the contact angle of a liquid drop placed on the surface. Both of these approaches can produce erroneous results arising from differences in surface roughness between an individual particle and the tablet or plate used.

Aveyard *et al.* (1994b) found that a Langmuir trough can be used to ascertain the wettability of small particles by surfactant solutions. Their results compared well with those obtained by measuring the contact angle of a drop on a flat surface of the same material treated with the same chemicals. However, there are limitations on the size of particle that can be used, their method is only viable for monodisperse spherical particles with a density of 2 g/cm³ with a diameter up to 3 μm . The particles found in flotation systems are usually in the size range of 10-300 μm .

Paunov (2003) developed the gel trapping technique to measure the contact angle of particles in the size range 2.15 μm to 9.6 μm . The particles are dispersed at a water-oil interface where the water has had gellan gum dissolved in it at 95° C. The system is kept at this high temperature whilst the particles are dispersed to prevent the gum setting. The temperature is then reduced and the gel sets, the oil is removed and a PDMS elastomer is poured on top of the gelled phase. Once the PDMS has set it is peeled off, taking the particles with it and replicating the interface around them. This sample can then be viewed with an SEM and the contact angle of the particles measured directly. This method was also used by Park *et al.* (2008) to measure the contact angle of colloidal particles (diameter 3.1 $\mu\text{m} \pm 0.2 \mu\text{m}$) at an interface.

2.4.3 PARTICLES AS SURFACTANTS

Surfactants and particles both stabilise foams, but through different mechanisms and generally on different scales, they do however also exhibit similarities, which were discussed by Binks (2002). It was proposed that just as a surfactant's properties can be described in terms of the hydrophile-lipophile balance (HLB), those of spherical particles can be described in terms of contact angle. The HLB is an important parameter used to characterise the relative efficiency of a surfactant's hydrophobic and hydrophilic parts. The hydrophobicity of a particle affects its readiness to adsorb at an interface. Once adsorbed it is held strongly at the two-phase interface whereas surfactant molecules are constantly adsorbing and desorbing from the interface over very short time scales.

Binks (2002) also reported that as nano or micro particles are not dissolved in the liquid phase there are no solubility based phenomena such as the formation of micelles, as found with surfactants. It is, however, possible for the particles to form loose aggregates in the film and become trapped between the opposite interfaces. Here they hold the opposite sides apart and prolong film lifetime (Kaptay (2006), Dickinson (2010)).

Binks (2002) used equation 2-4 to calculate the energy required to remove a particle from the interface, where r is the radius of the particle (in this case below a few microns so that gravity can be ignored) θ is

the contact angle, $\gamma_{\alpha\beta}$ is the surface tension of the oil-water interface the particle is attached to and E is the energy.

$$E = \pi r^2 \gamma_{\alpha\beta} (1 \pm \cos \theta)^2 \quad 2-4$$

The plus or minus signs represent the energy required to remove the particle into the oil or water phases respectively. E is at a maximum when $\theta=90^\circ$ and decreases rapidly either side of this. E also decreases with the square of r and particles of a size comparable to a surfactant model (5nm) are very easily detached, suggesting that there is a lower limit to the size of particle that can stabilise a film effectively.

2.5 PARTICLE STABILISATION OF FILMS

Foams are thermodynamically unstable systems and as soon as one is formed it begins to decay through several modes including gravity driven liquid drainage, film thinning and gas diffusion from smaller (higher pressure) to larger (lower pressure) bubbles. However, it is possible to increase the stability of foams with the addition of hydrophobic particles which act through a variety of mechanisms to stabilise the foam.

A particle stabilised foam differs from a two phase foam in that the films within it are stabilised by both the surfactant and the particles which are attached to the surface of the film. The surfactant stabilises the film on a molecular level and the attached particles act on a larger scale. The shape, size and surface properties of the particles used all have an effect on their ability to stabilise the films they are attached to.

In a detailed study, Aveyard *et al.* (1994a) found that particles of varying hydrophobicity can either stabilise or destabilise a foam, with a rapid increase in foam collapse once the contact angle of the particles is above 90° . Garrett (1994) also found that particles with a low contact angle ($\theta < 90^\circ$) promoted foam stability. Johansson and Pugh (1992) found that with small quartz particles (26 – 44 μm) the stability of the froth was maximised at an intermediate degree of hydrophobicity (contact angle of roughly 65°). It was also reported that the presence of particles with a lower hydrophobicity (smaller contact angle) did not have a noticeable effect on the froth properties. Particles of greater hydrophobicity ($\theta > 90^\circ$) were found to penetrate the film to a greater extent causing film failure. Schwarz and Grano (2005) also found that quartz particles with a contact angle of around 63° produced the most stable froth and Hunter *et al.* (2008) reported that foam and film stability varies with particle hydrophobicity. It was also found that the higher the concentration and smaller the particles, the greater the stability of the foam. Larger particles (74 – 106 μm) were found to have a less pronounced effect on the foam stability, showing that both the hydrophobicity and the particle size are important.

Koh *et al.* (2009) investigated the effect of particle shape and size on flotation performance. Ballotini was wet ground in a ball mill to produce samples of an irregular shape which were then sized into three different fractions -45+38 μm , -90+75 μm and -150+125 μm , samples of spherical ballotini were also

split into these size ranges. The samples were methylated to produce a range of contact angles between 0° and 90° and batch flotation tests were carried out.

It was found that the very hydrophobic particles destabilised the froth and also formed aggregates that made recovery difficult. It was also found that the ground ballotini had higher flotation rates than the spherical ballotini, a result that agrees with those of Kursun and Ulusoy (2006). Kursun and Ulusoy (2006) carried out flotation tests on talc ground in a ball mill or a rod mill. It was found that particles from the ball mill were of a more rounded shape whilst those from the rod mill were more elongated and flatter. This translated to a greater recovery of rod milled talc particles over ball milled ones. Hiçyilmaz *et al.* (2004) also reported that rod milled talc and quartz particles had a greater elongation and flatness when compared to ball milled or autogenous milled particles. The rod milled particles were also found to be more hydrophobic.

2.5.1 PARTICLE SHAPE AND FILM STABILITY

Shape also has an effect on the behaviour of individual particles at the interface. In a classic study, Dippenaar (1982) investigated the effect of shape on particle behaviour in a film. It was noted that bridging and subsequent dewetting of a film by a particle generally requires the contact angle to be above 90° but that some particles with specific shapes were able to bridge and dewet the film when $\theta < 90^\circ$. Four types of particle were used; galena, quartz, glass beads and crushed flowers of sulphur. The galena particles formed characteristically orthorhombic shapes and the glass beads were smooth spheres whilst the quartz and sulphur particles were described as being rough without any characteristic shape. Individual particles were placed in a film which was thinned to force them to bridge it and the behaviour observed. Dippenaar found that the smooth, spherical particles ruptured the film if their contact angle was greater than 90° through the bridging dewetting mechanism. This is the process by which the TPCs on opposite sides of a particle are drawn together at its surface whilst they try to maintain the contact angle. When the two TPC meet the film dewets the particle and the film fails. Bridging-dewetting occurred at all contact angles above 90° for spherical particles as soon as they bridged both sides of the film. If θ was less than 90° , the particles bridged the film but did not cause immediate failure. Rough particles (quartz and sulphur) also exhibited bridging-dewetting behaviour but if the contact angle was close to 90° their efficiency at rupturing films in this way was reduced. Galena particles, were found to behave in one of two ways, either bridging and dewetting the film immediately or reorienting themselves in the film and providing stability. In both cases the contact angle of the galena was less than 90° (72° - 88°) and the shape was roughly cubic.

Frye and Berg (1989) investigated the use of hydrophobic particles as antifoam agents and also noted that particles with asperities are more likely to bridge a film at lower contact angles and cause them to rupture more easily. Aronson (1986) also noted that particles with asperities are more likely to bridge an interface. It was proposed that when the asperities reach a certain size in relation to the particle and film thickness they are able to puncture the interface and attach the particle to the film. Kursun and Ulusoy (2006) noted

that the floatability of particles was increased the further their shape deviated from the ideal sphere. Koh *et al.* (2009) also observed that particles with the same surface properties but more jagged shapes showed better flotation performance.

Nano fabrication techniques are also allowing the production of shaped particles Brown *et al.* (2000) has produced a number of shaped particles including crosses, diamonds, disks and rectangles in the size range of 20-200 nm. It was found that curved disks at an air water interface arranged themselves into regular patterns which resulted in the least amount of film distortion. It was also observed that if one side is hydrophobic and the other hydrophilic the majority of particles had the corresponding face in the liquid or air phases.

2.6 EXPERIMENTAL INVESTIGATIONS

For a long time it was believed that a foam could not be stabilised by particles alone, but that a surfactant would also be required. However foams have been generated using only hydrophobic particles. Du *et al.* (2003) found that partially hydrophobised fumed silica particles with a nominal diameter of 20 nm can be used to stabilise air bubbles in double distilled water without the use of surfactant. Dickinson *et al.* (2004) also created particle stabilised foams using partially hydrophobised silica particles with a nominal diameter of 20nm and also found that the contact angle is an important factor in the formation of a stable foam.

Alargova *et al.* (2004) has also shown that super stabilised foams containing no surfactant can be generated using micro-rods of diameter 1 μ m and length of a few tens of μ m, synthesised from epoxy type photoresist SU-8. These rods form densely packed, interlocked structures at the film interfaces, which prevent the films from thinning and reduce the effects of gas diffusion between adjacent bubbles. The micro-rods steric repulsion of the film interfaces also ensure that any spaces left uncovered are too far apart for the capillary pressures present to cause film thinning to levels where they would rupture. It was also found that the addition of a surfactant (sodium dodecyl sulphate, SDS) to the mixture before foaming prevented the microrods from stabilising the foam. The addition of surfactant caused the rods to lose their affinity for adsorption at the interface. If SDS was added after the foam was formed the rods were expelled from the bubble surface and formed a sediment at the base of the foam.

This phenomenon was also studied by Subramaniam *et al.* (2006) and Abkarian *et al.* (2007) who investigated the effect of surfactant concentration on a bubbles completely covered in particles (an armoured bubble). After initial formation the armoured bubbles were spherical but as they lost gas over time, through dissolution, they progressively took on a non-spherical faceted shape which caused large distortion of the film surface. Eventually the dissolution ceased and the bubble stopped changing shape. However, upon the addition of surfactant to the liquid phase they became spherical once more and then began shrinking and shedding particles as they did so. Different concentrations of surfactant had remarkably different effects on the bubble. When surfactant was added at a concentration well above its

CMC (critical micelle concentration) the bubble quickly regained its spherical shape within 1s by ejecting particles, it then began shrinking and expelling more particles until it eventually dissolved. If surfactant was added at a concentration well below its CMC the particle retained its faceted shape but did expel particles and lose volume.

Fujii *et al.* (2006) generated aqueous foams stabilised with latex particles of various diameters. They were able to form stable foams using particles with diameters as low as 260 nm in diameter. SEM was used to image the films formed and it was found that the particle packing patterns in the films had a high degree of order for the larger diameters (roughly 1.62 μm) which decreased as the particles became smaller. The domains over which regular packing occurred were larger with particle size as well, particles of diameter 1.62 μm formed crystalline domains containing roughly 9600 particles whereas those with a diameter of 0.81 μm only contained around 100 particles. However, it should be noted that smaller particles have a larger degree of polydispersity and this correlates with reduction in size of crystalline domain. Although the effect of polydispersity on the crystalline domains was not directly studied the decrease in the size of domains with increasing polydispersity should be noted.

There are many similarities between particle stabilised foams and particle stabilised emulsions. (Kruglyakov *et al.* 2004a) investigated the effects of particles on the stability of emulsion films related to the capillary pressure. It was found that emulsion drops covered with compact layers of particles were more stable than those covered with friable layers of aggregated particles. It was concluded that the size and shape of particle aggregates on the film must be taken into account when calculating the critical capillary pressure required to rupture a film in a solid stabilised emulsion. It was also found that the experimental critical capillary pressure varied from the calculated one, at a contact angle of 35° it was 30 % and at 43° it was 85 % of the calculated value. This was attributed in part to packing defects on the film and highlights the large effect that even a small defect can have on the film stability.

2.6.1 PARTICLE COATED BUBBLES

Armoured bubbles display interesting properties as the closely packed particle shells can prevent gas dissolution from the bubble and distort its shape. Abkarian *et al.* (2007) used *Surface Evolver* (Brakke 1992) to confirm the experimental results obtained after investigating armoured bubbles and how the particles react to the bubble shrinkage due to dissolution of gas. It was found that as the gas volume decreases there is point at which the attached particles jam on the surface. If dissolution continues eventually the bubble surface and attached particles form a polyhedral structure representing a local energy minimum, at this point gas dissolution is also halted.

Gallegos-Acevedo *et al.* (2006) developed an analytical model to predict the mass of solids attached to a bubble and verified it experimentally. Certain assumptions had to be made when calculating bubble loading in the analytical model, especially regarding particle size and shape. Two approaches were used to estimate particle volume, one was to assume all particles are monodisperse and spherical, the other is to

assume rounded particles and introduce a shape factor. After generating a bubble it was manually loaded by sprinkling silica sand particles over it. Once fully coated the bubble was allowed to burst and the particles were collected and weighed to find the maximum loaded weight of material. It was also possible to record pictures of the loaded bubbles and analyse them to determine the surface coverage. A good correlation between the theoretical and experimental results was found for all approaches they used to predict the surface coverage. The most accurate one however, did not assume spherical particles and used the shape factor of Kelly and Spottiswood (1982). Gallegos-Acevedo *et al.* (2006) also imaged the particles on the film before they collected them, the pictures obtained clearly show the particle arrangement on the film. This approach could be used to help analyse the packing arrangements of particles in a thin film and verify theoretical models of particle-particle interaction on a thin film.

Bournival and Ata (2010) also visualised the particle arrangement on bubbles using spherical glass particles or galena particles. A series of particle packing models were used to fit the particle loading of the bubble surface, assuming monolayers only were present. The packing models used were based on hexagonal or square arrangements. Film coverage of particles was calculated for mono and bi disperse cases. It was found that for spherical particles the closest agreement to packing observed experimentally was gained from a monodisperse hexagonal model for all size classes whilst for galena both hexagonal and square packing models matched the experimental data, again for monodisperse cases. In both cases deviation from the true packing factor was less than 15 %.

Bournival and Ata (2010) and Ata (2009) also noted that when two, apparently fully loaded, bubbles coalesced very few particles were expelled. As there is a 20 % loss in surface area when coalescence occurs this implies that the particles are forced to adopt a new, tighter packing arrangement on the surface. It was concluded that the particles are able to adopt a variety of packing arrangements on the bubble surface based upon the interfacial forces and stresses they are subject to.

Sadr-Kazemi and Cilliers (2000) developed a method of sampling the particle loading of a flotation bubble lamella directly with use of a microscope slide. By touching the slide against the lamella the attached particles are transferred to the slide, the area of film sampled and the weight of solids attached to it can then be measured to give a particle bubble loading. If enough samples are taken under steady state conditions the solids can be assayed and the grade of the attached particles found. This technique has recently been expanded by Cole *et al.* (2009) to imaging lamellae sampled from a laboratory scale batch flotation with a scanning electron microscope.

2.6.2 PARTICLE AGGREGATION BEHAVIOUR

It is known that particles do not usually form completely regular patterns on films, even when monodisperse. At best a crystalline structure emerges with patches of regular distribution separated by fault lines. Horozov *et al.* (2005) used an experimental setup that allowed the formation of particle laden oil in water and water in oil films. Each film was formed in a glass lined PTFE ring connected to a syringe

which allowed the liquid in the film to be drawn out or forced in to it. The film was formed by starting with the PTFE ring in one phase and lowering or lifting it through the interface into the other. By distributing particles at the oil water interface it was possible to create particle laden films, which once formed were then allowed to settle over time so that the behaviour of the attached particles could be observed. The particles used were 3 μm diameter silica, which were treated to obtain a variety of contact angles. Using this method it is possible to generate films with monolayers at each interface and as the oil or water film is thinned the opposite monolayers are forced together. Monolayers of particles that bridged both sides of the film were formed when sparsely populated interfaces were brought together. When the opposite sides of the film were densely packed with particles however, a double layer of particles formed, separating the interfaces until the capillary pressure was large enough to force them into a monolayer. It was observed that the capillary pressure required to force a monolayer to form was much smaller than the capillary pressure required to cause failure of a double layer stabilised film.

2.7 ANALYTICAL AND COMPUTER MODELLING

2.7.1 ANALYTICAL MODELS OF PARTICLES IN FILMS

Ali *et al.* (2000) reduced the problem of particle stabilised thin films to 2D to study the effects inter particle separation distance and contact angle on film stability. Spherical particles were replaced with cylindrical rods of infinite length which stabilised the film. The particles were assumed to bridge both sides of the film and when the film between any two particles thinned to zero thickness ($h = 0$) the film would fail. It was found that as the distance between adjacent particles decreased, the capillary pressure required to rupture the film increased.

In addition to the work of Ali *et al.* (2000) several other models of particle in films are reported in the literature. Denkov *et al.* (1992) developed an axi-symmetric model of a spherical particle in three dimensions bounded by a circular cell. The total area of film in the circular cell was equal to the average area of film per particle in a packed film. In the Denkov model the area of film that remains when the particles are touching is taken into account and the minimum possible separation distance is adjusted accordingly. However, due to the circular boundary of the unit cell the shape of the film at the minimum separation distance does not accurately represent that of a film between hexagonally packed spherical particles at minimum separation distance. Kaptay (2004) also investigated the effect of attached particles stabilising a film and showed that if two layers of particles are attached to opposite sides of the film they can stabilise it at contact angles above 90° .

2.7.2 POROSIMETRY THEORY OF CAPILLARY DRIVEN FILM FAILURE

Porosimetry is a separate area of research that has used analytical approaches to describe the shape of liquid interfaces between solid surfaces with varying contact angles. Unlike particle stabilised films however, flow through porous media deals with the capillary pressure required to drive the liquid through

pores of varying cross-sectional shape. The analytical models have been developed to describe the shape of the interfaces in the area between particles which possess similarities with particle stabilised thin films.

Purcell (1950) approached the problem of a toroidal pore, effectively taking into account the converging-diverging nature whilst maintaining the axisymmetric nature of the system as shown in Figure 2-12.

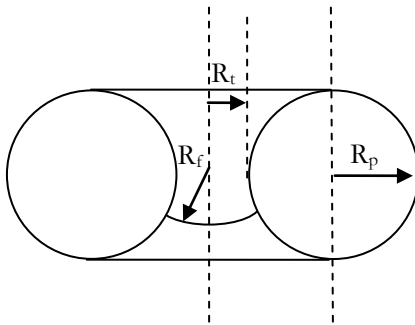


Figure 2-12. Cross section of the toroidal pore used by (Purcell 1950).

Where R_t is the radius of the throat of the torus, R_p is the radius of the torus wall and R_f is the radius of the film curvature. Mason and Morrow (1994) combined the Haines in sphere model (1927), Purcell (1950), Princen (1969a,b) and Mayer and Stowe (1965) approaches to calculating meniscus curvature in a pore made up of spherical bodies. Their theoretical results were consistent with their experimental data indicating that this method of modelling film shape for a non-axisymmetric pore can be used. However they also noted that the particle surface roughness and edge effects can decrease the effect of contact angle on the results obtained. To overcome this it was suggested that the receding contact angle for a rough surface be used instead of the equilibrium one for a smooth surface.

The Mayer Stowe-Princen method has also been applied to the problem of particle laden film stability for emulsions by Kruglyakov and Nushtayeva (2004) where it was also noted that knowledge of the structure of particle aggregates at the interface is needed to accurately predict the capillary pressure and curvature of the interface. Horozov *et al.* (2005) also used the method to calculate the capillary pressure required to cause film inversion in a double layer of particles for water in oil and oil in water films.

Hilden and Trumble (2003) used *Surface Evolver* (Brakke 1992) to investigate the pressure required to force the film through a converging diverging pore. They found that the pressure goes through a maximum as the liquid vapour interface traverses the pore. This has implications for particle stabilised film failure which will be described more thoroughly later on.

2.7.3 SIMULATING NON-SPHERICAL PARTICLES

Many experimental results have shown that particle shape has a profound effect on the properties and stability of foams and films. The effects of particle shape are now being simulated and investigated. De Graaf *et al.* (2009) used a triangular tessellation technique to calculate free energy associated with

adsorption of a colloidal particle at a flat interface. Interfacial deformation due to capillary, electrostatic and gravitational forces were neglected but the model is defined in a way that allows their implementation. The triangular tessellation technique was used to assess the adsorption energy of different particle shapes at an interface, these included ellipsoids, cylinder and sphero-cylinders. The adsorption free energies for these particle shapes obtained from the triangular tessellation technique were verified with a semi-analytical model derived from Dong and Johnson (2005). De Graaf *et al.* (2009) concluded that whilst the semi analytic technique was quicker it was time consuming to derive and prone to error, it was suggested the triangular tessellation technique could be used to verify the semi analytical models.

Lehle *et al.* (2008) developed an algorithm to investigate the capillary forces between ellipsoidal particles at an interface. The interaction between particles with contact angles other than 90° proved to have an effect on the particle interaction forces with a deviation from the quadrupole interaction. Further investigation of interaction forces between particles arising from capillary multipoles has been carried out by Danov *et al.* (2005) to investigate the aggregation of particles at a fluid interface. Equations were developed to describe the theoretical shape of the capillary multi-poles surrounding a particle with an undulating contact line on its surface. Capillary multi-poles of different modes can then be used to investigate the capillary forces between particles. This work has recently been developed further by Danov and Kralchevsky (2010) to obtain expressions that are applicable over a wider range of length scales than in Danov *et al.* (2005).

2.8 SUMMARY

This chapter has described the physics of a simple two phase foam system and expanded it to the three phase particle stabilised foams found in froth flotation. It is clear from the literature that particle stabilised thin films have many of variables affecting their behaviour and structure that have been investigated through experiment, theory and computer simulation over a long period of time. Three factors in particular are of note; the hydrophobicity of the particles, the shape of the particles and the packing arrangement of the particles on the film.

Contact angle affects the shape of the interface around the attached particles. The undulations in the TPC at the particle surface result in forces that act on the particle causing motion and aggregation. These forces can be calculated in a number of ways including 2D analytical models, numerical modelling and the development of capillary multipoles. The contact angle also affects the particle's ability to stabilise the film against increases in capillary pressure. A spherical particle with a small contact angle ($\theta < 90^\circ$) stabilises the film whilst a spherical particle with a contact angle above 90° will destroy a film through the bridging dewetting mechanism (Garrett, 1978). It is however, possible for particles with certain shapes (cubic, sharp edges, jagged) to rupture a film when the contact angle is below 90° (Dippenaar 1982).

The shape of a particle, as well as its contact angle can affect the shape of the interface surrounding it. Particles with asperities and sharp edges can enter an interface more easily as well as trap the TPC at their discontinuities. The orientation of non-spherical particles also affects the film stability and interface shape.

Monodisperse spherical particles can form regular, close packed hexagonal aggregates, either at an interface or in a foam film. These represent the maximum packing density for a single layer of spherical particles, however if the size or shape of the particles is more polydisperse the ordered structure does not form as easily. Non-spherical particles also form various types of aggregates with ellipsoidal particles linking up end to end or side to side (Hunter *et al.* 2008), micro rods forming interlocking structure at the interface (Alargova *et al.* 2004) and cylinders orienting themselves with or against film curvature (Lewandowski *et al.* 2008).

The results of investigations into these three particle properties are presented in this thesis. A series of models have been developed using the *Surface Evolver* (Brakke 1992) to investigate the effects of contact angle, shape and packing arrangement. These are presented along with results and insights gained into this complicated system.

3 MODELS AND METHODS

3.1 INTRODUCTION

Surface Evolver (Brakke 1992) is a program that minimizes the energy of a user defined surface and can be used to find its shape. It has been used extensively to simulate soap films, periodic and non-periodic foams (Wang and Neethling 2006), heavily laden particle encapsulated bubbles (Abkarian *et al.* 2007), droplets and particles at interfaces (Lewandowski *et al.* 2008) and is well suited to simulating the problem of particle stabilised thin films. It has therefore been chosen to simulate the particle stabilised films in this thesis.

3.2 SURFACE EVOLVER

The surfaces to be simulated are represented by a mesh of triangular facets which are evolved to the minimum energy surface using a gradient descent method. The energy of a surface that is evolved in *Surface Evolver* is made up of the sum of its component energies; the energy per unit area, gravity, prescribed pressure energy and user defined energies. The energy per unit area of a facet can be regarded as the surface tension of the interface it represents and the prescribed pressure energy is calculated as $E=PV$. E is energy, P the pressure of the gas phase and V the actual volume of the body concerned calculated directly from the model. Surfaces and boundaries can also be set to user defined constraints which limit their movement or positions and for the purposes of this dissertation allow the definition of boundary conditions and solid geometries.

3.2.1 BASIC MODEL GEOMETRY AND STRUCTURE

Surface Evolver can be used in both 2D (string model) and 3D (soap film model), in both cases the model uses four basic geometric elements to represent the line/surface to be simulated; vertices, edges, facets and bodies. Vertices are points defined in a Cartesian coordinate system with x, y and z coordinates ($v.x$, $v.y$, $v.z$). Edges join two vertices in a straight line and have a direction in which they are defined with a 1st and 2nd vertex ($ee.vertex[1]$ and $ee.vertex[2]$). Facets are triangular and are defined by listing the edges that make up their circumference, these also have an order and must be linked so that the ending vertex of edge n ($ff.edge[n].vertex[2]$) is the same as the starting vertex of edge $n+1$ ($ff.edge[n+1].vertex[1]$). The three vertices in a facet are also linked to the facet as $ff.vertex[1,2 \text{ or } 3]$. The facet normal is in the direction given by the right hand rule from the facet's edge order.

A body is defined by listing all of its bounding facets and can have a volume or pressure ascribed to it. In the 2D model each body only has one facet associated with it but in 3D there are as many as required to define the body surface. The facets listed for the body (in 3D) have all their normals pointing out from the body. The sign of the facet in the body list indicates whether the outward normal for the body is the same as the facet (positive) or not (negative).

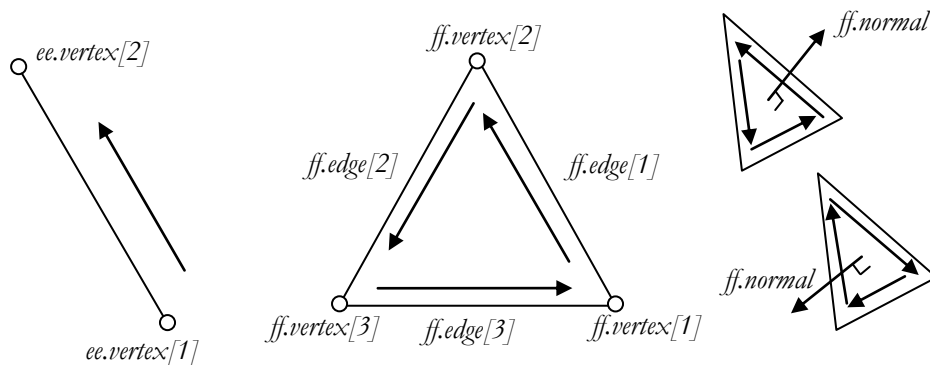


Figure 3-1. The vertex, edge and facet geometry of *Surface Evolver*. The facet normal ($ff.normal$) direction is governed by the direction in which the edges are linked.

Once a data file is loaded into *Surface Evolver* any facets that are listed with more than three edges are automatically split up into a set of triangles. This is achieved by placing a vertex in the centre of the facet and creating an edge from each vertex on the periphery of the facet to the centre vertex, as shown in Figure 3-2.

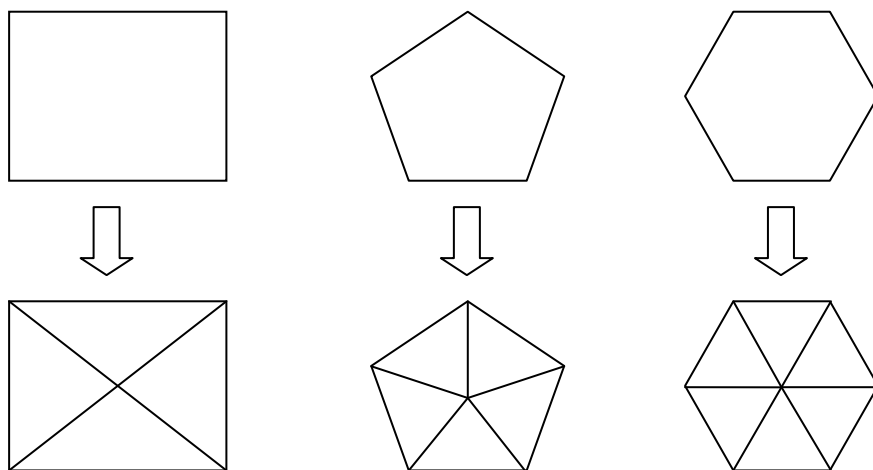


Figure 3-2. Facets before (top) and after (bottom) *Surface Evolver* has split them into a union of triangles.

In the 2D string model surfaces are represented by a (1D) line or curve whose position is expressed in 2D coordinates. In the 3D soap film model surfaces are represented by a union of triangular facets. In both models the resolution of the surface represented can be increased by refining the model. This is done by splitting the edges associated with the surface in two with the addition of a new vertex at the centre of each edge. In the string model this is enough to increase the resolution (Figure 3-3) but in 3D each new vertex (at the midpoint of the old edge) must be linked to others on opposite edges to increase the number of facets, as shown in Figure 3-4.

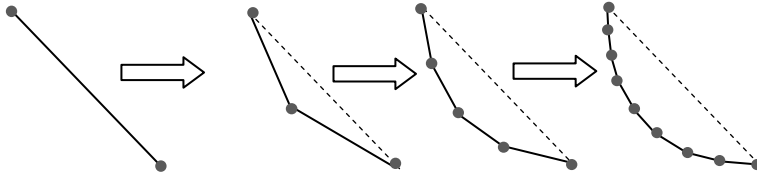


Figure 3-3. Refinement of an edge in the string model. Each dot represents a vertex.

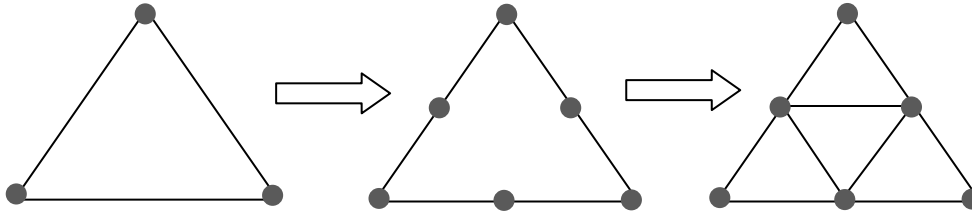


Figure 3-4. The method for refining a triangular facet; first the each edge is split into two next the new vertices are joined up to make 4 smaller triangles where there was originally one.

Once a surface has been defined and loaded into *Surface Evolver* it can be evolved to its minimum energy surface.

3.2.2 EXAMPLE MODEL - TWO JOINED BUBBLES

This example model is intended to demonstrate the basic model parameters introduced so far and expand upon them. Two bubbles sharing a common interface have been chosen, shown in Figure 3-5.

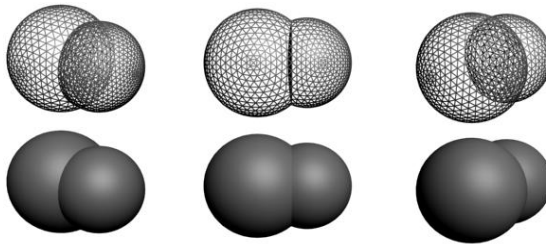


Figure 3-5. The double bubble model, wireframe (top), blank surfaces (bottom).

To begin the vertices must be defined. Each bubble will initially be defined as a cube, with eight vertices, one at each corner. As they share an interface, only twelve vertices need be defined as four vertices will be at the interface. The vertices are listed under the "vertices" header in numerical order followed by the x, y and z coordinates (Figure 3-6).

vertices	
1	0 0 0
2	1 0 0
3	1 1 0
4	0 1 0
5	0 0 1
6	1 0 1
7	1 1 1
8	0 1 1
9	1 2 0
10	0 2 0
11	0 2 1
12	1 2 1

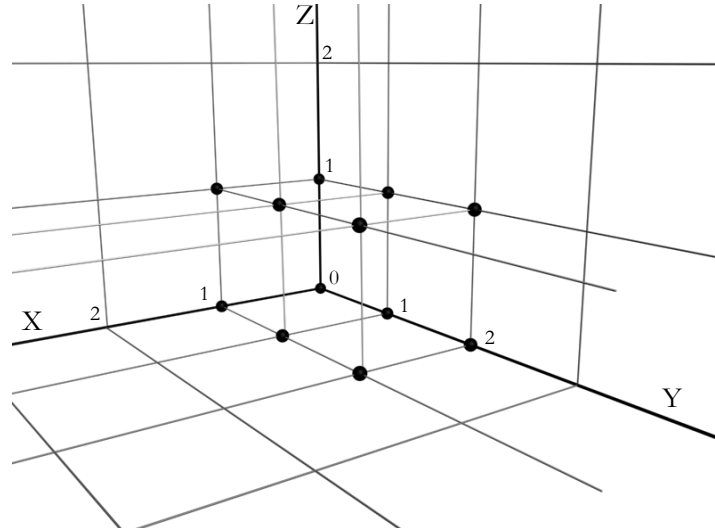


Figure 3-6. Vertices in data file and Cartesian coordinates.

The edges are made by listing the edge number, followed by its two vertex id numbers under the "edges" header. The lead vertex (*ee.vertex[1]*) is listed first, shown in Figure 3-7

edges	
1	1 2
2	2 3
3	3 4
4	4 1
..	
..	
16	7 12
17	9 10
18	10 11
19	11 12
20	12 9

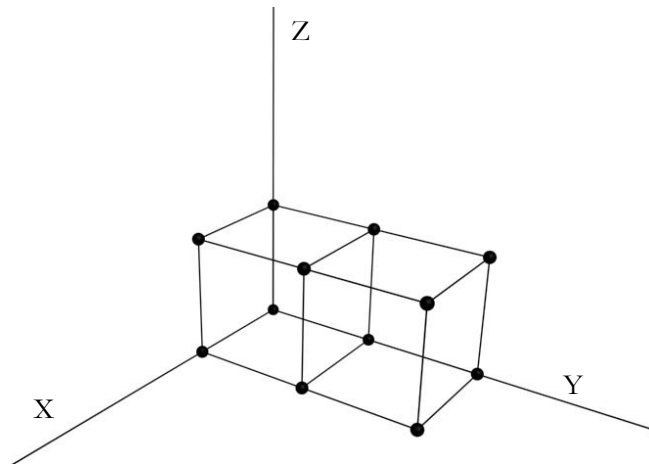


Figure 3-7. Edges in the data file and the model's current state.

Once edges and vertices are defined, the facets can be added to the data file. This is done by listing the facet number followed by the edge id numbers that make up its circumference. A "-" sign is included before the edge id number where it is necessary to reverse the direction of the edge to maintain the order of vertices, as shown in (Figure 3-8). Once the square facets are loaded into *Surface Evolver* it automatically adds a vertex to the centre of each one and extra edges to make all of the facets triangular.

faces

```

1 1 10 -5 -9
2 2 11 -6 -10
6 3 12 -7 -11
4 4 9 -8 -12
5 5 6 7 8
3 -4 -3 -2 -1
7 13 17 -14 -3
8 13 -20 -16 -11
9 17 18 19 20
10 14 18 -15 -12
11 16 -19 -15 -7

```

bodies

```

1 1 2 3 4 5 6 volume 1
2 -6 -7 8 9 -10 11 volume 0.5

```

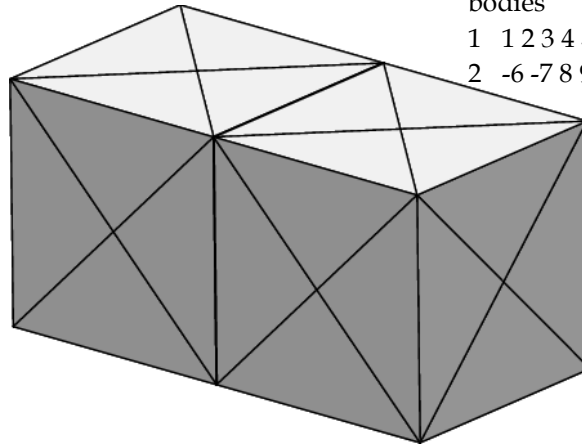


Figure 3-8. Facet list as it appears in the *Surface Evolver* data file and visual representation of the corresponding model.

The bodies are then created by listing the body id number followed by the facets id numbers, with "-" signs in front of the facet ids that need their normals reversing. After each body the volume or pressure can be prescribed, in this model the volume has been used, with one bubble half the volume of the other.

The model is now ready to be evolved to its minimum energy. By iterating the model in *Surface Evolver* and refining the mesh it is possible to generate the minimum energy surface approximating two bubbles joined together (Figure 3-9).

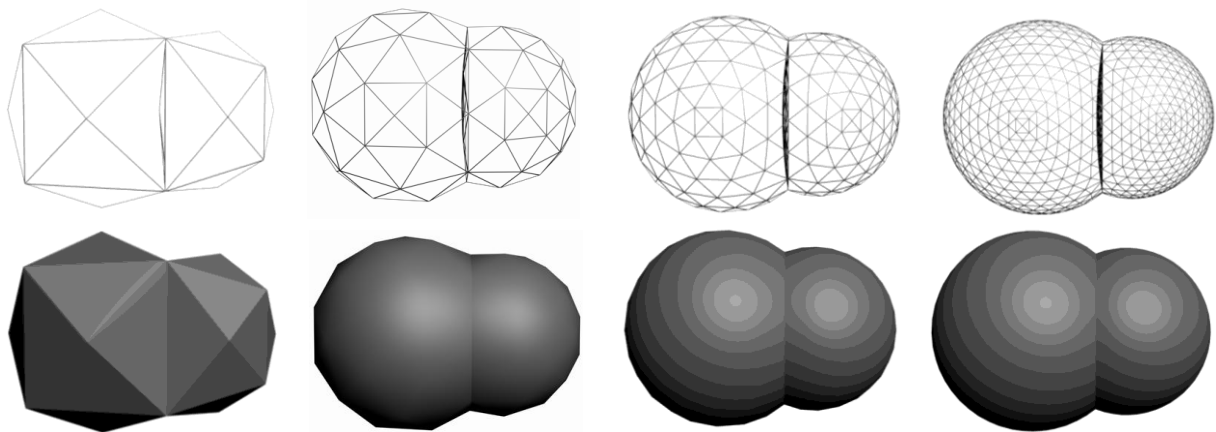


Figure 3-9. Showing the evolution of a model of two bubbles with 4 step of refinement.

This is a relatively simple case but it illustrates the steps required to generate a model in *Surface Evolver*, in the work presented in the following sections user defined constraints are also used to define boundary conditions and solid surfaces.

3.2.3 CONSTRAINTS FOR BOUNDARY CONDITIONS AND SOLIDS

A constraint is a formula that, when applied to a vertex, edge or facet forces it to satisfy the equation. These can be used to create solid surfaces and boundary conditions.

For example the formula $x^2+y^2=R_p^2$ defines a circle around the origin of radius R_p . Setting the vertices edges and facets of a model to this constraint will force them to adopt this surface. The left most image in Figure 3-10, shows an initially simple model of a flat, square surface defined in *Surface Evolver* with four vertices, four edges and four facets. Its outer edges and vertices are set to a circular constraint. As the model is refined, the new edges and vertices created at the boundary of the surface are forced onto the constraint, creating a circular film.

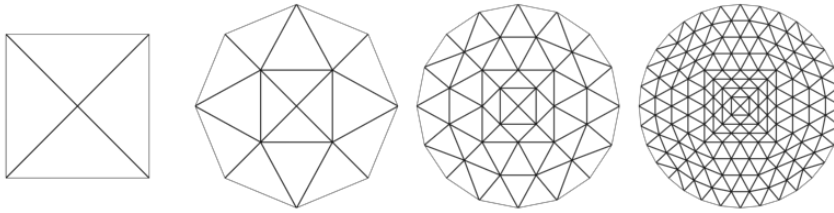


Figure 3-10. An initial model of a square face on a circular constraint adopting the circular boundary over 4 refinement steps.

To set a volume or pressure to the circular film it needs to form part of a body, to define a body an enclosed volume is needed. The simplest way to do this is to define an extra vertex some distance z away from the centre of the film, fix it in place and use it to define a series of edges and facets forming a cone. A vertex, edge or facet can be fixed in place by listing it as *fixed* in the data file, in this case only the vertex needs fixing. However the new facets that are defined to form the conic part of the model have a surface tension of 1, the default. This will distort the model when the minimum energy surface is found as they will contribute to the energy of the surface. This can be overcome by setting the conic wall facet to a surface tension of 0, they will still form the boundary of the volume but will not affect the film shape.

This model can be used to represent the circular interface between the two bubbles in the previous model. The radius of the constraint must be set to that of the interface and the pressure set to the difference in pressure between the two bubbles. When the surface is evolved it will have the same curvature as the interface.

When circular boundaries and spherical particles are defined in the *Surface Evolver* models in later chapters they must be put on a convex constraint. The convex constraint is used to keep the edges and vertices well spaced on the surface.

Surface Evolver minimises the energy of the surface(s) in a model but the straight edges of the facets cannot conform to any curved surfaces defined by constraints they are set to. This creates a small gap between the facet edge and the line or surface defined by the constraint. This gap does not contribute to the energy of the surface and it is therefore energetically favourable for the vertices to zip up at the boundaries to maximise this gap area and minimize the facet area and energy (Figure 3-11). This is an

undesirable effect that can be avoided by declaring the constraint to be convex, *Surface Evolver* will take a gap energy into account when minimising the surface, preventing the vertices from gathering.

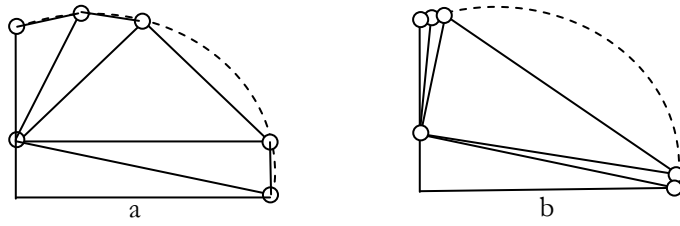


Figure 3-11. Showing the effect of a non-convex constraint on vertex behaviour at a curved constraint. Before evolution (a), after evolution, with vertices gathering (b).

Solid bodies can also be created by setting surfaces to constraints. Putting body 1 in the double bubble model on a convex constraint with the formula $x^2+y^2+z^2=R_p^2$ creates a spherical particle with a droplet attached to its surface. The model is evolved and refined in the same way as for the two bubbles but the resulting surfaces are different (Figure 3-12) with the spherical particle's curvature penetrating the droplet instead of the interface curving into the lower pressure large bubble as before (Figure 3-9).

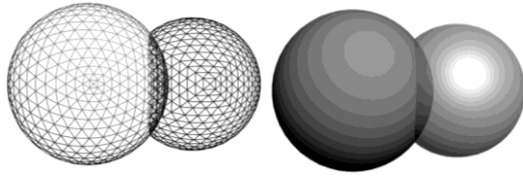


Figure 3-12. Showing the wireframe and surface renders of a spherical particle with a droplet attached. $R_p=0.62$

Figure 3-12 shows the results for the model when the energy per area (surface tension) is left at the default value of 1 for all facets. According to Young's equation (equation 3-1) this will give a contact angle of 90° . Contact angle is a key parameter in the simulation of particles in thin films and therefore it is required that this variable can be user defined.

$$\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV} \quad 3-1$$

3.2.4 DEFINING CONTACT ANGLE

The contact angle (θ) of a surface is defined according to Young's equation (equation 3-1). Where γ is the surface tension of an interface and SL , LV and SV represent the Solid-Liquid, Liquid-Vapour and Solid-Vapour interfaces respectively.

The default value for the surface tension of all facets (3D) or edges (2D) in *Surface Evolver* is the same which results in a θ of 90° . Therefore, the ratio of γ_{SL} , γ_{LV} and γ_{SV} must be balanced in accordance with

equation (3-1) to obtain the desired contact angle for the particle. For models in later chapters γ_{SL} is set to 0 and all other surface tensions are non-dimensionalised by γ_{LV} , resulting in equation (3-2).

$$\frac{\gamma_{SV}}{\gamma_{LV}} = \cos \theta \quad 3-2$$

The default value of γ_{LV} is 1, therefore by setting the surface tension of the solid-vapour interface to $\cos \theta$ the desired contact angle can be assigned. For models in section 4.6 the same approach was used but γ_{SL} was set to 0.1 and γ_{LV} to 1.1 meaning that equation (3-2) is expanded to equation (3-3) and the solid-vapour interfacial tension must be set to $\gamma_{SL} + \gamma_{LV} \cos \theta$ to obtain the desired contact angle.

$$\frac{\gamma_{SV}}{\gamma_{LV}} = \frac{\gamma_{SL} + \gamma_{LV} \cos \theta}{\gamma_{LV}} \quad 3-3$$

The change in approach to setting θ for section 4.6 was taken to make the models more robust. For the simple case of a single particle in a film used in section 4.4 a solid-liquid surface tension is not required as it is possible to monitor the model as it is running and adjust any meshing errors which may arise. However when using the more complicated series of models in the later stages of chapter 4 the addition of the solid-liquid surface tension prevents the mesh from distorting.

Using the above approach on the particle-droplet model from 3.2.3, it is possible to set the liquid phase contact angle to 45° , 90° and 135° (Figure 3-13).

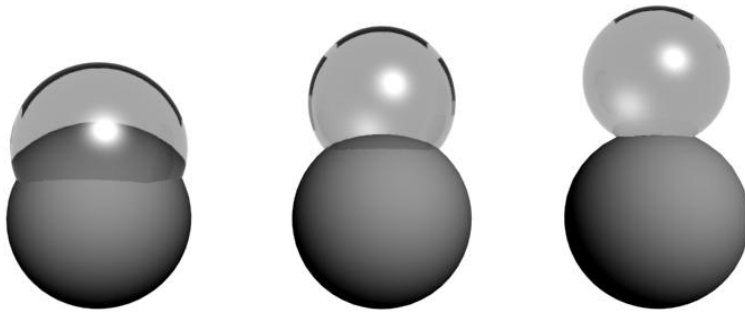


Figure 3-13. Spherical particle with liquid phase contact angle 45° , 90° or 135° (left to right) with a droplet attached.

3.3 PHYSICAL ASSUMPTIONS

Certain assumptions must be made to relate the *Surface Evolver* models used to the physical system they are approximating, these include the effects of gravity, particle size, conjoining and disjoining forces as well as the non-dimensionalisation of values in *Surface Evolver*.

3.3.1 NON-DIMENSIONALISATION OF LINEAR PARAMETERS

In the *Surface Evolver* models used throughout this dissertation all length parameters have been non-dimensionalised using the particle radius and all pressure parameters have been non-dimensionalised using the surface tension of the film (equations 3-4 and 3-5).

$$L^* = \frac{L_P}{R_P} \quad 3-4$$

$$P^* = \frac{P \times R_P}{\gamma_{LV}} \quad 3-5$$

Where L is length, R_P is the particle radius, P is pressure and γ_{LV} is surface tension of the liquid/vapour interface.

3.3.2 CONJOINING AND DISJOINING PRESSURES

The presence of conjoining and disjoining pressures acting on the film due to surfactants have been discounted in all models. Conjoining forces have been discounted as van der Waals forces are typically only of a similar magnitude to the surface tension forces in this system when the films are 10's of nm thick (Tcholakova *et al.*, 2008). Disjoining forces have been discounted as they only become strong enough to affect the film stability at a thickness of around 100 nm. Therefore the lower limit of particle diameter for this model will be around 20 μm . At this, lower size limit, disjoining pressures will begin to have an effect when the film thickness is 5 % the particle diameter

3.3.3 GRAVITY EFFECTS

The effect of gravity has also been discounted in this model. The Bond number, (equation 3-6) describes the balance between the effects of gravity and surface tension and must be much less than 1 to be able to discount gravity and can be rearranged to equation (3-7).

$$Bo = \frac{\rho d^2 g}{\gamma} \quad 3-6$$

$$\rho d^2 \ll \frac{\gamma}{g} \quad 3-7$$

The length scale d is the diameter of a particle, ρ is the difference in density of the two mediums, in this case the particle and water (about 2000 kg/m^3), g is gravitational acceleration and γ is the surface tension of water (about 0.07 N/m). For a particle of diameter 200 μm the Bond number is of the order of 0.011 and for a smaller particle size 30 μm it is 2.6×10^{-4} . Therefore the upper limit of this model is of the order of 200 μm at which point gravity begins to affect the film's shape.

3.4 2D MODELS OF PARTICLES IN A FILM

Section 3.2 introduced *Surface Evolver* and the basic approach to constructing simple models. This section will expand upon these to include the single particle in a film models in 2D that are used in section 4.4.

3.4.1 GEOMETRIC PARAMETERS

A schematic of a thin film loaded with spherical particles that bridge both its sides is shown in Figure 3-14. For the purposes of these models it has been assumed that the particles will spread evenly across the film, the separation distance S_p is defined as the distance between the centre of a particle to the midpoint of the film.

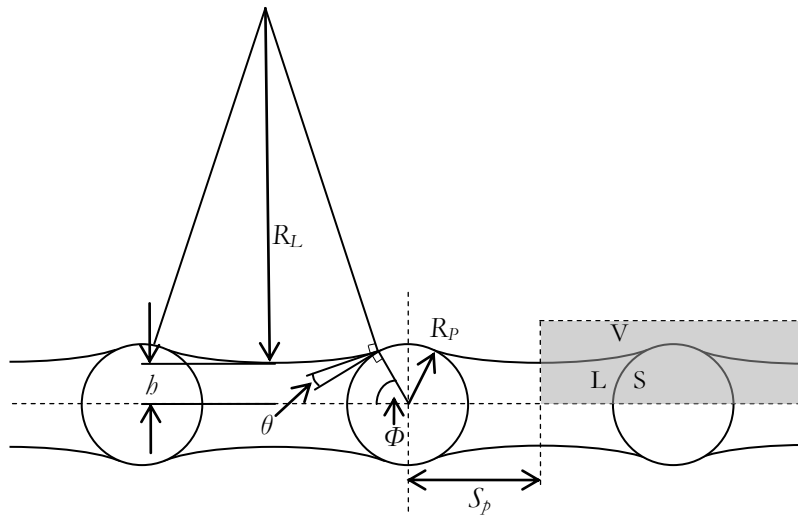


Figure 3-14. Showing a 2D particle laden film. Particles are bridging both sides of the film. The key parameters for the model are the separation distance S_p , the film thickness at its lowest point b , the particle radius R_p , and the contact angle of the particles θ . The 3 phases are also annotated with the vapour phase corresponding to V , the liquid phase L and the solid particle S . Grey area highlights the *Surface Evolver* model volume.

It is assumed that the particles are evenly spaced in the film (in reality, the particles will draw together to form rafts, some initial results dealing with particle aggregation can be found in Appendix A). b is defined as the film thickness at the lowest point in the film, this is at the mid-point between two particles in 2D. The constant radius of curvature and the uniform properties of the particles (size, shape and contact angle) mean that the arc describing film shape is symmetrical about the mid-point. Therefore, the lowest point on the arc and the films thinnest point for any given two particles will be situated at the midpoint between the two particles. If the particles are unevenly spaced, the thinnest point in the whole film will be between the two particles furthest apart.

3.4.2 STRUCTURAL DESCRIPTION OF 2D MODEL

The string model in *Surface Evolver* is used in the same way as the soap film model except that bodies are defined as a single facet, which does not have to be triangular and the energy minimisation is applied to

edges instead of facets. The model simulates the greyed section of the particle laden film depicted in Figure 3-14, corresponding to the midpoint of one film section to the midpoint of the next. Only the upper interface of the film is modelled as they are symmetrical. A circular particle is defined in the centre of the model (centred on $x=y=0$) and set on a convex circular constraint (equation 3-8), the midpoints of the film are placed on constraints corresponding to equation 3-9.

$$x^2 + y^2 = 1 \quad 3-8$$

$$x = \pm S_p^* \quad 3-9$$

A boundary is defined to represent the liquid phase of the film, allowing the capillary pressure to be prescribed in the model, and the film shape to be simulated, a typical refined and evolved model is shown in Figure 3-15.

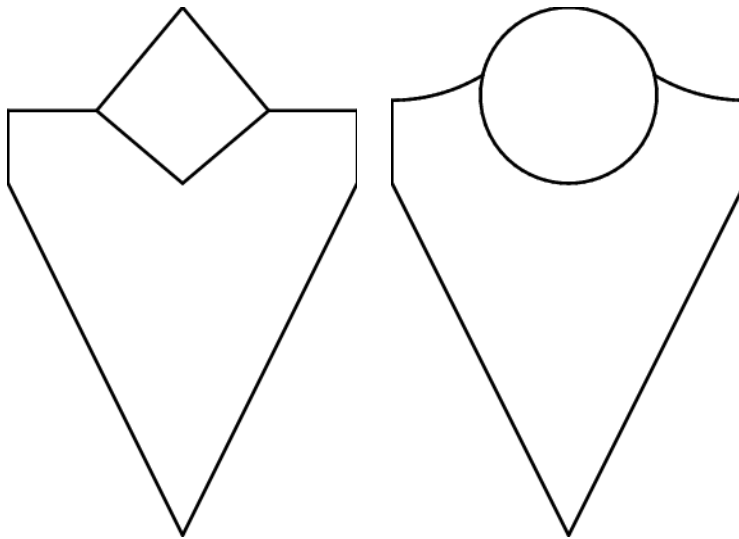


Figure 3-15. 2D model of a circular particle in a thin film. The initially defined coarse model is on the left, the refined and evolved one on the right.

The inter-particle separation distance can be changed with the value of S_p^* , which is set where the midpoint of the film lies, but does not constraint it in the y direction allowing it to move up and down freely as pressure is changed to find the line curvature that corresponds to the minimum surface energy for a prescribed pressure. The contact angle can be set as described in section 3.2.4 and the pressure can be changed once the model is loaded into *Surface Evolver*.

3.5 3D MODELS OF PARTICLES IN A FILM

Both the 2D and 3D models of particles in films used in this dissertation are subject to the same assumptions made in section 3.3. However, once expanded into 3D there are other spatial and geometric

parameters to take into account such as particle packing arrangement. The simplest particle stabilised film model to create in 3D is made by rotating the 2D model about the Z-axis creating a spherical particle in the centre of a circular film (Figure 3-16). Equation 3-8 Is now expanded to 3D in equation 3-10.

$$x^2 + y^2 + z^2 = 1 \quad 3-10$$

Whilst the model now represents a spherical particle in the film in 3D it is analogous to the 2D model as it is axisymmetric around the Z-axis. Both the 2D model in Figure 3-15 and the 3D model in Figure 3-16 will return the same critical capillary pressure for a given S_p^* and contact angle. However, by changing the shape of the boundary of the model in Figure 3-16 it is possible to simulate different regular packing arrangements.

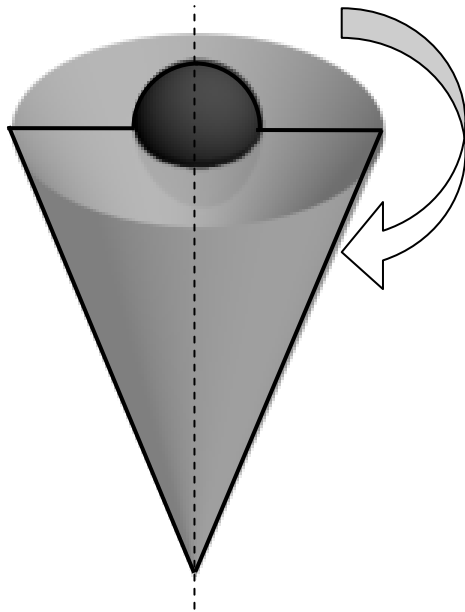


Figure 3-16. Rotation of 2D model to create a 3D model.

3.5.1 SQUARE AND HEXAGONAL PACKING GEOMETRY IN 3D

In 3D both the particle packing arrangement and particle separation distance must be taken into account, whereas in 2D only the interparticle distance need be considered. In 2D when $S_p^*=1$ there is no space between the particles for the film to move through, however in 3D, even when the particles are touching there is empty film space between them in the interstices between the particles. The shape of these interstices depends on the particle packing arrangement and affects capillary pressure required to rupture the film. Therefore modelling spherical particles in 3D can give more valuable insights into film stability than 2D analytical/simulation models. Two regular packing arrangements are considered in chapter 4, hexagonal and square, as illustrated in Figure 3-17.

The S_p^* is now expanded into two variables, S_{pp}^* and S_{pf}^* . S_{pp}^* is equivalent to S_p^* in 2D, representing the distance from the centre of a particle to the midpoint between it and its closest neighbour. S_{pf}^* is the distance from the centre of the particle to the midpoint of the film, i.e. the point furthest away from any particle, as shown in Figure 3-17. The relationship between S_{pf}^* and S_{pp}^* varies with packing pattern, for hexagonally packed particles it is defined by equation (3-11) and for square packing by equation (3-12).

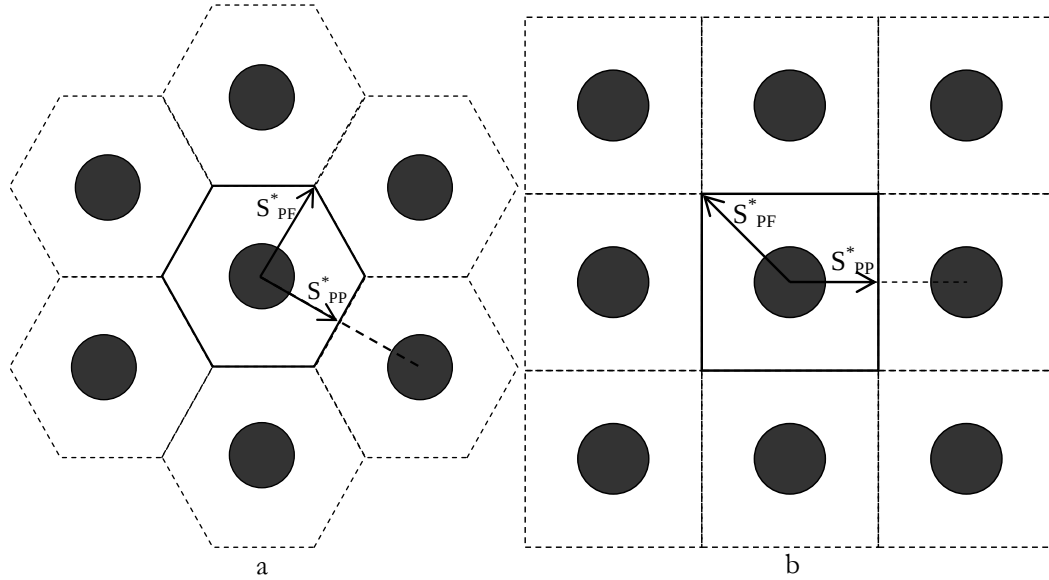


Figure 3-17. The separation distances and film boundaries for (a) hexagonal and (b) square packing. S_{pp}^* is half the distance between the centre of two adjacent particles. S_{pf}^* is distance from the centre of a particle to the midpoint of the film. The midpoint of the film is the point farthest from any surrounding particles.

$$S_{pf}^* = \frac{S_{pp}^*}{\cos 30} = 1.15S_{pp}^* \quad 3-11$$

$$S_{pf}^* = \frac{S_{pp}^*}{\cos 45} = 1.41S_{pp}^* \quad 3-12$$

Thus for a given S_{pp}^* , a square packing configuration will have a larger S_{pf}^* than a hexagonal one. The minimum separation distance allowed in both packing cases is $S_{pp}^*=1$ which, when written in terms of S_{pf}^* becomes $S_{pf}^*=1.15$ for hexagonal packing and $S_{pf}^*=1.41$ for square packing. As with the 2D models the pressure at which the film thickness h becomes zero is taken as P_{crit}^* .

3.5.2 STRUCTURAL DESCRIPTION OF REGULAR PACKING MODELS IN 3D

The dotted lines in Figure 3-17 show the boundaries around each particle with the solid black line highlighting the unit cell for the central particle. Each boundary line is at the midpoint between the two particles it separates. Therefore to simulate a periodic square packing arrangement a square outer boundary is required with edges on constraints defined by equations 3-13 and 3-14. Similarly the

hexagonal packing model requires a hexagonal outer boundary with constraints defined by equations 3-15, 3-16 and 3-17.

Square packing model boundary constraints:

$$x = \pm S_{PP}^* \quad 3-13$$

$$y = \pm S_{PP}^* \quad 3-14$$

Hexagonal packing model boundary constraints:

$$y = \pm S_{PP}^* \cos 30 \quad 3-15$$

$$x = S_{PP}^* \pm y \tan 30 \quad 3-16$$

$$x = -S_{PP}^* \pm y \tan 30 \quad 3-17$$

These constraints allow the particle packing distance to be changed by altering the values of S_{PP}^* and S_{PF}^* . The models are described with the minimum number of vertices, edges and facets needed, the initial models are shown in Figure 3-18. The model is then refined before evolution to the minimum energy surface for the prescribed pressure. The results and discussion for these models are presented in section 4.5.

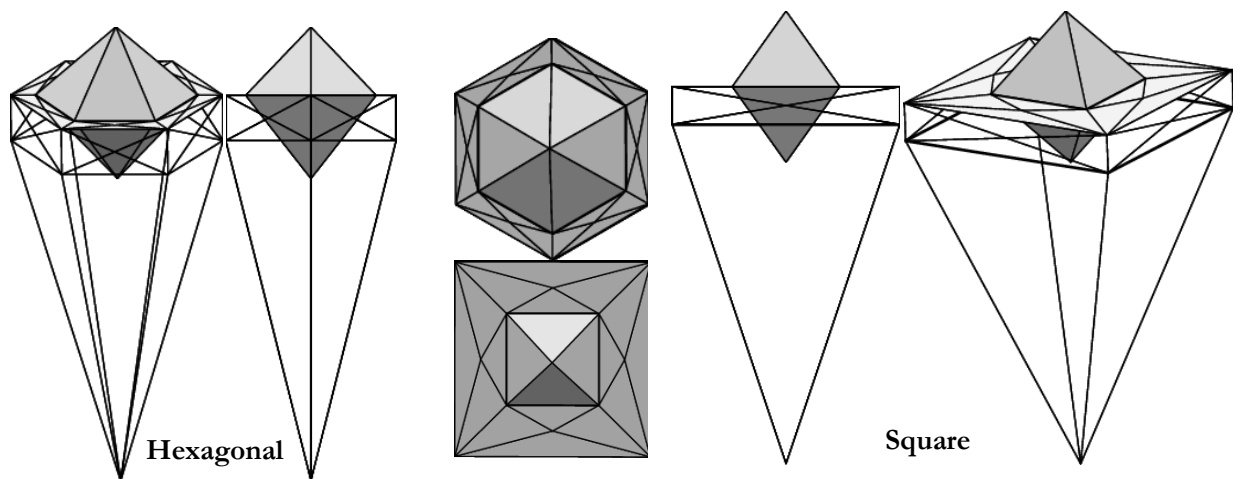


Figure 3-18. Showing the initial models for square and hexagonal packing of spherical particles.

3.6 RANDOM PACKING MODELS IN 3D

Particles do not always arrange themselves in regular packing distributions when at an interface. It is therefore necessary to develop a model which is capable of simulating systems where the particles are not all uniformly arranged in the film.

The assumptions made for both the 2D and 3D single particle models in section 3.3 hold true for the multiple particle models. It has also been assumed that the particles are arranged randomly in a flat film in a single layer with all particles bridging both sides of the film, all particles are assumed to be identical.

3.6.1 BOUNDARY CONDITIONS

3D models of regularly spaced particles described in sections 3.4 and 3.5 used constraints describing straight lines represent the boundaries of periodic cells. As the system being modelled is periodic and also symmetric along the boundary these constraints are a tractable way of defining a periodic cell. However for the larger systems containing more than one randomly spaced particle a true periodic surface is required. *Surface Evolver* can take its domain as a flat torus with an arbitrary parallelepiped as its unit cell by specifying the *torus* keyword at the beginning of the datafile. The size of the period cell can then be defined in the datafile. The geometry must be altered to take into account the periodic nature of the model as well, the film interfaces are defined as two individual surfaces as before but there are no boundary edges. Edges leave one side of the model and come back on the opposite side, this is defined in the *Surface Evolver* datafile using *, + and - characters after each of the edges listed, shown Figure 3-19.

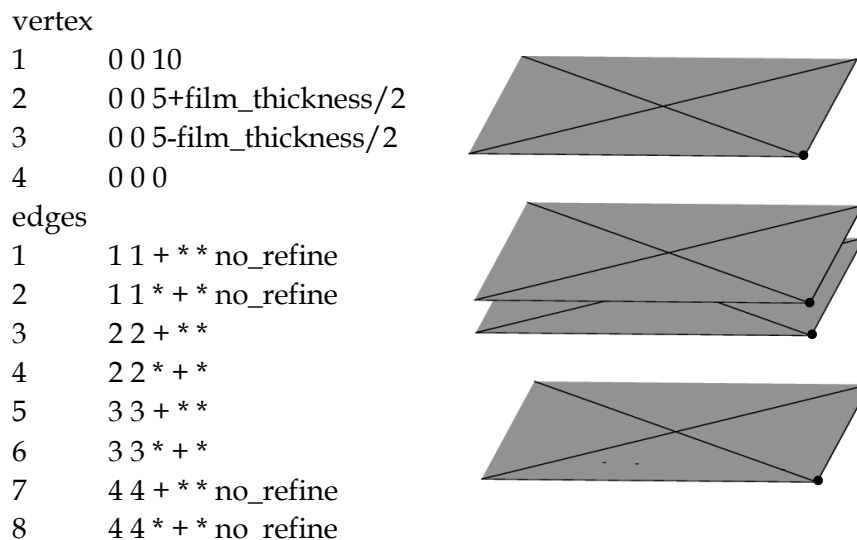


Figure 3-19. Showing the initial periodic cell once loaded into *Surface Evolver* and details of the vertex and edge description in the datafile. *no_refine* is a setting in the datafile that prevents *Surface Evolver* from needlessly refining the edges in the uppermost and lowermost facets. *film_thickness* is a constant that is used to set the initial film thickness in the model. Vertices 1-4 are highlighted by the small black circles in the lower right corner of each surface. Vertex 1 is at the top, 4 at the bottom, 2 and 3 in the middle.

For example an edge which leaves the boundary in the positive x-direction and comes back into the cell on the opposite side of the model will have the characters "+ * *" after its vertex listing. If it was the y or z-direction instead it would be "* + *" "* * +" respectively). This allows each interface to be specified with only one vertex, with that vertex acting as the head and tail for the two edges required to describe the facets as shown in Figure 3-19. The uppermost and lowermost surfaces in Figure 3-19 are used in conjunction with their closest respective film surface to describe the upper and lower bodies that allow the prescription of capillary pressure in the model.

The model pressure can be set as before and it can be refined and evolved in the same manner as the previous models. The film failure criteria remains the same, i.e. when $h=0$ which must be calculated slightly differently as the centre of the film is now at $\tilde{x}=0$. However there are no particles in the film, these need to be placed within it before the model can be used.

3.6.2 PARTICLE POSITIONING AND CONSTRAINTS

Particles are placed on spherical constraints as described in section 3.5, however equation 3-10 is for a sphere at the origin, therefore the spherical convex constraint is modified to equation 3-18 to allow the particle position to be defined.

$$(x - PP_{i1})^2 + (y - PP_{i2})^2 + (z - PP_{i3})^2 = 1 \quad 3-18$$

Where PP_{ij} is a matrix containing all of the particle positions, i is the particle number and subscript 1, 2 or 3 refer to the columns of the matrix storing the x, y or z coordinates respectively. All particles are set to have a non-dimensionalised radius of 1. By altering the values in the matrix PP_{ij} the constraint values that reference them and therefore the particle positions can be set or changed by the user. This method can be used in both periodic and non-periodic models.

3.6.3 PARTICLE CONSTRUCTION

A periodic film has been defined and the method by which the particle positions are set has been explained. Next the particles must be placed in the film. There are six steps required to insert a particle into an empty (periodic or non-periodic) film;

1. Identify the position of the particle and the facet closest to it.
2. Define particle edges (The vertices required already exist).
3. Define particle facets.
4. Assign facets to particle body.
5. Assign particle components (vertices, edges and facets) to spherical constraint.
6. Refine particle to a sphere.

The initial model in Figure 3-19 is refined several times until the facets are roughly 10 % of the particle cross-sectional area. Once the position of the particle is known (user defined or random coordinate) a facet in the upper film must be chosen as the seed for the particle. The coordinates of the centre of each facet are found by taking the average coordinate of its three vertices and then comparing the position of the centre of the facet to the desired particle position, the closest facet is then chosen as the seed. The facet directly below the seed facet, in the opposite interface, is also used. These two facets will become the solid-vapour interface of the particle (Figure 3-20a).

Edges are now created between the vertices of the two facets which are then used to define three new rectangular facets in between the two films. These facet are immediately split into four each as *Surface Evolver* automatically turns them into triangles. These newly defined facets will make up the solid-liquid interfaces of the new particle (Figure 3-20b).

The newly defined facets and the two chosen seed facets are now assigned to a new body, care must be taken to ensure all facets are listed in the correct direction (positive or negative) when defining the body. The facets, edges and vertices of the new particle are put on a constraint and the values of the particle position entered into the corresponding matrix positions (Figure 3-20c). The particle is now complete but is represented at a very low resolution, all the edges on the particle are now refined three times to create a well defined sphere (Figure 3-20d and e).

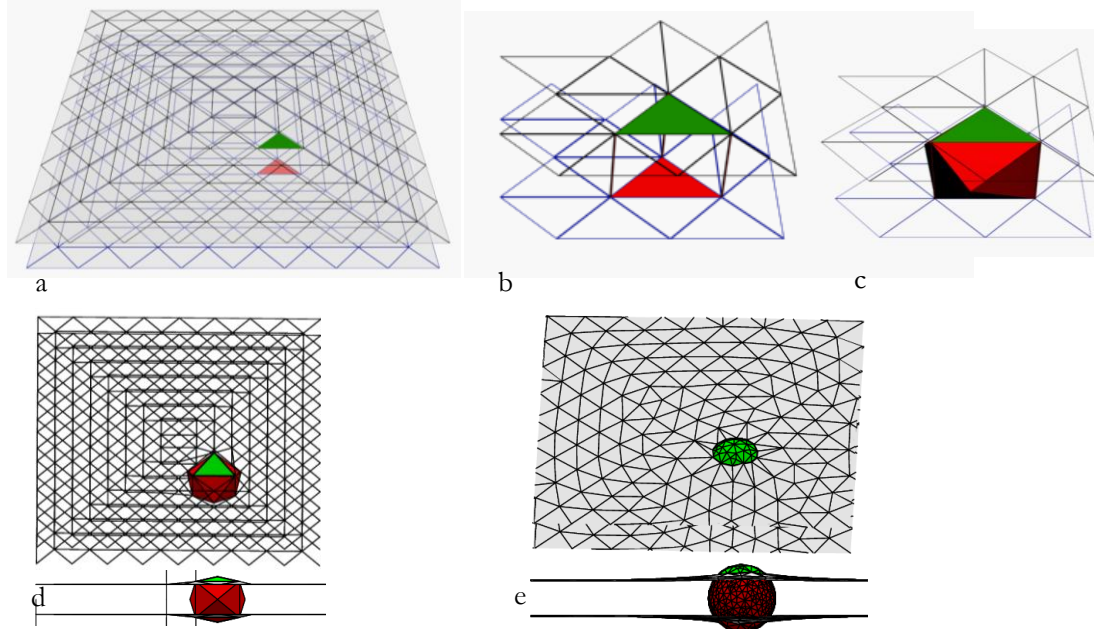


Figure 3-20. The steps involved in defining a particle; (a) Facets are chosen for the solid-vapour interfaces. (b) Edges are constructed. (c) Facets are defined to form a continuous surface. (d) Facets are assigned to particle body to form a coarse representation of the particle. (e) Particle edges are refined to produce a well-defined spherical particle.

This procedure can now be repeated for as many particles as are required to create a random distribution of particles in a thin film or a specific, user defined pattern.

3.6.4 CREATING PERIODIC MODELS

A square, periodic boundary with an edge of length of L_p^* is used for the periodic modelling of irregularly packed particles (Figure 3-21). As with all other length scales L_p^* is non-dimensionalised by R_p according to equation (3-4).

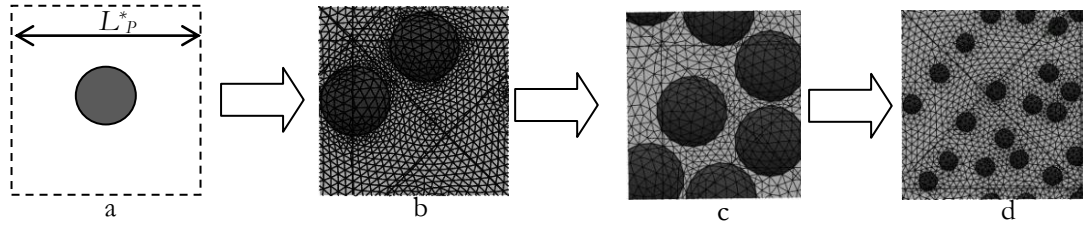


Figure 3-21. Original square period cell with one particle (a) and more complex irregularly placed particle models (b), (c) and (d)

By changing the number of particles placed in the film and the values of L_p^* it is possible to create models with varying packing densities. It is therefore possible to investigate the effect of variable $\mathcal{A}_{pp}^*$ for random packing arrangement by varying L_p^* and the number of particle in the film.

3.7 MESH REFINEMENT

The *r* command in *Surface Evolver* automatically refines the entire model as described in section 3.2, this command will ignore edges and facets that have *no_refine* specified in the datafile (e.g. Figure 3-19) but is otherwise a global command. Specific facets and edges can be refined using the *refine edge[i]* or *refine facet[i]* command, where *i* is the id number of the element. Maintaining a well balanced mesh in the model is an important factor when running the *Surface Evolver* simulations, if it is too coarse the curvature of the film cannot be accurately resolved, if it is overly refined the time taken to reach the minimum energy surface becomes prohibitively long.

Mesh geometry problems can also arise, especially at the Three Point Contact (TPC). If a facet has two edges on the TPC it prevents the edges from straightening out or curving in the opposite direction if they need to. This distorts the TPC and as a result the interface surrounding the particle. There is a command *edgeswap* which can be used on edges where this has occurred, it swaps the vertices of the edge as shown in Figure 3-22.

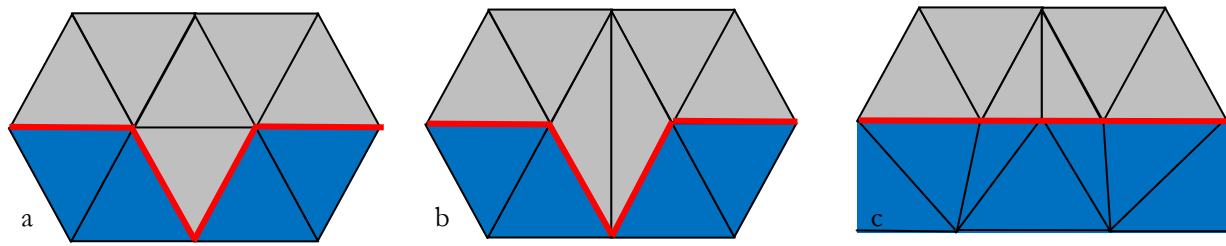


Figure 3-22. Shape of the TPC before (a) and after (b) *edgeswap* is used to correct the mesh geometry. (c) shows how the TPC can now reform to a straight line after evolution.

When finding the minimum energy surface for the single particle models the edge lengths are kept within certain bounds, each edge length is checked, if it is greater than $0.03 R_p^*$ it is refined and if it is lower than $0.012 R_p^*$ it is deleted. This prevents the film surface from developing large facets in areas where the TPC has moved away leaving a few, once small facets to cover a much larger area at lower resolution. The reverse is also true, where a large number of facets have been contracted into a smaller area, edges are deleted to increase computing efficiency.

Once the models become more complex and more particles are present, as in the multi-particle models, the simple approach used for single particle models is no longer the most computationally efficient way to manage the mesh. Therefore a method of refining the mesh in areas where extra resolution is needed but keeping it coarse in areas where there is little film curvature is used. Two lower and upper limits for edge length are defined, one set for edges falling in the fine resolution areas and one set for edges falling in the coarse areas. The film surface is at its most curved when it is near the particles in the film, at further distances from particles there is less curvature and a coarser mesh can be used. Therefore, the distance from the centre of a facet to the centre of the closest particle is used as a measure of whether its edges should be refined or not. Each particle has a radius of 1 and the mesh refinement criteria used are;

- An edge is refined if its associated facet is closer to a particle than $1.5 R_p^*$ and if its length is greater than $0.3 R_p^*$.
- If the associated facet is further than $2.5 R_p^*$ from its closest particle and is shorter than $0.75 R_p^*$ it is deleted.
- There is a universal check on all edges and if they are smaller than $0.05 R_p^*$ they are deleted.
- For all edges on a particle the upper and lower limits on edge length are $0.3 R_p^*$ and $0.05 R_p^*$.
- For facets with an area larger than $0.01 R_p^{*2}$ each edge length is checked. If they have any edges that are 2.5 times longer than any another in the same facet, the facet is refined. This prevents long thin facets distorting the film.

This is coupled with the TPC checks and the *edgeswap* command to ensure the TPC remains robust and the mesh remains computationally efficient. This collectively termed the *adaptive_mesh* procedure and can be read into *Surface Evolver* and run on any mesh, Figure 3-23 shows an example of an adaptively refined mesh.

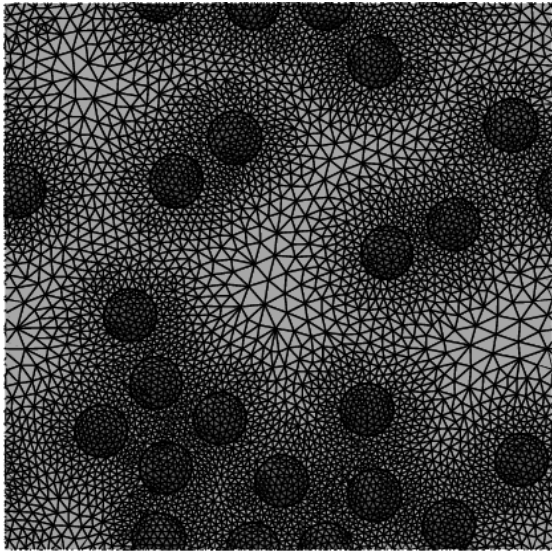


Figure 3-23. Periodic cell with an edge length of 15, containing 20 particles that has undergone 4 *adaptive_mesh* iterations.

3.8 DOUBLE PARTICLE LAYER MODELS

Chapter 5 investigates the stability of a hexagonally packed double layer of uniform spherical particles in a film using *Surface Evolver*. Two models are used in chapter 5, both of which are based upon the hexagonal packing model described in section 3.5.1. The 3D double layer of particles is more complex than the single layer as each particle must be in contact with three of the particle in the opposite layer. The vertical distance between particles in opposite layers is also dependent upon the lateral spacing of the particles in each layer.

3.8.1 STRUCTURE OF A DOUBLE LAYER

The structure of a double layer in a close packed hexagonal arrangement is very similar to that of a single layer except there are now two layers of particles, offset and one on top of the other. Additionally each layer only now bridges one interface (Figure 3-24).

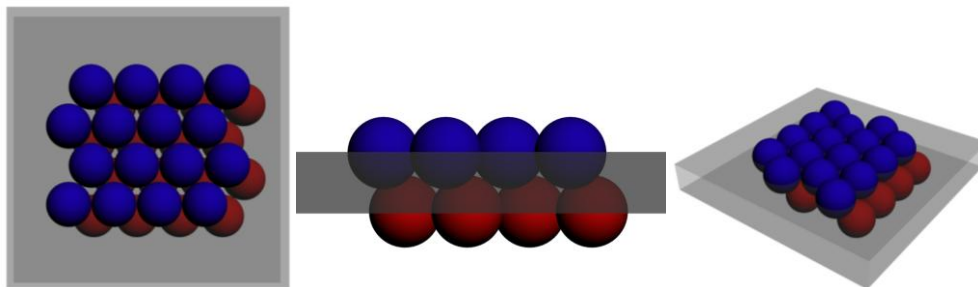


Figure 3-24. Close packed double layer of particles in a film.

As the separation distance between particles increases the layers begin to move into one another so that each particle maintains contact with the three nearest particles in the opposite layer. This also brings the

two film interfaces closer to the particles in the opposite layer and at some point they bridge the film. There is now still a distinct double layer of particles but they bridge both sides of the film (Figure 3-25).

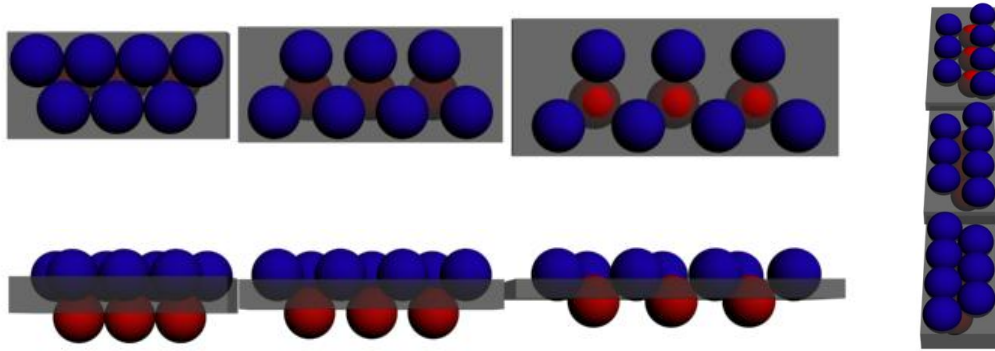


Figure 3-25. Double layers with different inter particle separation distances. ($S_{pp}^* = 1, 1.2, 1.5$) At larger separation distances particles bridge both sides of the film whilst maintaining a distinct double layer pattern.

There are therefore two distinct models required for a double layer of particles; one in which the film is bridged by only one layer of particles and one in which both layers of particles have bridged and both sides of the film.

3.8.2 UN-BRIDGED DOUBLE LAYER MODEL

This model is used in chapter 5 to identify the maximum capillary pressure that an un-bridged double layer can withstand and when particle bridging occurs. The conditions which are investigated are described in detail in section 5.2, but one of the factors that must be taken into account in the model design is that the capillary pressure will pass through a maximum.

As the particles only bridge one side of the film the same model as used for a single layer of particles in a hexagonal formation can be used. All geometric parameters and physical assumptions remain the same as in section 3.2, 3.3 and 3.5.1 except one, the prescribed pressure. Instead of prescribing the pressure and calculating the volume of the cell, the volume is prescribed and the pressure calculated. The reasons for this are explained in detail in section 5.3.1.

Therefore, in the *Surface Evolver* datafile the only change is to replace "pressure" with "volume" after the list of facets attributed to the body of the gas phase.

3.8.3 BRIDGED DOUBLE LAYER MODEL

Once the film has bridged both layers of particles the structure of the models changes. Now both layers of particles must be in the film at different levels. The unit cell used is still a hexagon, as the pattern still tessellates in this manner, but it is offset so that the centre of the model is now over one of the interstices between the particles. The unit cell is highlighted in Figure 3-26.

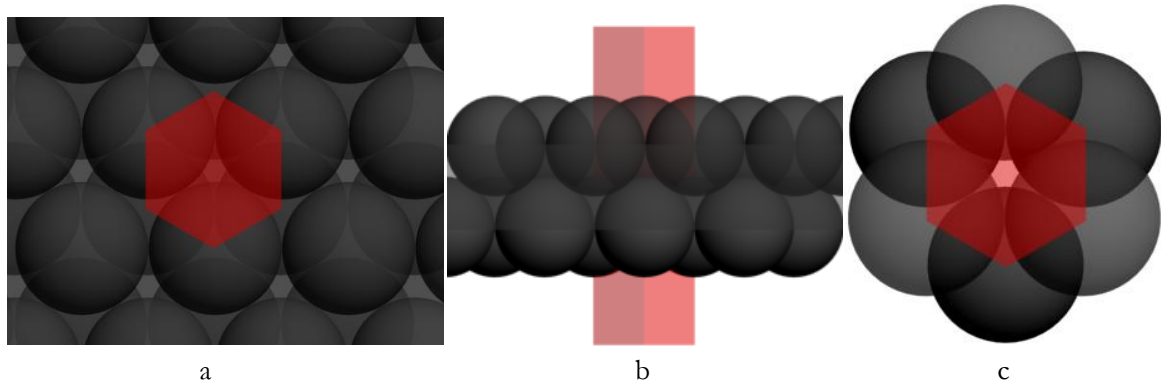


Figure 3-26. The unit cell for a double layer of particles. Red hexagon highlights the cell in the bulk double layer (a), from the side (b) and from just the surrounding particles (c).

The unit cell in Figure 3-26 is unbridged, but the particle packing is the same. The *Surface Evolver* model uses the same cell with six particles, one at each corner of the hexagon but with the films bridged by both layers. The initial model is shown in Figure 3-27. Each particle is on a convex constraint and the boundary shape is defined in the same way as for the hexagonally packed single layer of particles, as are the two gas phases. The particles in the two layers have their distance from the $z=0$ plane defined by equation 3-19, derived from basic geometric considerations of particles packed in regular hexagonal arrangements.

$$z = \pm \sqrt{\frac{2R_p^{*2} - \frac{4S_{pp}^{*2}}{3}}{2}} \quad 3-19$$

This model of a double layer is used to identify the critical capillary pressure at which the bridged film will fail for a range of contact angles and particle separations in chapter 5.

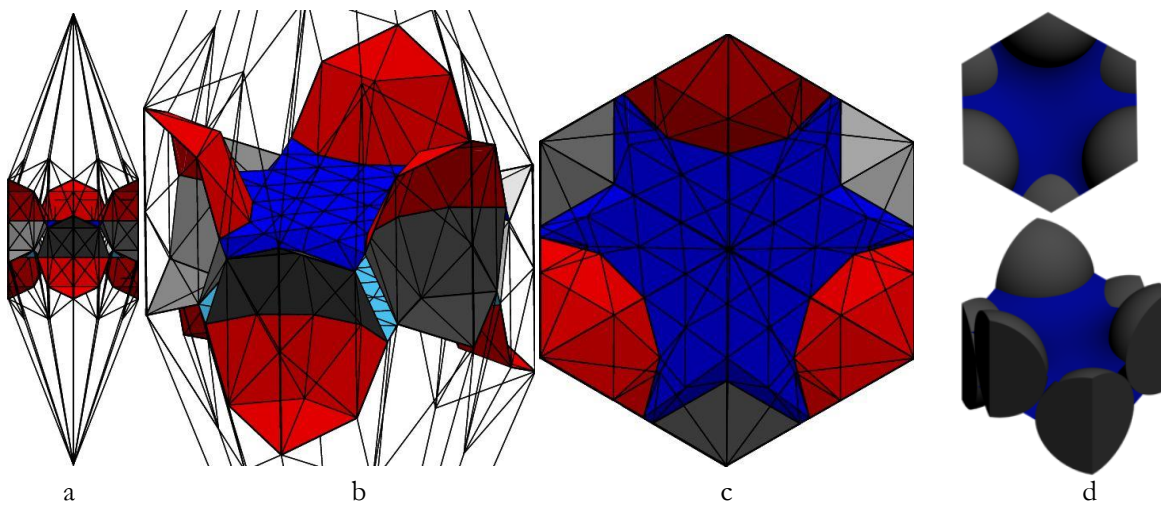


Figure 3-27. Basic bridged double layer mesh in *Surface Evolver*, viewed from the side (a), on angle (b) and top (c). (d) shows the evolved surface from the top and on angle.

3.9 NON-SPHERICAL PARTICLE MODEL

Many previous modelling and analytical studies, both in 2D and 3D have studied the effect of spherical particles and their properties on the film stability (Ali *et al.* (2000), Denkov *et al.* (1992) and Kaptay (2004)). However, the particles found in industrial foams and films are not usually spherical and are often irregularly shaped, possessing sharp edges and asperities which affect their behaviour in the film (Frye and Berg 1989, Dippenaar 1982). Whilst insights into film stability and particle behaviour can be gained from models of spherical particles, it is still desirable to develop them so that they can simulate non-spherical particles.

The use of a convex constraint to make a spherical particle has already been described in the previous sections, alternatively, the particle shape can be described as a series of surfaces with the vertices on each face of the particle set to a different constraint. For example a cylinder with $x^2+y^2=r^2$, $z=-r$, $z=r$ for the column and the two ends respectively (Figure 3-28).

It is clear that to study a large number of particle shapes this approach is inconvenient as each particle requires a different set of constraints to define it. Ideally, all particle shapes would be defined by a single constraint, and a single surface. The particle shape would then be controlled by altering the constants of the constraint. A superquadric equation can be used to create such a constraint.

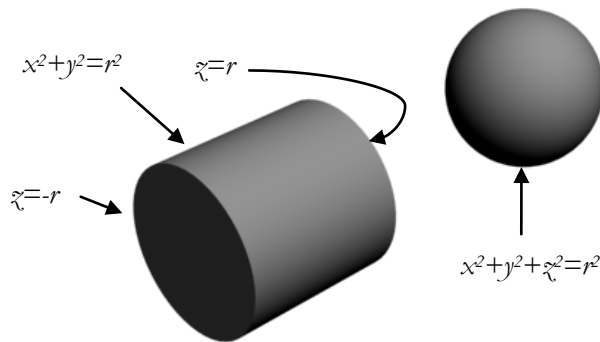


Figure 3-28. Equations used to define a cylinder and a sphere.

3.9.1 PARTICLE SHAPE

Many different shapes of particle can be generated using a superquadric equation to define the surface of the particle. A superquadric equation is capable of describing a parametric shape as a continuous surface in either 2D or 3D (Zhou 2001). Equation (3-20) shows the basic superquadric equation in 3D.

$$\left| \frac{x}{s_1 R_p} \right|^{\varepsilon_1} + \left| \frac{y}{s_2 R_p} \right|^{\varepsilon_2} + \left| \frac{z}{s_3 R_p} \right|^{\varepsilon_3} = 1 \quad 3-20$$

In equation (3-20), x, y and z are the coordinates of any point on the particle surface (for example the vertices of the particle in the *Surface Evolver* model). The squareness parameter ε_i (where $i=1, 2$ or 3) controls the shape of the superquadric while the values of s_i change the ratio of the length, width and height of the particle. Finally, R_p defines the particle size.

For example, if $s_1 = s_2 = s_3 = 1$ and $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 2$, equation 3-20 represents a sphere of radius R_p . If $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 20$ is used instead, the particle described is a cube with slightly rounded edges, and an edge length of $2R_p$. Increasing ε_i above 20 causes edges of the cube to become sharper. If $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 1$ the particle shape is an octahedron. It is also possible to alter the particle aspect ratio and size by changing the values of s_1, s_2 and s_3 . An increase in any one of the s_i will lengthen the particle along the corresponding axis. Figure 3-29 shows a selection of the particle shapes that can be generated by changing these values. Varying R_p will, of course, increase or decrease the particles overall size.

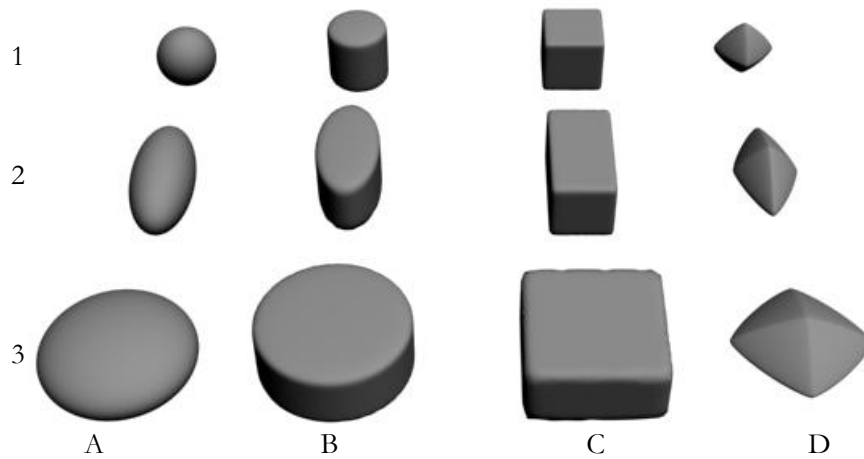


Figure 3-29. Examples of varying s_i and ε_i . Column A $\varepsilon_{1,2,3}=2$, B $\varepsilon_{1,2}=2, \varepsilon_3=20$, C $\varepsilon_{1,2,3}=20$, D $\varepsilon_{1,2,3}=1.25$. Rows (1) $s_{1,2,3}=1$, (2) $s_1=2, s_{1,3}=1$, (3) $s_{1,2}=2, s_3=1$.

The superquadric constraint defines the particle as a single continuous surface. Whilst this allows a great number of particle shapes to be easily created, care must be taken when simulating particles with sharp edges. When the contact line passes over a sharp edge, like that found on an orthorhombic crystal particle its contact angle can no longer be defined. Whilst the true contact angle remains constant, it appears trapped at the edge and its apparent value changes (Rusanov and Prokhorov 1996). It is, however, possible to create edges with very small radii of curvature that approximate these sharp edges by using large values of ε_i ($\varepsilon_i > 200$) an example is shown in Figure 3-30.

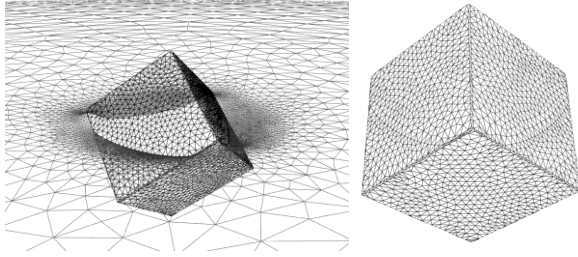


Figure 3-30. Cubic particle generated using $\varepsilon_i=200$.

As the particle surface and shape is defined by the constraint, the same simple initial particle surface can be used to create the desired shape of particle, in this case an octahedron which requires only six points. As the mesh is refined and the resolution of the model increases a more accurate representation of the desired shape emerges (Figure 3-31).

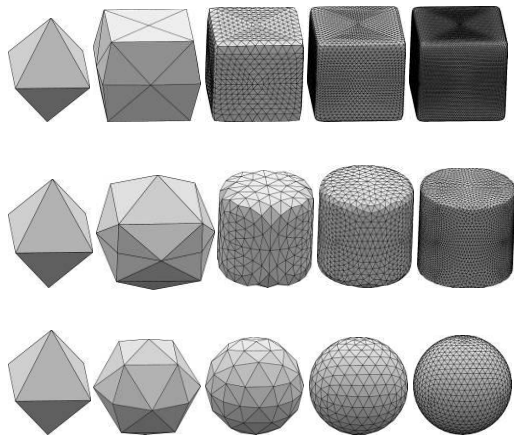


Figure 3-31. Examples of particle shapes at various mesh refinements all starting from the initially defined particle volume.

By reducing the number of variables required to create each new particle the complexity of the initial model can be reduced, making it more robust. It also makes it less time consuming to create particles whilst allowing their shape to be changed easily and quickly should this be required.

3.9.2 PARTICLE ROTATION

Once the particle is no longer spherical, its orientation will affect the film shape. For a particle of given shape and contact angle the film surface energy will change depending on its orientation. Therefore there are some orientations that produce a film with a lower energy than others. This results in energetically stable and unstable orientations that depend on particle contact angle and shape.

The orientation of a particle is accommodated by combining the shape constraint with a rotational matrix. By combining equation (3-20) with rotational matrices around the X, Y and Z axis it is possible to define a constraint that allows not only a user defined shape but also orientation of particle. This in turn allows the model to be used to investigate the effects of particle orientation on film energy and film stability.

Equation (3-21) results in equations (3-22), (3-23) and (3-24) for $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ which are then substituted into equation (3-20) in place of x , y and z . Where α , β and γ represent the angle of rotation around the X, Y and Z axis respectively and x , y and z are the Cartesian coordinates to be rotated.

$$\begin{bmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \left(\begin{bmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{bmatrix} \times \left(\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix} \right) \right) = \begin{bmatrix} \mathbf{x} \\ \mathbf{y} \\ \mathbf{z} \end{bmatrix} \quad 3-21$$

$$\mathbf{x} = x \cos \beta \cos \gamma + y \sin \alpha \sin \beta \cos \gamma + z \cos \alpha \sin \beta \cos \gamma - y \cos \alpha \sin \gamma + z \sin \alpha \sin \gamma \quad 3-22$$

$$\mathbf{y} = x \cos \beta \sin \gamma + y \sin \alpha \sin \beta \sin \gamma + z \cos \alpha \sin \beta \sin \gamma + y \cos \alpha \cos \gamma - z \sin \alpha \cos \gamma \quad 3-23$$

$$\mathbf{z} = -x \sin \beta + y \sin \alpha \cos \beta + z \cos \alpha \cos \beta \quad 3-24$$

The specification of particle rotation around the X, Y or Z axis is now controlled by changing the values of α , β and γ respectively (Figure 3-32). This theoretically allows any orientation to be defined, however, the actual rotation of the particle around the X axis changes when it is subsequently rotated around the Y axis. Whilst this can be compensated for, to better present results and describe the orientation more clearly it is necessary to develop an alternative method for referring to the particle orientation for an orthorhombic particle, described in the next section.

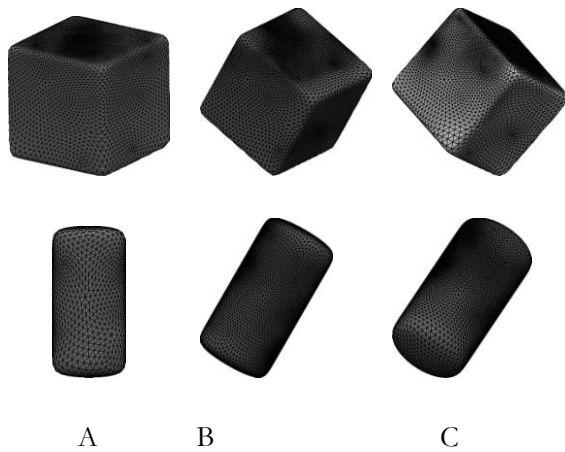


Figure 3-32. A cubic and cylindrical particle at orientations of (A) $\alpha=\beta=\gamma=0^\circ$, (B) $\alpha=30^\circ$, $\beta=\gamma=0^\circ$ and (C) $\alpha=\beta=30^\circ$, $\gamma=0^\circ$

3.9.3 DESCRIBING PARTICLE ORIENTATION

It is first assumed that there is a circular boundary to the film in the *Surface Evolver* model, allowing the rotation around the Z-axis (γ) to be discounted. When α , β and γ are equal to 0° the cube has two faces in

each of the XZ, YZ and XY planes. If the normals of three of the orthogonal faces are taken as N_1 , N_2 and N_3 , then the angles made between N_1 , N_2 and N_3 and the Z axis are shown in Figure 3-33 and can be written θ_{N1} , θ_{N2} and θ_{N3} . For all cases $\sin(\theta_{N1})^2 + \sin(\theta_{N2})^2 + \sin(\theta_{N3})^2 = 2$, i.e. any orientation can be described using only two of the angles θ_{N1} , θ_{N2} or θ_{N3} . These are related to the α and β values in the model by equations (3-25) and (3-26). This approach can be used to describe individual orientations for all particle shapes.

$$\beta = 90 - \theta_{N1} \quad 3-25$$

$$\alpha = \sin^{-1} \left(\frac{\cos \theta_{N2}}{\cos \beta} \right) \quad 3-26$$

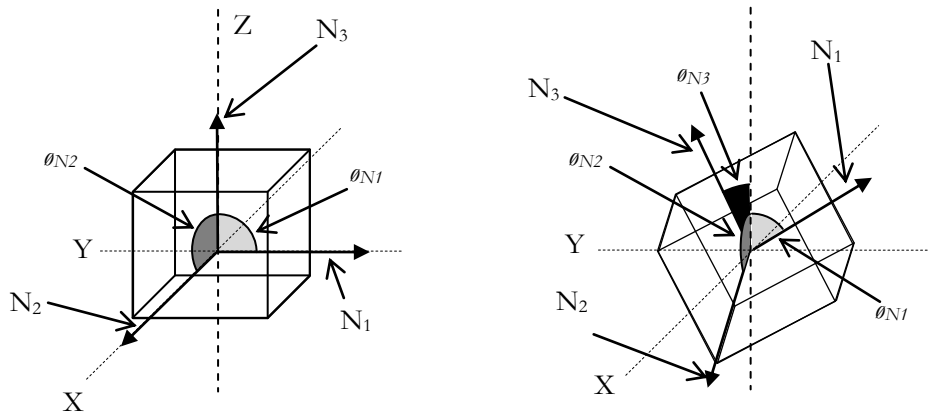


Figure 3-33. Showing the angles θ_{N1} , θ_{N2} and θ_{N3} , made by the facet normals (N_1 , N_2 and N_3) and the Z-axis.

It is now possible to define the shape of the particle as well as its orientation at an interface. If the particle is placed at an interface, the contact angle can be altered by changing the ratio of surface tension associated with the three interfaces γ_{SV} , γ_{SL} and γ_{LV} as detailed in section 3.2.4. This model can now be used to investigate the effect of contact angle on the stable orientations of particles in thin films or interfaces.

3.9.4 SURFACE EVOLVER MODEL

Two cases are investigated in chapter 6, one in which an orthorhombic particle is attached to a thick film and has bridged only one side of it (Figure 3-34a) and the second where the film has thinned sufficiently to allow the particle to bridge both sides of the film (Figure 3-34b). The outer boundary of the film, whilst constrained to a circle is free in the Z direction allowing the edges to move up and down. The first model is used to identify the stable orientations that a particle of given contact angle and shape will adopt in the film. Once these stable orientations have been identified the second model is used to investigate the effect of particle orientation on film stability.

In the experimental work carried out by Dippenaar (1982) the contact angle of the galena used was between 72° and 88° . In the simulations in chapter 6 contact angles between 45° and 90° were used. In the 2D analysis carried out by Dippenaar (1982) this was the range of contact angles over which either a horizontal or diagonal orientation was found to be stable. The single film model was set up with a single cubic particle in the centre of a circular film with a radius 15 times that of the particle edge length. This is in line with the experimental apparatus used by Dippenaar. The model used to investigate film failure used a circular film of radius $5R_p$.

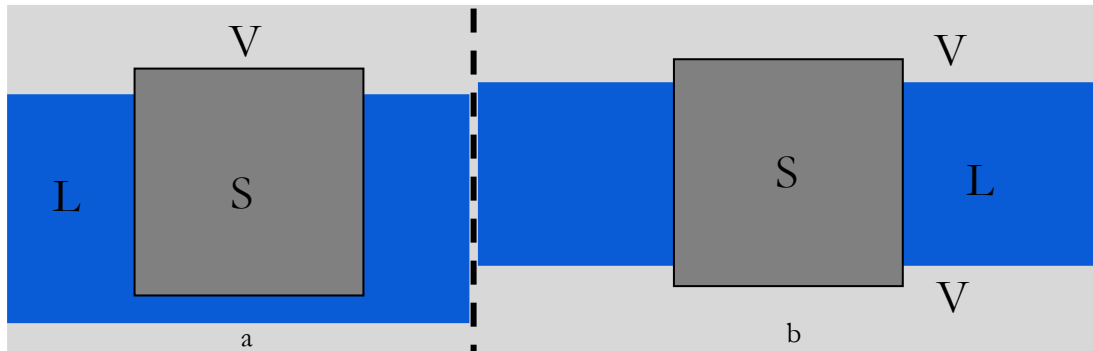


Figure 3-34. Galena particle bridging both sides of a film (a) and one side of a film (b). S is the solid phase, V the vapour phase and L the liquid phase

The contact angle of the particle is a key parameter as this determines the film's surface topology, energy and failure point. It is defined as described in section 3.2.4. Assumptions made regarding the effect of gravity, conjoining and disjoining pressure and non-dimensionalisation of length and pressure made in sections 3.3.1, 3.3.2 and 3.3.3 also remain the same for non-spherical particles.

3.9.5 SIMULATIONS TO IDENTIFY STABLE ORIENTATIONS

The model with only one surface bridged by the particle is used to investigate the effect of contact angle on particle orientation. To identify the stable orientations associated with a given contact angle the energy for each orientation must be found and used to create an energy surface.

To generate a point on the surface energy plot, the particle is assigned a contact angle and rotated to a specific orientation. The minimum energy film surface is then found using *Surface Evolver* and the energy of the model is extracted and stored for that orientation and contact angle. The energy used is the sum of the model's surface energy and prescribed pressure energy. The surface energy is the sum of the area of each facet multiplied by its surface tension plus the 'gap' energy associated with the convex constraints. The prescribed pressure energy is set to 0 and can be discounted as a contributing factor to the energy of the model. Therefore the energy calculated is the sum of surface energies, or the Gibbs energy. By repeating this process for many different particle orientations the data required to generate the surface energy plot is built up. This process is then repeated for various values of θ allowing the variation of stable orientation with θ to be found.

To generate a plot with sufficient resolution to identify the energy minima, the orientations need to be roughly 5° apart. Any further apart than this and the energy minima cannot be discerned. The model used has the particle inside a film with a circular boundary thus the liquid-vapour interface will be invariant with rotation around the Z-axis and only two θ_{Ni} need to be used. For the cases discussed in chapter 6 the angles used are θ_{N1} and θ_{N2} , which correspond to two orthogonal faces on a cubic particle with normals at 90° to the Z-axis when $\alpha=\beta=\gamma=0^\circ$. When the energy obtained from the evolved models is plotted against the corresponding values of θ_{N1} and θ_{N2} an energy landscape is created. This allows the identification of local minima, representing energetically stable orientations, circled in Figure 3-35.

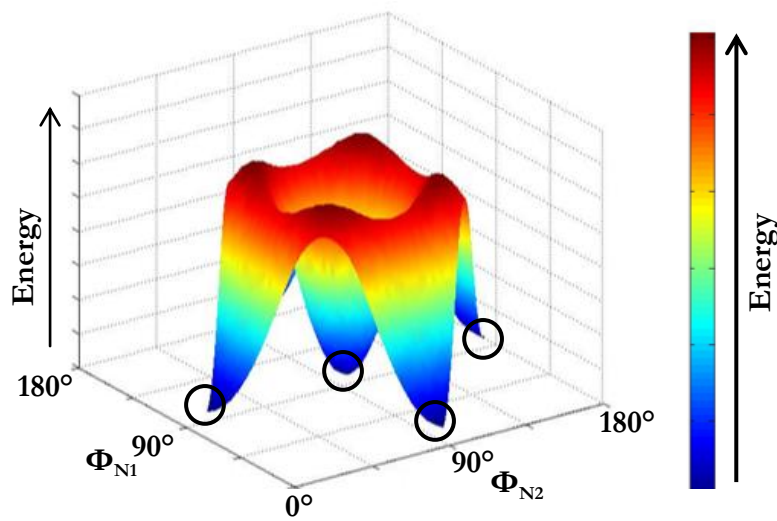


Figure 3-35. The energy surface landscape of a cubic particle with a contact angle of 45° . Circles highlight stable orientations at the energy minima where visible.

For any given particle in this model the limits for the full set of orientations of θ_{N1} and θ_{N2} are from 0 - 180° . At a 5° separation of values of θ_{N1} and θ_{N2} this requires roughly 1400 data points to fully resolve the complete set of particle orientations possible. This is not only computationally intensive but time consuming, thus it is desirable to reduce the number of simulations required.

For any particle with planes of symmetry many orientations are effectively duplicates of each other. For example the interfaces minimum energy surface is the same for a cubic particle sitting vertically in a film, whichever one of its faces are in the vapour phase.

For this model simulations were conducted with values of θ_{N1} and θ_{N2} bounded by $\theta_{N1}=0^\circ/\theta_{N2}=90^\circ$, $\theta_{N1}=90^\circ/\theta_{N2}=0^\circ$ and $\theta_{N1}=90^\circ/\theta_{N2}=90^\circ$. This still has a single line of symmetry in it through $\theta_{N1}=\theta_{N2}$, however for purposes of comparing data with non-cubic particles in later sections this is retained. These limits, with points spaced at 5° intervals have been used to identify the energetically stable orientations on an energy surface generated from 190 orientations.

3.10 SUMMARY

This chapter has introduced the *Surface Evolver* program and how to use it to create models of particles in thin films. The approaches used to generate and manipulate the models used in later chapters have been described here and finer detail of the running conditions can be found in the relevant chapters.

In the following chapters the single particle models in 2D and 3D are used to investigate film failure at various contact angles and separation distances for regularly packed particles in chapter 4. The 2D model will also be compared to analytical solution developed by Ali *et al.* 2000. The randomly spaced periodic models will also be used to investigate film failure over a range of contact angles and particle packing densities in chapter 4.

Chapter 5 uses the models developed in section 3.8 to identify the modes of failure of double layer. The same models are also used to compare P_{crit}^* with that of single layers. In chapter 6 the non-spherical particle models will be used to identify the energetically stable orientations of orthorhombic particles. Appendix A (chapter 10) contains further development of the 2D and 3D spherical particle models to simulate particle motion in the film and initial results obtained from these simulations.

4 STATIC SINGLE PARTICLE LAYERS

4.1 INTRODUCTION

The previous chapters have described the experimental, analytical and modelling techniques that have been used to study thin films and foams stabilised by hydrophobic particles. The formation of single and double layers of particles in thin films and the mechanisms through which they stabilise the film were also discussed. This chapter will present results from simulations run on the models described in sections 3.4, 3.5 and 3.6 which were used to investigate single layers of particles in the film.

Previous analytical studies of particle stabilised thin films have often approached the problem in 2D (Ali *et al.*, 2000, Kaptay, 2004), or assumed the film shape to be axisymmetric (Denkov *et al.*, 1992, Horozov *et al.*, 2005). Whilst these approaches allow investigation of the basic properties of these systems, they cannot represent the non-axisymmetric properties of film in the gaps between particles. Recent work on 3D analytical solutions for film shape and particle interaction using multi-poles have also been developed but only for simple cases (Danov and Kralchevsky, 2010).

By using the *Surface Evolver* to find the minimum energy surfaces of the film interfaces, the 3D surface behaviour can be investigated and the complex film shapes formed by close packed particles can be visualised. The *Surface Evolver* (Brakke 1992) was introduced as a program able to simulate this complex geometry and the models used in this chapter were described in chapter 3.

This chapter will present results from the investigation of monodisperse, spherical particles in a thin film in both ordered and random packing arrangements, in 2D and 3D. A section of these results have been published (Morris *et al.*, 2008), a copy of the manuscript can be found in Appendix B.

First, a 2D surface tension based model was verified against the analytical solution of Ali *et al.*, (2000), comparing the critical capillary pressure required to rupture a film at a given contact angle and particle separation. The model was then expanded into a 3D coordinate system to investigate the effect of square and hexagonal particle packing configurations on the film shape and stability. For both 2D and 3D models the approach to finding the critical capillary pressure was the same, however when expanded into the three dimensions extra variables for the particle spacing must be defined to take into account the particle packing arrangement. These models and geometric parameters are described in detail in chapter 3. Finally, models of randomly arranged particles in a thin film with periodic boundaries are used to find the critical capillary pressures for non-uniform packing arrangements.

4.2 FILM FAILURE CRITERIA

For a single layer of particles in a thin film it is assumed that the film fails when its opposite sides touch. For more complex geometries, the film failure criteria also becomes more complex, however these conditions will be described in detail in the relevant chapters. Failure of films containing single layers of particles can occur in one of two ways, either through capillary pressure driven failure (when $h=0$) or through particle bridging of the film.

4.2.1 CAPILLARY PRESSURE DRIVEN FILM FAILURE

In both 2D and 3D at a capillary pressure of zero the film is uniformly thick and attaches to the particle at a co-latitude equal to the contact angle. The point where the film meets the particle is termed the three point contact, or TPC. As capillary pressure increases, the film's radius of curvature decreases and the TPC moves down the particle to maintain the contact angle. This causes the film to thin as the value of h also decreases to maintain θ and the radius of curvature of the film (R_L). This results in the opposite sides of the film drawing closer together, until they touch, at which point the film fails.

4.2.2 PARTICLE BRIDGING OF THE FILM

If a particle has a sufficiently high contact angle it will draw the opposite sides of the film together on its surface, causing film failure. As the contact angle defines the equilibrium position of the TPC, if $\theta=90^\circ$ when the capillary pressure is zero, the TPCs for each interface will be drawn together at the particle equator, causing the film to rupture. It should be noted that this is only the case for particles in the film in single layers. If the film contains particles in the film in two or more layers it is possible for contact angles above 90° to stabilise the film, this will be considered in chapter 5.

4.2.3 FAILURE CRITERIA

For the models used in this chapter the failure criterion is that the film will fail when $h=0$ at some point in the model. This is true for both 2D and 3D cases and the capillary pressure that this occurs at will be taken as the critical capillary pressure, or P_{crit}^* .

4.3 MODELLING PROCEDURE

The following procedure was used to find P_{crit}^* for a given θ and particle separation: beginning at a capillary pressure of zero the surface is evolved to a minimum energy and the film checked to find h . If the film has not failed (i.e. $\theta < 90^\circ$), the capillary pressure is increased by a small amount P_{step}^* and the new minimum energy surface found. After each increase in pressure the new film thickness is calculated and, if the film has not ruptured, the pressure is increased again. The surface is re-evolved to its new minimum and the new film thickness is calculated. This procedure is continued until $h=0$, when the film fails. The pressure at which this occurs is the critical pressure, P_{crit}^* , for that combination of particle separation and contact angle.

4.4 2D SINGLE LAYER OF UNIFORM SPHERICAL PARTICLES

The 2D *Surface Evolver* model described in section 3.4 has been used to find the P_{crit}^* for circular particles with a contact angle between 0° and 90° and separation distances between 1 and 5. These results are then compared to those predicted by the 2D analytical solution developed by Ali *et al.*, (2000). The effects of particle separation distance and contact angle are then discussed. It should be noted that as the separation distance is taken from the centre of the particle, the minimum S_p^* will be $S_p^*=1$, corresponding to the case when two particles are touching, $S_{pmin}^* = S_{pmin}/R_p = R_p/R_p = 1$.

4.4.1 COMPARISON OF 2D AND ANALYTICAL (ALI *et al.* 2000) DATA

The analytical solution developed by Ali *et al.* (2000) is shown in equations 4-1 and 4-2. It is a 2D model based upon the geometry described in Figure 3-14 that can be used to calculate the capillary pressure of a film for a given contact angle, film curvature and particle separation distance.

$$P_C = \frac{\gamma_{LV}}{R_p} \left(\frac{R_L}{R_p} \right)^{-1} \quad 4-1$$

Where P_C is the capillary pressure, γ_{LV} the surface tension of the Liquid-Vapour interface, R_p the radius of the particle and R_L is the radius of curvature of the film. The formula linking R_L and R_p is given in equation (4-2).

$$(R_L + h)^2 + S_p^2 = R_p^2 + R_L^2 + 2R_p R_L \cos \theta \quad 4-2$$

Where h is film thickness, S_p is separation distance and θ is contact angle. When $h=0$ the film is at zero thickness and will fail. The P_C this occurs at is the critical capillary pressure required to rupture the film (P_{crit}^*). In 2D if $h=0$, $S_p=R_p$ and $0^\circ < \theta < 90^\circ$, R_L must be zero (equation 4-2) and therefore P_C tends to infinity (equation 4-1). Conversely if S_p tends to infinity R_L tends to infinity as well with P_C tending to 0. Figure 4-1 compares the P_{crit}^* values obtained from the 2D *Surface Evolver* model with the non-dimensionalised values of P_C at $h=0$ predicted using the analytical solution of Ali *et al.*, (2000) at a contact angle of 15° .

In Figure 4-1 it can be seen that the trends obtained from the *Surface Evolver* model match the analytical. On average the P_{crit}^* for analytical solution is 0.97 % lower than the *Surface Evolver* results, with a low of -0.06 % at $S_p^*=1.16$ and high of -3.7 % at $S_p^*=4.48$.

The value of P_{step}^* used in all simulations for the results shown in Figure 4-1 was 0.005. This is 0.09 % of the P_{crit}^* found for $S_p^*=1.16$ but 4.8 % of the P_{crit}^* for $S_p^*=4.48$. At larger values of S_p^* the P_{step}^* is a larger

fraction of the P_{crit}^* . This causes the increased difference between the final values of P_{crit}^* returned from *Surface Evolver* as compared to the analytical values.

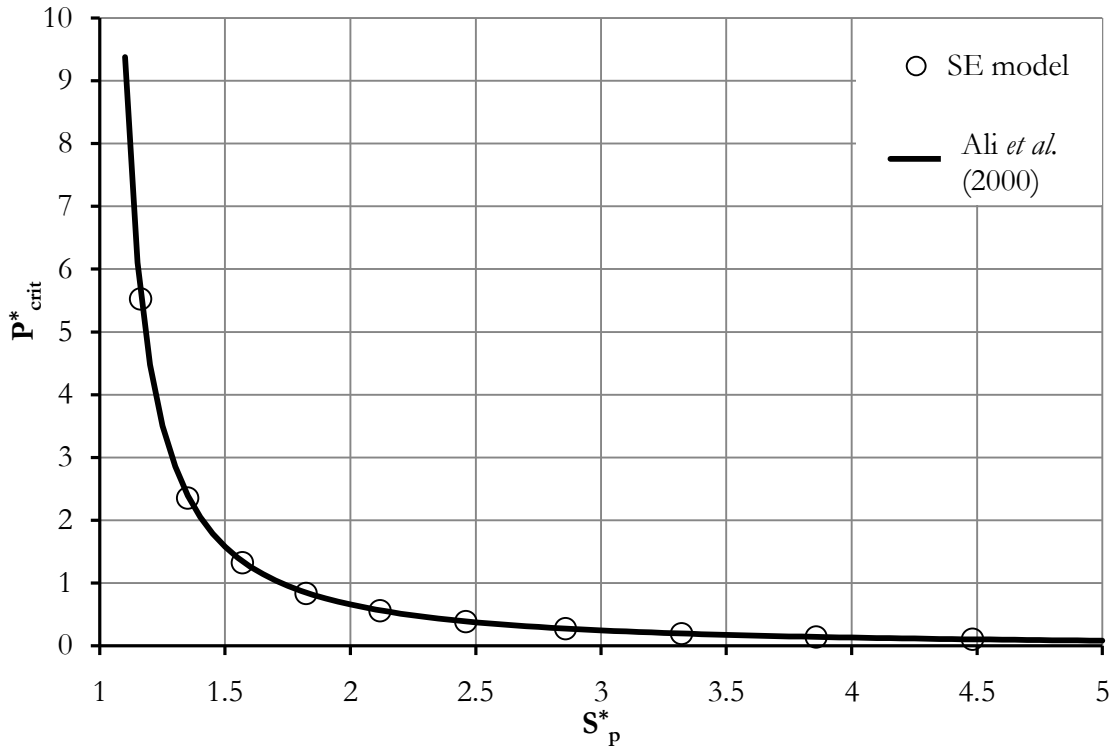


Figure 4-1. Comparison between the P_C^* from the analytical solution of Ali *et al.*, (2000) and simulated results for P_{crit}^* as a function of S_p^* , $\theta=15^\circ$, $P_{step}^*=0.005$.

Figure 4-2 compares the results for P_{crit}^* at a contact angle of 75° for two set of results, one using a P_{step}^* of 0.005 and one a P_{step}^* of 0.0005. The average difference between P_{crit}^* for the analytical and *Surface Evolver* models is 3.5 % for $P_{step}^*=0.005$ and 1.35 % for $P_{step}^*=0.0005$. At $S_p^*=4.48$ a P_{step}^* of 0.005 is 16 % of the returned value of P_{crit}^* and has an 11 % difference to the analytical model. When reduced by a factor of ten to 0.0005, P_{step}^* is only 1.8 % of the P_{crit}^* returned and the difference to the analytical model value is now 5 %.

Comparing the values of P_{crit}^* obtained for different contact angles (Figure 4-3) it can be seen that the analytical solution and *Surface Evolver* results compare favourably. There is an average difference of around 1.3 % between the two for contact angles in the range of θ of 10° and 75° . At 85° the difference increases to around 10 %, this however can be attributed to the value of P_{step}^* used (0.005). The error bars shown in Figure 4-3 for higher contact angles highlight how the use of a constant P_{step}^* increases the error associated with models of low P_{crit}^* . However this can be remedied by running the model with a smaller P_{step}^* , once a low P_{crit}^* has been identified. Generally, the P_{step}^* used should be less than 5 % of P_{crit}^* .

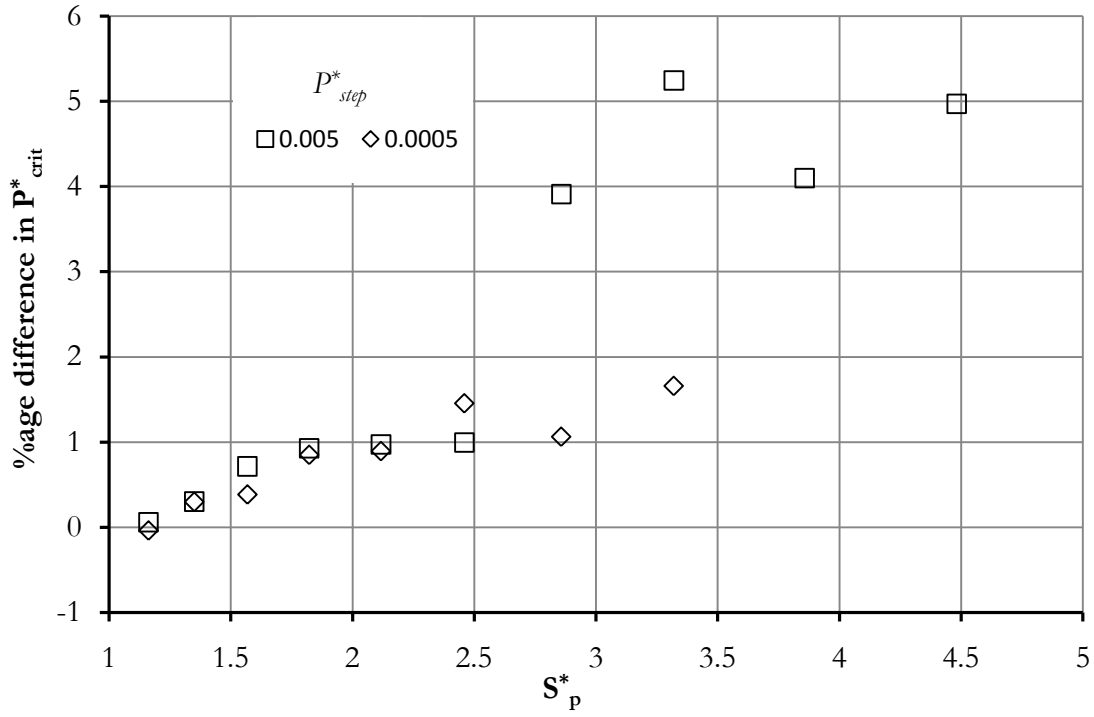


Figure 4-2. Percentage difference between simulated and calculated P^*_{crit} as a function of S^*_p for $P^*_{step} = 0.005$ and 0.0005 , $\theta = 75^\circ$.

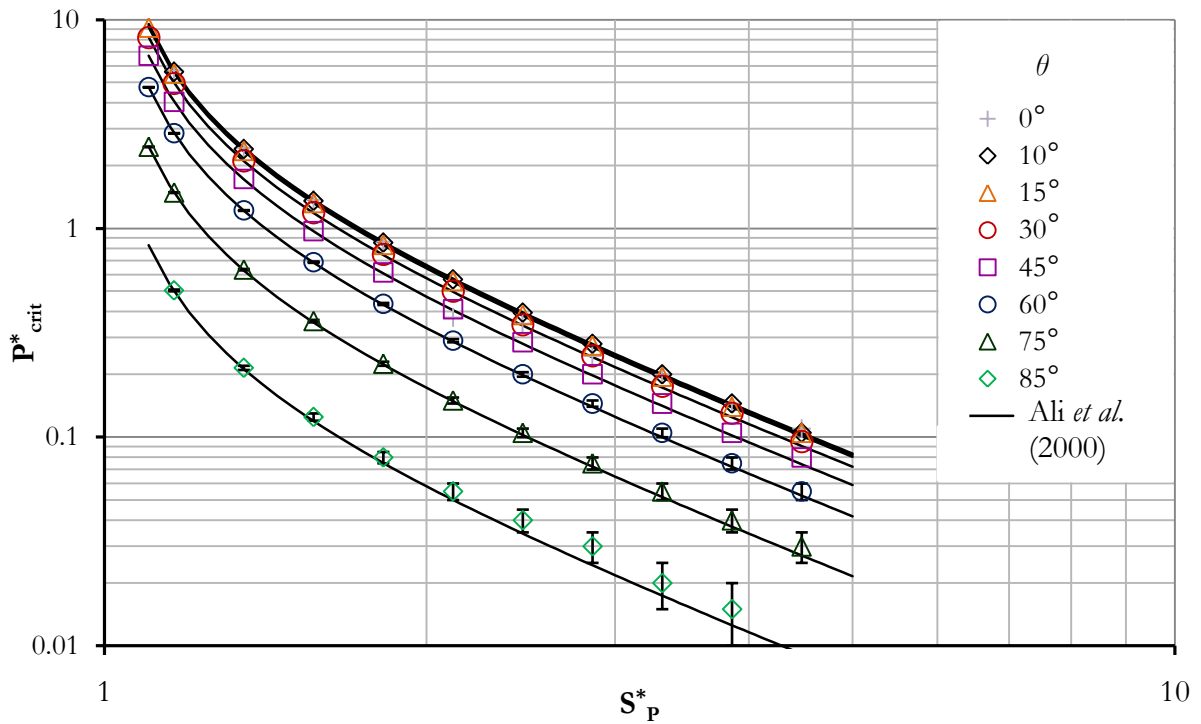


Figure 4-3. P^*_{crit} as a function of S^*_p for analytical solution (Ali *et al.* 2000) and *Surface Evolver* models at different contact angles. Range bars for θ of 60° , 75° and 85° of 0.005 are shown to demonstrate the effect of P^*_{step} at low P^*_{crit} .

The *Surface Evolver* model shows an increase in P_{crit}^* as the separation distance decreases (Figure 4-3) with a good agreement to the analytical model. Therefore, if the particles are evenly distributed on the film surface the film will be more stable for a greater particle loading. A higher particle loading corresponds to a lower S_p^* and as S_p^* decreases P_{crit}^* and thus film stability increases.

Figure 4-4 shows the results from the 2D *Surface Evolver* model re-plotted with P_{crit}^* as a function of θ instead of S_p^* , using contact angles between 0° and 90° and separation distances between 1.2 and 4.5. It can be seen that for a given separation distance as contact angle decreases P_{crit}^* and film stability increase. It is also apparent that at smaller separation distances the effect of a change in contact angle becomes more pronounced.

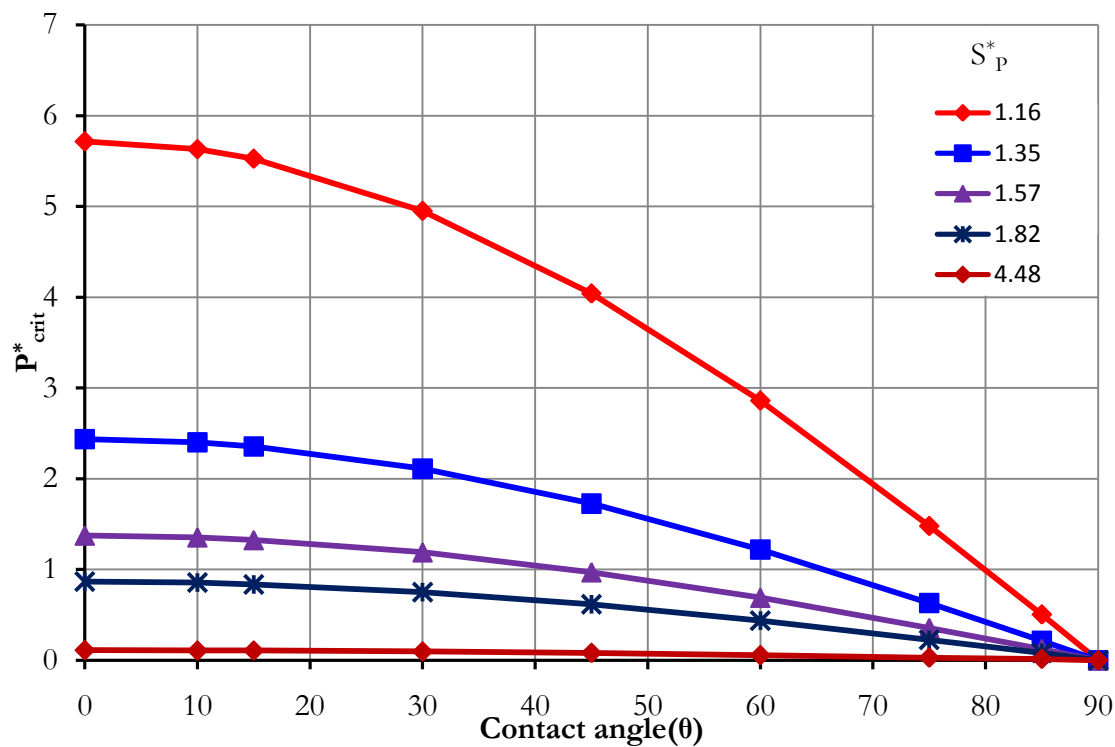


Figure 4-4. The effect of θ on P_{crit} whilst keeping the separation distance between particles constant.

For all separation distances it was found that when θ decreases below approximately 15° P_{crit}^* does not change by more than 4.5 %. However, as θ tends to 90° a small change in its value has a much larger effect on P_{crit}^* . When $S_p^* = 1.16$ a change in θ from 75° to 85° results in a 66 % drop in P_{crit}^* . This drop in P_{crit}^* is on average 62 % until S_{pp}^* is roughly greater than 4.5. Therefore films stabilised by particles with a small contact angle ($\theta < 15^\circ$) are relatively insensitive to a change in contact angle, but the stability of films with particles that have a θ close to 90° will be affected by small changes in θ .

4.4.2 SUMMARY OF 2D RESULTS

The results obtained using the analytical solution developed by Ali *et al.*, (2000) have been accurately reproduced using the 2D string model in *Surface Evolver*. Results show that with decreasing particle

separation distance the pressure required to rupture the film increases. The 2D models have shown that as contact angle decreases below approximately 15° there is little change in P_{crit}^* . However, at contact angles approaching 90° a change in contact angle has a larger effect on the value of P_{crit}^* . The general trend shown has been that for a given particle separation, the lower the contact angle the greater P_{crit}^* .

4.5 3D SINGLE LAYERS OF UNIFORM SPHERICAL PARTICLES

The 2D single particle model is now expanded into the 3D *Surface Evolver* model described in section 3.5 and used to investigate the effect of particle packing arrangements in the film on P_{crit}^* . The same approach has been used to find P_{crit}^* , but new geometric parameters must be introduced. These are explained in detail in section 3.5.1 but are required to take into account particle packing arrangements, separation distance and the 3D nature of the film.

4.5.1 COMPARISON OF SEPARATION DISTANCES IN 3D

Figure 4-5 compares the P_{crit}^* results for 3D hexagonal packing, 3D square packing and 2D models with varying S_{pp}^* at a contact angle of 45° . All three models produce a similar P_{crit}^* for separation distances above 3, however, below this they diverge from each other.

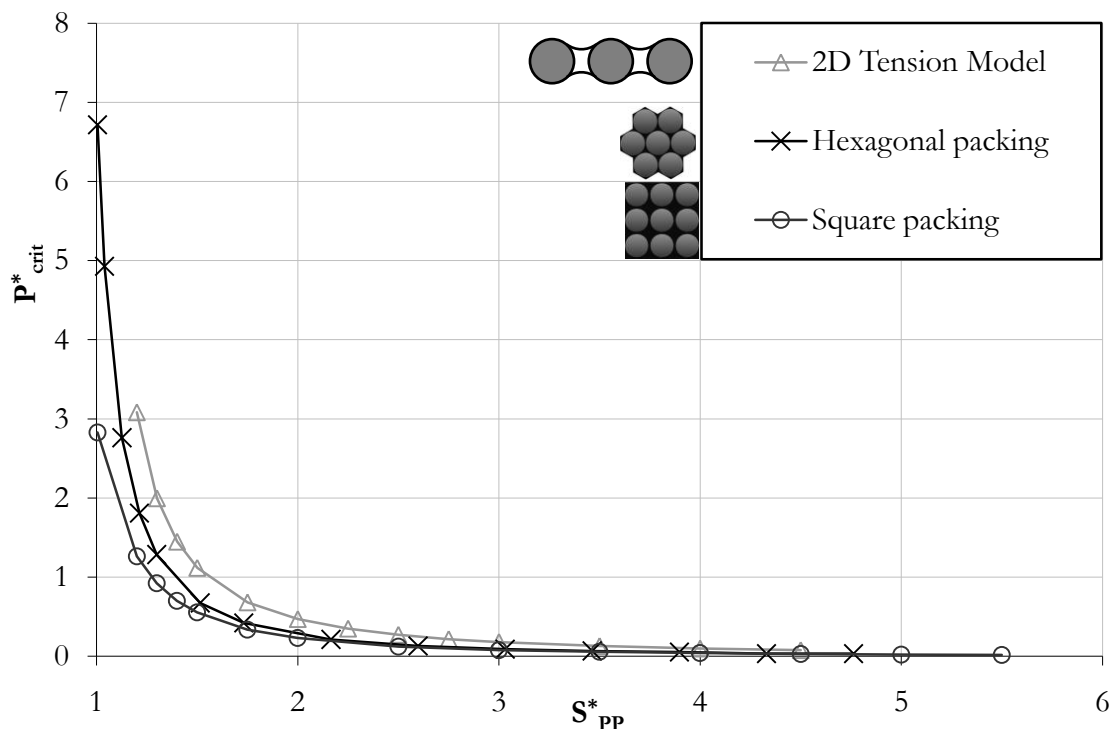


Figure 4-5. Comparison of square, hexagonal and 2D P_{crit}^* as a function of S_{pp}^* . $\theta=45^\circ$ in all cases.

For a given S_{pp}^* , the P_{crit}^* results for the 2D case are highest and diverge from the 3D results at around $S_{pp}^*=3$. The square packing P_{crit}^* results are lower than those of hexagonal packing. At an S_{pp}^* of 1.5 the

P_{crit}^* for hexagonal packing begins to diverge from that of square packing and at an S_{pp}^* of 1.005 (which corresponds to a very closely packed layer) P_{crit}^* is around half that of the hexagonal packing. Thus based on P_{crit}^* as function of S_{pp}^* hexagonal packing stabilises the film to greater extent than square packing as for all separations P_{crit}^* is higher for a hexagonal arrangement.

Figure 4-6 shows P_{crit}^* as a function of S_{PF}^* . The order of the results is reversed compared to Figure 4-5; for a given S_{PF}^* the square packing has the highest P_{crit}^* , diverging at an S_{PF}^* of approximately 2.5, whilst the results for hexagonal and 2D P_{crit}^* are much closer, diverging at an S_{PF}^* of 1.5. It should be noted that the minimum S_{PF}^* for both packing arrangements is found using equations (3-11) and (3-12) when $S_{pp}^*=1$. This means the lower limit of S_{PF}^* for the two packing arrangements shown in Figure 4-6 is different.

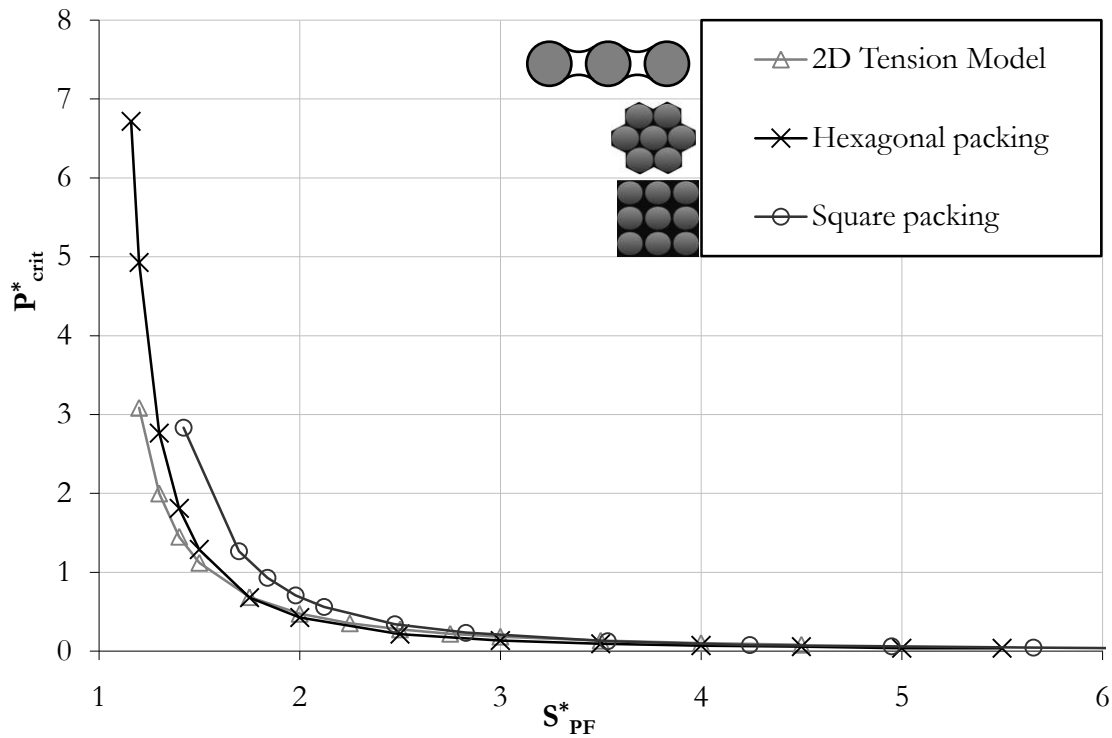


Figure 4-6. Comparison of square, hexagonal and 2D P_{crit}^* as a function of S_{PF}^* for all cases $\theta=45^\circ$.

2D results showed that as the distance from the particle to the midpoint of the film increases, P_{crit}^* decreases. For a given S_{pp}^* a square packed film will always have a larger S_{PF}^* and thus a point in the film further away from any particles than its equivalent in a hexagonally packed film. Therefore, a square packed film will always fail at a lower P_{crit}^* for a given S_{pp}^* . Film area is directly related to separation distance and a hexagonally packed film, capable of packing to a lower S_{PF}^* , is able to achieve the highest value of P_{crit}^* .

Square packing has a higher P_{crit}^* than hexagonal packing for a given S_{PF}^* but the smallest possible S_{PF}^* for square packing is larger than that for hexagonal packing (see equation 3-11 and 3-12). It is still therefore possible to obtain the highest P_{crit}^* from a hexagonal arrangement when plotting as a function of S_{PF}^* .

Plotting P_{crit}^* as a function of S_{pp}^* shows that hexagonal packing gives a higher P_{crit}^* for a given S_{pp}^* (see Figure 4-5) whereas the reverse is true when S_{PF}^* is used. If further investigation of particle stabilised films in 3D is to be carried out it is clear that a better measure of particle loading on the film needs to be developed to compare results over different packing patterns. One such measure that can be used is the area of film per particle.

4.5.2 COMPARISON OF FILM AREA WITH P_{CRIT}^*

The area of the unit cell not occupied by the particle when viewed from above can be calculated using (equations 4-3 and 4-4) for hexagonal and square cells respectively.

$$area_{hex} = \left(\frac{3\sqrt{3}}{2} S_{PF}^{*2} \right) - \pi = (2\sqrt{3} S_{PP}^{*2}) - \pi \quad 4-3$$

$$area_{square} = 2 S_{PF}^{*2} - \pi = 4 S_{PP}^{*2} - \pi \quad 4-4$$

The area of film for hexagonal packing when $S_{PP}^*=1$ is 0.3225 whilst for square packing at this value it is 0.8584. The exposed area of film in a hexagonal cell is therefore 37.6 % of that for a square cell when the particles are close packed. As S_{PP}^* increases, the difference in film area between the two cells decreases and at $S_{PP}^*=1.5$ the hexagonal cell has an area that is 80 % of the square cell (Figure 4-7). The large decrease in percentage area occurs below 1.5, this is also the S_{PP}^* below which the values of P_{crit}^* for hexagonal and square packing diverge.

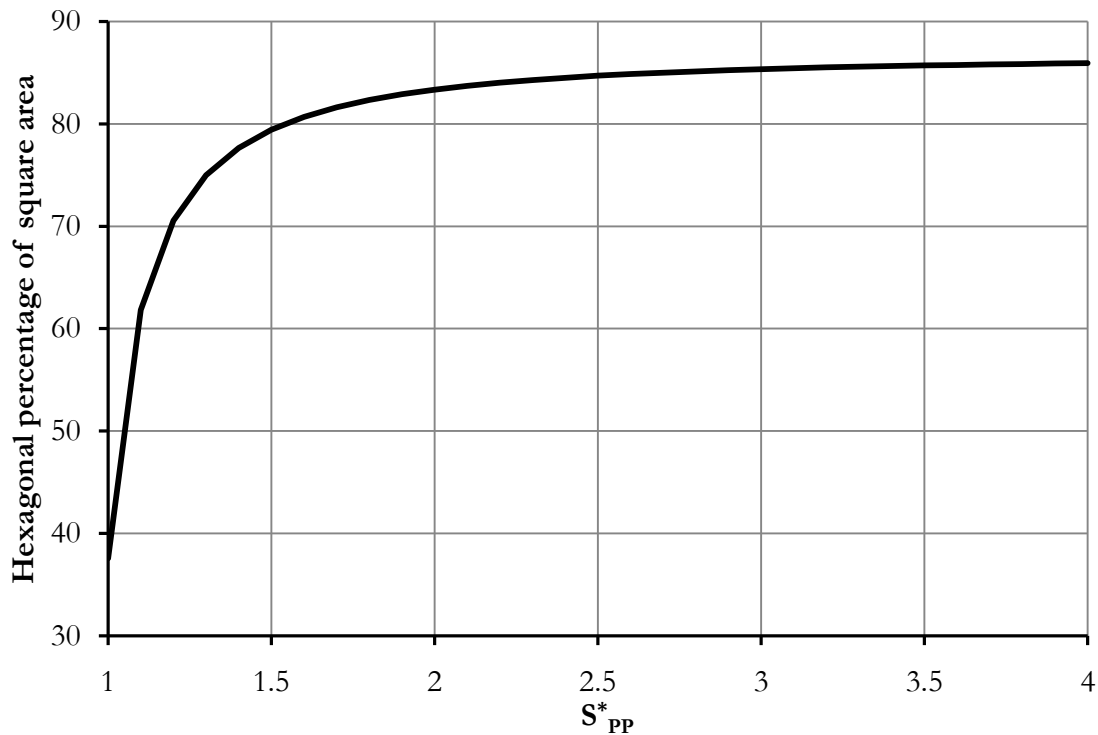


Figure 4-7. Percentage free film area of a square cell taken up by a hexagonal cell as a function of S_{PP}^* .

Figure 4-8 shows the results for P_{crit}^* re-plotted as a function of area of film instead of S_{pp}^* . It can be seen that the curves are almost identical, showing that the relation between the area of free space around the particle and P_{crit}^* is a more appropriate method for comparing the stability of particle packing arrangements.

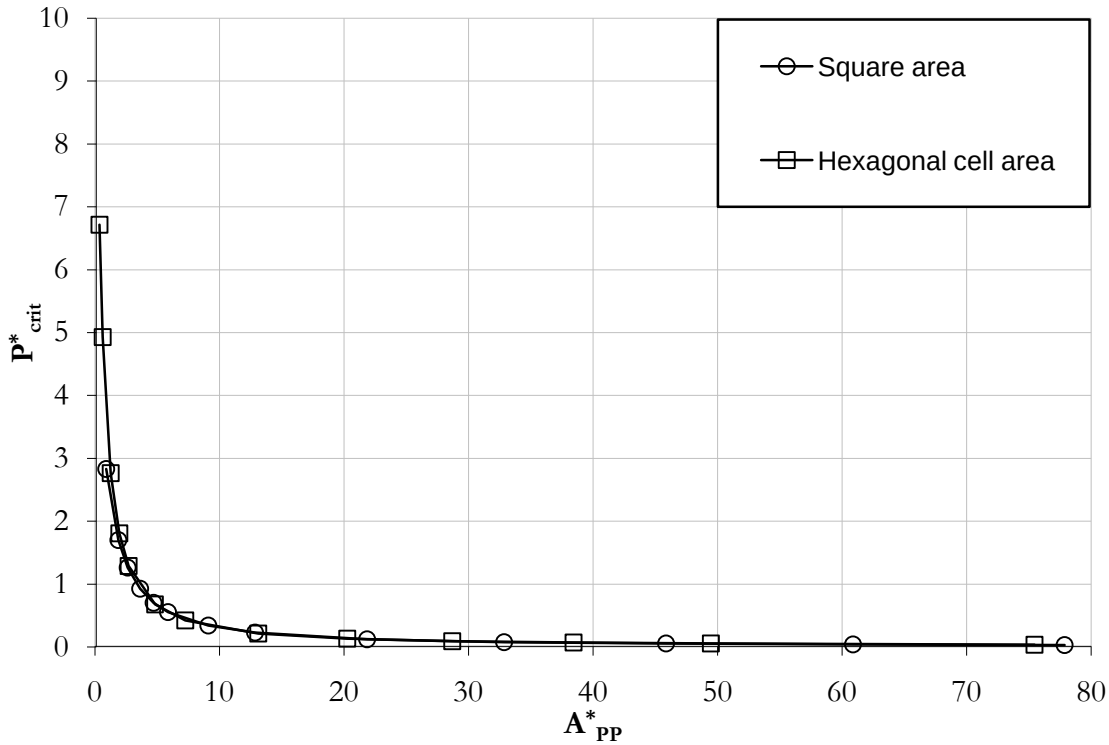


Figure 4-8. Comparison of square and hexagonal packing P_{crit} as a function of film area for both cases $\theta=45^\circ$.

The very high P_{crit}^* of the hexagonal packing seen at low A_{pp}^* in Figure 4-8 is possible because the hexagonal packing arrangement has a smaller minimum A_{pp}^* than the square one. Re-plotting the graph on a log-log axis (Figure 4-9) shows that the point at which the values for P_{crit}^* diverge from each other corresponds to a non-dimensional film area of around 2.7 (thin dotted line in Figure 4-9). The thick dashed line represents the minimum area of film with hexagonal packing (0.3225) and the thin dashed line represents the minimum area for square packing (0.8584). At areas below 2.7 (which roughly correspond to S_{pp}^* of 1.3 for hexagonal and 1.2 for square packing arrangements) the packing pattern has a small effect on P_{crit}^* . However, even at areas below this the results are very similar until A_{pp}^* gets close to the square packing limit, at this point P_{crit}^* for square packing is roughly 65 % of that for hexagonal packing. The P_{crit}^* at the minimum A_{pp}^* for square packing is around half of the P_{crit}^* at the minimum A_{pp}^* for hexagonal packing, which is the same as comparing P_{crit}^* for the two packing arrangements at $S_{pp}^*=1$.

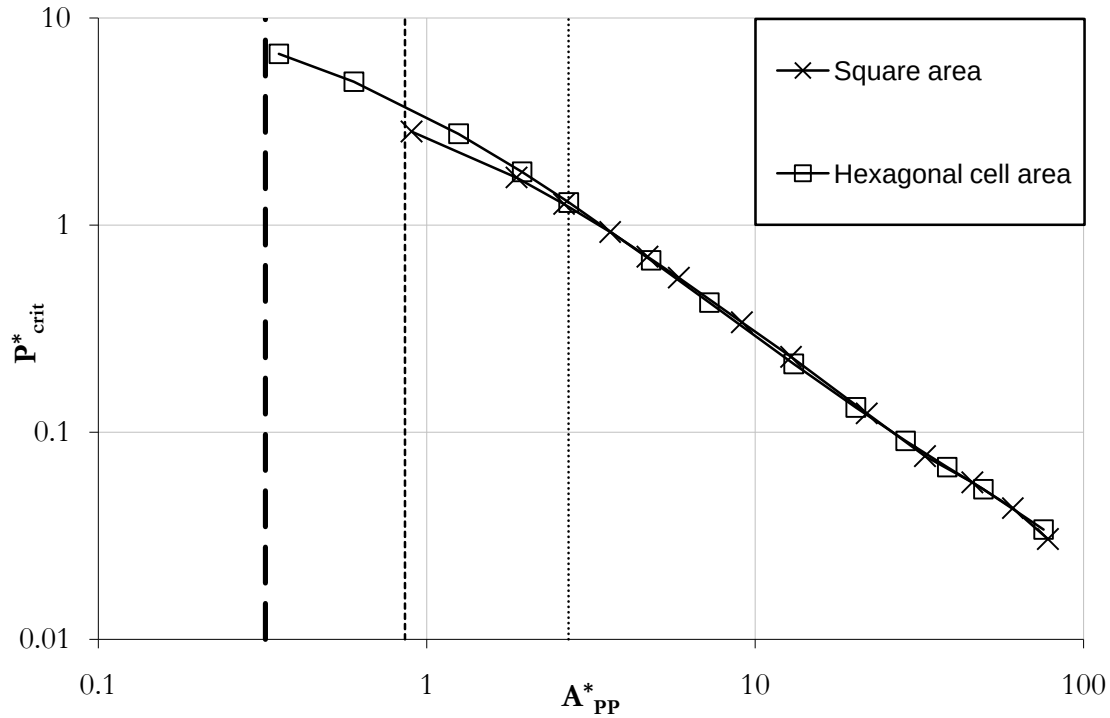


Figure 4-9. Comparison of P_{crit} for square and hexagonal packing as a function of film area on log-log axis, $\theta=45^\circ$. Thick dashed line represents the minimum cell area achievable for hexagonal packing and the thin dashed line the same for square packing. The dotted line is the point at which P_{crit}^* begins to diverge.

4.5.3 EFFECT OF PACKING ARRANGEMENT ON TPC POSITION

Surface Evolver also stores the film geometry. Figure 4-10 shows a plot of the film height on the surface of a spherical particle ($\theta=45^\circ$, $S_{pp}^*=1.13$) for square and hexagonal packing.

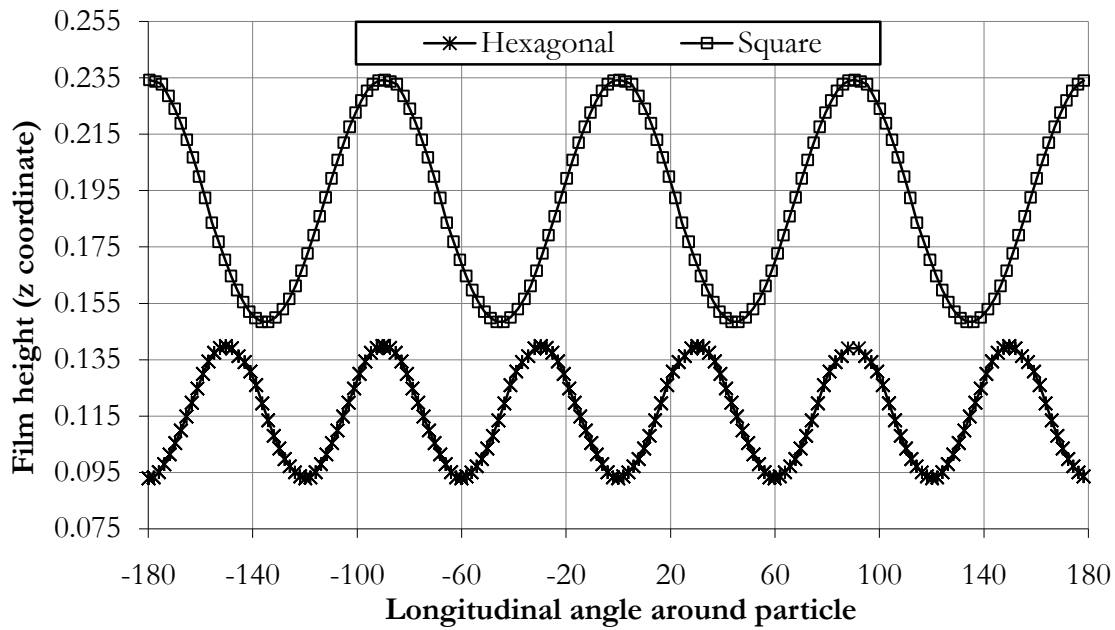


Figure 4-10. The z coordinate of the film at the three phase contact plotted against the longitudinal angle around the particle at $S_{pp}^*=1.13$, $\theta=45^\circ$ at the point of failure.

The TPC is much higher on the surface of the particle for the square packing case, i.e. more of the particle is in the liquid phase. This is because there is a greater A_{pp}^* for the square case and the four corners of the cell are further away from the particle (S_{PF}^* is greater for square packing than hexagonal for a given S_{PP}^*). This means the film is able to reach a zero thickness with less film curvature and as a result the TPC is not forced down the side of the particle as far as it is for hexagonal packing.

4.5.4 FILM DISTORTION

Figure 4-11 and Figure 4-12 show the simulated shape of the film after evolution at P_{crit}^* for both square and hexagonal boundaries.

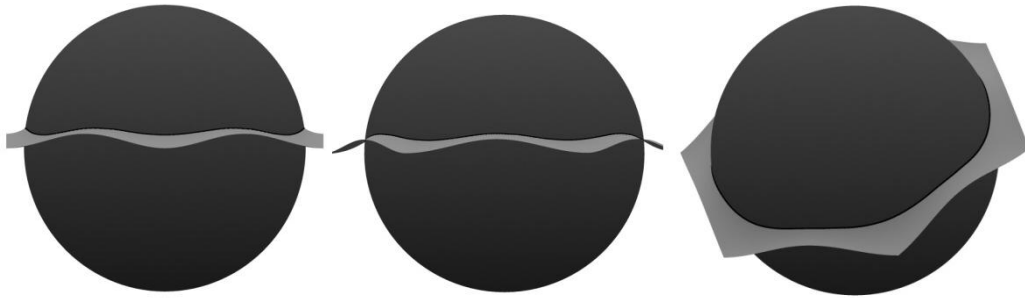


Figure 4-11. The Evolved surface for hexagonal packing at $S_{PP}^*=1.13$, $\theta=45^\circ$ and P_{crit}^* . Figure only shows the upper surface of the film.

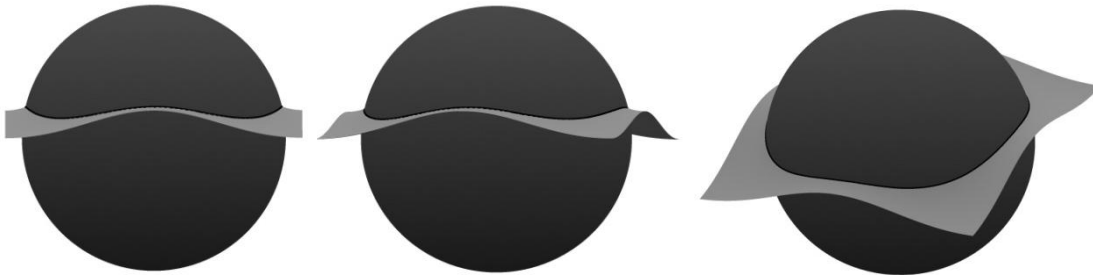


Figure 4-12. Evolved surface for square packing at $S_{PP}^*=1.13$, $\theta=45^\circ$ and P_{crit}^* . Figure only shows the upper surface of the film.

4.5.5 SUMMARY OF REGULAR 3D PACKING RESULTS

The comparison of results has shown that whilst the 2D model produces the same trends for critical capillary pressure as the 3D models it consistently predicts a higher value for P_{crit}^* . This is because the 2D model does not take into account the effects of particle packing configurations and zero separation distances between particles. It should be noted that in 3D the film also becomes highly distorted at low separation distances, a feature that cannot be captured using a 2D model.

The packing pattern and distance between the particles attached to the film affects the capillary pressure required to rupture the film. When considering the separation distance between particles, hexagonally close packed particles have a higher P_{crit}^* than square packed ones. However, as the separation distance

increases above $S_{pp}^*=3$ the difference in P_{crit}^* for the two different particle packing configurations becomes negligible.

For low contact angles ($\theta < 15^\circ$) a small change in contact angle has relatively little effect on P_{crit}^* but at larger contact angles (θ greater than roughly 60°) there is a much greater change in the P_{crit}^* with change in θ . Therefore, much greater care needs to be taken when dealing with particles at high levels of hydrophobicity as a small change in contact angle will have a large effect on P_{crit}^* .

If film area per particle is considered instead of S_{pp}^* both packing arrangements provide a similar level of film stability for a given contact angle indicating that the film area per particle, not the separation distance, is the variable that should be used to compare the stability of different particle arrangements. A close packed hexagonal pattern is able to achieve much lower film areas per particle than square packing enabling a greater film stability. This implies that when considering films with evenly distributed attached particles, packing configuration has a large effect on film stability only when the particles are densely packed.

In 2D the film fails at the midpoint between two particles, where it is the thinnest, in 3D the film fails at the point furthest from any particle. If the particles are not regularly spaced in the film, as is likely to occur in a flotation froth, there will be larger areas of empty space in the film, which will lower P_{crit}^* of the film. The implications of irregularly arranged particles leaving empty areas on the film and the effect this has on film stability will be considered in the next section.

4.6 RANDOMLY PACKED UNIFORM SPHERICAL PARTICLES

4.6.1 INTRODUCTION

Section 4.4 and 4.5 investigated the effect of regular particle packing arrangements on film stability. It established that as the packing density increases and area of film per particle decreases, the critical capillary pressure increases. 3D models of square and hexagonal packing arrangements were found to return a similar P_{crit} for a given contact angle when the area of film per particle was the same. However, flotation froths contain particles with a much less ordered packing structure on the film. It is therefore necessary to expand the model used so that irregularly spaced particles can be investigated. The average area of film per particle will be used as a measure of comparison between models as it has already been established that this can be used to compare different packing arrangements. In this section the periodic models that were described in section 3.6 are used to generate a series of models of particle stabilised films with different packing densities, periodic edge lengths (L_p^*) and contact angles, these models are then used to investigate P_{crit}^* .

4.6.2 RANDOM PACKING MODEL

Empty periodic films with an L_p^* of 5, 7, 10 and 15 were created and then populated with varying numbers of particles to create a set of models with different packing densities. Details of the models are shown in Table 1.

L_p^*	A_{pp}^* Range	Number of particles placed in film
5	1.9-21.9	1, 2, 3, 4, 5
7	1.8-45.9	1, 2, 3, 4, 5, 7, 10
10	1.858-96.9	1, 2, 3, 4, 5, 10, 15, 20
15	8.1-221.9	1, 2, 3, 4, 5, 10, 15, 20

Table 1. Showing the combination of particle numbers, A_{pp}^* and L_p^* for periodic models

The particles were placed in the film at random locations without overlapping. The coordinates for the particle locations were determined from random numbers generated by *Surface Evolver*. The full details of the method used to place the particles in the film can be found in section 3.6. Once the particles are placed they are all assigned the same contact angle and the critical capillary pressure is found using the method detailed in section 4.3. Examples of various periodic cells are shown in Figure 4-13.

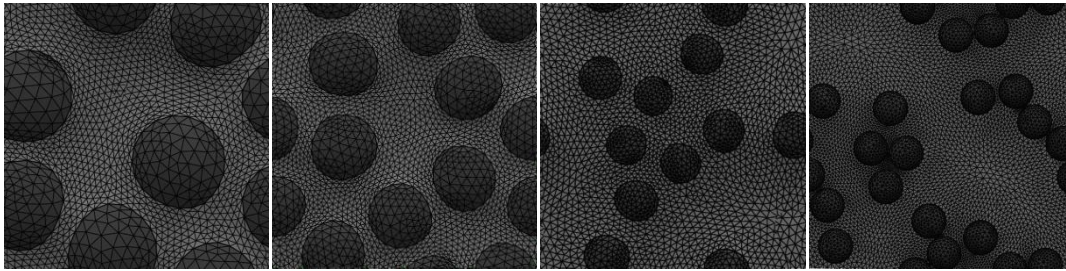


Figure 4-13. Periodic cells of edge length 5, 7, 10 and 15 containing 5, 10, 10 and 20 particles respectively.

For each combination of L_p^* and particle number an average of 9 different models were created by changing the random seed attribute in *Surface Evolver*. This is the seed from which the random numbers are generated, by changing it, different random numbers are generated creating different particle arrangements. The exceptions to this were the models containing only one particle, due to the periodic cell, no matter where a single particle is placed it is effectively in a square packing arrangement. Therefore only one model containing a single particle was created for each L_p^* .

4.6.2.1 Packing densities

The average area of film per particle has been used as the measure of particle packing density for the periodic film models and is calculated using equation (4-5).

$$A_{pp}^* = \frac{L_p^{*2} - n_p \pi}{n_p} \quad 4-5$$

Where $\mathcal{A}_{pp}^*$ is the area of film per particle and n_p is the number of particles in the film. $\mathcal{A}_{pp}^*$ can therefore be changed by altering either L_p^* or n_p .

4.6.2.2 Contact angle

The contact angle has been defined as detailed in section 3.2.4, however, for the more complex models used in this section surface tension is defined using equation 3-3 instead of 3-2.

The contact angles used in the models were 29° , 38° , 50° , 63° or 76° , with each model containing uniform, monodisperse spherical particles. The P_{crit}^* for each combination of L_p^* , n_p and θ was found for each set of random particle arrangements on the film. The P_{crit}^* results from all the models with the same L_p^* and n_p were averaged for each value of θ to get a value of P_{crit}^* for a given θ and $\mathcal{A}_{pp}^*$.

4.6.3 PARTICLE PACKING CONSIDERATIONS FOR PERIODIC CELLS

It has been shown that for uniform packing a lower film area per particle results in a higher P_{crit}^* . This is because an unoccupied area of film is thinnest at the point farthest from any particles, which is due to the constant radius of curvature in the film. If this distance, or unoccupied area is increased by increasing the $\mathcal{A}_{pp}^*$ then P_{crit}^* decreases. Therefore, for a given number of particles in a film of a given area, the highest P_{crit}^* is achieved by a uniformly spaced arrangement of particles in the film as this minimises the maximum area of unoccupied film. Conversely, if the particles agglomerate, the largest area of unoccupied film increases, lowering P_{crit}^* accordingly.

There is an effect of cell size for periodic models, consider two periodic cell models, one with an L_p^* of 5 containing 5 particles and one with an L_p^* of 10 containing 20 particles. Both of these models will have an $\mathcal{A}_{pp}^*$ of 1.858. However, if during random placing of the particles in the film they end up close together it is possible for the larger period to have a much greater exposed area of film. If the $L_p^*=5$ model has all its particles closely packed together the maximum space of empty film will still be smaller than for the larger period, as shown schematically in Figure 4-14.

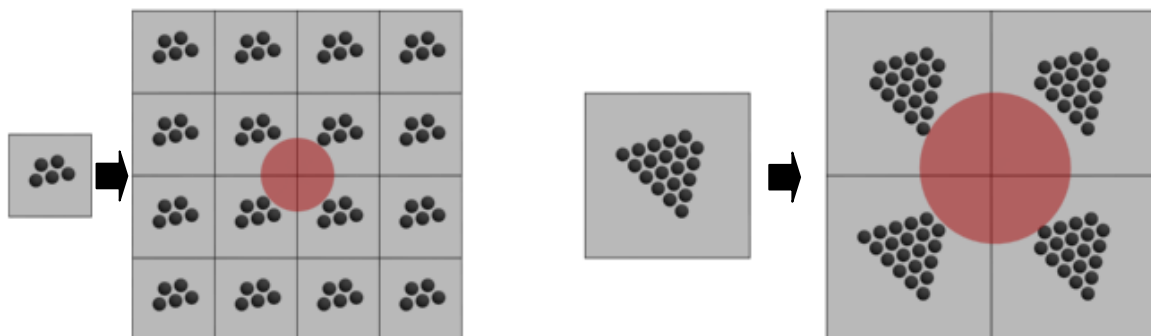


Figure 4-14. Showing the large scale uniformity of smaller periodic boundaries, close particle packing has been exaggerated to illustrate the empty film areas. Shaded area highlights the difference in area of exposed film.

Smaller period models will have larger scale uniformity in packing, which will lead to a higher predicted P^*_{crit} . The examples shown in Figure 4-14 are exaggerated, and if the particles are spread out in the smaller period as well as the larger period the P^*_{crit} will tend to the same value as the particle spacing becomes more regular. This is why there is a disparity in results between the larger and smaller scale models.

It is therefore desirable to use as large an L_p as possible to minimise the effects of small periods on particle packing. However as the model size increases, many more particles are required to reach the low values of A^*_{pp} . These models take much longer to construct, using the random placement method and also take much longer to run in *Surface Evolver*, for example a model with an L_p of 10 with 20 particle in it has twice as many vertices as one containing only 10 particles. Therefore it is still necessary to use the smaller period models to simulate high packing densities to prevent the models complexity producing prohibitive computing times.

4.6.4 PACKING DENSITY AND CRITICAL CAPILLARY PRESSURE

The P^*_{crit} as a function of A^*_{pp} and θ for a period with $L_p=5$ are shown in Figure 4-15. They show the same trends as observed for both 2D and 3D models with uniform packing. P^*_{crit} increases abruptly as A^*_{pp} decreases but for a given A^*_{pp} there is little change in P^*_{crit} once θ is below roughly 40° . For all contact angles the P^*_{crit} for an A^*_{pp} of 21.85 (1 particle in the film) is roughly 13.5 % of that for an A^*_{pp} of 1.86 (5 particles in the film) and for all A^*_{pp} the P^*_{crit} for a contact angle of 76° is roughly 36 % of that for a contact angle of 29° .

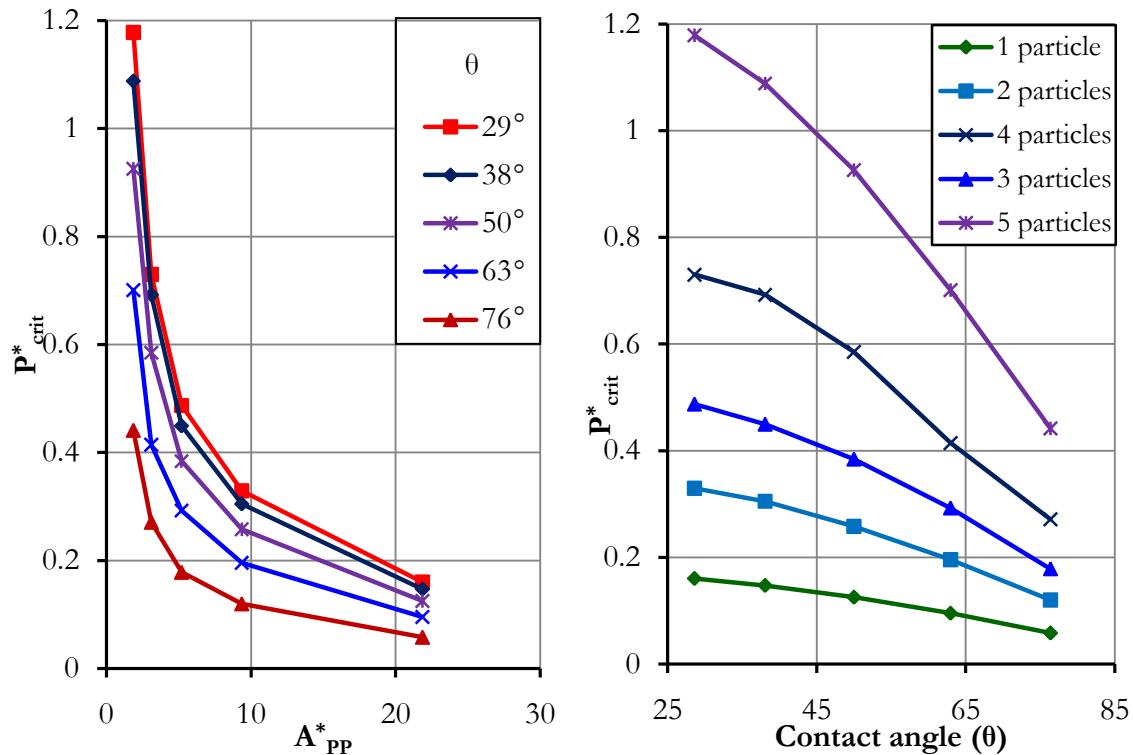


Figure 4-15. P^*_{crit} vs A^*_{pp} for various θ and P^*_{crit} vs θ for various A^*_{pp} for a period with edge length of 5 and contact angles of 29° , 38° , 50° , 63° and 76° .

These are features also seen for the larger periods (Figure 4-16, Figure 4-17 and Figure 4-18) with greater numbers of particles and a wider range of $\mathcal{A}_{pp}^*$. As the film area per particle decreases the critical capillary pressure increases. As θ decreases P_{crit}^* does not change more than 20 % once the contact angle is below roughly 40° . For a given $\mathcal{A}_{pp}^*$ the P_{crit}^* at a contact angle of 76° is on average 62 % of that for a contact angle of 63° . This is in line with the results from section 4.4 showing that over low contact angles ($\theta < 40^\circ$) there is relatively little difference in P_{crit}^* for a given $\mathcal{A}_{pp}^*$ but as θ approaches 90° P_{crit}^* begins to decrease quickly.

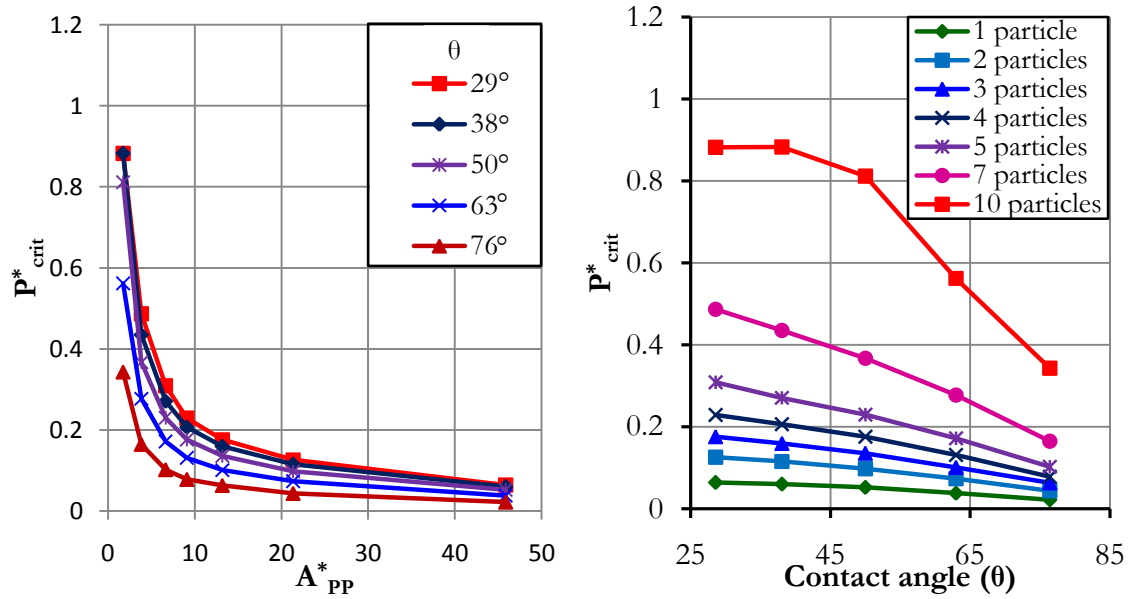


Figure 4-16. P_{crit}^* vs $\mathcal{A}_{pp}^*$ and P_{crit}^* vs θ for a period with edge length of 7 for contact angles of $29^\circ, 38^\circ, 50^\circ, 63^\circ, 76^\circ$.

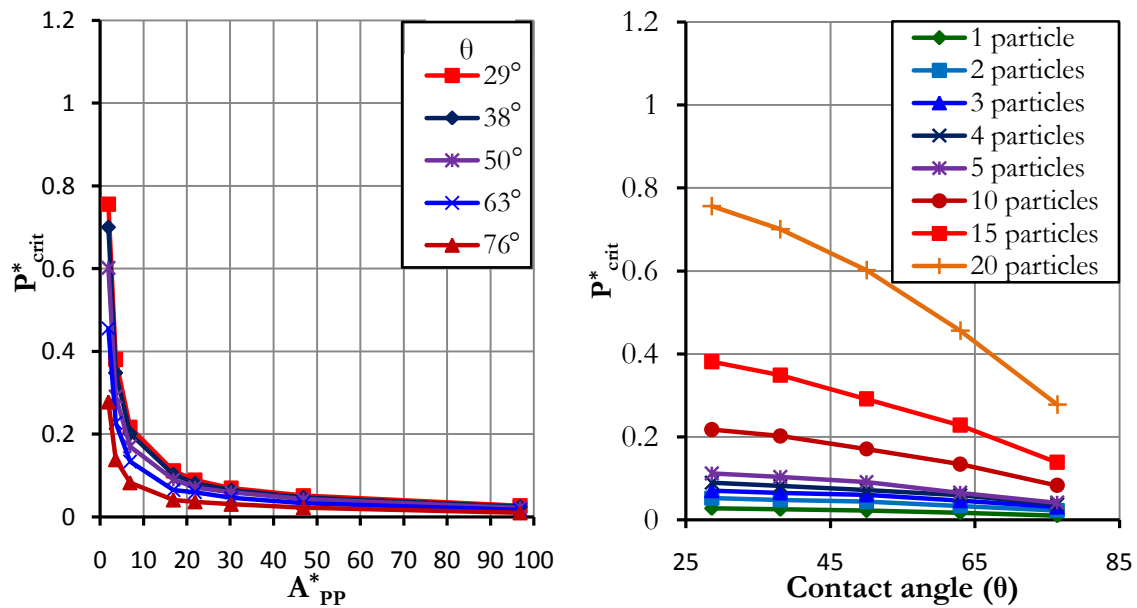


Figure 4-17. P_{crit}^* vs $\mathcal{A}_{pp}^*$ and P_{crit}^* vs θ for a period with edge length of 10 for contact angles of $29^\circ, 38^\circ, 50^\circ, 63^\circ, 76^\circ$.

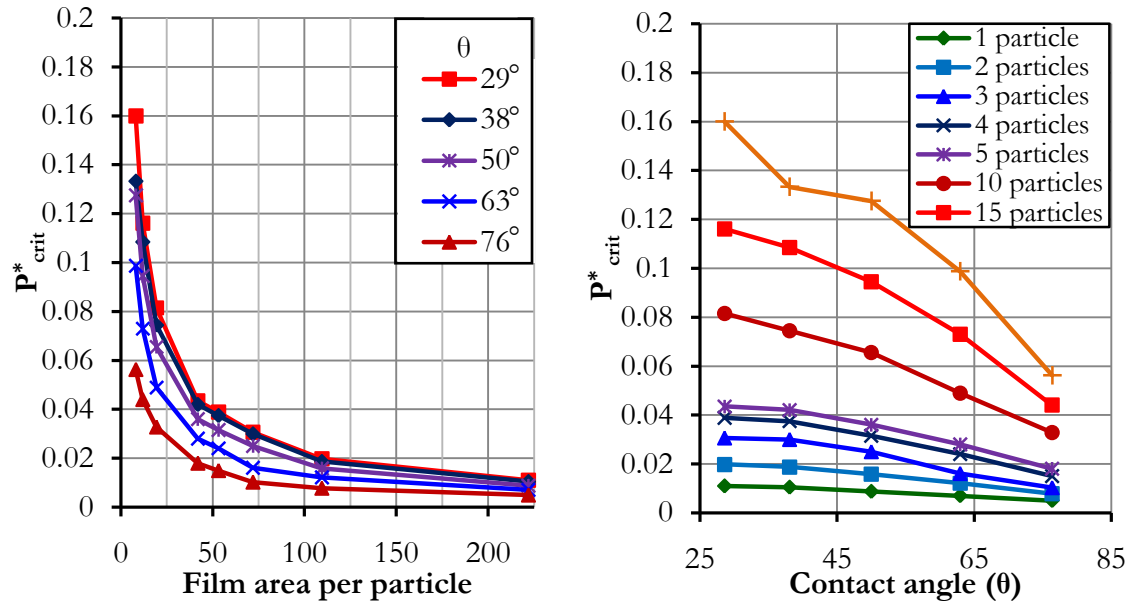


Figure 4-18. P^*_{crit} vs A^*_{pp} and P^*_{crit} vs θ for a period with edge length of 15 for contact angles of 29°, 38°, 50°, 63°, 76°.

However if the P^*_{crit} vs A^*_{pp} is compared for different L^*_p an additional feature can be identified (Figure 4-19). The P^*_{crit} found for a given A^*_{pp} is lower for larger values of L^*_p . At an A^*_{pp} of 21 and a contact angle of 29° the P^*_{crit} found for $L^*_p=10$ is 40 % of that for $L^*_p=5$ and at a contact angle of 76° this difference is 44 %. This can be attributed to a combination of periodic cells and regular packing described in section 4.6.3.

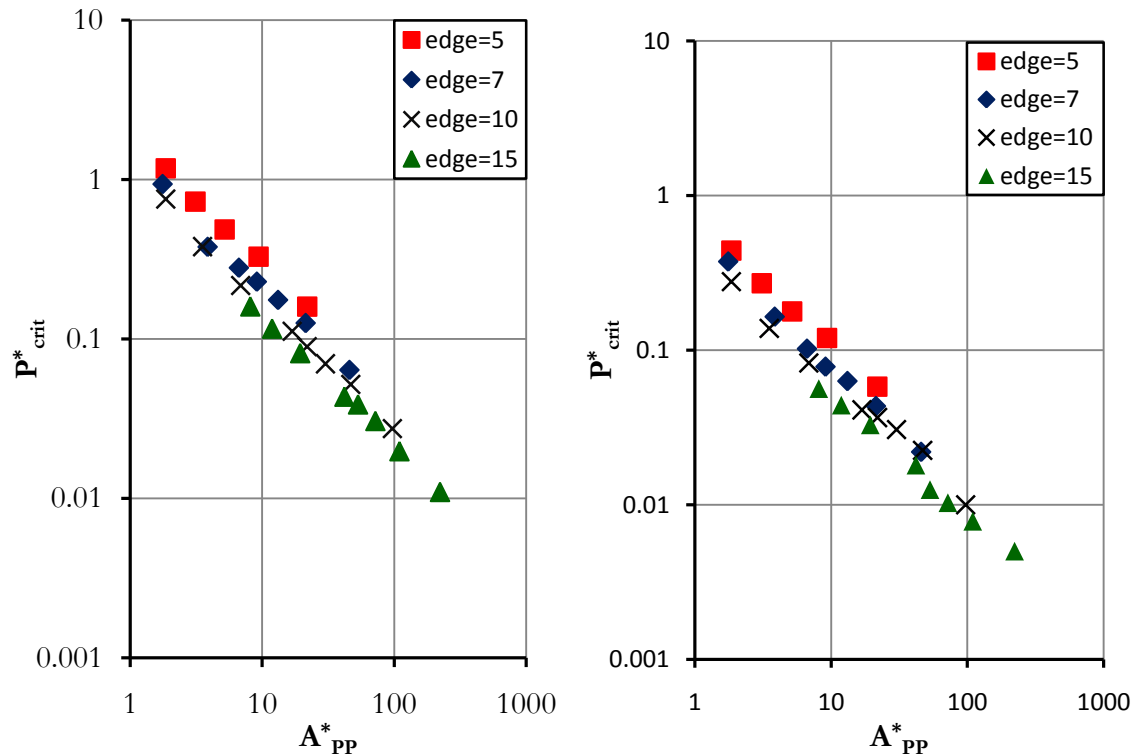


Figure 4-19. P^*_{crit} vs A^*_{pp} for contact angles of 29° (left) and 76° (right).

4.6.5 STATISTICAL ANALYSIS

Each value of P_{crit}^* plotted in figures Figure 4-15 - Figure 4-19 is a mean value, calculated from an average of 9 individual simulations, run at the same A_{pp}^* and θ . The 95 % confidence intervals for this data, calculated using the student t-test show no trend in size with A_{pp}^* or θ . All data for contact angles of 29° , 38° , 50° , 63° and 76° is plotted in Figure 4-20 with the 95 % confidence intervals shown on all data.

4.6.6 COMPARISON OF COMBINED MODEL DATA

The data from all the models is plotted together as P_{crit}^* against A_{pp}^* in Figure 4-20. For each contact angle, a trend line of the form $P_{crit}^* = KA_{pp}^{*\alpha}$ can be fitted to the data.

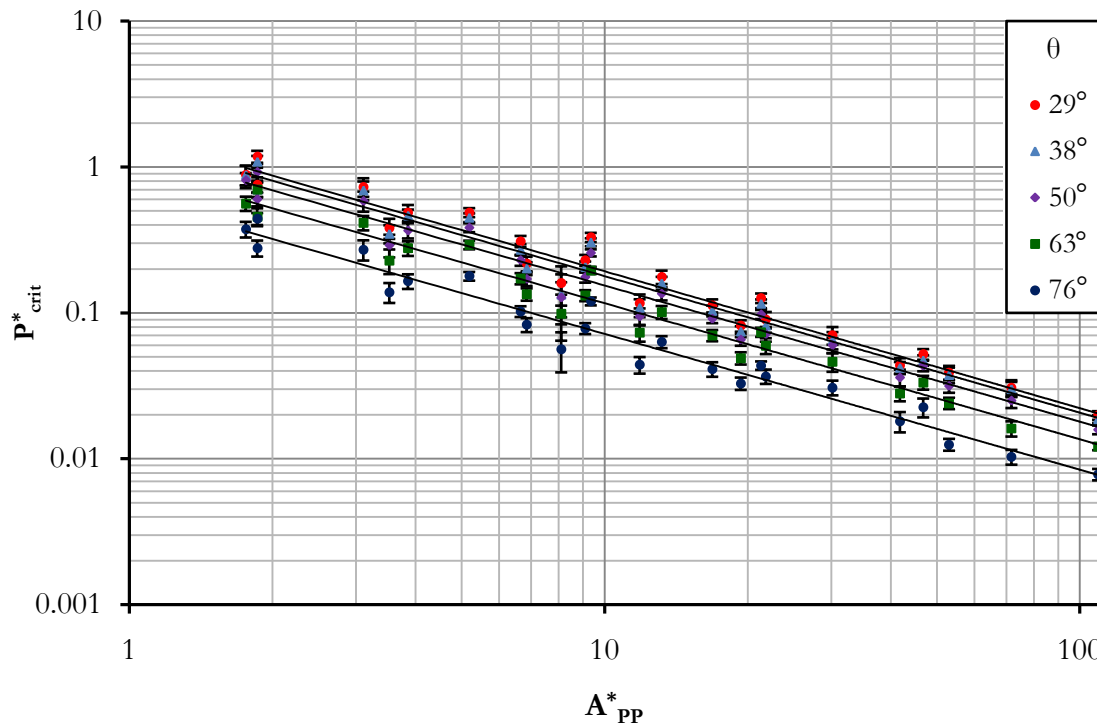


Figure 4-20. P_{crit}^* vs A_{pp}^* for randomly packed particles with contact angles of 29° , 38° , 50° , 63° or 76° . Error bars show the 95 % confidence interval.

Contact angle	K	α
29	1.6741	-0.939
38	1.5401	-0.936
50	1.321	-0.934
63	0.9924	-0.932
76	0.6103	-0.93

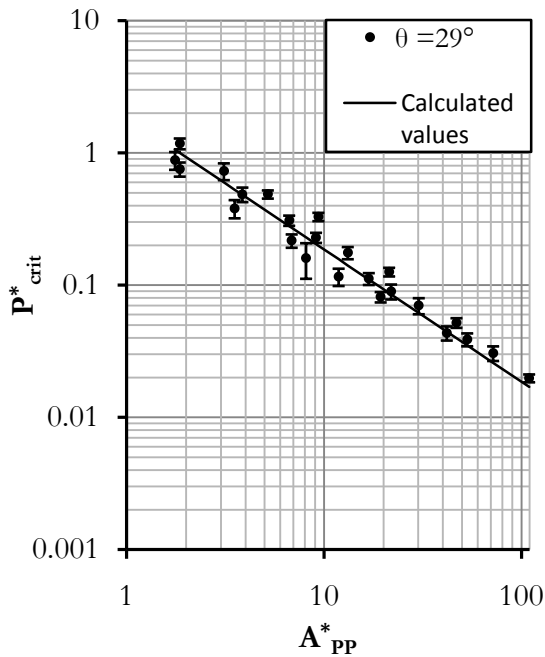
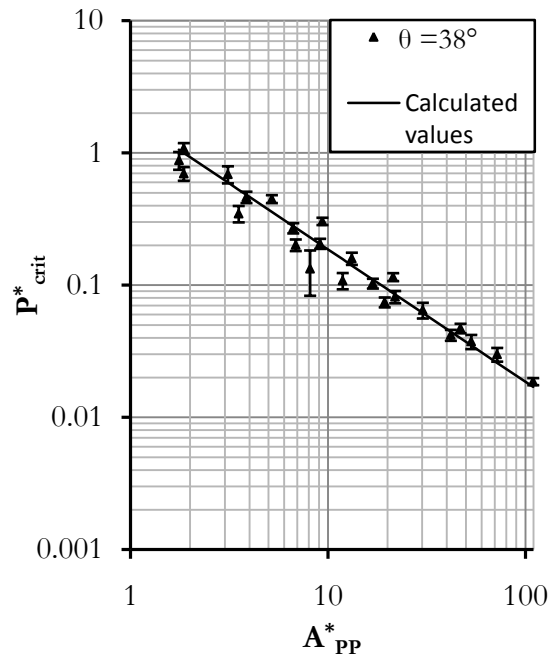
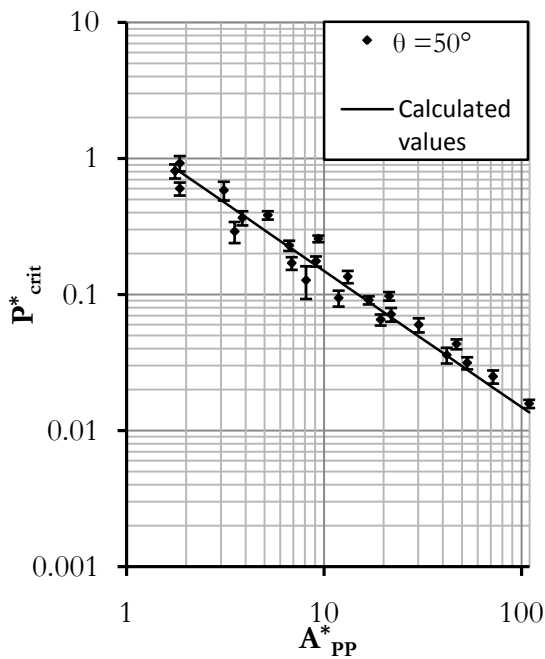
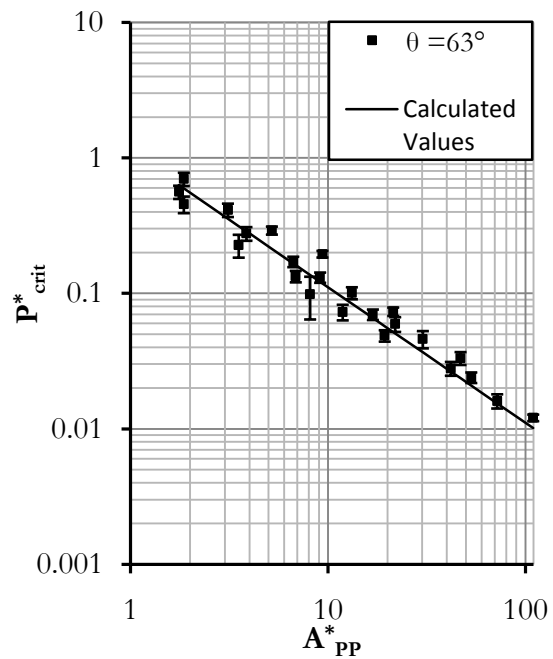
Table 2. Values of K and α for different θ .

The values of K and α for different θ are shown in Table 2. The proximity of all the values of α to -1 indicates that a relationship of the form shown in equation 4-6 may be fitted to the data.

$$P_{crit}^* = \frac{K}{A_{pp}^*}$$

4-6

The fitted value of K is found for each contact angle using an iterative procedure aimed at minimising the difference between P_{crit}^* calculated using equation (4-6) and the P_{crit}^* found using *Surface Evolver*. The fitted lines of P_{crit}^* using equation (4-6) and their comparison to the simulated results are shown in Figure 4-21, Figure 4-22, Figure 4-24 and Figure 4-25.

Figure 4-21. $\theta=29^\circ$, $K=1.859$.Figure 4-22. $\theta=38^\circ$, $K=1.734$.Figure 4-23. $\theta=50^\circ$, $K=1.440$.Figure 4-24. $\theta=63^\circ$, $K=1.057$.

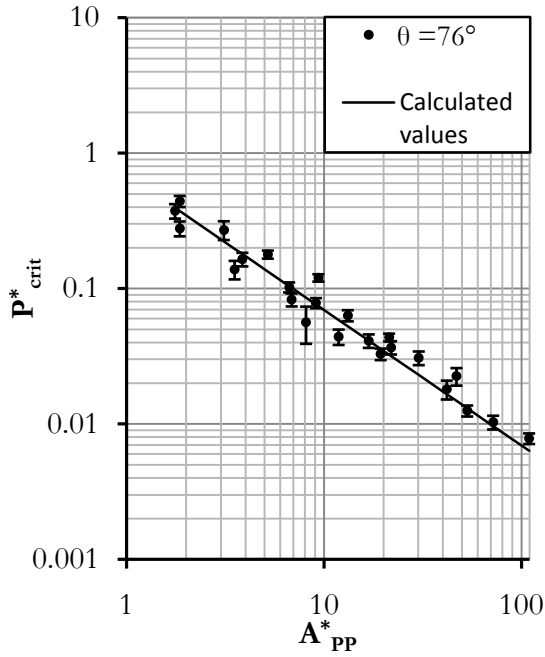


Figure 4-25. $\theta=76$, $K=0.661$

The fitted values for P^*_{crit} match with the trends obtained from the *Surface Evolver* models over the range used and by plotting the K values against contact angle the relationship in Figure 4-26 is seen.

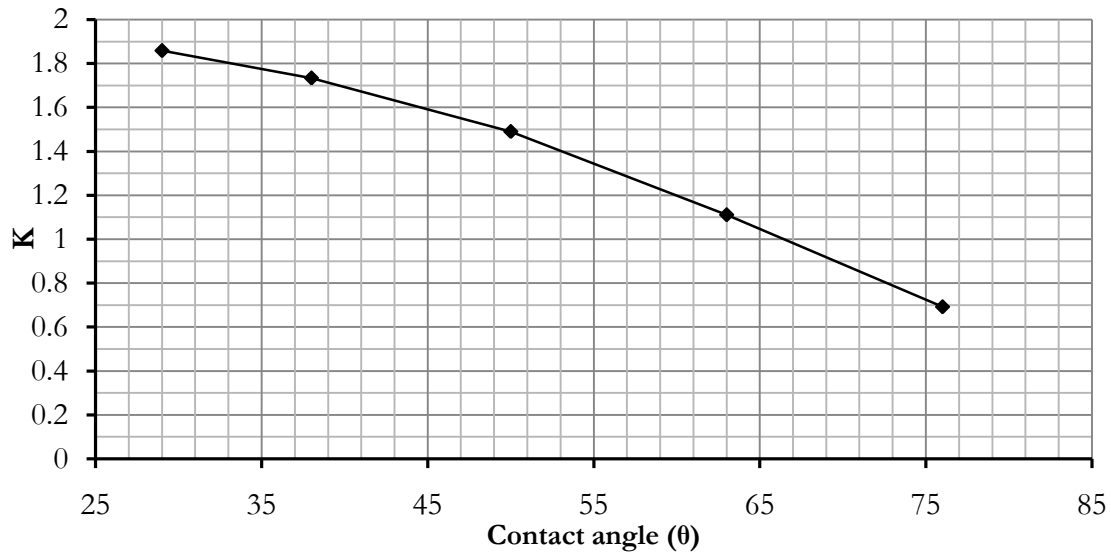


Figure 4-26. K vs contact angle.

With a relation between K and contact angle established it is now possible to use Figure 4-26 to obtain a value of K for a given θ which can then be used in equation (4-6) to find the P^*_{crit} for film with a given A^*_{pp} . This has been shown to fit well with the irregularly packed particle films in Figure 4-21, Figure 4-22, Figure 4-23, Figure 4-24 and Figure 4-25. However if plotted against the values for P^*_{crit} obtained for the hexagonal and square packing models the values returned by equation (4-6) for a θ of 45° are below those

found using the models (Figure 4-27). The values predicted by equation (4-6) are an average of 53 % less than those found by the square and hexagonal packing models. This disparity in modelled and predicted values is due to the same reasons as the difference in P_{crit}^* found between large and small scale periods. If particle size and shape are uniform, a uniform packing arrangement results in the highest P_{crit}^* achievable for a given contact angle and $\mathcal{A}_{pp}^*$.

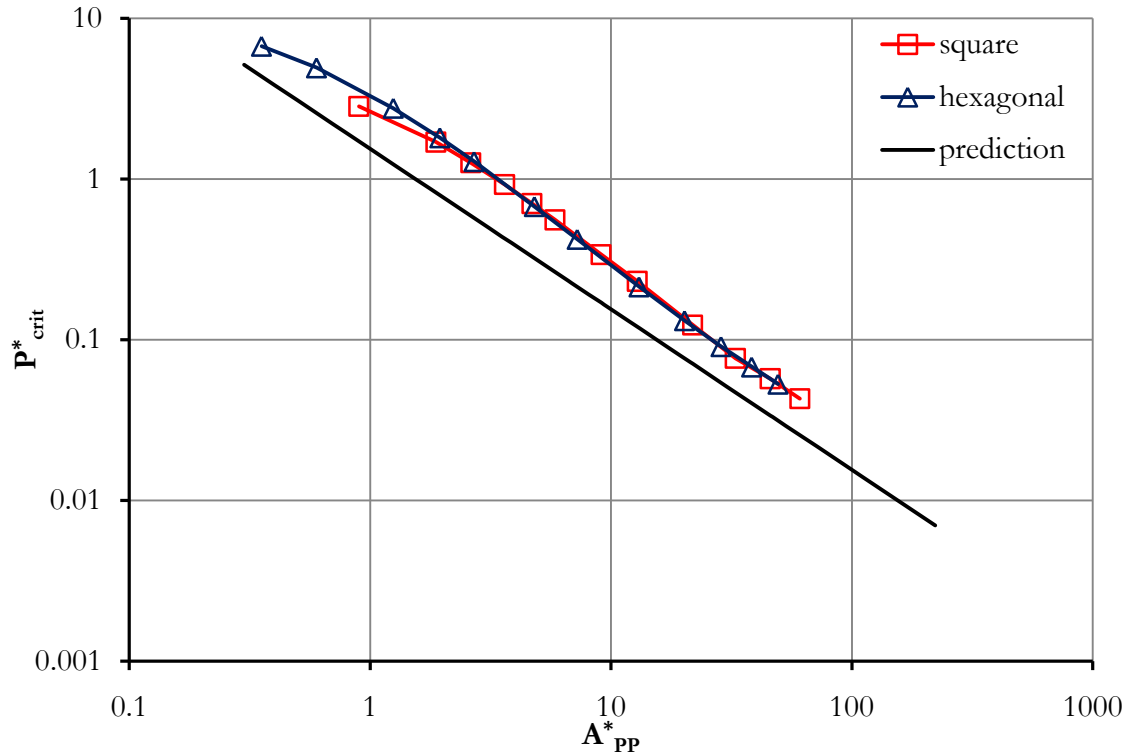


Figure 4-27. P_{crit}^* vs $\mathcal{A}_{pp}^*$ for square and hexagonal packing, with the predicted values of P_{crit}^* from equation (4-6), $K=1.547$.

4.6.7 SUMMARY FOR RANDOMLY PLACED PARTICLES

Equation (4-6) and Figure 4-26 can be used together to predict the P_{crit}^* of particle loaded films if it is assumed that the particle packing will adopt a random non-uniform arrangement and the $\mathcal{A}_{pp}^*$ and θ are known. The predicted P_{crit}^* can then be used in simulations of froth behaviour and as a parameter to define coalescence between two bubbles in the froth. This allows the bubble size distribution and therefore bulk foam properties to be simulated with a greater degree of accuracy.

4.7 SUMMARY

For 2D models the separation distance has potentially a much larger effect on P_{crit}^* than θ , however the limiting factor with these models is that when particles are touching the P_{crit}^* tends to infinity. They are also limited by their inability to take into account particle packing pattern which has been shown to have a large impact on the film stability. For these reasons it is preferable to use 3D simulations wherever possible as they give much greater insight into the effect of particles on the stability of thin films.

Expanding the *Surface Evolver* models into 3D has shown that when particles are evenly spaced, the area of film per particle (A_{pp}^*) can be used to compare the P_{crit}^* of different packing arrangements. This has been expanded to include films containing randomly spaced particles over larger areas. A_{pp}^* can also be used to compare film stability and loading between experimental and modelled systems. Sadr-Kazemi and Cilliers (2000) developed a method of directly sampling and measuring the particle laden bubble lamella. This approach has been used to measure film loading in experimental and industrial systems and allows the particle size distribution, film sample area and particle size to be measured. This data can be combined to provide an A_{pp}^* which can be used with equation 4-6 to calculate a P_{crit}^* for the films.

P_{crit}^* is highest at a given A_{pp}^* and θ when the particles are packed in a regular hexagonal or square arrangement. If the particles are randomly placed in the film they open up larger areas of empty space in the film, reducing the P_{crit}^* it can sustain. It is therefore desirable to have particles as evenly spaced in the film as possible to maximise film stability. However, flotation froths do not generally contain particles in uniform packing arrangements, indeed capillary pressure and surface tension actively drive particle agglomeration in a film. Uniform particle spacing is often a feature seen when charged particles are found at an interface, when the particles tend to adopt the hexagonal packing patterns investigated in section 4.4. If additional film stability were desired in a flotation froth by charging the particles they would be forced to form more regular packing arrangements, stabilising the froths to a greater extent.

As the particles in the film will agglomerate, the true packing arrangement will be somewhere between the random or uniform packing arrangements simulated. It has been shown that the P_{crit}^* of the film can be related to the packing arrangement of the particles it contains. It is also necessary to consider the impact that more than one layer of particles has on the stability of the film, as flotation froths are often heavily laden with particles.

5 DOUBLE LAYERS OF PARTICLES IN A THIN FILM

5.1 INTRODUCTION

Flotation films are often heavily laden and consequently contain areas with more than one layer of particles in them. Chapter 4 discussed results obtained from investigation into single layers of particles attached to a thin film, this chapter will investigate the effects of a double layer of hexagonally packed particles on the stability of a thin film.

A double layer of particles is a more complicated system than a single layer one, as particles must be in contact with those in the opposite layer, but not necessarily those in the same layer. As a result there are more geometric considerations when formulating models and investigating their stability.

There are three modes of failure for a film containing a double layer of particles, as opposed to the two described in section 4.2. The first section of this chapter will describe these different modes of failure and the conditions under which they apply as well as introducing the geometry of double layers. The conditions under which specific modes of film failure occur is then investigated, followed by an analysis of how this affects the film stability.

5.2 FAILURE CRITERIA

5.2.1 PACKING GEOMETRY AND MAXIMUM STABLE CONTACT ANGLE

Chapter 4 considered single layers of particles bridging both sides of a thin film, when it is only possible for them to stabilise the film if their contact angle is below 90° . However, when considering a double layer of particles in the film (Figure 5-1) it is possible to have particles bridging only one side of the film. In this case, the film interfaces are held further apart and the TPC can exist below a particles equator without rupturing the film (Kaptay 2004, Horozov *et al.* 2005). Kaptay (2004) derived equation 5-1 to find the maximum sustainable contact angle for a close packed hexagonal double layer. $F_{i,max}^{CP2}$ is the interfacial force and R_i is the particle radius and when $F_{i,max}^{CP2}=0$ equation 5-1 predicts the maximum stable θ for a close packed hexagonal double layer to be 129° . However hexagonally packed double layers of particles can still exist when not close packed in which case the maximum stable θ is dependent on the separation distance of the particles. The geometry for a hexagonally packed double layer is shown in Figure 5-2. The maximum stable contact angle that can be accommodated by the double layer as a function of particle separation distance S_{PP}^* is shown in equation 5-4 which can be derived from simple geometric considerations (equations 5-2 and 5-3). Where H is the vertical distance between two particle centres in opposite layers and l_{max} is the distance from a particle equator to the top of the particles in the opposite

layer. The maximum sustainable contact angle at $P^*=0$ will be the one at which the flat film interface is in the $\xi=-l_{max}^*$ plane relative to the upper particle layer. This leads to equation 5-4. As S_{PP} increases the particles in the lower layer move into the upper layer and the maximum sustainable contact angle, H and l_{max}^* (when $P^*=0$ and the interface is flat) decrease. The relationship between θ_{maxhex} and S_{PP}^* is shown in Figure 5-3.

$$F_{i,max}^{CP2} = 4\pi R_s \gamma (\cos\theta + 0.633) \quad 5-1$$

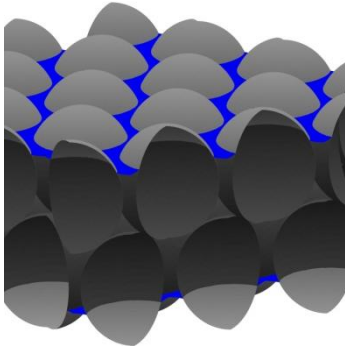


Figure 5-1. Double layer of particles in a film.

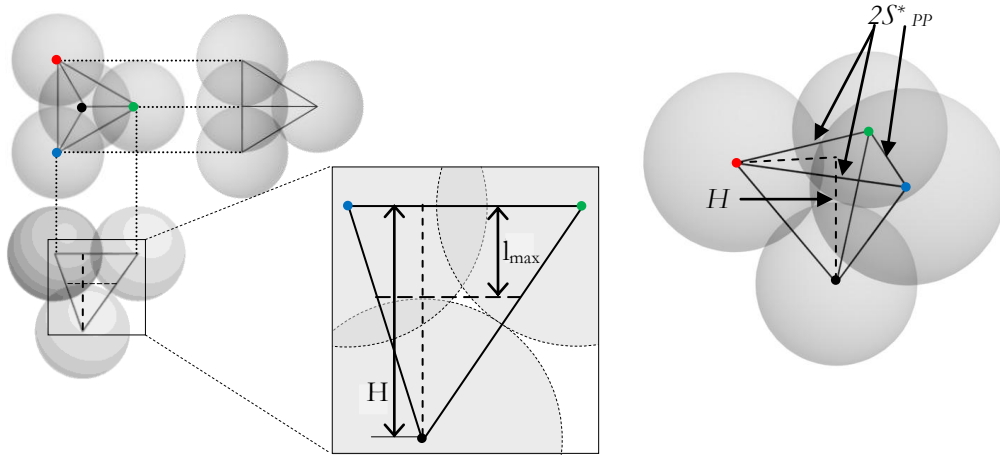


Figure 5-2. Showing the geometry of a close packed hexagonal double layer. Coloured dots represent the centre of a particle.

$$H = \sqrt{4R_p^{*2} - \frac{S_{PP}^{*2}}{\cos 30^2}} \quad 5-2$$

$$l_{max}^* = H - R_p^* \quad 5-3$$

$$\theta_{maxhex} = 180 - \cos^{-1} \left(\frac{l_{max}^*}{R_p^*} \right) \quad 5-4$$

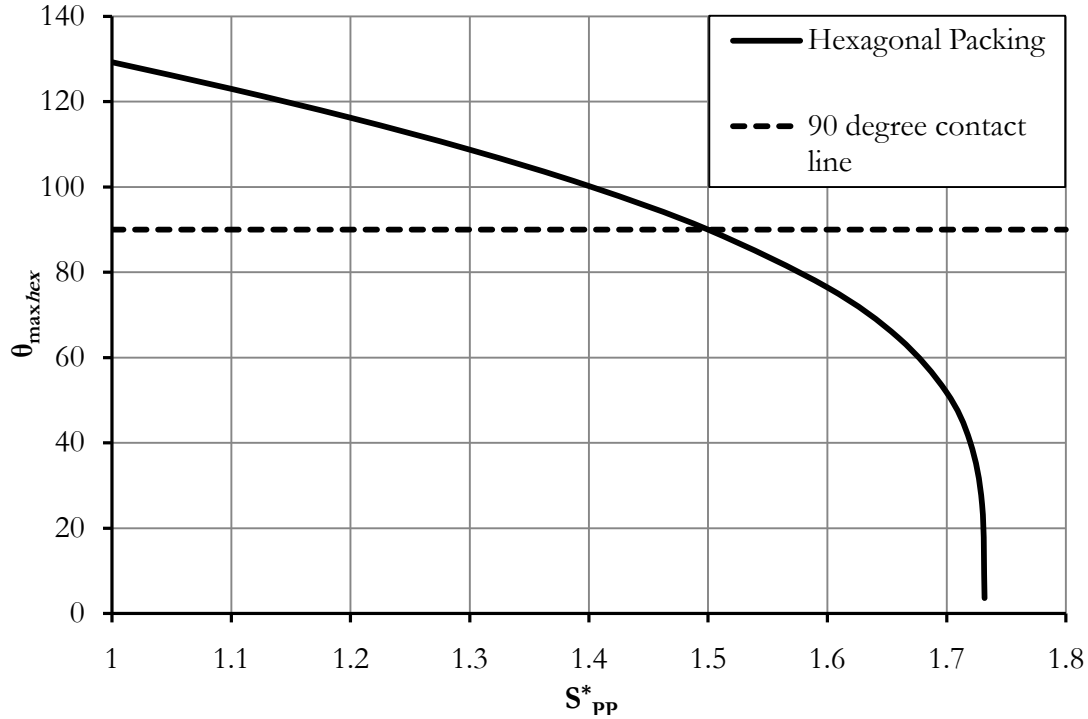


Figure 5-3. The maximum θ that does not bridge the opposite layer of particles as a function of the separation distance (S_{pp}^*) between particles in the same layer.

Both equations 5-1 and 5-4 show that if the particles are close packed hexagonal and $P^*=0$, the liquid vapour interface will not bridge the opposite layer of particles until its contact angle exceeds 129° . This is therefore the maximum sustainable contact angle for a double layer of particles. However it is also highly unstable, a slight increase in particle separation distance anywhere in the double layer will cause the interface to bridge the opposite layer, immediately rupturing the film. Conversely an infinitesimal increase in capillary pressure will cause the interface to curve, again bridging the opposite particle and causing immediate failure.

5.2.2 FAILURE MODES

For a single layer of particles the failure criterion was defined as the capillary pressure at which the opposite sides of the film come into contact with each other. Particle bridging was considered but as it results in the immediate destruction of the film it was discounted. However, contact angles at which particle bridging can occur in a single layer are stable under certain conditions in a double layer. There are now three different modes of failure to consider;

5.2.2.1 Particle Bridging

For contact angles above 90° (horizontal dashed line in Figure 5-3) the film will fail when it touches a particle in the layer below regardless of whether the double layer is close packed or spread out. In this case when the film interface bridges the opposite layer of particles the only energetically stable position for the TPC is beyond that occupied by the TPC on the opposite side of the film. As a result, the two

TPCs are drawn together on the particles surface and the film fails. The effect is similar to the case of a single layer of particles with a contact angle above 90° (chapter 4) and is shown below in Figure 5-4.

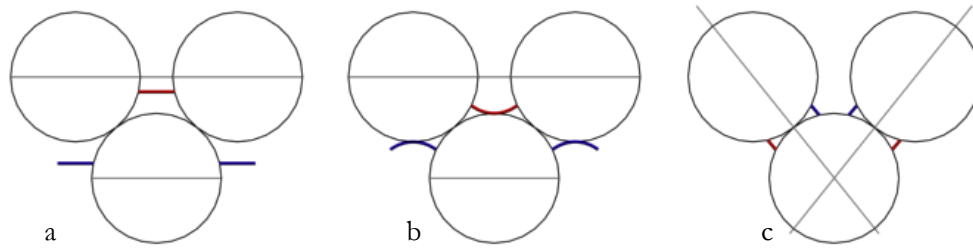


Figure 5-4. 2D representation of particle bridging in a double layer. Initially the films are flat at $P^*=0$ but sitting below the particle equator at (a). P^* increases and the film curvature brings the interfaces in contact with the particles in the opposite layer (b). Once the particles bridge the opposite layer the interfaces move to the new "below equator" line which involves them passing through each other (c). Clearly this involve the opposite sides coming into contact with each other resulting in failure of the film.

5.2.2.2 Capillary Pressure driven Failure

Consider the case of the liquid-vapour interface bridging the particles in the opposite layer as stated above but for a contact angle of less than 90° . As $\theta < 90^\circ$ the film will not necessarily fail immediately, failure instead depends on the P^* and S_{pp}^* . Both liquid-vapour interfaces are attached to the upper and lower layer of particles creating a highly distorted surface. As P^* is increased the film curvature increases as well and the film eventually fails when its opposite sides touch in the gaps between particles, as shown in Figure 5-5 and Figure 5-6.

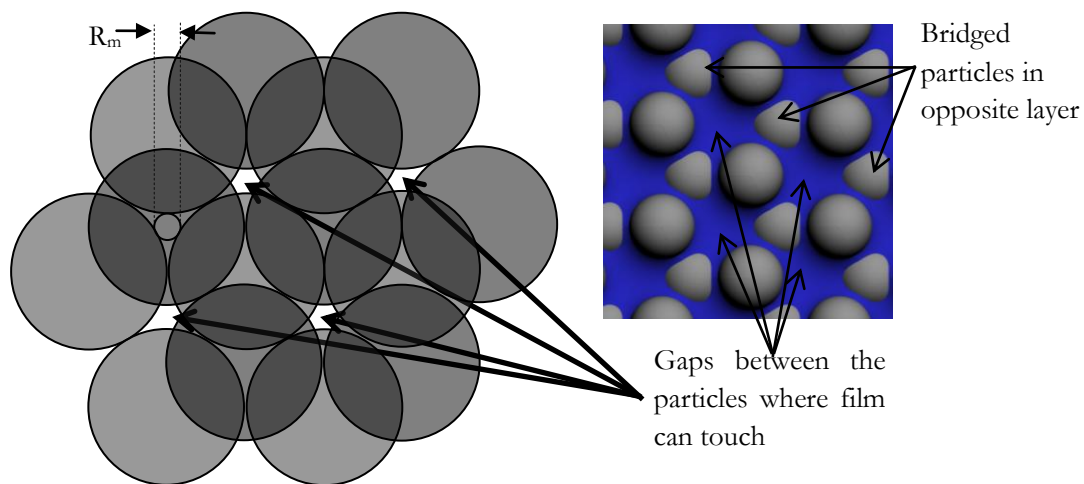


Figure 5-5. The gaps in between double layers of particle where the opposite sides of the film can meet. The figure also shows a bridged double layer of particles.

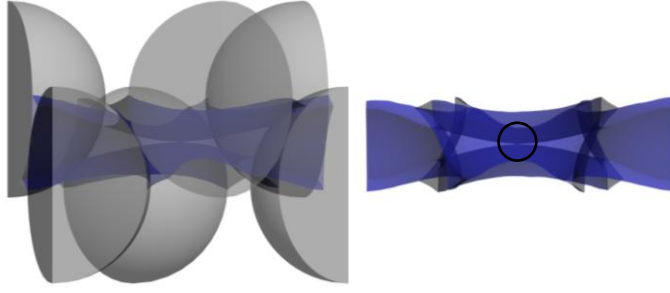


Figure 5-6. Single unit cell for a double layer at capillary driven failure. Particle and film (left), just film side view (right), point at which the interfaces meet highlighted by circle.

5.2.2.3 Film Inversion

This relates to the maximum capillary pressure the film can withstand before it inverts for an unbridged double layer. Consider the interface in the interstice between three hexagonally close packed particles. For each contact angle there is a maximum capillary pressure that this liquid-vapour interface can withstand before it becomes energetically more favourable for the TPC to exist on the other side of the particle, effectively flipping the film. A film loaded with a single layer of particles will fail long before the maximum sustainable capillary pressure is reached ($P^*_{critmax}$), even when close packed. However, for a double layer of particles it is possible to reach $P^*_{critmax}$ before particle bridging occurs. As P^* increases so does the interfacial curvature, the TPC also moves down the surface of the bubble as shown in Figure 5-7. When the maximum sustainable P^* is exceeded the interfaces on both sides of the film become unstable and the TPCs try to move through each other, in a similar manner to the bridging dewetting mechanism, to re-establish themselves in an energetically stable geometry. When this occurs the TPCs from opposite sides of the film touch causing immediate failure of the film.

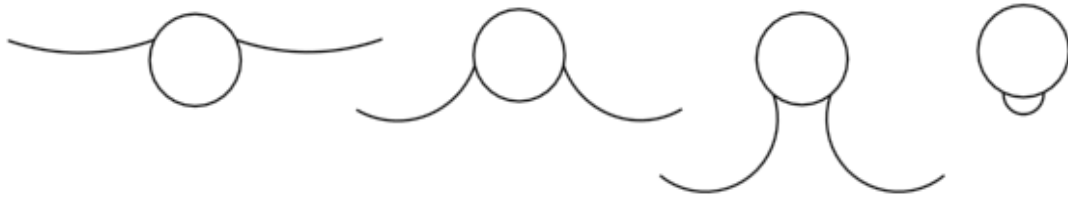


Figure 5-7. Increase in film curvature (exaggerated for illustration) with P^* (left to right) until film inversion occurs (far right).

5.3 IDENTIFYING FAILURE MODES

5.3.1 IDENTIFYING $P^*_{CRITMAX}$

To identify the $P^*_{critmax}$ for a given θ and S^*_{pp} the *Surface Evolver* (Brakke 1992) model used in previous sections was modified. It is possible to prescribe either a target volume or target pressure to a body in *Surface Evolver* with the prescribed variable contributing to the surface energy and the non-prescribed one calculated from the model. As $P^*_{critmax}$ is the maximum stable capillary pressure, if pressure is the

prescribed variable in the model as in chapter 4, once $P^*_{critmax}$ is exceeded the model will crash as the surface inverts. To accommodate this the *Surface Evolver* model was run in a similar fashion as in section 4.3 except that volume was used as the prescribed value instead of pressure. At each step the volume was reduced by a small amount V^*_{step} and the surface was evolved to the minimum energy, then the pressure and lowest point of the film (z_{LP}) were recorded, the volume was then reduced by a small amount and the process repeated. All of the data for P^* was then plotted as a function of volume and the highest capillary pressure attained was identified and taken as $P^*_{critmax}$. At the same time its corresponding z_{LP} was also recorded. A typical plot of P^* as a function of volume is shown in Figure 5-8, the $P^*_{critmax}$ is clearly identifiable at a volume of 10.1.

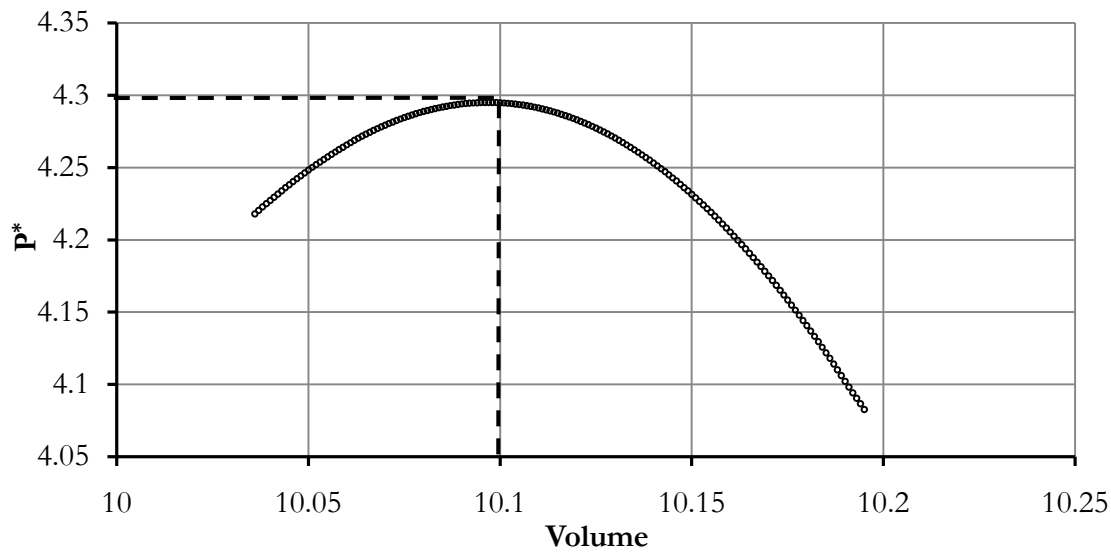


Figure 5-8. P^* as a function volume, $\theta=30^\circ$, $S^*_{pp}=1.13$.

$P^*_{critmax}$ for a range of contact angles is shown as a function of S^*_{pp} in Figure 5-9 where it can be seen that the trends are similar to those seen in chapter 4. If $P^*_{critmax}$ is compared to P^*_{crit} as in Figure 5-10 it can be seen that a double layer of particles stabilise the film to a greater extent for all separation distances. On average the capillary pressure required to rupture the film for a single layer of particles is 75 % of that for a double layer, for all contact angles up to 90° . Here S^*_{pp} has been used instead of $\mathcal{A}^*_{pp}$ as the same packing arrangement is being compared (hexagonal) so the relative trends will be the same regardless of the packing density measure used. S^*_{pp} in the double layer case refers to the spacing between particles in the same layer.

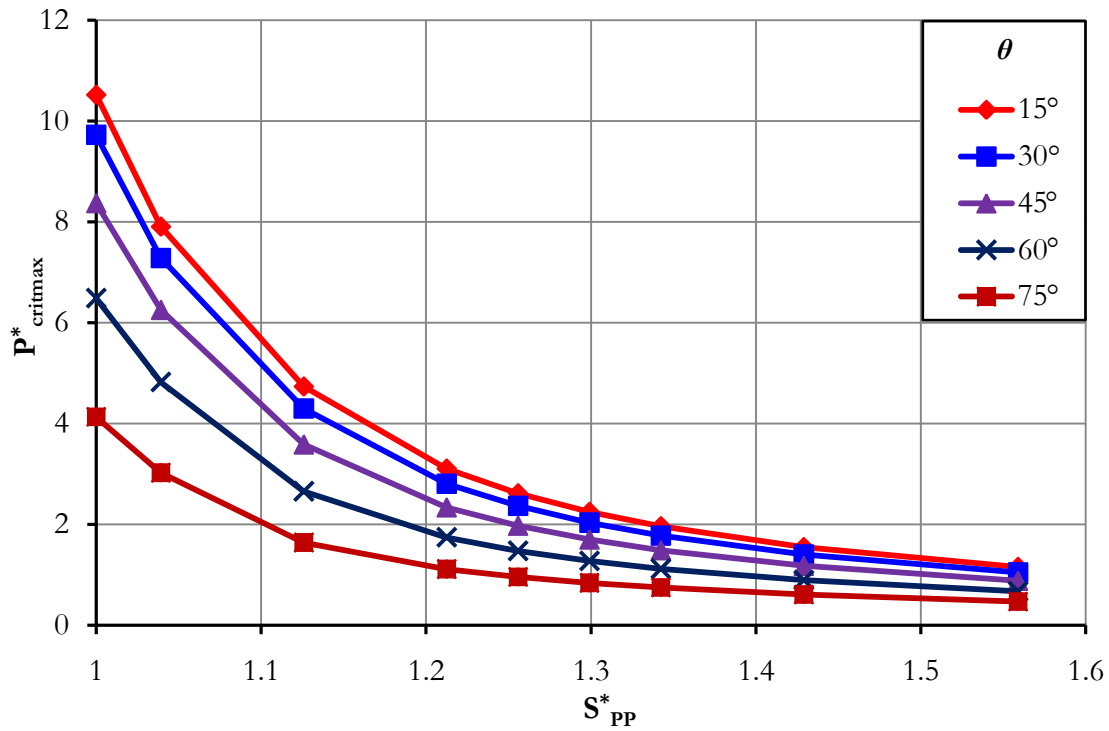


Figure 5-9. $P_{critmax}^*$ as a function of S_{pp}^* for varying contact angle.

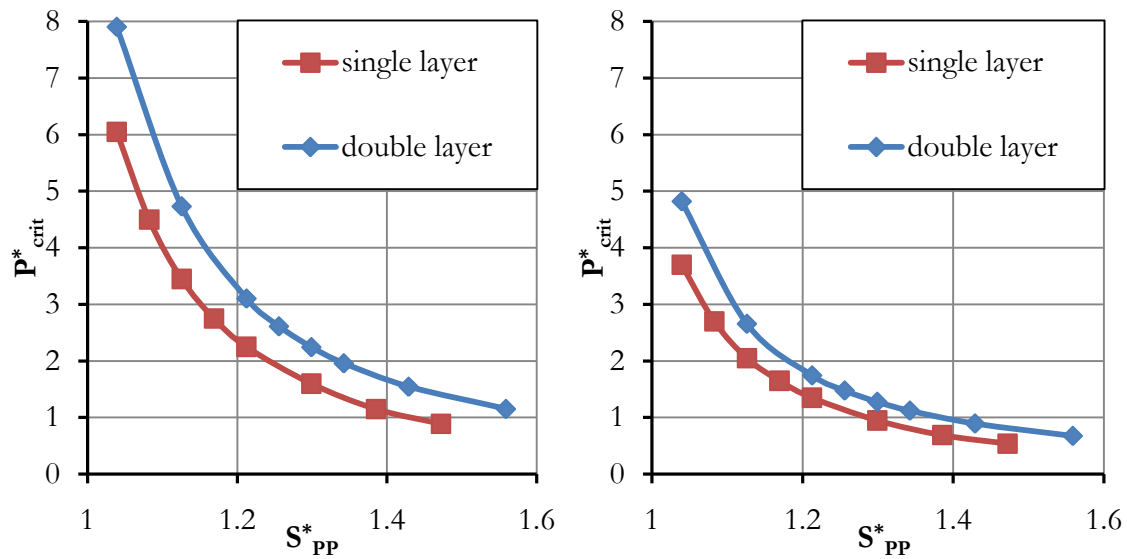


Figure 5-10. P_{crit}^* and $P_{critmax}^*$ as functions of S_{pp}^* for contact angles of 15° (left) and 60° (right).

Mason and Morrow (1994) and Horozov *et al.* (2005) used a toroidal pore model to calculate $P_{critmax}^*$ for an interface passing through the gap between three particles. The radius of the torus throat is taken as $2R_m$, where R_m is the radius of a cylinder that can fit through the gap between three closely packed spheres, as identified in Figure 5-5. The formulae used by Horozov *et al.* (2005) are shown in equations 5-5 and 5-6;

$$P_{critmax}^* = \frac{2\gamma_{LV}\sqrt{1 - 3\sin^2\theta/4}}{R_p\left(\frac{2}{\sqrt{3} - \sin\alpha_{max}}\right)} \quad 5-5$$

$$\alpha_{max} = \theta + \cos^{-1}\left(\frac{\sqrt{3}\sin\theta}{2}\right) \quad 5-6$$

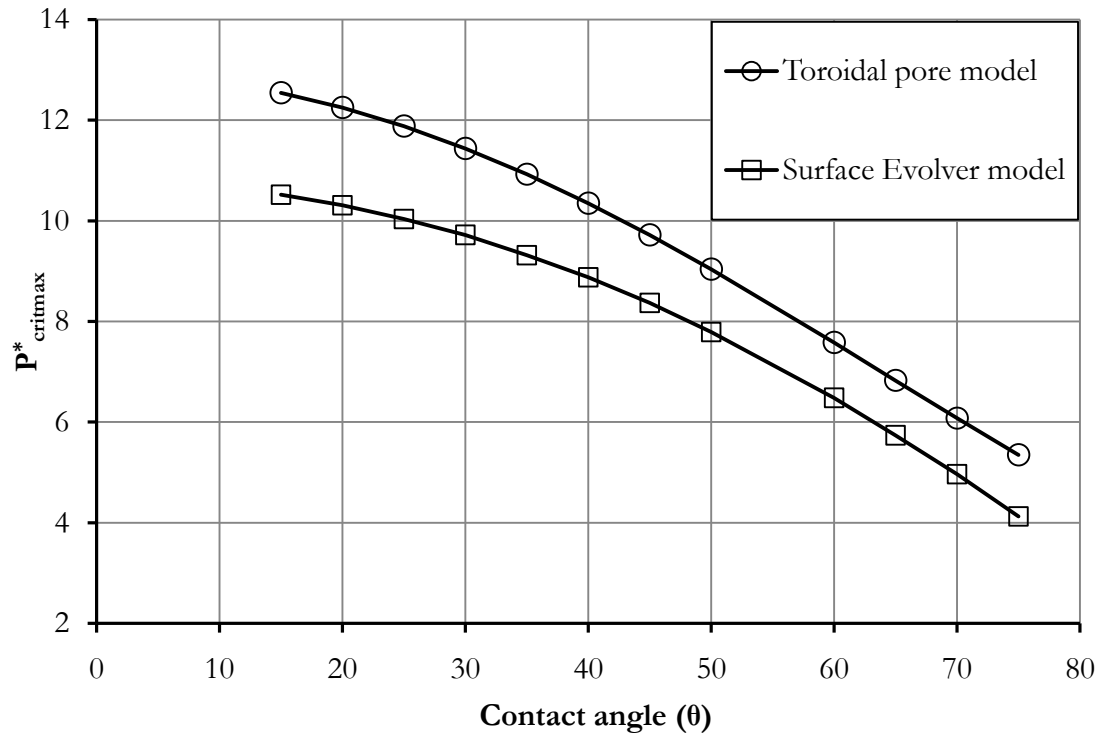


Figure 5-11. $P_{critmax}^*$ as a function of θ , comparing toroidal pore model and *Surface Evolver* model. $S_{pp}=1$.

Comparing the $P_{critmax}^*$ obtained from *Surface Evolver* and the toroidal pore model (Figure 5-11) it is clear that both approaches produce the same trends, but the *Surface Evolver* model returns consistently lower values. They are on average 84 % of the toroidal pore model ± 2.4 % with a slightly decreasing trend in difference with θ . At $\theta=15^\circ$ the *Surface Evolver* model is 84 % of the toroidal pore model and at $\theta=75^\circ$ it is 77 %.

It was shown in chapter 4 when the particles are close packed, the film shape at failure pressure is highly distorted. The capillary pressure at which film inversion occurs is much higher than P_{crit}^* . This results in an even more distorted interface (Figure 5-12), the shape of which is affected by the TPC at the particle's surface. The toroidal model cannot take this into account, which may account for its consistently higher $P_{critmax}^*$.

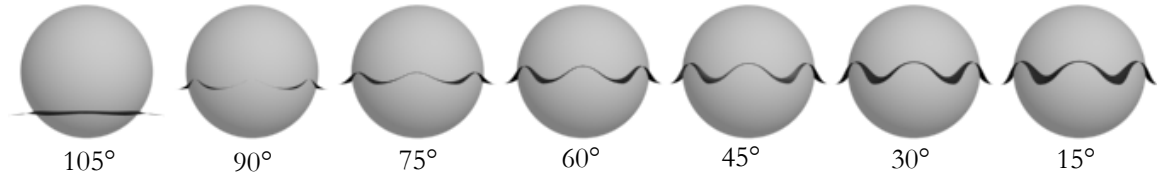


Figure 5-12 Showing the increase in distortion in film surface from $\theta=15^\circ$ to $\theta=105^\circ$.

When $P^*_{critmax}$ is found, the corresponding film shape is also extracted from the model and stored. This makes it possible to find the lowest point that the film reaches before it inverts (z_{LP} shown as a function of S^*_{pp} and θ in Figure 5-13). The z_{LP} varies with θ and S^*_{pp} as well as $P^*_{critmax}$ however, unlike $P^*_{critmax}$ it passes through a maximum at a θ of 60° for all separation distances. There is a steep drop at contact angles above 60° . At a contact angle of 45° the value of z_{LP} is 4 % lower than that for 60° value but at 75° it is 19 % lower. If values further from the minimum are taken (30° and 90°) they are 15 % and 85 % lower respectively, showing the steep drop off in z_{LP} at $\theta > 90^\circ$. It can be seen in Figure 5-12 that the film will distort to a greater degree before it inverts the further the contact angle is below 60° . At contact angles greater than 60° the film is less distorted but sits further below the particle equator which allows it to travel further down the particle before inverting.

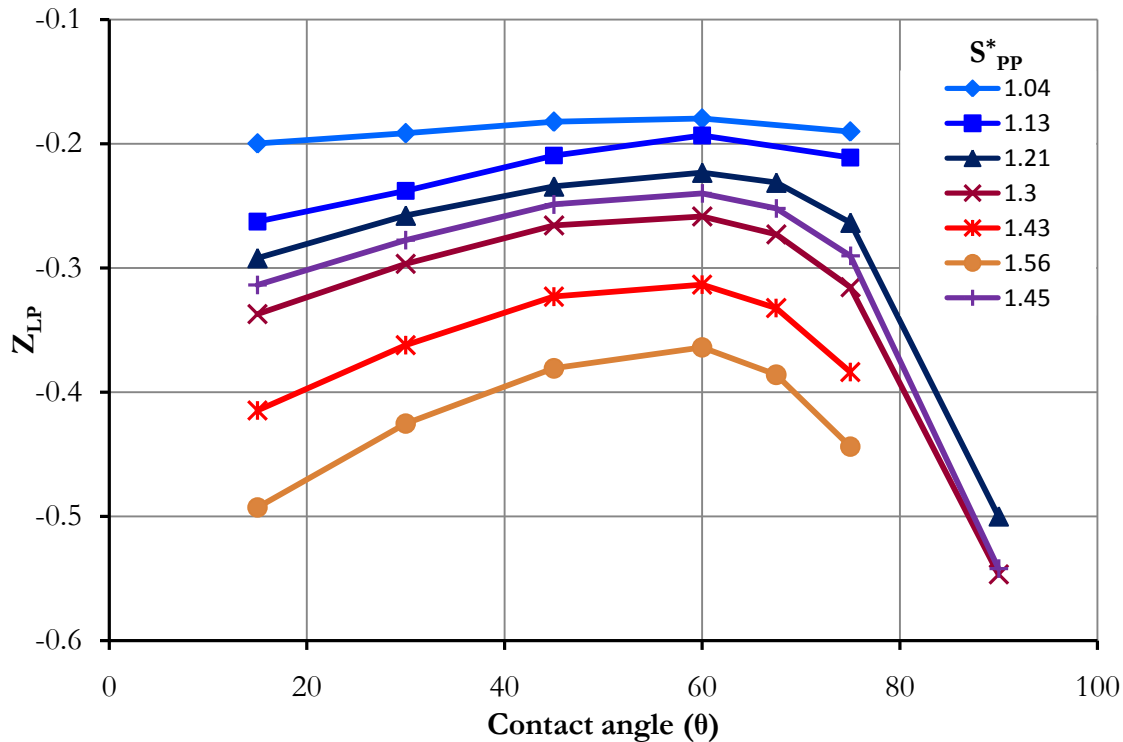


Figure 5-13. z_{LP} as a function of θ for various S^*_{pp} .

So far it has been assumed that the film will fail through *film inversion* at all S^*_{pp} . However, as the separation distance increases and z_{LP} becomes lower there is a point at which the liquid-vapour interface bridges the particle in the opposite layer before it inverts. This changes the mode of film failure. The z_{LP}

data, when combined with the particle packing geometry can therefore be used to identify the criteria under which the liquid vapour interfaces of the film will bridge the particles in the opposite layer, changing the failure mode.

5.3.2 DETERMINING FILM FAILURE MODE

This section will investigate the conditions under which a particular failure mode will occur for a double layer of spherical particles. When the particles are closely packed together and the contact angle is below 90° , the film will invert before it bridges the particles in the opposite layer. As S_{pp}^* increases the $P_{critmax}^*$ decreases, however, the ξ_{LP} also decreases bringing the interface closer to the particles in the opposite layer. At a specific S_{pp}^* the liquid-vapour interface will bridge the opposite layer of particles before it inverts. At this point the mode of failure changes from film inversion and its associated $P_{critmax}^*$ to either *particle bridging* (if $\theta > 90^\circ$) or *capillary pressure driven failure*. It is possible to identify the point at which this transition in failure mode occurs by comparing the values of ξ_{LP} and the coordinates of the top of a particle in the opposite layer (l_{max} in Figure 5-2). At values of θ below 90° , when bridging occurs, P_{crit}^* must be found for the bridged double layer, using the same approach as in section 4.3. If $\theta > 90^\circ$ when bridging occurs the film will fail immediately due to *particle bridging*.

5.3.2.1 Transition from film inversion to particle bridging

The ξ_{LP} at a θ of 45° are plotted as a function of S_{pp}^* in Figure 5-14. The position of the top of the particle in the opposite layer ($-l_{max}^*$) is also plotted using equations 5-2 and 5-3.

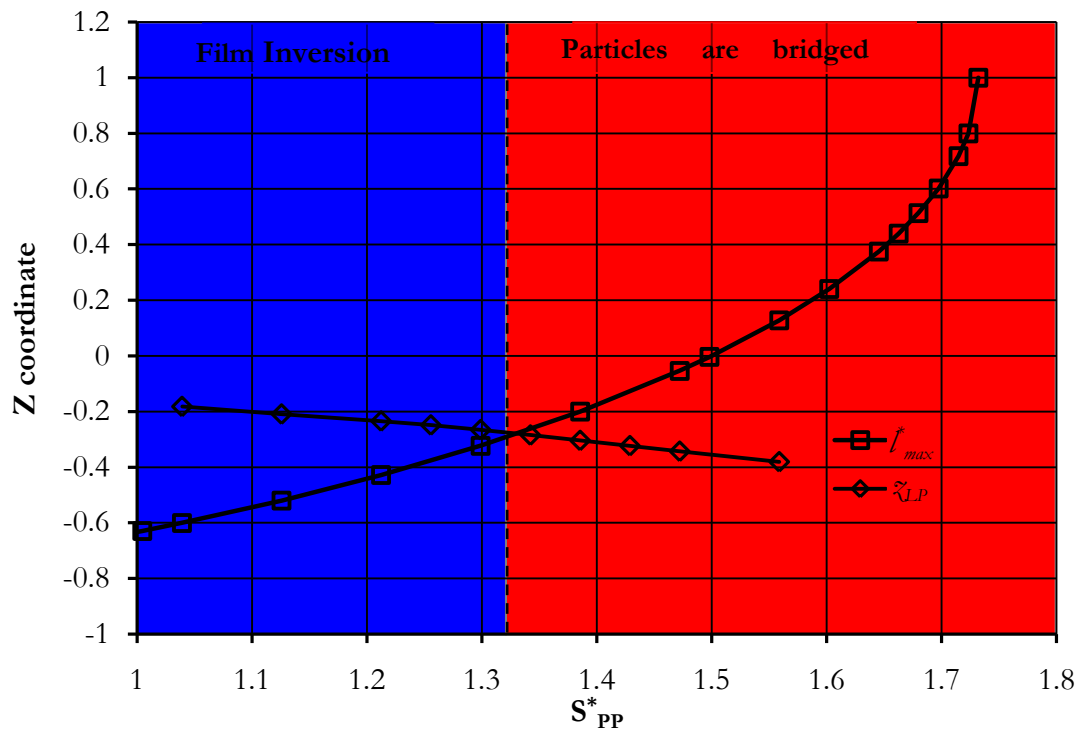


Figure 5-14. ξ_{LP} and $-l_{max}^*$ as a function of S_{pp}^* . Red background represents values of S_{pp}^* at which film bridges particles, Blue values at which film fails through *film inversion*.

If the z_{LP} is greater than $-l_{max}^*$ then the film will fail at $P_{critmax}^*$ (film inversion). For the corresponding S_{PP}^* , if the opposite is true then the film will fail when its opposite sides touch, i.e. at P_{crit}^* (capillary pressure driven failure). For $\theta=45^\circ$ the S_{PP}^* at which failure mode changes (S_{PPC}^*) is roughly 1.33, as highlighted in Figure 5-14.

It was established in section 5.3.1 that as contact angle changes so does the z_{LP} , meaning that the value of S_{PPC}^* is also dependant on θ . Figure 5-15 shows the variation of z_{LP} with contact angle and S_{PP}^* whilst Figure 5-16 shows the S_{PPC}^* for contact angles from 15° to 105° .

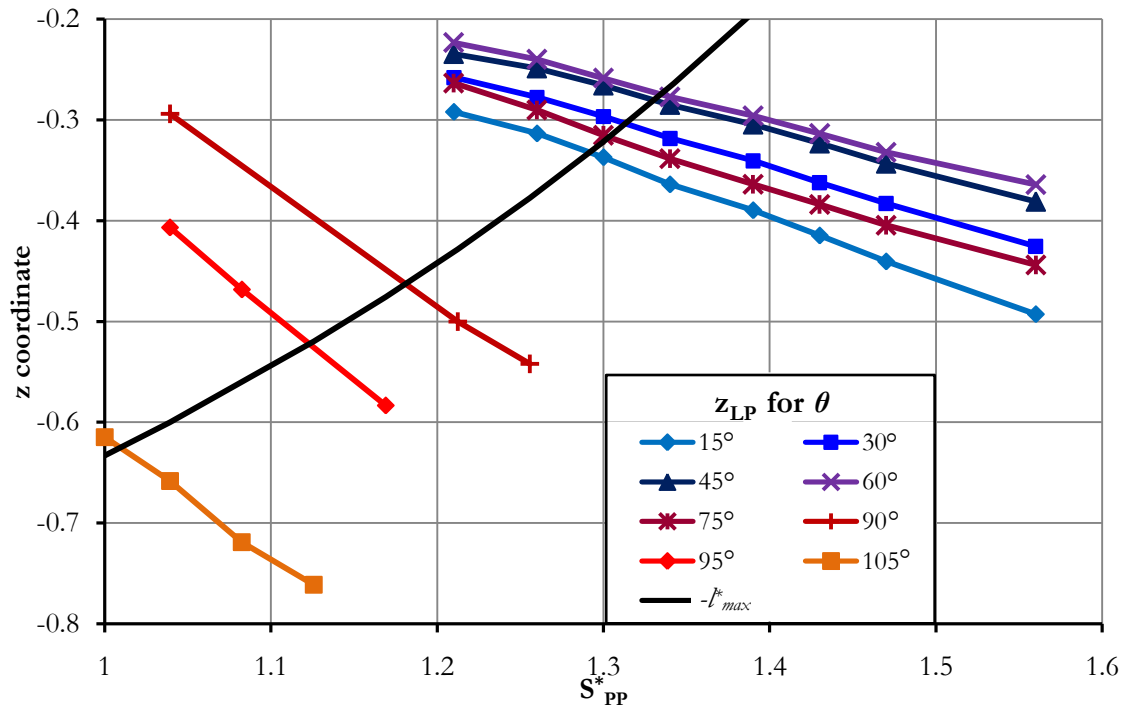


Figure 5-15. z_{LP} and $-l_{max}^*$ as a function of S_{PP}^* for contact angle of 15° , 30° , 45° , 60° and 75° .

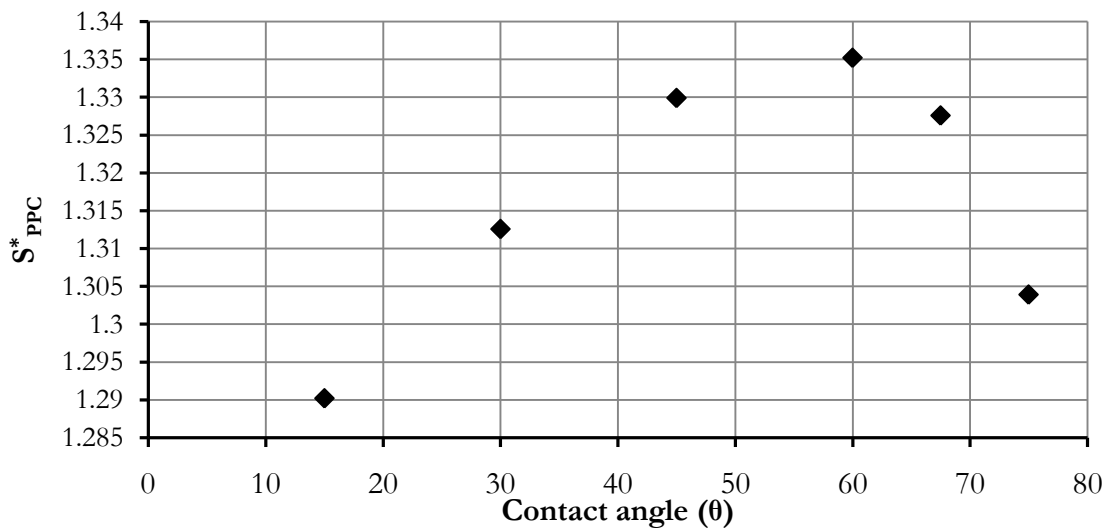


Figure 5-16. S_{PPC}^* as a function of θ , showing a peak at $\theta=60^\circ$.

It can be seen that the largest value of S_{PPC}^* is at $\theta=60^\circ$ at around $S_{PPC}^*=1.34$. The steep drop in S_{PPC}^* is also shown for values above 75° . At some contact angle between $60^\circ < \theta < 75^\circ$ the highest point on the film moves below the particle equator, once this occurs it is energetically much easier for the film to move down the surface of the particle with increasing P^* . This causes the ξ_{LP} to decrease a lot faster, the film curvature also decreases as can be seen in Figure 5-12 between contact angles of 90° and 105° .

This agrees with results from section 5.3.1 where a contact angle of 60° was shown to produce the highest value of ξ_{LP} for a given S_{PP}^* . At a contact angle of 60° the particles must be 5 % further apart than at 15° to allow the film to bridge both sides of the particle layers before *film inversion* causes the film to fail.

5.4 FAILURE CRITERIA FOR HEXAGONAL DOUBLE LAYER

Combining the results for $P_{critmax}^*$, P_{crit}^* and S_{PPC}^* the mode of failure and capillary pressure at which the film fails can be found for a double layer and plotted as a function of θ and S_{PPC}^* (Figure 5-17 and Figure 5-18). When the liquid-vapour interface bridges the particles there is a jump in P_{crit}^* , for a contact angle of 45° this increase is roughly 14 % of the $P_{critmax}^*$. For contact angles up to 75° the P_{crit}^* for single layers is, on average, 74 % of that for double layers before particle bridging occurs and 55 % after bridging occurs.

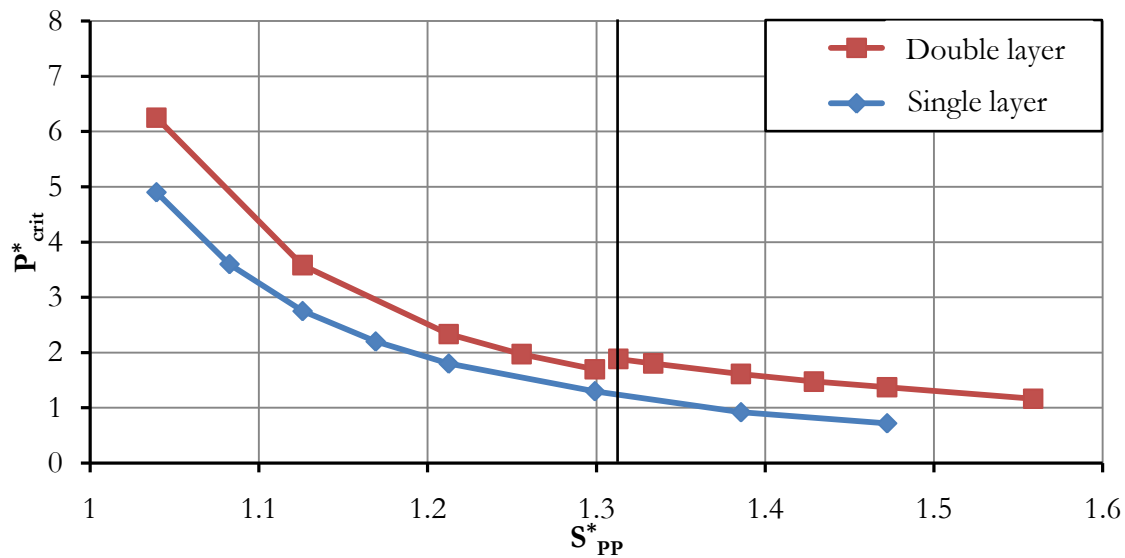


Figure 5-17. P_{crit}^* as a function of S_{PP}^* , the vertical line represents S_{PPC}^* , $\theta=45^\circ$.

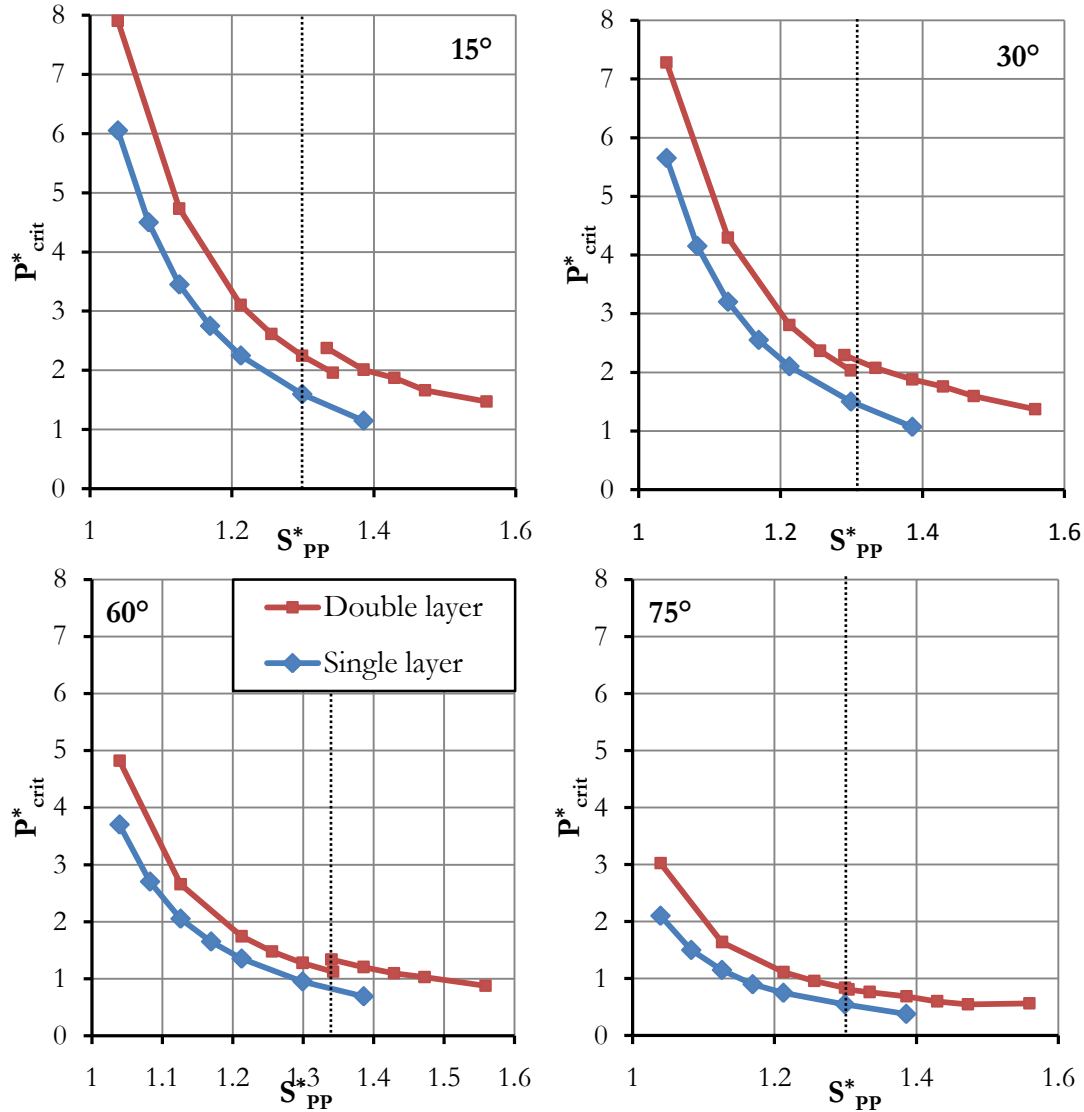


Figure 5-18. Comparison of P^*_{crit} for double and single layers for contact angles of 15°, 30°, 60° and 75°. Dotted lines highlight transition from one failure mode to another.

In Figure 5-17 and Figure 5-18 it appears that the value of $P^*_{critmax}$ gets closer to P^*_{crit} as θ increases. However $P^*_{critmax}$ is on average 0.87 ± 0.032 of the P^*_{crit} for all values of θ except $\theta=75^\circ$ (Figure 5-19). At $\theta=75^\circ$ $P^*_{critmax}$ is roughly equal to P^*_{crit} . This is attributed to the TPC moving completely past the particle equator at $P^*_{critmax}$ between 60° and 75°. Once the film is completely below the particle's equator the capillary pressure required for *film inversion* drops significantly. Figure 5-12 illustrates how at around $\theta=60^\circ$ this occurs and there is an associated sharp drop in the values of $\mathcal{Z}_{LP}$ for contact angles above 60° (Figure 5-15). At $\theta=75^\circ$ S^*_{ppc} has passed through its maximum and is now smaller than at $\theta=60^\circ$. Now, for a given S^*_{pp} ($\theta>60^\circ$) the pressure at which the film will bridge the particles in the opposite layer is much lower. This results in a lower P^*_{crit} as the bridged particles draw the TPCs much closer together at higher contact angles. Consequently this increases the percentage value of $P^*_{critmax}$ relative to P^*_{crit} .

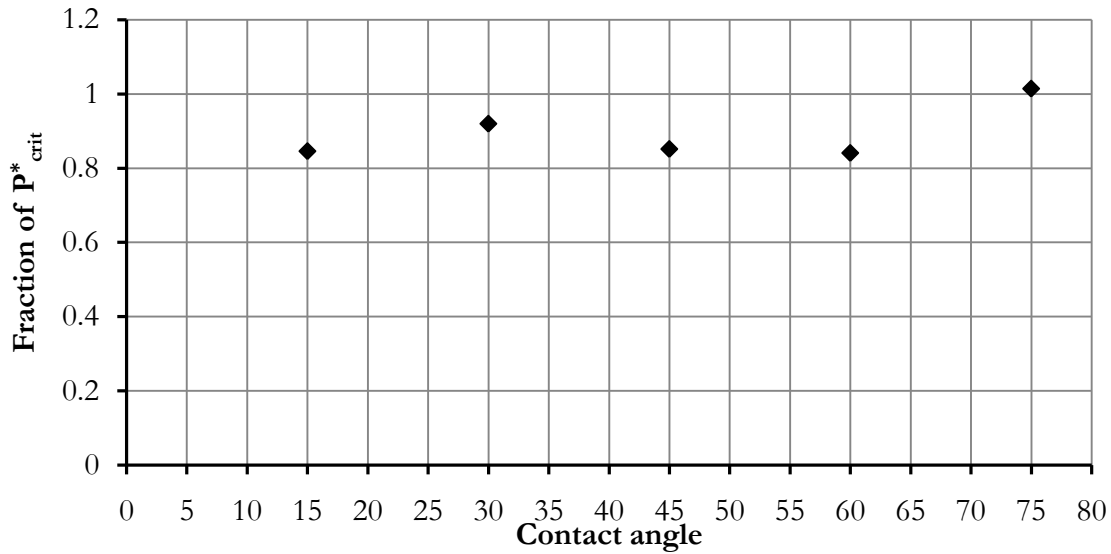


Figure 5-19. $P^*_{critmax}$ as a fraction of P^*_{crit} plotted as a function of contact angle.

When a film contains a close packed double layer of spherical particles in a hexagonal arrangement ($S^*_{pp}=1$) it will fail when the capillary pressure reaches a point at which the interface inverts itself on the particle surface for all contact angles below 110° . This occurs before particles in the opposite layer are bridged and before the opposite sides of the film touch in the gaps between the particle layers. For a close packed hexagonal arrangement ($S^*_{pp}=1$), P^*_{crit} for the single layer is on average 80 % of the value of $P^*_{critmax}$ for the double layer up to contact angles of around 75° . However above this contact angle the difference in failure pressure increases abruptly and at contact angles approaching 90° the P^*_{crit} is only 10 % of $P^*_{critmax}$ (Figure 5-20). For a close packed double layer of particles $P^*_{critmax}$ levels off above $\theta=100^\circ$ at a value of roughly 1.

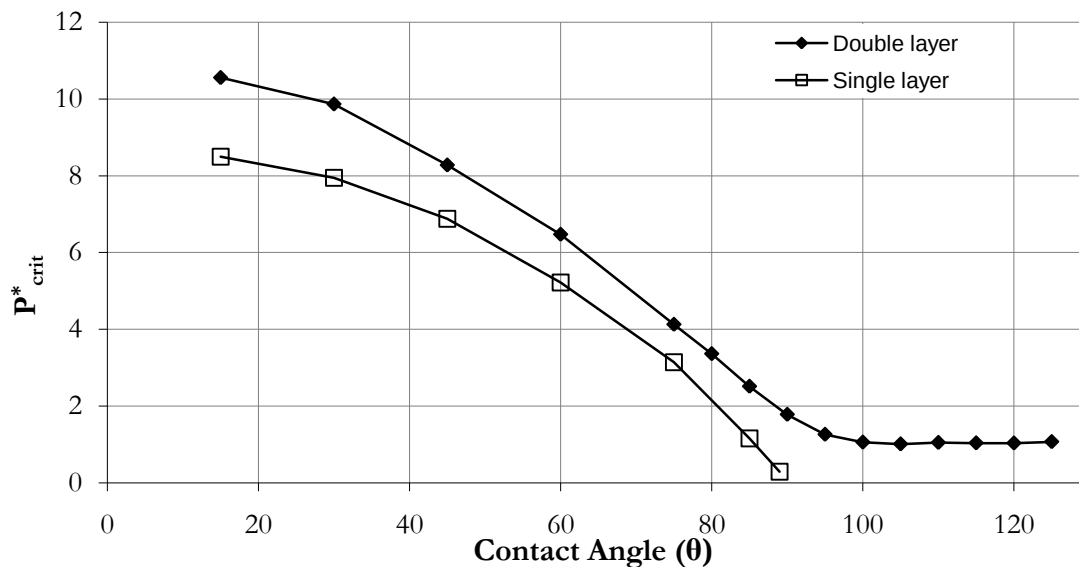


Figure 5-20. showing the difference in P^*_{crit} and $P^*_{critmax}$ for varying contact angles.

5.5 SUMMARY

In summary, a uniform double layer of particles in a close packed hexagonal arrangement will stabilise a film to a much greater extent and over a larger range of contact angles than a single layer of particles in a close packed hexagonal arrangement.

The extra stability is derived from the particles in opposite layers interlocking with each other and holding the opposite sides of film further apart than in a single layer. This means that the film can distort to a much greater degree before it ruptures, supporting the much higher capillary pressures. However, whilst it is possible for a double layer remain stable when the contact angle of the particles is greater than 90° this is only whilst the liquid-vapour interface does not bridge the opposite layer of particles. As soon as the capillary pressure is high enough to cause particle bridging above a contact angle of 90° the film will fail immediately.

It is also apparent that a bridged double layer is more stable than its un-bridged counterpart at the transition between inversion and bridging. The more complex geometry of these bridged films makes this a little more difficult to explain. If, however, it is thought of once more in terms of film area per particle, or perhaps as a ratio of interfacial areas it becomes apparent that when the particles bridge the opposite interface they reduce the amount of film area. A film however, is only as strong as its weakest point, which in this case remains in the interstices between particles in different layers (Figure 5-5). When the particles bridge the film they impinge on this area slightly, hence the increase in P_{crit}^* .

It has also been seen that trends based on contact angle for double layers are constantly upset by, or peak at $\theta=60^\circ$. Particles with a contact angle of 60° must be furthest apart before bridging occurs. This indicates that at around $\theta=60^\circ$ there is change in regime, further analysis has shown that at some point between $60^\circ < \theta < 75^\circ$ the highest point of the interface moves below the particle equator. This can be attributed to the sudden change in behaviour and drop in ζ_{LP} above 60° .

The major trends seen in chapter 4 have also been observed in double layers too, as contact angle decreases the P_{crit}^* increases and as separation distance increases P_{crit}^* decreases, however the failure mode is more complex and the range of contact angles supported is wider. Regarding particles with contact angles over 90° , whilst it is possible for them to stabilise the film, as soon as the film area expands and one of the particles bridges the both sides of the film it will collapse. As this is likely to occur in any loaded film at some point, especially those found in flotation froths it is undesirable to use particles above 90° to stabilise.

This chapter has assumed a static model for the particles, as the particles are of uniform property and are equally spaced all the forces are balanced, creating a quasi stable arrangement. However if one of the particles is disturbed this will cause an imbalance which will cause a change in the organisation of the

double layer. To investigate this in depth it is necessary to calculate the forces acting on the particles, preliminary results from dynamic models can be found in Appendix A (chapter 10).

6 NON-SPHERICAL PARTICLES

6.1 INTRODUCTION

Many previous modelling and analytical approaches, both in 2D and 3D have studied the effect of spherical particles and their properties on the film stability. Results presented in chapters 4 and 5 as well as work done by Ali *et al.* (2000), Denkov *et al.* (1992) and Kaptay (2004) agree that, for a given particle spacing, the film stability increases as the contact angle (θ) decreases whilst for a given θ , the film stability decreases as the particle separation (2D) or A^*_{pp} (3D) increases. However, the particles found in many industrial foams and films are not usually spherical and are often irregularly shaped, possessing sharp edges and asperities which affect their behaviour in the film (Frye and Berg 1989, Dippenaar 1982, Koh *et al.* 2009, Hiçyılmaz *et al.* 2004). Whilst it is possible to gain insights into film stability and particle behaviour from simulations of spherical particles, as shown in chapters 4 and 5, it is still desirable to extend simulations so that they can model non-spherical particles (De Graaf *et al.* 2009, Lehle *et al.* 2008, Lewandowski *et al.* 2008).

This chapter will describe and discuss results obtained using *Surface Evolver* to simulate non-spherical particles. The method used to create models of non-spherical particles and define their orientation is described in section 3.9. Results from the models are compared with those of Dippenaar (1982), who investigated cubic (galena) particles at an interface and the effect of contact angle and orientation on the film stability. This is followed by an expansion of the investigation to include oblong and flattened cubic particles at an interface.

6.2 CUBIC PARTICLES AT AN INTERFACE

6.2.1 INTRODUCTION

This section discusses results obtained from the *Surface Evolver* model that was defined in section 3.9 and used to simulate a cubic particle at an interface. They are also compared to the findings of Dippenaar (1982).

Dippenaar (1982) showed that orthorhombic particles with contact angles between 72° and 88° , when placed at an interface, could adopt one of two stable orientations. One of these orientations drastically reduced the stability of a film when the particle bridged both of its sides. Moreover, the orientation of non-spherical particles at an interface also affects the shape of the film surface, which is difficult to observe experimentally. The results presented in this section have been published, (Morris *et al.* 2010a) a copy of the manuscript is included in Appendix C.

6.2.2 MODEL AND SIMULATIONS

The particle shape is described as a single surface using a superquadric equation as defined in section 3.9. For the particles simulated in this section the parameters used in equation 3-20 were $s_i=1$, $\varepsilon_i=20$ and $R_p=1$, which creates a cubic particle as shown in Figure 3-29.1c.

The energy surfaces and values for minimum surface energy were obtained using the methods described in section 3.9.5. The P_{crit}^* for cubic particles bridging both sides of a film were found using a model with a circular boundary of $5R_p^*$. The method used to find P_{crit}^* was the same as described in section 4.3, however the film thickness was also specifically checked at the surface of the particle in addition to the film boundary. This additional failure criteria was added to take into account the possibility of bridging-dewetting.

6.2.3 RESULTS AND DISCUSSION

Only two distinct, stable orientations for a cubic particle in a thin film were found: rotated and horizontal shown in Figure 6-1a and Figure 6-1b respectively. The horizontal particle sits in the film with four vertical faces in the liquid phase and the upper and lower faces in the vapour phase. In the rotated case the particle has turned around both its X and Y axes and has three faces in the upper vapour phase and three in the lower, all of which have some portion in the liquid phase as well. In this orientation the normal of each of the three upper faces of the cube are at an angle of 55° with the Z axis ($\theta_{N1} = \theta_{N2} = \theta_{N3} = 55^\circ$). Dippenaar (1982) observed the horizontal orientation when the particle was sat in the film. However, the rotated orientation was only seen when the particle bridged the film and caused immediate failure. Instead, Dippenaar (1982) observed a stable, diagonal orientation when the particle bridged one side of the film, Figure 6-1c. In this case the normals of two of the faces are at 45° to the Z-axis and one is at 90° ($\theta_{N1} = \theta_{N2} = 45^\circ$, $\theta_{N3} = 90^\circ$). It was reported that the diagonal and horizontal orientations had roughly equal rates of occurrence.

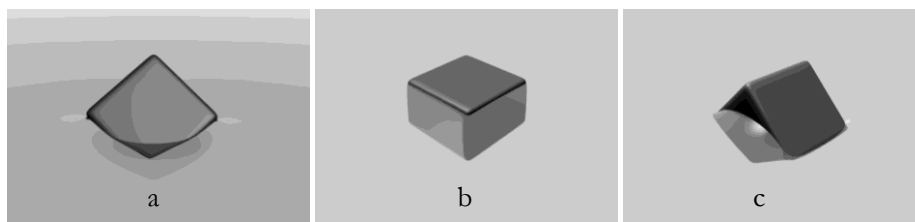


Figure 6-1. Rotated (a), horizontal (b) and diagonal (c) orientations of cubic particles at an interface.

Whilst two stable orientations were identified using *Surface Evolver*, they are not energetically stable across the whole range of contact angles investigated. A cubic particle with a contact angle of 45° is only energetically stable in the horizontal orientation and this is also the lowest energy orientation it can adopt highlighted in Figure 6-2a. The rotated orientation at this contact angle is the highest energy orientation possible and is surrounded by lower energy orientations making it energetically unstable. There are no other local surface energy minima so whatever the initial orientation of the particle at the interface, it will

always move to a horizontal one. At $\theta=85^\circ$ the situation is reversed (Figure 6-2c) and the only stable orientation is a rotated one with the energy maximum at the horizontal particle orientation. In the mid-range of contact angles both orientations are energetically stable (Figure 6-2b).

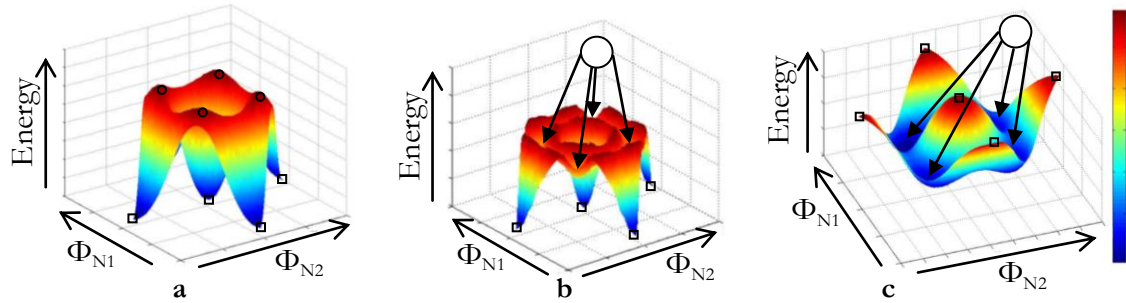


Figure 6-2. Energy surface orientations for cubic particles at contact angles of 45° (a), 70° (b) and 85° (c). Circles highlight the rotated orientation, squares the horizontal orientation.

In between these two contact angles there is a transition from horizontal stability to rotated stability and there are a range of contact angles for which either orientation is energetically stable. In this case both orientations are situated at a local minimum in energy and are separated from each other by a set of unstable, higher energy orientations. For a specific contact angle, both stable orientations have different energies with the lower energy orientation being the more energetically favourable one. As the contact angle increases from approximately 60° , the difference in energy between the two orientations becomes less, and the horizontal orientation is energetically most favourable. At a contact angle of about 72.5° , the surface energies for the two orientations are the same, and, as θ increases further, the rotated orientation becomes the more stable of the two.

The two stable orientations are located at energy minima in the surface energy landscape defined by θ_{N1} , θ_{N2} and model energy (the surface energy landscape is explained in more detail in section 3.9.5). For any particular contact angle, there is a particle orientation that has the maximum surface energy. This maximum energy may be considered as a ridge in the energy surface. The height of this ridge corresponds to the amount of energy required to move a particle from one stable orientation to another (i.e. over the ridge). It is calculated as the difference in energy between the ridge and an energy minimum and is referred to as ΔE_s .

The line representing ΔE_s for a horizontal orientation in Figure 6-3 decreases and therefore the horizontal orientation becomes less energetically stable as θ increases. At $\theta=80^\circ$, ΔE_s for the horizontal orientation is zero and it is no longer a stable orientation. The line representing ΔE_s for the rotated orientation is zero for values of $\theta < 65^\circ$ and is energetically unstable for these values. For $\theta > 65^\circ$ the ΔE_s for a rotated orientation increases and the rotated orientation becomes more energetically stable. It can be seen in Figure 6-3 that at $\theta=72.5^\circ$ the ΔE_s for the stable horizontal and rotated orientations is the same and there is no net energy gain by moving from one orientation to the other. Above $\theta=72.5^\circ$ the rotated

orientation is energetically the most stable and hence more favourable, while below $\theta=72.5^\circ$ it is the horizontal orientation. When ΔE_s is 0 that orientation is also the orientation with the maximum energy, making it unstable. If ΔE_s is non-zero for either of the two orientations it is at a local energy minimum and therefore stable. This is only true for these two orientations. Taking these criteria it can also be seen from Figure 6-3 that for contact angles below 65° the only stable orientation is the horizontal one and for $\theta>80^\circ$ the only stable orientation is the rotated one.

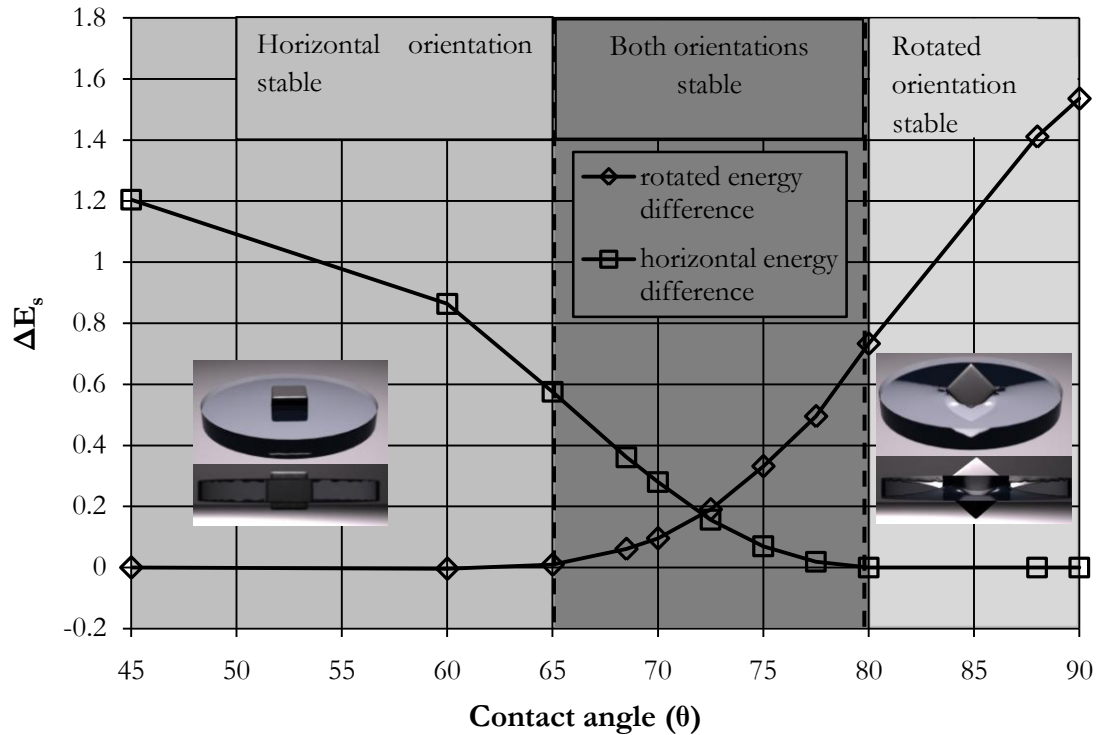


Figure 6-3. The difference in surface energy and the maximum energy orientation for both the horizontal or rotated orientations as it changes with θ .

Figure 6-3 indicates further that the energy required to move from one stable orientation to the other also changes as the contact angle changes, and that it is not symmetrical. When $\theta<72.5^\circ$, less energy is required to move the particle from a rotated to a horizontal orientation than the other way around, while for $\theta>72.5^\circ$ the opposite is true. At $\theta=70^\circ$ the energy required to move over the maximum energy point from a rotated orientation to a horizontal one is 34.2 % of what is required to move the other way. At $\theta=75^\circ$ to move from a horizontal to a rotated orientation the energy required is 21.0 % that of going the other way.

As noted earlier, a 2D geometric analysis of a cubic particle in a film indicates stability in both horizontal and diagonal orientations for $45^\circ<\theta<90^\circ$, which is not equivalent to the 3D results. However, the diagonal orientation found from a 2D analysis is not the same, true orientation adopted when analysed in 3D as the rotation cannot occur in two directions. This may be the reason that only one stable orientation is found in 3D for $45^\circ<\theta<60^\circ$ and $80^\circ<\theta<90^\circ$ instead of two, as in 2D. It should also be noted that for a cubic particle the diagonal orientation observed by Dippenaar and seen in the 2D case forms a saddle

point in the surface energy landscape, so that if rotation around only one axis was possible it would be stable. If the particle is elongated along one axis this changes the film shape and energy of the system and affects the stable orientations. This will be considered in greater detail in section 6.3.

6.2.4 FILM STABILITY WITH CUBIC PARTICLES

It has been shown that contact angle dictates the energetically stable orientations of cubic particles at an interface. However eventually a film will thin to the point where the particle will bridge both of its sides. At this point both the contact angle and the particle orientation will have an effect on the film stability. A *Surface Evolver* model in which the particle has bridged both sides of a film was used to determine the critical capillary pressure required to rupture the film. The critical capillary pressure has been found for horizontal particles with contact angles of 45-80° and for rotated particles with contact angles between 65° and 90°. Dippenaar (1982) observed that when a diagonally oriented particle bridged a film it either rotated to a horizontal orientation and the film continued to thin until failure or it twisted around its second axis and ruptured the film at its edges. The simultaneous two-axis rotation of the particle and film thinning as it bridges the surface is highly complex and cannot at present be simulated. Instead the particle was first rotated to its energetically stable orientation in the film, which was then further thinned until failure.

The horizontally orientated particle stabilises the film by holding its opposite sides apart at the upper and lower faces, as shown in Figure 6-1. As the capillary pressure increases so does the film curvature, but the TPC remains at the rounded edges of the particle. Eventually the P^* becomes large enough to force the TPC to slide down the vertical faces thinning the film further. The rotated orientation particle initially draws the opposite sides of the film close together near the edges running around its centre forming a highly distorted surface. This forces the initial film surfaces much closer together and as a result there is a decrease in the capillary pressure required to destroy the film.

It can be seen in Figure 6-4 that as the contact angle of a horizontally oriented particle increases, the critical capillary pressure for film failure decreases. This trend was reported previously for spherical particles by Ali *et al.* (2000) and was expanded upon in chapter 4. The same trend is also observed for particles in the rotated orientation. The critical capillary pressure is much lower than for a horizontally oriented particle with the same contact angle and decreases linearly as θ increases. For contact angles in the range of 65-80° both orientations are energetically stable. The critical capillary pressure of a rotated particle at $\theta=65^\circ$ is 29.2 % of the horizontal one and at $\theta=80^\circ$ it is 27.9 %. A cubic particle with a given contact angle can therefore have its stabilising effect on the film reduced by as much as 72.1 %, depending on its orientation.

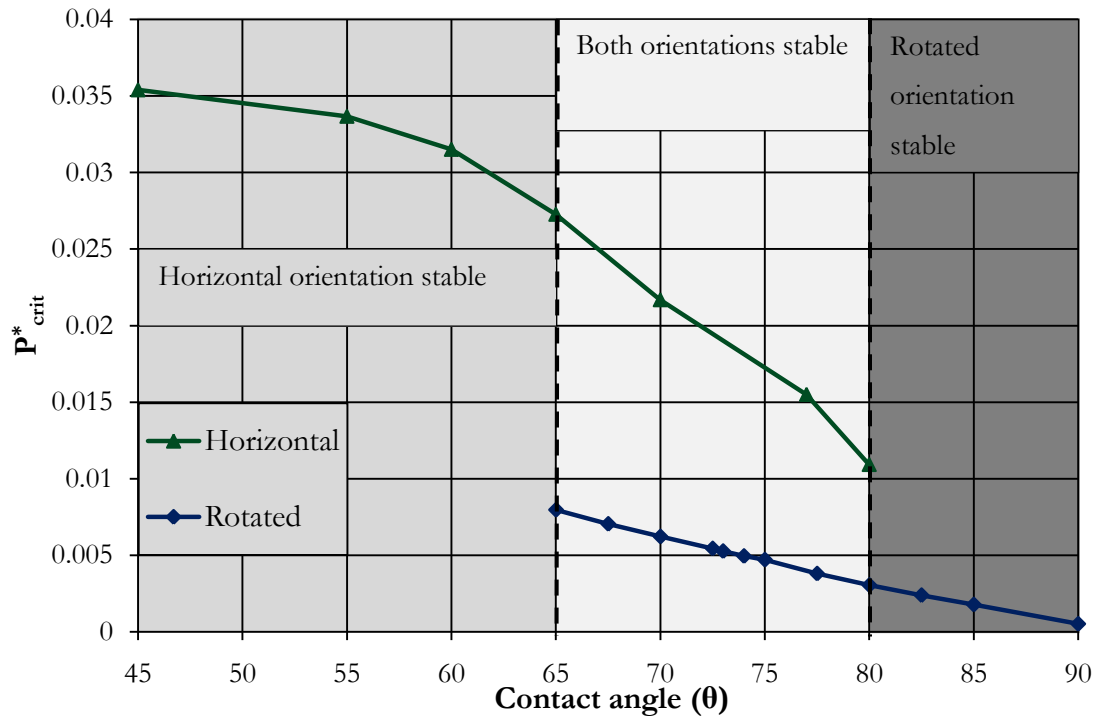


Figure 6-4. Critical capillary pressure as a function contact angle for cubic particles bridging a thin film. Dashed lines represent the limiting contact angles at which both orientations are stable.

If it is assumed that a particle enters the film at an initially random orientation then its final orientation and stabilising effect will depend on which side of the unstable maximum energy ridge it lands. If it is on one side it will move to the horizontal orientation, if it is on the other it will prefer the rotated orientation, with a much lower stabilising effect.

The position of the energy ridge separating the stable orientations changes with the contact angle. This changes the range of initial orientations that will move to one stable orientation instead of another. Once the positions of the stable orientations are known as well as the position of the energy maximum separating them it is possible to identify whether a particle with a given contact angle and initial orientation will end up horizontal or rotated in the film. This information can also be used to calculate the probability of a particle entering the film with a random orientation ending up in a particular stable orientation. Consider P_H as the probability that a particle will end up in the horizontal orientation.

The results indicate that if a cubic particle enters the film with a random orientation then the higher the contact angle the higher the probability it will adopt a rotated orientation. This means it will have a severely reduced stabilising effect when it bridges the opposite interface. Figure 6-5 shows that for a particle with a contact angle of 65° there is a 0.97 chance that it will align itself horizontally in the film and require a high critical capillary pressure to rupture the film (0.027, Figure 6-4). Nonetheless, there is a 0.03 chance that the particle will align itself in a rotated orientation (critical capillary pressure = 0.008, Figure 6-4) reducing the pressure required for failure by 70.8 %.

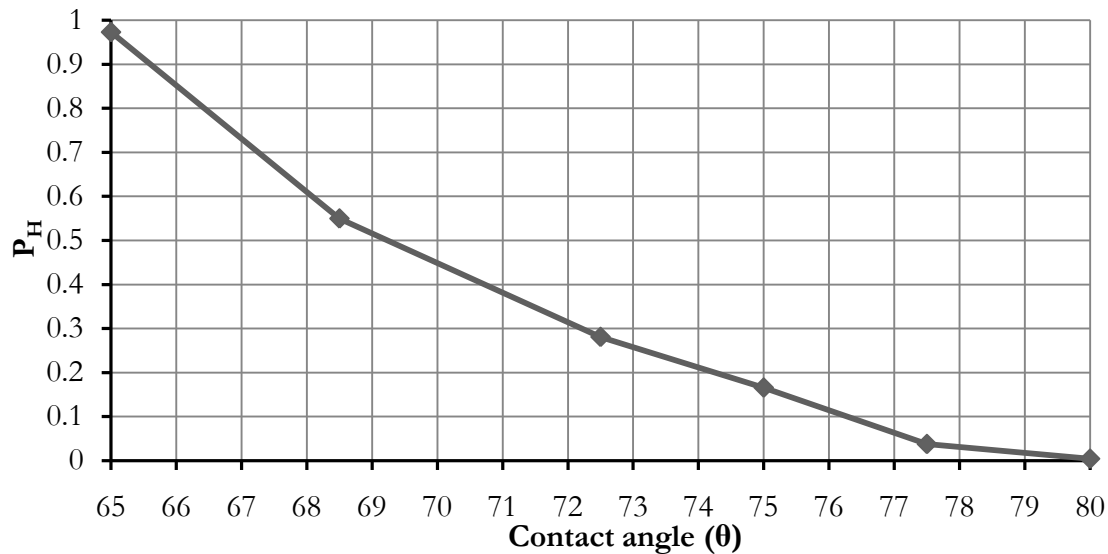


Figure 6-5. P_H against contact angle. Below $\theta=65^\circ$ it is 1, above 80° it is 0.

As θ increases the probability that a rotated orientation will ensue also increases and at $\theta=72.5^\circ$ it is 0.72. Above $\theta=80^\circ$ and the particle always enters a rotated orientation as the horizontal one is no longer energetically stable. This drastically reduces the pressure required for failure and produces a less stable film.

6.2.5 SUMMARY

It has been shown that a cubic particle has two stable orientations, horizontal or rotated, when attached to a film. The preference for one orientation over the other depends on its contact angle and the orientation with which it enters the film. Both particle orientations will help stabilise a film, but the horizontal orientation is more effective. A diagonal particle orientation is energetically unstable for a cubic particle but sits in an energy saddle. As galena breaks up into orthorhombic particles but not necessarily cubic ones its height to length to width ratio can have an effect on film stability and this is covered in the following sections.

2D geometric analysis shows that there are two stable orientations for a square particle in a film when it has a contact angle between 45° and 90° , however 3D modelling has shown that for a cubic particle the two stable orientations are horizontal and rotated (three facet normals of the cube at 55° to the Z axis) and they are only both stable between contact angles of 65° and 80° .

For any given contact angle in the range of $65^\circ < \theta < 80^\circ$ (where both orientations are energetically stable) the critical capillary pressure required to rupture a film bridged with a rotated particle is approximately 70 % lower than one with a horizontal particle in it. The probability that a particle entering the film with a random orientation will adopt either a horizontal or rotated orientation has also been found. As θ increases from 65° to 80° the likelihood of the particle adopting a rotated orientation in preference a horizontal one increases from 0 to 1. Therefore, if greater film stability is desired it is important to keep

the particle contact angle below 65° under which conditions the particle will prefer a horizontal orientation and stabilise the film more readily. If the contact angle increases above 65° , the probability of a particle adopting a rotated orientation in the film also increases, which will result in a much reduced film stability around that particle and therefore the whole film.

However whilst it was observed experimentally (Dippenaar 1982) that a particle with a contact angle of $80^\circ \pm 8^\circ$ orientated itself in the film horizontally or diagonally with roughly equal probability, the results obtained from simulations are different. For a particle with a contact angle above 80° the probability it will rotate in the film is 1 and even for a particle with a contact angle of 72° the probability it will rotate in the film is still roughly 0.7. However these results are for a cubic particle and the effect of particle length (and width) on the preferred orientation will be considered in the next section.

6.3 OBLONG AND FLATTENED SQUARE PARTICLES

6.3.1 INTRODUCTION

Section 6.2 identified the stable orientations for a cubic particle. It also showed the effect that particle shape can have on the stable orientations. This section will use the same model to investigate other orthorhombic particles, particularly oblong and flat square particles.

A cubic particle has been shown to be energetically stable in the rotated orientation ($\theta_{N1} = \theta_{N2} = 55^\circ$, Figure 6-1a) or the horizontal orientation (Figure 6-1b). However, Dippenaar (1982) observed that orthorhombic particles sometimes adopt a diagonal orientation (Figure 6-1c) where two faces are vertical and four are at an angle of 45° to the horizontal. It is possible that this is an effect of particle shape, whereby elongation of the particle affects its energetically stable orientations. This effect is investigated for both oblong and flattened square particles.

6.3.2 MODEL PARAMETERS

The same model as in section 6.2 was used, however s_3 was changed between 1.1 and 2 to create oblong particles which could be placed at the interface in various orientations. To make the flattened square particles s_2 and s_3 were changed, between 1.1 and 1.7 to alter the aspect ratio of the particle.

6.3.3 OBLONG PARTICLES

It has been established that a cubic particle will be energetically stable in either a horizontal or rotated orientation, however there is a saddle point in energy at orientations corresponding to a diagonal particle (where two of $\theta_{Ni} = 45^\circ$ and one $\theta_{Ni} = 90^\circ$). If the particle is extended along one axis to form an oblong shape this saddle gradually becomes an energy minimum and the orientation becomes energetically stable.

6.3.3.1 Comparison with the Dippenaar results

Whilst the *Surface Evolver* simulation results show that horizontal or rotated orientations are stable at different contact angles for cubic particles, Dippenaar did not report any particles rotating about both axes whilst attached to a single film interface. Rotation about both axes was only reported once the particle had bridged the film. There are many variables that could affect the stable orientations of a particle that are not explicitly taken into account in the model; for example differences in advancing and receding contact angles, surface roughness and non-cubic particle shape. Whilst the first two of these causes are beyond the limitations of this model it is plausible that the galena particles used by Dippenaar (1982) were not completely cubic. The effect of this can be investigated by altering the particle shape in *Surface Evolver*.

The same procedure was used for an oblong particle with $\theta=70^\circ$ and using $s_1=s_2=1$, but s_3 was increased to 1.4. In this case the stable orientation with the lowest energy corresponds to a particle lying horizontally in the film. However there is also a stable orientation corresponding to a particle in a diagonal orientation as observed by Dippenaar, the two orientations are shown in Figure 6-6a and Figure 6-6b.

The model was also used to obtain results for the same oblong-shaped particle ($s_3=1.4$) for $\theta=60^\circ$ and $\theta=80^\circ$ to investigate how the stable orientations are affected by contact angle. When $\theta=60^\circ$, the horizontal orientation is stable but there is no local minimum for a diagonal orientation. There is also a small local minimum for a particle sitting in the film with its long axis vertical indicating that this orientation is also stable. At $\theta=80^\circ$ the horizontal orientation becomes unstable and the lowest energy point is for a particle rotated 45° around its long axis. These results are also in line with Dippenaar's observation that a single particle which is elongated along one axis can stably orientate itself in a film when rotated around only one axis.

6.3.3.2 Stable orientations

The stable orientations for contact angles between 45° and 90° for particles with an s_3 between 1.1 and 2 have been identified in the same manner as section 6.2. The minimum energy surface was found for orientations of θ_{N1} and θ_{N2} between 0° and 90° at intervals of 5° , s_1 and s_2 were held constant at 1.1. The different stable orientations for differing s_3 and θ are listed in Table 3 and shown in Figure 6-6.

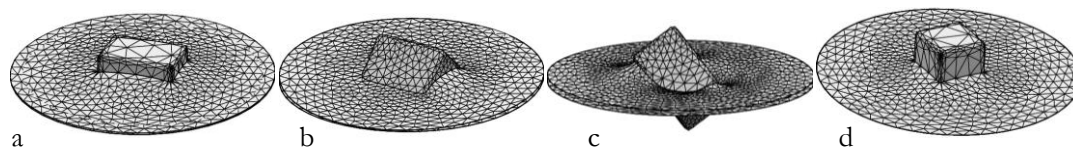


Figure 6-6. Four stable orientations for an oblong particle horizontal(a), diagonal(b), rotated(c) and vertical(d), a- ($\theta_{N1}=0^\circ/\theta_{N2}=90^\circ$ or $\theta_{N1}=90^\circ/\theta_{N2}=0^\circ$), b- ($\theta_{N1}=\theta_{N2}=45^\circ$), c- ($\theta_{N1}=\theta_{N2}=55^\circ$), d- ($\theta_{N1}=\theta_{N2}=90^\circ$).

The horizontal orientation (a) is stable for all values of s_1 up to a contact angle of 75° , above which either orientation (b) or (c) are stable, corresponding to a diagonal ($\theta_{N1}=\theta_{N2}=45^\circ$) or rotated ($\theta_{N1}=\theta_{N2}=55^\circ$) orientation respectively. However there is now also a discernable vertical orientation (d) corresponding to $\theta_{N1}=\theta_{N2}=90^\circ$, where the particle is sitting with its long axis in line with the Z-axis. At a contact angle of 45° the vertical orientation is stable for all values of s_3 . As θ increases the maximum value of s_3 that can sustain a stable vertical orientation decreases until θ reaches 75° , above this contact angle the vertical orientations is no longer stable at all. The diagonal orientation (b) is the only stable orientation above contact angles of 80° and $s_3>1.5$. When $\theta<65^\circ$ only the vertical or horizontal orientations are stable. At lower values of s_3 (<1.5) the diagonal orientation is stable at intermediary contact angles but becomes unstable for all θ below $s_3=1.2$, except when $\theta=70^\circ$. The rotated orientation seen for cubic particles is the only stable orientation at high contact angles and small s_3 .

Particle	$s_3 \backslash \theta$	45°	60°	65°	70°	75°	80°	90°
	1.1	a-d	a-d	a-c-d	a-c-d	a-c-d	c	c
	1.2	a-d	a-d	a-d	a-b-d	a-c-d	c	c
	1.3	a-d	a-d	a-d	a-b-d	a-b	b-c	c
	1.5	a-d	a-d	a-b-d	a-b	a-b	b	b
	1.7	a-d	a-d	a-b	a-b	a-b	b	b
	1.9	a-d	a	a-b	a-b	a-b	b	b
	2	a-d	a	a-b	a-b	a-b	b	b

Table 3. Showing the stable orientations for different combinations of s_3 and θ . Orientations are; horizontal (a), diagonal (b), rotated (c) and vertical (d) from Figure 6-6.

Even though the vertical orientation is stable at $s_3=2$ and $\theta=45^\circ$ the energy minimum it inhabits is very shallow and completely disappears at higher contact angles as shown in Figure 6-7. At a contact angle of 65° the shallow energy minimum for a diagonal orientation (b) can also be seen. The stable orientations are therefore a function of both particle shape and contact angle.

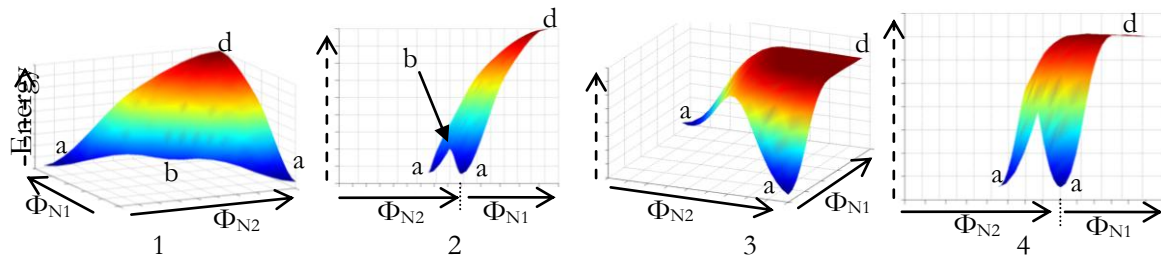


Figure 6-7. Surface plot of energy as a function of θ_{N1} and θ_{N2} at $s_3=2$, $s_2=s_3=1.1$, $\theta=65^\circ$ (1, 2) and $\theta=45^\circ$ (3, 4). Orientations (a), (b) and (d) are labelled.

Plotting the surface energy as a function of θ_{N1} and θ_{N2} it can be seen how the stable orientations change with contact angle and particle length (Figure 6-8, Figure 6-9, Figure 6-10). Figure 6-8 shows how, as s_3 increases, the vertical orientation (d) becomes less energetically stable, whilst the horizontal orientation (a) remains stable throughout. At contact angles of 75° (Figure 6-9) it can be seen that the vertical orientation is unstable for all cases except $\theta=75^\circ$ and $s_3=1.2$. However, as s_3 increases the horizontal orientation remains stable. At $\theta=90^\circ$ (Figure 6-10) the vertical orientation has the highest surface energy and is unstable for all values of s_3 . Whilst the horizontal orientation is unstable for all values of s_3 , it can be seen that as s_3 increases the respective surface energy associated with the horizontal energy decreases.

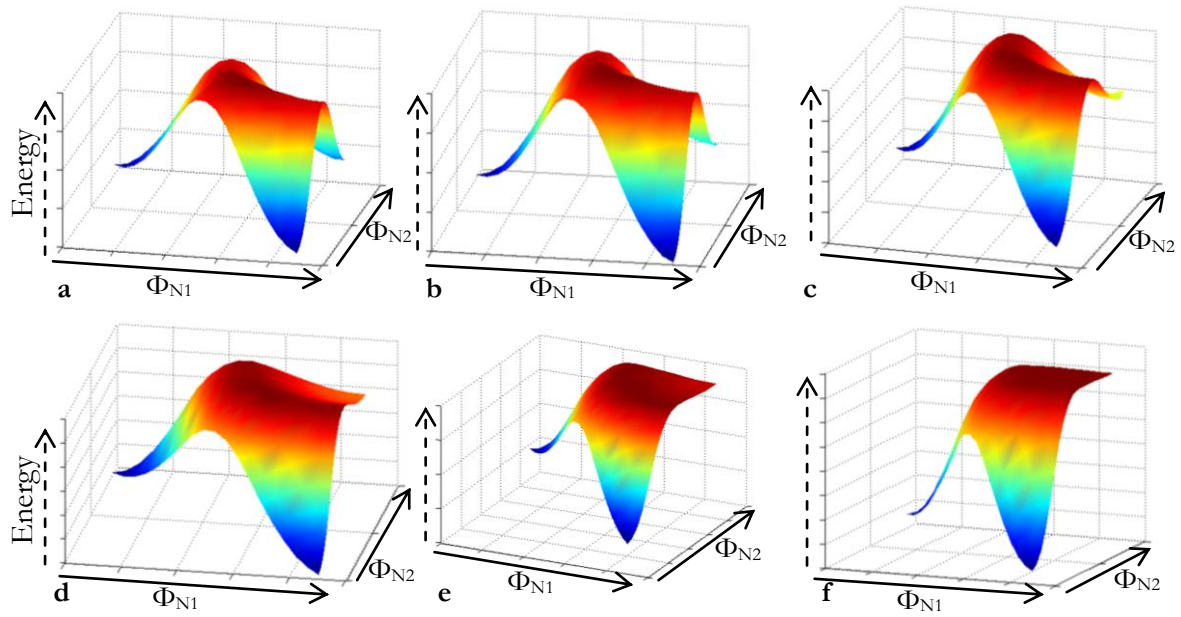


Figure 6-8. Energy surfaces for $\theta=45^\circ$, $s_3=1.2$ (a), 1.3 (b), 1.5 (c), 1.7 (d), 1.9 (e), 2 (f).

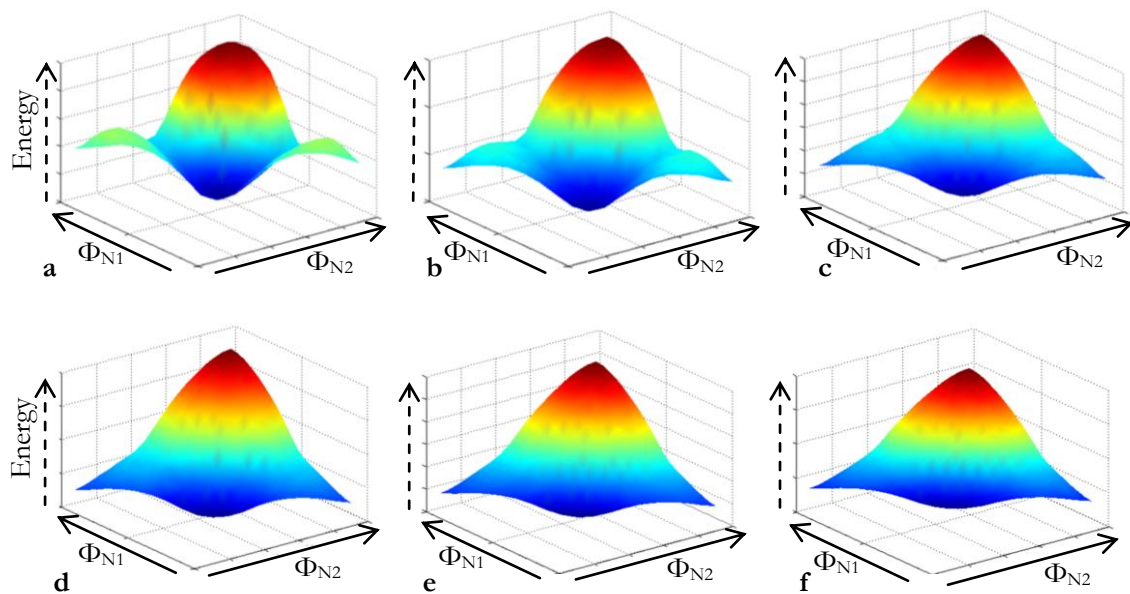


Figure 6-9. Energy surfaces for $\theta=75^\circ$, $s_3=1.2$ (a), 1.3 (b), 1.5 (c), 1.7 (d), 1.9 (e), 2 (f).

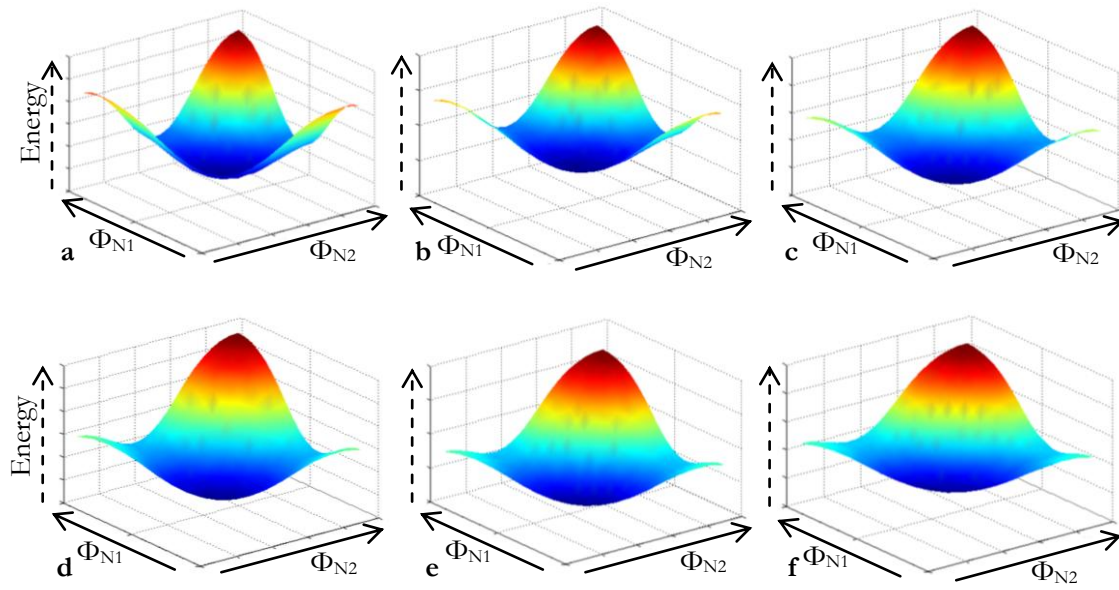


Figure 6-10. Energy surfaces for $\theta=90^\circ$, $s_3=1.2$ (a), 1.3 (b), 1.5 (c), 1.7 (d), 1.9 (e), 2 (f).

6.3.3.3 Comparisons of ΔE_s

The relative stability of orientations can be compared by finding the difference in surface energy between the orientation concerned and the maximum surface energy orientation (ΔE_s). Plotting these differences as a function of contact angle (as in Figure 6-3) shows that as s_3 increases the contact angle at which the vertical orientation becomes the maximum energy (i.e. the difference in energy is 0) decreases (Figure 6-11, Figure 6-12 and Figure 6-13).

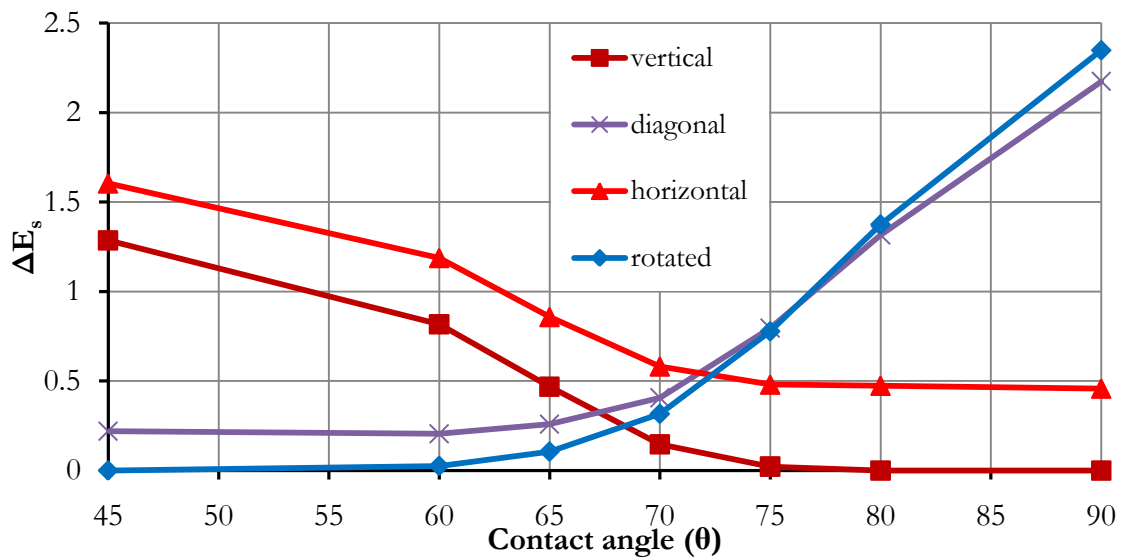


Figure 6-11. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_3=1.2$.

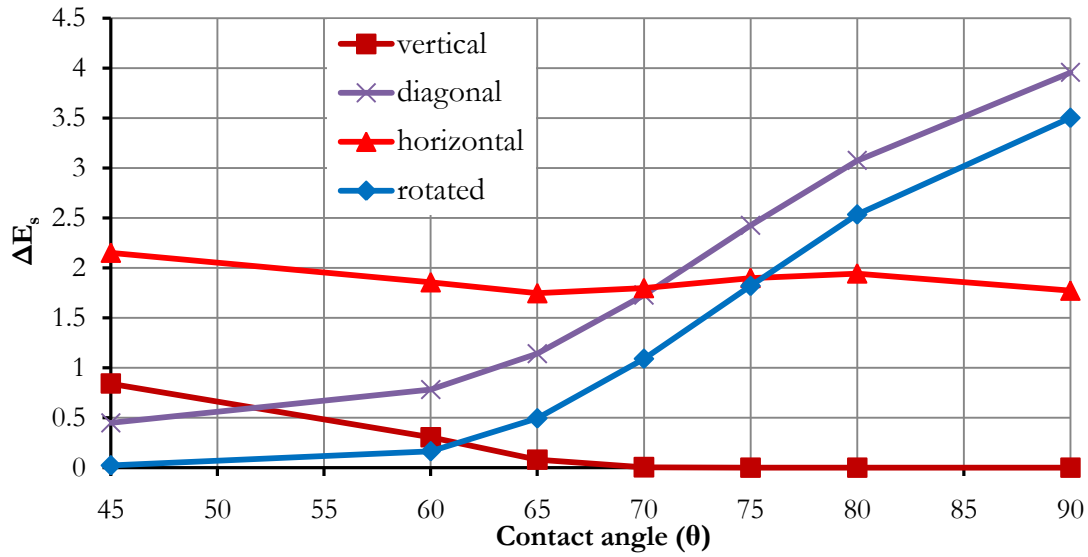


Figure 6-12. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_3=1.5$.

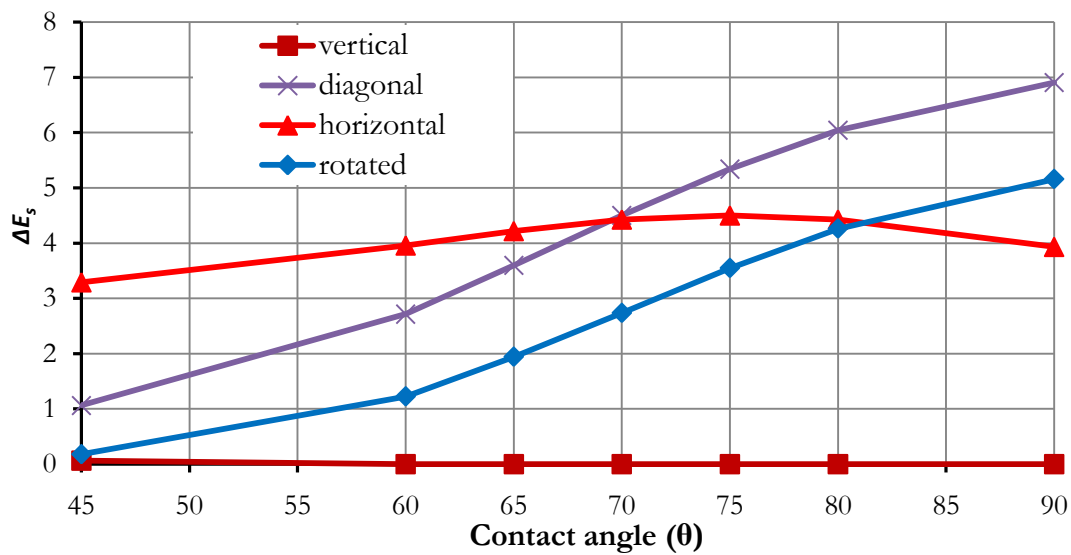


Figure 6-13. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_3=2$.

Unlike the results for a cubic particle, an oblong particle orientation with a ΔE_s greater than 0 does not necessarily mean it is stable, it only means it is not the highest energy. In section 6.2, when only two orientations were considered they were either the maximum (unstable energy) or at a minimum (stable), so if the energy is not 0 the orientation for that contact angle is stable.

When $s_3=1.2$, the ΔE_s of the rotated orientation becomes greater than the ΔE_s of the diagonal orientation at $\theta=75^\circ$, this corresponds to the point at which the rotated orientation becomes the stable one instead of the diagonal one. However it should be noted that the diagonal orientation is only stable for contact

angles above around 70° when $s_3=1.2$. When $s_3>1.2$ the diagonal orientation has the greater ΔE_s for all values of θ and s_3 except when $s_3=1.3$ and $\theta=90^\circ$ where both orientations have the same ΔE_s . The rotated orientation is not stable for values of $s_3>1.3$. The ΔE_s of both the horizontal and vertical orientations show the same trends in Figure 6-11, with the horizontal orientation on average 0.41 higher than the vertical. As s_3 increases the ΔE_s of the vertical orientation becomes 0 at lower contact angles whilst the ΔE_s of the horizontal orientation begins to flatten out and then form a peak at around $\theta=75^\circ$. At $s_3=2$ ΔE_s for the vertical orientation is 0 for all contact angles except 45° . At $\theta=45^\circ$ it is 0.0618, which is 2 % of the ΔE_s for the horizontal orientation.

For a cubic particle, the contact angle at which the rotated orientation becomes more energetically stable than the horizontal one is roughly 72.5° , for a particle of $s_3=1.2$ this point is also at around 72.5° , however as s_3 increases, the rotated orientation becomes energetically unstable. In its place the diagonal orientation becomes more energetically stable than the horizontal one. This is around $\theta=70^\circ$ for all s_3 simulated above $s_3=1.2$. If the ΔE_s for horizontal orientations is compared for different values of s_3 (Figure 6-14) it can be seen that it forms a peak at around $\theta=75^\circ$ for values of $s_3>1.5$, this corresponds to the maximum contact angle at which it is energetically stable.

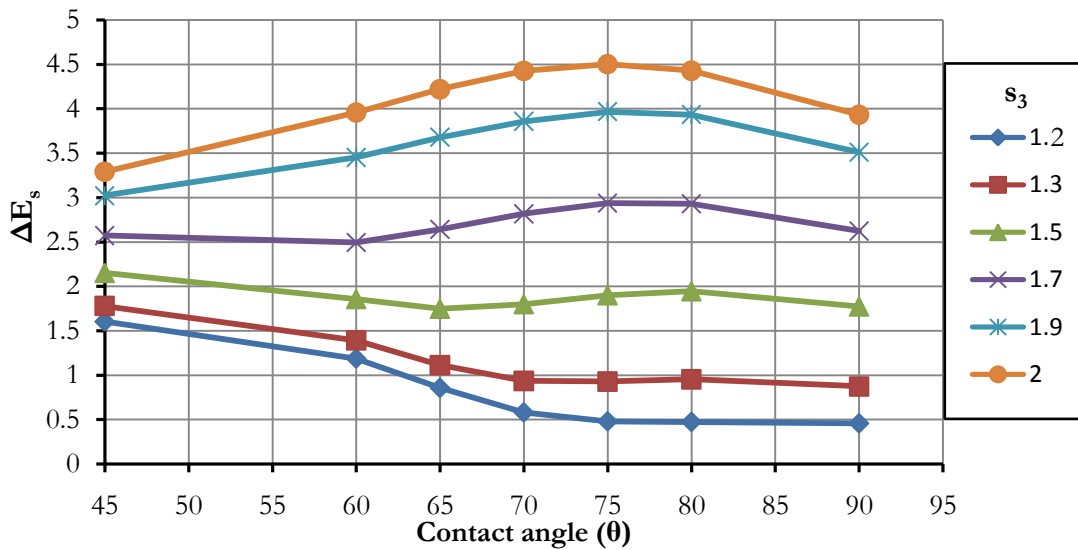


Figure 6-14. ΔE_s for horizontal orientations as a function of contact angle for $1.2 < s_3 < 2$.

It has been shown that an elongated particle will sit at the interface in a horizontal orientation over a similar variety of contact angles to a cubic one as the value of s_3 increases. However, as s_3 increases, the diagonal orientations becomes energetically preferable to the rotated one.

In 6.2.4 it was found that a film containing a cubic particle in a rotated orientation had a P^*_{crit} of only around 30 % of a film containing a particle in a horizontal orientation. The same approach will now be

used to investigate the effect on film stability of the stable orientations for an oblong particle that have been identified.

6.3.3.4 Film failure for oblong particles

The stable orientations for a given combination of s_3 and θ were identified in section 6.3.3.2. The P^*_{crit} for these stable orientations has been found using the same methods as described in section 4.3. The P^*_{crit} was found for $45^\circ < \theta < 90^\circ$ and for values of s_3 of 1.2, 1.5 and 2. Figure 6-15 shows the P^*_{crit} as a function of contact angle for stable orientations at $s_3=1.2$, $s_1=s_2=1.1$, again the same trends seen in Figure 6-4 are present here for all orientations. The diagonal and rotated orientations both have much lower P^*_{crit} than the horizontal and vertical ones, at roughly 43 % and 28 % respectively. The vertical and horizontal orientations both have very similar P^*_{crit} but as the particle is only slightly non-cubic this can be attributed to the close values of s_1 , s_2 and s_3 . The diagonal orientation provides more stability to the film than a rotated orientation with an average difference of 0.0034.

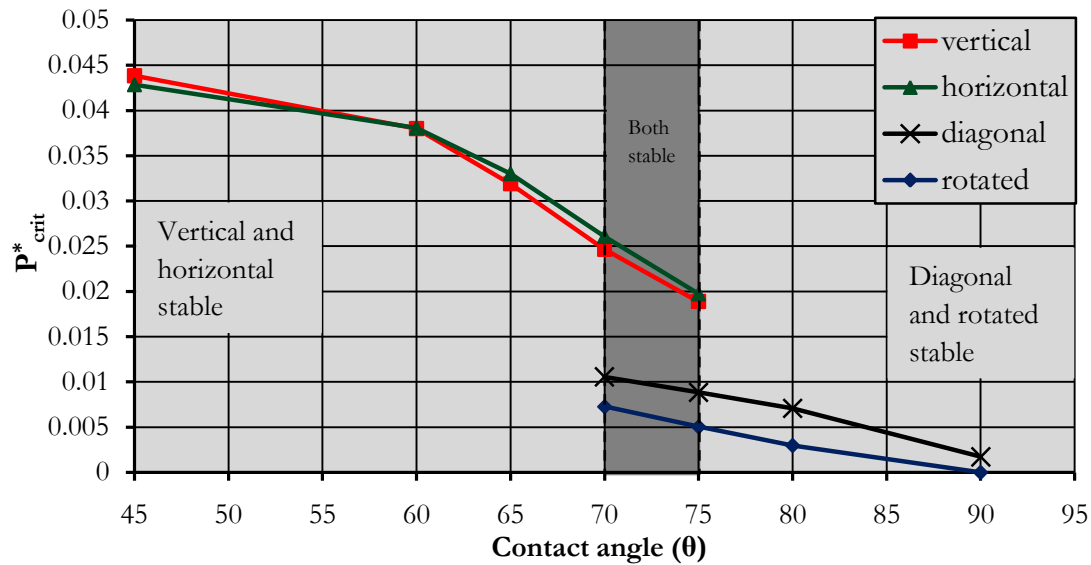


Figure 6-15. P^*_{crit} as a function of contact angle for vertical, horizontal, rotated and diagonal orientations $s_3=1.2$. Black lines highlight contact angles where stable orientations overlap.

When s_3 is increased to 1.5 the rotated orientation is no longer energetically stable and is not shown in Figure 6-16. The vertical orientation is only stable up to a contact angle of 65° , whereas the horizontal orientation is stable up to $\theta=75^\circ$. There is now a discernable difference between the P^*_{crit} at different contact angles for the vertical and horizontal orientations. Whilst the horizontal P^*_{crit} decreases in the same fashion as for $s_3=1.2$, the vertical orientation decreases slightly more linearly, dropping to roughly 80 % of the P^*_{crit} of the horizontal orientation at $\theta=60^\circ$ and 65° .

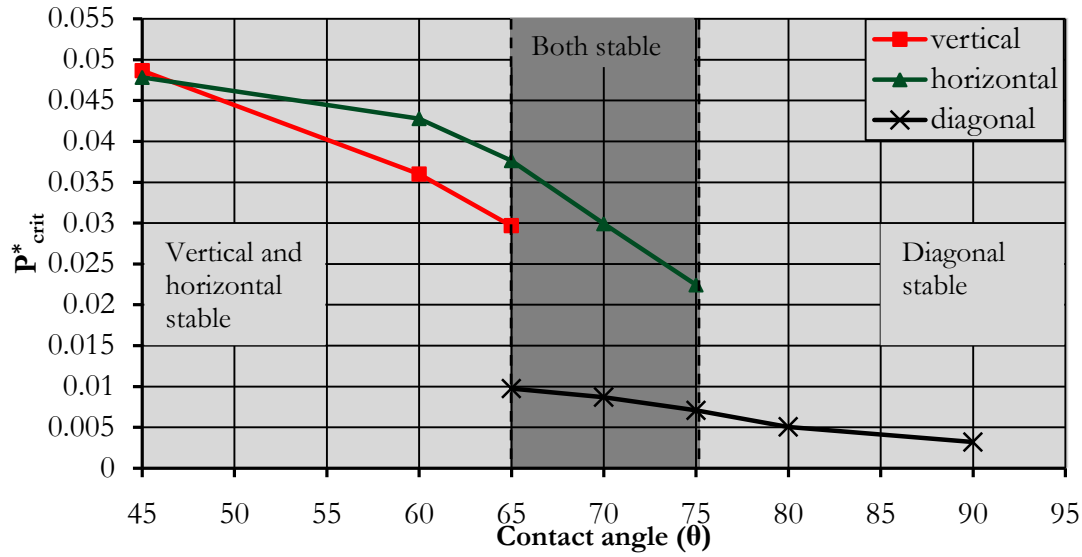


Figure 6-16. P^*_{crit} as a function of contact angle for vertical, horizontal, rotated and diagonal orientations $s_3=1.5$. Black lines highlight contact angles where stable orientations overlap.

As the film sits at the corners of the particle before film failure it would be expected that the vertical orientation would give more stability to the film than the horizontal one, as the opposite sides of the film are held further apart. This is not the case for two reasons; firstly the cell area for the model is the same for all particles and as has previously been seen, when the film space surrounding a particle decreases the P^*_{crit} increases very quickly. A horizontally orientated particle sits in the film with a larger surface area exposed to the vapour phase, effectively taking up more space than the vertical orientation. The second reason is that the film hangs at the edges of the particle as P^* increases and the film curvature increases. Eventually it is more energetically favourable for the TPC to move down the side of the particle to reduce curvature of the film. Once this occurs, the TPC will continue to move down the flat side of the particle as this continues to reduce the film surface energy, causing rupture. A vertical particle will cause much greater film curvature than the horizontal orientation as the P^* increases, and the critical curvature will be reached at a lower P^* .

At $s_3=2$ (Figure 6-17) the vertical orientation is only stable at a contact angle of 45° , the rotated orientation is unstable at all θ and the particle has moved into a new stability regime. If cubic particle has the horizontal and rotated orientations associated with it then an oblong one has the horizontal and diagonal ones, whilst the intermediary particle has all three plus the vertical orientation. At $s_3=2$, when $65^\circ < \theta < 75^\circ$ both orientations are stable and the diagonal orientation has a P^*_{crit} that is on average 22 % of the horizontal P^*_{crit} value.

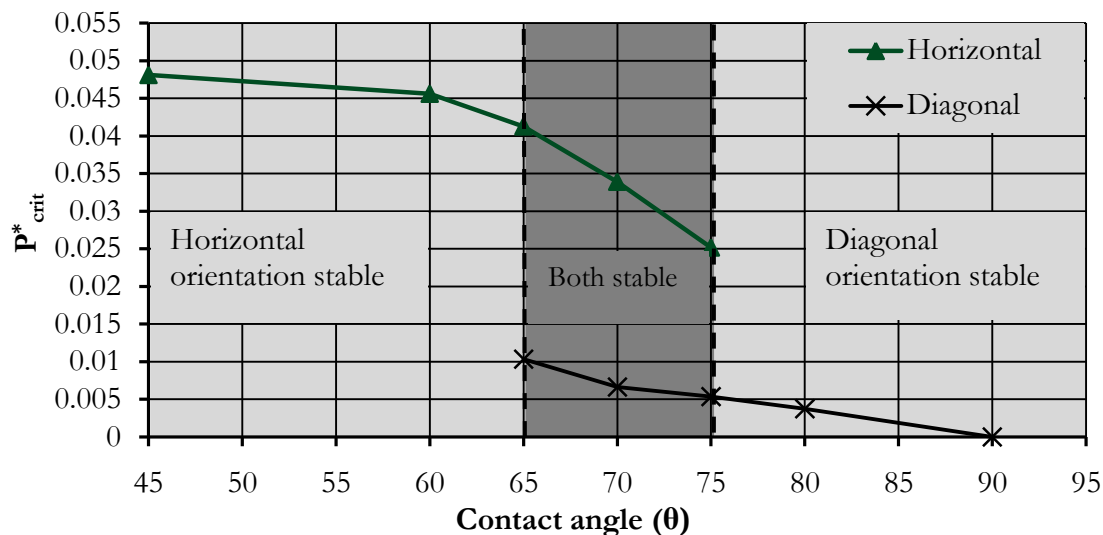


Figure 6-17. P^*_{crit} as a function of contact angle for vertical, horizontal, rotated and diagonal orientations $s_3=2$. Black lines highlight contact angles where stable orientations overlap.

6.3.3.5 Summary

It has been found that the length of a particle can affect the energetically stable orientations that it adopts at an interface. As the particle length increases and it becomes oblong instead of cubic there is a transitional period where the orientations associated with both particle shapes are energetically stable. This occurs between the values of $1.1 < s_3 < 2$, where vertical, horizontal, rotated and diagonal orientations are all stable at some point. When $s_3 > 2$ there are only two stable orientations, horizontal and diagonal which are both energetically stable at intermediary contact angles ($65 < \theta < 75^\circ$) with the horizontal orientation stabilising the film to a greater extent. Whilst the vertical orientation remains energetically stable for some value of θ up to an s_3 that is 82 % longer than s_1 and s_2 , the rotated orientation is only stable for values of s_3 that are up to 18 % longer than s_1 and s_2 . Diagonal orientations at values of $s_3 < 1.5$ require a P^*_{crit} roughly 40 % of the horizontal orientations one. At an s_3 of 2 this has dropped to 22 %.

6.3.4 FLAT SQUARE PARTICLES

Section 6.3.3 investigated the effect of particle elongation on film stability and the energetically stable orientations that the particle can adopt. This section expands upon this further by presenting results obtained from the same model but expanding both length and width to create a flat, square particle. Contact angles between 45° and 90° were used for particles of dimension $s_1=1.1$ and $s_2=s_3=1.2, 1.3, 1.5$ and 1.7 .

6.3.4.1 Stable orientations

If the energy landscapes for four particles of differing aspect ratio are compared, (Figure 6-18), it can be seen how the increase in aspect ratio causes the energy difference between the stable orientations to change. As s_2 and s_3 increase so does the energy difference between the horizontal orientation Figure 6-6(a) and the vertical orientation Figure 6-6(d) with the horizontal one becoming increasingly more

energetically stable. It should be noted here that the new particle shape means that a vertical orientation (d) has replaced one of the horizontal orientations (a) in the film as circled in Figure 6-18a.

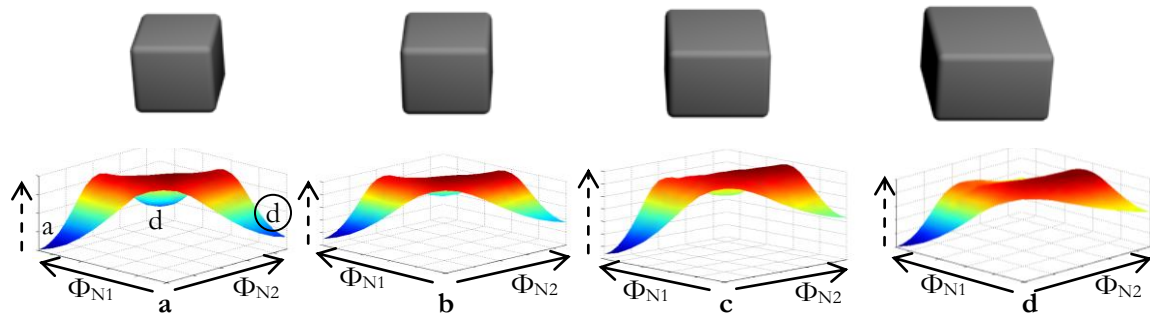


Figure 6-18. Energy surfaces for ratios of (a) $s_1=1.1$, $s_2=s_3=1.2$, (b) $s_1=1.1$, $s_2=s_3=1.3$, (c) $s_1=1.1$, $s_2=s_3=1.5$, (d) $s_1=1.1$, $s_2=s_3=1.7$, $\theta=45^\circ$, particle shapes for each model are shown above the relevant model.

If the particle shape is held constant and the contact angle is changed, the stable orientation changes. For a particle defined by $\varepsilon_{1,2,3}=20$, $s_1=1.1$, $s_2=s_3=1.2$ and $45^\circ < \theta < 90^\circ$ (particle (a) in Figure 6-18), a kink forms in the energy surface as θ increases. This kink slowly deepens into a local minima (Figure 6-19) and a new stable orientation (c) whilst orientations (d) and (a) get shallower and eventually turn into local maxima. Orientation (c) corresponds most closely to the rotated orientation discussed in 6.2 and will be referred to as such from here on.

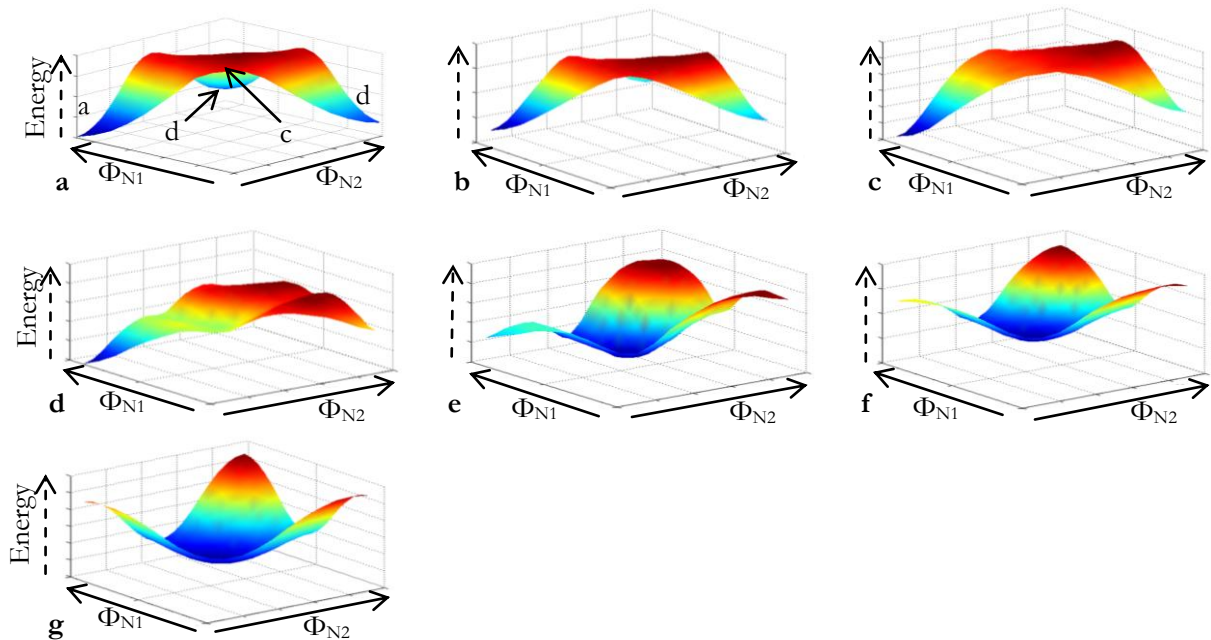


Figure 6-19. Energy surfaces for particle with aspect ratios of $s_1=1.1$, $s_2=s_3=1.2$ and contact angles of (a) $\theta=45^\circ$, (b) $\theta=60^\circ$, (c) $\theta=65^\circ$, (d) $\theta=70^\circ$, (e) $\theta=75^\circ$, (f) $\theta=80^\circ$ and (g) $\theta=90^\circ$.

However, the kink is not in a single position, it first appears at a contact angle of 70° and $s_1=1.1$ $s_2=s_3=1.2$ when it is situated at $\theta_{N1}=45^\circ$, $\theta_{N2}=55^\circ$. As the values of s_2 and s_3 rise, the contact angle at which the kink orientation becomes energetically stable also increases, at $\theta=80^\circ$ all values of $s_2=s_3<1.7$ have a stable orientation in the region of $\theta_{N1}=45^\circ$, $\theta_{N2}=55^\circ$. The combination of s_i values and θ at which the various orientations are stable is shown in Table 4.

Particle	$s_{2,3} \setminus \theta$	45	60	65	70	75	80	90
 a	1	a-d d	a-d	a-d	a-c-d	a-c-d	c	c
 c	1.2	a-d	a-d	a-d	a-c-d	a-c-d	c	c
	1.3	a-d	a-d	a-d	a-d	a-c-d	c	c
	1.5	a-d	a-d	a-d	a-d	a-c-d	c	c
	1.7	a-d	a-d	a-d	a	a	a-c	c

Table 4. stable orientations for given values of s_2 , s_3 and θ . Orientations are; horizontal (a), diagonal (b), rotated (c) and vertical (d) from Figure 6-6. For flat cubic particles in rotated orientations the θ_{N1} and θ_{N2} are between 45° and 60° .

6.3.4.2 Comparisons of ΔE_s

Calculating ΔE_s for these stable orientations as well as the horizontal and vertical ones and plotting them as a function of θ (Figure 6-20, Figure 6-21, Figure 6-22 and Figure 6-23) shows similar trends to those found in sections 6.2 and 6.3.3. For all cases the ΔE_s of the vertical orientation decreases to 0 at a lower contact angle as s_2 and s_3 increase. It becomes the most energetically unstable orientation for $\theta > 70^\circ$, when $s_2=s_3=1.7$ but at $s_2=s_3=1.2$ this increases to 80° . The horizontal orientation has a higher ΔE_s than the vertical orientation for all values of θ . As s_2 and s_3 increase this difference increases too, when $\theta=45^\circ$ the ΔE_s for a vertical orientation is 16 % lower than the ΔE_s for a horizontal orientation at $s_2=s_3=1.2$. At $s_2=s_3=1.7$ this difference has increased to 58 % of the horizontal ΔE_s . As the particle moves away from a cubic shape to a flat square, the horizontal orientation becomes much more stable than the vertical one.

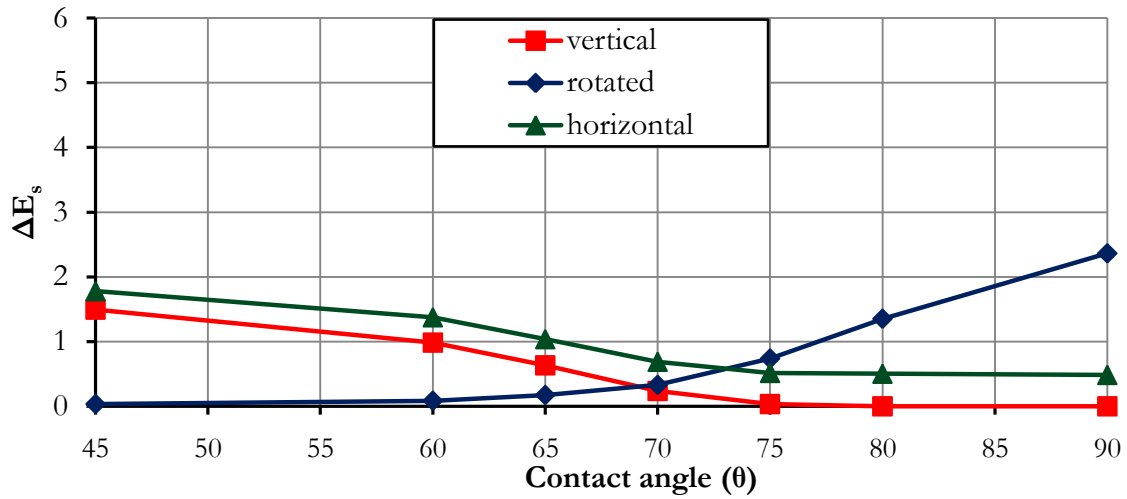


Figure 6-20. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1, s_2=s_3=1.2$.

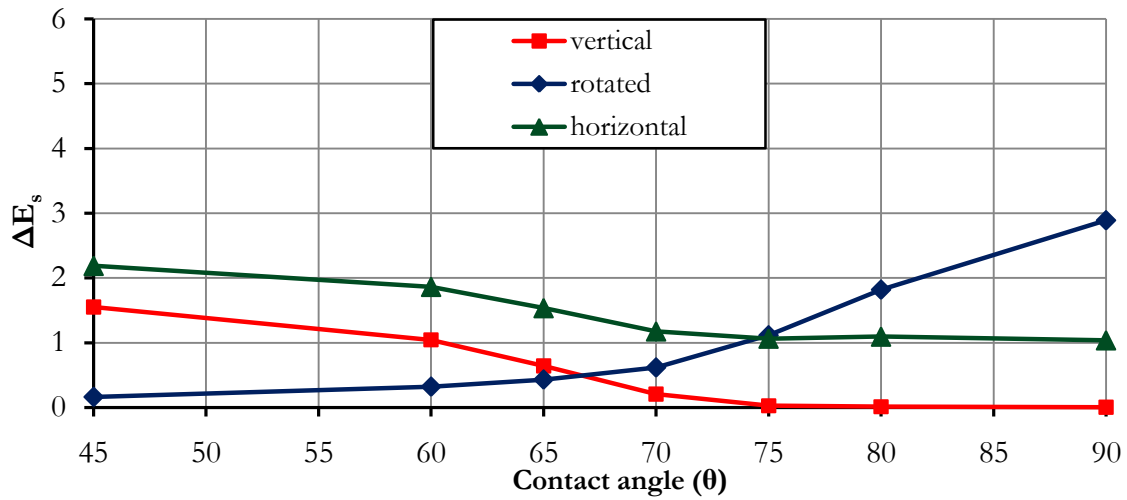


Figure 6-21. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1, s_2=s_3=1.3$.

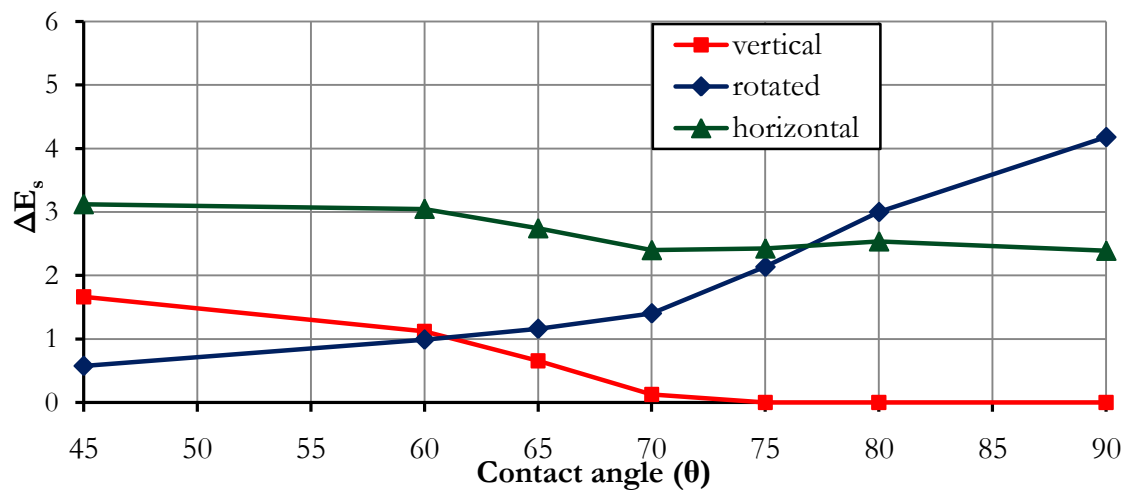


Figure 6-22. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1, s_2=s_3=1.5$.

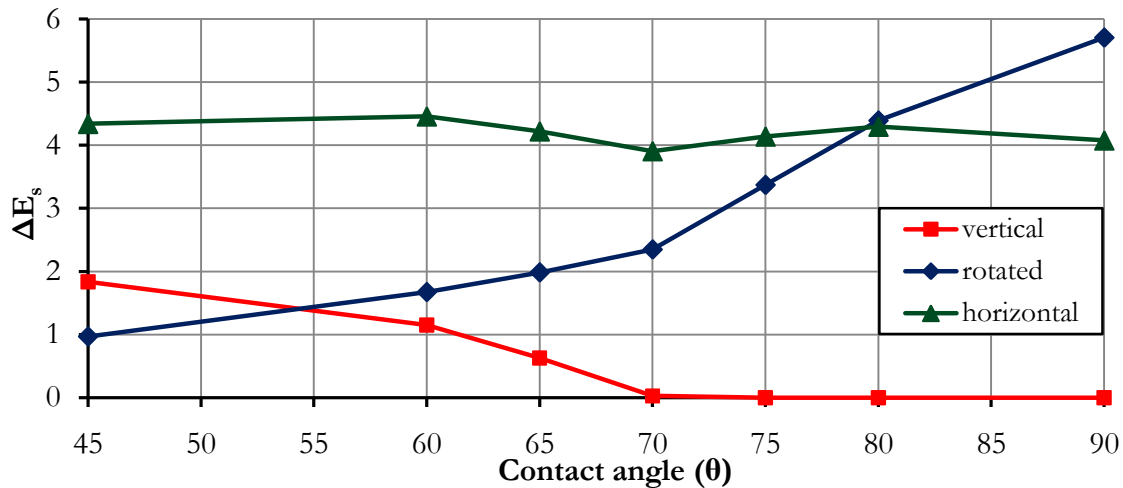


Figure 6-23. The difference in surface energy between a given orientation and the maximum energy orientation as a function of contact angle for $s_1=1.1$, $s_2=s_3=1.7$.

6.3.4.3 Film failure for flat square particles

Using *Surface Evolver* to find the P^*_{crit} at each stable orientation and contact angle shows similar trends as have been seen for oblong particles. The rotated orientation has a P^*_{crit} of roughly 28 % of the vertical or horizontal ones but the range of contact angles that the three orientations are all stable for is greatly reduced. For $s_2=s_3=1.2$ and $s_2=s_3=1.3$ (Figure 6-24) the horizontal and vertical orientations are both stable up to a contact angle of 75° , but as the aspect ratio increases the difference in P^*_{crit} does too. At $s_2=s_3=1.2$ the P^*_{crit} for a vertical orientation is on average 94 % of the horizontal orientation, at $s_2=s_3=1.5$ (Figure 6-25) this has dropped to 80 % and at $s_2=s_3=1.7$ (Figure 6-26) it is 75 %. This drop is associated with the increase in film distortion caused by the particle's increasing aspect ratio distorting the film surface and lowering the pressure at which the TPC leaves the curved edge of the particle and rides down the side.

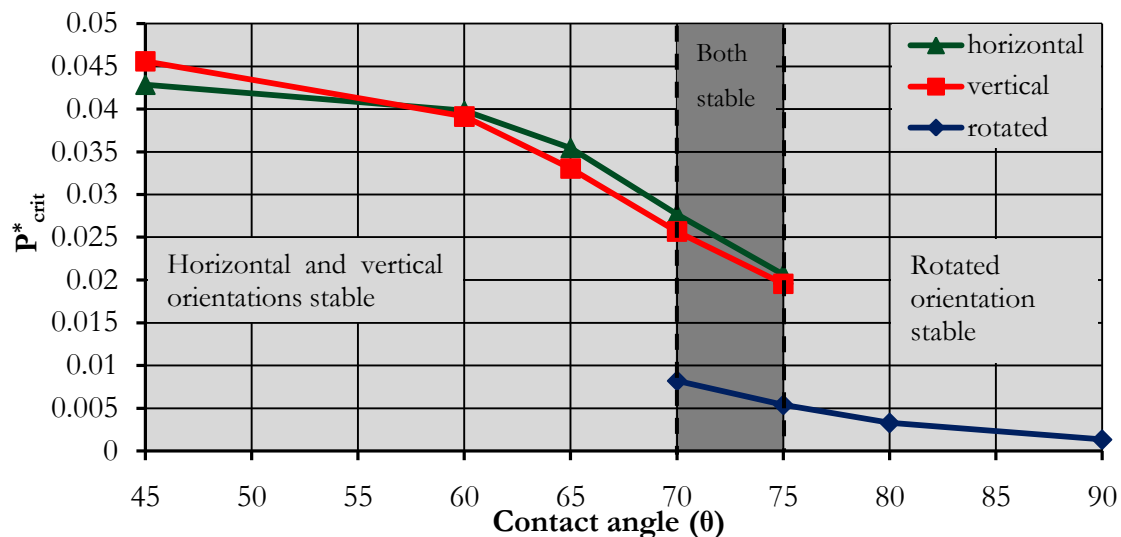


Figure 6-24. P^*_{crit} as a function of contact angle, $s_2=s_3=1.2$.

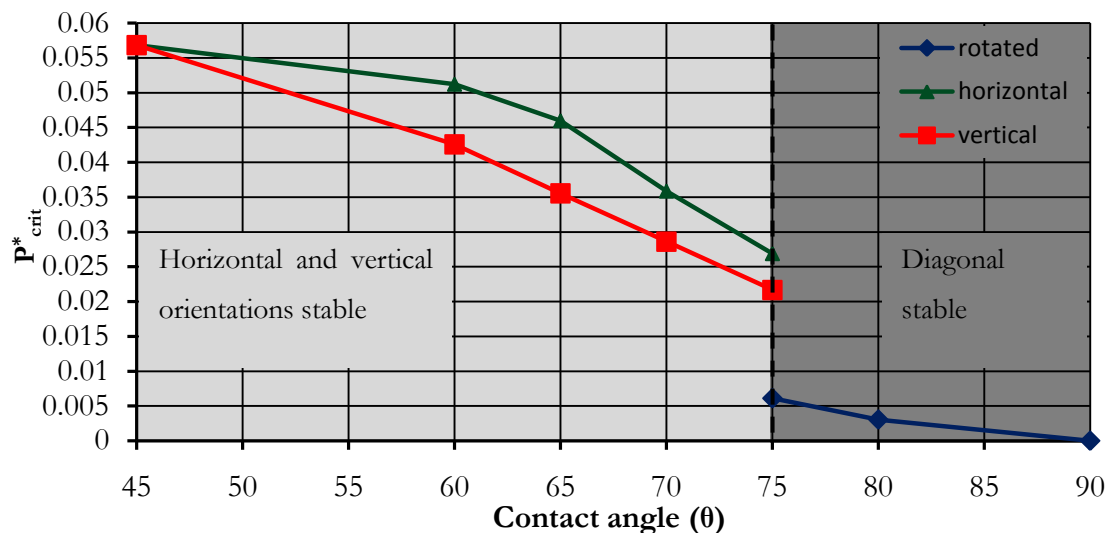


Figure 6-25. P^*_{crit} as a function of contact angle, $s_2=s_3=1.5$.

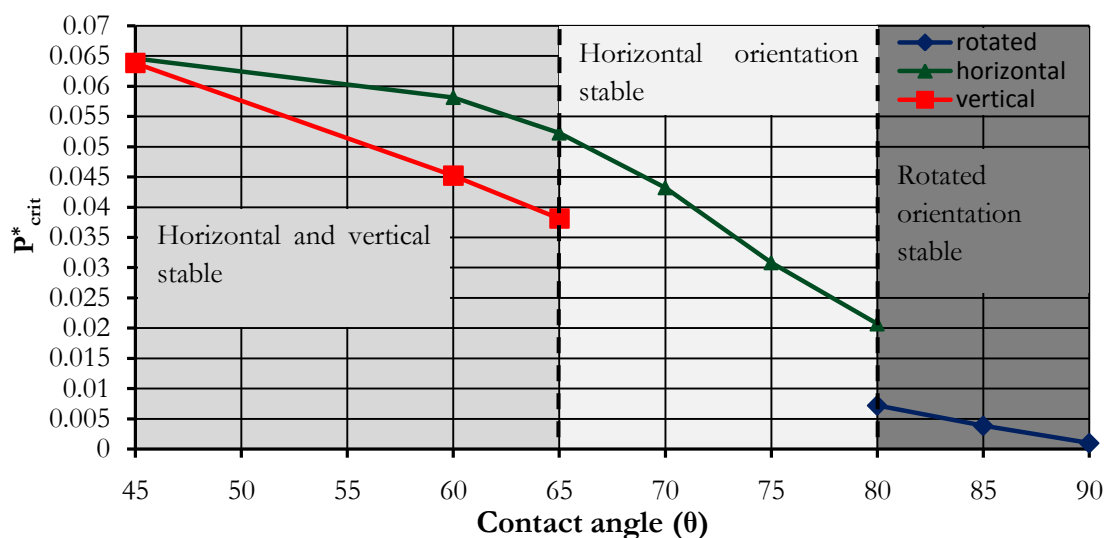


Figure 6-26. P^*_{crit} as a function of contact angle, $s_2=s_3=1.7$.

It has been shown that the horizontal orientation requires the highest P^* to rupture the film and that by increasing the aspect ratio of the particle it is possible to widen the range of contact angles over which this orientation is stable. It is therefore desirable to have wider, flatter particles attached to thin films to increase stability over more cubic ones.

The higher critical capillary pressures are associated with orientations that initially have a single face in each vapour phase (horizontal, vertical). The TPC for each interface sits at the edges bounding each of these faces. As P^* increases the curvature of the film does as well, however the TPC remains attached to the rounded edges of the particle to maintain the contact angle (Figure 6-27b). This effectively holds the film interfaces further apart at a given P^* producing a higher P^*_{crit} in comparison to a rotated or diagonal orientation. This effect is more apparent at lower contact angles, nearer $\theta=90^\circ$ the TPC is more mobile.

When the particle is rotated the edges that the TPCs are drawn to are the same for both interfaces, i.e. the equatorial edges running in a zigzag around the particle (Figure 6-27a). This causes much more film distortion but also draws the opposite sides closer together at lower P^* thereby reducing the P_{crit}^* associated with that orientation. For a diagonal orientation the TPCs are drawn together along the two edges in the long axis that are in the midpoint of the film (Figure 6-27c,d). Whilst this results in less film distortion than a rotated orientation there is still considerable thinning of the film at the particle edges, reducing the P_{crit}^* .

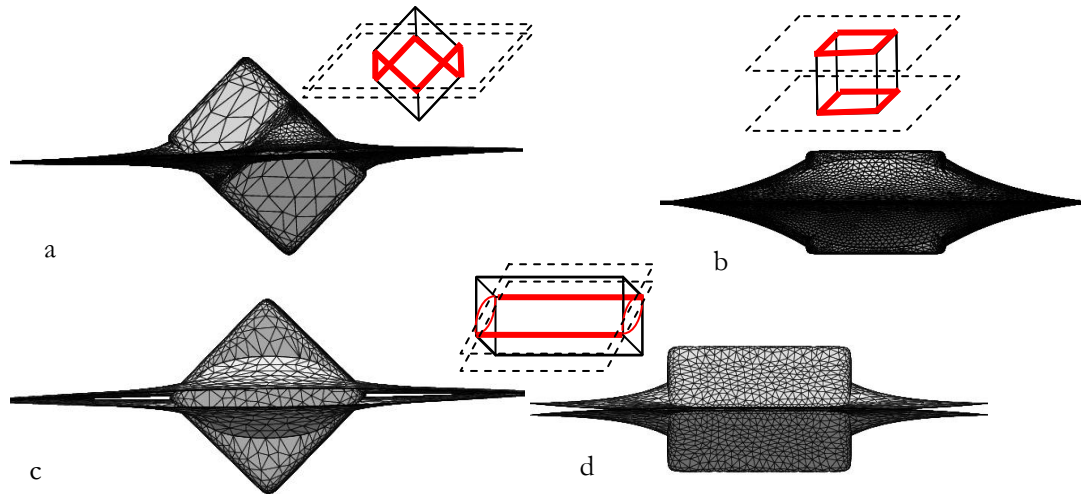


Figure 6-27. Showing the film distortion for rotated (a), horizontal (b) and diagonal orientations (c, d).

The propensity for sharp edged particles to reduce film and foam stability was observed by Frye and Berg (1989) who noted that particles with asperities noticeably reduced the foam stability at high contact angles, but that below $\theta=45^\circ$ the effect was diminished. At lower contact angles orthorhombic particles are only energetically stable in the horizontal and vertical orientations, which have been shown to produce a greater P_{crit}^* . However at higher θ when rotated and diagonal orientations become energetically stable the P_{crit}^* is much lower. This agrees with the observations of Frye and Berg (1989) that the foam stability is greatly reduced or actively destroyed by a combination of high contact angles and particles with asperities. Kursun and Ulusoy *et al.* (2006) conducted column flotation tests on talc and found that particles that were characteristically flatter or longer were more floatable than those that were rounded. A higher P_{crit}^* can be achieved with orthorhombic particles that are flatter or longer as opposed to cubic (rounder).

6.3.4.4 Summary

It has been shown that as s_2 and s_3 increase, the stable orientations that the particle can adopt change in a similar way to those for an oblong particle as it lengthens. Initially the vertical, horizontal and rotated orientations are stable but as the particle aspect ratio increases the vertical orientation becomes less stable and the rotated orientation coordinates change. As contact angle increases both the vertical and horizontal orientations become less stable but by increasing the particle aspect ratio it is possible to maintain the horizontal orientation's energetic stability at higher contact angles.

As s_2 and s_3 increase, initially there is no change in the maximum contact angle that the horizontal and vertical orientations are stable for, however at $s_2=s_3=1.7$ the horizontal orientation is stable up to $\theta=80^\circ$. The vertical orientation is also stable at higher contact angles for a given s_i than for the oblong particle. This is due to the lengthening of one axis in the vertical orientation, so that the area and shape of particle in the vapour phase is the same as for an oblong particle in a horizontal orientation. The added stability of this change in area is mitigated by the increase in particle length, making the vertical orientation more stable than for an oblong particle but still less than the horizontal orientation of the flat square particle.

Comparing the P^*_{crit} for the energetically stable orientations over a range of particle aspect ratios shows the rotated orientation to be the least stabilising orientation whilst the P^*_{crit} for vertical and horizontal orientations is significantly higher for those contact angles where all of the orientations are energetically stable. As aspect ratio increases, not only does the horizontal orientation become more energetically stable over the vertical one but the difference in P^*_{crit} also increases, leading to the conclusion that the higher the aspect ratio, or flatter the particle the higher the P^*_{crit} required to rupture the films.

6.4 CONCLUSIONS AND SUMMARY

This chapter has identified the energetically stable orientations of a series of orthorhombic particles at an interface and found the P^*_{crit} of films containing these particles in their stable orientations. It has used the method for simulating a non-spherical particle at an interface described in section 3.9.

A cubic particle was found to have only two energetically stable orientations in the film, horizontal and rotated. The contact angle was found to govern which orientation was most energetically stable with the horizontal orientation favouring contact angles below 80° and the rotated orientation favouring contact angles above 65° . Films containing a particle in a rotated orientation had a P^*_{crit} of around 30 % of the ones containing a horizontal particle. This behaviour was also seen for particles with either one or two axis extended to create oblong or flattened square particles. At low aspect ratios both types of particle showed rotated, vertical or horizontal orientations to be energetically stable over a similar range of contact angles to cubic particles. However, when $\theta > 75^\circ$, as the aspect ratio increased the oblong particles became more energetically stable in the diagonal orientation than the rotated one. Under the same conditions the flattened square particles were more energetically stable in the rotated orientation but at slightly altered values of θ_{N1} and θ_{N2} .

These results are in line with Dippenaar's research where it was observed that orthorhombic galena particles sat either horizontally or diagonally in the film. As it is very difficult to hand pick a completely cubic particle it is likely that the particles were elongated along at least one axis, affecting their stable orientation in the film, hence the observed diagonal orientation over a rotated one. The horizontal and diagonal orientations were observed with roughly equal probability by Dippenaar and the particles had

contact angles between $72\text{-}88^\circ$ which falls within the bounds where both orientations are energetically stable for oblong particles.

The film failure models used for the stable orientations showed that the horizontal or vertical orientations for all particle aspect ratios and contact angles had a significantly higher P_{crit}^* than the rotated or diagonal orientations which were roughly 30 % of the former values. In the cases where both diagonal and rotated orientations were energetically stable the diagonal orientation had the higher P_{crit}^* . Therefore to ensure the highest P_{crit}^* , a horizontal or vertical orientation is desirable. This can be achieved by keeping the contact angle of the particles below 65° or increasing the particle aspect ratio to form a flattened square.

The modelling of multiple, non-spherical particles is a more complex problem than that of multiple spherical particles. As orientation plays such a large role in the film stability it must be taken into account and when multiple particles are considered their positioning relative to each other will affect the stable orientations they will adopt. This requires more in depth investigation and will be discussed in the further studies chapter.

7 CONCLUSIONS

The aim of this thesis has been to investigate some of the fundamental aspects affecting particle stabilisation of thin films, with application to films found in flotation froths. Three main areas have been investigated; particle shape, packing arrangement and contact angle.

The expansion of existing 2D analytical models into 3D using the *Surface Evolver* program (Brakke 1992) has made it possible to simulate much more complicated systems of particles in thin films. These initial models developed in this thesis were used to investigate the effects of particle packing on film stability in 3D. The simple geometry of regular hexagonal and square arrangements of particles in a thin film were studied in more depth than previously possible with 2D approximations. These models were expanded to random particle arrangements in the film, allowing the investigation of particle packing density on the film. A model of a hexagonally packed double layer of particles in a film was also developed from the initial single layer models. Whilst models of spherical particles in films give insight into the geometric packing factors affecting film stability it is also necessary to take into account particle shape. A 3D model of non-spherical particles has therefore been developed and used to study the effect of shape and contact angle on the orientation of a particle within the film and its resulting effect on the capillary pressure required to rupture the film.

7.1 SINGLE LAYERS OF PARTICLES

Assuming a regular hexagonal or square packing pattern of particles in a film for given particle spacing the greatest sustainable capillary pressure is achieved when the particle contact angle is as low as possible. For a given contact angle the highest sustainable capillary pressure is achieved by minimising the particle separation distance on the film, increasing the packing density.

In 3D the simple measure of inter particle distance (S^*_p) used in 2D cannot be used to compare particle the packing densities for different arrangements in the film. Using S^*_{pp} or S^*_{pf} as measures of particle packing density produces different trends for hexagonal or square packing, instead the average film area per particle should be used. This has been shown to be a good measure of comparison for the P^*_{crit} across different regular packing arrangements. Moreover this allows easier comparison with experimental results as the $\mathcal{A}^*_{pp}$ is a measurable property of surface lamellae in flotation froths (Sadr-Kazemi and Cilliers, 2000).

The $\mathcal{A}^*_{pp}$ can also be use to compare the stability of films containing particles in random packing arrangements. A relationship between the contact angle of the particles and the $\mathcal{A}^*_{pp}$ has been established which allows the P^*_{crit} of a film to be calculated provided these two variables are known. The P^*_{crit} is a useful factor in the bulk simulation of foams, if it is known it can be used to help simulate the bubble coalescence throughout the froth. This in turn allows the bubble size distribution to be more accurately

calculated. Randomly packed films exhibit the same trends as regularly packed ones; a higher packing density (lower A_{pp}^*) results in a higher P_{crit}^* at a given contact angle. For a given A_{pp}^* the highest P_{crit}^* is found at the lowest contact angle. However, regular packing arrangements provide the highest stability for a given A_{pp}^* and θ . The film always fails at the point furthest from any particles, hence a lower packing density producing a lower P_{crit}^* . Clumped particle aggregates on the film will also result in a lower P_{crit}^* than regularly spaced ones. For a given A_{pp}^* a regular packing arrangement provides the highest P_{crit}^* . If the particles are regularly spaced (hexagonal or square packing) the calculated value of P_{crit}^* from equation 4-6 will be roughly 53 % of the values obtained from *Surface Evolver*.

At very low contact angles ($\theta < 15^\circ$) a small change in θ has little effect on the P_{crit}^* for a given packing arrangement, whilst at values of θ closer to 90° there is a larger change in P_{crit}^* with contact angle. Therefore, when using particles with large contact angles care needs to be taken that it is measured or attributed correctly.

7.2 DOUBLE LAYERS OF PARTICLES

The investigation into the stability of double layers highlights the complex geometry that arises when more than one layer of particles is present in a film. The effects of inter particle spacing and contact angle on the stability of a hexagonally packed double layer was simulated using *Surface Evolver*. Three separate failure criteria were identified; capillary driven failure, film inversion and particle bridging.

Capillary pressure driven failure is the same mechanism through which films containing single layers of particles are ruptured and is well understood. However the *Surface Evolver models* developed allowed a thorough investigation of the P_{crit}^* for partially bridged double layers, where particles in both layers have been bridged by both interfaces forming a highly complex film shape. Similar trends to those seen for single layers were observed for particle spacing and contact angle in double layers. Lower contact angles and closer particle packing produced higher P_{crit}^* . For a given particle spacing double layers always returned a higher value of P_{crit}^* than single layers.

However, a film containing a double layer of particles can also fail through film inversion. This occurs when the capillary pressure reaches a level high enough that it becomes energetically more favourable for the interface to switch to the other side of the particle. If the inversion capillary pressure is reached before the particles in the opposite layer are bridged the film will fail immediately. The conditions under which film inversion occurs instead of capillary pressure driven failure have been identified and a more complete picture of double layer film stability developed. The particle spacing in the double layer at which the film failure changes regime depends upon the contact angle, with a peak in S_{PPC}^* at $\theta = 60^\circ$. Above this contact angle and the S_{PPC}^* rapidly drops off. For both failure regimes a double layer has a higher P_{crit}^* than a single layer, but at the S_{PPC}^* , capillary pressure driven failure has the largest P_{crit}^* . When considering closely packed double layers of particles it is safe to assume that the film will invert before it bridges and fails

through capillary pressure. However, for less densely packed double layers it necessary to take into account the geometry of the particles and calculate the mode through which the film will fail. It has also been shown that a toroidal pore model over-predicts the failure capillary pressure, much like the 2D approximations of single layers.

7.3 NON-SPHERICAL PARTICLES

The development of a modelling technique that can quickly and easily simulate non-spherical particles at an interface has allowed an in depth study of orthorhombic particles and their energetically stable orientations. Cubic particles were found to have two stable orientations, whilst orthorhombic particles such as flattened squares or oblongs had three or four, depending on their dimensions. However, two distinct types of energetically stable orientation were observed and the adoption of one over the other has a large impact on the critical capillary pressure of the film.

In *flat* orientations the orthorhombic particle has its faces aligned either with the undisturbed interface or at 90° to it (termed horizontal or vertical orientations). In *twisted* orientations, the normals of the upper faces of the particle make an angle of between 45° and 60° to the Z-axis (rotated or diagonal orientations) depending on particle shape and contact angle. For all particle shapes the film has a significantly higher P_{crit}^* when the particle is *flat* instead of *twisted*. In the case of a cubic particle the *twisted* P_{crit}^* is roughly 70 % lower than the *flat* P_{crit}^* . In general the *flat* orientations are energetically stable at lower contact angles ($\theta \sim 45^\circ$), whilst the *twisted* ones are energetically stable closer to $\theta = 90^\circ$. However, the aspect ratio of the particle also affects the stable orientations. As the length of a cubic particle increases the rotated orientation is replaced by the diagonal orientation and the vertical orientation becomes unstable. If both the length and the width are increased and a flat square particle is formed the vertical orientation remains stable at greater aspect ratios but the horizontal orientation is stable at much higher contact angles (80° instead of 75°).

Therefore, to increase the stability of a film or froth stabilised by orthorhombic particles (e.g. a galena froth), the contact angle should be kept below about 65° . This will ensure the *flat* orientations remain more energetically favourable, reducing the chances of *twisted* particles in the film. If it is possible to control particle shape then flat particles with a higher aspect ratio have *flat* orientations that are more energetically favourable at higher contact angles. Conversely if film destabilisation is sought then cubic particles with a high contact angle should be used as the rotated orientation has the lowest P_{crit}^* of any orientation investigated and is stable over the largest range of contact angles for a cube. This agrees with experimental work of Hiçilmaz *et al.* (2004), and Kursun and Ulusoy(2006) who found that talc particles with a characteristically elongated or flat shape were more floatable than those with a more rounded shape.

7.4 SUMMARY

Three main aspects have been investigated in this thesis; contact angle, particle spacing in the film and particle shape. All three have an important role to play in the structure and dynamics of a film and therefore flotation froth. Keeping the contact angle as low as possible will provide the most stability for a given particle arrangement but there is evidence that the contact angle itself affects the final arrangement of the particles (Appendix A, chapter 10). Films can sustain a higher capillary pressure (and are therefore more stable), the greater their particle loading. Wide, flat particles offer the most film stability as they will sit flat in the film and are less able to twist in it, which stops them bringing the opposite sides together and causing failure through bridging dewetting. However a film is only as stable its weakest point; even if one particle in the film has a high contact angle or shape conducive to bridging dewetting it is there that the film is most likely to fail.

The results presented in this thesis have also shown that it is possible resolve the interfacial shape of a film stabilised by large numbers of particles using the *Surface Evolver* program. Three papers have been published using the results from this work (Morris *et al.* 2008, Morris *et al.* 2010a, Morris *et al.* 2010b).

The models developed here have been designed with versatility in mind and are capable of being used to investigate many more configurations in their current form. There is also scope for further development to investigate, among other areas, particle dynamics in the film.

8 FUTURE WORK

Several models and tools have been developed over the course of this thesis, including single and double layers of regularly packed particles, non-spherical particles and large scale particle placement. Whilst the results obtained from these models have expanded on previous work there is still much to do in this area of research.

- The investigation of non-uniform properties of particles on film stability can easily be investigated using the current models. As each particle is placed it can be assigned random size, contact angle and even shape and orientation to allow more in depth analysis of bulk effects on film stability.
- If non-spherical particles are inserted into a film their energetically preferred orientations will have to be taken into account. The studies in this thesis have only considered a singular non-spherical particle. If there are many non-spherical particles in close proximity to each other the film distortion they cause could affect the stable orientations of adjacent particles. It is computationally inefficient to approach the problem of energetically stable orientations of multiple particles in the same way as was done here for individual particles. It can be solved using the film shape data at the TPC of the non-spherical particles. The resultant force acting on a particle can be calculated from the facets at the TPC and this same data can be used to calculate the moment acting on a non-spherical particle. If the moment is known the same approach used for moving spherical particles can be used to rotate non-spherical particles to their energetically stable orientation. This makes it possible to populate a film with non-spherical particles and find their energetically stable positions relative to each other before finding the critical capillary pressure required to rupture the film.
- The 3D models of spherical particle motion in Appendix A (chapter 10) are currently limited to single layers in flat films. Implementing a film curvature to account for pressure differences between adjacent bubbles will allow a more accurate representation of the particle stabilised films found within a flotation froth. This is not a particularly difficult problem, by altering the pressure in the two gas phases of the model a curvature can be induced in the film and the force calculations on the particles will automatically take into account the effects of film curvature. However the tools that populate the film as well as manipulate the mesh need to be improved before this is tractable.
- Whilst developing the model for dynamic particles several forces are calculated and added to find the resultant force acting on the particle. Implementing the calculation of additional forces acting on the particle such as electrostatic repulsion is therefore a matter of adding an extra force calculation in the DEM step of the model.

- Expanding the dynamic 2D model of double layers into 3D is also an improvement that can be made to the dynamic 3D model. This would allow the investigation of the effect of film expansion on a close packed double layer of particles and comparison the 2D data.
- The models described in this thesis have all been used to investigate various individual aspects of particle stabilised thin films. There is, however, scope to combine them into one model capable of simulating large scale dynamic models of non-spherical particles in a thin film. A model like this would enable the investigation of the bulk properties of realistic particle stabilised thin films on a scale much larger than previously accomplished.

9 REFERENCES

- Abkarian M., Subramaniam A.B., Kim S.H., Larsen R.J., Yang S.M., Stone H.A., Phys. Re. ltr. (2007) **99** 188301
- Alargova R.G., Warhadpande D.S., Paunov V.N., Velev O.D., Langmuir **20** (2004) 10371
- Ali S.A., Gauglitz P.A., Rossen W.R., Ind. Eng. Chem. Res. **39** (2000) 2742-2745
- Ata S. J. Colloid and Interface Sci. **338** (2009) 558-65.
- Aveyard R., Binks B.P., Clint J.H., Adv. Colloid and Interface Sci. **100-102** (2003) 503–546
- Aveyard R., Binks B.P., Fletcher P.D.I., Peck T.G. and Rutherford C.E., Adv. Colloid and Interface Sci. **48** (1994a) 93-120
- Aveyard R., Binks B.P., Fletcher P.D.I., Rutherford C.E., Colloids and Surfaces A: Physicochem. and Eng. Asp. **83** (1994b) 89
- Aronson MP. Langmuir. (1986) **2** 653-659.
- Binks B.P. Current Opinion in Colloid and Interface Sci. **7** (2002) 21
- Bournival G, Ata S. *Minerals Engineering*. **23** (2010) 111-116.
- Brakke K., Exp. Math. **1** (1992) 141-165.
- Brown A.D.B., Smith C.G., Rennie A.R., Phys. Rev. E **62** (2000) 951
- Cole K, Morris G, Cilliers J.J. Minerals Engineering (2010) 1-5.
- Danov K.D., Kralchevsky P.A., Naydenov B.N., Brenn G., J. Colloid and Interface Sci. **287** (2005) 121-34.
- Danov K.D., Kralchevsky P.A., Adv. Colloid and Interface Sci. **154** (2010) 91-103.
- Dickinson E. Current Opinion in Colloid & Interface Science. **15** (2010) 40-49.
- Dickinson E., Ettelaie R., Kostakis T., Murray B.S., Langmuir **20** (2004) 8517
- Dippenaar A., Int. J. Mineral Processing, **9** (1982) 1-14
- Du Z., Bilbao-Montoya M.P., Binks B.P, Dickinson E., Ettelaie R., Murray B.S., Langmuir **19** (2003) 3106
- Denkov N.D., Ivanovi B., Kralchevsky P.P., Wasan T., J. Colloid and Interface Sci. **150**, No.2 (1992) 589-593

- Exerowa D., Kruglyakov P.M., Foam and foam films, (1997)
- Fujii S., Iddon P.D., Ryan A.J., Armes S.P., Langmuir **22** (2006) 7512-7520
- Frye G.C., Berg J.C., Journal of Colloid and Interface Science. **130** (1989) 54-59.
- Gallegos-Acevedo P.M., Pérez-Garibay R., Uribe-Salas A. Min. Eng. **19** (2006) 12-18
- Garrett P.R., Colloids and Surfaces A: Physicochem. Eng Aspects **85** (1994) 159-197
- Garrett P.R., Journal of Colloid and Interface Science **69** (1979) 107-121
- Haines W.B., J. Agri. Sci. **17** (1927) 264-290
- Hiçyılmaz C., Ulusoy, U., Yekeler M., Applied Surface Science **233** (2004) 204-212
- Horozov T.S., Aveyard R., Clint J.H., Langmuir **21** (2005) 2330
- Hunter T.N., Pugh R.J., Franks G.V., Jameson G.J., Adv. Colloid and Interface Sci. **137** (2008) 57-81
- Hilden J.L., Trumble K.P., J. Colloid and Interface Sci. **267** (2003) 463
- Johansson G., Pugh R.J., Int. J. Mineral processing **34** (1992) 1-21
- De Graaf J., Dijkstra M., van Roij R., Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top. **80**, (2009), 0514505
- Kaptay G., Colloids and Surfaces A: Physicochem. Eng. Aspects **230** (2004) 67-87
- Kelly E.G., Spottiswood D.J., Introduction to Mineral Processing. John Wiley & Sons (1982) 491
- Koh P.T.L., Hao F.P., Smith L.K., Chau T.T., Bruckard W.J. Int. J. Miner. Process. **93** (2009) 128-134
- Kruglyakov P.M., Nushtayeva A.V., Vilkova N.G., J. Colloid and Interface Sci. **276** (2004) 465-474
- Kruglyakov P.M., Nushtayeva A.V., Adv. Colloid and Interface Sci. **108-109** (2004) 151-8.
- Kursun H., Ulusoy U., Int. J. Miner. Process. **78** (2006) 262-268
- Lewandowski E.P., Bernate J.A, Searson P.C., Stebe K.J., Langmuir. **24**, (2008), 9302-9307
- Lehle H., Noruzifar E., Oettel M., Eur. Phys. J. E: Soft Matter Biol. Phys. **26**, (2008), 151-160
- Mason G., Morrow N.R., J. Colloid and Interface Sci. **168** (1994) 130-141
- Mayer R.P., Stowe R.A., J. Colloid and Interface Sci. **20** (1965) 893
- Morris G., Pursell M.R., Neethling S.J., Cilliers J.J., J. Colloid and Interface Sci. **327** (2008) 138-144

- Morris G., Neethling S.J., Cilliers J.J., Minerals Engineering **23** (2010a) 979-984
- Morris G., Neethling S.J., Cilliers J.J., J. Colloid and Interface Sci. (2010b) doi:10.1016/j.jcis.2010.10.039
- Paunov V.N., Langmuir. **19** (2003) 7970-7976
- Park B.J., Pantina J.P., Furst E.M., **24** (2008) 1686-94.
- Princen H.M., J. Colloid and Interface Sci. **30** (1969) 69-75
- Princen H.M., J. Colloid and Interface Sci. **30** (1969) 359-371
- Purcell W.R., Trans AIME **189** (1950) 369
- Rusanov A.I., Prokhorov V.A., Interfacial Tensiometry, Elsevier (1996)
- Schwarz S., Grano S., Colloids and Surfaces A: Physicochem. Eng. Aspects **256** (2005) 157–164
- Sadr-Kazemi N., Cilliers J.J. Minerals engineering **13** (2000) 773-776
- Subramaniam A.B., Mejean C., Abkarian M., Stone H.A., Langmuir **22** (2006) 5986
- Weire D., Hutzler S. The Physics of Foams, (2005) Clarendon Press Oxford
- Wills B.A., Mineral processing technology, (1997) Butterworth-Heinemann
- Wang Y, Neethling S. *Minerals Engineering*. **19** (2006) 1069-1076.
- Zhou L., Kambhamettu C., Graphical Models. **63(1)**, (2001), 1-20

10 APPENDIX A: DYNAMIC MODELS OF PARTICLES IN FILMS

10.1 INTRODUCTION

Particles attached to a film are subject to a series of forces that arise from the shape of the interface around them, the pressure of the liquid and gas phases and charges on the particles. The forces acting on the particles are often unbalanced causing particle motion in the film which can be simulated if the film shape is known. In 2D the film shape and resulting particle motion can be found analytically for a single layer of particles in the film (Ali *et al.* 2000). However, for a 2D double layer the particle-particle interaction coupled with the film shape swiftly becomes intractable for large scale simulations. It is possible to use the 2D string model in *Surface Evolver* to calculate the forces acting on the particles in a double layer on a large scale and simulate the particle reaction to disturbances which is described in section 10.2. This section will present some initial results from simulations run with the model described in section 10.2, investigating particle reaction to a disturbance in a quasi stable double layer and film expansion.

Whilst it has previously been shown that 2D models cannot resolve many aspects of 3D film systems they have been proven to reliably reproduce the trends seen in 3D and it is for this reason that these models have been used. The 3D double layer system is complicated, making a 2D approach a tractable way of investigating the behaviour of particles in a film and gaining insight into the trends and behaviour they produce.

The approach used to simulate particle forces and motion in 2D can easily be expanded to 3D as described in section 10.3 and used to simulate the aggregation of spherical particles in a flat film. 3D particle motion also allows the generation of more realistic packing arrangements on a film. The regular and random packing arrangements used in chapter 4 offer insight into the stabilisation of films by particles but it is clear that the particle arrangement is an important factor. Simulating particle motion on the film will allow more realistic particle packing arrangement to be generated.

The results presented in this appendix represent an expansion of the static models to dynamic, and a step change in complexity, applicability and computation intensity. However, the results obtained are qualitative showing expected particle behaviour on small a small scale. The largest scale models run require large amounts of computer time and as a result not enough results have been obtained to perform rigorous statistical analysis, instead the results presented show work in progress, which will be expanded upon. The planned development of these models is described in the chapter 8.

10.2 DYNAMIC MODELS IN 2D

The static 2D model introduced in section 3.4.2 is used as the base for the dynamic 2D model but in this section the focus is on particle behaviour in the film driven by the forces that arise from film curvature, capillary pressure and particle interaction.

10.2.1 PHYSICAL ASSUMPTIONS

All the assumptions made in section 3.3 are held for the dynamic model. The effects of drag from the liquid (and gas phases) and charges on the particles have also been ignored. All forces are also non-dimensionalised using equation 10-1.

$$F^* = \frac{F}{\gamma_{LV} R_p} \quad 10-1$$

10.2.2 MODELLING STEPS

The forces that have been used to calculate particle motion are those arising from surface tension, liquid and vapour pressures and particle-particle interaction. It is assumed the motion of the particles is quasi-dynamic, the steps used in the model are as follows;

1. The film is evolved to its minimum energy.
2. Particles are checked to see if any are ejected from or enter into the film.
3. The total force acting on each particle is calculated from the *Surface Evolver* model data.
4. Each particle is moved in proportion to force acting on it over a time interval scaled to force. The time scale is set so that a particle will not move further than the minimum edge length in a given time step.
5. The particle positions are used to check if particles are overlapping. If not, back to step 1.
6. If overlapping a repulsive reaction force for each particle is calculated as a function of the overlap distance.
7. The particles are moved a small amount in the direction of their resultant reaction forces.
8. Return to step 5.

This is continued until a stable configuration is reached or all the particles have bridged the film or the film fails. The following section will investigate each step in more detail.

10.2.3 EVOLVING MODEL TO MINIMUM ENERGY SURFACE

Once the particle positions and surface properties have been fixed the model is evolved to the minimum energy. During this step the edge lengths of the film and particles are checked to ensure detail, accuracy and computational efficiency are maintained. The upper and lower bounds of the edge length are set at $0.03R_p$ and $0.01R_p$ respectively (non-dimensionalised to $0.03R_p^*$ and $0.01R_p^*$).

10.2.4 ENTERING OR LEAVING A FILM

Particles are considered to be ejected from a film (dewetting) in 2D when two TPCs touch, if they are from opposite sides of the film it will fail, but if the particle is forced up or down then the TPCs on its left and right hand sides can come into contact, which will result in its ejection from the film (Figure 10-1)

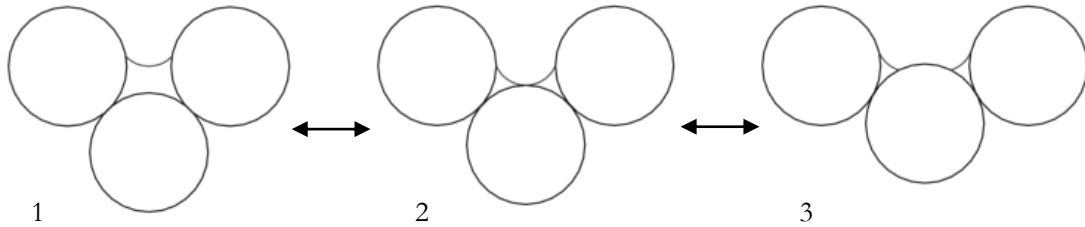


Figure 10-1 Particle entering the film (1, 2, 3) or being ejected from it (3, 2, 1).

Likewise, if the particle comes into contact with the opposite side of the film it is assumed it will bridge it. It is assumed that bridging/dewetting occurs instantaneously, i.e. the new minimum energy surface is attained in a negligible amount of time and reactions arising from the unbalanced forces as the film travels to its new equilibrium position have no effect on the particle behaviour.

10.2.5 CALCULATION OF PARTICLE FORCES

The forces are calculated separately and are extracted from the data in the *Surface Evolver* model. In 2D this comes from the values for surface tension, pressure, particle position, edge properties and vertex position. The forces due to surface tension are calculated first.

10.2.5.1 Surface Tension Forces

The forces acting on a particle due to surface tension arise from the angle that the liquid vapour interface makes with the horizontal at TPC (θ_γ) as well as the surface tension of the liquid vapour phase as shown in Figure 10-2.

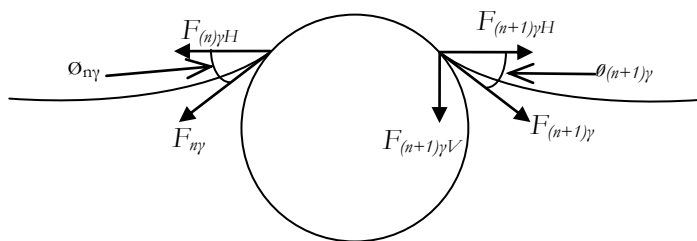


Figure 10-2 Surface tension forces acting on a particle in 2D.

F_γ is calculated in two separate parts, horizontal and vertical (equations 10-2 and 10-3) for each TPC on the particle, these are then summed to get a resultant horizontal and vertical force for the tension component (equations 10-4 and 10-5).

$$F_{nyH} = \gamma_{LV} \cos \phi_{ny} \quad 10-2$$

$$F_{nyV} = \gamma_{LV} \sin \phi_{ny} \quad 10-3$$

$$F_{totyH} = \sum_{n=1}^n F_{nyH} \quad 10-4$$

$$F_{totyV} = \sum_{n=1}^n F_{nyV} \quad 10-5$$

10.2.5.2 Pressure Forces

The liquid and vapour pressure forces are calculated by multiplying the pressure in the corresponding phase by the cross sectional area of the particle in that phase. In the *Surface Evolver* model this is done by considering each edge in turn. Each edge has several attributes, including tension, length (ee.l), a base (ee.x) and a height (ee.y) which are used in these calculations (Figure 10-3). Each edge will contribute an x-component and a y-component to the resultant pressure force, calculated as shown in equations (10-6), (10-7), (10-8) and (10-9).

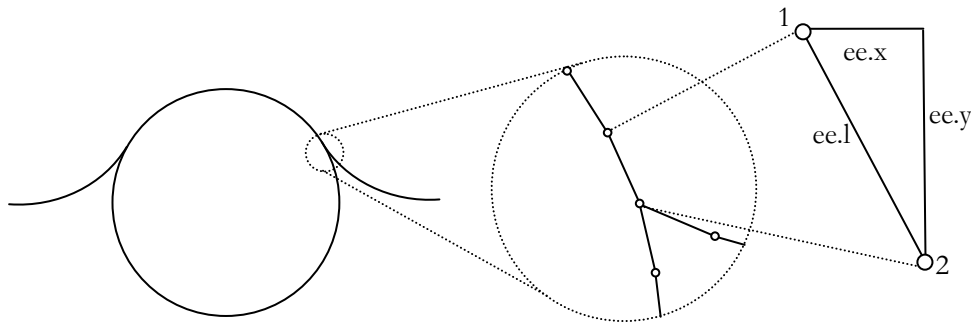


Figure 10-3 Breakdown of the structure of a 2D model.

The pressure force direction is controlled by the edge direction, the edge shown in Figure 10-3 is measured from 1 to 2 with up and right as positive in the x and y directions respectively. Therefore *ee.x* will have a positive value and *ee.y* a negative one, when used with equations (10-6) and (10-7) they will return forces to the left and down. The model is defined so that all the edges are organised in a clockwise fashion around the particle so that equations (10-6-10-9) return the correct values for force and direction.

$$F_{VPx} = \sum ee.y \times P_V \quad 10-6$$

$$F_{VPy} = \sum -ee.x \times P_V \quad 10-7$$

$$F_{LPx} = \sum ee.y \times P_L \quad 10-8$$

$$F_{LPy} = \sum -ee.x \times P_L \quad 10-9$$

Where P_V is the pressure of the vapour phase, P_L is the pressure of the liquid phase and ee represents a specific edge within the vapour or liquid phases. Both the x- and y-components of F_{VP} and F_{LP} are the sum of the individual components of all the edges in that phase.

10.2.5.3 Particle-particle reaction force

This force, used in the DEM phase of the simulation, uses the particle position coordinates to calculate the particle overlap and reaction. Again, the x- and y-components are calculated separately for each overlapping particle and summed to give a total force in the X and Y directions. The particle positions are stored in the PP_j matrix where i is the particle number and j is the X or Y direction introduced in section 3.6. If it is assumed that two particles are overlapping then the reaction force from particle 2 to particle 1 is calculated as;

$$Sep_{12} = \sqrt{(PP_{1x} - PP_{2x})^2 + (PP_{1y} - PP_{2y})^2} \quad 10-10$$

$$Sep_{12x} = \left(\frac{(PP_{1x} - PP_{2x})}{Sep_{12}} \right) \left(\frac{Sep_{12} - 2R_P}{2} \right) \quad 10-11$$

$$Sep_{12y} = \left(\frac{(PP_{1y} - PP_{2y})}{Sep_{12}} \right) \left(\frac{Sep_{12} - 2R_P}{2} \right) \quad 10-12$$

$$F_{PPx} = (100Sep_{12x})^3 + (100Sep_{12x})^5 \quad 10-13$$

$$F_{PPy} = (100Sep_{12y})^3 + (100Sep_{12y})^5 \quad 10-14$$

Equation (10-10) is used to find whether the two particles are overlapping, if they are then the relevant overlap (Sep_{12x} , Sep_{12y}) is calculated using equations (10-11) and (10-12), equations (10-13) and (10-14) are used to generate the reaction force on particle 1 from particle 2. In equations (10-10) and (10-11) the

overall overlap and therefore the reaction force, is divided by two as the reaction force will be equally distributed between the two overlapping particles respectively. The process is repeated for particle 2 to calculate the forces acting on it from particle 1.

This simple case can be expanded if more than two particles are overlapping each other. If it is assumed there are many particles, some overlapping others, equation (10-10) is used to calculate the distance between each particle. If it is less than $2R_p^*$ for any case then those two particles overlap and the separation between them (Sep_{ijx} , Sep_{ijy}) is calculated and stored for each particle. The resultant x- and y-components of overlap are then summed for each particle and F_{ppx} and F_{ppy} can be calculated for each particle. These values are stored and added to when other overlap forces from different particles are calculated to find the final, resultant force and direction of motion for the particle. It is moved a small amount in that direction and the process is begun again until the maximum non-dimensional force acting on any particle is less than 0.001, this corresponds to an overlap of 4.65×10^{-4} .

10.2.6 PARTICLE MOTION

The particle reaction forces are used in a separate particle motion step to the film and pressure forces but both use the same approach which is described here. The particle reaction forces can be calculated quickly from the particle positions data whilst the pressure and film forces can only be calculated from the evolved model. It is therefore quicker to evolve the film, calculate the forces on the particles and move them accordingly in one step. The overlapping particle positions can then be corrected in the DEM step on a much finer time step. In the case of particle-particle interaction the resultant force on each particle is used, in the case of film and pressure driven motion the sum of the tension, vapour pressure and liquid pressure forces are used, herein collectively referred to as reaction force (F_R) and film force (F_F) respectively. As each particle is moved in proportion to the force acting on it in both cases the motion is due to an effective viscosity acting on the particles.

First the particles are moved in the direction of the resultant film force, the new particle positions are then used to calculate the reaction force for each particle as described in section 10.2.5.3 and they are then moved in that direction proportional to the force acting on them. The reaction force is then recalculated and the particles moved again, this step is repeated until there is no overlap. At this point the new film surface is found using *Surface Evolver* and the process begun again.

The distance a particle is moved in a given step is related to the force acting upon it, however, if the particles are suddenly moved large distances it can cause problems with the model integrity in *Surface Evolver*. To prevent sudden large motion a maximum movement constant is set so that in any one step no particle can move further than this M_{max} which is set as $0.1R_p^*$ for the F_F step and $0.02R_p^*$ for the F_R step. It is assumed that the maximum resultant force acting on any one particle will result in that particle moving M_{max} (equation 10-15), where K_t is equivalent to a dynamic time step.

$$K_1 = \frac{M_{max}}{F_{Fmax}} \quad 10-15$$

The position of the particles and shape of the film is saved at regular intervals denoted by K_{step} , if F_{Fmax} is very small K_1 can become much larger than K_{step} so to prevent this, if K_1 is greater than $0.4K_{step}$ it is made equal to $0.4K_{step}$. Once K_1 has been calculated it is used in equation (10-16) to calculate the distance moved by each particle. Where i represents the a particle in the model and j is the x or y component of position or force, t is the current time step and $t+K_1$ is the next.

$$PP_{ij}^{t+K_1} = PP_{ij}^t + K_1 F_{Fij} \quad 10-16$$

After each time step to calculate the motion due to film force the DEM step is used to move particles that overlap. This is approached in the same way as for film forces but the calculation of forces and movement of the particles is repeated until none of the particles are overlapping anymore.

10.2.7 CHANGING FILM PROPERTIES

The film properties can be changed with time by tying the particular property in question (pressure, volume, dimensions etc.) to the total K . Defining K_{tot} as the sum of all K_1 gives a non-dimensionalised time passed for the model. The film boundary can be contracted or expanded by changing the constraint(s) defining the its position by some fraction of time, negative values contracting the film, positive values expanding it.

10.3 DYNAMIC MODELS IN 3D

This section describes a model, in *Surface Evolver*, that calculates the particle motion that arises from the distortion of the film due to particle contact angle and capillary pressure in 3D. The 2D model in chapter 10 is built upon and expanded into 3D to look at packing arrangements on the film. The model is however, limited to single layers of spherical particles in a flat film, but it is still able to provide insight into the complex problem of particle motion and behaviour.

10.3.1 MODEL PARAMETERS

Assumptions made in chapter 10 regarding gravity, conjoining and disjoining pressures, non-dimensionalisation, contact angle, viscosity and particle charge have all been maintained.

The models used to investigate the forces acting on particles are non-periodic, flat film models. The spherical particles are placed in the film in random or user defined positions as described in section 3.6. Unlike the 2D model, surface tension force is now calculated from facet and edge attributes instead of edge and vertex attributes, whilst pressure forces are now calculated from facet attributes. The simulation steps are detailed below for clarity;

1. The film is evolved to its minimum energy.
2. The total force acting on each particle is calculated from the *Surface Evolver* model data.
3. Each particle is moved in proportion to force acting on it over a time interval scaled to force.
4. The particle positions are used to check if particles are overlapping. If not, back to step 1.
5. If overlapping a repulsive reaction force for each particle is calculated as a function of the overlap distance.
6. The particles are moved a small amount in the direction of their resultant reaction forces.
7. Return to step 4.

As the models used in this section are composed of particles in a single layer, spread out in the film it is not necessary to check if they are ejected from or enter the film.

10.3.2 SURFACE TENSION FORCES

The surface tension force is calculated from the facets that have one edge attached to the particle at the TPC and the other two in the film as shown in Figure 10-4. Each facet has three edges (ff_{eei} where $i=1, 2$ or 3) and a normal with x, y and z components $ff.x$, $ff.y$, $ff.z$, which are used to calculate the component of force that it contributes.

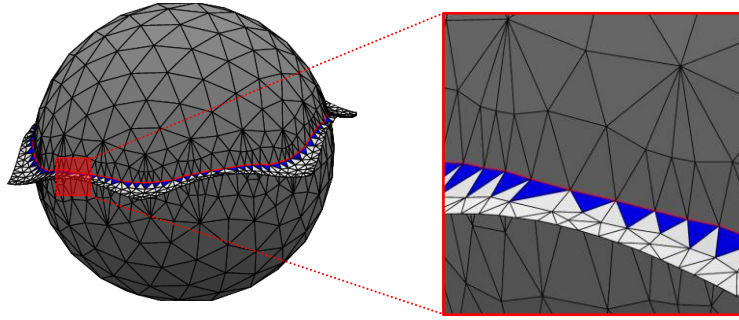


Figure 10-4 Particle surrounded by a TPC (red edges), highlighting the facet used to calculate the surface tension component of force (coloured blue).

The facet and TPC edge data is used to calculate the direction of the force, acting along the length of the TPC edge (in red, Figure 10-4), this is then multiplied by the facet tension (ff) to get the force and direction acting on the particle from that section of the TPC. This is repeated for all edges on the TPC and the forces summed to find the resultant force acting on the particle (equation 10-17).

$$\hat{F}_\gamma = \sum \hat{F}_{\gamma e} \quad 10-17$$

Where $\hat{F}_\gamma$ is the total force vector and $\hat{F}_{\gamma e}$ is the force vector for an individual edge on the TPC. $\hat{F}_{\gamma e}$ is calculated using equation (10-18).

$$\hat{F}_{\gamma e} = \left(\frac{\gamma_{LV} v_{i\gamma}}{\sqrt{ee_j^2 + ee_k^2}} + \frac{\gamma_{LV} v_{j\gamma}}{\sqrt{ee_i^2 + ee_k^2}} + \frac{\gamma_{LV} v_{k\gamma}}{\sqrt{ee_j^2 + ee_i^2}} \right) \quad 10-18$$

Where $\hat{v}_\gamma$ is the direction vector for the surface tension force calculated from the facet using equation (10-19);

$$\hat{v}_\gamma = \hat{n}_{ee} \times \hat{n}_{ff} \quad 10-19$$

Where $\hat{n}_{ee}$ is the normalised direction vector of the TPC edge ee and $\hat{n}_{ff}$ is the normalised direction vector of the facet ff (equations 10-20 and 10-21). The cross product of the two gives the direction of the plane of the facet normal to the TPC edge as shown in Figure 10-5.

$$\hat{n}_{ee} = \frac{ee_x}{ee_l} + \frac{ee_y}{ee_l} + \frac{ee_z}{ee_l} \quad 10-20$$

$$\hat{n}_{ff} = \frac{ff_x}{ff_{area}} + \frac{ff_y}{ff_{area}} + \frac{ff_z}{ff_{area}} \quad 10-21$$

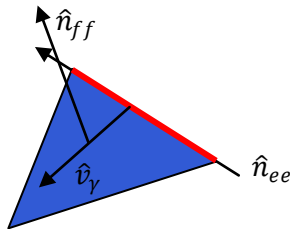


Figure 10-5 Vector used to find the direction of tension.

10.3.3 PRESSURE FORCES

Pressure forces are calculated by multiplying the facet normal in each direction with the pressure of the phase the facet is in using equations (10-22) and (10-23), where *phase* can be liquid or vapour. $\hat{n}_{ff}$ is the vector describing the facet normal, $\hat{F}_{ffphase}$ is the pressure force vector of a single facet and $\hat{F}_{phase}$ is the pressure force vector for either liquid or vapour phases.

$$\hat{F}_{ffphase} = \hat{n}_{ff} P_{phase} ff_{area} \quad 10-22$$

$$\hat{F}_{phase} = \sum \hat{F}_{ffphase} \quad 10-23$$

10.3.4 PARTICLE MOTION

The particle motion in 3D is calculated in the same manner as described for 2D in chapter 10. First the total force acting on each particle due to pressure and surface tension ($\hat{F}_{tot}$) is found using equation (10-24).

$$\hat{F}_{tot} = \hat{F}_L + \hat{F}_V + \hat{F}_\gamma \quad 10-24$$

The $\hat{F}_{tot}$ for each particle is stored in a matrix and the largest $F_{x, y \text{ or } z}$ is found and used to calculate K_I using equation (10-15). M_{max} is set equal to the minimum edge length used in the mesh ($0.05R^*_p$). If K_I is greater than $0.4K_{step}$ then it is set equal to $0.4K_{step}$ to ensure that there are at least 3 movement steps between each time section that is stored. Time is measured by adding K_I to K_{tot} during every step, the model an data is saved whenever K_{tot} reaches a multiple of K_{step} , if $K_I + K_{tot} > K_{out}$ where K_{out} is a multiple of K_{step} then $K_I = K_{out} - K_{tot}$.

Once K_I has been identified the motion for each particle is calculated using equation (10-25), where PP is the particle position, i is the particle identification number and j is the force or position in the x, y or z direction.

$$PP_{ij}^{t+K_1} = PP_{ij}^t + K_1 \hat{F}_{totij} \quad 10-25$$

10.3.5 PARTICLE INTERACTION FORCES

However, before the new particle positions are implemented there is a DEM step which is used to simulate particle interaction. Once the new particle positions have been calculated, the distance between all particles is found (S_{ij} , where n and m denote a particle each) (equation 10-26). If it is less than $2R^*_p$ the overlap distance and direction ($\hat{S}_{nm}$) is found (equation 10-27) and the reaction force between particle n and m ($\hat{F}_{PPnm}$) is calculated for that overlap (equations 10-28 and 10-29).

$$S_{nm} = \sqrt{(PP_{nx} - PP_{mx})^2 + (PP_{ny} - PP_{my})^2 + (PP_{nz} - PP_{mz})^2} \quad 10-26$$

$$\hat{S}_{nm} = \left(\frac{S_{nm} - 2R_p}{2} \right) \left(\left(\frac{(PP_{nx} - PP_{mx})}{S_{nm}} \right) i + \left(\frac{(PP_{ny} - PP_{my})}{S_{nm}} \right) j + \left(\frac{(PP_{nz} - PP_{mz})}{S_{nm}} \right) k \right) \quad 10-27$$

$$f_{overlap} = 10 + 10(2R_p - S_{nm}) \quad 10-28$$

$$\hat{F}_{PPnm} = \frac{\hat{S}_{nm}(|f_{overlap}| + f_{overlap}^2 + f_{overlap}^4)}{S_{nm}} \quad 10-29$$

Boundary conditions are also implemented at this stage, the particle positions are compared to the coordinates of the model boundaries. If the edge of the particle is outside of it a boundary force is calculated in the same way as that for particle interaction and added to the total force acting on the particle. The resultant reaction force acting on particle n ($\hat{F}_{res}$) is the sum of all $\hat{F}_{PPnm}$ acting on that particle (equation 10-30).

$$\hat{F}_{res} = \sum_{m=1}^m \hat{F}_{PPnm} \quad 10-30$$

The particle movement is calculated in the same way as for the film forces except that the movement between steps is smaller ($M_{max}=2.5 \times 10^{-3}R_p^*$) and K_{touch} (the time step coefficient for the resultant force) is never greater than $0.1R_p^*$. The DEM step is run continuously until none of the particles are overlapping each other. It is run at much smaller time intervals to ensure that when particles move apart the gap between them is as small as possible. The calculation of forces acting on the particles is also much quicker than the evolution of the film surface to its minimum energy so it is possible to run the DEM steps at much finer intervals with little loss in computing time.

10.4 DYNAMIC PARTICLES IN 2D FILMS

The dynamic 2D model described in section 10.2 has been used to investigate the behaviour of particles in a double layer in a thin film. Two separate aspects of particle behaviour were modelled; the reaction of a double layer to the perturbation of a single particle and the behaviour of a close packed double layer of particles when the film is expanded around them.

10.4.1 PARTICLE PERTURBATION

The initial model is set up with a regular double layer of 21 particles (Figure 10-6). The central particle is then displaced up or down by altering its S_p^* on either side. The particles in the rest of the model are moved apart or together by an equal amount to maintain the initial, regular spacing. The model is then run as described in chapter 10 for contact angles of 15° , 30° , 45° and 75° and the particle reactions observed.

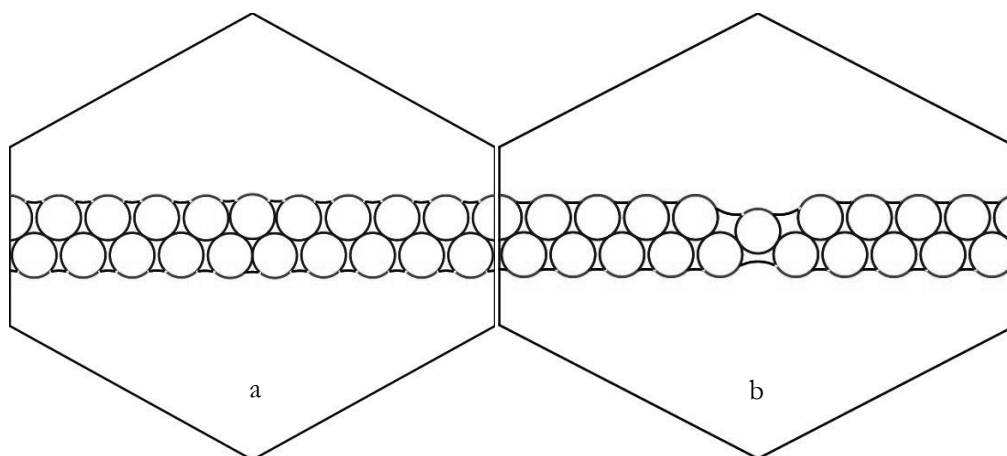


Figure 10-6. 2D model of 21 particles in a double layer $S^*=1.1$, central particle perturbed up (a) or down (b) by decreasing or increasing the separation of surrounding particles, $\theta=15^\circ$.

10.4.2 PARTICLE PERTURBATION

10.4.2.1 75° Contact angle

At high contact angles the film sits closer to the particles in the opposite layer for a given capillary pressure. This means that comparatively less particle motion is required before the films are bridged. However the initial particle separation is also a factor that must be taken into account. The closer the particles start together, the less room there is for rearrangement of the double layer structure for a given film area.

For particles with a contact angle of 75° in a double layer it was found that if the particle was perturbed down, towards the interface on the opposite side of the film it seeded the formation of a single layer of particles around it. This single layer expands, absorbing particles into it from the double layer, until the film is covered by a close packed array of particles. The further apart the initial spacing of particles in the double layer, the larger the proportion of single layer in the final film as shown in Figure 10-7.

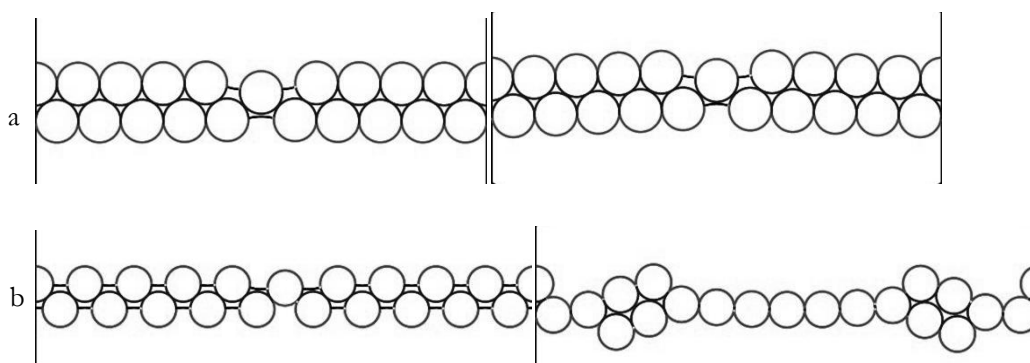


Figure 10-7 Particles with an initial perturbation down causing a single layer to form and spread, $\theta=75^\circ$, initial separation is 1.1 (a) and 1.4(b).

If however, the central particle is perturbed up it acts as a seed for a double layer of particles, which form in the centre of the film. If the particles begin close together ($S_p^*=1.2$) then three distinct regions of double layer form, separated by a single particle fault line. As the initial separation increases this fault line turns into a distinct single layer that again expands in size with initial separation distance (Figure 10-8).

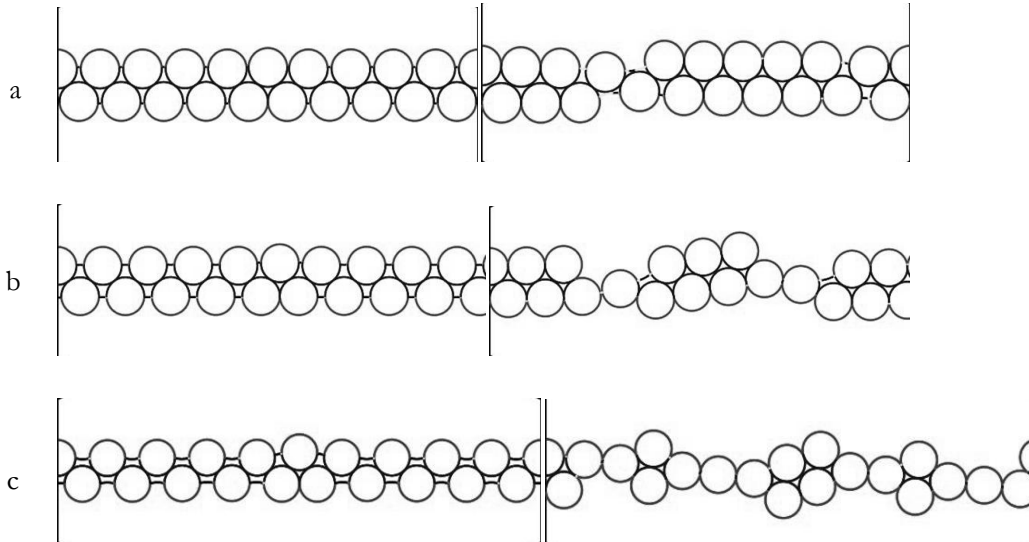


Figure 10-8 Particle perturbed up in the film acting as a seed for double layers, $\theta=75^\circ$, separations are 1.1 (a), 1.2 (b), 1.4 (c).

At large separation distances (Figure 10-8c) it can be seen that the double layers diminish into a series of small islands separated by single layers of particles, however the full packing of the film is maintained. The high contact angle used here results in particles bridging the film much more readily, when lower contact angles are used the trends are the same but the order of the particles remains more regular.

10.4.2.2 Contact angles of 15° , 30° and 45°

The trends seen for lower contact angles are the same as those seen for 75° , with particles perturbed down seeding single layers and particles perturbed up seeding double layers as shown in Figure 10-9, Figure 10-10 and Figure 10-11.

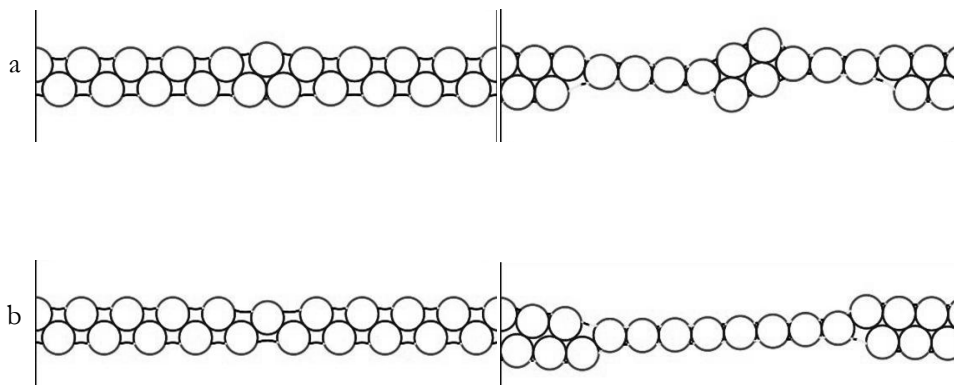


Figure 10-9 Contact angle of 45° initial separation of 1.4, central particle perturbed up (a) and down (b)

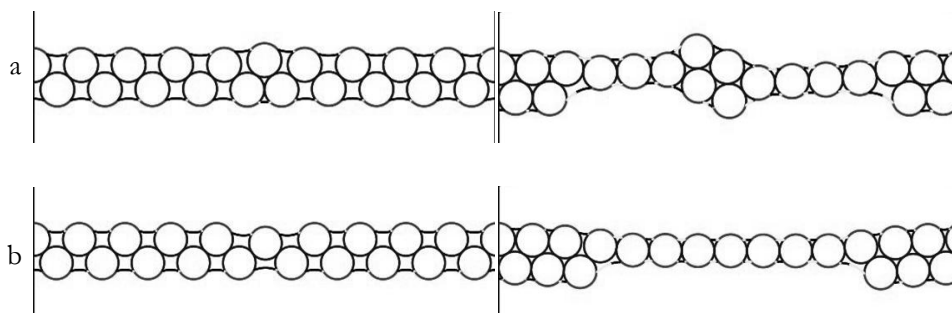


Figure 10-10 Contact angle of 30° initial separation of 1.4, central particle perturbed up (a) and down (b).

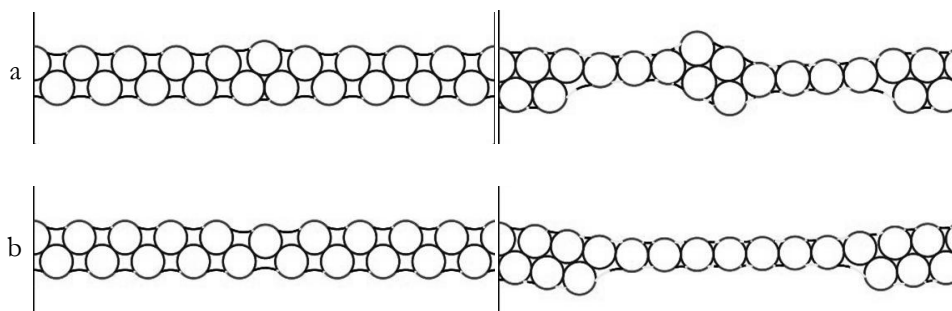


Figure 10-11 Contact angle of 15° initial separation of 1.4, central particle perturbed up (a) and down (b).

It should be noted that at a contact angle of 75° , when the central particle is perturbed up at large separations ($S^*=1.4$) the central clump of double layer is accompanied by two small double layers of 2 particles, one on each side. The other, lower contact angle models did not show this, however all the models used had relatively low numbers of particles (twenty one) and this may be a phenomenon observed at larger scales. It can also be seen in Figure 10-10b and Figure 10-11b that the presence of a single layer between two double layers creates a slight curvature on the film again a feature that may be a construct of the relatively small number of particles.

10.4.2.3 Effects of Initial Separation

For all contact angles the initial separation between particles in the same layer effects the final packing in 2D. For a lower separation distance there is less room for particles to compact into and so a smaller proportion of single layer will form as the film will quickly reach a point where the particles have jammed. As the initial separation increases it requires a larger number of particles to adopt a single layer formation to ensure that the film is fully loaded with particles and has minimised its liquid vapour interfacial area. This leads to a larger proportion of the final structure adopting a single layer formation.

10.4.3 PARTICLE SPREADING

The second model started with a close packed double layer and the film was expanded with each time step at a constant rate of $0.05K_l$. A contact angle of 45° was used in all cases.

The previous section showed that particle laden films in 2D tend towards a close packing arrangement, with particles in a loose double layer expanding into gaps as a tightly packed single layer until the film is completely covered by particles. If the film begins as a tightly packed double layer then disturbing a particle has little effect other than to thin the film where the particle has been disturbed. However, thin films often stretch over the course of their life time, increasing the area of film to be taken up by particles. If this occurs the particles in the double layer will spread out into a single layer to accommodate the increase in free film area as shown in Figure 10-12.

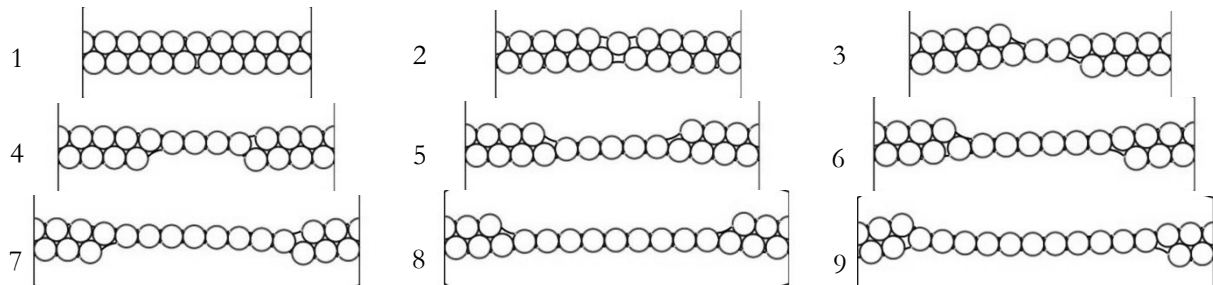


Figure 10-12 Expanding film containing a double layer of particles, $\theta=45^\circ$.

The central particle in frame 1 is perturbed down slightly and as the film is stretched this acts as the seed for the single layer to form. The particles on either side, remain in a tight packed double layer due to surface tension forces pulling them towards their closest neighbour, on the opposite side to the disturbed particle. As the film expands the central particle drops until it bridges the film below, it is followed by a particle to its right, then left. The particle leaving the double layer and entering the single layer alternate from right to left as the film continues to stretch. This will continue until there is no double layer left, at which point the particles will remain as a clump in the centre and free film will begin to expand from the edges of the agglomerate with an associated sudden drop in critical film stability as the film area increases.

10.4.4 SUMMARY

A 2D approach to modelling double layers of particles can be used to gain an insight into particle dynamics on thin films. Whilst a 2D approach cannot resolve certain aspects of the 3D system it allows a much simpler and faster approach to investigating the problem, from which valuable insights can be obtained. Particles in thin films generally move towards their closest neighbours, in a 2D model this can be seen to cause the formation of zones of double and single layers of particles which helps to maintain film stability. A tightly compacted double film forms and the empty area left by this is filled by a single layer of particles, again tightly compacted. As the film expands, the double layer acts as a store for particles, feeding them into the single layer maintaining a film completely covered by particles. Once the film becomes large enough that there are no double layers left the particles remain as a raft and an empty patch will form. This is analogous to the windows often seen forming on the top of bubbles in flotation froths.

10.5 DYNAMIC MODELS OF SINGLE LAYERS

10.5.1 INTRODUCTION

It was shown in section 4.6 that models of many particles in a thin film can be used to gain insight into their effect on film stability. It is also clear that the arrangement of the particles in the film has a profound effect on the film stability, be it regular or random, however particles found in flotation froths and other particle stabilised foam systems are often neither regularly packed nor randomly spaced. They are somewhere between the two, forming aggregated, fractal arrangements, as shown in Figure 10-13.

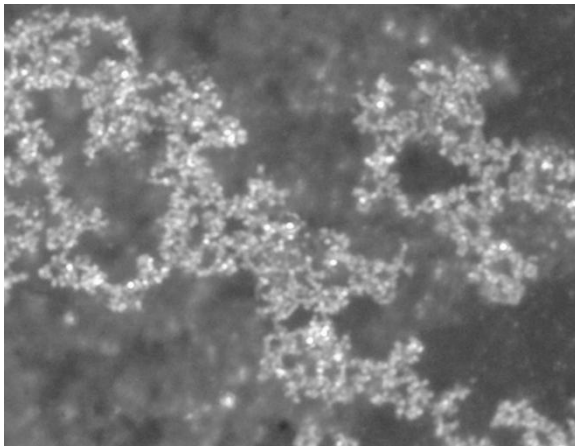


Figure 10-13 Particles attached to a thin film forming rafts.

These patterns form due to the unbalanced forces that arise from, among other things, the shape of the film surrounding the particles. The shape of the film interfaces are responsible for surface tension based forces on the particle whilst the liquid and vapour phases create a pressure force on the particle. These combine to produce the unbalanced forces on the particles in the film which cause the aggregation. By modelling these forces on the particles it is possible to create more accurate particle arrangements in films, which in turn will improve the accuracy of the film stability.

10.5.2 SMALL SCALE MOTION

Section 10.3 described how a *Surface Evolver* model containing particles in a film can be used to calculate the forces acting on that particle due to surface tension and liquid and vapour pressures. This approach has been applied to a small number of particles in a circular film of radius $5R_p^*$ to investigate their simulated behaviour and check it against theoretical models and observed behaviour. The models have been run with a P^* of 0.01 and the film boundary has been set to a thickness of R_p^* , which results in a film thickness of $0.76R_p^*$ in the absence of any particles. The combination of values have been chosen to create a film that is stable without the attached particles and with an outer boundary that is far enough from the particles that it will not interfere with their initial motion. Several initial models have been built with using the techniques described in section 3.6 except that a non-periodic model has been used and

the particle positions are user defined, not random. The particle motion is calculated as described in section 10.3.

10.5.2.1 Simple particle models (3-4 particles)

Several models were created, featuring three or four uniform spherical particles in simple geometric arrangements with uniform contact angles of 45° . The models were the run for 200 iterations and the particle behaviour observed. The initial models are shown in Figure 10-14.

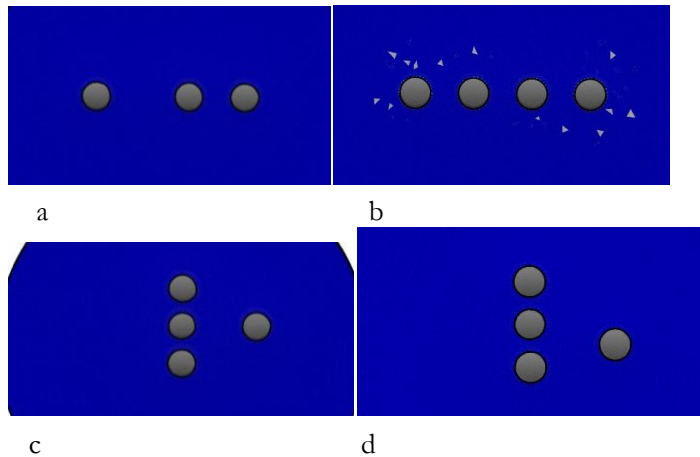


Figure 10-14 Initial particle models.

The simple models have been used to investigate the behaviour of particles in the film on a small scale. Figure 10-14 shows three particles in a line in the film along $x=0$ the y coordinates are 4, -1 and -4 from left to right. As the model is iterated, the two closest particles move towards each other much quicker than the one on the left moves towards them. Once they are in contact the two rightmost particles move towards the leftmost one, which has been moving towards them all the time. The sequence is shown in Figure 10-15a. The initial model in Figure 10-14b has four particles placed at equal distances from each other in the film at $x=0$ and $y=4.5, 1.5, -1.5, -4.5$. The particles initially form two dimers, with the central particles moving out towards the outer two. Once the dimers have formed they move back in towards each other, forming a chain of four particles. Once the chain has formed however the particles begin to slide over each other to form a close packed hexagonal arrangement of four particles.

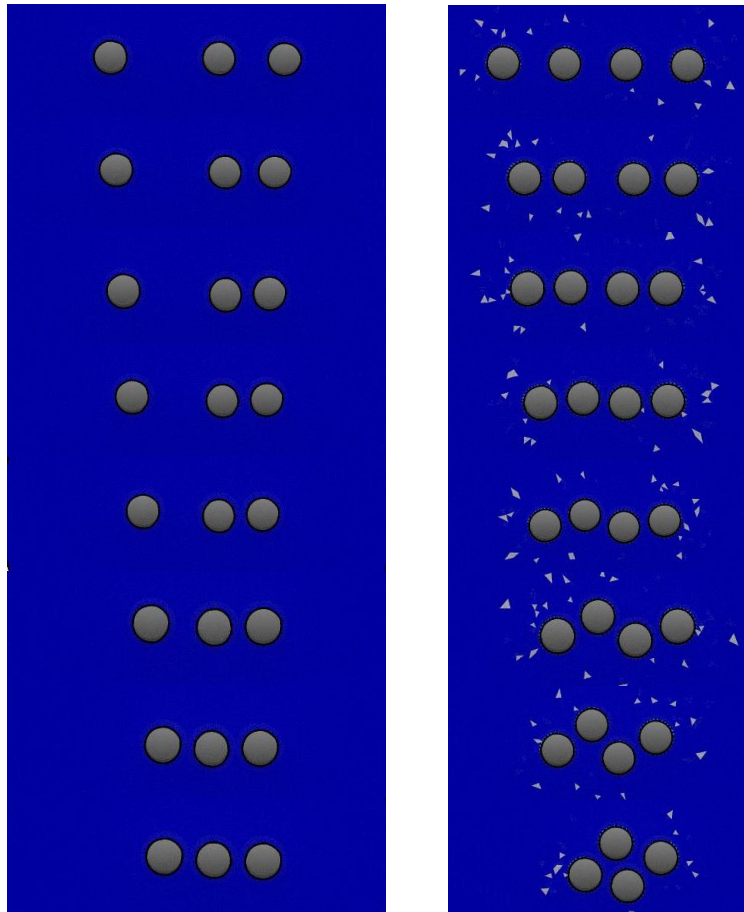


Figure 10-15 Showing particle agglomeration for initial models (a) and (b)

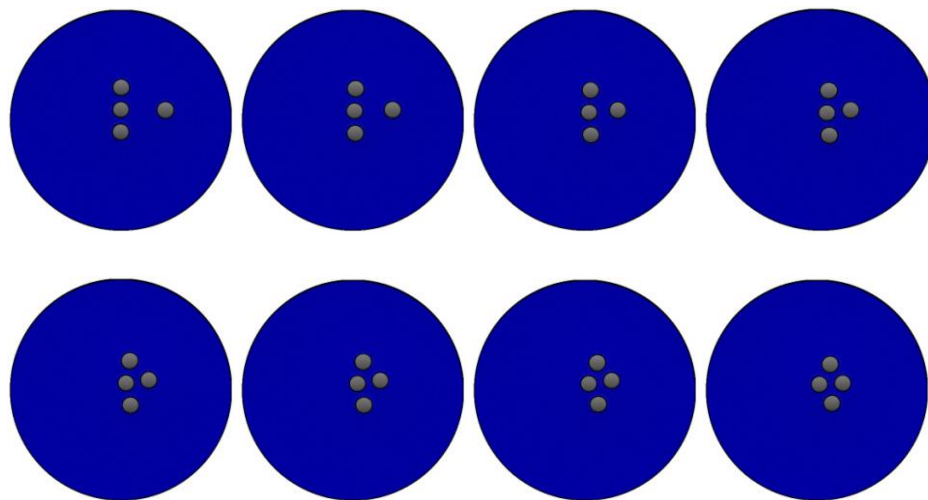


Figure 10-16 The evolution of the initial model found in (c).

Figure 10-16 shows the behaviour of the particles when three are initially touching, in a line centred at the origin with one particle further out, perpendicular to the line of particles. Initially the single particle moves towards the three in a line. As it draws closer the two particles at either end of the trimer begin to

fractionally curl in towards it however even when the lone particle meets the central particle in the trimer the three particles are still relatively straight. The initially lone particle now moves up towards one of the trimer, which curls in towards it much quicker than the one below. Eventually the end configuration is that of four particles in a hexagonally close packed arrangement, the same as in Figure 10-15b, but with a different orientation.

If, as in Figure 10-17, the initial particle is offset so that it is in line with the interstice between two particles the end result for the four particles is again the same, a close packed hexagonal arrangement, reached via a slightly different route to Figure 10-16 and Figure 10-15b. This time as the particle closes on the lower end of the trimer the lower particle swings up towards it much more noticeably than in Figure 10-16, to the point that the lone particle comes into contact with both the mid and lower particles at roughly the same time. The motion of uppermost particle in the trimer now accelerates and it curls down to form the close packed hexagonal arrangement.

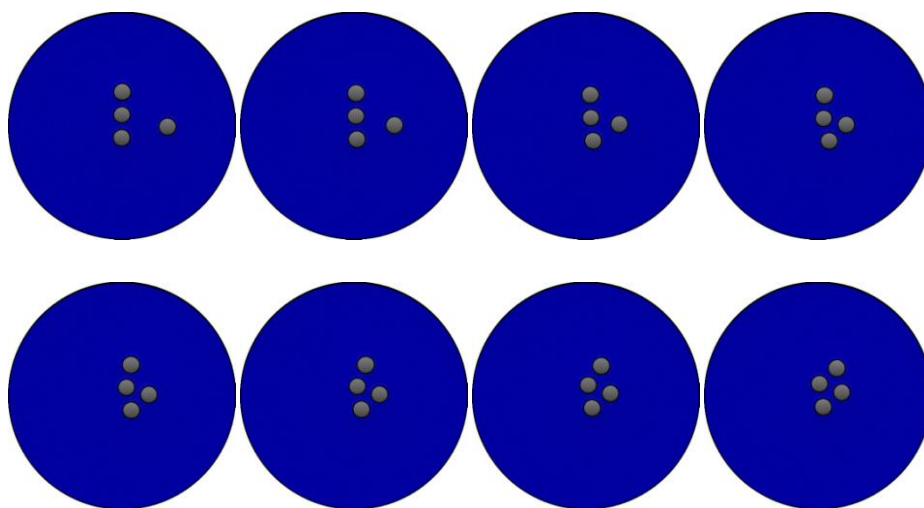


Figure 10-17 Evolution of four particle to a close packed hexagonal arrangement.

It has been seen in some way in all four cases shown that the particles move towards their closer neighbour in the film and the closer they are, the faster they move, however their motion is also affected by where their closest neighbours other neighbours are. The model shown with three particles in Figure 10-15a can be easily imagined in 2D as three particles in a line, the two particles that are closer have a more horizontal film between them at the given capillary pressure and therefore a stronger attractive force. This results in them moving towards each other to form a dimer. Once the dimer is formed the two particles can get no closer and act as a single entity. The film is less curved between the central particle and the far one than it is between the outer particle in the dimer and the model boundary so they are drawn together.

The four particles in the model in Figure 10-15b could be expected to move towards each other at the same rate as they are all initially equally spaced, however, the particles on the outer edges have a large

empty space of film next to them. This allows an increased curvature on their outer hemispheres which results in a lower surface tension pull in that direction which sums to a lower overall force in that direction. The position of the interface on the other side of the particle provides a stronger tug towards the particles in the centre and the outer particles move in slightly. Meanwhile the central particles have balanced forces on either side, leaving them stationary. Now the distance between the outer particles and their adjacent centre particle is slightly less than between the two central particles, unbalancing the forces and causing them to move out, forming the two dimers. Once the dimers are formed, they act as one and contract into the centre, however once in the centre, small, unbalance forces result in the particles sliding over each other to form the hexagonal close packed arrangement.

Therefore, on a small scale, like the 2D case, particles in a 3D film will generally move towards those closer to them before aggregating into close packed hexagonal arrangements.

10.5.2.2 Three particles equally spaced

In this model three particles have been placed at the corners of an equilateral triangle of edge length $3R_p^*$, centred around the origin. They have a contact angle of 45° and the model has been iterated at three different P^* of 0.01, 0.03 and 0.05. The initial model set up is shown in Figure 10-18.

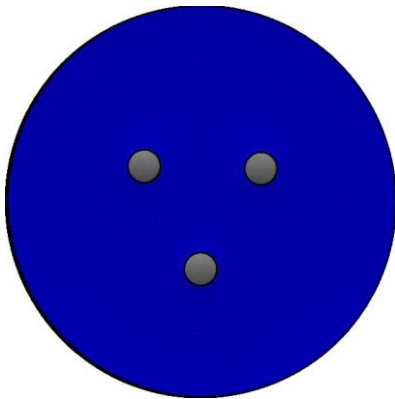


Figure 10-18 Initial model for three particle set out at the corners of an equilateral triangle of edge length $3R_p^*$ centred around the origin.

In all cases the particle move towards each other, meeting at the origin. The number of iterations this occurs at depends on the P^* of the model. At higher capillary pressures the film has a higher curvature which causes a higher force to act on the particles as shown in Figure 10-19, Figure 10-20 and Figure 10-21. The magnitude of the non-dimensional force acting on the particles is plotted against their distance from the origin as a measure of the particle-particle separation.

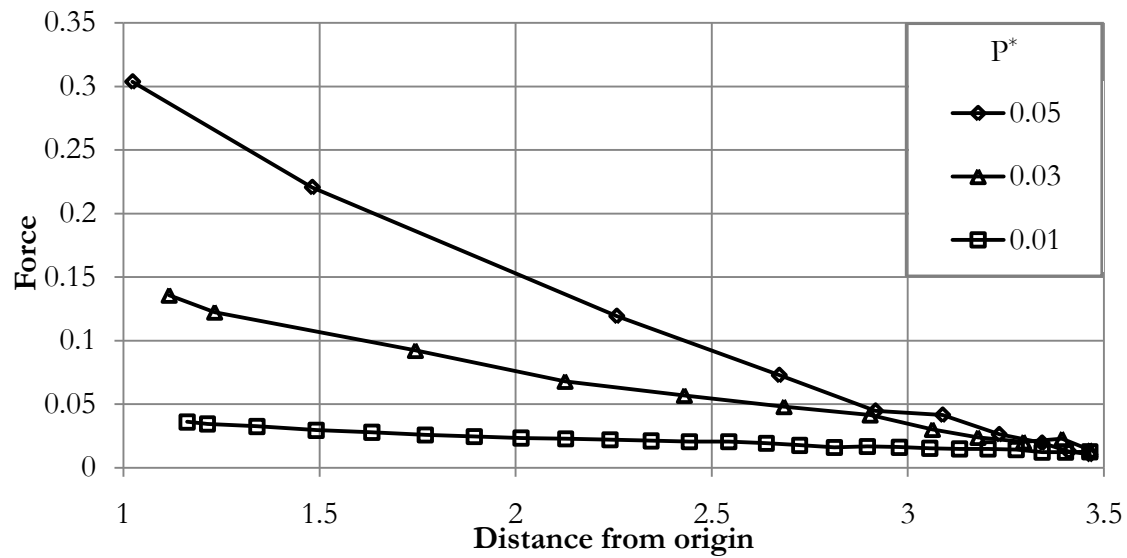


Figure 10-19 Non-dimensional force as a function of distance from the origin for particle 1 for capillary pressures of 0.05, 0.03 and 0.01.

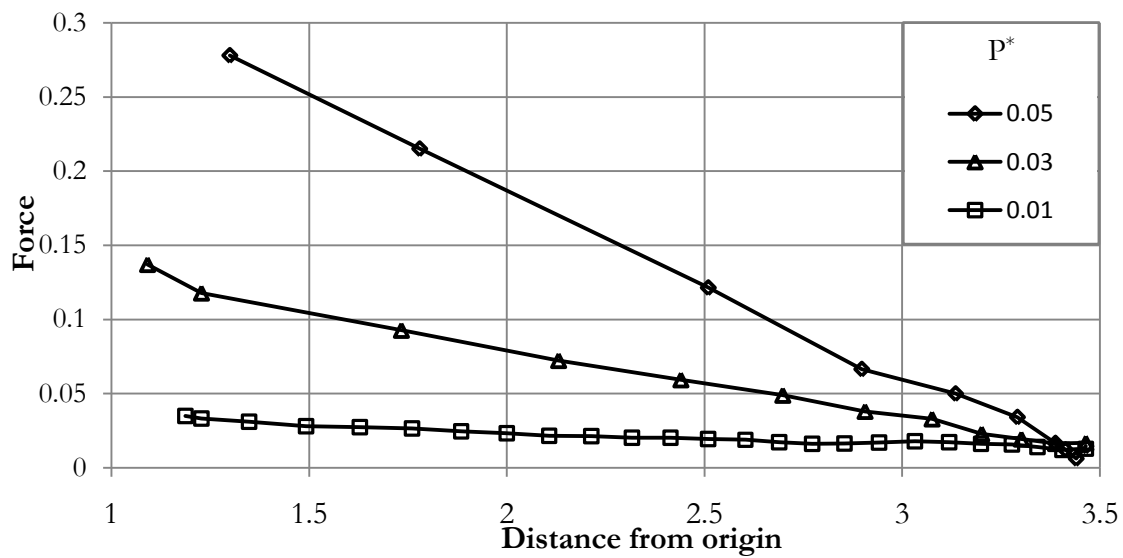


Figure 10-20 Non-dimensional force as a function of distance from the origin for particle 2 for capillary pressures of 0.05, 0.03 and 0.01.

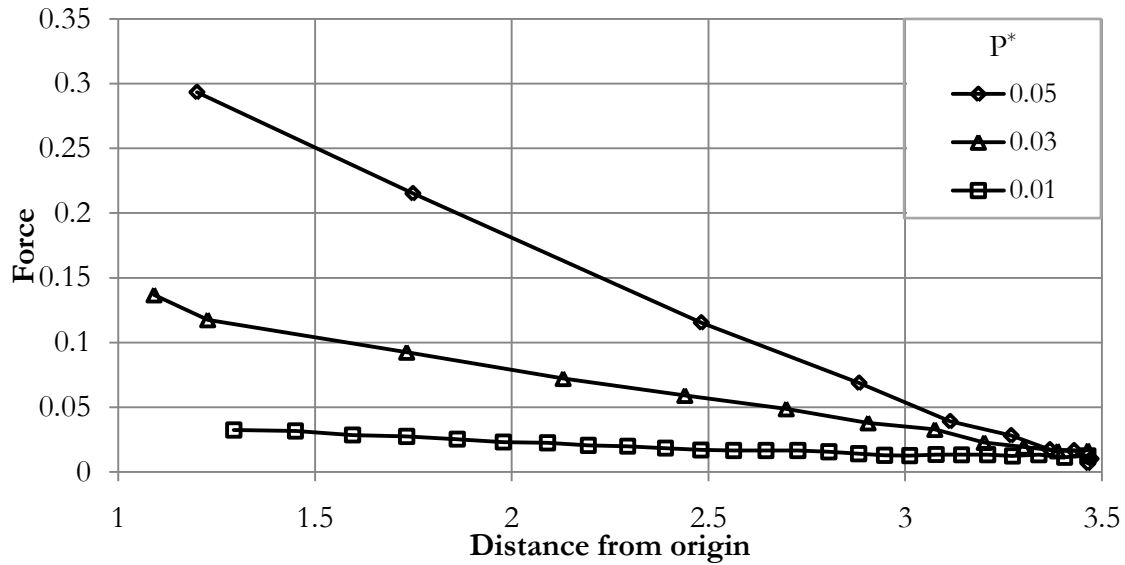


Figure 10-21 Non-dimensional force as a function of distance from the origin for particle 2 for capillary pressures of 0.05, 0.03 and 0.01.

All the forces acting on the particle begin at similar magnitudes of force, around 0.013. However as the particles move towards each other the force acting on them increases with capillary pressure. Just before the particles touch the magnitude of the force acting on them at $P^*=0.01$ is 12 % of the force acting on them at $P^*=0.05$ whilst at $P^*=0.03$ it is 45 % of the force at $P^*=0.05$. This fits qualitatively with results from the 2D analytical model from Ali *et al.* (2000) which shows the non-dimensional force to increase with capillary pressure and decrease with particle separation distance.

10.5.2.3 Medium scale models (10 particles)

The models presented in the previous section all had the particles placed in user defined positions, but the approach for randomly placing particles in the film as described in section 3.6 and used in section 4.6 can also be used here, in a non-periodic boundary. Monodisperse, spherical particles of uniform surface property are placed in random positions in a film with a circular boundary of $20R_{part}^*$. The boundary is also constrained to a film thickness of R_p^* . The model is the run at $P^*=0.01$ to find the particle behaviour when the contact angle is 15° , 30° , 45° and 60° , the initial particle positions are shown in Figure 10-22.

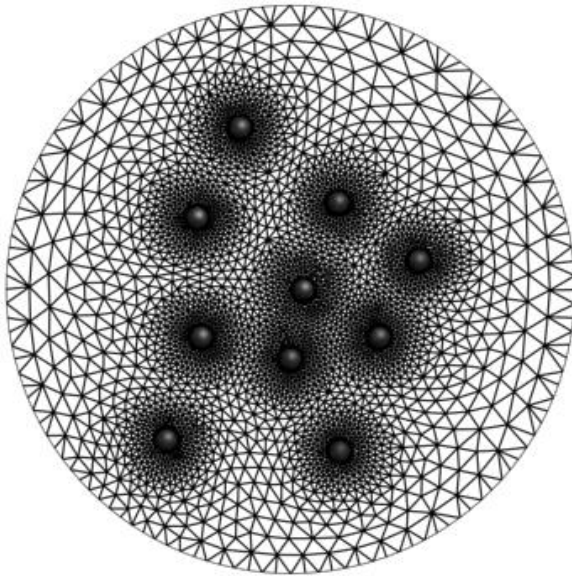


Figure 10-22 Initial positions of particles before iteration, film radius is $20R^*_p$, all particles in any one model are given the same θ .

When the models are iterated, the particle motion changes with contact angle and the final arrangements of the particles in the film are different.

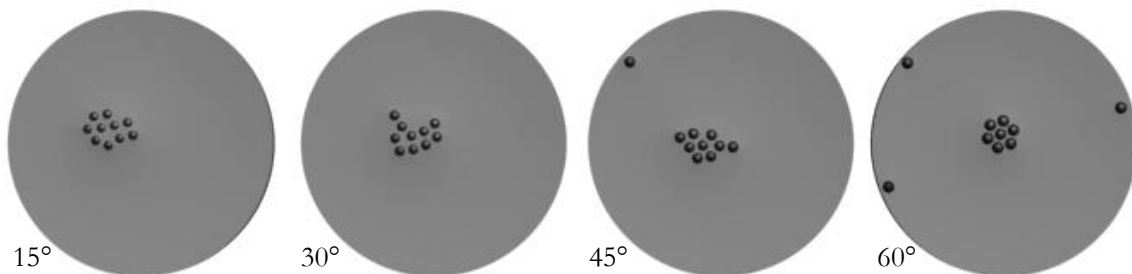


Figure 10-23 Packing of particles at different contact angles after 73 time steps.

It can be seen in Figure 10-23 that the particles end up in very different arrangements based on contact angle. The low contact angles (15° and 30°) both result in particles packed in the central part of the film in one cluster, although the configurations of the cluster are different. At $\theta=45^\circ$ one of the particles is at the edge of the film and at $\theta=60^\circ$ three particles move to the film boundary. In this simple, 10 particle case, contact angle clearly has a marked effect on the behaviour of the particles and the arrangements they form in the film.

The models shown are on the 73rd time step as defined in section 10.3 as in the 74th time step at $P^*=0.01$ the film containing particles at $\theta=15^\circ$ fails when the opposite sides touch. This is unexpected, all previous data has shown that the lower the contact angle the more stable the film. However, previous data has only been compared for different θ applied to the same particle packing arrangements. Figure

10-23 shows that different contact angles result in different particle behaviour producing different packing arrangements. Difference in packing arrangement has also been shown to heavily affect the film P^*_{crit} . However, if the other models are iterated further, the next one to fail is at $\theta=60^\circ$ at a time step of 75, followed by $\theta=45^\circ$ at 91 and $\theta=30^\circ$ at 99 which conform with expectations from previous results that a higher θ will result in a less stable film.

The particle arrangement in the film was discussed in chapter 4 and it was shown that the more evenly spaced the particles, the greater the P^*_{crit} . Particles with a lower contact angle stabilise the film more effectively in part because the low value of θ causes the TPC to sit higher on the side of the particle, which slows the film thinning. This also means that the film will be closer to the horizontal at the TPC, which will result in a larger force from surface tension acting on the particle. A larger force acting on the particle will cause the particle to move faster in the film, agglomerating more quickly, as can be seen in Figure 10-24.

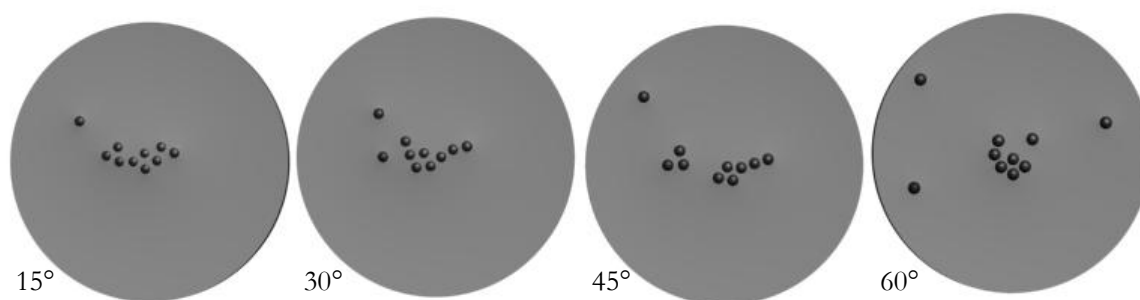


Figure 10-24 Packing of particles at different contact angles after 50 time steps.

The models with lower contact angles are much closer together at a time step of 50 than the models with particles at higher contact angles. Larger areas of free film space form faster in the models with lower contact angles, which reduces film stability leading to the failure of the 15° model. It should be noted however that these models represent films that are very lightly loaded, they have an $\mathcal{A}^*_{pp}$ of 122.5, films with more particles in them may behave differently.

10.6 SUMMARY

At present the results are of a qualitative nature as multiple particle motion in 2 and 3D is a complex problem, however the models have been able to offer insight into the basic behaviour of particles in films. In 2D the simulation of a double layer has shown that whilst a spread out double layer is quasi stable, as soon as a disturbance is introduced the particles zip up. As the particles move together to form a close packed double layer extra space is created which is filled by a single layer of particles. As a film is only as stable as its weakest point (the single layer) the double layer adds no stability unless it covers the entire

film in a close packed arrangement. A slight gap between particles will see them move into it, with the creation of a single layer left in their wake.

It was also observed that a film is completely covered with close packed double and single layers will maintain close packing for as long as possible when it expands. As film area increases the double layers of particles unzip to form close packed single layers, taking up more space as they do, maintaining close packing and film stability. Therefore a film containing both double and single layers can expand and maintain the stability offered by a close packed single layer of particles as the extra particles in the double layer unzip to fill the space created by the expanding film.

The 3D dynamic model has been used to simulate single layers of particles and the results have shown particle behaviour which would be expected. Small scale (2-4 Particles) models of three particles show forces changing with capillary pressure and particles aggregating into close packed hexagonal arrangements.

At larger scales (10 particles) the simulations have highlighted how contact angle can affect the behaviour of the particles. The same initial model, run several times with different contact angles but the same initial particle positions results in different final positions. As the particle positions in a film as well as the contact angle affect the film stability this is an important consideration.

11 APPENDIX B

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The effect of particle hydrophobicity, separation distance and packing patterns on the stability of a thin film

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ABSTRACT

Hydrophobic particles attached to bubble films in foams can increase the capillary pressure required to cause coalescence or bursting. Previous studies have considered the effects of changing particle spacing and contact angle in 2 dimensions (2D), but there are limitations to this approach; in 2D when the separation distance is zero and the particles are touching, the critical capillary pressure tends to infinity as there is no exposed film. In 3 dimensions (3D) spherical packing ensures that there are always exposed sections of film between particles even when they are close packed. Using Surface Evolver, the effects of contact angle and particle separation on the stability of a particle laden film were investigated in 2D and 3D. The 2D model was compared and validated with an analytical approach developed by Ali et al. [Ind. Eng. Chem. Res. 39 (2000) 2742–2745] and a 3D model was used to investigate the critical capillary pressures of square and hexagonal packing of monodisperse particles. It was found that when the stability of the film was compared with the area of film per particle both packing patterns have the same stability.

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1. Introduction

Particle stabilised foams are found in many industrial processes, however the physical processes through which the particles stabilise the foams are not well understood. These systems are difficult both to examine in real life and to model but through better understanding of the mechanisms which affect foam stability the many industrial processes reliant on particle laden foams and films may be improved. One such industrial process is froth flotation which uses air bubbled through an ore slurry to concentrate valuable minerals. Chemicals added to the slurry render the surfaces of the valuable mineral particles hydrophobic. The hydrophobic particles attach to the surface of the bubbles as they rise through the slurry and form a concentrated mineralised froth when they reach the surface. This concentrate is then collected and processed. Every time a laden bubble on the surface of the froth bursts, the particles attached to it enter the network of channels running along the edges of films called Plateau borders and move freely. This reduces the efficiency and selectivity of the process. Similarly if a film separating two bubbles within the froth ruptures causing coalescence, the particles attached to the ruptured film will also be lost to the Plateau borders. The causes of coalescence and bursting within the froth are complex and difficult to predict but the fact that attached particles affect the stability of froths, foams and emulsions has

been known for a long time, see the work of Aveyard et al. [2]. Understanding how the hydrophobicity of the particles affects the film stability will allow more efficient operation of flotation cells and therefore it is appropriate to examine this further.

In flotation, hydrophobicity is often characterised in terms of contact angle. In this case contact angle is defined as the angle made between the surface of the particle and the film at the three phase boundary made where the film meets the particle. It is shown in Fig. 1 as θ . The contact angles of particles found in flotation froths usually lie within the range of 0–90° with low hydrophobicity being around 0–30°, intermediate 30–70° and high over 70°. In a detailed study, Aveyard et al. [3] found that particles of varying hydrophobicity can either stabilise or destabilise a foam, with a rapid increase in foam collapse once the contact

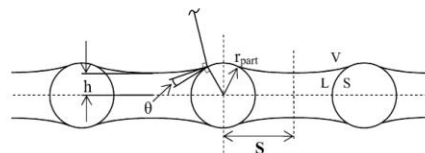


Fig. 1. Showing a 2D particle laden film. Particles are bridging both sides of the film. The key parameters for the model are the separation distance S , the film thickness at its lowest point h , the particle radius r_{part} , and the contact angle of the particles θ . The 3 phases are also annotated with the vapour phase corresponding to V, the liquid phase L and the solid particle S.

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angle of the particles is above 90° . Garrett [4] also found that particles with a low contact angle ($\theta < 90^\circ$) promoted foam stability. Johansson and Pugh [5] found that with small quartz particles (26–44 μm) the stability of the froth was maximised at an intermediate degree of hydrophobicity (contact angle of roughly 65°). It was also reported that the presence of particles with a lower hydrophobicity (smaller contact angle) did not have a noticeable effect on the froth properties. Particles of greater hydrophobicity ($\theta > 90^\circ$) were found to penetrate the film to a greater extent causing film failure. It was also found that the higher the concentration and smaller the particles, the greater the stability of the foam. Larger particles (74–106 μm) were found to have a less pronounced effect on the foam stability, showing that both the hydrophobicity and the particle size are important. Schwarz and Grano [6] also found that quartz particles with a contact angle of around 63° produced the most stable froth and Hunter et al. [7] reported that foam and film stability varies with particle hydrophobicity.

The shape of the particle also has a pronounced effect on its ability to rupture a film. Dippenaar [8] showed that galena particles with a contact angle of less than 90° will rupture films and therefore destabilise a froth if they have a shape that forces the two three phase boundaries to the same point on a wetted particle. This effect was observed using crushed galena particles.

The interaction of particle size, shape and hydrophobicity can have significant effects on the flotation process, but due to the complexity of the system it is difficult to uniquely predict how these properties will affect froth stability experimentally. To successfully investigate properties of particle laden bubbles and foams theoretically, the problem must be simplified. Ali et al. [1] successfully studied the problem of particle stabilised bubbles by treating the particles as being 2 dimensional (2D). Spherical particles were replaced with cylindrical rods of infinite length which stabilised the film between two particle laden bubbles. The particles bridged both sides of the film and were laid out as shown in Fig. 1, it was assumed that when the film between any two particles thinned to zero thickness ($h = 0$) and the opposite sides touched, the film would rupture. Ali et al. [1] found that as the distance between adjacent particles decreased, the capillary pressure required to rupture the film increased.

The capillary pressure and geometry are linked via the Young–Laplace law. The geometry of the system determines the curvature of the film linking the particles which is then related to the capillary pressure of the liquid using surface tension and the Young–Laplace law, equation

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right). \quad (1)$$

Here Δp is the difference in pressure between the liquid and vapour, γ is surface tension of the interface, R_1 is the radius of the arc of the curvature of the surface in one direction and R_2 is the radius in the other, perpendicular direction. For 2D cases $R_2 = \infty$ and the $1/R_2$ term becomes zero. However a 2D model has limitations: when the rods touch (i.e. the separation distance is zero) there is no exposed film between them and the capillary pressure required to rupture the film increases to infinity. In 3 dimensions (3D) even when the particles are close packed there is still exposed film surface in the interstices between any three adjacent particles.

In addition to the model of Ali et al. several other models of particles in films are reported in the literature. Denkov et al. [9] developed an axi-symmetric model of a spherical particle in three dimensions bounded by a circular cell. The total area of film in the circular cell was equal to the average area of film per particle in a packed film. In the Denkov model the area of film that remains when the particles are touching is taken into account and the minimum possible separation distance is adjusted accordingly.

However, due to the circular boundary of the unit cell the shape of the film at the minimum separation distance does not accurately represent that of a film between hexagonally packed spherical particles at minimum separation distance. Kaptay [10] also investigated the effect of attached particles stabilising a film and showed that if two layers of particles are attached to opposite sides of the film they can stabilise it at contact angles above 90° .

To investigate the effects of particle packing and irregular film shape on the critical pressure in 3D several models were developed using the Surface Evolver [11] program. Surface Evolver [11] is a modelling package that minimizes the energy of a user defined surface subject to various constraints. It can be used to generate and analyse models of surface tension based systems and as such is well suited to simulating problems in films and foams. Using Surface Evolver [11] the problem of a spherical particle stabilising a thin film can be simulated in 2D and 3D. This paper will first verify a 2D surface tension based model against the analytical approach of Ali et al. [1], comparing the critical capillary pressure required to rupture a film at a given contact angle. In this 2D model either film surface can be represented by a (1D) curve but as they are symmetrical only one side of the film is simulated and although a 1D curve its position is expressed in 2D coordinates. The model is then expanded into a 3D coordinate system to investigate the effect of square and hexagonal particle packing configurations on the film shape and stability. The particles simulated are monodisperse and spherical with uniform hydrophobicity over their surface. As with the 2D system only one side of the film is simulated as they are symmetrical. When considering particle packing configurations and their effect on film stability and shape the coordinates defining the locations of the film surface need to be expressed in 3D in order to describe the curvature of the 2D film. The system being simulated is therefore referred to as a 3D one, even though the film itself is 2D.

2. Approach

Surface Evolver [11] was used to create 2D and 3D surface tension based models of a single, spherical particle in a thin film. Similar to the approach of Ali et al. [1], it was assumed that the particles bridged both sides of the film and particles were assumed to have a contact angle of less than 90° . At contact angles above 90° the opposite sides of the film must overlap each other to reach a stable three point contact. As the film failure criteria has been defined as when opposite sides of the film touch, a film on a particle with a contact angle above 90° will fail immediately. It should be noted that this is only for single particles bridging both sides of the film. If there are two or more layers of particles they can stabilise a film above a contact angle of 90° , as demonstrated by Kaptay [10].

A thin film loaded with spherical particles that bridge both sides of the film is shown in Fig. 1. It was assumed that the particles spread evenly across the film in 2D and the separation distance S is defined as the distance between the centre of a particle to the midpoint of the film. At any separation distance, when the film thins to a critical thickness, the opposite sides touch and it will fail. The assumption of evenly spaced particles is used as a basis for the purpose of simulation, however in reality the particles will draw together to form rafts (Ali et al. [1]). If a repulsive force between particles were present for example if the particles were charged, there would be the possibility for evenly spaced particles but this is beyond the scope of this paper.

Assuming a regular packing pattern, the film will fail at a point on the exposed film's surface central to the surrounding particles. However, its exact location will depend on the particle packing arrangement. Two 3D packing patterns will be investigated in this paper, square packing and hexagonal packing.

The key parameters for the model in 2D, after applying symmetry to reduce complexity, are shown in Fig. 1. They are the separation distance S , the film thickness at its lowest point h , the particle radius r_{part} , and the contact angle of the particles θ . The 3 phases are also annotated with the vapour phase corresponding to V, the liquid phase L and the solid particle S.

The 2D model developed in Surface Evolver used the string model to represent the particle in a film. The hydrophobicity of the particle was set by altering the surface tension of the dry surface of the particle (surface bounded by phases V and S, surface tension referred to as γ_{SV}) in accordance with Young's equation,

$$\gamma_{\text{SL}} + \gamma_{\text{LV}} \cos \theta = \gamma_{\text{SV}}. \quad (2)$$

The energy of a surface that is minimised in Surface Evolver is made up of the sum of its component energies; one of these is the energy per unit area which can also be regarded as surface tension. The default value for surface tension in the model is 1, as the total surface area of solid is fixed, only the difference between γ_{SV} and γ_{SL} affects the energy minimisation process. To minimise the variables γ_{SL} is kept constant and set to 0. All interfacial surface tensions are then non-dimensionalised by γ_{LV} which has the effect setting γ_{SV} to $\cos \theta$, γ_{SL} to 0 and γ_{LV} to 1. Young's equation (2) is satisfied and γ_{SV} can be changed with θ , altering the hydrophobicity of the particle for each simulation. γ_{SL} was kept constant at 0 throughout the simulations for simplicity. A cell boundary was defined to allow the capillary pressure within the film to be set. The capillary pressure of a film in a foam is caused by the adjacent Plateau borders drawing liquid out of the film as the foam drains, if the surfaces of the film are curved into a concave shape then owing to the Laplace pressure the pressure in the film will be lower than that in the surrounding vapour. This then tends to counteract the capillary pressure trying to suck water out of the film. With the correct curvature of each film surface the pressures will be matched and an equilibrium film can be sustained. It should also be noted that in 2D the shape of the film is the arc of a circle whilst in 3D it is a surface of uniform mean free curvature.

The presence of disjoining and conjoining forces acting on the film can also affect its stability but in this case have been neglected. As there is little surfactant found in a flotation froth (of the order of 20–100 g/t ore) and it is assumed the model is quasi static so viscosity can be ignored, disjoining forces have been discounted. Conjoining forces have also been discounted as Van der Waals forces are typically only of a similar magnitude to the surface tension forces in this system when the films are tens of nm thick (Tcholakova et al. [12]). This is a very small consideration when the system being modelled is many orders of magnitude larger (the particles found in a flotation froth are typically between 10 and 100 μm). It should be noted that as conjoining forces act over a slightly larger scale than disjoining forces a film will fail slightly more easily than this model predicts. The effect of particle distribution is the focus of this paper and although disjoining pressure forces will have an effect on film rupture it is at a scale much smaller than the particle diameter and initial thinning of the film which is being investigated.

The effect of gravity on the model has also been ignored. The Bond number, Eq. (3) describes the balance between the effects of gravity and surface tension and must be much less than 1 to be able to discount gravity:

$$\text{Bo} = \frac{\rho d^2 g}{\gamma}. \quad (3)$$

The length scale d is the diameter of a particle, ρ is the difference in density of the two mediums, in this case a flotation particle and water (about 2000 kg/m^3), g is gravitational acceleration and γ is the surface tension of water (about 0.07 N/m). For a large flotation particle (100 μm in diameter) it is of the order of 0.003 and for a

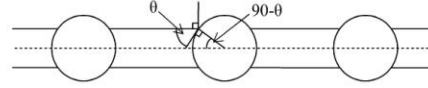


Fig. 2. Showing the shape of the film when the pressure is equal in the liquid and the vapour phases.

more typical particle size (30 μm) it is 2.6×10^{-4} . At the higher end of the scale gravity does begin to play a role in the particle–film interaction but as most flotation particles are around 30 μm it is safe to ignore the effects of gravity in this model.

In this paper, all linear parameters have been non-dimensionalised using the particle radius and all force parameters have been non-dimensionalised using the surface tension of the film as shown in Eqs. (4) and (5):

$$L^* = \frac{L}{r_{\text{part}}}, \quad (4)$$

$$P^* = \frac{P \times r_{\text{part}}}{\gamma_{\text{LV}}}, \quad (5)$$

where L is length, r_{part} is the particle radius, P is pressure and γ_{LV} is surface tension of the liquid/vapour interface.

The following procedure was used to find the critical pressure at which a film would fail for a given θ and S : beginning at a capillary pressure of zero the surface was evolved to a minimum energy and the film checked to find h . While h was greater than zero the film was taken to be stable. At a capillary pressure of zero the film is uniformly thick and attaches to the particle at a co-latitude equal to the contact angle as shown in Fig. 2. As the capillary pressure is increased the film surface's curvature increases, the film becomes thinner and its point of attachment to the particle moves closer to the equator. If the film had not ruptured the pressure was increased by a small amount P_{step}^* . The surface was re-evolved to its new minimum and the film was checked again. This procedure was continued until h reached zero, when the film fails. The pressure at which this occurred was taken as the critical pressure, P_{crit}^* , for that combination of separation distance and contact angle. P_{crit}^* is the minimum capillary pressure required to overcome the Laplace pressure exerted by the film surface in order to cause the film to thin and rupture and is calculated from Eq. (5). By repeating this approach, a set of results for varying contact angles and particle separations were collected which could then be compared to the analytical results of Ali et al. [1]. It should be noted that as the separation distance is taken from the centre of the particle, the minimum S^* will be $S^* = 1$, corresponding to the case when two particles are touching, $S_{\text{min}}^* = S_{\text{min}}/r_{\text{part}} = r_{\text{part}}/r_{\text{part}} = 1$.

The 2D model was expanded to 3D to investigate the effect of particle packing configurations on P_{crit}^* . The initial 3D model was set up to simulate hexagonal packing of spherical particles with a varying separation distance, as shown in Fig. 3a. The symmetry of hexagonally packed particles allowed the model to be simplified to one particle with a hexagonal boundary which tessellates to form a particle laden film represented by the solid hexagonal boundary shown in Fig. 3a. The symmetry condition used for the film is that it must be perpendicular to the boundary of the periodic cell wherever it meets it. The surface tensions γ_{VS} , γ_{SL} and γ_{LV} , for the 3D model are the same as for the 2D model. The pressure checking algorithm was modified for the 3D model to find h for a film surface instead of a 2D line, before increasing the pressure by a step.

In 3D the packing arrangement of the spherical particles can be compared. A hexagonally packed configuration is the densest possible distribution for a layer of spherical particles of equal size and when they are touching it produces the smallest possible area of exposed film. However, due to the hexagonal shape of the cell, the

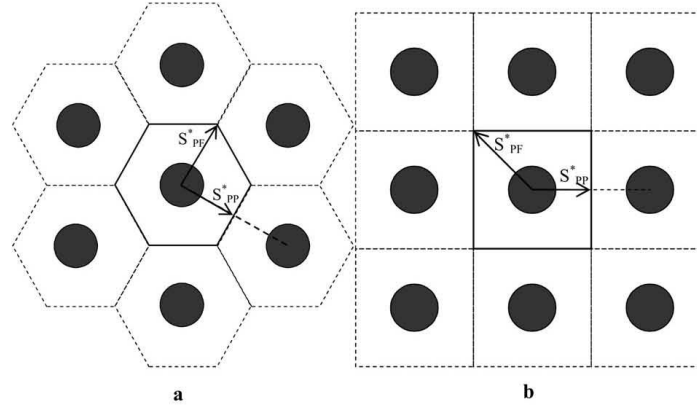


Fig. 3. Showing the separation distances and film boundaries for hexagonal (a) and square (b) packing. S_{PF}^* is half the distance between the centre of two adjacent particles. S_{PP}^* is distance from the centre of a particle to the midpoint of the film. The midpoint of the film is the point farthest from any surrounding particles.

boundary is not a uniform distance from the centre of the particle. As such there are two possible measures of particle separation, shown in Fig. 3a as S_{PF}^* and S_{PP}^* . The use of two different definitions of separation distance affects the relative trends obtained and both will be used. S_{PF}^* is the distance from the centre of the particle to the point in the film farthest from any adjacent particle and S_{PP}^* is half the distance from the centre of the particle to the centre of any adjacent particle. When the film fails it is at the lowest point and for identical particle laden films this will always be at the point farthest from any of the particles, i.e. the point corresponding to the maximum separation distance S_{PF}^* . The relationship between S_{PF}^* and S_{PP}^* varies with packing pattern, for hexagonally packed particles $S_{PF}^* = S_{PP}^* / \cos 30^\circ = 1.15 S_{PP}^*$, and for a square packed configuration $S_{PF}^* = S_{PP}^* / \cos 45^\circ = 1.41 S_{PP}^*$. Thus for a given S_{PP}^* a square packing configuration will have a larger S_{PF}^* . As both S_{PF}^* and S_{PP}^* are taken from the centre of the particle, the minimum separation distance allowed in the model is $S_{PP}^* = 1$ which represents the surface of the particle. After non-dimensionalisation the only free parameters in the model are non-dimensional separation distance S^* and non-dimensional contact angle θ . Therefore particle radius cannot be altered in the model. The pressure at which the film thickness h became zero was taken as the critical pressure P_{crit}^* . A square packing model was also set up using a similar approach as that to the hexagonal model with the boundary defined as shown in Fig. 3b. The effects of separation distance and particle hydrophobicity on P_{crit}^* were then simulated and compared.

3. Results and discussion

Fig. 4 compares the results of the 2D surface tension model at a contact angle of 0° with those obtained using the analytical approach developed by Ali et al. The analytical solution is shown in equation:

$$P_c = \frac{\gamma}{R_p} \left(\frac{R_L}{R_p} \right)^{-1}, \quad (6)$$

where P_c is the capillary pressure, γ the surface tension, R_p the radius of the particle and R_L is the radius of curvature of the film. The formula linking R_L , R_p is given in equation:

$$(R_L + h)^2 + a^2 = R_p^2 + R_L^2 + 2R_p R_L \cos \theta, \quad (7)$$

where h is film thickness, a is separation distance (defined as the distance from the centre of a particle to the midpoint of the film)

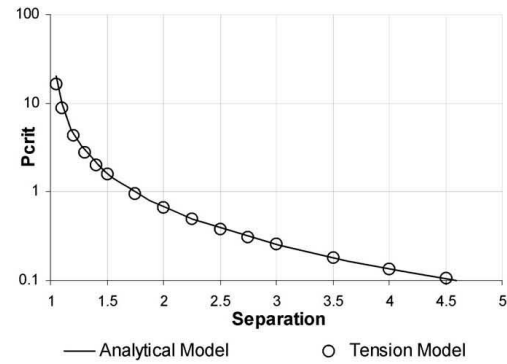


Fig. 4. Comparison of analytical and simulated results showing the values for P_{crit}^* at a given separation distance between particles. P_{crit}^* is taken as the dimensionless pressure at which the film thickness is zero ($h = 0$).

and θ is contact angle. When $h = 0$, $a = R_p$ and $0 < \theta < 90^\circ$ R_L must be zero and therefore P_c tends to infinity. Conversely if a tends to infinity R_L tends to infinity as well. In Fig. 4 it can be seen that the trends obtained from the surface tension model match the analytical ones very closely. The separation distance and pressure are both dimensionless as defined in Eqs. (4) and (5).

The 2D tension model was used to generate results using contact angles between 0° and 90° and separation distances between 1.2 and 4.5 to see how they affected P_{crit}^* . In Fig. 5 it can be seen that for a given separation distance as contact angle decreases (and hence the particle becomes less hydrophobic), P_{crit}^* and film stability increase. It is also apparent that at lower separation distances the effect of a change in contact angle becomes more pronounced. For all separation distances it was found that when θ decreases below 15° there is little change in P_{crit}^* however as it tends to 90° a small change in θ has a much larger effect on P_{crit}^* . Therefore films stabilised with particles with a low θ ($\theta < 15^\circ$) are insensitive to changes in θ , but the stability of films with particles that have a θ close to 90° will be affected by small changes in θ . This has implications for experimental work conducted on particles with θ close to 90° .

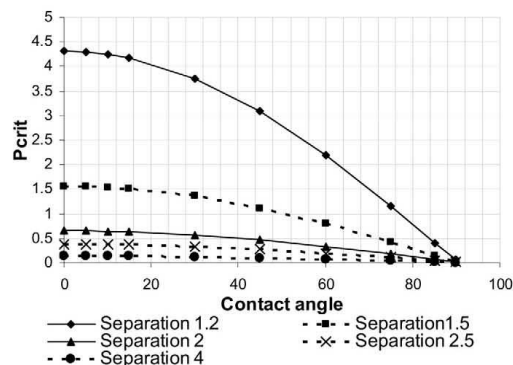


Fig. 5. Comparison of the effect on P_{crit} by changing θ whilst keeping the separation distance between particles constant. For each series plot the separation distance is held constant and P_{crit} is taken at $h = 0$.

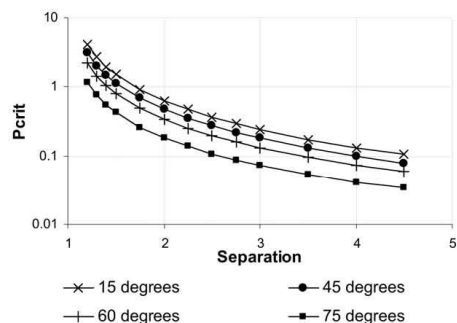


Fig. 6. Plot of P_{crit} against separation distance comparing various values of θ . For each series plot θ is held constant and P_{crit} is taken at $h = 0$.

It can be seen in Fig. 6 that the surface tension model shows an increase in P_{crit}^* as the separation distance decreases. The results also show the same trends as those predicted by Denkov [9] although they are not directly comparable as different values for surface tension and particle size were used. This implies that if the particles are evenly distributed on the film surface the film will become more stable the greater the particle loading. A higher particle loading corresponds to a lower S^* and as S^* decreases P_{crit} and thus film stability increase.

Fig. 7 compares the P_{crit}^* results for 3D hexagonal packing, 3D square packing and 2D models with varying S_{pp}^* separation distances at a contact angle of 45° . All three models produce a similar P_{crit}^* for separation distances above 3, however, below this they diverge from each other. For a given S_{pp}^* , the P_{crit}^* results for 2D are highest and diverge from the 3D results at around $S_{pp}^* = 3$, whilst the square packing P_{crit}^* results are lower than those of hexagonal packing. At an S_{pp}^* of 1.5 the P_{crit}^* for hexagonal packing begins to diverge from that of square packing and at an S_{pp}^* of 1.005 (which corresponds to a very closely packed layer) P_{crit}^* is less than half that of the hexagonal packing. Thus based on S_{pp}^* hexagonal packing is more stable than square packing.

Fig. 8 shows P_{crit}^* as a function of S_{pf}^* . The order of the results is reversed; for a given S_{pf}^* the square packing will have the highest P_{crit}^* , diverging at an S_{pf}^* of approximately 2.5, whilst the results for hexagonal and 2D P_{crit}^* are much closer, diverging at an S_{pf}^* of

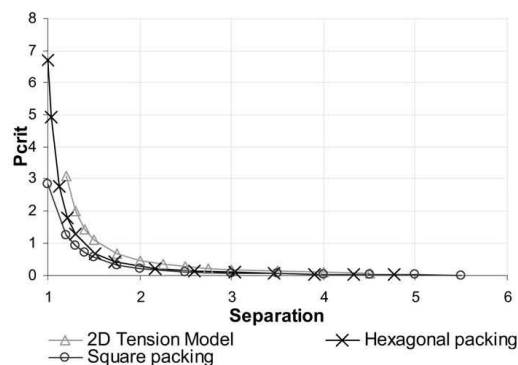


Fig. 7. Comparison of square, hexagonal and 2D P_{crit} as a function of S_{pp}^* for all cases $\theta = 45^\circ$.

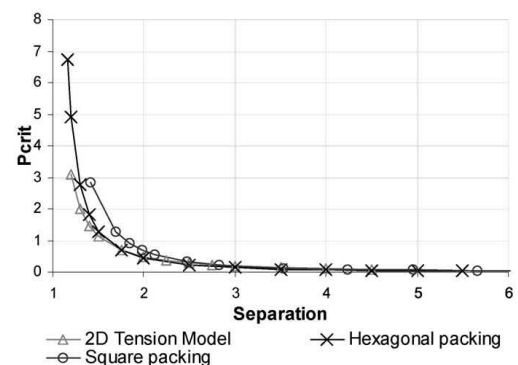


Fig. 8. Comparison of square, hexagonal and 2D P_{crit} as a function of S_{pf}^* for all cases $\theta = 45^\circ$.

1.5. It should be noted that the minimum S_{pf}^* for square packing is 1.41 hence its lower final value for P_{crit} in Fig. 8.

The 2D results have shown that as the distance from the particle to the midpoint of the film increases, P_{crit}^* decreases. For a given S_{pp}^* a square packed film will always have a larger S_{pf}^* and thus a point in the film further away from any particles than its equivalent in a hexagonally packed film. Therefore, a square packed film will always fail at a lower P_{crit}^* for a given S_{pp}^* . Film area is directly related to separation distance and a hexagonally packed film, capable of packing to a lower S_{pf}^* is able to achieve the highest value of P_{crit}^* . Although square packing has a higher P_{crit}^* for a given S_{pf}^* the particles cannot pack as tightly and so reach their maximum possible P_{crit}^* before hexagonal packing. As hexagonal packing continues to pack tighter for lower film areas that square packing cannot reach, the P_{crit}^* increases and thus the maximum P_{crit}^* for hexagonal packing is much higher than that for square packing. Plotting P_{crit}^* against S_{pp}^* shows hexagonal packing has a much higher P_{crit}^* at $S_{pp}^* = 1$ (see Fig. 7) but at $S_{pp}^* = 1$ the S_{pf}^* for square packing is larger than S_{pf}^* for hexagonal packing. At $S_{pp}^* = 1$ the exposed area of film for hexagonal packing is 37.6% that of square packing.

The area of the film in the cell can be calculated using Eqs. (8) and (9) for hexagonal and square cells respectively.

$$\text{Area}_{\text{hex}} = \left(\frac{3\sqrt{3}}{2} (S_{pf}^*)^2 \right) - \pi r_{\text{part}}^2 = (2\sqrt{3} (S_{pp}^*)^2) - \pi r_{\text{part}}^2, \quad (8)$$

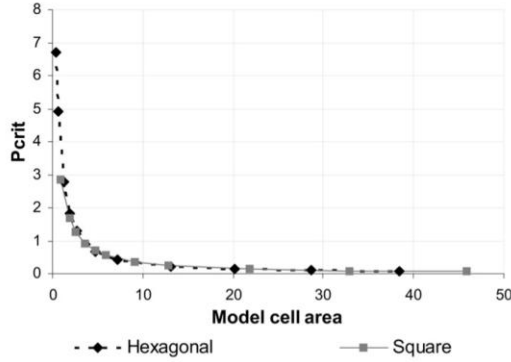


Fig. 9. Comparison of square and hexagonal packing P_{crit} as a function of film area for both cases $\theta = 45^\circ$.

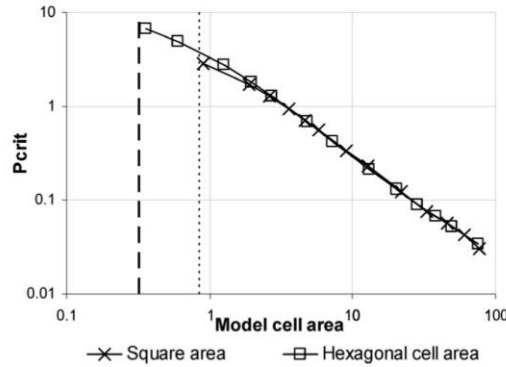


Fig. 10. Comparison of P_{crit} for square and hexagonal packing as a function of film area on log-log axis for both cases $\theta = 45^\circ$. The dashed line represents the minimum cell area achievable for hexagonal packing and the dotted line the same for square packing.

$$\text{Area}_{\text{square}} = 2(S_{pp}^*)^2 - \pi r_{\text{part}}^2 = 4(S_{pp}^*)^2 - \pi r_{\text{part}}^2 \quad (9)$$

Fig. 9 shows the results for P_{crit}^* re-plotted against area of film instead of S_{pp}^* , it can be seen that the curves are almost identical, showing that the relation between the area of exposed film per particle and P_{crit}^* is almost independent of packing pattern. The much higher P_{crit}^* of the hexagonal packing is only reached because it allows smaller film areas to be reached. Re-plotting the graph on a log-log axis as shown in Fig. 10 the point at which the values for P_{crit}^* diverge from each other corresponds to an area of around 2.7, however even at areas below this the results remain very close. The thick dashed line represents the minimum area of film with hexagonal packing (0.3225) and the thin dotted line represents the minimum area for square packing (0.8584). Fig. 10 shows that at small areas the packing pattern has a small effect on P_{crit}^* . At each packing arrangement's minimum area ($S_{pp}^* = 1$) the P_{crit}^* for square packing is around half of that for hexagonal packing and above film areas of approximately 2, the packing arrangement of the particles has a negligible effect on the film stability. As S_{pp}^* increases the percentage difference in area between the two cells decreases and at $S_{pp}^* = 1.5$ the hexagonal cell has an area 80% that of the square packing. It should also be noted that 2D results used to create an axi-symmetric model with a circular boundary diverge from the 3D results at much higher separation

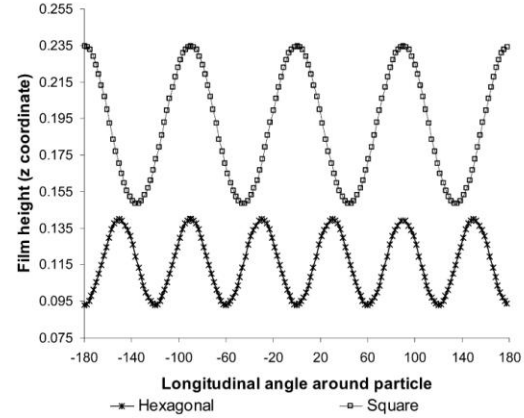


Fig. 11. Showing the z coordinate of the film at the three phase contact plotted against the longitudinal angle around the particle at $S_{pp}^* = 1.13$, $\theta = 45^\circ$ and P_{crit} .

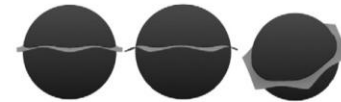


Fig. 12. The evolved surface for hexagonal packing at $S_{pp}^* = 1.13$, $\theta = 45^\circ$ and P_{crit} . Figure only shows the upper surface of the film.



Fig. 13. Evolved surface for square packing at $S_{pp}^* = 1.13$, $\theta = 45^\circ$ and P_{crit} . Figure only shows the upper surface of the film.

distances highlighting the importance of taking into account 3D packing patterns.

Fig. 11 shows a plot of the film height on the surface of the particle for square and hexagonal packing. The film height is much higher on the surface of the particle for the square packing case. As the boundary for the square case is further away from the particle, the film is able to distort more to reach a zero thickness and as a result the three phase contact point is not forced down the side of the particle as far as it is for hexagonal packing.

Figs. 12 and 13 show the shape of the film after evolution at P_{crit}^* for both square and hexagonal boundaries. The complex shape formed by the film in 3D cannot be captured by the 2D model and further highlights the difference in results in 2D and 3D.

4. Conclusions

The results obtained using the analytical model developed by Ali et al. [1] can be matched with a 2D surface tension based model using Surface Evolver. Results show that with decreasing particle separation distance the pressure required to rupture the film increases. The 2D model also shows that as contact angle decreases below approximately 15° at a constant separation where $S_{pp}^* < 3$, P_{crit}^* does not change by more than 5.5%. At contact angles approaching 90° P_{crit}^* is very low regardless of separation distance, indicating that when single particles with a high hydrophobicity bridge both sides of a thin film they have little effect on film stability. However, it is possible for a double layer of particles with

contact angles above 90° to stabilise the film but these cases are beyond the scope of this paper. The separation distance has potentially a much larger effect on P_{crit}^* than θ but it should be noted that the probability of a particle attaching to a film (and therefore packing density) decreases with hydrophobicity.

A 2D model is limited in the sense that although it shows the same trends as the 3D model it cannot take into account particle packing configurations and zero separation distances between particles so it always returns a higher P_{crit}^* than a 3D model for a given separation distance. In 3D the film also becomes highly distorted at low separation distances.

The packing pattern and distance between the particles attached to the film affects the capillary pressure required to rupture the film implying that they are important parameters when considering the stability of a film or foam. When considering the separation distance between particles, hexagonally close packed particles appear to stabilise thin films to a greater extent than square packed ones by increasing the capillary pressure required to rupture them. However, as the separation distance increases above $S_{\text{pp}}^* = 3$ the difference in P_{crit}^* for different particle packing configurations drops significantly. If film area per particle is considered instead of S_{pp}^* both types of packing arrangement considered have similar effects on the film stability indicating that the film area per particle not the separation distance is a useful property to use as a comparison factor. A close packed hexagonal pattern is able to achieve much lower film areas per particle than square packing enabling a greater film stability. This implies that when considering films with evenly distributed attached particles, packing configuration has a large effect on film stability only when the particles are densely packed. The difference in P_{crit}^* at contact angles of 0° and 90° at an $S_{\text{pp}}^* = 4$ is 2.7% of the same difference in P_{crit}^* at $S_{\text{pp}}^* = 1.2$. Separation distance is directly related to the particle packing density on the film so for low particle loadings the positioning does not have a large effect on film stability. These results fit with the results of Johansson and Pugh [5] indicating that

there is an optimum combination of packing fraction, packing arrangement, hydrophobicity and size that maximises foam and film stability. The authors are unaware of any published experimental results which could be used to validate this model and experimental techniques are currently being developed to verify the findings of this paper. Future experimental work will investigate the effects of particle hydrophobicity and packing density on packing arrangement and critical capillary pressure of thin films. Future investigations will look at the effects of particle size and distribution on the film as well as the effect of multiple layers of particles within a film.

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References

- [1] S.A. Ali, P.A. Gauglitz, W.R. Rossen, *Ind. Eng. Chem. Res.* 39 (2000) 2742–2745.
- [2] R. Aveyard, B.P. Binks, J.H. Clint, *Adv. Colloid Interface Sci.* 100–102 (2003) 503–546.
- [3] R. Aveyard, B.P. Binks, P.D.I. Fletcher, T.G. Peck, C.E. Rutherford, *Adv. Colloid Interface Sci.* 48 (1994) 93–120.
- [4] P.R. Garrett, *Colloids Surf. A Physicochem. Eng. Aspects* 85 (1994) 159–197.
- [5] G. Johansson, R.J. Pugh, *Int. J. Miner. Process.* 34 (1992) 1–21.
- [6] S. Schwarz, S. Grano, *Colloids Surf. A Physicochem. Eng. Aspects* 256 (2005) 157–164.
- [7] T.N. Hunter, R.J. Pugh, G.V. Franks, G.J. Jameson, *Adv. Colloid Interface Sci.* 137 (2008) 57–81.
- [8] A. Dippenaar, *Int. J. Miner. Process.* 9 (1982) 1–14.
- [9] N.D. Denkov, B. Ivanov, P.P. Kralchevsky, T. Wasan, *J. Colloid Interface Sci.* 150 (2) (1992) 589–593.
- [10] G. Kaptay, *Colloids Surf. A Physicochem. Eng. Aspects* 230 (2004) 67–87.
- [11] K. Brakke, *Exp. Math.* 1 (1992) 141–165.
- [12] S. Tcholakova, N.D. Denkov, A. Lips, *Phys. Chem. Chem. Phys.* 10 (2008) 1608–1627.

12 APPENDIX C

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The effects of hydrophobicity and orientation of cubic particles on the stability of thin films

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ABSTRACT

A three-dimensional model of a single cubic particle in a thin liquid film has been developed using the Surface Evolver (Brakke, 1992) program. It has been used to investigate the effect of a particle's contact angle on its energetically stable orientations at a liquid–vapour interface and how these, in turn, affect the particle's ability to stabilise a thin film. It has been found that depending on the contact angle there are two possible stable orientations for a cubic particle (termed horizontal and rotated) at a liquid–vapour interface. For a film containing a cubic particle in a rotated orientation it has been found that the capillary pressure required to rupture the film is roughly 30% of that required for a film containing a particle of the same contact angle but in a horizontal orientation. The probability of a particle adopting one orientation over another is also investigated, showing that this too is affected by contact angle and leading to the conclusion that contact angle has a profound effect on non-spherical particles behaviour in thin films.

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1. Introduction

Particle-stabilised foams are present in many industrial processes. A foam is made up of a series of thin films which form the walls of the individual cells or bubbles. Capillary pressure is exerted on the films as liquid drains from the foam under gravity, causing them to thin. The film fails when it reaches a critical thickness, at which point the opposite sides touch and rupture occurs. However, when particles are attached to the film they hold the opposite sides apart and increase the capillary pressure required to draw liquid out of the film. This slows the thinning process and increases film lifetime and stability. It has long been known that the particle hydrophobicity affects the froth stability (Aveyard et al., 2003), however, the mechanism by which attached particles stabilise a bubble film is not well understood. This is due to the dynamic behaviour of particles when in a thin film and the complex effects of particle size, shape, hydrophobicity, packing arrangement and physical distribution. Furthermore, the system is experimentally difficult, as these factors are not readily controlled. By design, flotation froths are highly unstable, bubbles enter the froth with a diameter of around 1 mm but overflow or burst at the surface with a diameter of around 5 cm. When bubbles coalesce within the froth, film surface area is lost and the attached particles

become detached, enter the Plateau borders and flow back into the pulp so decreasing the efficiency and selectivity of the process.

Experimental investigation of the effect of particle contact angle (θ) on film and foam stability has been conducted by Aveyard et al. (1994) which found that when the contact angle of the particles increased above 90° the foam stability rapidly decreased. Schwarz and Grano (2005) reported that quartz particles with a contact angle of approximately 63° maximised froth stability, whilst Johansson and Pugh (1992) found that small quartz particles ($26\text{--}44\text{ }\mu\text{m}$) with an intermediate level of hydrophobicity (contact angle $\sim 65^\circ$) stabilised the froth to the greatest extent.

Previous analytical and modelling work on film stability in both two-dimensions (2D) and three-dimensions (3D) has concentrated on the effects of the hydrophobicity and particle spacing of spherical particles. Ali et al. (2000), Denkov et al. (1992), Kaptay (2004) and Morris et al. (2008) found that, for a given particle spacing, the film stability increased as θ decreased and that for a given θ film stability decreased as the particle separation increased. However, the irregular shape of particles found in flotation films also has an effect on film stability. Frye and Berg (1989) noted that particles with asperities enter a film more easily and are capable of destroying them at much lower contact angles than smooth particles.

In a classic study, Dippenaar (1982) investigated the effect of particle shape and contact angle on the stability of a film containing particles of crushed galena treated with xanthate to give them a contact angle of $80^\circ \pm 8^\circ$. Galena breaks into orthorhombic shapes when crushed and the sharp rectangular edges of the particles affect their behaviour when attached to thin films. The cubic

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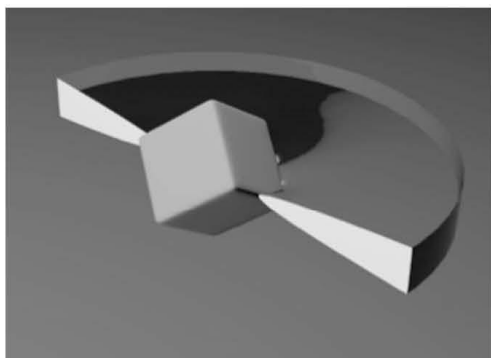


Fig. 1. Cross section of a cubic particle in a film orientated in such a way as to draw the opposite sides together at the edges and cause failure of the film.

particles were placed on a thin film so that they were only attached to the upper surface and the film was thinned until the lower part of the galena particle came into contact with the lower film surface. At this point the lower surface of the galena bridged the film and depending on its orientation and contact angle either ruptured the film almost immediately or moved to the side whilst the film continued to thin. The galena particles initially orientated themselves in the film in one of two ways, either horizontally or rotated through 45° around the viewing axis (X -axis). When the lower face of the horizontally orientated galena bridged the lower surface of the film it was moved to the side and film continued to thin to failure. However, when in the diagonal orientation the particle either rotated 45° about the X -axis, to the horizontal orientation and moved to the edge of the film as before, or it rotated 45° around the Y -axis. When the latter occurred the opposite sides of the film were drawn together at the edges of the cube (Fig. 1) causing the film to fail. Dippenaar (1982) reported that the two initial orientations occurred with roughly equal probability.

Using 2D analysis Dippenaar (1982) showed that for a cubic particle in a thin film two orientations were stable, a horizontal particle or a diagonal. Both orientations are stable when the contact angle is in the range of 45° – 90° and the galena particles used in the experiments had contact angles between 72° and 88° allowing either orientation to be adopted. However, in 3D the film takes on a highly distorted shape, in particular when the cubic particle rotates around two axes and an analytical solution is not possible.

In this study we will use a surface energy minimisation approach to model and further analyse the Dippenaar (1982) experiments. Validation of single particle results will allow extension to multiple particle systems and, ultimately, an understanding of the mechanism of particle stabilisation of thin films.

2. Computational methodology

2.1. Surface Evolver model

Surface Evolver (Brakke, 1992) is a program used to study the topology of surfaces governed by energies such as surface tension, gravity and other user defined energies. It uses a gradient descent method to evolve a user defined surface towards its minimum energy and as such is a powerful tool for the study of foams and films. It was used to create a model which is able to simulate an orthorhombic particle in a thin film in 3D. Two cases are investigated, one in which the particle is attached to a thick film and has bridged

only one side of it (Fig. 2a) and the second where the film has thinned sufficiently to allow the particle to bridge both sides of the film (Fig. 2b).

In the first case the model has been used to investigate the stable orientations of the particle in the film and how they vary with the particle contact angle. The initial simulations used contact angles between 45° and 90° so that the complete range of contact angles that support either orientation in 2D could be expanded to 3D. Once the stable orientations were identified the second model was used to investigate the effect of particle orientation on film stability. The single film model was set up with a single cubic particle in the centre of a circular film with a radius 15 times that of the particle edge length in line with the experimental apparatus used by Dippenaar (1982). The model used to investigate film failure used a circular film of radius 2.5 the particle edge length. In both cases the outer boundary of the film, whilst constrained to a circle was free in the Z direction allowing the edges to move up and down.

The particle is defined as a single surface within Surface Evolver and its hydrophobicity is characterised by the contact angle θ , defined as the angle formed between the surface of the particle and the liquid–vapour interface (Fig. 3). The contact angle of the particle is a key parameter as this determines the film's stability and surface energy and so the preferred orientation of the particle. Mineral flotation particles generally have contact angles between 0° and 90° , with a low hydrophobicity defined as 0 – 30° , intermediate 30 – 70° and high over 70° .

In Surface Evolver the contact angle is set by altering the surface tension values for the facets that make up the dry surface of the particle in accordance with Young's equation, (Eq. (1)); γ_{ij} refers to the surface tension of the solid–liquid (SL) solid–vapour (SV) and liquid–vapour (LV) interfaces.

$$\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV} \quad (1)$$

The energy of a surface that is minimised in Surface Evolver is made up of the sum of its component energies; one of these is the energy per unit area which can also be regarded as surface tension. The default value for surface tension in the model is 1, as the total surface area of solid is fixed, only the difference between γ_{SV} and γ_{SL} affects the energy minimisation process. γ_{SL} is kept constant and set to 0 and all interfacial surface tensions are non-dimensionalised by γ_{LV} which has the effect setting γ_{SV} to

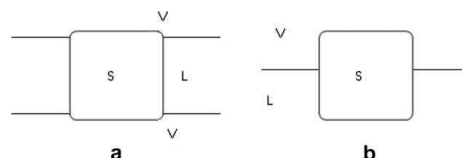


Fig. 2. Galena particle bridging both sides of a film (a) and one side of a film (b). Where S is the solid phase, V the vapour phase and L the liquid phase.

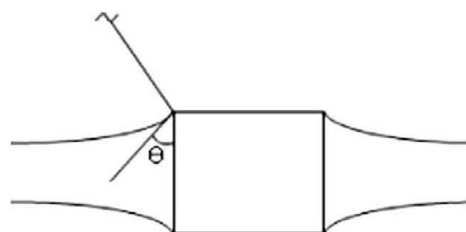


Fig. 3. The contact angle (θ) on the surface of an orthorhombic particle.

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$\cos \theta$, γ_{SL} to 0 and γ_{LV} to 1. This satisfies Young's equation and θ can be changed by altering γ_{SV} . As there is little surfactant found in a flotation froth (in the range of 20–100 g/t ore) disjoining forces have been discounted. Conjoining forces have also been discounted as Van der Waals forces are typically only of a similar magnitude to the surface tension forces in this system when the films are tens of nm thick (Tcholakova et al., 2008). This is a very small consideration when the system being modelled is many orders of magnitude larger (the particles found in a flotation froth are typically between 10 and 100 μm). In this paper, all linear parameters have been non-dimensionalised using r_{part} (half the cube edge length) and all force parameters have been non-dimensionalised using the surface tension of the film (Eqs. (2) and (3)):

$$L^* = \frac{L}{r_{\text{part}}} \quad (2)$$

$$P^* = \frac{P \times r_{\text{part}}}{\gamma_{LV}} \quad (3)$$

where L is length, P is pressure and γ_{LV} is surface tension of the liquid/vapour interface. It should be noted that the curvature of a 2D film surface such as the one being simulated has two orthogonal radii of curvature, r_1 and r_2 associated with it. These are related to the pressure using Eq. (4).

$$P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (4)$$

However, if r_1 and r_2 are equal, the curvature can be characterised by a single radius of curvature r_{curve} .

$$\frac{1}{r_{\text{curve}}} = \frac{1}{r_1} + \frac{1}{r_2} \quad (5)$$

Substituting Eq. (5) into Eq. (4) and the result into Eq. (3) it can be seen that P^* is a measure of particle radius to film curvature Eq. (6).

$$P^* = \frac{r_{\text{part}}}{r_{\text{curve}}} \quad (6)$$

2.2. Particle shape model

The particle shape is described as a single surface using a superquadric equation which is capable of describing a parametric shape as a continuous surface in both 2D and 3D (Zhou and Kambhampati, 2001). Eq. (7) shows the basic superquadric equation in 3D.

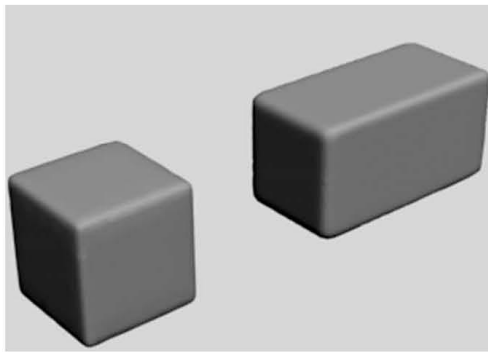


Fig. 4. Cube ($s_1 = 1$) and oblong ($s_1 = 2$) particles defined by Eq. (7).

$$\left| \frac{x}{s_1} \right|^{s_1} + \left| \frac{y}{s_2} \right|^{s_2} + \left| \frac{z}{s_3} \right|^{s_3} = r_{\text{part}} \quad (7)$$

In Eq. (7) x , y and z are the coordinates of a point on the surface, in this case the vertices in the Surface Evolver model. The squareness parameter s_i (where $i = 1, 2$ or 3) controls the shape of the superquadric; $s_1 = s_2 = s_3 = 20$ was used throughout. The values of s_i change the ratio of the length, width and height of the particle, whilst r_{part} controls its size. For the purposes of this model $r_{\text{part}} = 1$, $s_2 = s_3 = 1$ and s_1 was varied between 1 and 1.4 to change the length of the particle. Fig. 4 shows two of the particles shapes generated.

2.3. Simulations

Initially the model with only one surface bridged by the particle was used to investigate the effect of contact angle on particle orientation. First the particle was assigned a contact angle and rotated to a specific orientation. Surface Evolver was then run through a series of iterations and mesh adjustments until the minimum energy surface had been reached. This process was then repeated for 190 different particle orientations to produce the data required to find the energetically stable orientations for that contact angle. The whole process was then repeated for different contact angles ($\theta = 45^\circ, 60^\circ, 65^\circ, 68.5^\circ, 70^\circ, 72.5^\circ, 75^\circ, 77.5^\circ, 80^\circ, 88^\circ, 90^\circ$).

Once the stable orientations were identified the model with a particle that has bridged both sides of the film was used to investigate the effect of orientation and contact angle on film stability. The model was initially set with a capillary pressure of 0 and the film evolved to find the film shape. The entire film surface was then tested to see if at any point the opposite sides were touching (this indicating film failure). If not, the capillary pressure was increased by a small amount, the new surface evolved and tested for failure. This was repeated until the film failed and so the critical capillary pressure of the film was ascertained.

3. Results and discussion

The total energy of the evolved model was found for cubic particles with contact angles between 45° and 90° and rotations between 0° and 90° around the X -axis and 0° and 45° around the Y -axis. Only two distinct, stable orientations for a cubic particle in a thin film were found: horizontal and rotated (Fig. 5). The horizontal particle sits in the film with the lower horizontal and four vertical faces in the liquid phase whilst the upper horizontal face is in the vapour phase. In the rotated case the particle has turned around both its X - and Y -axes and has its three upper faces in the vapour phase and three lower faces in the liquid phase. All three of the upper faces also have some portion of their surface in the liquid phase. The direction of the normal from each of the three of the upper faces forms an angle of 55° with the Z -axis. Dippenaar (1982) observed the horizontal orientation, however the rotated orientation was only seen when the particle bridged both sides of the film, instead the diagonal orientation was found to be stable for a particle bridging a single film interface.

When both sides of the film are bridged the horizontally orientated particle stabilises the film by holding its opposite sides apart at the upper and lower faces as shown in Fig. 3. As the capillary pressure gradually increases the film surfaces slide down the vertical faces and the film curvature increases until the opposite sides touch and the film fails. The particle in a rotated orientation initially draws the opposite sides of the film together near the edges running around its centre forming a highly distorted surface. This forces the initial film surfaces much closer together and as a result there is a decrease in the capillary pressure required to destroy the film.

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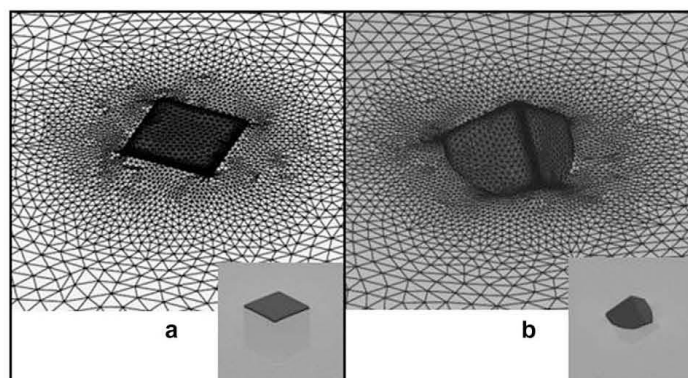


Fig. 5. The two stable orientations of a cubic particle ($\theta = 45^\circ$) in a thin film, horizontal (a), rotated (b).

A cubic particle with a contact angle of 45° is only energetically stable in the horizontal orientation and this is also the lowest energy orientation it can adopt. The rotated orientation at this contact angle is the highest energy orientation possible and is surrounded by lower energy orientations making it energetically unstable. There are no other local surface energy minima so whatever the initial orientation in the film, the particle will always move to a horizontal one. At $\theta = 90^\circ$ the situation is reversed and the only stable orientation is a rotated one with the energy maximum at the horizontal particle orientation.

In between these two contact angles there is a transition from horizontal stability to rotated stability and there is a range of contact angles for which either orientation is energetically stable. In this case both orientations are situated at a local minimum in energy and are separated from each other by a set of unstable, higher energy orientations. For a specific contact angle, both stable orientations have different energies with the lower energy orientation being the more energetically favourable one. Whilst the horizontal orientation is energetically most favourable at a contact angle of 60° , as it increases above this value, the difference in energy between the two orientations decreases. At about a 72.5° contact angle, the surface energies for the two stable orientations are the same whilst still separated by a ridge of higher energy orientations. As θ increases further, the rotated orientation becomes more stable of the two.

There is a surface energy landscape, defined by the X and Y rotation coordinates, for a particle with a specific contact angle. The two stable orientations are located in low energy points in the landscape. For any particular contact angle, there are also particle orientations that have a maximum in surface energy; consider this energy as a ridge in the energy surface. The difference in height between the ridge and a stable orientation is the amount of energy required to move a particle from one stable orientation to another (i.e. over the ridge).

It can be seen in Fig. 6 that at $\theta = 72.5^\circ$ the difference in energy between the stable horizontal and rotated orientations and the energy peak is the same and there is no net energy gain by moving from one orientation to the other. Above $\theta = 72.5^\circ$ the rotated orientation is energetically the most stable and hence more favourable, whilst below $\theta = 72.5^\circ$ it is the horizontal orientation. It can also be seen that for $\theta < 65^\circ$ the only stable orientation is the horizontal one and for $\theta > 80^\circ$ the only stable orientation is the rotated one.

Fig. 6 indicates further that the energy required to move from one stable orientation to the other also changes as the contact an-

gle changes, and that it is not symmetrical. When $\theta < 72.5^\circ$, less energy is required to move the particle from a rotated to a horizontal orientation than the other way around, whilst for $\theta > 72.5^\circ$ the opposite is true. At $\theta = 70^\circ$ the energy required to move over the maximum energy point from a rotated orientation to a horizontal one is 34.2% of what is required to move the other way. At $\theta = 75^\circ$ to move from a horizontal to a rotated orientation the energy required is 21.0% that of going the other way.

As noted earlier, a 2D geometric analysis of a cubic particle in a film indicates stability in both horizontal and diagonal orientations for $45^\circ < \theta < 90^\circ$, which is not equivalent to the 3D results. However, the diagonal orientation found from a 2D analysis is not the same, true orientation adopted when analysed in 3D as the rotation cannot occur in two directions. This may be the reason that only one stable orientation is found in 3D for $45^\circ < \theta < 60^\circ$ and $80^\circ < \theta < 90^\circ$ instead of two. It should also be noted that for a cubic particle the diagonal orientation observed by Dippenaar (1982) and seen in the 2D case forms a saddle point in the surface energy landscape, so that if rotation around only one axis was possible it would be stable. If the particle is elongated along one axis this

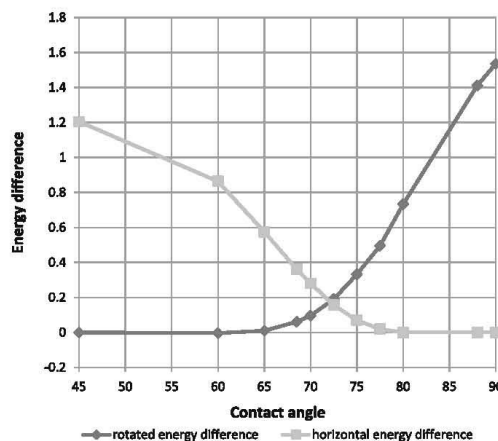


Fig. 6. The difference in surface energy between horizontal or rotated orientations and the energy of the orientation with the largest energy for a given contact angle.

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changes the film shape and energy of the system and affects the stable orientations which will be considered in the next section.

3.1. Comparison with the Dippenaar results

It should be noted that whilst the Surface Evolver simulation results show that horizontal or rotated orientations are stable at different contact angles, Dippenaar (1982) did not report any particles rotating about both axes whilst attached to a single film interface. Rotation about both axes was only reported once the particle had bridged the film. There are many variables that could affect the stable orientations of a particle that are not explicitly taken into account in the model; for example differences in advancing and receding contact angles, surface roughness and non-cubic particle shape. Whilst the first two of these causes are beyond the scope of this study it is plausible that the galena particles used experimentally by Dippenaar (1982) were not exactly cubic. The effect of this can be investigated by altering the particle shape in Surface Evolver.

The same procedure that was followed for the cubic particle was used for an oblong particle with $\theta = 70^\circ$ and using $s_2 = s_3 = 1$. However, s_1 was increased to 1.4 thereby increasing the particle length by 40%. In this case the stable orientation with the lowest energy corresponds to a particle lying horizontally in the film. There is also a stable orientation corresponding to a particle lying along its long axis but rotated 45° around it and both orientations (shown in Fig. 7) were observed by Dippenaar (1982). When θ is decreased to 60° , the horizontal orientation is stable but there is no local minimum for a diagonal orientation. At $\theta = 80^\circ$ the horizontal orientation becomes unstable and a particle rotated 45° around its long axis becomes the stable orientation.

3.2. Film stability with cubic particles

It has been found that contact angle has a large effect on the orientation of cubic particles bridging one side of a film, however eventually a film will thin to the point where the particle will bridge both of its sides. At this point both the contact angle and the particle orientation will have an effect on the film stability. A Surface Evolver model in which the particle has bridged both sides of a film was used to determine the critical capillary pressure required to rupture the film. The critical capillary pressure has been found for horizontal particles with contact angles of 45° – 80° and for

rotated particles with contact angles between 65° and 90° . Dippenaar (1982) observed that when a diagonal particle bridged a film it either rotated to a horizontal orientation and the film continued to thin until failure or it twisted around its second axis and ruptured the film at its edges. The simultaneous two-axis rotation of the particle and film thinning as it bridges the surface is highly complex and cannot at present be simulated. Instead the particle was first rotated to its stable orientation in the film, which was then further thinned until failure.

It can be seen in Fig. 8 that as the contact angle of a horizontally orientated particle increases, the critical capillary pressure for film failure decreases. This trend was reported previously for spherical particles by Ali et al. (2000) and Morris et al. (2008). The same trend is also observed for particles in the rotated orientation however the critical capillary pressure is much lower than for a horizontally orientated particle with the same contact angle. For contact angles in the range of 65° – 80° both orientations are energetically stable. The critical capillary pressure of a rotated particle at $\theta = 65^\circ$ is 29.2% of the horizontal one and at $\theta = 80^\circ$ it is 27.9%. A cubic particle with a given contact angle can therefore have its stabilising effect on the film reduced by as much as 72.1%, depending on its orientation.

If it is assumed that a particle enters the film at an initially random orientation then its final orientation and stabilising effect will depend on which side of the unstable maximum energy orientations it lands. If it is on one side it will move to the horizontal orientation, if it is on the other it will prefer the rotated orientation, with a much lower stabilising effect. However, the position of the energy maximum separating the stable orientations changes with the contact angle. This changes the range of initial orientations that will move to one stable orientation instead of another. Once the positions of the stable orientations are known as well as the position of the energy maximum separating them it is possible to identify whether a particle with a given contact angle and initial orientation will end up horizontal or rotated in the film. This information can also be used to calculate the probability of a particle entering the film with a random orientation ending up in a particular stable orientation. Consider P_H as the probability that a particle will end up in the horizontal orientation.

The results indicate that if a cubic particle enters the film with a random orientation then the higher the contact angle the higher the probability it will adopt a rotated orientation, significantly lowering its stabilising effect on the film when it bridges the opposite

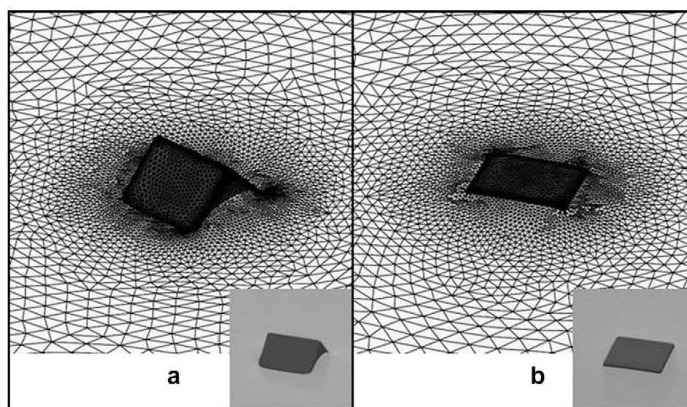


Fig. 7. Stable orientations of an oblong particle, diagonal (a) and horizontal (b), $\theta = 70^\circ$, $s_1 = 1.4$, $s_2 = s_3 = 1$.

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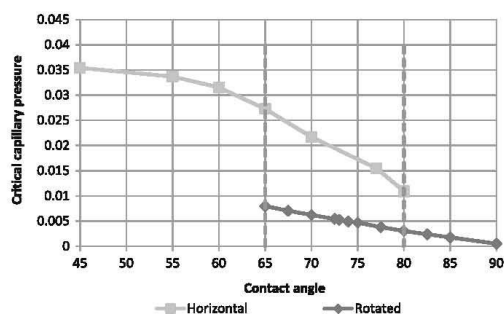


Fig. 8. Critical capillary pressure taken from the Surface Evolver model vs. contact angle for cubic particles bridging a thin film. Dashed lines represent the limiting contact angles at which both orientations are stable.

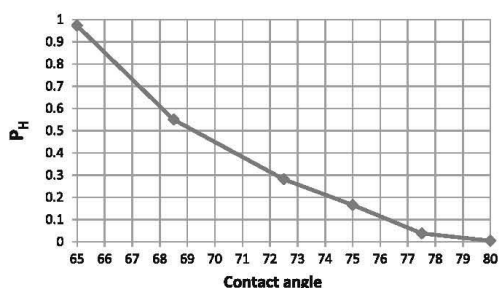


Fig. 9. P_H against contact angle. Below $\theta = 65^\circ$ it is 1, above 80° it is 0.

interface. Fig. 9 shows that for a particle with a contact angle of 65° there is a 0.97 chance that it will align itself horizontally in the film and require a high critical capillary pressure to rupture the film (0.027, Fig. 8). Nonetheless, there is a 0.03 chance that the particle will align itself in a rotated orientation (critical capillary pressure = 0.008, Fig. 8) reducing the pressure required for failure by 70.8%. As θ increases the probability that a rotated orientation will ensue also increases and at $\theta = 72.5^\circ$ it is 0.72. Above $\theta = 80^\circ$ the particle always enters a rotated orientation as the horizontal one is no longer energetically stable. This drastically reduces the pressure required for failure and produces a less stable film.

4. Conclusions

It has been shown that a cubic particle has two stable orientations, horizontal or rotated, when attached to a film. The preference for one orientation over the other depends on its contact angle and the orientation with which it enters the film. Both particle orientations will help stabilise a film, but the horizontal orientation is more effective. A diagonal particle orientation is energetically unstable for a cubic particle, but if its length along one axis is increased the diagonal orientation becomes stable and the rotated one unstable which is in line with Dippenaar's (1982)

work. As galena breaks up into orthorhombic particles but not necessarily cubic ones this means that its height to length to width ratio will have an effect on film stability. Whilst an investigation of the effect of particle length on the stability of the film is beyond the scope of this paper it has been shown that a slight elongation of the particle has a profound effect on its preferred orientation within the film which has already been shown to heavily affect the film stability.

As the rotated orientation of a cubic particle reduces its ability to stabilise the film by 70% more research is required into the effect of particle shape on film stability. 2D geometric analysis shows that there are two stable orientations for a square particle in a film when it has a contact angle between 45° and 90° , however 3D modelling has shown that for a cubic particle the two stable orientations are horizontal and rotated (three facet normals of the cube at 55° to the Z-axis) and they are only both stable between contact angles of 65° and 80° .

For any given contact angle in the range of $65^\circ < \theta < 80^\circ$ (where both orientations are energetically stable) the critical capillary pressure required to rupture a film bridged with a rotated particle is approximately 70% lower than one with a horizontal particle in it. The probability that a particle entering the film with a random orientation will adopt either a horizontal or rotated orientation has also been found. As θ increases from 65° to 80° the likelihood of the particle adopting a rotated orientation in preference to a horizontal one increases from 0 to 1. Therefore, if greater film stability is desired it is important to keep the particle contact angle below 65° under which conditions the particle will prefer a horizontal orientation and stabilise the film more readily. If the contact angle increases above 65° , the probability of a particle adopting a rotated orientation in the film also increases, which will result in a much reduced film stability around that particle and therefore the whole film.

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References

- Ali, S.A., Gauglitz, P.A., Rossen, W.R., 2000. Industrial Engineering and Chemical Research 39 (8), 2742–2745.
- Aveyard, R., Binks, B.P., Clint, J.H., 2003. Advances in Colloid and Interface Science 100–102, 503–546.
- Aveyard, R., Binks, B.P., Fletcher, P.D.I., Peck, T.G., Rutherford, C.E., 1994. Advances in Colloid and Interface Science 48, 93–120.
- Brakke, K., 1992. Experimental Mathematics 1, 141–165.
- Denkov, N.D., Ivanovi, B., Kralchevsky, P.P., Wasan, T., 1992. Journal of Colloid and Interface Science 150 (2), 589–593.
- Dippenaar, A., 1982. International Journal of Mineral Processing 9 (1), 1–14.
- Frye, G.C., Berg, J.C., 1989. Journal of Colloid and Interface Science 130 (1), 54–59.
- Johansson, G., Pugh, R.J., 1992. International Journal of Mineral Processing 34 (1–2), 1–21.
- Kaptay, G., 2004. Colloids and Surfaces A: Physicochemical and Engineering Aspects 230 (1–3), 67–80.
- Morris, G., Pursell, M.R., Neethling, S.J., Cilliers, J.J., 2008. Journal of Colloid and Interface Science 327 (1), 138–144.
- Schwarz, S., Grano, S., 2005. Colloids and Surfaces A: Physicochemical and Engineering Aspects 256 (2–3), 157–164.
- Tcholakova, S., Denkov, N.D., Lips, A., 2008. Physical Chemistry Chemical Physics 10 (12), 1608–1627.
- Zhou, L., Kambhampati, C., 2001. Graphical Models 63 (1), 1–20.