

On the origin of surface tension and its application to micro/nano-scale devices

By

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Statement of Originality

The author claims that the work reported in this thesis is his own work except where due reference is made in the thesis itself. This work has not previously been submitted for a degree or diploma in any university.

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Abstract

Surface tension, which is an important interfacial property of inhomogeneous systems, strongly affects the phase transition in a system. At the macro-scale, the surface tension is regarded as constant. However, a curvature dependence of the surface tension at the nano-scale has been predicted in the seminal work of Gibbs (1928), Tolman and co-workers (1949).

This thesis investigates the curvature dependence of the surface tension and the Tolman length with molecular dynamics simulations. It is found that the curvature starts to affect the surface tension and Tolman length when the curvature radius decreases to around 20 molecular diameters. The magnitude of the effect of curvature on the surface tension and Tolman length is similar for nanobubble and nanodroplet interfaces while they act oppositely.

Governed by the scaling law, the surface tension dominates at millimeter-scale and below. To utilise the large Laplace pressure across liquid menisci caused by surface tension, liquid ring bearings have recently been developed. In this thesis, I present a detailed experimental and theoretical performance analysis of such bearings.

Building on the study of the liquid ring bearings, a thrust bearing consisting of an air cushion formed within a liquid ring has been developed. An important discovery is that the performance of this bearing is greatly enhanced by the sealed cushion of air within the ring. Factors which affect the performance of the liquid ring and the liquid ring sealed air bearing have been studied both experimentally and numerically providing results that can be used to optimise the design of such bearings.

To conclude, the surface tension and Tolman length have a curvature dependence only when the length-scale decreases down to molecular scale. The surface tension can be utilized to confine liquid menisci at millimeter-scale and below to support the load and effectively lubricate bearings.

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Table of Contents

Statement of Originality.....	I
Copyright Declaration.....	II
Abstract.....	III
Acknowledgement	IV
Table of Contents.....	V
List of Figures	VIII
List of tables.....	XIII
Nomenclature.....	XIV
Chapter 1 Introduction	1
1.1 Research Background and Aims.	1
1.2 Research objectives.....	4
1.3 Outline of the thesis.	5
Chapter 2. Literature review	6
2.1 Surface tension and the Tolman length of a curved liquid/gas interface	6
2.1.1 Thermodynamic deduction of the relationship between the surface tension and Tolman length.....	7
2.1.2 Simulations on the curvature dependence of the surface tension and Tolman length .	10
2.1.3 Experimental investigation of the curvature dependence of the surface tension.	15
2.2 Tribological problems of Micro-Electro-Mechanical Systems (MEMS).....	17
2.2.1 MEMS devices involving contacts and sliding	18
2.2.2 Tribological problems	22
2.2.3 MEMS bearings	24
2.3 The surface tension at micro/nano-scales	26
2.3.1 Avoiding adhesion of surfaces	26
2.3.2 MEMS liquid ball/ring bearings	29
2.4 Superhydrophobic surface.....	31
2.4.1 Properties of superhydrophobic surface.....	31
2.4.2 Preparation methods of superhydrophobic surface	34
2.5 Conclusions.....	37
Chapter 3 Molecular dynamics simulations of surface tension of flat gas-liquid interface	6
3.1 Introduction.....	38

3.2 Methodology	39
3.2.1 Theoretical investigation of the way for calculating the surface tension	39
3.2.2 Numerical simulations	41
3.3 Results and discussion	46
3.3.1 The ‘average after’ procedure of calculating the surface tension and Tolman length. 46	
3.3.2 The ‘average before’ procedure of calculating the surface tension and Tolman length	50
3.3.3 The surface tension and Tolman length	52
3.3.4 The effect of curvature on the surface tension and Tolman length.....	56
3.5 Fitted Tolman equation considering both effects of density ratio and curvature.....	59
3.4 Conclusions.....	60
Chapter 4. Liquid ring bearings	38
4.1 Introduction.....	62
4.2 Experimental and Numerical Methods.....	63
4.2.1 Fabrication of the liquid ring thrust bearing	63
4.2.2 Theoretical model for the static maximum supporting force of the liquid ring	66
4.2.3 Mathematical model for the profile of the liquid/air interface and the maximum dynamic supporting force of the bearing	69
4.2.4 Mathematical model for the frictional torque	74
4.3 Results and discussion	75
4.3.1 Supporting force of the bearing.....	75
4.3.2 Profile of the outer liquid/air interface.....	80
4.3.3 The maximum dynamic supporting force of the bearing	82
4.3.4 Bearing torque: comparison between experimental results and predictions	83
4.4 Other possible design of the bearing.....	86
4.4.1 The concave model	87
4.4.2 The convex model.....	88
4.4.3 The wavy model.....	90
4.5 Conclusions.....	93
Chapter 5. Liquid ring sealed air bearing.....	62
5.1 Introduction.....	94
5.2 Methods.....	95
5.1.1 Design and experimental methods	95

5.1.2 Theoretical model for the maximum static supporting force	97
5.1.3 Theoretical model for the stiffness of the bearing	100
5.1.4 Liquid evaporation model	102
5.1.5 Air diffusion model	103
5.1.6 Pressurized liquid ring test	103
5.1.7 The wettability transition model	104
5.3 Results and discussion	105
5.3.1 The maximum static supporting force of the bearing	105
5.3.2 The effect of air diffusion	112
5.3.3 The effect of liquid evaporation	112
5.3.4 The stiffness of the bearing	117
5.3.5 The dynamic supporting force of the bearing	121
5.4 Conclusions	122
Chapter 6 Conclusions and future work	123
6.1 Summary of the thesis achievements	123
6.2 Future work and research	125
References	127
List of Published Work	137
Published Articles	137
Articles Under Preparation in the Moment	137
Presentations in Academic Conferences	137
Appendix	138
Appendix A Deduction of the Tolman equations for cylindrical interfaces	138
Appendix B Volume of the liquid ring	138
Appendix C Volume of the air cushion	141

List of Figures

Figure 2.1. Size dependences of surface tension [35]. Dotted line – [36] (Tolman), solid line – [37] (GTKB), semidotted line [9] (Gibbs formula), dashed line – [34].	9
Figure 2.2. A two-dimensional system of hard rectangular particles with length L and width σ either (a) confined by a circular hard wall that forms a cavity with radius R or (b) surrounding a circular hard wall that forms an obstacle with radius R . Adapted from [55].	13
Figure 2.3. Tolman length (δ) of the nucleus droplet and bubble (as indicated) (a) vs scaled overpressure and (b) vs curvature radius of the surface of tension (R_T). The inset displays δ vs $1/R_T$. Adapted from [57].	15
Figure 2.4. (a) Experimental scheme of shear-mode quartz-tuningfork–based (QTF-based) AFM. The inset shows the artistic view of the water meniscus having a highly negative curvature at molecular scale. (b) Typical scanning electron microscopic (SEM) image of a quartz tip with radius of about 40 nm that is glued to one of the QTF prongs. (c) Geometry of the water meniscus. The liquid-vapor interface of the meniscus is in mechanical equilibrium by having the constant mean curvature. Here, r_1 and r_2 are the two principal radii-of-curvature ($r_1 \sim -1$ nm is negative and $r_1 \sim 10$ nm positive in ambient condition) and d is the tip-surface distance. Here, θ_1 and θ_2 are the contact angles [63].	17
Figure 2.5. Micro gas turbine generator cross-section. [73]	19
Figure 2.6. Exploded view of main mechanical design structure for the gyro/accelerometer [86].	21
Figure 2.7. The scaling of different types of forces [103].	22
Figure 2.8. Formation of liquid meniscus at the interface between two rough hydrophilic surfaces [103].	23
Figure 2.9. Schematic of the microturbine device used to test the micro-scale rolling elements [110].	24
Figure 2.10. Cross section diagram of a micro gas levitated bearing [81].	25
Figure 2.11. Schematic drawings of polysilicon surfaces produced by the release treatments [132].	27
Figure 2.12. Schematics of SAM formation process [136].	27
Figure 2.13. Micro-structures fabricated around grain boundaries [140].	28
Figure 2.14. Artistic impression of a mechanically reconfigurable zigzag metasurface (cross-section) infiltrated with a liquid crystal [141].	29
Figure 2.15. (a) Schematic of the cross section of the liquid bearing structure with variations in contact angle from non-wetting to wetting regions; forces acting on the rotor due to surface tension to (b) centre the rotor (c, d) support the rotor in compression and tension [142].	30
Figure 2.16. (a) Satellite bearing retention locations defined by SHP micro-patterns. (b) Cross section A–A showing relationship of rotor, liquid bearings, and stator. (c) Mechanism for tip/tilt restoring torque resulting from an induced rotor tilt [21].	30

Figure 2.17. Exploded view of the side-driven rotary stage on conductive liquid rings [20].	31
Figure 2.18. Liquid droplet on a solid surface.	32
Figure 2.19. Droplet on an inclined solid surface.	33
Figure 2.20. Contact angle at different contacting state. (a) Wenzel state. (b) Cassie state	34
Figure 2.21. Typical optical images of a water droplet on a superhydrophobic coating [162].	35
Figure 2.22. (a) Picosecond laser processing system. (b) SEM images of the periodic microgrooves fabricated on solar glass surface at different laser line intervals [168].	36
Figure 3.1. Typical simulation box showing the coordinate system, equimolar surface and surface of tension schematically for the flat interface case. y_e and y_s are the location of the equimolar surface and surface of tension, respectively. Red particles are the liquid molecules (L), blue particles are the gas molecules (G).	42
Figure 3.2. Typical simulation boxes showing the coordinate system, equimolar surface and surface of tension schematically. (a) and (b) are nanodroplet and nanobubble cases, respectively. R_e and R_s are the curvature radii of the equimolar surface and the surface of tension. Red particles are the liquid molecules (L), blue particles are the gas molecules (G), yellow particles are the hydrophilic wall molecules (S_{phi}) and pink particles are the hydrophobic molecules (S_{pho}). The nanodroplet and nanobubble have a cylindrical shape and the z axis is along the length of the cylinder.	43
Figure 3.3. Snapshots of droplets on a homogeneous solid surface with different ϵ_{SL} . (a) Initial configuration of all the simulations in this figure. (b), (c) and (d) Snapshots of the simulations after systems were balanced with ϵ_{SL} being 0.2, 0.4 and 0.7, respectively.	44
Figure 3.4. Nanodroplets with different sizes confined on the solid surface by alternate hydrophobic and hydrophilic patterns.	45
Figure 3.5. A typical density profile of a nanobubble case. The three-dimensional Cartesian coordinate system at the down-left corner was used in the MD simulation. The cylindrical coordinate system was established by fitting the equal-density profile. The z axis is along the length of the cylindrical bubble. In the r direction, the integration of the surface tension starts from the bulk gas region inside the bubble (the inner red circle) and ends at the bulk liquid region (the outer red circle).	46
Figure 3.6. Local profiles of a flat interface case. (a) Local density profile. (b) and (c) Local normal and tangential pressure component profiles.	47
Figure 3.7. Surface tension, γ , and Tolmann length, δ , along a flat liquid/gas interface.	48
Figure 3.8. Local profiles of a nanobubble case. (a) Local density profile. (b) and (c) Local normal and tangential pressure component profiles.	49
Figure 3.9. Surface tension and Tolman length along the liquid/gas interface of a nanobubble case.	49
Figure 3.10. Density and pressure component profiles for both flat and curved interfaces. (a), (c) and (e) Density, normal and tangential pressure component profiles for flat, nanodroplet and nanobubble interfaces, respectively. (b), (d) and (f) Kinetic and virial components of the normal and tangential pressure for flat, nanodroplet and nanobubble interfaces, respectively.	50

Figure 3.11. The surface tension for nanodroplet cases depicted as γ_D (a) and the Tolman length for nanodroplet cases depicted as δ_D (b) calculated with different procedures.	52
Figure 3.12. Surface tension depicted as γ_F (a) and Tolman length depicted as δ_F (b) for flat interfaces with different ρ_G/ρ_L	53
Figure 3.13. Schematic diagram showing typical force state of liquid molecules.	53
Figure 3.14. Nanodroplets with close curvature radii but different intrusions into the simulation domain.	54
Figure 3.15. The surface tension and Tolman length as a function of R_e . (a) and (b) Surface tension VS for nanodroplets (γ_D) and nanobubbles (γ_B), respectively. (c) and (d) Tolman length VS R_e for nanodroplets (δ_D) and nanobubble (δ_B), respectively. This figure shows all curved interface cases run.	55
Figure 3.16. Effect of curvature on the surface tension and Tolman length obtained by subtracting the effect of ρ_G/ρ_L from the results in figure 3.15. (a) and (b) Curvature dependence of surface tension for nanodroplets and nanobubbles, respectively. (c) and (d) Curvature dependence of Tolman length for nanodroplets and nanobubbles, respectively.	57
Figure 3.17. Effect of curvature on (a) the surface tension and (b) Tolman length.	58
Figure 3.18. Surface tension for (a) nanodroplets and (b) nanobubbles obtained from MD simulations and the (fitted) Tolman equation for interfaces with different curvature.	59
Figure 3.19 Surface tension for (a) nanodroplets and (b) nanobubbles obtained from MD simulations and the fitted Tolman equation for interfaces with different ρ_G/ρ_L	60
Figure 4.1. Schematic diagram of a liquid ring bearing.	63
Figure 4.2. Fabricating process of the bearing.	64
Figure 4.3. (a) Experimental setup. (b) Schematic diagram depicting the testing status of the bearing.	65
Figure 4.4. (a) Schematic diagram depicting the geometric features of the liquid ring. (b) Cross-sectional view of the liquid ring showing the stress analysis (The dashed blue lines show the critical condition of the liquid ring). (c) Cross section of ring showing geometry and stress analysis of the contact line at the critical condition when slip occurs (dashed lines in (b)).	67
Figure 4.5. (a) The cross-sectional view of the liquid ring and the coordinate system. (b) Assumed laminar velocity profile in the liquid ring.	70
Figure 4.6. The coordinate system used to simulate the profile of the liquid/air interface numerically.	71
Figure 4.7. The flow chart of simulating profile of the liquid/air interface for a given load and gap height.	72
Figure 4.8. Simulated profiles of the liquid/air interface (jointed black line) and the junction point of the superhydrophobic and hydrophilic strips on the upper and lower plates (red dots). (a) Simulated profile with the upper contact angle or the load being too small. (b) Simulated profile with the upper contact angle or the load being too big. (c) The right simulated profile.	73

Figure 4.9. The flow chart of simulating profile of the liquid/air interface for a given upper contact angle and gap height.	74
Figure 4.10. The supporting force of the bearing as a function of the gap height. Inserts: Schematic curvature radii in the cross-sectional plane.	75
Figure 4.11. Contributions from the Laplace pressure and the surface tension on the three-phase contact line to the supporting force of the bearing without misalignment.	77
Figure 4.12. Supporting force as a function of gap height for different misalignments at different advancing contact angle on the superhydrophobic surface. (a) Advancing contact angle equals 130°. (b) Advancing contact angle equals 150°. (c) Advancing contact angle equals 170°.	78
Figure 4.13. Supporting force as a function of gap height for different advancing contact angle on the superhydrophobic surface at different misalignments. (a) No misalignment. (b) Misalignment of 50 μm . (c) Misalignment of 100 μm	79
Figure 4.14. Critical gap height and supporting force of the bearing for different misalignments.	80
Figure 4.15. Profile of the outer liquid/air interface at different rotational speeds: 0, 500 and 1000 rpm for two gap heights: (a) 200 and (b) 400 μm	81
Figure 4.16. Profile of the outer liquid/air interface with different liquid ring width: 1, 2 and 3 mm for three different rotational speeds: (a) 0, (b) 500 and 1000 rpm. The gap height of the bearing is all 200 μm	82
Figure 4.17. Maximum dynamic supporting force as a function of the rotational speed for the superhydrophobic surface with an advancing contact angle of (a) 130°, (b) 150° and (c) 170°.	82
Figure 4.18. Maximum dynamic supporting force as a function of the rotational speed for bearings with different liquid ring widths. The gap heights of the bearing are (a) 200 and (b) 400 μm . The advancing contact angle on the superhydrophobic surfaces is 150° for both (a) and (b).	83
Figure 4.19. The torque of the bearing as a function of Re for different gap heights. There are four pairs of curves in every graph. Each pair contains a solid curve which represents the experimental data and a dashed curve which represents the theoretical data. From top to bottom, the four pairs of curves representing 4 gap heights which are yellow for 100 μm , green for 200 μm , purple for 300 μm and blue for 400 μm . For certain conditions, the ration of the experimental torque to the measured torque is labelled with vertical arrows.	84
Figure 4.20. Torque of the bearing as a function of Re. There are four pairs of curves in this graph representing the same data as in figure 4.19 (b). The two red dotted lines around each curve of the experimental data are the fitted lines using the upper and lower limit of the experimental data. The red solid curve represents the critical Res.	84
Figure 4.21. (a) Geometry of the artificial textures on the outer edge of the liquid ring. (b) Torque of the bearing with artificial textures on the edges of the superhydrophobic strips.	85
Figure 4.22. Schematic diagram showing the vortices induced by the outer menisci. The width of the liquid ring in (b) is twice that in (a) and hence the unstable region in (b) affects a smaller fraction of the liquid flow.	86

Figure 4.23. Stress analysis of the concave liquid ring bearing.	87
Figure 4.24. Supporting force of the concave bearing. (a) Supporting force at different gap height for concave bearings with different slant angles. (b) Supporting force of the concave bearing as a function of the slant angle for different advancing contact angle on the superhydrophobic surface.	88
Figure 4.25. Stress analysis of the convex water ring bearing.	89
Figure 4.26. Supporting force of the convex bearing. (a) Supporting force at different gap height for convex bearings with different slant angles. (b) Supporting force of the convex bearing as a function of the slant angle for different advancing contact angle on the superhydrophobic surface.	90
Figure 4.27. Stress analysis of the wavy water ring bearing.	90
Figure 4.28. Supporting force of the wavy bearing. (a) Supporting force at different gap height for wavy bearings with different slant angles. (b) Supporting force of the wavy bearing as a function of the slant angle for different advancing contact angle on the superhydrophobic surface. (c) Supporting force per unit width parallel to the gap of the wavy bearing as a function of the slant angle for different advancing angle on the superhydrophobic surface.	92
Figure 5.1. Schematic diagram of the liquid ring sealed air bearing.	96
Figure 5.2. Sketch of the bearing showing geometrical features in their most general configuration. (a) Sketch of the upper and lower contact lines of the liquid ring. (b) Cross-sectional view of the liquid ring at $\varphi=0$	98
Figure 5.3. Flow chart of theoretical model for the stiffness of the bearing.	102
Figure 5.4. Models for pressurized liquid ring test. Left: stator without liquid ring. Right: stator with a liquid ring on it (the liquid is dyed red).	104
Figure 5.5. Transition band between the hydrophilic and superhydrophobic patterns. (a) A liquid bridge between two plates confined by alternating hydrophilic and superhydrophobic patterns. (b) Schematic diagram of the transition band. (c) SEM image of the transition band.	105
Figure 5.6. The static supporting force of the bearing. (a) Numerical results with different misalignments. (b) Experimental and simulated results.	106
Figure 5.7. Different contributions to the supporting force of the air bearing.	107
Figure 5.8. Contributions of the Laplace pressure inside the chamber and the liquid ring at different misalignment.	108
Figure 5.9. Supporting force as a function of gap height for different θ_{phiR} at different misalignments. (a) No misalignment. (b) Misalignment of 50 μm . (c) Misalignment of 100 μm	109
Figure 5.10. Supporting force as a function of gap height for different θ_{phoA} at different misalignments. (a) No misalignment. (b) Misalignment of 50 μm . (c) Misalignment of 100 μm	110
Figure 5.11. Effect of θ_{phiR} and θ_{phoA} on the critical gap height and the global maximum supporting force of the bearing. (a) and (b) Effect of θ_{phiR} and θ_{phoA} on the critical gap height. (c) and (d) Effect of θ_{phiR} and θ_{phoA} on the global maximum supporting force. ..	111

Figure 5.12. The effect of W_{ring} on $F_{\text{Supporting}}$.	112
Figure 5.13. Concentration of nitrogen in the liquid ring, showing effect of diffusion. (a) 3D plot showing concentration of N_2 as a function of time and position along the liquid ring. (b) 2D plots showing snapshots in time.	113
Figure 5.14. Variation in $F_{\text{Supporting}}$ over time (h constant) showing effect of evaporation. (a) Effect of RH on $F_{\text{Supporting}}$. (b) Effect of ring width W_{ring} on $F_{\text{Supporting}}$.	114
Figure 5.15. Pressurized liquid ring test results.	116
Figure 5.16. The stiffness of the bearing: experimental vs. modelling results. It should be noted here, the gap height of the bearing is decreasing as the bearing is being compressed. Thus, the results in this figure go from right to left in each individual plot.	117
Figure 5.17. Effect of the volume of the air chamber on the stiffness of the bearing. Note here that the results go from right to left as the bearing is being compressed.	118
Figure 5.18. Effect of surface wettability on the stiffness of the bearing. (a) Effect of θ_{phoA} on the stiffness. (b) Effect of θ_{phiR} on the stiffness. Note here that the results go from right to left as the bearing is being compressed.	119
Figure 5.19. The stiffness of the bearing. (a) Effect of ΔR on stiffness. (b) Effect of W_{ring} on stiffness. Note here that the results go from right to left as the bearing is being compressed.	120
Figure 5.20. Experimental dynamic $F_{\text{Supporting}}$ and frictional torque of the bearing. The solid and dashed lines are the experimental and theoretical results (based on the Laminar assumption), respectively. (a) The dynamic $F_{\text{Supporting}}$ of the bearing at different h . (b) The frictional torque of the bearing at different h .	121
Figure A.1. Stress state of a strip in a longitudinal plane of a cylindrical interface.	138
Figure B.1. The volume of section ①. (a) Coordinate system used for calculation. (b) Infinitesimal element of the liquid ring.	140

List of Tables

Table 2.1. Tolman length (δ) obtained with thermodynamic and mechanical routes[38].	12
Table 2.2 The overview of some micro turbines [81].	20
Table 3.1. Values of LJ potential parameters used in the MD simulations.	44
Table 4.1. DHR-1 Technical specifications	65
Table 5.1. Pressurised liquid ring test results.	115

Nomenclature

Chapter 1				
ΔP	Pressure drop across a curved interface		γ	Surface tension
R	Radius of the sphere		δ	Tolman length
γ_R	Surface tension for an interface with a radius of R		γ_∞	Surface tension for a flat interface
R_e	Curvature radius of the equimolar interface		R_s	Curvature radius of the surface of tension
Chapter 2				
γ	Surface tension		Γ	Superficial density
μ	Gibbs potential of the fluid molecules		p'	Pressure in the bulk gas region
p'	Pressure in the bulk liquid region		ρ'	Density in the bulk gas region
ρ'	Density in the bulk liquid region		R	Droplet radius
x	Variable measuring the radial distance from the surface of tension in the direction from liquid to vapour		$\mathbf{P}$	Pressure tensor of the system
r, θ, φ	Three directions of the coordinate system		P_T	Tangential pressure component
P_N	Normal pressure component		m	An integer
$P_{\alpha,\beta}(r; R_s)$	Pressure which equals P_α for r between R_α and R_s and P_β for r between R_s and R_β		k_B	Boltzmann constant
R_c	Mean curvature radius of the interface		v_l	Molecular volume of liquid
T	Temperature		h	Clearance between the contacting surfaces
$\frac{p}{p_e}$	Ratio of the external vapour pressure to the saturation pressure		γ_{SG}	Surface tension of solid/gas interface
θ_c	Contact angle of the liquid on the contacting surface		γ_{LG}	Surface tension of liquid/gas interface
γ_{SL}	Surface tension of solid/liquid interface		S_0	Surface area of a smooth surface
S	Real wetted surface area of a rough surface		ΔS_0	Increment of the apparent wetted surface area
C_r	Roughness factor		ΔE_f	Surface free energy variation
θ_W^*	Apparent contact angle in Wenzel wetting state		A_{SL}	Area of the solid/liquid contacting interface
ϕ_{SL}	Solid-liquid interface fraction		ϕ_{LG}	Liquid/gas interface fraction
A	Total area of the solid surface		θ_C^*	Apparent contact angle of a droplet in the Cassie state
Chapter 3				
γ_∞	Surface tension		P_N	Normal pressure component
P_T	Tangential pressure component		y	Axis normal to the gas/liquid interface
y_G	Location deep inside the bulk gas region		y_L	Location deep inside the bulk liquid region

γ_s	Location of the surface of tension		ρ_G	Molecule number density in the bulk gas region
ρ_L	Molecule number density in the bulk liquid region		ρ_y	Molecule number density at location y
γ_e	Location of the equimolar surface		δ_∞	Tolman length for a flat interface
R_α	Deep inside the bubble (or droplet) region		R_β	Deep inside the outer bulk-liquid (-gas) region
R_s	Curvature radius of the surface of tension		R_e	Equimolar radius of the curved interface
δ_B	Tolman length for nanobubble		δ_D	Tolman length for nanodroplet
γ	Surface tension		U_{ij}	Lennard-Jones potential
r_{ij}	Distance between molecules i and j		ϵ_{ij}	Interacting strength between molecules i and j
σ_{ij}	Characteristic length between molecules i and j		r_{i0}	Equilibrium bond distance
G	Gas molecule		L	Liquid molecule
S_{phi}	Hydrophilic solid molecule		S_{pho}	Hydrophobic solid molecule
T_s	Tether site molecule		r_{yi}	Distance between molecule i and the location of the wall
ϵ_{SL}	Interacting strength between solid and liquid molecules		ρ_G/ρ_L	Gas/liquid density ratio
T_{set}	Temperature of the system		$P_{xx}, P_{yy}, P_{zz}, P_{xy}, P_{xz}, P_{yz}$	6 pressure components of a pressure tensor in a x,y,z coordinate system
r, θ, z	A cylindrical coordinate system		γ	Surface tension
δ	Tolman length		ρ	Density
γ_F	Surface tension for a flat interface		δ_F	Tolman length for a flat interface
γ_D	Surface tension of nanodroplet interface		γ_B	Surface tension of nanobubble interface
$\Delta\gamma_D$	Effect of curvature on the surface tension for nanodroplet		$\Delta\gamma_B$	Effect of curvature on the surface tension for nanobubble
$\Delta\delta_D$	Effect of curvature on the Tolman length for nanodroplet		$\Delta\delta_B$	Effect of curvature on the Tolman length for nanobubble
γ_{R_s}	Surface tension of a curved interface with a curvature radius of R_s		W_z	Width of a longitudinal strip

Chapter 4

R	Radius of the bearing		h_r	Height of the gap
w_{pho}	Width of the superhydrophobic strip		r_{1in_limit}	Upper limit of r_{1in}
w_{phi}	Width of the hydrophilic strip		$r(z)$	Profile of the air/water interface
r_i	Inner radius of the water ring		m	Load on the rotor
r_o	Outer radius of the water ring		g	Gravitational acceleration
γ	Surface tension of the air/water interface		θ_A	Advancing contact angle on the superhydrophobic surface
ΔP	Pressure difference cross the air/water interface		ΔL	Misalignment between the patterns on the rotor and the stator

R_c	Curvature radius of the air/water interface		r_{2in}	Curvature radius of the inner air/water interface in the horizontal plane
r_1	Curvature radius of the air/water interface in the cross-sectional plane		r_{2out}	Curvature radius of the outer air/water interface in the horizontal plane
r_2	Curvature radius of the air/water interface in the horizontal plane		$F_{Laplace}$	Supporting force provided by the Laplace pressure
r_{1in}	Curvature radius of the inner air/water interface in the cross-sectional plane		F_γ	Vertical component of the surface tension
r_{1out}	Curvature radius of the outer air/water interface in the cross-sectional plane		ρ η	Density of water Kinematic viscosity of water
ω	Local rotational speed in the water ring		Ω	Rotational speed of the rotor
T	Frictional torque exerted on the rotor			

Chapter 5

R	Radius of the bearing		R_{in}	Inner radius of the hydrophilic strip
R_{out}	Outer radius of the hydrophilic strip		w_{phi}	Width of the hydrophilic strip
$F_{Supporting}$	Supporting force of the bearing		$F_{Laplace}$	Vertical force induced by the Laplace pressure
$F_{Capillary}$	Vertical component of the capillary force		γ_{LA}	Liquid/air surface tension
θ_{in}	Inner local contact angle of the liquid ring		θ_{out}	Outer local contact angle of the liquid ring
φ	Circumferential angle in the coordinate system		O_U	Center point of the upper patterns
O_L	Center point of the lower patterns		O_s	Origin of the coordinate system
ΔP_{in}	Laplace pressure crossing the inner meniscus of the liquid ring		ΔP_{out}	Laplace pressure crossing the outer meniscus of the liquid ring
r_{in}	Mean curvature radius of the inner meniscus		r_{out}	Mean curvature radius of the outer meniscus
r_{1in}	Curvature radius of the inner meniscus on the cross-sectional plane		r_{1out}	Curvature radius of the outer meniscus on the cross-sectional plane
r_{2in}	Curvature radius of the inner meniscus on the horizontal plane		r_{2out}	Curvature radius of the outer meniscus on the horizontal plane
θ_{inmin}	Minimum inner local contact angle of the liquid ring		θ_{outmax}	Maximum outer local contact angle of the liquid ring
h	Gap height of the bearing		$\Delta R_{in}'$	Local misalignment of the inner contact line
ΔR	Misalignment of the patterns on the rotor and stator		W_{ring}	Width of the liquid ring
$\Delta R_{out}'$	Local misalignment of the outer contact line		θ_{phiR}	Receding contact angle on the hydrophilic surface
θ_{phoA}	Advancing contact angle on the superhydrophilic surface		n	Molar mass of the air inside the air cushion
R_{gas}	Ideal gas constant		T	Temperature
P_{air}	Pressure inside the air cushion		V_{air}	Volume of the air cushion

V_{ring}	Volume of the liquid ring		α	Liquid evaporation coefficient
v	Air flow velocity around the bearing		A	Area of the outer liquid/air interface
L_e	Amount of liquid evaporated per second		X	Actual humidity ratio of the environmental air
X_s	Maximum humidity ratio of the environmental air		C_j	Concentration of gas j in the liquid ring
K_{Hj}	Henry's constant of gas j		t	Time
P_j	Partial pressure of gas j		Δn_j	Molar mass of gas j diffused through the liquid ring
D_j	Diffusion coefficient of gas j in the liquid		ρ	Density of water
T	Frictional torque exerted on the rotor		Ω	Rotational speed of the rotor
η	Kinematic viscosity of water			

Chapter 1 Introduction

The research background and objectives along with the outline of the thesis are presented in this chapter.

1.1 Research Background and Aims

The surface tension is an important interfacial property of an inhomogeneous system. It results from the intermolecular forces at the interface between two bulk phases. Forces induced by the surface tension are usually proportional to the length scale. Typical forces are the capillary force acting on the three-phase contact line of a droplet or a bubble and the force induced by Laplace pressure inside a curved interface. These forces increase linearly with the length and are very small at the macroscale compared to surface forces (such as the drag force) and body forces (such as gravity and inertial forces) which scale with length quadratically and cubically, respectively. Thus, in engineering, where phenomena are most often observed at the macroscale, the effect of surface tension is usually neglected in theoretical work while the results agree well with practical applications. However, as the length scale decreases, forces induced by the surface tension scale down much lower than the surface forces and body forces. This leads to the fact that at the micro-/nano-scale, forces induced by the surface tension outweighs the surface and body forces. This effect causes strong adhesion between wetted surfaces and parts and thus has a profound influence on the design of machines operating at the micro-/nano-scale.

To understand the role which the surface tension play at the micro-/nano-scale, it is important to know the intrinsic properties of the surface tension first. The surface tension is directly related to the pressure tensors to which the intermolecular force is also a main contributor. The pioneering work on the surface tension dates back to the nineteenth century when the Young-Laplace equation [1, 2] was derived using continuum arguments to rationalise its effect at the macroscale. It reads:

$$\Delta P = \frac{2\gamma}{R} \quad (1.1)$$

where ΔP is the pressure drop across a curved interface, γ is the surface tension and R is the radius of the sphere that best matched the local shape of the interface being studied (spherical interface). At the macroscale the surface tension is treated as constant with regard to the curvature of the interface. Equation (1.1) shows great accuracy and has been used for decades. In an inhomogeneous system, two bulk phases (such as liquid and vapour) transit to each other through a layer where the physical properties change dramatically. But there is not an exact physical interface which separates the two bulk phases. Mathematically, two interfaces which separate the two phases explicitly were defined by Gibbs [3]. One is the equimolar surface where the superficial number density of particles (molecules) vanishes. The other one is the surface of tension where the surface tension is supposed to act. We can see that

different particles would contribute equally to the equimolar surface if they are at the same position, as the contribution to the equimolar surface depends on the number of particles. However, this is not the case for the surface of tension, where the intermolecular forces differ between different types of particles (molecules) even if they are at the same position. Thus, the contribution of different types of particles to the surface of tension differs from each other. Given the above, it is not hard to understand that the equimolar surface and the surface of tension normally do not coincide [4-8]. Tolman [9, 10] was among the first several researchers who investigated the distance between the equimolar surface and the surface of tension which was later named as Tolman length (δ). At the macroscale, the curvature radius of a curved interface is much larger than the intermolecular interaction distance. The stress state of a molecule on a curved interface can be simplified as one on a flat interface. Thus, the curvature does not show appreciable effect on the surface tension, which can in turn be regarded as constant for curved interfaces. However, when the curvature radius of the interface reduces to molecular interacting scales, the curvature shows a strong effect on the surface tension. Tolman has derived an equation to show the curvature dependence of the surface tension [9, 10]. By neglecting terms $\mathcal{O}(\delta/R)$ and assuming that δ is constant, the equation for a spherical interface reads:

$$\frac{\gamma_R}{\gamma_\infty} = \frac{1}{1 + \frac{2\delta}{R}} \quad (1.2)$$

where γ_R and γ_∞ are the surface tension for an interface with a radius of R and a flat interface, respectively. However, there are studies in recent decades showing that δ also has a curvature dependence [5, 6, 11-15]. Neglecting the terms $\mathcal{O}(\delta/R)$ may also have an appreciable effect on the results. Mathematically, the Tolman length is normally defined as $\delta = R_e - R_s$, where R_e and R_s are the curvature radius of the equimolar interface and the surface of tension, respectively [5]. Sometimes, this definition can be ambiguous. For example, a curvature radius cannot be defined for a flat interface, while the Tolman length can. Moreover, this definition can lead to opposite results between bubbles and droplets; this will form part of my investigation and will be discussed later in this thesis [16-18]. For a long time, people assume that nanobubbles and nanodroplets resemble each other and would follow the same law regarding surface tension at the scale governed by molecular interactions. However, it is not clear whether this assumption holds true or not. If it is true, what is the law that these two counterparts share?

With the rapid development of micro-electro-mechanical systems (MEMS), micro-turbines, micro-gyroscopes, and micro-generators are becoming increasingly important due to their crucial functions in a system. The size of those devices in MEMS usually ranges from 1 to 1000 microns. However, the friction and wear are severe at such small contacts due to the high surface-to-volume ratio and lubrication methods that are efficient at macro-scale are not directly transferable to the micro-scale. In micro-devices, friction and wear are much more sensitive to the surface roughness and wear debris,

which is very difficult to control at micro-/nano-scales; this renders the use of rolling element bearings, conventionally used in macroscopic systems, unfeasible.

Liquid lubrication which utilizes pressurized liquid between two sliding surfaces to support load is widely used at the macroscale. Because the contacting surfaces of two counter sliding parts are separated by a liquid film, low friction and wear can be achieved. There are two types of liquid lubrication: hydrostatic and hydrodynamic methods. The hydrostatic method uses external energy to pump or pressurize the lubricant into the space between the sliding surfaces. This method can realize low friction at all speeds. However, this method needs external energy input and auxiliary pressurization devices. The hydrodynamic method uses the convergent profile formed by the contacting surfaces to entrain lubricant into the contacting area and lubricate the system. This method does not need auxiliary pressurization devices; however, a full lubricant film can only be formed at high sliding velocity. These two methods are efficient and reliable at the macroscale; however, is not feasible at the micro-/nano-scale because the liquid viscous force would dominate and result in overdamping in such small systems due to the high surface-to-volume ratio.

The fact that lubricating methods efficient at macroscale do not work for MEMS has prompted the development of different systems. Examples are air bearings suspended by electromagnetic or electrostatic forces. These bearings are effective as the sliding surfaces are totally separated by air, however, they all have a complex design and require a control system and auxiliary energy inputs.

It is important to note that at the micro-scale surface tension has a strong effect and is likely to dominate the behaviour of the fluid instead of inertial forces, which tend to dominate at larger scales. This provides a novel way of anchoring the liquid between two solid surfaces and provides an alternative path to lubricate bearings. In the past decade, the idea of liquid lubricated thrust bearings had been proposed and studied. Alternate superhydrophobic/hydrophobic and hydrophilic patterns have been used to create surface energy barriers, which help to pin water droplets on the hydrophilic areas of the rotor surface [19-22]. At such small scales, the surface tension is strong enough to stop the droplets from deforming and the Laplace pressure inside the water droplets supports the load of the rotor. In this way, the solid contact between the rotor and the stator is replaced by a liquid/solid contact [19]. The annular scattered water droplets [21] have later been replaced by water rings, which were continuously deployed along the shear direction [20]. Comparing with the water droplets, this modification eliminated the contact angle hysteresis along the shear direction, thus reducing the frictional torque of the rotor. The startup torque and wobble of the liquid ring bearing has also been studied while the relationship between the frictional torque, the height of the liquid ring and the rotational speed is yet to be investigated. The design of such systems needs to be improved, their performance and potential benefits need to be investigated in detail. A more advanced bearing based on improved theory and further exploitation of these promising concepts can be designed.

The overall aim of this project is to understand the intrinsic properties of the surface tension and utilize the specific properties of the surface tension to design a liquid ring sealed air bearing at the micro-scale. The assumption made at the macroscale that the surface tension is constant with regard to the curvature of the interface may not hold true at the micro-/nano-scale and this, along with other potential factors affecting the strength of surface tension, will be investigated with molecular dynamics (MD) simulations. With the intrinsic understanding of the surface tension obtained with MD simulations, a micro thrust bearing lubricated with liquid rings which are confined with alternate hydrophilic and superhydrophobic patterns can be designed. Based on the experimental conditions in the lab, a prototype of such bearings will be made and tested. The experimental results will be used to optimize the design and the performance of the bearing.

1.2 Research objectives

The research objectives to be completed in this project are listed below:

- i Build a MD model with nanobubbles and nanodroplets confined on a solid surface by alternate hydrophilic and hydrophobic patterns. Through the whole simulation, the contact line of the nanobubbles and nanodroplets needs to be anchored by the patterns.
- ii Deduce a mechanical route to obtain the surface tension based on MD simulations in a cylindrical coordinate system.
- iii Run MD simulations to investigate the effect of potential factors (such as the curvature of the interface and the gas/liquid density ratio across the interface) on the strength of surface tension.
- iv Design a liquid ring lubricated micro thrust bearing and build a numerical model to predict the performance of the bearing, such as the supporting force and the frictional drag of the bearing.
- v Make a prototype of such a bearing with liquid rings confined by alternate hydrophilic and superhydrophobic patterns. Use a rheometer to investigate the performance of the bearing experimentally. Obtain the key performance characteristics of the bearing.
- vi Corroborate the numerical model with experimental results and use the validated model to optimize the design of the bearing.
- vii Upgrade the liquid ring bearing design to a liquid ring sealed air bearing. Build a numerical model of the air bearing and predict its performance.
- viii Make a prototype of the air bearing and use a rhometer to investigate the performance of the air bearing experimentally.
- ix Corroborate the numerical model with experimental results and use the validated model to optimize the design of the air bearing.

1.3 Outline of the thesis

The thesis is divided into 6 chapters. A summary of the content in each chapter is presented below:

Chapter 1 gives an introduction to the research background and aims of the project. The objectives which need to be accomplished are briefly discussed in this chapter along with the outline of the thesis.

Chapter 2 reviews the relevant literature in all areas pertinent to the work carried out in the thesis, from the MD simulations of the surface tension, to tribological problems and potential methods of lubricating devices at the micro-/nano-scale.

Chapter 3 presents methods to investigate surface tension at the nano-scale using MD simulations. The results of the simulations are also discussed in this chapter. The main factors which affect the strength of the surface tension are studied and important trends are obtained.

Chapter 4 presents the design of a liquid ring bearing utilizing the surface tension to build up pressure in the liquid rings and support load. The deformation of the liquid ring interface, the supporting force of the bearing and the frictional torque of the bearing are investigated numerically and experimentally. Experimental results are used to validate the numerical models.

Chapter 5 presents a novel design of a liquid ring sealed air bearing which uses the liquid ring to seal pressurized air in the air chamber and to support the load on the rotor. The air diffusion through the liquid ring, the slip of the contact line and the rigidity of the bearing are investigated numerically and experimentally. Experimental results are used to validate the numerical models.

Chapter 6 summarizes the main findings of the project and provides a perspective overview of the possible avenues to follow in future work.

References lists all cited literature in the thesis.

Published work and Appendix.

Chapter 2. Literature review

The literature relevant to the study of surface tension and the Tolman length, tribological problems in MEMS and potential lubricating methods at the micro-/nano-scale are reviewed in this chapter. The first part summarizes investigations about the surface tension at micro-/nano-scale. Reviewed research topics in this part include the Tolman length and the curvature dependence of the surface tension. In the second part, MEMS devices involving contacting and sliding and the tribological problems encountered in those devices are reviewed. MEMS bearings which have recently been developed are also reviewed. The third part reviews published studies conducted to explore important contributions of the surface tension at the micro-scale. The two different roles the surface tension plays at the micro-scale are then briefly summarized. In the final part, properties of superhydrophobic surfaces and the existing preparation methods are reviewed.

2.1 Surface tension and the Tolman length of a curved liquid/gas interface

Phenomena related to the experimental evidence that the water level in a glass tube with a small inner diameter (as small as the diameter of a hair) is higher than the bulk water level into which the glass tube is dipped, and a metal needle with a higher density than water can float on the water surface, promoted people's understanding of the surface tension. The first seminal progress was made by Young [1] and Laplace [2] in the early nineteenth century. By assuming intermolecular forces (the understanding of molecules and intermolecular forces were not clear at that time), they deduced (separately) the well-known Young-Laplace equation (equation (1.1)), which describes the relationship between the pressure difference across a liquid/gas interface and the surface tension. The surface tension was defined as the tension per unit length along a line on the liquid/air interface and should be equal to the work done by creating a unit area of the interface. An intuitive perspective explanation of the origin of the surface tension is that the liquid molecules possess attractive force to each other. For a molecule in the bulk fluid, the attractive forces from neighbouring molecules are balanced. While for a molecule at the liquid surface, it receives less attractive force from the gas side and thus experience a net inward force. This net force causes molecules on the liquid surface to retract and resist the deformation of the liquid/gas interface. Except equation (1.1), which can be used to study surface tension of spherical interfaces at the macro scale, not much information can be obtained from Young and Laplace's deduction of the equation. When considering a curved interface with smaller and smaller scale, the concept of bulk properties used in Young-Laplace equation, such as the bulk pressure in the liquid and gas regions and the radius of the spherical interface, no longer have unique characteristics. Even the interface itself cannot be uniquely defined as the width of the transition region from liquid to gas become comparable to the curvature radius. With the progress in the understanding of molecules, intermolecular forces,

physics of fluids, thermodynamics and statistical mechanics, more elaborated and accurate equations describing surface tension have been deduced in the following century [23, 24].

2.1.1 Thermodynamic deduction of the relationship between the surface tension and Tolman length

Thermodynamically, relationships between the surface tension of a flat interface and a spherical interface of a droplet surrounded by its vapour were deduced in a spherical coordinate system (r, θ, z) . It is found that the curvature radius of the interface will have an effect of the surface tension when it goes down to the molecular scale. Among those relationships, the Tolman equation [9] (also known as the Gibbs–Tolman–Koenig–Buff (GTKB) equation [25-29]) is the most well-known and broadly used. This equation was deduced based on two interfaces defined by Gibbs [3, 30]. One is the equimolar surface where the superficial number density of particles (molecules) vanishes. The other one is the surface of tension where the surface tension actually acts. A length scale parameter, which was later named after Tolman as the Tolman length, is defined as the distance from the surface of tension to the equimolar surface in the direction from liquid to gas. Based on the Gibbs [3] thermodynamic theory of capillary, a relationship between the surface tension and the Tolman length was deduced by Tolman [9] for a spherical droplet interface within a one-component two-phase system. This has later been extended to multicomponent systems by Koenig [31]. The deduction starts with the dependence of surface tension on potential obtained by Gibbs:

$$d\gamma = -\Gamma d\mu \quad (2.1)$$

where γ is the surface tension, Γ is the superficial density and μ is the Gibbs potential of the fluid molecules. Gibbs also obtained the dependence of the pressure of a homogeneous phase on its state, which in this case can be written as:

$$d\mu = dP' / \rho' = dP'' / \rho'' \quad (2.2)$$

where P' , ρ' and P'' , ρ'' are the pressure and density in the bulk liquid and the bulk gas regions, respectively. Combining equation (2.1) and equation (2.2) along with equation (1.1), after some rearrangement we obtain:

$$\frac{1}{\gamma} \frac{d\gamma}{dR} = \left(\frac{2}{R^2} \right) \left(\frac{\Gamma}{\rho' - \rho''} \right) \left/ \left[1 + \left(\frac{2}{R} \right) \left(\frac{\Gamma}{\rho' - \rho''} \right) \right] \right. \quad (2.3)$$

Let us now consider the superficial molecule number density relative to the surface of tension; this can be obtained by integrating the density profile as follows:

$$\Gamma = \int_{-a}^0 (\rho - \rho') \left(1 + \frac{1}{R}x\right)^2 dx + \int_0^b (\rho - \rho'') \left(1 + \frac{1}{R}x\right)^2 dx \quad (2.4)$$

where x is a variable measuring the radial distance from the surface of tension in the direction from liquid to vapour. $x = -a$ and b are deep inside the bulk liquid and vapour region, respectively. R is the droplet radius. By defining a length δ as the distance from the surface of tension to the equimolar surface in the direction from the liquid to gas, the superficial density at the equimolar surface can be expressed as:

$$\begin{aligned} \Gamma_e = 0 = \int_{-a}^0 (\rho - \rho') \left(1 + \frac{1}{R}x\right)^2 dx + \int_0^b (\rho - \rho'') \left(1 + \frac{1}{R}x\right)^2 dx \\ + \int_0^\delta (\rho - \rho') \left(1 + \frac{1}{R}x\right)^2 dx - \int_0^\delta (\rho - \rho'') \left(1 + \frac{1}{R}x\right)^2 dx \end{aligned} \quad (2.5)$$

Substituting equation (2.4) into (2.5) and rearranging gives:

$$\frac{\Gamma}{\rho' - \rho''} = \delta \left(1 + \frac{1}{R}\delta + \frac{1}{3R^2}\delta^2\right) \quad (2.6)$$

Substituting equation (2.6) into (2.3) we obtain:

$$\frac{1}{\gamma} \frac{d\gamma}{dR} = \frac{\left(\frac{2\delta}{R^2}\right) \left(1 + \frac{\delta}{R} + \frac{1}{3}\left(\frac{\delta}{R}\right)^2\right)}{1 + 2\frac{\delta}{R} \left(1 + \frac{\delta}{R} + \frac{1}{3}\left(\frac{\delta}{R}\right)^2\right)} \quad (2.7)$$

Researchers have also obtained the exact solution to equation (2.7) and many other simplified solutions [6, 32-35]. By assuming that δ is a constant with respect to the curvature of the interface, the exact solution of equation (2.7) can be written as [34]:

$$\gamma = \gamma_\infty \frac{\left(\frac{R}{\delta}\right) \exp\left\{0.647 \cdot \left[\tan^{-1}\left(0.2046 + 0.8967 \cdot \frac{R}{\delta}\right) - \frac{\pi}{2}\right]\right\}}{\left(\frac{R}{\delta} + 1.5437\right)^{0.8012} \left[\left(\frac{R}{\delta}\right)^2 + 0.4563 \cdot \frac{R}{\delta} + 1.2956\right]^{0.0994}} \quad (2.8)$$

By assuming that $\frac{\delta}{R} \ll 1$, equation (2.7) can be simplified as:

$$\ln \frac{\gamma}{\gamma_\infty} = \int_\infty^R \frac{2\delta}{R^2} dR \quad (2.9)$$

Equation. (2.9) can be integrated as:

$$\gamma = \gamma_\infty e^{-\frac{2\delta}{R}} \quad (2.10)$$

Also by assuming that the δ is a constant with respect to the curvature of the interface and integrating both sides from $R = \infty$ to a radius of interest R while ignoring terms $\frac{\delta}{R}$ and $\left(\frac{\delta}{R}\right)^2$ as being commonly one of more orders of magnitude lower than the other terms in the expansion (see equation (2.7)), the well-known Tolman equation (equation (1.2)) which gives the curvature dependence of the surface tension can be obtained. As Tolman pointed out himself, neglecting the terms $\frac{\delta}{R}$ and $\left(\frac{\delta}{R}\right)^2$ might cause an appreciable error in the evaluation of the surface tension when the curvature radius is comparable to the Tolman length. He compared the results obtained with equation (2.7) and of those without neglecting terms $\frac{\delta}{R}$ and $\left(\frac{\delta}{R}\right)^2$ and found that a 5% divergence would occur when $\frac{\delta}{R}$ increases to a value of 0.3. Further assuming that $\frac{\delta}{R} \ll 1$, equation (2.2) can be rewritten as:

$$\gamma = \gamma_{\infty} \left(1 - \frac{2\delta}{R}\right) \quad (2.11)$$

A comparison between different solutions (shown in figure 2.1) has been made by Kalová and Mareš [35]:

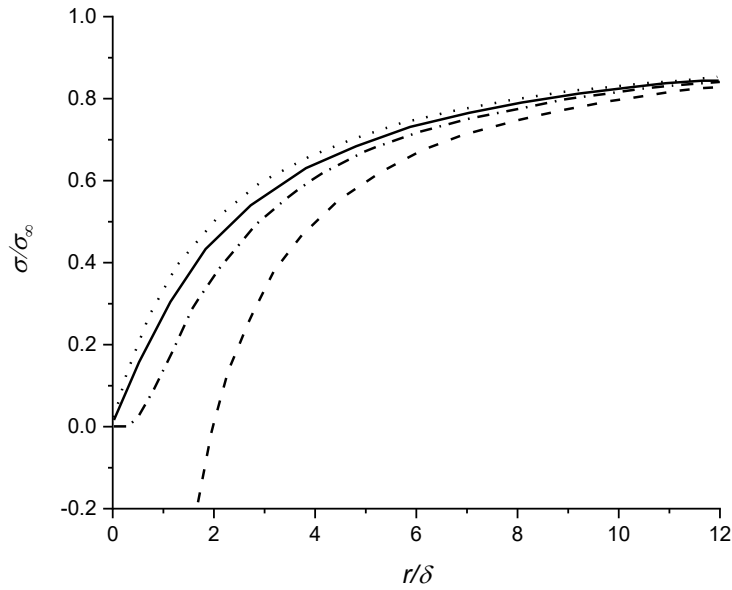


Figure 2.1. Size dependences of surface tension [35]. Dotted line – [36] (Tolman), solid line – [37] (GTKB), semidotted line [9] (Gibbs formula), dashed line – [34].

Combining equation (1.1) and (1.2) a thermodynamic way of calculating the radius of the surface of tension can be obtained [38]:

$$R_s = \frac{3\gamma_{\infty} - \left[9\gamma_{\infty}^2 - 4R_e\gamma_{\infty}\Delta P\right]^{1/2}}{\Delta P} \quad (2.12)$$

2.1.2 Simulations on the curvature dependence of the surface tension and Tolman length

As can be seen, equation (2.7) predicts the relationship between the surface tension and the curvature of the interface. The radius of the surface of tension can also be obtained with equation (2.12) [38]. But this method needs the surface tension for the flat interface to be known first. To obtain equation (2.12), δ was considered as independent of the interface curvature; however, this might not be valid and needs further investigation. Thus, different simulation methods have been developed to calculate the curvature dependence of the surface tension and the Tolman length [5, 7, 8, 11-13, 15, 26, 39-43]. Typical ways include the use of first principle concepts from mechanics, which calculate the surface tension and the radius of surface tension through formally calculating the pressure tensors [38, 44-46]. However, the microscopic definition of the pressure tensors is not unique and difference exists between different definitions [47]. The surface tension can also be obtained based on the change in free energy of an isothermal system with constant volume due to an increase in the interfacial surface area [48, 49]. This method gives an alternate way of calculating surface tension, but curvature radius of the surface of tension cannot be obtained with this method. Researchers have also conducted density functional theory calculations to investigate the curvature dependence of surface tension and Tolman length [50-52].

Adopting the mechanical method, the equations for the surface tension and the radius of the surface of tension for a nanodroplet immersed in its vapour are deduced below [4]. The system can be simplified as a droplet of phase α immersed in its vapour β within a spherical coordinate system r, θ, φ . The pressure tensor of the system is:

$$\mathbf{P} = P_N(\mathbf{e}_r\mathbf{e}_r) + P_T(\mathbf{e}_\theta\mathbf{e}_\theta + \mathbf{e}_\varphi\mathbf{e}_\varphi) \quad (2.13)$$

Let us now consider a flat radial strip with an angular width of $d\theta$, stretching from R_α (in the bulk α region) to R_β (in the bulk β region) in the r direction, at a constant φ . The surface of tension is at R_s in the radial, r , direction. The force acting on one side of the strip can be expressed in two ways: as an integral of $P_T(r)$ over the strip, or, as a resultant action of the pressure P_α acting on the surface between R_α and R_s , the pressure P_β acting on the surface between R_s and R_β , and of the surface tension γ acting at R_s . The two expressions of the force and the moment of the force about the z axis can be equated to give:

$$\int_{R_\alpha}^{R_\beta} r^n P_T dr = \int_{R_\alpha}^{R_s} r^n P_\alpha dr + \int_{R_s}^{R_\beta} r^n P_\beta dr + R_s^n \gamma \quad (2.14)$$

where $n = 1$ and 2 represent the force acting on the strip and its moment about the origin, respectively. Here we define a pressure $P_{\alpha,\beta}(r; R_s)$ which equals P_α for r between R_α and R_s and P_β for r between R_s and R_β . Then from equation (2.14) we have:

$$\gamma = \int_{R_\alpha}^{R_\beta} \left(\frac{r}{R_s}\right)^n (P_{\alpha,\beta}(r; R_s) - P_T) dr \quad (2.15)$$

At the same time, from the hydrostatic equilibrium condition of the system $\nabla \cdot \mathbf{P}=0$ we have:

$$\int_{R_\alpha}^{R_\beta} \frac{dr^m P_N}{dr} dr = \int_{R_\alpha}^{R_\beta} r^{m-1} [(m-2)P_N + 2P_T] dr \quad (2.16)$$

where m is an integer. Integrating the left side of equation (2.16) we obtain:

$$R_\beta^m P_\beta - R_\alpha^m P_\alpha = \int_{R_\alpha}^{R_\beta} r^{m-1} [(m-2)P_N + 2P_T] dr \quad (2.17)$$

In the meanwhile, from the integration of $mr^{m-1}P_{\alpha,\beta}(r; R_s)$ we can write:

$$\begin{aligned} \int_{R_\alpha}^{R_\beta} mr^{m-1}P_{\alpha,\beta}(r; R_s) dr &= \int_{R_\alpha}^{R_s} mr^{m-1}P_\alpha dr + \int_{R_s}^{R_\beta} mr^{m-1}P_\beta dr \\ &= R_\beta^m P_\beta - R_\alpha^m P_\alpha + (P_\alpha - P_\beta)R_s^m \end{aligned} \quad (2.18)$$

Substituting equation (2.17) into equation (2.18) gives:

$$(P_\alpha - P_\beta)R_s^m = \int_{R_\alpha}^{R_\beta} (mr^{m-1}P_{\alpha,\beta}(r; R_s) - r^{m-1}[(m-2)P_N + 2P_T]) dr \quad (2.19)$$

At the surface of tension we have:

$$P_\alpha - P_\beta = \frac{2\gamma}{R_s} \quad (2.20)$$

Substituting equation (2.20) into equation (2.19) gives:

$$\gamma = \frac{1}{2} \int_{R_\alpha}^{R_\beta} \left(m \left(\frac{r}{R_s}\right)^{m-1} P_{\alpha,\beta}(r; R_s) - \left(\frac{r}{R_s}\right)^{m-1} [(m-2)P_N + 2P_T] \right) dr \quad (2.21)$$

Equation (2.15) times 3 for $n = 2$ minus equation (2.21) times 2 for $m = 3$:

$$\gamma = \int_{R_\alpha}^{R_\beta} \left(\frac{r}{R_s}\right)^2 (P_N - P_T) dr \quad (2.22)$$

Equation (2.22) divided by equation (2.21) for $m = 0$:

$$R_s^3 = \frac{\int_{R_\alpha}^{R_\beta} r^2 (P_N - P_T) dr}{\int_{R_\alpha}^{R_\beta} \frac{1}{r} (P_N - P_T) dr} \quad (2.23)$$

Equation (2.22) and (2.23) are the equations used to calculate the surface tension and the radius of the surface of tension for a nanodroplet immersed in its vapour. The Tolman length can be obtained by $R_e - R_s$, where R_e is the radius of the equimolar surface.

By applying the mechanical equilibrium condition ($\nabla \cdot \mathbf{P} = 0$), a relationship between P_N and P_T can be obtained. For a spherical coordinate system, the relationship is:

$$P_T = P_N + \frac{r}{2} \frac{dP_N}{dr} \quad (2.24)$$

Substituting equation (2.24) into equation (2.22) and (2.23), different equations can be obtained. Many researchers have conducted simulations calculating the surface tension and the Tolman length with the mechanical approach described above.

Rowlinson *et al.* [38] conducted MD simulations to calculate the surface tension and the Tolman length of a liquid droplet surrounded by its vapour using both the thermodynamic and the mechanical methods. For the mechanical method, the tangential component of the pressure tensor was computed using equation (2.24). Both the Irving Kirkwood [53] and the Harasima [54] pressure tensors were used.

Table 2.1. Tolman length (δ) obtained with thermodynamic and mechanical routes[38].

Source	A. IK pressure tensor				Thermodynamic route			Mechanical route		
	T^*	N	p_t^*	p_s^*	γ_s^*	R_s^*	δ	γ_s^*	R_s^*	δ
C	0.71	54	0.208	0.016	0.17	1.79	0.63	0.12	1.23	1.18
C	0.71	138	0.220	0.012	0.27	2.56	0.69	0.21	2.03	1.23
C	0.71	250	0.225	0.009	0.34	3.15	0.65	0.34	3.11	0.68
C	0.71	454	0.207	0.009	0.43	4.33	0.56	0.38	3.88	1.00
C	0.71	896	0.184	0.006	0.52	5.85	0.27	0.48	5.41	0.71
C	0.80	54	0.043	0.026	0.02	1.98	0.95	0.04	4.26	— 1.34
C	0.80	138	0.121	0.023	0.11	2.37	0.87	0.14	3.20	0.03
C	0.80	454	0.161	0.017	0.30	4.18	0.52	0.25	3.47	1.23
C	0.80	896	0.143	0.015	0.34	5.36	0.38	0.32	5.04	0.70
O	0.63	256	0.330	0.004	0.56	3.46	0.57	0.47	2.88	1.15
O	0.69	256	0.208	0.007	0.31	3.10	0.74	0.27	2.69	1.15
O	0.77	256	0.081	0.012	0.09	2.53	1.00	0.09	2.73	0.80
O	0.63	2048	0.205	0.001	0.85	8.33	0.05	0.74	7.27	1.11
O	0.76	2048	0.152	0.005	...	...	...	0.54	7.38	0.96
C ^b	0.71	138	0.506	0.0046	0.78	3.09	0.27	0.77	3.07	0.29
B. H pressure tensor										
O	0.63	256	0.320	0.004	...	...	...	0.38	2.4	1.63
O	0.63	2048	0.210	0.001	...	...	...	0.60	5.7	2.7
O	0.76	2048	0.153	0.005	...	...	...	0.32	4.3	4.04

The molecules in their study interact with each other through a shifted Lennard-Jones (LJ) potential cutoff at 2.5σ , where σ is the distance at which the inter-particle potential is zero. The main results are shown in table 2.1. In their study, Tolman lengths between 0.05σ and σ were found using the thermodynamic method with the radius of the droplet ranging from 2σ to 9σ . For the mechanical method, Tolman lengths between 0.03σ and 1.23σ were obtained with the Irving Kirkwood pressure tensors, while much larger values were obtained with the Harasima pressure tensors (Tolman lengths

between 1.63σ and 4.04σ were obtained with the radius of the droplet ranging from 4σ to 8σ). The Tolman length did not show a clear curvature dependence due to the high uncertainties in their study.

The Tolman length of a flat solid/liquid interface in out-of-equilibrium conditions has been calculated with atomistic simulations by Cheng and Ceriotti [41]. In their method, first they used metadynamics to calculate the surface tension of a localized version of the Gibbs dividing surface defined based on an atomic-scale order parameter and its fluctuations. Then, the surface energy change between the localized Gibbs surface and the equimolar dividing surface was obtained. After that, they computed the Tolman length for a model potential, and found a good agreement with the ones obtained by fitting homogeneous nucleation free energy profiles using classical nucleation theory expressions. In their work, a Tolman length ranging from -0.8 to -0.2 reduced LJ units was obtained.

Calvo [43] used the mechanical method to calculate the surface tension of Ag-Au liquid alloys. In this study it was found that the surface tension decreases as the droplet radius of the droplet decreases. A Tolman length for a flat interface of around 2 molecular diameters was inferred from the size variations of the surface tension. The curvature dependence of the Tolman length was not obtained from these simulations.

Wilhelmsen *et al.* [8] used a “hybrid” square gradient theory to investigate the leading correction of the curvature expansion of the surface tension. In their study a negative Tolman length ranging from -0.5 to -0.6 Å was obtained. They found that the Tolman length decreases slightly with the temperature of the system.

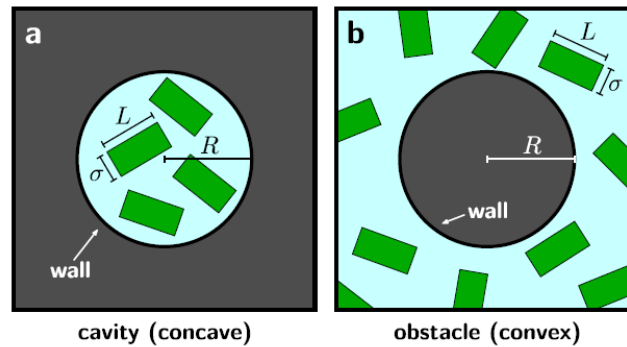


Figure 2.2. A two-dimensional system of hard rectangular particles with length L and width σ either (a) confined by a circular hard wall that forms a cavity with radius R or (b) surrounding a circular hard wall that forms an obstacle with radius R . Adapted from [55].

The curvature dependence of the surface tension for a system with orientable hard rectangles is a two-spatial-dimension system (with the hard rectangles serving as liquid particles) has been explored by Sitta *et al.* [55] with an analytical method, Monte Carlo simulations and density functional theory. Two different curved interfaces had been investigated, which are the cavity and obstacle interfaces. For the cavity interface, the rectangles are held in a circular cavity, while for the obstacle interface, a hard-circular obstacle is surrounded by the rectangles (shown in figure 2.2). By fitting the slope of

relationship between the surface tension to curvature, the Tolman length for different curved interfaces were obtained. They found that the Tolman length increases all the way as the area fraction (similar to density) occupied by the rectangular particles increases from 0 to 0.5. The increasing rate increases with the aspect ratio (length to width ratio) of the rectangles. For rectangles with an aspect ratio of 4, the Tolman length increases from -0.2 to 0.15 times of the width of the rectangles as the area ratio increases from 0 to 0.5.

The curvature dependence of the surface tension of a fluid consisting of spherical particles and a mixture of ethane and butane had been investigated by Philipp and Joachim [56] using non-local classical density functional theory based on the perturbed chain statistical associating fluid theory. They compared two simple approximations of the surface tension, of which one is a first-order expansion of the Tolman length and the other one is a second-order expansion. They found that the second-order expansion had a good agreement with the results obtained with density functional theory for the simple fluid. The results showed that the Tolman length increases almost linearly (with a slightly positive curvature) with the curvature of the droplet. The slope of the linear relationship strongly depends on the temperature of the system. The limits of the Tolman length for a flat interface at different temperatures are relatively close which is around -0.1 in reduced LJ units. For the liquid consisting of alkanes, the Tolman length for flat interface has a value of about -0.38 Å for low temperatures. The Tolman length for flat interfaces with more strongly non-spherical substances turns positive with the temperature approaching the critical point.

Using spherical solid clusters in equilibrium with fluid, Montero de Hijos [15] calculated the surface tension and Tolman length of curved solid/liquid interfaces with classical nucleation theory. Negative values of Tolman length ranging from -0.12 to -0.36 sigma were obtained with the radius of the solid cluster in the range of 7.4 to 30.6 sigma. The Tolman length of a flat interface was obtained by fitting the surface tension linearly with $(1/R_s)$. They found that this Tolman length coincided with that calculated with the classical nucleation theory.

Based on the framework of the Gibbs theory of nucleation, a key equation which allows an approximation of the work for homogeneous nucleation at any overpressure of a metastable single-component fluid was deduced by Kashchiev [57]. By fitting this equation with results obtained by other researchers, a parameter A was obtained. With the parameter A, the overpressure (defined as the pressure difference of the actual pressure of the bulk old phase and that pressure of the bulk new phase at which the chemical potentials of the two bulk phases are equal at the temperature T of the system) dependence of the Gibbs equimolar radius, of the surface tension of the nucleus, and of the Tolman length can be obtained. Then, by fitting these values to corresponding equations, the Tolman length of a flat interface was obtained providing that the surface tension of the flat interface and the spinodal overpressure are independently known. In their work, the Tolman length is defined as the curvature

radius of the equimolar surface minus the curvature radius of the surface of tension. Thus, the Tolman length was negative for droplets and positive for bubbles. The absolute value of the Tolman length (shown in figure 2.3) obtained in their work decreases from around 2.6 (for a curvature radius of surface of tension around 0) to 0.2 (for a curvature radius of surface of tension around 14) reduced LJ units for bubble nucleation. The absolute value of the Tolman length decreases from around 0.8 (for a curvature radius of surface of tension around 0) to 0 (for a curvature radius of surface of tension around 14) reduced LJ units for droplet nucleations.

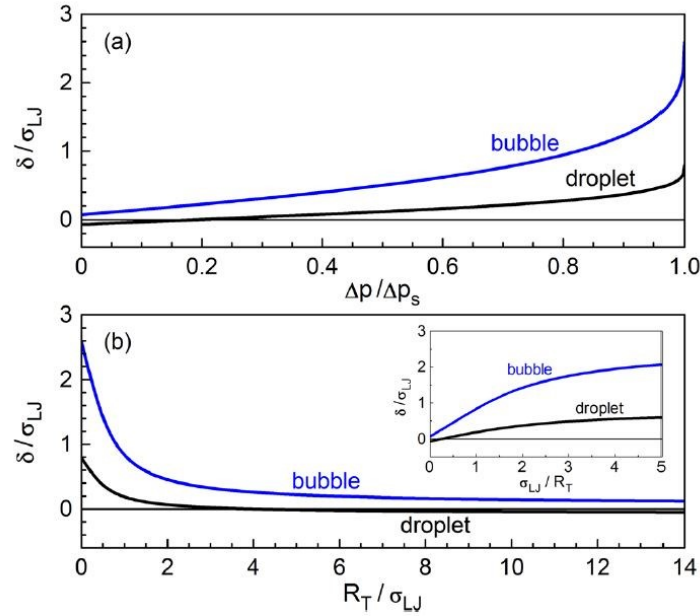


Figure 2.3. Tolman length (δ) of the nucleus droplet and bubble (as indicated) (a) vs scaled overpressure and (b) vs curvature radius of the surface of tension (R_T). The inset displays δ vs $1/R_T$. Adapted from [57].

2.1.3 Experimental investigation of the curvature dependence of the surface tension

While the Tolman theory of the curvature dependence of surface tension was well established, experimental measurement of the surface tension for interface with high curvature is extremely sparse. This has always been an objective of researchers, which in this case is not made particularly easy by the lack of techniques able to explore surfaces of nanobubbles and/or nanodroplets. There were some experiments related to the nano-scale liquid meniscus between two curved solid surfaces, but were not direct measurement of the surface tension [58].

Chioi *et al.* [59] performed experiments to investigate the curvature dependence of the surface tension and the theory of solubility. The curvature of the interface is created by the solute gas molecules (He, Ne, H₂, N₂ etc.) in the solvent (C₆H₆, C₆H₁₂ and CCl₄). The diameters of the cavity created by the solute gas molecules were between 4 and 5 Angstrom. They found that the surface tension can be lowered by two thirds of the value for a plane surface.

Fisher and Israelachvili [60-62] performed experiments to validate the Kelvin and Tolman relation by measuring the adhesion force between two curved mica surfaces with a meniscus of hydrocarbon fluid connecting them. They found that the Kelvin relation is valid for liquid bridges having a curvature radius down to 4 nm. It was also shown that the agreement could be slightly improved for smaller curvature radius by applying the Tolman's correction to the surface tension due to the curvature of the interface.

Similarly, using a Surface Forces Apparatus, Christenson [58] investigated the adhesion force between two molecularly smooth mica surfaces with a liquid bridge between them. They conducted experiments with 3 different liquids (cyclohexane, n-hexane, and water) and the relative vapour pressure of the system was controlled during the experiments. The distance between the solid surfaces was reduced below 4 nm. The adhesion force between the two solid surfaces experienced different stages as the gap width and the relative vapour pressure varied. Those are well explained with the changing of the dominating force between the solid forces. However, their measurements did not give any direct information on the curvature dependence of the surface tension.

Most recently, Seongsoo *et al.* [63] provided relatively direct evidence for the curvature dependence of the surface tension in capillary condensation experimentally (see the schematic diagram in figure 2.4). They obtained a Kelvin-Tolman equation by combining the Kelvin and the Tolman equation:

$$\frac{1}{R_c} = \frac{k_B T}{v_l \gamma_\infty} \left(1 + \frac{\delta}{R_c} \right) \ln \frac{P}{P_e} \quad (2.25)$$

where R_c is the mean curvature radius of the interface, k_B is the Boltzmann constant, T is the temperature, v_l is the molecular volume of the liquid, and $\frac{P}{P_e}$ is the ratio of the external vapour pressure to the saturation pressure. By fitting of equation (2.25) to their experimental results, the values of δ can be obtained. They found that when the curvature dependence of the surface tension is taken into account, the Kelvin equation is valid down to 0.5 nm. However, a direct measurement of the surface tension and the Tolman length for interface with extremely high curvature is still impossible.

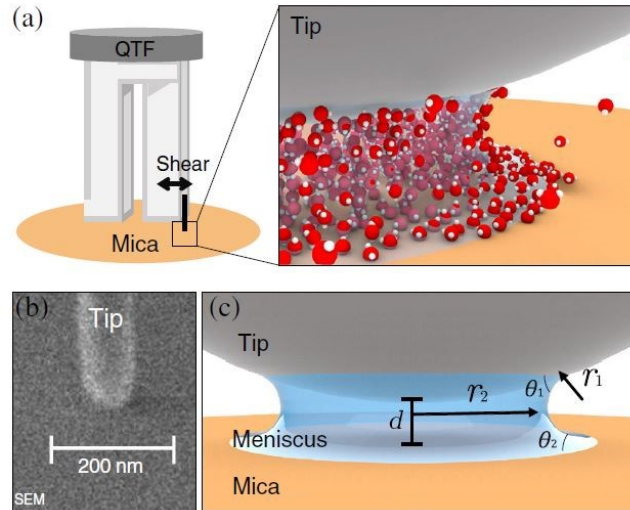


Figure 2. 4. (a) Experimental scheme of shear-mode quartz-tuningfork–based (QTF-based) AFM. The inset shows the artistic view of the water meniscus having a highly negative curvature at molecular scale. (b) Typical scanning electron microscopic (SEM) image of a quartz tip with radius of about 40 nm that is glued to one of the QTF prongs. (c) Geometry of the water meniscus. The liquid-vapor interface of the meniscus is in mechanical equilibrium by having the constant mean curvature. Here, r_1 and r_2 are the two principal radii-of-curvature ($r_1 \sim -1$ nm is negative and $r_1 \sim 10$ nm positive in ambient condition) and d is the tip-surface distance. Here, θ_1 and θ_2 are the contact angles[63].

Except the liquid bridge condensed between two solid surfaces, the long lifetime of nanobubbles on a solid surface submerged in water [64–68] also draws people’s attention to the curvature dependence of surface tension for interfaces with nano-scale curvature radius. The existence of these nano bubbles has been widely reported with the atomic force microscopy (AFM) [69, 70] and through optical visualization [71, 72]. These nano bubbles have smaller contact angles than the predicted by the Young’s equation and can survive much longer than expected. With such small radius, the Laplace pressure inside these bubbles is expected to be very high and gas inside the bubble is expected to dissolve into the liquid within a time scale of μ s. Understanding the curvature dependence of surface tension could shed light on this phenomenon.

Nicolas and Frédéric [14] investigated the surface tension and Tolman length of ethanol and n-heptane with experiments on nucleation of bubbles. A Tolman length ranging from -0.05 to -0.15 nm was obtained for flat interface. They also found that the Tolman length has a temperature dependence which leads to a slight decrease of the Tolman length as the temperature increases.

2.2 Tribological problems of Micro-Electro-Mechanical Systems (MEMS)

The second main area relevant to the work performed in this thesis requiring an extensive literature review is that of bearings and tribology of microscopic devices. Micro-electro-mechanical systems (MEMS) are micro machines/devices that range in size from 1 to 1000 microns. They have been widely used in both civilian and military equipment, such as the accelerometers in vehicles, inkjet printer heads and micromirrors in display devices. However, few of these MEMS applications involve contacts and

sliding. Many other MEMS devices rely on the use of assemblies and surface interactions, such as micro-motors and turbines for micro-harvesters, which can generate power even with very slow wind speeds, and gyroscopes in mobile equipment. These are limited by severe tribological problems, such as stiction, high friction and severe wear problems resulting from high surface forces. Surface forces, which are negligible at the macroscale such as capillary forces, electrostatic forces and Van der Waals forces can be comparable to or even larger than the actuation forces at the micro-scale. These forces cause the high friction, severe wear, short life and sticking during operation in MEMS devices.

2.2.1 MEMS devices involving contacts and sliding

In the 20th century, due to the lack of effective methods for dealing with the severe tribological problems at the micro-scale, the development of MEMS only saw a significant growth in devices that do not make use of surface interactions to transmit power, such as thermal, electrostatic, piezoelectric and magnetic driving sensors and actuation systems. However, in the recent decades, researchers have realised the need and the importance of developing MEMS devices involving contacts and sliding, such as micro-motors, -turbines, -accelerometers and gyroscopic systems. With the help of more advanced MEMS fabrication methods such as Deep Reactive Ion Etching, many devices such as triaxis accelerometers and MEMS gyroscopes have been commercialised. Facing the severe wear and friction problems in MEMS devices, many techniques aimed at reducing wear and friction at the micro-scale have been proposed and tested. MEMS technology has also been applied in the fields of biotechnology, medical technology and information communication technology. It has already become an important part of our daily life.

Micro-engines

Micro-engines are one type of MEMS devices involving contacts and sliding. In 1997, a group from MIT proposed a new class of MEMS engine (see figure 2.5) which was as efficient as the best large sized machines produced then [73]. With considerable design, analytical, and experimental work, they proved that micro-heat engines are feasible, and this opened up a host of possibilities including various thermodynamic machines. The MIT micro-engine project was one of the earliest projects funded by the Defense Advanced Research Projects Agency (DARPA) in this area. Their work encouraged further research and investment in the field of micro-engines.

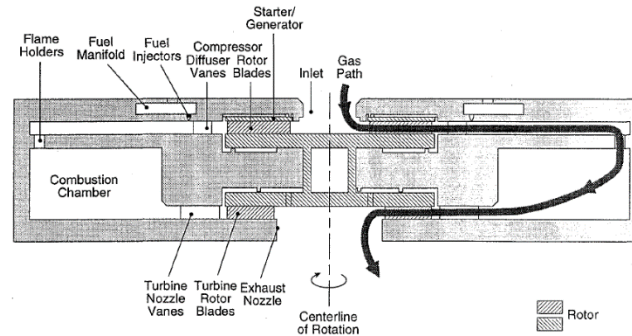


Figure 2.5. Micro gas turbine generator cross-section. [73]

This micro-engine was optimized in following work conducted by the same group. As the construction of combustion engines and associated components at the micro-scale is unprecedented, they verified the fundamental engine functions and theory before complex systems were attempted. With their progress in combustion, high-speed gas bearings and the principle of electric induction [74-77], they were able to make far more advanced systems with higher levels of system functionality. Following their work, many other groups made progress in micro-engines. For example, other micro-combustors have been proposed and fabricated and a few of them appeared to operate with good combustion efficiency [78-80].

An integrated system called micro FIRE, was a MEMS electrical power generator, designed by Maruta and co-workers in 2001 [79]. The system consisted of a combustor, a counterflow heat exchanger and thermoelectric power generation devices. The catalytic combustion technique for producing thermal energy in the system was studied numerically. The combustion took place in small diameter (1 mm) flow reactor tubes at low Reynolds numbers. Coupling the FLUENT code to external subroutines, which model the surface chemistry at the channel wall, the process was studied numerically, and the results proved the validity of the potential application of catalyst combustion technique.

A gas turbine engine having a length of about 10 cm was designed [80] in 2004. This solution was aimed at replacing those small power units, which were relatively inefficient, heavy and inconvenient. To improve the efficiency of the gas turbine, an active way of controlling the clearance between the compressor blades and the shroud was invented. In this technique, the tip clearance was measured and used to actively control the gap between the moving and stationary parts by a feedback loop; this can be in turn used to improve the efficiency of the micro-turbines.

Although the funding initiative from DARPA has ended, the MIT micro-engine project has triggered the enthusiasm around the micro combustion engine. Many micro combustion engines have been fabricated in labs (see table 2.2) [81]. As the micro-scale manufacturing techniques drastically improve, technological advancements are enabling the development of new solutions that will hopefully make well-designed micro-engines part of our daily lives in the near future.

Table 2.2 The overview of some micro turbines [81].

Region	Organization	Type	Diameter/mm	Rotational speed/rpm	Output/W
US	MIT	radial	4	2,400,000	60
	MIT	radial	6	1,200,000	52
	Stanford	axial-radial	12	800,000	—
Asia	Utokyo	axial-radial	8	1,170,000	300
	Tohoku Univ.	axial-radial	10	870,000	475
	XJTU	radial	10	930,000	485
	SIMTech	radial	8.4	—	—
	KIMM	radial	—	400,000	500
Europe	KUL	axial	10	250,000	44
	AIT	radial	10	35,000	10
	ICL	axial	12	140,000	10
	ETH Zurich	radial	16	500,000	100
	WUT	disk	30	176,500	800

Micro-gyroscopes

Micro-gyroscopes based on levitation effects also involve contacts and sliding. They have been shown to be capable of reaching tactical-grade (the In Run Bias Stability (IRBS) in the gyroscope is between 0.5 and 5 degrees per hour) while it cannot be reached by equivalent vibratory counterpart because of structural constraints. Therefore, there is much significance and potential benefit in the development of levitated micro-gyroscopes.

One of the methods adopted for levitating the rotor of micro-gyroscopes is magnetic levitation. The idea of magnetic levitation originated in 1939 [82, 83], when people found that a conducting plate can be levitated stably above two groups of concentric circumferential coils. After that, in 1997, Williams et al. [84] invented a frictionless micromotor with an aluminium rotor levitated, constrained laterally and rotated by electromagnetic induction. The levitation and torque were produced by the high-frequency magnetic fields generated by a monopole stator coil. In their initial test, they achieved angular velocities more than 1000 rpm and the motor ran for over 100 hours without degradation. However, their version of micromotor did not have a displacement sensing system.

A few years later, in 2000, Shearwood et al. [85] improved the design of the micro-gyroscope. In their design, electrodes are integrated into the planar coil allowing the angular-rate of the device to be measured about two orthogonal axes, and acceleration along the third, which worked as a multimode inertial sensor. The rotor was levitated and constrained laterally by the repulsive force produced by the interaction between the eddy currents in the rotor which is induced by a high frequency AC current, and the excitation current. The rotation of the rotor was induced by a temporally and spatially phase-distributed current. However, limited by the output torque, viscous drag, and the stiffness of the magnetic suspension, the maximum rotating speed was still 1000 rpm, which limited the angular sensitivity of the system.

In 2004, a micro-gyroscope with its rotor levitated electromagnetically and having separated rotation, levitation and stability coils was invented by a group at Shanghai Jiao Tong University (see Figure 2.6) [86]. They presented a detailed design structure of a rotational gyroscope with an electroforming nickel rotor employing low-cost UV-LIGA (Ultra Violent Lithographie (Lithography), Galvanoformung (Electroplating) and Abformung (Molding)) technology. Almost every aspect was considered in the

design for their micro-gyroscope, such as gyroscopic action of micro rotor, methods of stable levitation, micro displacement detection and control, rotation drive and speed control, vacuum packaging and microfabrication.

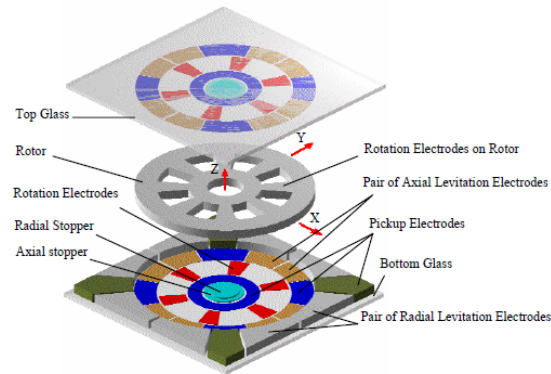


Figure 2.6. Exploded view of main mechanical design structure for the gyro/accelerometer [86].

In 2005, a concept of a magnetically levitated gyroscope packaged with magnetic actuator quadrants and a U-shaped stator was reported by Dauwalter et al. [87, 88]. In their prototype tests, they adopted four techniques for position sensing.

Besides magnetically-induced levitation, many other ways to levitate the rotor of the MEMS gyroscope have been tested. Electrostatic levitation is another popular method. Early in the 1990s [89], an electrostatically levitated micromechanical rate gyroscope prototype consisting of a motor drive, position sensors, and non-rotary actuators for rebalance and suspension was first demonstrated by SatCon Technology Co.; they proved that the design of the magnetically levitated micro gyroscope could be fabricated using the techniques available at that time.

Tokimec and Tohoku universities have also carried out some work in this area [90-93]. In 2006, they developed a ring-shaped gyroscope having radial stators with a narrow gap formed by deep reactive ion etching (DRIE). The rotational speed of the rotor could be maintained at 74,000 rpm. Compared with the disc-shaped rotational gyroscope, a lower voltage was needed for the ring-shaped gyroscopes to control the levitation along the radial axes. A turntable with a resolution of 0.001 deg/s was used to test the performance of the gyroscope; the results showed that the measured noise of the gyroscope output was about 0.002 deg/s/Hz^{1/2}.

Another group at the University of Southampton also described a system which could levitate a disk using electrostatic force [94, 95]. Due to the very small frictional torque of the disk when it is rotating, it could be used as a micro-gyroscope. After that, a prototype of a gyroscope with an electrostatically levitated rotating disk was designed and made [96, 97] by a microfabrication technique [98] based on micro-molding and electroplating using a dry film thick negative photoresist.

Thanks to all the contributions made by the researchers working in this area, electrostatically levitated micro-gyroscopes have been made commercially available and used in industry. In the electrostatically levitated system, there is no contacting friction and air-film damping dominates. In the 21st century, many researchers started to optimize the control system of the electrostatically levitated gyroscope [99-102].

2.2.2 Tribological problems

In MEMS systems, capillary forces and electrostatic forces which are negligible at macro-scale start to dominate due to size effect and their contribution at the micro-scale. The roles, which different forces play at different scales, are related to the physical properties of the object such as volume, mass, surface area, surface topography etc. All these physical parameters are related to the length of the object and these relationships are governed by scaling laws [103]. When the length scale l goes down, the capillary force decreases proportionally, the electrostatic force and the frictional force decrease at a scaling of l^2 , the weight, the inertia force and the electromagnetic force decrease at a scaling of l^3 , while the electromagnetic force decrease at a scaling of l^4 . Figure 2.7 shows the scaling of different types of forces as a function of the critical system length (radius in this example) in a log-log plot. Therefore, in MEMS devices, capillary, Van der Waals and electrostatic forces outweigh weight and inertial forces, and this causes strong stiction, high friction and significantly reduces the lifetime of the sliding parts.

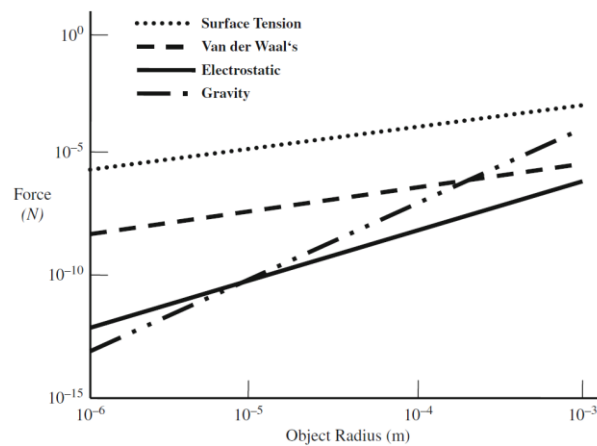


Figure 2.7. The scaling of different types of forces [103].

Capillary force

At the micro-scale, the capillary force causes the strongest adhesion and stiction. When liquid vapour (from a lubricant or water in the atmosphere) condenses in the gap between contacting surfaces and forms a liquid film, a pressure difference will form between the two sides of the liquid/air interface, which can be calculated using the Laplace equation:

$$\Delta p = \frac{\gamma \cos \theta_c}{h} \quad (2.26)$$

where γ is liquid/air interface tension, h is the clearance between the contacting surfaces and θ_c is the contact angle of the liquid on the contacting surface. If θ_c is smaller than 90° , the pressure inside the liquid film will be smaller than that outside the film. This pressure difference can cause severe adhesive force between the contacting surfaces and results in high friction [104]. Due to the significant adhesion, in some cases the friction force has been found to be larger than the normal load, giving a friction coefficient greater than one [103] – see also mechanisms responsible for this described in figure 2.8. De Boer et al. showed the dependency of adhesion energy on relative humidity [105]. They used the length of a one-end anchored micro cantilever to quantify the adhesion energy. At high relative humidity, the gap between the two surfaces becomes filled with liquid and hence, the measured work of adhesion is expected to equal twice the water surface tension [103]. Mastrangelo and co-workers found that for a silicon against silicon contact, with a roughness of around 3 nm, the adhesion energy resulting from water condensation could reach 0.14 Jm^{-2} under 100% relative humidity [106].

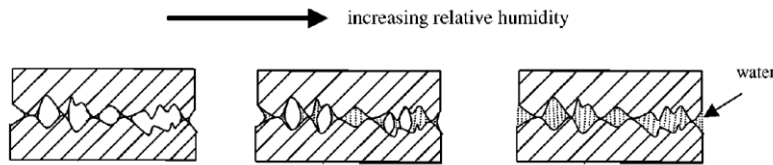


Figure 2.8. Formation of liquid meniscus at the interface between two rough hydrophilic surfaces [103].

Electrostatic Force and Van der Waals Force

Electrostatic and Van der Waals forces might be also important at the micro-scale, although capillary forces are always the strongest. Electrostatic attracting forces usually arise from the electrostatic charging [103], while tribo-charging of sliding surfaces and electrons trapped in the oxide layer of MEMS surfaces would also result in electrostatic forces within MEMS contacts [107]. Thus, electrostatically actuated devices and systems characterised by low humidity are more likely to suffer from electrostatic attraction. Van der Waals forces, and in some cases “chemical” forces such as hydrogen bonding and solid bridging also plays a very important role in MEMS devices. It results from the mutual electric interaction of the induced dipoles in the contacting surfaces [108]. However, the Van der Waals force drops much faster than other contributions and it is usually negligible at distances larger than 20 nm [34] and can often have little effect on adhesion. Van der Waals adhesion is much smaller than the capillary condensation adhesion normally and is only dominant when the relative humidity is very low (<30%) or the contacting surfaces is water-repellent [104, 109]. The Van der Waals adhesion is mostly affected by the surface roughness as the force is determined by the real contact area.

2.2.3 MEMS bearings

Micro ball bearings

Many methods have been studied to reduce the wear and friction at the micro-scale. Micro ball bearing is one solution which has been proposed and studied [110-114]. Although widely used in large components, ball bearings do not work well at the micro-scale. Ta-Wei Lin et al. [111] characterized the friction behaviour of micro ball bearings using an in-situ non-contact experimental system whose measuring error was less than 2%. They showed that the micro ball bearings have an average static COF of 0.01 and an average dynamic COF of 0.007 between stainless-steel and silicon-micromachined contacting surfaces without load at 27 C° and 40% relative humidity. However, the average static COF and the average dynamic COF increased to 0.07 and 0.045 respectively when the load was 40 g in the same configuration.

Hanrahan et al. [110, 114] investigated the wear mechanism in micro ball bearings (see figure 2.9). They found that ball material adhesion, which was mainly caused by the free surface energy, was the primary wear mechanism. Therefore, it is very important to minimize the free surface energy in order to achieve low wear in micro-scale rolling bearings. Thus, unlike macro-scale ball bearings, where the minimization of contact pressure, and thus maximization of contact area, is desired, the systems using micro-scale rolling bearings should be designed to minimize contact area and/or surface free energy. They also found that surface properties had a significant effect on the friction of the micro-scale rolling bearing. Thus, controlling surface roughness which is very hard to do at the micro/nano-scale is crucial to reduce wear and friction. The difficulties encountered in controlling the shape and the surface properties of the micro-balls and raceways limited the application of the micro-scale rolling bearings.

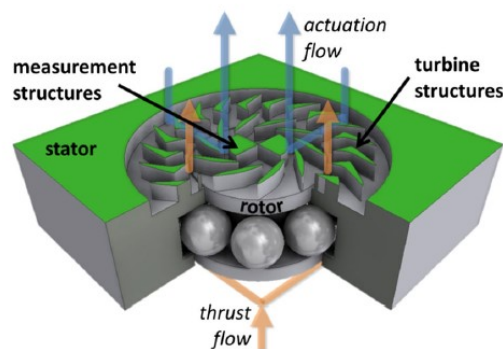


Figure 2.9. Schematic of the microturbine device used to test the micro-scale rolling elements [110].

Microscopic liquid film bearings

Liquid lubrication as a prevalent method of reducing friction at the macro-scale has also been tested at the micro-scale. In large components, the liquid is entrained into the small gap between two contacting surfaces and is pressurized. When the sliding speed between the two contacting surfaces becomes

sufficiently high, the pressure in the lubricant film is high enough to enable separation of the two surfaces. Thus, the friction is significantly reduced. However, at the micro-scale it may be very hard to maintain a speed which is sufficiently high to form a stable thin film between the two sliding surfaces. Moreover, the viscous drag force has been considered to be too high for a micro-bearing [115]. Researchers also found that the maximum rotation speed of the liquid lubricated bearing is small, because the viscous drag force would dominate when the speed becomes high, hence causing overdamping. Therefore, liquid lubrication was concluded to be inappropriate for micro lubrication by some researchers and limited research has been conducted in this area.

However, in recent years, Reddyhoff et al. [116] have measured the friction of micro silicon surfaces lubricated with liquids having very low viscosities such as hexadecane, toluene silicone oil and water. They found that the friction coefficient of low viscosity liquid lubricated silicon surfaces could also be reduced to values below 0.1 at high rotational speeds (5000 rpm), which indicated that liquid lubrication might be feasible for micro devices operating at high speeds [117]. Further studies need to be conducted before this method is used in MEMS devices.

Gas levitated micro bearings

Compared with rolling-element or liquid-lubricated micro bearings, the gas levitated micro bearing (see figure 2.10) has the smallest friction, near-zero wear and no contamination which makes it a popular candidate to support the rotating devices in MEMS. With the development of the micro combustion engines, where micro-bearings with high working speed ($\sim 10^5$ rpm) and high-temperature resistance are needed, gas levitated micro-bearings have been well studied [118-123]. Much research and many advances have been made in gas levitated micro-bearings and the study of their lubrication characteristics [124], damping stiffness analysis [125, 126], nonlinear dynamic characteristics [127] performance testing [127-129] and manufacturing [119, 122, 130].

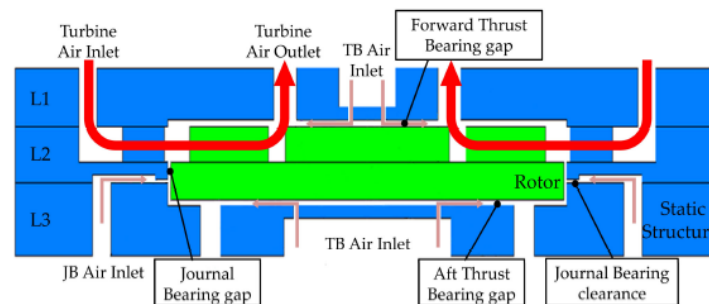


Figure 2.10. Cross section diagram of a micro gas levitated bearing [81].

To summarise the findings from the literature in the field of micro-scale bearings, different issues seem to emerge with different potential solutions being developed. On one hand, when rolling element bearing solutions have been trialled it was found that they were negatively affected by the fact that the surface roughness and the shape of the rolling balls is very hard to control while friction and wear are

very sensitive to the surface roughness. On the other hand, air levitated bearings can deliver reduced friction, but the continuous injection of air consumes extra energy. Moreover, a complicate control system is needed to operate the air-levitated bearings. Thus, a more efficient lubricating method is still urgently needed.

2.3 The surface tension at micro/nano-scales

As mentioned above, as the scale reduces, different forces contribute according to different scaling laws. At the micro-scale, the capillary force which is caused by surface tension causes the strongest adhesion and stiction and dominates the performance of MEMS devices. Thus, it is very important to obtain a good understanding of the effects generated by surface tension at the micro-scale.

2.3.1 Avoiding adhesion of surfaces

Considering a molecule/atom in the bulk of a homogeneous liquid/solid, the forces acting on it are statistically distributed in all directions. However, a surface molecule at the air-liquid/air-solid interface has strong forces acting upon it and “pulling” it toward the liquid/solid; this is due to the fact that the air-liquid/air-solid adhesive forces are much smaller than the liquid-liquid/solid-solid cohesive forces. Surface tension is the net intermolecular force acting on the surface molecules of a liquid. Surface energy is the relevant energy of these bonds for both liquids and solids. The molecules on the surface have more energy compared with the molecules in the bulk of the material and show an attraction to other molecules sufficiently close to the surface. Compared to other forces at the macro-scale, such as gravity force and initial forces, these surface forces are small enough to be neglected. However, at the micro-scale, the contribution of such forces can be significant (can become the dominant force) and cause severe wear and friction.

As has been mentioned above, the transformation of the lubricant vapour or water vapour to liquid phase (condensation) in MEMS devices causes the formation of liquid films between two surfaces. However, there are also methods to reduce the adhesive forces caused by the surface tension. One such method is to increase the contact angle of the contact surface (decrease the surface energy) [22, 131] and the other one is to decrease the liquid condensed area (wetting area) [109].

Hydrogen termination

To reduce the surface energy, and thus increase the contact angle of the contacting surface at the micro-scale, a variety of surface modifications have been developed such as hydrogen termination [132, 133], self-assembled monolayers (SAM) [134-137] and plasma-polymerized polymers (58). Hydrogen termination is an effective method to reduce surface energy, and thus stiction, of MEMS contacts; this method makes the silicon surface hydrophobic with hydrofluoric acid (HF) or ammonium fluoride (NH₄F). By doing this, the hydrophilic oxide layer of the silicon surface is etched away by the fluorine

acid or the ammonium fluoride, and the contact angle of the surface is increased. Houston et al. [132] found that the work of adhesion is reduced by a factor of 2000 through treating the oxide-coated surface with NH_4F . Using x-ray photoelectron spectroscopy and atomic force microscopy they found that the reduction is not only due to the effect of the surface chemistry but also to topographical changes (see figure 2.11). The roughness on the surface will further decrease the work of adhesion and this also has been shown using advanced modelling techniques [138].

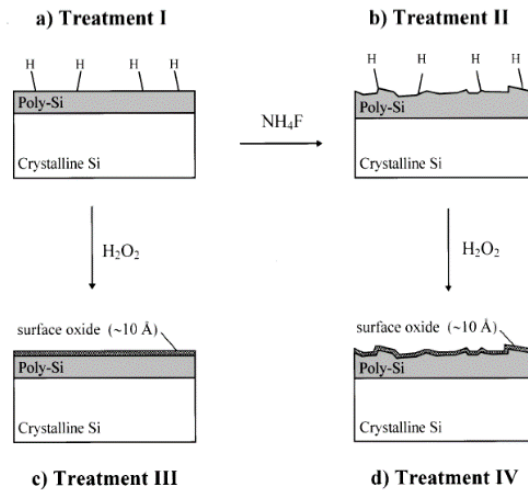


Figure 2.11. Schematic drawings of polysilicon surfaces produced by the release treatments [132].

Self-assembled monolayers

Self-assembled monolayers (SAM) is another way to reduce the stiction at the micro-scale (see Figure 2.12). Using cantilever beam arrays, Maboudian et al. [136] demonstrated that self-assembled monolayers have the ability to reduce the work of adhesion, although the extent of such reduction depends on the surface topography, e.g., surface roughness. The friction and wear characteristics of SAM coated surfaces was tested using a lateral friction force method. They found that the static coefficient of friction decreased from 2.0 for SiO_2 to 0.1 for SAM-coated microstructures; the authors also showed that such a reduction could be maintained after 1 million contact cycles at an equivalent contact pressure of 26 kPa.

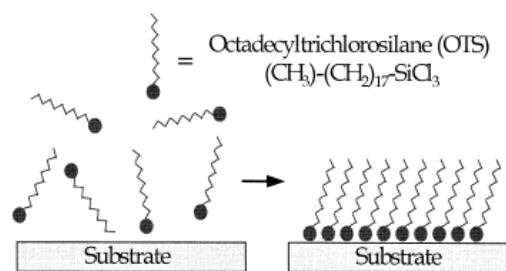


Figure 2.12. Schematics of SAM formation process [136].

Surface texturing

Typical ways of decreasing the liquid condensed area include texturing, roughening the surfaces and using “spacers” [134, 137, 139]. Increasing the surface roughness can be done by using longer HF or BHF (HF with a buffering salt) etch times, which result in an over-etching of the Si micro-structures. The etching can also be done in a $\text{CCl}_4/\text{He}/\text{O}_2$ plasma after the release has been completed. The etching speed of the SiO_2 is much smaller than that of etching the silicon. Thus because the oxide layer thickness is not uniform, the silicon surface is affected by spatially-varying etching rates/amounts, which increases the surface roughness significantly [139].

Yee and co-workers increased the silicon surface roughness by fabricating micro holes (micro textures) over the surface [140]. Phosphorus is used to speed up the oxidization process at the grain boundaries, which results in a thicker oxide layer around the grain boundaries. Because of the difference between thickness of oxide layers around the grain boundary and the rest of the surface, the etching process can be conducted to an extent where the thinner oxide layer is removed whereas the thicker oxide layer around grain boundaries remains. The remaining oxide layer can function as a mask and further etching can be conducted in the masked region and micro textures generated around the surfaces. Figure 2.13 below demonstrates the micro textures formed using this technique.

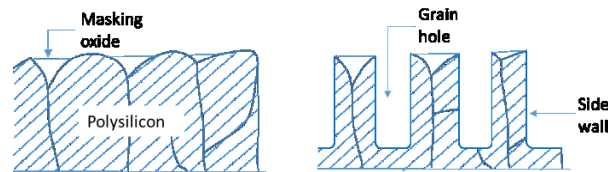


Figure 2.13. Micro-structures fabricated around grain boundaries [140].

The RMS roughness of the silicon surface after this process could reach 52.7 nm. The roughness of untreated silicon surfaces is about 0.3 nm. The adhesion energy density is largely reduced (around 20 times) as a result of the smaller contact area (wetting area) resulting from the increased roughness.

Liquid crystals

In recent years liquid crystals have also been used to control stiction in MEMS devices (see figure 2.14) [141]. Using a NEMS-based tunable photonic metamaterial, where reliable switching of optical response was achieved for the entire range of nanoscopic structural displacements, the authors demonstrated that stiction can be eliminated by infiltrating NEMS with nematic liquid crystals. Compared to the existing methods, their way of eliminating stiction is straightforward and easy-to-implement. Such methods introduced an active mechanism for controlling stiction, which enabled a reversible transition between stiction-free and the stiction-limited regimes of NEMS operation.

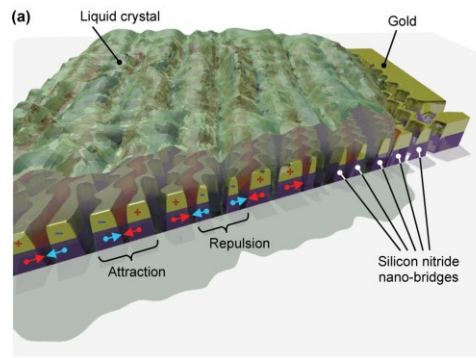


Figure 2.14. Artistic impression of a mechanically reconfigurable zigzag metasurface (cross-section) infiltrated with a liquid crystal [141].

Among all the methods of avoiding stiction in MEMS devices, few of them could be used under the situations where contacting and friction are integral part of the system design, such as MEMS bearings. The use of hydrophobic coatings, micro-texturing and modified surface topography is usually limited as they are vulnerable and can be removed easily due to the direct interaction between surfaces; changes to the rubbing surfaces usually implies that the hydrophilic substrates or smoother surfaces will again come into contact and cause severe stiction and wear.

2.3.2 MEMS liquid ball/ring bearings

Other innovative solutions have also been developed in the past decade. Instead of reducing surface energy to reduce the adhesion induced by surface tension, these solutions rely on a new method of lubricating thrust bearings using liquid balls or rings (shown in figure 2.15), which has been recently proposed and studied [19-21, 142-144]. In 2011, Chan et al. [19, 142] measured the performance of rotating micro device incorporating a liquid bearing. In their design, the fluid is confined between the rotor and the stator using hydrophobic patterns on a hydrophilic substrate. The hydrophobic patterns were fabricated by patterning a 2 μm thick Cytop (Asahi) hydrophobic layer on the silicon substrate. Because there were no micro- and/or nano-structures on the substrate, the water contact angle on the hydrophobic patterns could only reach ~ 99 degrees. The load capacity of such liquid bearing was provided by the Laplace pressure inside the liquid ring, which means the load capacity increases as the gap between the rotor and the stator decreases. When a transverse force is applied to the rotor, the contact angle of the liquid bearing changes following opposite trends on the different sides of the liquid ring; thus, a restoring force due to changes in the surface tension arises. In their design, the bearing could support a maximum transverse load equal to approximately 10% of the rotor's weight.

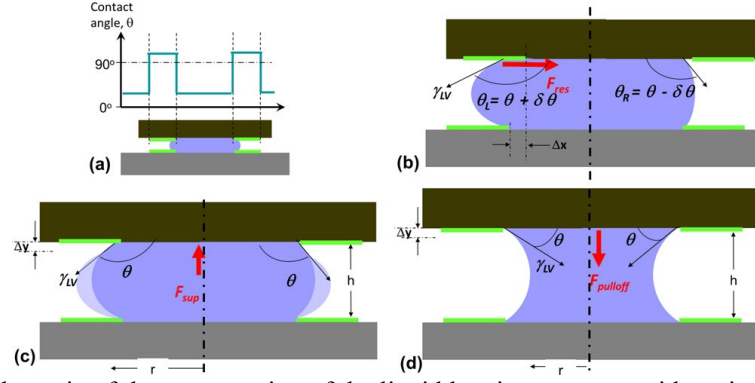


Figure 2.15. (a) Schematic of the cross section of the liquid bearing structure with variations in contact angle from non-wetting to wetting regions; forces acting on the rotor due to surface tension to (b) centre the rotor (c, d) support the rotor in compression and tension [142].

In the example studied in Ref. [142], the rotor was actuated by magnetic forces. The diameter of the silicon rotor which was used to characterize the liquid bearing was 10 mm and the fluid thickness between the rotor and the stator ranged from 20 to 200 microns. A minimum torque of $0.15 \mu\text{Nm}$ is required to overcome static friction and initiate rotation. The maximum rotation rate of 1800 rpm was tested in these experiments and it was found that the planar vibration was less than $\pm 1 \text{ mrad}$ for rotation rates above 720 rpm. The drag coefficient of the bearing was $1.2 \times 10^{-3} \mu\text{Nm/rpm}$.

In the same year, the design of the bearing was improved [21]. Compared to the early edition [19, 142], the new design was improved both in the hydrophobicity and the geometry of the patterns (see figure 2.16).

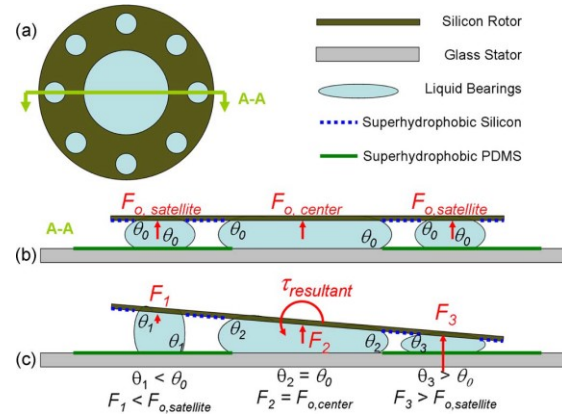


Figure 2.16. (a) Satellite bearing retention locations defined by SHP micro-patterns. (b) Cross section A–A showing relationship of rotor, liquid bearings, and stator. (c) Mechanism for tip/tilt restoring torque resulting from an induced rotor tilt [21].

The hydrophobicity of the new bearing was significantly increased by creating micro- and nano-structures under the superhydrophobic patterns, which were only hydrophobic in the previous edition. By optimizing the shape of the geometries of the microstructures, the contact angle of the superhydrophobic coating was increased to 156.1 degrees. The increment of the hydrophobicity significantly increased the load capacity and transverse force resistance. Moreover, several satellite

droplets were added to the former edition, which increased the tip/tilt stiffness ($5.4 \mu\text{Nm/deg}$). However, these satellite droplets also slightly increased the frictional torque of the bearing due to the sliding friction caused by the contact angle hysteresis of the droplets on the laser-roughened polydimethylsiloxane raceway when the bearing was rotating. The drag coefficient of the new bearing was $0.94 \times 10^{-3} \mu\text{Nm/rpm}$, and compared to the previous edition, the minimum torque required to initiate the bearing for the satellite bearing was smaller and measured at about $0.3 \mu\text{Nm}$, with a larger wobble, measured at $\pm 3 \text{ mrad}$.

In 2014 [20], conductive liquid was used in the two liquid rings which passed two independent electric signals separately, allowing a direct electrical path between the substrate and potential components on the rotor (see figure 2.17). The minimum torque to initiate the rotation of the bearing ($\sim 2.5 \text{ nNm}$) was hundreds of times smaller than the previous ones.

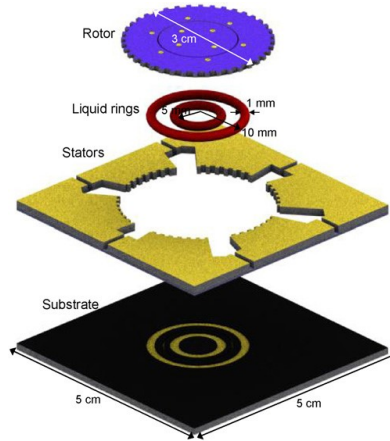


Figure 2.17. Exploded view of the side-driven rotary stage on conductive liquid rings [20].

Although the liquid ball/ring bearings have already been invented, the performance of the bearings is yet to be well understood. For example, due to the limitation of the testing platform, the frictional torque of the bearings as a function of the rotational speed and the load capacity as a function of the ring thickness have not been given. Thus, further investigation needs to be conducted, and this is the aim of the first phase of this PhD project, which has been reported in chapters 4 and 5. Also, in our preliminary investigations we found that the load capacity of the liquid ring bearing can be dramatically increased by sealing air in the liquid rings. Thus, a thrust bearing using liquid rings to seal air and increase the load capacity is studied here.

2.4 Superhydrophobic surface

2.4.1 Properties of superhydrophobic surface

Liquid wetting a solid surface is a common phenomenon in our daily life, such as inkjet printing and spray coating. The wetting state is determined by the liquid and solid surface properties and

characterised by the contact angle (see figure 2.18). The contact angle is the angle between the line tangential to the liquid/air interface and the solid/liquid interface. It is governed by the Young's equation [145]:

$$\cos \theta = (\gamma_{SG} - \gamma_{SL})/\gamma_{LG} \quad (2.27)$$

where γ_{SG} , γ_{SL} and γ_{LG} are the surface tension of solid/gas, solid/liquid and liquid/gas interfaces, respectively.

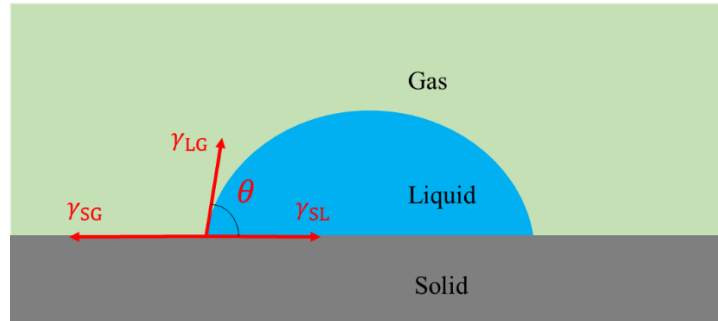


Figure 2.18. Liquid droplet on a solid surface.

The contact angle is affected by the surface roughness and the intermolecular interacting strength between solid, liquid and gas molecules. Theoretically, the contact angle of a solid surface is constant. However, due to the inhomogeneity of the chemical composition and surface roughness, the contact angle of a solid surface has a range. If a droplet is placed on a solid surface and tilt the surface gradually (see figure (19)). The liquid droplet will slip off the surface when the slant angle of the surface reaches a critical value. At this critical point, the contact angle on the leading and trailing edges of the contact line are the acceding contact angle (θ_A) and the receding contact angle (θ_R) of the surface, respectively. And the difference between the acceding and receding contact angles is the contact angle hysteresis ($\theta_A - \theta_R$).

Depending on the water contact angle, a solid surface is hydrophilic if the contact angle of water on it is smaller than 90° , and is hydrophobic when the water contact angle is bigger than 90° . The surface is superhydrophilic if the water contact angle is smaller than 5° and superhydrophobic when the water contact angle is bigger than 150° and the contact angle hysteresis is less than 5° .

The contact angle on an atomically smooth solid surface is called the intrinsic contact angle. While the contact angle for a solid surface with roughness is called the apparent contact angle. The maximum contact angle obtained by decreasing the surface free energy of a smooth solid surface is around 120° [146, 147]. While solid surface with a contact angle larger than 150° can be found in nature, such as the lotus leaf. Wenzel [148] introduced a parameter which is the roughness factor into the Young's equation to explain this phenomenon.

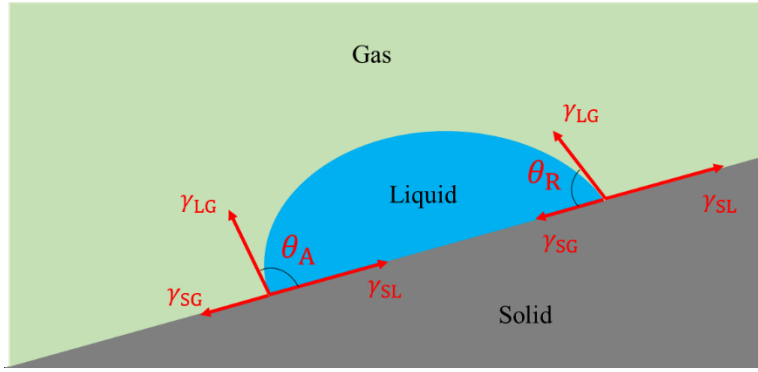


Figure 2.19. Droplet on an inclined solid surface.

Wenzel believes that real wetted surface area of a rough surface (S) is larger than a smooth surface (S_0), which is caused by the side surfaces of the roughness structures (see figure (2.20 (a))). The roughness factor is defined as $C_r = S/S_0$. When the contact line moves and leads to an increment of the apparent wetted surface area (the area of projection onto the horizontal plane) of ΔS_0 . The real increment wetted area of the surface is $C_r \Delta S_0$. Then the change of the surface free energy of the system is:

$$\Delta E_f = (C_r(\gamma_{SL} - \gamma_{SG}) + \gamma_{LG} \cos \theta_W^*) \cdot \Delta S_0 \quad (2.28)$$

where θ_W^* is the apparent contact angle in Wenzel wetting state (the surface roughness is totally wetted as shown in figure 2.20 (a)). When the system is balanced, the surface free energy variation should be $\Delta E_f = 0$. Wenzel obtained the following equation by substituting equation 2.28 into 2.27:

$$\cos \theta_W^* = C_r \cos \theta \quad (2.29)$$

where θ is the intrinsic contact angle of the solid surface. This equation can be used to calculate the apparent contact angle of a rough surface in Wenzel wetting state. We know that the roughness factor for a roughness surface C_r is always larger than 1, Thus we can see from equation 2.29 that for a hydrophilic surface ($\theta < 90^\circ$), the apparent contact angle in Wenzel wetting state decreases with C_r . While for a hydrophobic surface ($\theta > 90^\circ$), the apparent contact angle in Wenzel wetting state increases with C_r . This means that the surface roughness makes a hydrophilic surface more hydrophilic and a hydrophobic surface more hydrophobic in Wenzel wetting state.

However, the contact state of a droplet on a porous surface is not always in the Wenzel state where the water penetrates into the gap between the surface roughness structures. Such as a droplet on a lotus leaf where air pockets were trapped in the aspc between the surface roughness structures (see figure 2.20 (b)). Cassie and Baxter analysed this contact state and deduced an equation to predict the apparent contact angle of a droplet of a rough surface in such state. This state was later named as the Cassie state [149].

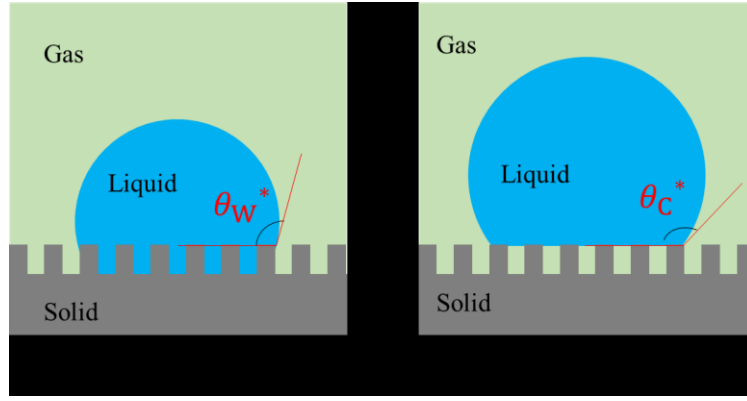


Figure 2.20. Contact angle at different contacting state. (a) Wenzel state. (b) Cassie state

In the Cassie state, liquid and solid contact only on the top of the surface roughness structures and a solid-liquid interface fraction is defined as $\phi_{SL} = \frac{A_{SL}}{A}$, where A_{SL} and A are the area of the solid-liquid contacting interface and entire composite surface beneath the liquid, respectively. Accordingly, the liquid-gas interface fraction is $\phi_{LG} = 1 - \phi_{SL}$. Similar to Wenzel's deduction, when the contact line moves and leads to an increment of the apparent wetted surface area of ΔS_0 , the variation of the solid-liquid and liquid-gas interface Areas are $\phi_{SL} \cdot \Delta S_0$ and $(1 - \phi_{SL}) \cdot \Delta S_0$. The surface free energy of the system would change by

$$\Delta E_f = (\phi_{SL}(\gamma_{SL} - \gamma_{SG}) + \gamma_{LG}(1 - \phi_{SL}) + \gamma_{LG} \cos \theta_C^*) \cdot \Delta S_0 \quad (2.30)$$

where θ_C^* is the apparent contact angle of a droplet in the Cassie state. When the system is balanced, the Cassie obtained the following equation by substituting equation 2.30 into 2.27:

$$\cos \theta_C^* = \phi_{SL}(1 - \cos \theta) - 1 \quad (2.31)$$

We can see from equation 2.31 that for a hydrophobic surface ($\theta > 90^\circ$) with roughness structures, the apparent contact angle in Cassie wetting state increases (θ_C^*) as ϕ_{SL} decreases. Which means the air pockets trapped between the surface roughness structures on a hydrophobic surface increases the hydrophobicity.

2.4.2 Preparation methods of superhydrophobic surface

Superhydrophobic surface can be found widely in nature, such as lotus leaf [150], water strider leg [151] and butterfly wing [152]. With the development of material science, scientists have invented artificial superhydrophobic surfaces. They are widely used in our daily lives, such as the non-stick pan, waterproof cloth, underwater drag reduction [153-155], anti-icing surfaces [156, 157] and anti-fouling [158-161] surfaces. According to the Cassie-Baxter theory, the hydrophobicity of a solid surface can be improved by increasing the liquid-gas contacting interface fraction which can be achieved by the combination of increasing the surface roughness and decreasing the surface free energy. Based on this

theory, two strategies were adopted to prepare superhydrophobic surfaces. One is creating roughness structures on the surface of hydrophobic materials. The other one is creating a rough surface first and then decreasing the surface free energy of the rough surface.

Sol-gel method

Xu *et al.* [162] prepared a superhydrophobic surface on a floating glass substrate using a sol-gel method based on removable polymeric nanospheres. In their method, a mixed sol-gel containing 0.014% removable nanometer-sized polymeric spheres with a diameter of 500 nm and 2.5% silica colloid particles with a diameter of 50 nm was coated on the glass first. Then the polymeric spheres were removed by heat treating the surface at 500 °C for 10 minutes. By doing this, nano-scale holes were obtained on the surface which increase the roughness and as a result increases the hydrophobicity of the surface. With this method, they managed to obtain a surface with a water contact angle as high as 160° (see figure 2.21) and the sliding angle is close to 0°.

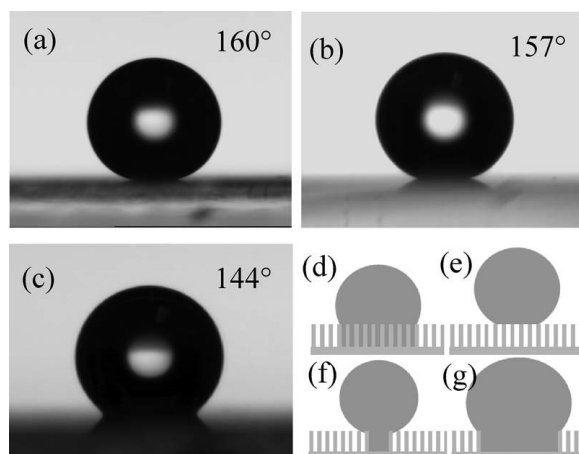


Figure 2.21. Typical optical images of a water droplet on a superhydrophobic coating [162].

Shang *et al.* [163] obtained an optically transparent superhydrophobic film using the sol-gel processing with self-assembly. The surface roughness of the film can be controlled by tuning the microstructures of the sol-gel through controlling the hydrolysis and condensation reactions during the process. The coatings they obtained showed an optical transparency higher than 90%. The advancing and receding water contact angles can be as high as 165° and 115°. A one-step approach which is the sol-gel processing of long-chain fluoroalkylsilane was adopted by Liu *et al.* [164] to prepare superhydrophobic coatings. The coating has a water contact angle of 169° and a sliding angle of 5°.

Phase separation method

Zhao *et al.* [165] used a mixture of Bisphenol A polycarbonate and *N,N'*-dimethylformamide to prepare superhydrophobic surface through vapor-induced phase separation. This method is simple one-step method. The hydrophobicity of the surface can be tuned by controlling relative humidity of the drying atmosphere. The maximum water contact angle achieved with this method is 162°. Wei *et al.* [166]

synthesized the styrene and 2,2,3,4,4,4-hexafluorobutyl methacrylate copolymers by bulk polymerization. Then, they used it to prepare the superhydrophobic copolymer films using the phase separation technique. To induce phase separation, the copolymer was dissolved in tetrahydrofuran, and then ethanol was added into the solution. They found that the microstructures of the polymer films could be enhanced by the concentration of ethanol. With this method, they obtained a superhydrophobic surface with a contact angle of 154.38° and a sliding angle of 5.88° . Liu *et al.* [167] used a method which involves the in situ polymerization of butyl methacrylate and ethylene dimethacrylate in the presence of co-porogens of 1,4-butanediol and N-methyl-2-pyrrolidone to prepare superhydrophobic surfaces. The superhydrophobic surface obtained with this method could achieve a water contact angle of 159.5° and a sliding angle of 3.1° . Moreover, it shows better resistance to acid, alkali and salt aqueous solutions and can maintain proper hydrophobicity at a temperature of 190°C .

Surface etching

Surface roughness structures are important in making superhydrophobic surfaces. Different surface etching methods had been used to make those surface structures, such as laser etching, chemical etching and reactive-ion etching. Wang *et al.* [168] obtained micro and nano-scale roughness on a glass surface by etching the surface with picosecond laser (see figure 2.22 (a)). They found that increasing the roughness (see figure 2.22 (b)) of glass surface makes the surface more hydrophilic as smooth glass surface is hydrophilic. After the rough glass surface is treated with 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane, it turns superhydrophobic. With this method they managed to obtain a superhydrophobic surface with a contact angle of 172° .

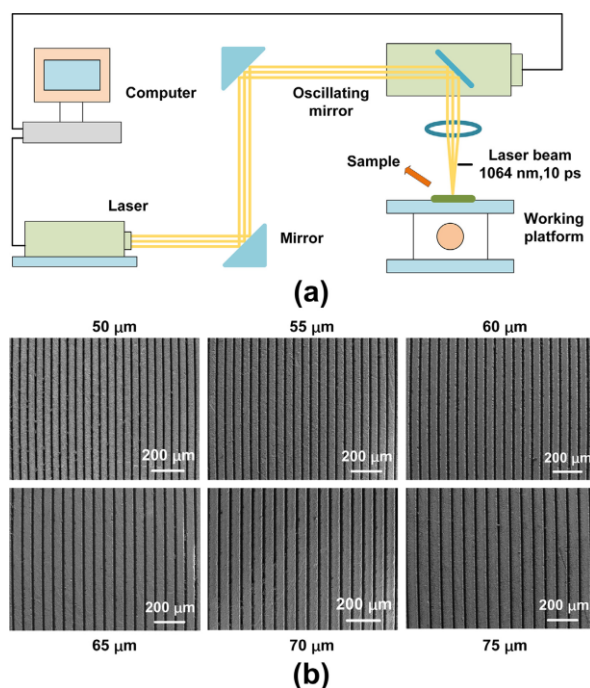


Figure 2.22. (a) Picosecond laser processing system. (b) SEM images of the periodic microgrooves fabricated on solar glass surface at different laser line intervals [168].

A method using KOH etching and metal assisted etching has been adopted by Xiu *et al.* [169] to make the hierarchical structures on a silicon wafer. The KOH etching was used first to make the relatively large micro-scale structures. Then, nano-scale structures were made on the micro-scale structures with the metal assisted etching. They found that the superhydrophobic surface fabricated in this method is more robust than superhydrophobic surfaces fabricated from polymeric materials or from silicon that contains only nanostructures. Kwon *et al.* [170] has adopted a reactive-ion etching method to make the hierarchical structures. In their method, the Bosch process was used first to make the micro-scale pillars. After that, nano-scale roughness was fabricated on the micro-scale pillars with XeF_2 etching. With this method, they managed to obtain extremely superhydrophobic surfaces with a contact angle of 173° .

2.5 Conclusions

From the literature reviewed in this chapter, we can see that the surface tension has a curvature dependence, and this effect could be significant at the nano-scale. The magnitude and sign of the Tolman length, which is the key parameter related to the curvature dependence of the surface tension still needs to be investigated. Furthermore, a systematic comparison between droplets and bubbles is yet to be conducted. Based on existing research, the curvature dependence of the surface tension seems to diminish for systems at the micro-scale and larger. This provides a potential method of lubricating micro-scale systems taking advantage of the dominance of the surface tension at micro-scale. However, such systems are not well designed and there are also many other potential methods to be investigated. The main aim of this thesis is to provide improved understanding and to contribute with original research to these interesting topics.

Chapter 3 Molecular dynamics simulations of surface tension for nano-scale gas-liquid interface

Stable cylindrical nanobubbles and nanodroplets are obtained in MD simulations with three-phase contact lines pinned by alternate hydrophobic and hydrophilic patterns. The surface tension and Tolman length for both types of curved interfaces and flat interfaces are obtained with a mechanical method based on the difference between normal and tangential pressure components. Results show that the surface tension decreases linearly while the Tolman length increases linearly with the gas/liquid density ratio. By subtracting the surface tension and Tolman length for flat interfaces with the same gas/liquid density ratio as that of curved interfaces, effects of curvature on the surface tension and Tolman length are obtained. It is found that such effects start to be seen when the equimolar curvature radius goes down to 20 reduced LJ units. And they have the same magnitude but act with opposite signs for nanobubble and nanodroplet interfaces. Results obtained by the mechanical method agree well with those obtained by Tolman's theoretical equation except at very small curvature radius (<10 LJ reduced units) due to the accumulation of the curvature dependence of the Tolman length.

3.1 Introduction

As has been discussed in Chapter 2, the surface tension which has a strong effect on bubble/droplet nucleation is an important interfacial property of an inhomogeneous system. The relationship between the surface tension and the pressure had been derived by Young and Laplace (equation (1.1)). It shows that the pressure difference across an interface equals the surface tension times the curvature of the interface. And the pressure is higher on the side to which the interface is curved. This equation shows good agreement with the experimental results at macro scale and has been widely used. The surface tension is regarded as constant when using the Young-Laplace equation at the macro scale. However, Tolman, Gibbs et al. had predicted that the surface tension has a curvature dependence at molecular scale. They found that the surface of tension where the surface tension acts and the equimolar surface of an inhomogeneous system do not coincide with each other. The distance between them was named after Tolman as the Tolman length. The surface tension of a curved interface at the molecular scale can be predicted by a simplified equation (equation (1.2)). This equation gives the relationship between the surface tension, the curvature of the interface and the Tolman length which is regarded as a constant in the derivation of this equation. Meanwhile, researchers have found that the Tolman length also has a curvature dependence [5, 6, 13-15, 171, 172]. The widely used definition of the Tolman length, which is the difference between the curvature radius of the equimolar interface and the curvature radius of the surface of tension, can be ambiguous. For example, the curvature radius of a flat interface is not uniquely defined.

For a long time, it was believed that bubbles and droplets are the counterparts of each other and follow the same rules at the molecular scale. However, detailed comparisons between bubble and droplet systems have not been conducted. One can see that the definition of the Tolman length for the two systems can be different as the liquid region is in the inner area for droplets while the gas region is in the inner area for a bubble. A simple subtraction between the curvature radii of the equimolar surface and the surface of tension can lead to equal and opposite results of the Tolman length for bubbles and droplets. Thus, a more restricted definition should be used.

In this chapter, a statistic mechanical technique based on Molecular Dynamics (MD) simulations was adopted to simulate the surface tension and Tolman length of flat, nanobubble and nanodroplet interfaces. A restricted definition of the Tolman length from Tolman's original work was used. The results were compared with that obtained through Tolman's equation. The research systems and methods adopted are introduced in section 3.2. In section 3.3.1 and 3.3.2, two procedures of calculating the surface tension and Tolman length are presented. The effect of the gas/liquid density ratio (ρ_G/ρ_L , where ρ_G and ρ_L are the gas density and liquid density, respectively) on the surface tension and Tolman length for a flat interface is discussed in section 3.3.2. In section 3.3.3, the results of surface tension and Tolman length for nanobubble and nanodroplet interfaces are compared and discussed. The curvature dependence of the surface tension and Tolman length is obtained and discussed in section 3.3.4. In section 3.3.5, fitted Tolman equations which consider both effects of the gas/liquid density ratio and curvature are introduced. Finally, in section 3.4, we conclude the main results of this chapter.

3.2 Methodology

3.2.1 Theoretical investigation of the way for calculating the surface tension

The surface tension of the flat, cylindrical nanobubble and nanodroplet interfaces were simulated with classical MD simulations. The equations for calculating the surface tension with pressure tensors of a flat interface are well defined:

$$\gamma_{\infty} = \int_{y_G}^{y_L} (P_N - P_T) dy \quad (3.1)$$

$$\gamma_{\infty} y_s = \int_{y_G}^{y_L} y (P_N - P_T) dy \quad (3.2)$$

where γ_{∞} is the surface tension, P_N and P_T are the normal and tangential pressure components, respectively. y is the direction normal to the gas/liquid interface, y_G and y_L are two locations deep inside the bulk gas and the bulk liquid regions, respectively. y_s is the location of the surface of tension where the surface tension acts.

The location of the equimolar surface can be obtained by the following equation:

$$\int_{y_G}^{y_e} \rho_G dy + \int_{y_e}^{y_L} \rho_L dy = \int_{y_G}^{y_L} \rho_y dy \quad (3.3)$$

where ρ_G and ρ_L are the molecule number density in the bulk gas and bulk liquid regions, respectively. ρ_y is the molecule number density at location y . y_e is the location of the equimolar surface.

Thus the magnitude of the Tolman length for a flat interface (δ_∞) can be obtained:

$$\delta_\infty = y_e - y_s \quad (3.4)$$

In this thesis, the Tolman length is defined as the distance from the surface of tension to the equimolar surface in the direction from liquid to gas.

For a cylindrical interface, the equations for the surface tension and radius of the surface of tension based on pressure tensors can be deduced following the method similar to that for a spherical interface (see the appendix A for detailed derivation):

$$\gamma = \int_{R_\alpha}^{R_\beta} \frac{r}{R_s} (P_N - P_T) dr \quad (3.5)$$

$$R_s^2 = \frac{\int_{R_\alpha}^{R_\beta} r (P_N - P_T) dr}{\int_{R_\alpha}^{R_\beta} \frac{1}{r} (P_N - P_T) dr} \quad (3.6)$$

where R_α and R_β are deep inside the bubble (or droplet) and outer bulk-liquid (gas) regions, respectively. R_s is the curvature radius of the surface of tension. Equations (3.5) and (3.6) are used in this chapter to calculate the surface tension and the curvature radius of the surface of tension. The equimolar radius of the curved interface cases (R_e) can be obtained by the following equation [173]:

$$R_e^2 = \frac{\int_{R_\alpha}^{R_\beta} r^2 \rho dr}{\int_{R_\alpha}^{R_\beta} \rho dr} \quad (3.7)$$

As the Tolman length is defined as the distance from the surface of tension to the equimolar surface in the direction from liquid to gas in this thesis, the Tolman length for nanodroplet case is

$$\delta_D = R_e - R_s \quad (3.8)$$

While the Tolman length for nanobubble case is

$$\delta_B = R_s - R_e \quad (3.9)$$

Based on the Gibbs [3] thermodynamic theory of capillary, a relationship between the surface tension and the Tolman length was deduced by Tolman [9] for a spherical droplet interface within a one-component two-phase system which has later been extended to multicomponent systems by Koenig [31]:

$$\frac{1}{\gamma} \frac{d\gamma}{dr} = \frac{\left(\frac{2\delta}{r^2}\right) \left(1 + \frac{\delta}{r} + \frac{1}{3} \left(\frac{\delta}{r}\right)^2\right)}{1 + 2\frac{\delta}{r} \left(1 + \frac{\delta}{r} + \frac{1}{3} \left(\frac{\delta}{r}\right)^2\right)} \quad (3.10)$$

By assuming that δ is constant and neglecting the terms $\frac{\delta}{r}$ and $\left(\frac{\delta}{r}\right)^2$, a simplified equation (equation (1.2)) was obtained. Following this method, similar equations can be deduced for the cylindrical nanobubble and nanodroplet interfaces. Based on the definition of the Tolman length in this work, the equation for the cylindrical nanodroplet interface is

$$\frac{1}{\gamma} \frac{d\gamma}{dr} = \frac{\left(\frac{\delta}{r^2}\right) \left(1 + \frac{1}{2} \frac{\delta}{r}\right)}{1 + \frac{\delta}{r} \left(1 + \frac{1}{2} \frac{\delta}{r}\right)} \quad (3.11)$$

The equation for the cylindrical nanobubble interface is

$$\frac{1}{\gamma} \frac{d\gamma}{dr} = \frac{-\left(\frac{\delta}{r^2}\right) \left(1 - \frac{1}{2} \frac{\delta}{r}\right)}{1 - \frac{\delta}{r} \left(1 - \frac{1}{2} \frac{\delta}{r}\right)} \quad (3.12)$$

Adopting the same assumptions which Tolman used, equation (3.11) and (3.12) can be integrated from the flat interface to a radius of interest $r = R_s$ respectively:

$$\frac{\gamma_{R_s}}{\gamma_{\infty}} = \frac{1}{1 + \frac{\delta}{R_s}} \quad (3.13)$$

$$\frac{\gamma_{R_s}}{\gamma_{\infty}} = \frac{1}{1 - \frac{\delta}{R_s}} \quad (3.14)$$

3.2.2 Numerical simulations

Simulation Setup

The surface tension of flat, cylindrical nanobubble and nanodroplet interfaces were simulated with classical MD simulations using the open-source code LAMMPS (the large-scale atomic/molecular massively parallel simulator). All length units used in the MD simulations are reduced LJ units if units are not explicitly specified. Two types of molecules were used in the flat interface cases: one type of gas molecules (G) and one type of liquid molecules (L). A liquid slab was placed in the middle of the simulation domain which has a size of $30 \times 30 \times 60$ (see figure 3.1). Periodic boundary conditions were applied in all three directions. The molecules interact with each other through a truncated Lennard-Jones potentials with a cut off of 5 sigma:

$$U_{ij}(l) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right] \quad (3.15)$$

where $U_{ij}(l)$ and r_{ij} are the potential and distance between molecules i and j . ϵ_{ij} and σ_{ij} are the interacting strength and the characteristic length between molecules i and j .

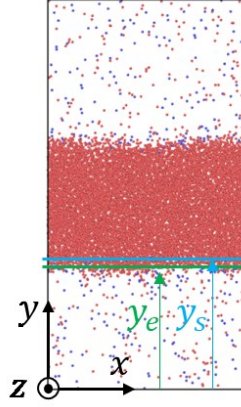


Figure 3.1. Typical simulation box showing the coordinate system, equimolar surface and surface of tension schematically for the flat interface case. y_e and y_s are the location of the equimolar surface and surface of tension, respectively. Red particles are the liquid molecules (L), blue particles are the gas molecules (G).

Three more molecule types were used in the nanodroplet and nanobubble interface cases: two types of solid molecules (hydrophilic (S_{phi}) and hydrophobic (S_{pho})) and one type of tether site molecules (T_s). The G, L, S_{phi} and S_{pho} molecules in the nanobubble and nanodroplet cases interact with each other through truncated Lennard-Jones (LJ) potentials (formula 3.15) with a cut-off of 5. The T_s molecules are fixed in a *fcc* lattice at the wall region during the whole simulation for nanodroplet and nanobubble cases. The S_{phi} and S_{pho} molecules are tethered to the T_s molecules one by one through the following potential with a cut off of 5 sigma:

$$U_{ij}(l) = \epsilon_{ij}(r_{ij} - r_{i0})^2 \quad (3.16)$$

where $\epsilon_{ij} = 150$ is the interacting strength and $r_{i0} = 0$ is the equilibrium bond distance. Thus, the S_{phi} and S_{pho} molecules can vibrate around the T_s molecules.

The nanobubbles and nanodroplets have a cylindrical shape (see figure 3.2). Periodic boundary conditions were employed in the x and z directions. The top of the simulation domain has a wall boundary condition which interacts with G and L molecules through the following potential:

$$U(r_{yi}) = \epsilon \left[\frac{2}{15} \left(\frac{\sigma}{r_{yi}} \right)^9 - \left(\frac{\sigma}{r_{yi}} \right)^3 \right] \quad (3.17)$$

applied to molecules within a distance 2.5 from the wall. Where $\epsilon = 1.0$ and $\sigma = 1.0$ are the interacting strength and the characteristic length between the wall and molecules. r_{yi} is the distance between molecule i and the location of the wall. The thickness of the simulation domain in the z direction is set to 5, making the simulations effectively two dimensional.

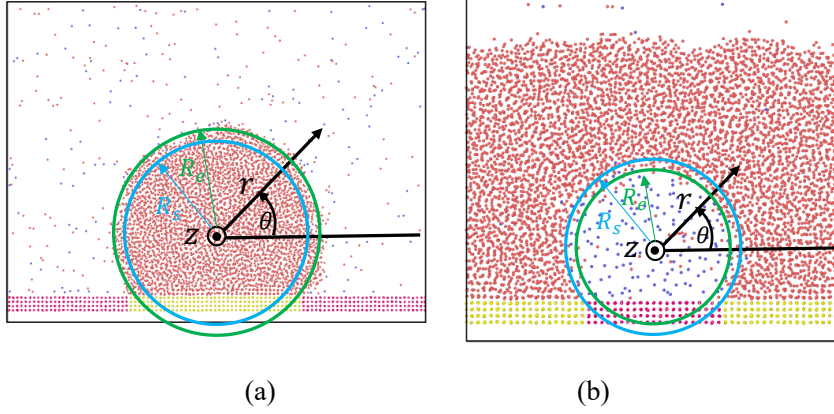
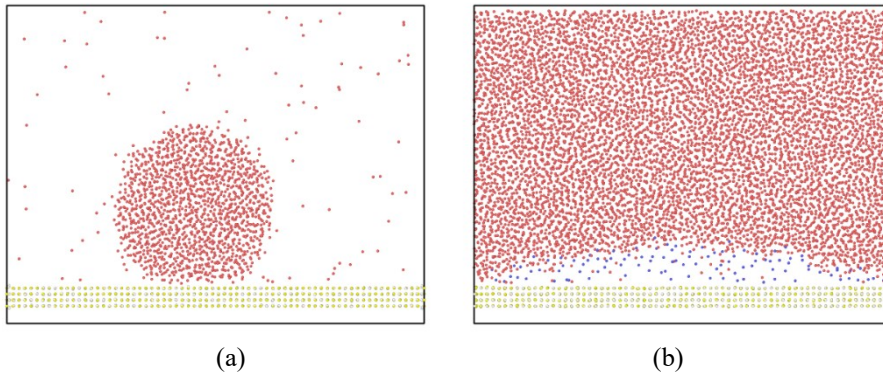


Figure 3.2. Typical simulation boxes showing the coordinate system, equimolar surface and surface of tension schematically. (a) and (b) are nanodroplet and nanobubble cases, respectively. R_e and R_s are the curvature radii of the equimolar surface and the surface of tension. Red particles are the liquid molecules (L), blue particles are the gas molecules (G), yellow particles are the hydrophilic wall molecules (S_{phi}) and pink particles are the hydrophobic molecules (S_{pho}). The nanodroplet and nanobubble have a cylindrical shape and the z axis is along the length of the cylinder.

For curved interface cases, there is a hydrophilic (hydrophobic) strip in the middle of the wall while the other part of the wall is hydrophobic (hydrophilic) for the nanodroplet (nanobubble) cases to control the size and anchor the position of the droplet (bubble). The hydrophobicity of the solid walls is controlled by tuning the interacting strength (ϵ_{SL}) between solid and liquid molecules. A series of simulations were conducted to investigate this effect and the results are shown in figure 3.3. The interacting strength and characteristic length between different molecules are the same except ϵ_{SL} , which is set to 0.2 for (a) and (b), 0.4 for (c) and (d) and 0.7 for (e) and (f). Each image is a snapshot of the simulation when the system is balanced. As we can see that the liquid contact angle of the droplet on the solid wall decreases as ϵ_{SL} increases while the air contact angle of the bubble increases. In this thesis, ϵ_{SL} is 1.0 for hydrophilic surface and 0.1 for hydrophobic surface.



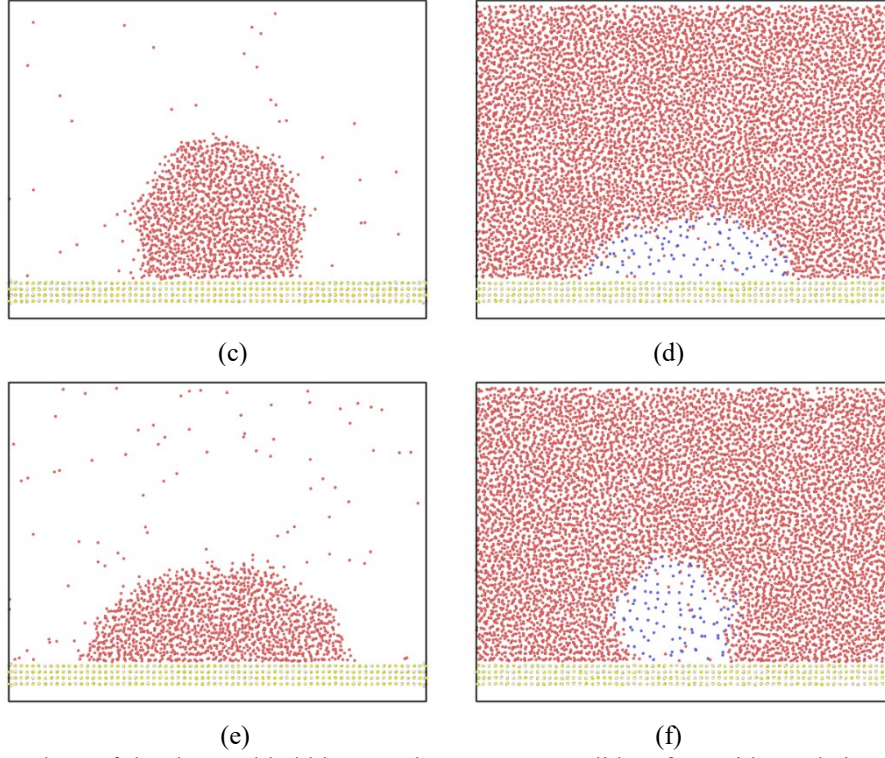


Figure 3.3. Snapshots of droplets and bubbles on a homogeneous solid surface with ϵ_{SL} being 0.2 for (a) and (b), 0.4 for (c) and (d) and 0.7 for (e) and (f).

The LJ potential parameters for all the simulations in this chapter are listed in table 3.1.

Table 3.1. Values of LJ potential parameters used in the MD simulations

$i - j$	ϵ_{ij}	σ_{ij}
L - L	1.0	1.0
S _{phi} - L	1.0	1.0
S _{pho} - L	0.1	1.0
L - G	0.52	1.18
S _{phi} - G	0.1	1.18
S _{pho} - G	0.5	1.18
G - G	0.5	1.7

With the alternate hydrophobic and hydrophilic patterns, nanodroplets and nanobubbles can be anchored on the solid surface. Examples of nanodroplets with different contact angles and sizes are shown in figure 3.4. As we can see, the alternate hydrophobic and hydrophilic patterns strongly pin the contact lines of the droplets at the boundaries of the patterns. With such patterns, the position and size of the nanobubbles and nanodroplets can be controlled.

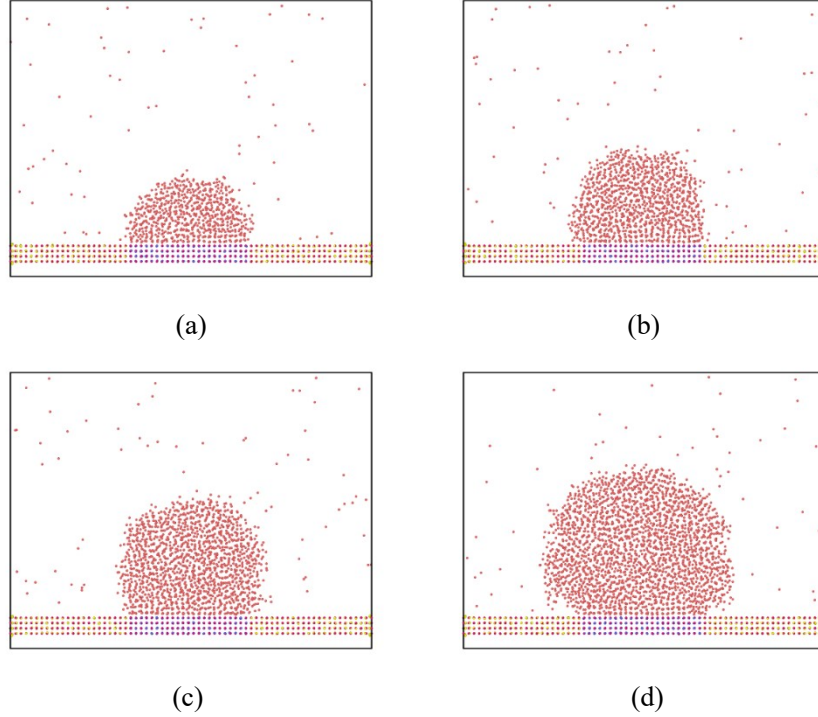


Figure 3.4. Nanodroplets with different sizes confined on the solid surface by alternate hydrophobic and hydrophilic patterns.

Simulation procedures

All the simulations were performed in a three-dimensional Cartesian coordinate system. For the flat interface cases, initially, regions of gas and liquid molecules are added to the simulation domain. The thickness of the liquid slab is around 20. Then the system is thermostatted at a temperature of $T_{set} = 0.8$ with a heat bath size of $Q=100$ dt for 3 million time steps in an NVT ensemble using a Nose-Hoover thermostat [174, 175]. After that, measurements of the density and pressure tensor are obtained using a grid of chunks with the size being 0.5×0.5 covering the $x - y$ plane. The results are collected from an NVE ensemble run over 500,000 time steps with the time-average values calculated by taking a sample every 50 time steps. As the flat liquid/gas interface is parallel to the $x - y$ plane, the normal pressure component is $P_N = P_{yy}$ and the tangential pressure component is $P_T = P_{xx}$.

For the nanodroplet and nanobubble cases, initially, gas and liquid molecules were placed on the hydrophobic and hydrophilic surfaces, respectively. Then the system was equilibrated for 3 million time steps in an NVT ensemble using a Nose-Hoover thermostat with the temperature of the wall molecules S_{phi} and S_{pho} thermostatted using $T_{set} = 0.8$ with a heat bath size of $Q=100$ dt. When the system is equilibrated, gas molecules tend to stay on the hydrophobic surfaces and the liquid molecules preferentially stay on the hydrophilic surfaces. In this way, we were able to form cylindrical nanodroplets and nanobubbles on solid surfaces. Data collection follows the same process as the flat-interface case, with time-averaged density and pressure tensor measurements obtained in a grid of

chunks with the size being 0.5×0.5 covering the $x - y$ plane in an NVE ensemble. Time-average values are calculated for 500,000 time steps by taking a sample every 50 time steps. After that, a cylindrical coordinate system was established by fitting a circle to the location halfway between bulk liquid and bulk gas density. Then the pressure tensors in the three-dimensional Cartesian coordinate system were transferred to the cylindrical coordinate system (figure 3.5) using the following equations:

$$P_N = P_{xx}(\cos(\theta))^2 + P_{yy}(\sin(\theta))^2 + P_{xy}\sin(2\theta) \quad (3.18)$$

$$P_T = P_{xx}\left(\cos\left(\theta + \frac{\pi}{2}\right)\right)^2 + P_{yy}\left(\sin\left(\theta + \frac{\pi}{2}\right)\right)^2 + P_{xy}\sin(2\theta + \pi) \quad (3.19)$$

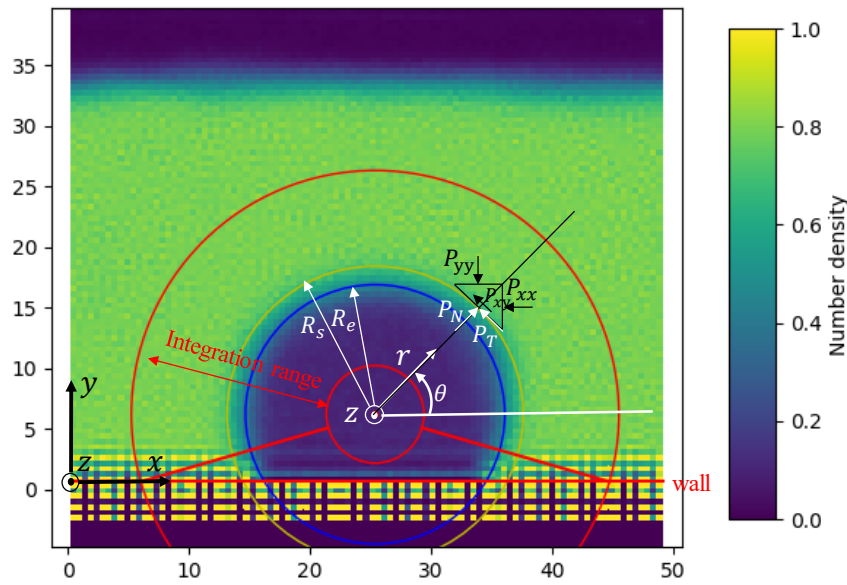


Figure 3.5. A typical density profile of a nanobubble case. The three-dimensional Cartesian coordinate system at the down-left corner was used in the MD simulation. The cylindrical coordinate system was established by fitting the equal-density profile. The z axis is along the length of the cylindrical bubble. In the r direction, the integration of the surface tension starts from the bulk gas region inside the bubble (the inner red circle) and ends at the bulk liquid region (the outer red circle).

3.3 Results and discussion

3.3.1 The ‘average after’ procedure of calculating the surface tension and Tolman length

To calculate the surface tension (γ) and the Tolman length (δ) with the density (ρ), normal (P_N) and tangential (P_T) pressures, there are two procedures available. Procedure i) (referred to as ‘average after’) is to get the local profiles of ρ , P_N , and P_T in the normal direction (y and r directions for the flat and curved interface cases, respectively). These profiles are then used to calculate the local γ and δ in the whole range of the tangential direction (x and θ directions for the flat and curved interface cases, respectively). Finally, the mean values of γ and δ can be obtained by averaging the local values along the tangential direction. Procedure ii) (referred to as ‘average before’) is to obtain the mean profiles of

ρ , P_N , and P_T in the normal direction first by averaging the local profiles along the tangential direction. Then, the mean value of γ and δ can be calculated using the mean profiles of ρ , P_N , and P_T .

As has been mentioned, the density and pressure tensors are obtained in a grid of chunks with the size being 0.5×0.5 in the $x - y$ plane. The results are collected from an NVE ensemble run over 500,000 time steps taking a sample every 50 time steps. An example for each of the local profiles for ρ , P_N , and P_T at three positions in x direction for a flat interface case is shown in figure 3.6. The profiles start from deep inside the gas region and end in the liquid region.

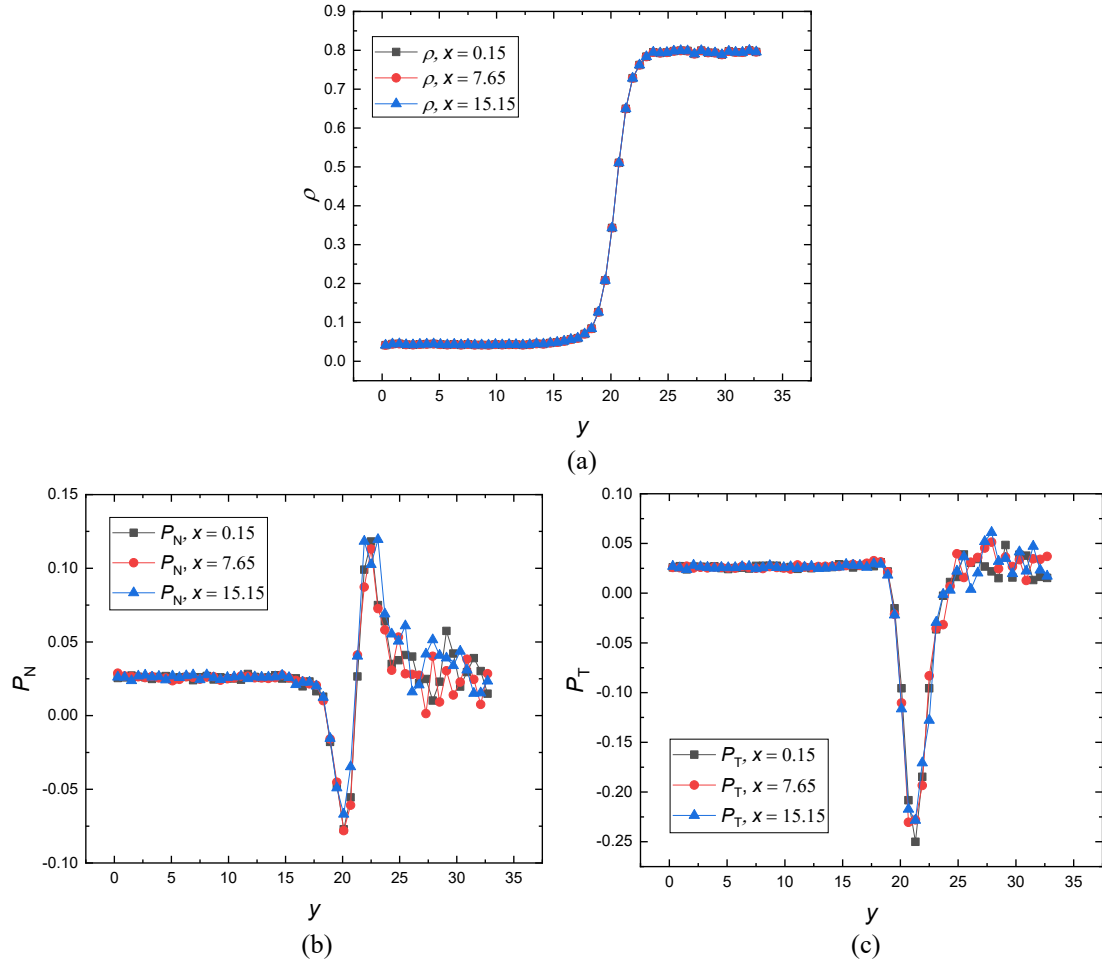


Figure 3.6. Local profiles of a flat interface case. (a) Local density profile. (b) and (c) Local normal and tangential pressure component profiles.

As we can see from figure 3.6 (a) that the ρ profile at different positions in the x direction are all very smooth and coincide with each other as periodic boundary conditions were applied in all directions. The P_N and P_T profiles at different positions also coincide with each other well. They are smooth in the gas region while they have larger fluctuation in the liquid region. The local γ and δ of the liquid/gas interface at different positions in the x direction can be obtained with the ρ , P_N and P_T profiles.

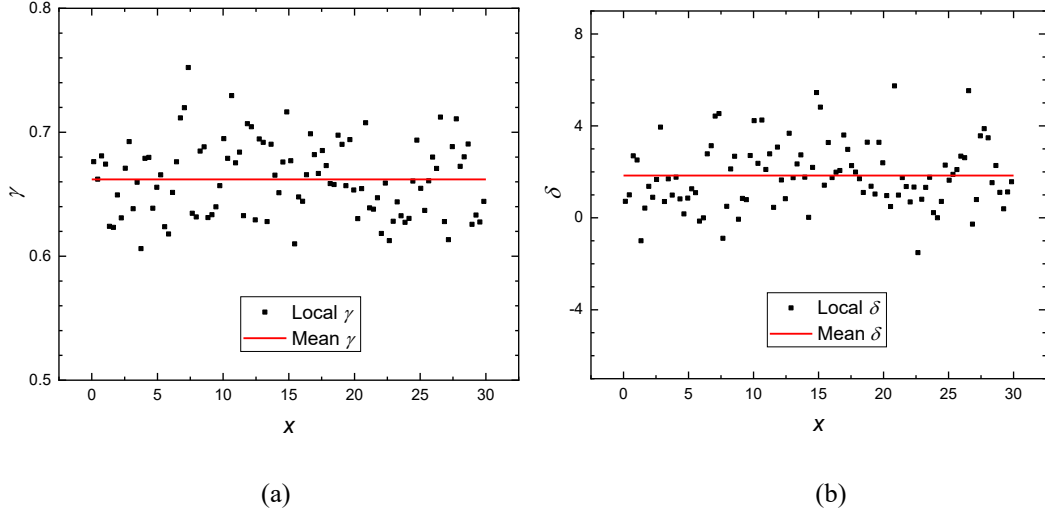
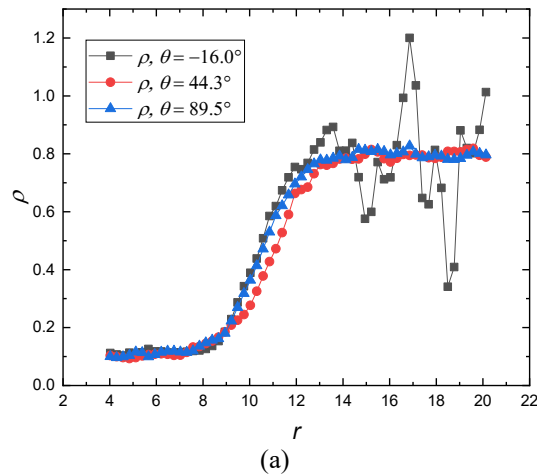


Figure 3.7. Surface tension, γ , and Tolmann length, δ , along a flat liquid/gas interface.

Figure 3.7 shows the local and mean values for γ and δ along a flat liquid/gas interface. The mean γ and δ are obtained by averaging the local values along the whole range in the x direction which is parallel to the interface. It can be seen that the local γ slightly fluctuates while the data points are evenly scattered around the mean value. Because periodic boundary conditions are applied in all directions, the lateral boundaries do not show any effect on the local surface tension. The fluctuation of the local δ is relatively high compared to the mean value, but the data points are also evenly scattered around the mean value.

Figure 3.8 (a) shows the ρ profiles along the r direction at three different locations in the θ direction for the nanobubble case shown in figure 3.5. The profiles start deep inside the nanobubble and go deep into the bulk liquid region. We can see that the profile at $\theta = -16.0^\circ$, which is a measurement near the three-phase contact line, shows fluctuations in density when r is larger than around 13. This is a result of the stacking when liquid molecules are close to the solid wall (see figure 3.5), which has a nearly fixed molecular structure and induces ordering in the structure of the adjacent liquid atoms [176]. The profiles far from the solid wall do not observe this effect and appear smoother.



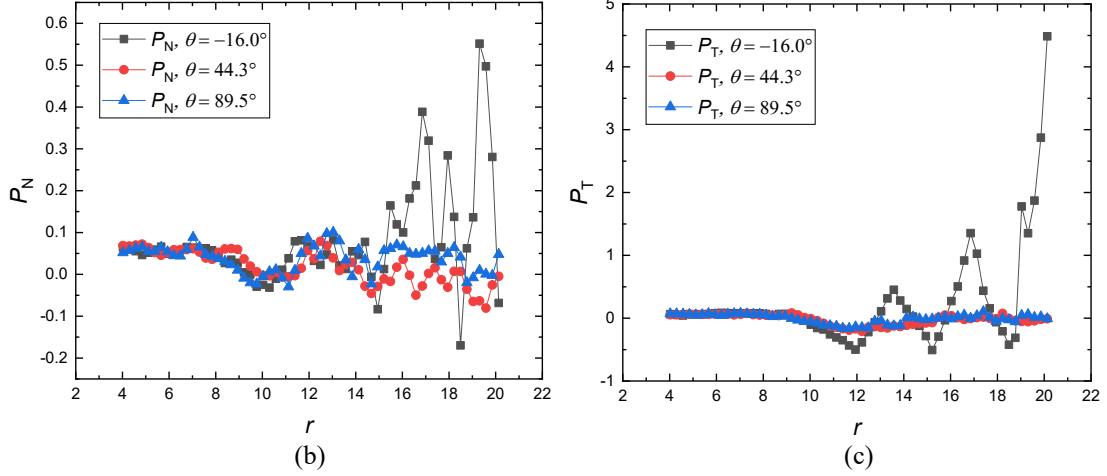


Figure 3.8. Local profiles of a nanobubble case. (a) Local density profile. (b) and (c) Local normal and tangential pressure component profiles.

Figure 3.8 (b) and (c) show the P_N and P_T profiles along the r direction. Although averaged for 10,000 time steps, the profiles of the pressure components are not smooth, especially the one at $\theta = -16.0^\circ$ due to the strong effect of the solid wall. Compared to P_N , P_T has a larger fluctuation. The local γ and δ of the interface in θ direction can be calculated with the local pressure component profiles.

A distribution of the local surface tension γ and Tolman length δ in the θ direction obtained with the local ρ , P_N and P_T profiles is shown in figure 3.9. We can see that the effect of the solid wall on the pressure components near the wall region is passed to the surface tension. As the focus of this work is on the liquid/gas interface, the mean surface tension is obtained by averaging the value in the middle flat area which is far from the wall region for the ‘average after’ procedure of calculating the surface tension. It is shown that the distribution of the local γ and δ as a function of θ for the nanobubble interface far from the wall region is similar to that for the flat interface case.

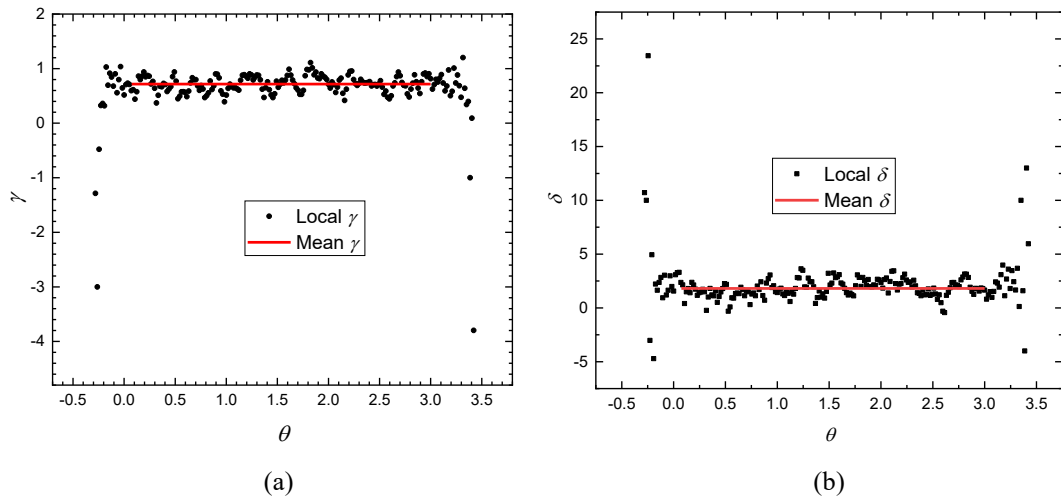


Figure 3.9. Surface tension (a) and Tolman length (b) along the liquid/gas interface of a nanobubble case.

3.3.2 The ‘average before’ procedure of calculating the surface tension and Tolman length

The ‘average before’ procedure of calculating the surface tension is shown in this section. In this procedure, the profiles of the mean density, normal and tangential pressure components are obtained first by averaging the local profiles along the tangential direction. The surface tension is then calculated using the mean pressure component profiles with equation (3.1) and (3.5).

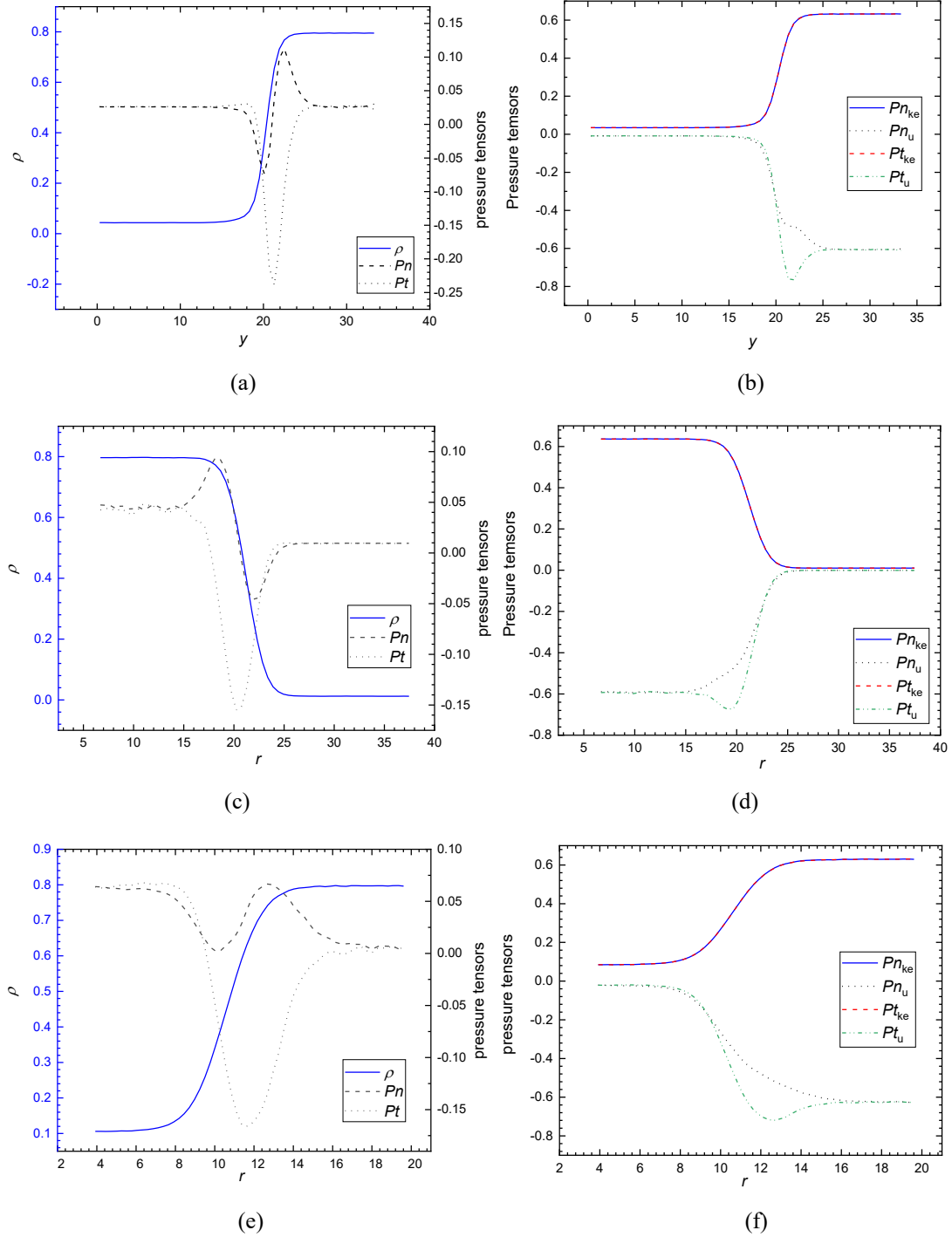


Figure 3.10. Density and pressure component profiles for both flat and curved interfaces. (a), (c) and (e) Density, normal and tangential pressure component profiles for flat, nanodroplet and nanobubble interfaces, respectively.

(b), (d) and (f) Kinetic and virial components of the normal and tangential pressure for flat, nanodroplet and nanobubble interfaces, respectively.

Figure 3.10 shows examples of the mean density and pressure component profiles for both flat and curved interfaces. As has been discussed that the wall has a strong effect on the density and pressure components for curved interface cases, the mean profiles are calculated using data from the range of θ far from the wall. While there is no solid wall in the flat interface cases, the mean profiles are obtained using data in the whole range of x . We can see that the mean profiles for density and pressure components are much smoother than the local profiles.

For the flat interface (figure 3.10 (a) and (b)), the profiles start from the bulk gas region and ends in the bulk liquid region. Thus, the density profile in figure 3.10 (a) increases from the gas region to the liquid region. For the droplet (figure 3.10 (c) and (d)) cases, the origin of the system is at the centre of the nanodroplet and the profile starts from inside the droplet and ends deep inside the bulk gas region. Thus, the density profile in figure 3.10 (c) decreases from inside the droplet to the outer bulk gas region. For the nanobubble (figure 3.10 (e) and (f)) cases, the origin of the system is at the centre of the nanobubble and the profile starts from inside the bubble and ends deep inside the bulk liquid region. Thus, the density profile in figure 3.10 (e) increases from inside the bubble to the outer bulk liquid region.

For normal and tangential pressure components of the flat interface case, we can see from figure 3.10 (a) that they equal each other in bulk gas and liquid regions which means there is no pressure difference cross the flat interface. Near an interface in a balanced system, a constant normal pressure is required for momentum balance. While this is known to not occur for solid–liquid interfaces with the virial or IK1 (note here that IK1 is the first term in the Irving Kirkwood expansion which is the same as the virial from LAMMPS) pressure [177] which is the default pressure measured by LAMMPS. This observation motivates the use of the VA and MOP formulations for solid-liquid cases [178, 179]. However, even applying the VA and MOP approach to the liquid–vapour interface, the normal component of the intrinsic pressure does not show momentum balance [180] and a full time evolving surface tracing is needed to give a flat profile [181]. In this work, the simplified IK1 pressure is used as the resulting form of normal pressure does not affect the resulting surface tension (as the integration of the two opposite peaks in the normal pressure component with respect to radius is zero) or Tolman length which are the focus of this work. Thus, for all the interfaces, the normal pressure component (figure 3.10 (a), (c) and (e)) shows a higher peak on the liquid side and a lower peak on the gas side. While for the tangential pressure component, it shows a single deep valley. It is this difference between the normal and tangential pressure component results in the surface tension.

Figure 3.10 (b) (d) and (f) show the kinetic and virial parts of the normal and tangential pressure components. It can be seen that no matter the interface is curved or not, the magnitude of both the kinetic and virial parts of the normal and tangential pressure components increase monotonically

(except the virial part of the tangential pressure shows a peak on the liquid side near the interface) from the gas region to the liquid region. The kinetic part of the pressure is positive while the virial part is negative. When these kinetic and virial parts are added up, the total pressure follows the Young-Laplace law which predicts a higher total pressure on the side to which the interface is curved. It is also shown that the kinetic parts of the normal and tangential pressure components equal each other for all interfaces which means that the kinetic part of the pressure does not contribute to the surface tension. The difference between the virial parts of the normal and tangential pressure components near the interface is the origin of the surface tension.

3.3.3 The surface tension and Tolman length

The errors for all the results are from time-average values of four subsequent subsets of 500,000 time steps. The γ and δ calculated using the two different procedures are compared. The results show that the γ and δ of the flat interface calculated using the two procedures are the same while those for curved interfaces are slightly different. Examples of the γ and δ for nanodroplet interfaces calculated with two procedures are shown in figure 3.11. As we can see, the differences of γ calculated by the two procedures are small while the differences in δ increase slightly as the curvature radius of the nanodroplet increases. The results discussed later in this chapter are all calculated using the ‘average before’ procedure (“average before” chosen arbitrarily given no clear advantage of either, but not expected to affect conclusions.).

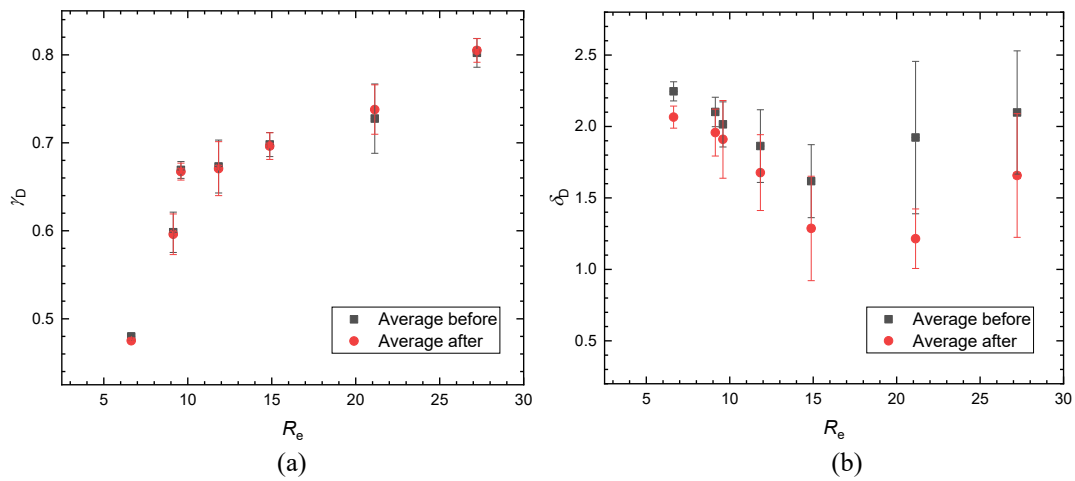


Figure 3.11. The surface tension for nanodroplet cases depicted as γ_D (a) and the Tolman length for nanodroplet cases depicted as δ_D (b) calculated with different procedures.

The effect of ρ_G/ρ_L on γ and δ is studied with flat interface cases and the results are shown in figure 3.12, we change ρ_G/ρ_L by change the number of gas molecules in the gas region of the system which has a fixed volume. It should be noted here that the density used in this chapter is the particle number density. The density is directly related to pressure at the same temperature. The smallest ρ_G/ρ_L we can get is the case where there are no gas molecules in the gas region, with the gas region filled by the liquid

vapour molecules. The highest ρ_G/ρ_L we can get is around 0.25, above which the boundary between the gas and liquid is hard to identify. It should be noted that in the whole density ratio range, the density of the liquid region is quite stable and stays around 0.8. That is because liquid is less compressible than gas. We can see from figure 3.12 (a) that γ decreases as ρ_G/ρ_L increases (or as the density difference between gas and liquid decreases).

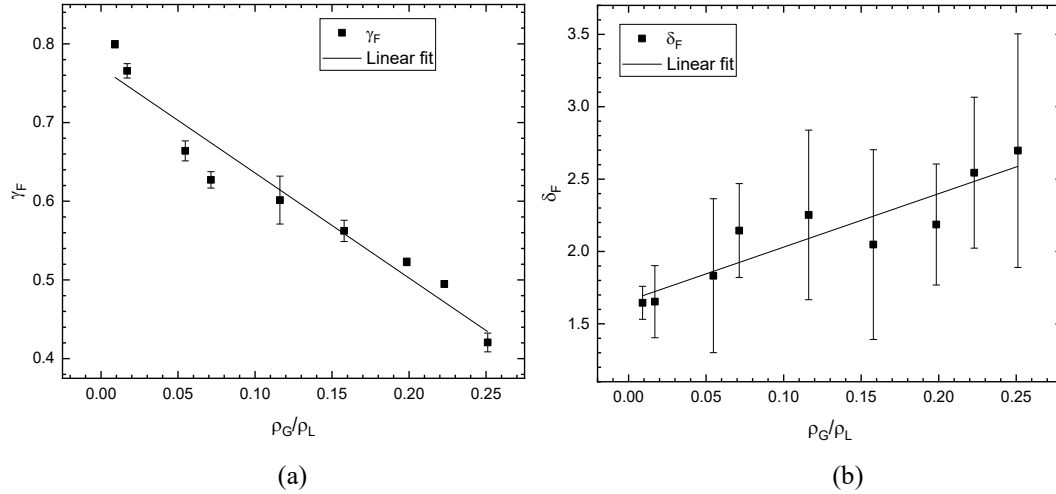


Figure 3.12. Surface tension depicted as γ_F (a) and Tolman length depicted as δ_F (b) for flat interfaces with different ρ_G/ρ_L .

The reason for this decrease is that γ results from the unbalanced intermolecular forces at the interface between the gas and liquid regions (as shown schematically in figure 3.13). The molecules on the interface experience a resultant force pointing into the liquid which means it tends to contract. As the liquid density is relatively constant, when there are fewer gas molecules in the gas region, they contribute less force to the interface which results in an unbalanced force state at the interface and a higher surface tension. When the gas density increases, the unbalanced force state of the interface eases and the surface tension decreases.

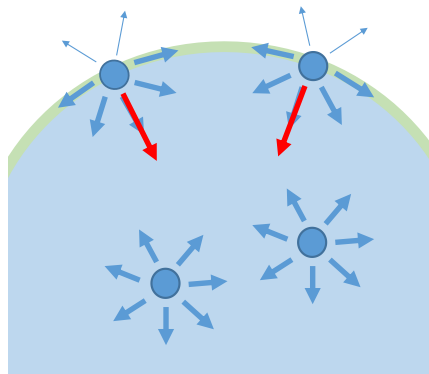


Figure 3.13. Schematic diagram showing typical force state of liquid molecules.

It is shown in figure 3.12 (a) that the surface tension of a flat interface (γ_F) has an approximately linear relationship with ρ_G/ρ_L , which is in agreement with results from other researches where the surface tension decreases linearly with the supersaturation ratio [51]. Thus, a linear fitting is applied to the data:

$$\gamma_F = -1.3352 \frac{\rho_G}{\rho_L} + 0.7695 \quad (3.20)$$

Moreover, ρ_G/ρ_L also shows an effect on the Tolman length (see figure 3.12 (b)). The Tolman length ranges from 1.2 to 3.5 reduced units. Similar to the results of surface tension, a linear relationship is used to fit the increase of the Tolman length with ρ_G/ρ_L :

$$\delta_F = 3.6941 \frac{\rho_G}{\rho_L} + 1.6605 \quad (3.21)$$

where δ_F represents the Tolman length for a flat interface. It should be noted here that as the relative uncertainty of δ_F is high, the linear fit can have a big variation.

These linear fits will be used to subtract γ_F and δ_F (with the same ρ_G/ρ_L as the curved interfaces) from curved interfaces to obtain the effect of curvature.

Molecular dynamics simulations necessarily contain a finite number of molecules, with periodic boundaries used at the edges. In order to ensure the finite-size of these systems do not affect the observed γ and δ , simulations have been performed to parameterise the effect of the simulation domain size. To demonstrate this, a set of simulations (referred to as ‘larger simulation domain’) which use twice as much space between the nanobubble/nanodroplet and the boundary as the remaining simulations were conducted.

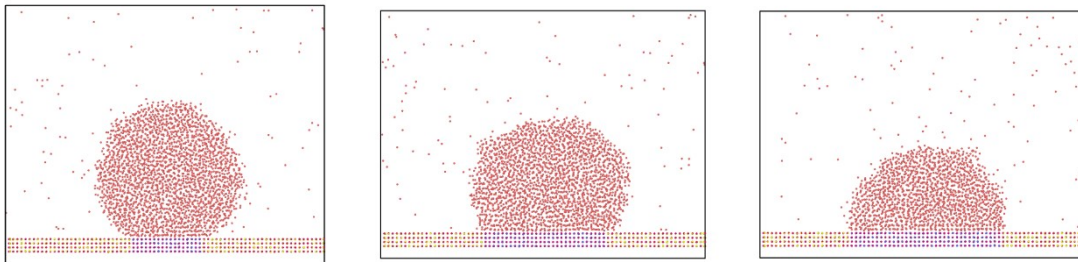


Figure 3.14. Nanodroplets with close curvature radii but different intrusions into the simulation domain.

The effect of the intrusion of the curved interface into the simulation domain on γ and δ has also been studied. Here, the intrusion of the curved interface is defined as distance between the fitted origin of the interface and the flat wall in the direction from wall to the curved interface normalised by the equimolar radius of the curved interface. It is determined by the curvature radius of the curved interface and the length of the pinning pattern. By controlling the length of the pinning pattern and the number of the liquid molecules, droplets with similar curvature radii but different intrusion can be obtained (referred to as ‘different intrusions’ and examples of droplets with close curvature radius but different intrusions are shown in figure 3.14).

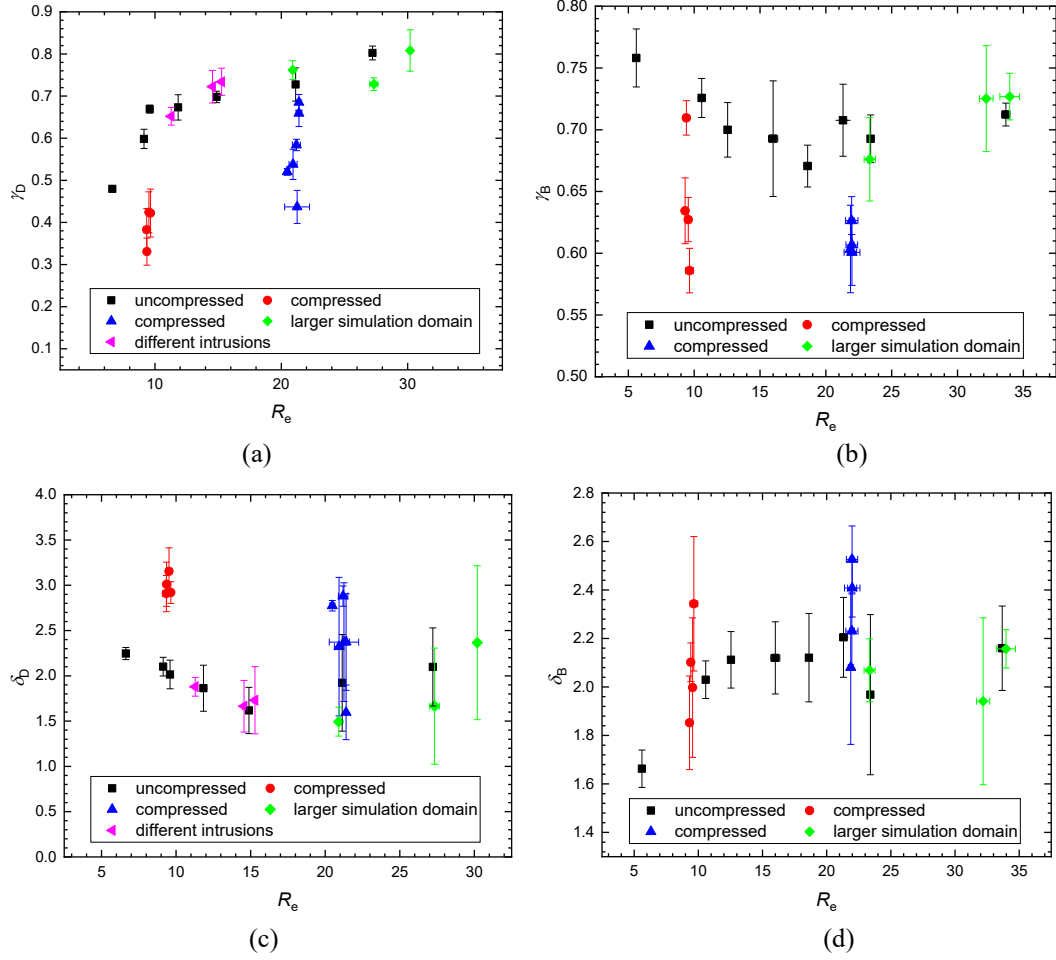


Figure 3.15. The surface tension and Tolman length as a function of R_e . (a) and (b) Surface tension VS for nanodroplets (γ_D) and nanobubbles (γ_B), respectively. (c) and (d) Tolman length VS R_e for nanodroplets (δ_D) and nanobubble (δ_B), respectively. This figure shows all curved interface cases run.

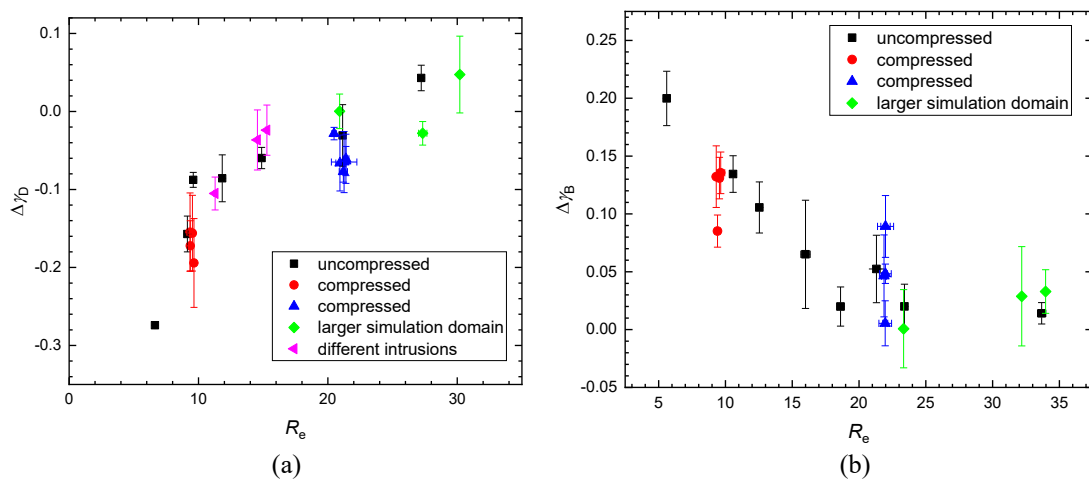
Figure 3.15 shows γ and δ for all curved interface cases run in this work. Results labelled ‘larger simulation domain’ and ‘different intrusions’ show similar values of γ and δ to the remaining results which confirms that the size of the simulation domain used in the remaining studies is sufficient to avoid finite size effects, and the intrusion of the nanodroplet interface does not affect the measured values of γ and δ . Figure 3.15 (a) and (b) show the surface tension of nanodroplet (γ_D) and nanobubble interfaces (γ_B) with different R_e and ρ_G/ρ_L . In all simulations, nanodroplets stay on the solid surfaces and are surround by gas region (see in figure 3.2 (a)). For the uncompressed nanodroplet cases (labelled as ‘uncompressed’), there are no gas molecules added in the system, thus the pressure in the bulk gas region is the saturated liquid-vapour pressure. While the pressure inside the droplet is governed by the Yong-Laplace law. For the compressed nanodroplet cases (labelled as ‘compressed’), different amounts of gas molecules are added in the bulk gas region to adjust the pressure of the system. All the nanobubbles stay on the solid surface and are submerged in liquid (see in figure 3.2 (b)). For the uncompressed nanobubble cases (labelled as ‘uncompressed’), there is a vapour region above the liquid region which ensures that the pressure in the bulk fluid equals the saturated liquid-vapour pressure.

While the pressure inside the bubble is determined by the Young-Laplace law. For the compressed nanobubble cases (labelled as ‘compressed’), there is no vapour region above the bulk liquid region, and the pressure of the system can be adjusted by the number of gas molecules added inside the bubble.

As we can see from figure 3.15 (a), γ_D of uncompressed nanodroplets increases monotonically with the molecular curvature radius and levels off at a R_e of around 20. Meanwhile, γ_D of compressed droplets is smaller than that of the uncompressed droplets with the same R_e which is in accordance with the flat interface cases where γ_F decreases as ρ_G/ρ_L increases. γ_B of the uncompressed nanobubble interface (shown in figure 3.15 (b)) decreases first and then increases slightly as R_e increases. Similarly, γ_B of compressed bubbles is smaller than that of the uncompressed bubbles with the same R_e . When R_e is smaller than 20, γ_D shows an opposite trend compared to γ_B , where γ_D decreases as R_e decreases while γ_B increases.

The results for Tolman length of the nanodroplet (δ_D) and nanobubble (δ_B) interfaces are shown in figure 3.15 (c) and (d), respectively. For both nanobubble and nanodroplet results, δ for compressed cases is slightly higher than the uncompressed cases which is in accordance with the flat interface cases where higher ρ_G/ρ_L leads to bigger δ_F . When R_e is smaller than 20, δ also shows opposite trends for the nanodroplet and nanobubble interfaces, where δ_D increases as R_e decreases while δ_B decreases. When R_e is larger than 20, the δ_D levels off smoothly while δ_B shows a slight decrease and then levels off. The results show that γ and δ for nanodroplet and nanobubble interfaces have different trends with the curvature radius. However, this is a combination of the effect of ρ_G/ρ_L and curvature. In the following section, the effect of curvature is obtained and discussed.

3.3.4 The effect of curvature on the surface tension and Tolman length



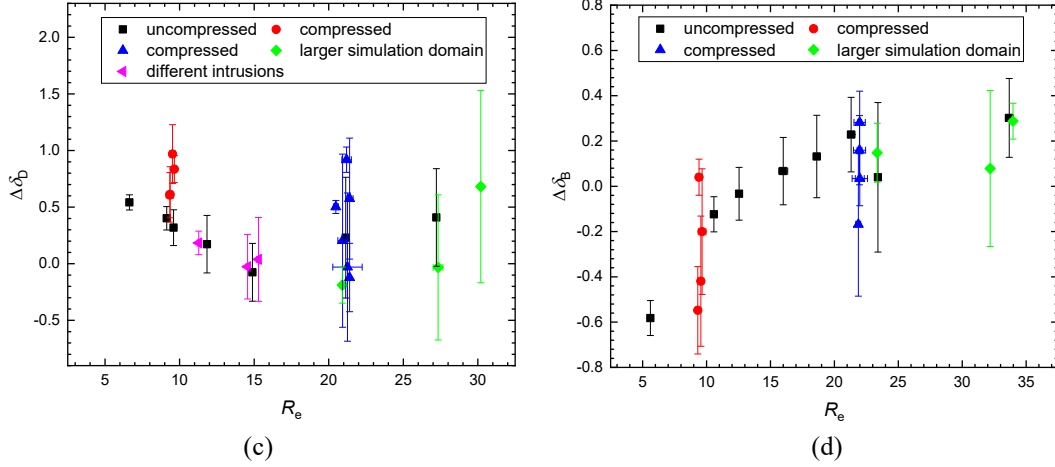


Figure 3.16. Effect of curvature on the surface tension and Tolman length obtained by subtracting the effect of ρ_G/ρ_L from the results in figure 3.15. (a) and (b) Curvature dependence of surface tension for nanodroplets and nanobubbles, respectively. (c) and (d) Curvature dependence of Tolman length for nanodroplets and nanobubbles, respectively.

As figure 3.12 (a) has shown, the effect of ρ_G/ρ_L on γ_F can be fitted to a linear relationship described with equation (3.20). Thus, the effect of the density ratio can be corrected in the droplet and bubble cases by using γ_F with the same ρ_G/ρ_L . Then, the difference between γ_F and γ for the curved interface (γ_D for nanodroplet interface and γ_B for nanobubble interface) can be regarded as the effect of curvature on γ ($\Delta\gamma$), which is

$$\Delta\gamma_D = \gamma_D - \gamma_F \quad (3.22)$$

for nanodroplet cases and

$$\Delta\gamma_B = \gamma_B - \gamma_F \quad (3.23)$$

for nanobubble cases.

The results for the effect of curvature on γ are shown in figure 3.16 (a) and (b). As we can see, when the effect of ρ_G/ρ_L on γ is corrected, the effect of the curvature on γ for both compressed nanodroplets and nanobubbles follows the uncompressed trends. Moreover, it is shown that the curvature shows an opposite effect on γ_D and γ_B . The same method applied here was used to obtain the effect of curvature on δ ($\Delta\delta$), which is

$$\Delta\delta_D = \delta_D - \delta_F \quad (3.24)$$

for nanodroplet cases and

$$\Delta\delta_B = \delta_B - \delta_F \quad (3.25)$$

for nanobubble cases.

The results for the effect of curvature on δ are shown in figure 3.16 (c) and (d). It is shown that, as with the results for γ , by subtracting the flat interfaces value of δ from both compressed nanodroplet and

nanobubble cases, it can be made to agree with the uncompressed trends. Similarly, the curvature presents opposite effects on δ_D and δ_B .

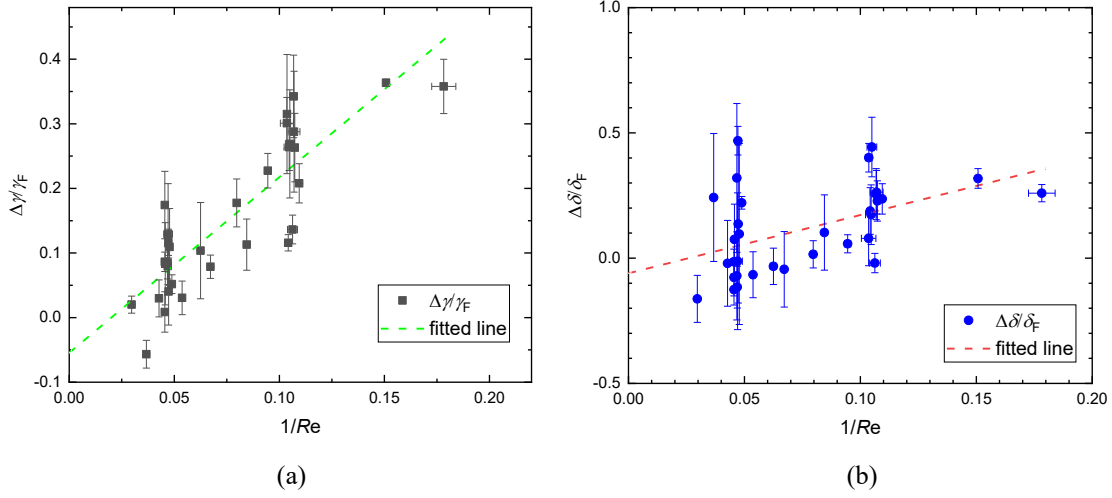


Figure 3.17. Effect of curvature on (a) the surface tension and (b) Tolman length.

Figure 3.17 (a) shows $\Delta\gamma$ normalised by γ_F with the same ρ_G/ρ_L (note here that opposite values to the results for nanodroplet interfaces are used). We can see that $\Delta\gamma/\gamma_F$ increases with the curvature of the interfaces. As the effect of curvature is expected to fade away when the curvature decreases, a linear relationship is fitted to the curvature dependence of the surface tension. The data points agree well with the fitted line as the effect of ρ_G/ρ_L is corrected. The results scatter evenly around the fitted line within the error bars. The effect of curvature on the surface tension vanishes at a curvature of around 0.02 where the fitted line intersects the x axis. Figure 3.17 (b) shows $\Delta\delta$ normalised by δ_F with the same ρ_G/ρ_L (note here that opposite values of the results for nanobubble interfaces are used). Similar to the surface tension, a linear relationship is fitted to the Tolman length. The data points do not agree as well as that for the surface tension with the fitted line. The reason is that the relative uncertainty of the Tolman length for the flat interface case is high [8, 43] (as shown in figure 3.12 (b)) and the linear fit to Tolman length and ρ_G/ρ_L for flat interface has a big possible variation.

As the effects of ρ_G/ρ_L and curvature on $\Delta\gamma$ are investigated separately, the results for surface tension in figure 3.15 can be discussed more thoroughly. For the uncompressed nanobubble cases, on the one hand, the pressure in the bulk liquid region is the saturated liquid-vapour pressure as there is a vapour region above the bulk-liquid region. However, inside the nanobubbles the pressure follows the Young-Laplace law and it increases when R_e decreases which causes the density inside the nanobubble increase, while the density of the liquid stays relatively the same. Then ρ_G/ρ_L increases and leads to a decrease of the surface tension as R_e decreases. On the other hand, the curvature also has an effect on the surface tension which leads to an increase of the surface tension as R_e decreases. When R_e is larger than 20, the effect of ρ_G/ρ_L dominates, and the surface tension shows a slight decrease as R_e decreases. When R_e is smaller than 20, the effect of curvature dominates, and the surface tension shows an increasing trend as

R_e decreases. For the uncompressed nanodroplet cases, there are no gas molecules in the vapour region and the pressure there is the saturated liquid vapour pressure. While inside the nanodroplets, the pressure follows the Young-Laplace law and increases as R_e decreases. However, because the liquid is incompressible, its density stays relatively constant. Thus ρ_G/ρ_L does not change for the nanodroplet cases and there is only the effect of the curvature. This is why the surface tension of the nanodroplet cases decreases monotonously as R_e decreases. Similar effects can also be seen from the results for Tolman length in figure 3.15.

3.3.5 Fitted Tolman equation considering both effects of density ratio and curvature

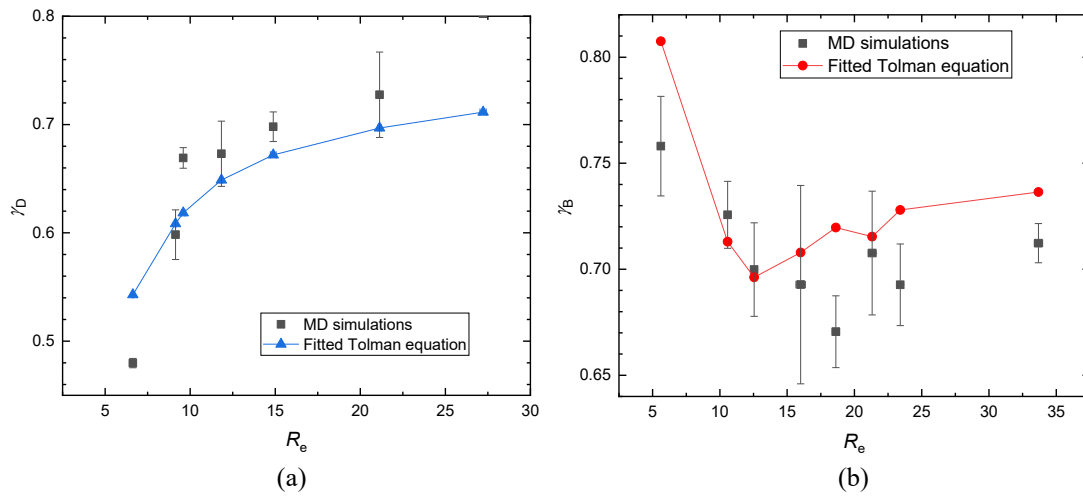


Figure 3.18. Surface tension for (a) nanodroplets and (b) nanobubbles obtained from MD simulations and the (fitted) Tolman equation for interfaces with different curvature.

As has been discussed that the relationship between the surface tension and the Tolman length for cylindrical nanobubble (equation (3.13)) and nanodroplet (equation (3.14)) interfaces were obtained following the methods adopted by Tolman. By substituting the fitted surface tension (equation (3.20)) and Tolman length (equation (3.21)) for flat interface into equation (3.13) and (3.14), we obtain the fitted Tolman equation for cylindrical nanodroplets and nanobubbles, respectively:

$$\gamma_{R_s} = \frac{R_s \left(-1.3352 \frac{\rho_G}{\rho_L} + 0.7695 \right)}{R_s + \left(3.6941 \frac{\rho_G}{\rho_L} + 1.6605 \right)} \quad (3.26)$$

$$\gamma_{R_s} = \frac{R_s \left(-1.3352 \frac{\rho_G}{\rho_L} + 0.7695 \right)}{R_s - \left(3.6941 \frac{\rho_G}{\rho_L} + 1.6605 \right)} \quad (3.27)$$

With the fitted Tolman equations, γ for nanodroplet and nanobubble cases with a certain curvature radius and ρ_G/ρ_L were obtained. The results are compared with the MD simulations in figure 3.18. It is shown that the surface tensions obtained with the MD simulations and the fitted Tolman equation show similar trends for both nanodroplet and nanobubble interfaces. When the curvature radius is larger than 10 for nanodroplets and 12 for nanobubbles, γ obtained with the two methods agree relatively well.

For smaller curvature radius, γ obtained with the fitted Tolman equation tends to be higher than that obtained with MD simulations. Such difference at the small curvature radius might come from the assumption that δ is constant, while from the results shown earlier in this chapter, we know that it varies with curvature radius when the curvature is smaller than 20. Equation (3.13) and (3.14) are obtained by integrating equation (3.15) and (3.16) with respect to R from infinite (flat interface) to the radius of interest (R_s). Thus, the effect of the curvature dependence of Tolman length will accumulate when the curvature radius is smaller than 20. And it causes the higher values of the results from the fitted Tolman equation for curvature radius smaller than around 10 for nanodroplets (around 12 for nanobubbles).

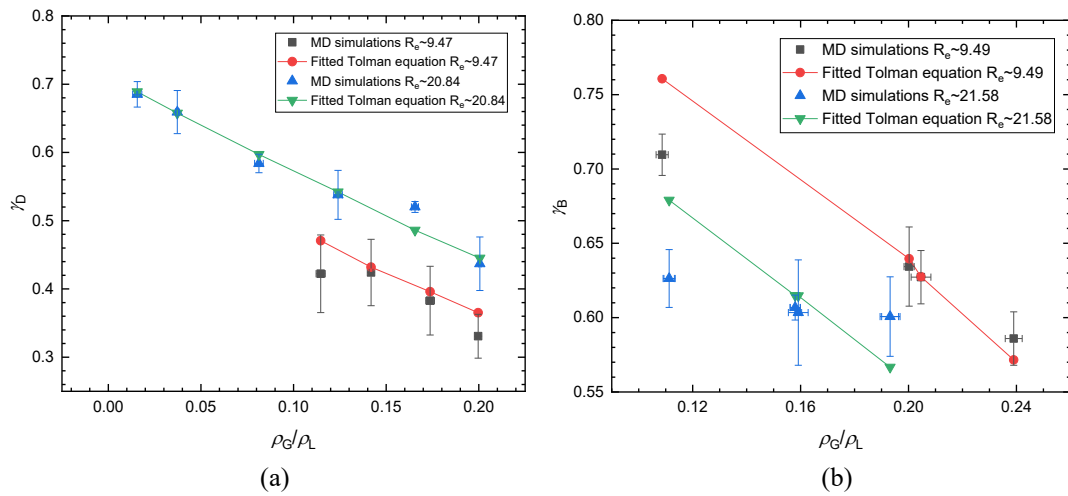


Figure 3.19 Surface tension for (a) nanodroplets and (b) nanobubbles obtained from MD simulations and the fitted Tolman equation for interfaces with different ρ_G/ρ_L .

The same comparison of γ obtained with the MD simulations and the fitted Tolman equation was done for nanobubble and nanodroplet interfaces with similar curvature but different ρ_G/ρ_L . Each data set in figure 3.19 represents cases with similar curvature radius. As we can see from figure 3.19 (a), γ obtained with the fitted Tolman equation is slightly higher than that obtained with the mechanical method when ρ_G/ρ_L is small. While for the nanodroplet cases, γ obtained with the two methods agree well with each other.

3.4 Conclusions.

In this chapter, positive values for the Tolman length, are obtained for flat, nanobubble and nanodroplet interfaces with MD simulations using a mechanical method based on the difference in mechanical pressure components. The Tolman length is defined as the distance from the surface of tension to the equimolar surface in the direction from liquid to gas. The effect of the gas/liquid density ratio is parameterised using the case of a flat interface, measuring the surface tension and Tolman length using flat liquid slabs sandwiched inside the gas region. It is found that the surface tension decreases linearly while the Tolman length increases linearly with the gas/liquid density ratio. Fittings are obtained which parameterise both surface tension and Tolman length as a function of density ratio. Next, the surface

tension and Tolman length for nanobubbles and nanodroplets confined on solid surfaces with alternate hydrophobic and hydrophilic patterns are simulated for various curvature radii. Using the density ratio relations from the flat interface case, the effect of gas/liquid density ratio is removed and the curvature dependence of the surface tension and Tolman length for cylindrical nanobubble and nanodroplet interfaces were obtained and compared. The curvature started to show an effect when the radius of the equimolar surface is smaller than 20 LJ reduced units. The droplet and bubble show equal but opposite trends in both surface tension and Tolman length as a function of radius. Using the effect of gas/liquid density ratio obtained from flat interface cases, a fitted Tolman equation can be obtained to predict the surface tension of a curved interface with certain curvature radius and gas/liquid density ratio. Results showed that the surface tension obtained with the fitted Tolman equation are comparable with those obtained with the MD simulations. They agree well except the higher values obtained with the fitted Tolman equation at smaller curvature radius due to the accumulation of the curvature dependence of the Tolman length.

Chapter 4. Liquid ring bearings

Having explored the effect of surface curvature and its effect on surface tension and Tolman length at the smallest of scales in chapter 3, I now turn my attention to the study of surface tension and its exploitation at larger scales. Liquid menisci at millimeter length scale and smaller exhibit large Laplace pressures. To utilise these effects, liquid ring bearings have recently been proposed, which consist of liquid rings confined between alternate superhydrophobic and hydrophilic patterns. In this chapter, we present a detailed experimental and theoretical performance analysis of an embodiment of such bearings. For a single, 100 μm thickness, liquid ring, the maximum supporting force is 0.13 N, which decreases with increasing the ring misalignment. The frictional torque increases linearly with rotational speed until a critical Reynolds number is reached. Above this, an instability occurs due the concave liquid ring meniscus, which further increases friction. These results show how liquid ring bearings can be optimised and their efficiency should increase as the scale of the bearing decreases.

4.1 Introduction

With the rapid development of microelectromechanical systems (MEMS), micro-turbines [182, 183], micro-gyroscopes [87, 88, 184, 185], and micro-generators [183, 186] are becoming increasingly important due to their compact size and the unique function they perform. However, as the length scale reduces to millimeter sizes and below, capillary forces induced by surface tension, dominates other forces such as electrostatic and inertia force. This causes strong adhesion in MEMS [187], which combined with high surface-to-volume ratio [110-112, 114] causes severe friction and wear in micro-scale contacts. Furthermore, at the micro-scale, friction and wear are much more sensitive to surface roughness, which is very difficult to control, and this renders the use of micro rolling element bearings unfeasible. These challenges prompted the development of novel lubricating systems for micro-scale examples of these are bearings levitated by air flow [119, 122, 123, 130, 188], electromagnetic or electrostatic force [92, 101, 102, 189]. These techniques are highly effective of reducing friction, however need auxiliary energy input and complex control systems. Liquid film lubrication - a prevalent method of reducing friction at the macro-scale - is often overlooked as a means of lubricating micro-bearings due to the perception that viscous drag force would be excessively high [115]. However, it has been shown that these problems are overcome if very low viscosity lubricants are used in combination with appropriate boundary lubricating additives [116, 117].

Recent years, a liquid thrust bearing which has a simple design and does not require external control has been reported by researchers [19-21, 142]. The liquid bearing takes advantage of the Laplace pressure, which increases as the curvature radius of the liquid/gas interface decreases, thus has the potential to lubricate at micro-scale. Alternate hydrophobic and hydrophilic patterns which form surface free energy barriers on a solid surface are used to anchor the liquid. The patterns are produced by a

hydrophobic chemical coating (liquid contact angle ~ 99 degrees) on the silicon substrate [19, 142]. With those patterns, a liquid droplet is confined on the central hydrophilic area of the stator. When the droplet is compressed, the Laplace pressure builds up inside the droplet and provides a supporting force to the upper rotor. Thus, the sliding rotor and stator were totally separated by the liquid droplet and the solid-solid contact is replaced by solid-liquid shearing which significantly reduced friction. Moreover, due to the increasing/decreasing contact angles on opposing sides of the liquid droplet, a restoring force results to balance any transverse force that is applied to the rotor. In subsequent designs [21], several small annularly located satellite droplets were placed around the central droplet to increase the tilt stiffness of the bearing at a cost of a $0.3 \mu\text{N}\cdot\text{m}$ increase to the startup torque. Later, those annular liquid droplets were replaced by liquid rings which were continuously deployed along the shear direction [20]. Compared to the droplets, the rings eliminate contact angle hysteresis along the shear direction and thus reduce the frictional torque of the rotor. Moreover, the two liquid rings are conductive which enables both energy and signal transmissions between the rotor and the substrate. However, additional liquid rings are possible for such bearings as shown in Figure 4.1. In fact, multiple rings are likely to be advantageous due to an increased solid/liquid interfacial area and a greater total contact line length. So far, the startup torque had been obtained by estimating the torque generated by the electrostatic force using finite element analysis (FEA). While many other mechanical properties, such the frictional torque as a function of the rotational speed and the supporting force as a function of the gap height between the rotor and the stator, have not been studied.

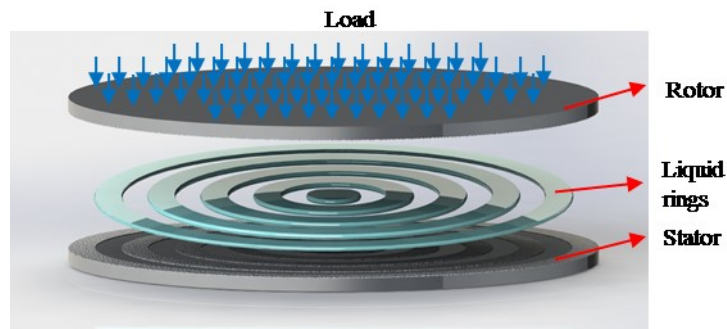


Figure 4.1. Schematic diagram of a liquid ring bearing.

In this chapter, a liquid ring thrust bearing is designed, made and tested using a rheometer and the working liquid is water. The supporting force and the frictional torque of the bearing was measured as a function of the gap height between the rotor and the stator and the rotational speed systematically. Numerical simulations are conducted to better understand the effects of the parameters on the performance of the bearing which can be used to optimize the design.

4.2 Experimental and Numerical Methods

4.2.1 Fabrication of the liquid ring thrust bearing

In order to reduce measurement errors and better understand the performance of the bearing, only one liquid ring was tested in this chapter (shown in Figure 4.2 (b)). The inner and outer radii of the liquid ring are $r_i = 16 \text{ mm}$ and $r_o = 18 \text{ mm}$. Since the liquid rings all have the same geometry, the results obtained from one liquid ring could be applied to the other liquid rings. The bearing consists two plates both with radius $R = 20 \text{ mm}$, one serves as the upper rotor, the other one serves as the lower stator. The rotor (shown in figure 4.2 (f)) and the stator (shown in figure 4.2 (e)) are the same except that an air hole was drilled at the centre of the stator to connect the inside chamber and the ambient environment to help eliminate any influence of air pressure. Alternate superhydrophobic and hydrophilic annular patterns are made on the bottom surface of the rotor and the upper surface of the stator by masked spraying of a commercial paint (Ultra-Ever Dry, Ultra Tech International)[190]. To make these patterns, first, the aluminium plates are polished with a surface roughness smaller than $R_a 1.6 \text{ }\mu\text{m}$. (figure 4.2 (a)) Next, annular vinyl strips with the width being the value expected for the width of the liquid ring was pasted on the plate surface which serve as the mask (figure 4.2 (b)). Then the superhydrophobic paint is spread on the surface of the plate (figure 4.2 (c)). It should be noted here that in order to make it easier to remove the vinyl strip when the coat is dry, only the top coat of the commercial is used in our experiments. After that, the superhydrophobic coat is dried at room temperature for 2 hours. Last, the vinyl strip is removed carefully and the glue residue is cleaned with ethanol (figure 4.2 (d)). The annular aluminium surface protected by the vinyl strip is still hydrophilic while the painted surface becomes superhydrophobic. The advancing contact angle of the superhydrophobic surface obtained in this work is 160° .

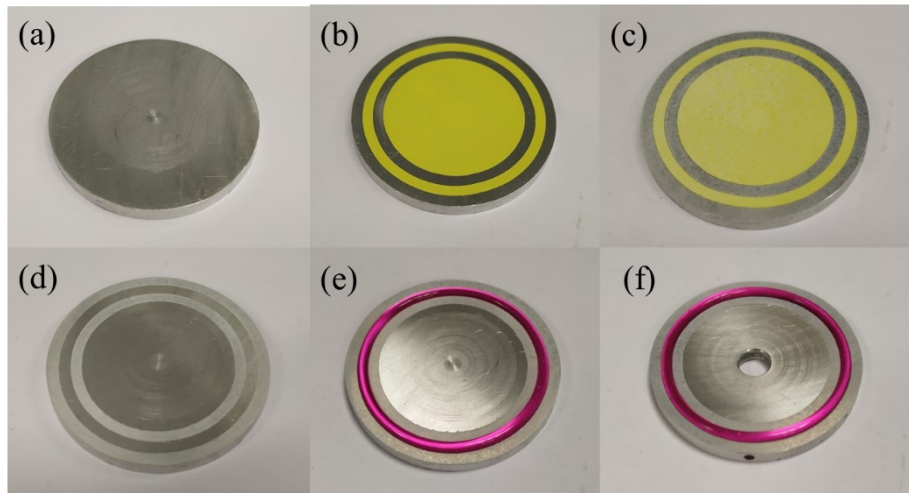


Figure 4.2. Fabricating process of the bearing. The diameter of the bearing is 40 mm.

A rheometer (DHR-1, TA instruments, USA) is used in this chapter to measure the frictional torque and the supporting force of the bearing (see from figure 4.3 (a)). The main specifications of the rheometer is shown in table 4.1. In the experiments, the rotor was attached to the rotatable shaft of the rheometer which could rotate or move vertically. The stator was attached to the base of the

rheometer and remains stationary during the test. The temperature was set to be 25 °C for all the tests. As the aluminium rotor is attached to the main axle of the rheometer, it changes the momentum of inertia of the shaft and the gap between the upper and lower geometries. Thus, they are calibrated before the experiments. During the experiments, firstly, a controlled volume of liquid is injected onto the hydrophilic strip of the stator. Confined by the surface free energy barrier at the boundary of the superhydrophobic and hydrophilic surfaces, the liquid forms an annular ring on the hydrophilic strip. When compressed, the pressure in the liquid ring becomes higher than atmospheric pressure according to the Young-Laplace Equation and provides a supporting force to bear the load on the rotor. Thus, the rotor and the stator are totally separated and the solid/solid contact is replaced by solid/liquid contact which reduces the friction when the rotor rotates.

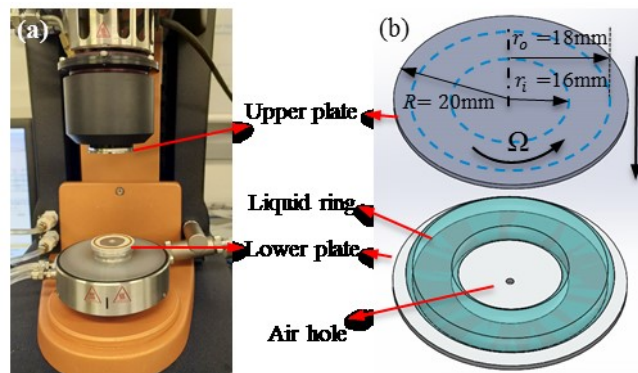


Figure 4.3. (a) Experimental setup. (b) Schematic diagram depicting the testing status of the bearing.

Table 4.1. DHR-1 Technical specifications

Item	Specification
Minimum torque oscillation	10 nN·m
Minimum torque steady shear	20 nN·m
Maximum torque	150 mN·m
Torque resolution	0.1 nN·m
Minimum frequency	1.0E-07 Hz
Maximum frequency	100 Hz
Minimum angular velocity ¹	0 rad/s
Maximum angular velocity	300 rad/s
Displacement resolution	10 nrad
Step time, strain ²	15 ms
Step time, rate ²	5 ms
Maximum normal force	50 N
Normal force sensitivity	0.01 N
Normal force resolution (mN)	1mN

When measuring the supporting force of the bearing, the rotor moves down gradually to compress the liquid ring. The axial force exerted on the rheometer shaft (*i.e.* the load support of the bearing) and the vertical location of the shaft (*i.e.* the gap height between rotor and stator) were recorded at a rate of 2 Hz. When measuring the frictional torque of the bearing, the gap height of the bearing was fixed. Then

the rotational speed of the rotor increased to a certain value. After allowing 5 s for the rotational speed to stabilize, the frictional torque exerted on the rheometer shaft was recorded for 10 s at a rate of 2 Hz.

4.2.2 Theoretical model for the static maximum supporting force of the liquid ring

The contribution of an individual liquid ring to the static supporting force of the bearing as depicted in figure 4.3 was investigated theoretically. Figure 4.4 describes the geometrical features of the liquid ring under investigation. According to the Young-Laplace equation, the pressure difference between the outside atmosphere and the inside of the liquid ring is $\Delta P = \gamma/R_C$, where γ is the liquid/air surface tension. R_C is the curvature radius of the liquid/air interface and it equals $1/(1/r_1 + 1/r_2)$, where r_1 and r_2 are the curvature radii of the liquid/air interface in the cross-sectional and horizontal planes respectively. The curvature radii of the inner and outer liquid/air interfaces in the cross-sectional plane are depicted in figure 4.4 (a) with r_{1in} and r_{1out} respectively, while the curvature radii in the horizontal plane are $-r_{2in}$ and r_{2out} respectively. As shown in figure 4.4 (b), the Laplace pressure difference across the liquid/air interface provides a force ($F_{Laplace}$) directed upwards which helps to support the rotor. The capillary force ($\gamma \cdot l$, where l is the length of the contact line), which acts on the contact line of the liquid ring, has a vertical component F_γ . This acts to pull the rotor and stator together. Thus, the static supporting force of the bearing is $F = F_{Laplace} - F_\gamma$ which balances the load on the rotor. Although F_γ is small enough to be neglected for the bearing in this work, it can be important and should be considered at the micro-scale.

When the load on the rotor increases, r_1 decreases with the gap height (h_r) between the rotor and the stator which leads to a higher Laplace pressure inside the liquid ring to balance the increased load. In the whole process, the curved inner and outer liquid/air interfaces should give the same Laplace pressure. Because the inner liquid/air interface has a negative curvature on the horizontal plane, it gives a negative contribution to the pressure in the liquid ring. Thus, r_{1in} needs to be smaller than r_{1out} in order to give the same pressure difference. As the load is increased further, the curvature radius of the liquid/air interface on the inner side of the liquid ring r_{1in} reaches the upper limit (r_{1in_limit}) first and leads to the collapse of the liquid ring (see figure 4.4 (b)). So, when considering the maximum static supporting force of the rotor, the smallest r_{1in} is analyzed (see figure 4.4 (c)). The critical condition is that the contact angle on the inner side of the liquid ring reaches the advancing contact angle (θ_A) on the superhydrophobic surface. In the model, the inevitable, small misalignment between the patterns on the rotor and the stator induced in the fabrication and assembly processes has been considered as ΔL .

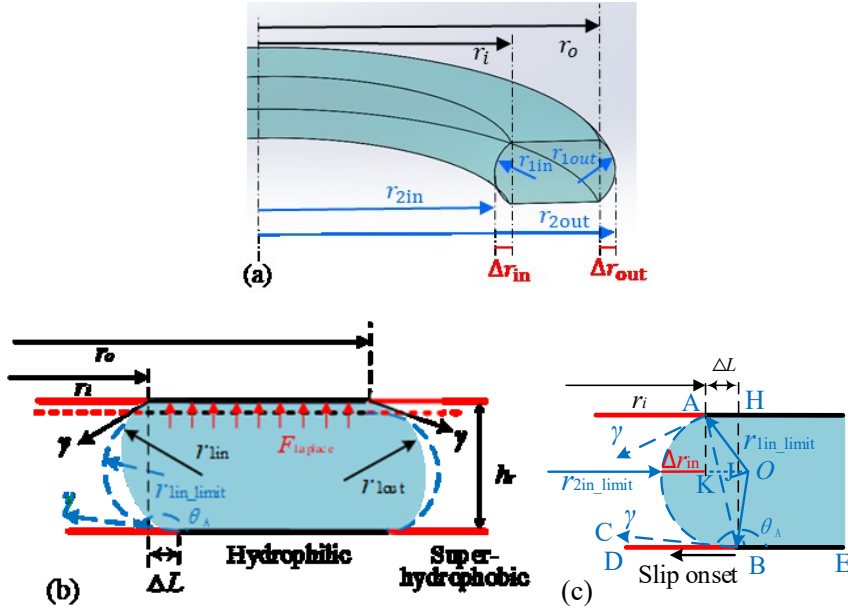


Figure 4.4. (a) Schematic diagram depicting the geometric features of the liquid ring. (b) Cross-sectional view of the liquid ring showing the stress analysis (The dashed blue lines show the critical condition of the liquid ring). (c) Cross section of ring showing geometry and stress analysis of the contact line at the critical condition when slip occurs (dashed lines in (b)).

When the applied load reaches a certain value, the contact line will slip, and the bearing will collapse – *i.e.*, for any given gap height, there is an upper limit to the load support that the bearing can provide. This maximum static supporting force is an important bearing performance parameter and is analyzed as follows. First, the limit of the curvature radius for a single liquid ring, must be found. This can be achieved with reference to figure 4.4 (c), which depicts the geometry of the contact line at the critical condition when the critical contact angle is reached and contact line slip occurs.

In figure 4.4 (b) and (c), the black line represents the hydrophilic strip and the red line represents the superhydrophobic surface. ΔL is the misalignment between patterns on the rotor and the stator. Point A and B in figure 4.4 (c) are the joint point of the alternate superhydrophobic and hydrophilic patterns which are also the location where the three-phase contact line is pinned. Point O is the centre of the curved liquid/air interface. Point K is the midpoint of line AB. As can be deduced from the isosceles triangle ABO, the limiting curvature radius in cross sectional plane of the inner meniscus is

$$r_{1in_limit} = \frac{AB/2}{\cos(\angle ABO)} \quad (4.1)$$

Because the liquid/air surface tension (γ) is tangential to the outline of the interface, we know that $\angle CBO$ is a right angle. Then

$$\angle ABO = \angle CBO - \angle CBA = 90^\circ - \angle CBA \quad (4.2)$$

In the right triangle ABH, $\angle ABH$ can be obtained as

$$\angle ABH = 90^\circ - \arctan\left(\frac{h_r}{\Delta L}\right) \quad (4.3)$$

As has been mentioned that at the critical state, the inner contact angle of the liquid ring reaches the advancing contact angle of the superhydrophobic surface (θ_A) which gives

$$\angle CBE = \theta_A \quad (4.4)$$

Thus $\angle CBD$ can be obtained as

$$\angle CBD = 180^\circ - \angle CBE = 180^\circ - \theta_A \quad (4.5)$$

It is also known that $\angle DBH$ is a right angle. Then $\angle CBE$ can be obtained

$$\angle CBA = \angle DBH - \angle CBD - \angle ABH = 90^\circ - \angle CBD - \angle ABH \quad (4.6)$$

Substitute equation (4.6) into (4.2)

$$\angle ABO = \angle CBD + \angle ABH \quad (4.7)$$

Substitute equation (4.3) and (4.5) in to (4.7), we have

$$\angle ABO = 290^\circ - \theta_A - \arctan\left(\frac{h_r}{\Delta L}\right) \quad (4.8)$$

Substitute equation (4.7) into (4.1), the limiting curvature radius in the horizontal plane of the inner meniscus can be obtained

$$r_{1in_limit} = \frac{\sqrt{(\Delta L)^2 + h_r^2}}{2\cos(270^\circ - \theta_A - \arctan(\frac{h_r}{\Delta L}))} \quad (4.9)$$

The limiting curvature radius in the horizontal plane of the inner meniscus can also be deduced from figure 4.4 (c) as

$$r_{2in_limit} = -(r_i - \Delta r_{in}) \quad (4.10)$$

where Δr_{in} is depicted in figure 4.4 (a) and (c) using a solid red line and can be calculated as

$$\Delta r_{in} = r_{1in_limit} - KJ - JO = r_{1in_limit} - \Delta L - JO \quad (4.11)$$

where JO can be obtained in the right triangle JOB as

$$JO = r_{1in_limit} \cdot \cos(\angle JOB) = r_{1in_limit} \cdot \cos(\angle OBE) = r_{1in_limit} \cdot \cos(\theta_A - 90^\circ) \quad (4.12)$$

Substitute equation (4.11) and (4.12) into (4.10), the limiting curvature radius in the horizontal plane of the inner meniscus can be obtained as

$$r_{2in_limit} = -(r_i - \Delta r_{in}) = -\left(r_i - \left(r_{1in_limit} \cdot (1 - \cos(\theta_A - 90^\circ) - \Delta L)\right)\right) \quad (4.13)$$

The term $(r_{1in_limit} \cdot (1 - \cos(\theta_A - 90^\circ) - \Delta L))$ in equation (4.13) is small enough to be neglected compared to the inner radius of the liquid ring r_i . So we have $r_{2in_limit} \approx -r_i$ and then the Laplace pressure is

$$\Delta P = \frac{2\gamma \cos(270^\circ - \theta_A - \arctan(\frac{h_r}{\Delta L}))}{\sqrt{(\Delta L)^2 + h_r^2}} - \frac{\gamma}{r_i} \quad (4.14)$$

The supporting force provided by the Laplace pressure is

$$\begin{aligned} F_{Laplace} &= \Delta P \cdot \pi(r_o^2 - r_i^2) \\ &= \left(\frac{2\gamma \cos(270^\circ - \theta_A - \arctan(\frac{h_r}{\Delta L}))}{\sqrt{(\Delta L)^2 + h_r^2}} - \frac{\gamma}{r_i} \right) \cdot \pi(r_o^2 - r_i^2) \end{aligned} \quad (4.15)$$

where r_o is the outer radius of the liquid ring. Actually the ratio of the gap height to the misalignment $(h_r/\Delta L)$ has a strong influence on the supporting force of the bearing and if we define $\alpha = \arctan(h_r/\Delta L)$ here, equation (4.15) can be rewritten compactly as

$$F_{Laplace} = \left(\frac{2\gamma \cos(270^\circ - \theta_A - \alpha) \cdot \sin(\alpha)}{h_r} - \frac{\gamma}{r_i} \right) \cdot \pi(r_o^2 - r_i^2) \quad (4.16)$$

The vertical component of the surface tension is

$$F_Y = \gamma \cdot \cos(\theta_A - 90^\circ) \cdot 2\pi(r_i + r_o) \quad (4.17)$$

Thus the static maximum supporting force is

$$F = F_{Laplace} - F_Y \quad (4.18)$$

4.2.3 Mathematical model for the profile of the liquid/air interface and the maximum dynamic supporting force of the bearing

As the rotor rotates, the liquid in the liquid ring flows in an annular direction due to the shear force from the rotor. The liquid at different vertical locations have different azimuthal speeds and thus experience centrifugal forces with different magnitudes. This will cause asymmetric deformation to the meniscus and finally leads to the collapse of the liquid ring. Here a mathematical model is used to simulate the

deformation of the meniscus when the rotor is rotating at different speeds. Figure 4.5 (a) shows the coordinate system used in the model. The vertical location z is the independent variable and the radial location r is the dependent variable. So the profile of the liquid/air interface reads $r(z)$.

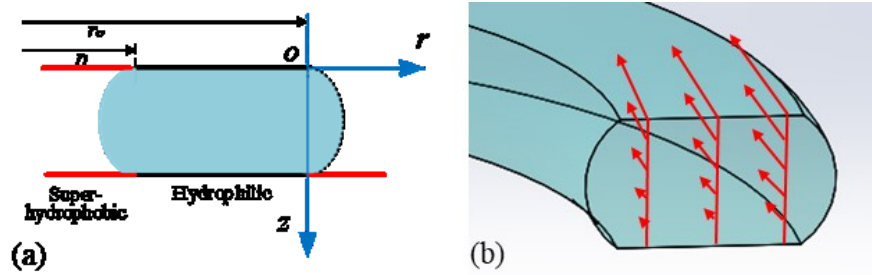


Figure 4.5. (a) The cross-sectional view of the liquid ring and the coordinate system. (b) Assumed laminar velocity profile in the liquid ring.

The curvature of the liquid/air interface[191] is

$$\frac{1}{R_c} = \frac{|r''|}{(1 + (r')^2)^{\frac{3}{2}}} \quad (4.19)$$

The pressure inside the liquid ring contains four contributions which are the pressure induced by the load, the pressure induced by the capillary force, the pressure induced by the centrifugal acceleration and the pressure induced by the gravitational acceleration. The pressure induced by the load is:

$$\frac{m \cdot g}{\pi(r_o^2 - r_i^2)} \quad (4.20)$$

where m is the load on the rotor, g is the gravitational acceleration.

The pressure induced by the capillary force is:

$$\frac{\gamma \cdot \cos(\theta - 90^\circ) \cdot 2\pi(r_i + r_o)}{\pi(r_o^2 - r_i^2)} \quad (4.21)$$

where θ is the actual contact angle on the contact line.

To calculate the pressure induced by the centrifugal force in the liquid ring, the velocity profile in the liquid ring needs to be calculated. First we defined the Reynolds number as $Re = \frac{\rho \cdot h_r \cdot \Omega \cdot r_o}{\eta}$, where ρ is the density of liquid, Ω is the rotational speed of the rotor and η is the kinematic viscosity. The maximum rotational speed tested in the experiment is 104.7 rad/s and the maximum height of the liquid ring is 400 μm , which gives a maximum Re of 750. For Re smaller than 750, we assume here that the flow inside the liquid ring is laminar and the velocity in the liquid ring decreases linearly from the upper

plate to the lower plate as shown in figure 4.5 (b). Thus the local rotational speed in the liquid ring is $\omega = \frac{(h_r - Z)}{h_r} \Omega$. Therefore, the pressure induced by the centrifugal acceleration is:

$$\int_{r_i}^r (\rho \cdot \omega^2 r) dr = \rho \left(\frac{Z}{h_r} \Omega \right)^2 \frac{(r^2 - r_i^2)}{2} \quad (4.22)$$

The pressure induced by the gravitational acceleration is $\rho \cdot g \cdot z$

Considering all the four contributions, the pressure difference between the inside and the outside of the liquid/air interface is

$$\Delta P = \frac{m \cdot g + \gamma \cdot \cos(\theta - 90^\circ) \cdot 2\pi(r_i + r_o)}{\pi(r_o^2 - r_i^2)} + \rho \left(\frac{h_r - Z}{h_r} \Omega \right)^2 \frac{(r^2 - r_i^2)}{2} + \rho \cdot g \cdot z \quad (4.23)$$

Substituting equation (4.18) and (4.23) into the Young-Laplace equation, we have the equation of the liquid/air interface:

$$\frac{|r''| \gamma}{(1 + (r')^2)^{\frac{3}{2}}} = \frac{m \cdot g + \gamma \cdot \cos(\theta - 90^\circ) \cdot 2\pi(r_i + r_o)}{\pi(r_o^2 - r_i^2)} + \rho \left(\frac{h_r - Z}{h_r} \Omega \right)^2 \frac{(r^2 - r_i^2)}{2} + \rho \cdot g \cdot z \quad (4.24)$$

This differential equation (4.24) has no known analytical solution, and is therefore solved numerically in a coordinate system shown in figure 4.6.

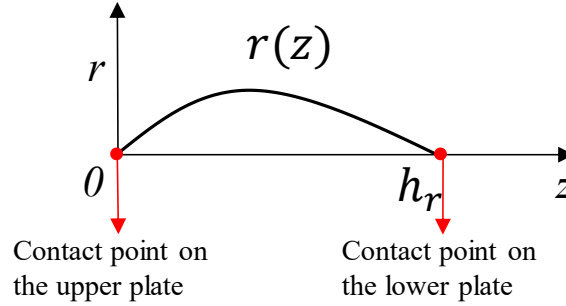


Figure 4.6. The coordinate system used to simulate the profile of the liquid/air interface numerically.

There two different ways of simulating the profile of the liquid/air interface. One of them is that the load and the gap height of the bearing are given as the boundary conditions. Then the profile of the liquid/air inter face is simulated. The other one is that the upper contact angle and the gap height of the bearing are given as the boundary condition. With the first method, the profile of the liquid/air interface under a certain load, gap height and rotational speed can be obtained. With the second method, the maximum dynamic load of the bearing can be obtained when the upper contact angle is given as the advancing contact angle on the superhydrophobic surface.

$$\text{Differential equations of the air/water surface profile:}$$

$$\frac{|r''|\gamma}{(1 + (r')^2)^{\frac{3}{2}}} = \frac{mg + \gamma \cdot \cos(\theta - 90^\circ) \cdot 2\pi(r_i + r_o)}{\pi(r_o^2 - r_i^2)} + \rho \left(\frac{h_r - Z}{h_r} \Omega \right)^2 \frac{(r^2 - r_i^2)}{2} + \rho g z$$

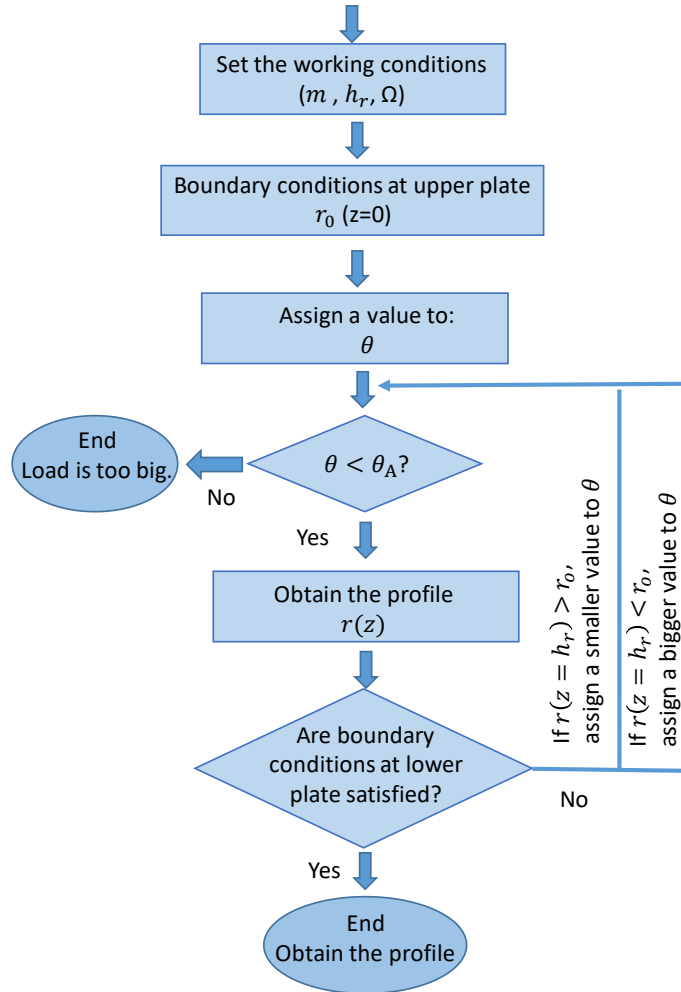


Figure 4.7. The flow chart of simulating profile of the liquid/air interface for a given load and gap height.

The flow chart of the first method is shown in figure 4.7. In the simulation, firstly, boundary conditions on the upper plate which are the coordinates of the contact point of the liquid/air interface there (0, 0) as well as the load and gap height of the bearing are used. Then, a value is assigned to the upper contact angle (θ) in the differential equation (4.24). If the assigned value is larger than the advancing contact angle on the superhydrophobic surface (θ_A), it means the load on the plate is too big and the simulation ends with an error. If the applied value is smaller than θ_A , the simulation continues. After that, equation (4.24) is solved numerically. This gives a profile of the outer liquid/air interface. From the simulated profile, the coordinates ($h_r, (z = h_r)$) of the contact point on the lower plate is obtained. However, this point might not coincide with the junction point of the superhydrophobic and hydrophilic strips on the lower plate. Then a larger value is assigned to θ if $r(z = h_r)$ is smaller than r_o (see figure 4.8 (a)), otherwise, a smaller value is assigned to θ and the loop circulates (see figure 4.8 (b)). When

the point $r(z = h_r)$ is close enough to r_o , the circulation ends and the profile of the liquid/air interface is obtained (see figure 4.8 (c)).

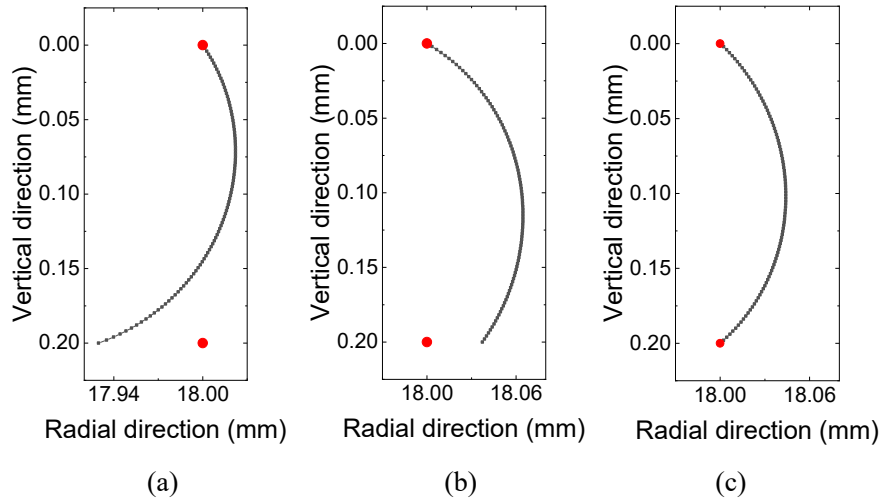


Figure 4.8. Simulated profiles of the liquid/air interface (jointed black line) and the junction point of the superhydrophobic and hydrophilic strips on the upper and lower plates (red dots). (a) Simulated profile with the upper contact angle or the load being too small. (b) Simulated profile with the upper contact angle or the load being too big. (c) The right simulated profile.

The flow chart of the second method is shown in figure 4.9. In the simulation, instead of the load of the bearing, the upper contact angle of the liquid ring is given as one of the boundary conditions while the others are the same as those used in the first method. Then, a value is assigned to the load of the bearing (m) in the differential equation (4.24) and the equation is solved numerically. This gives a profile of the outer liquid/air interface. From the simulated profile, the coordinates $(h_r, (z = h_r))$ of the contact point on the lower plate is obtained. If the simulated $r(z = h_r)$ is smaller than r_o (see figure 4.8 (a)), a bigger value is assigned to m . Otherwise, a smaller value is assigned to m (see figure 4.8 (b)). Then the loop circulates until the lower contact point is close enough to the junction point of the superhydrophobic and hydrophilic strips on the lower plate (see figure 4.8 (c)).

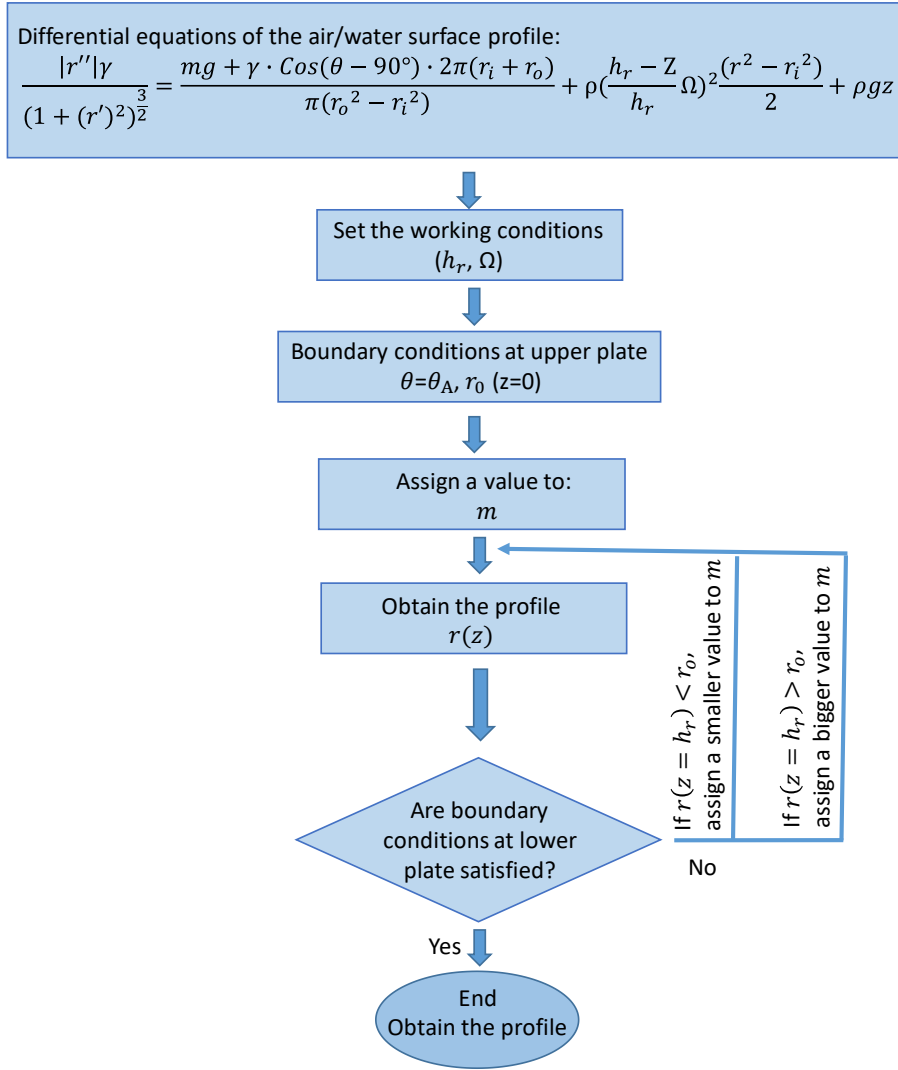


Figure 4.9. The flow chart of simulating profile of the liquid/air interface for a given upper contact angle and gap height.

4.2.4 Mathematical model for the frictional torque

As has discussed previously, the flow in the liquid ring is assumed to be laminar. Based on the laminar assumption, neglecting the effect of the concave meniscus, the frictional torque (T) can be deduced. The velocity gradient in the radial direction is

$$\tau = \mu \frac{dv}{dh} = \mu \frac{\Omega r}{h_r} \quad (4.25)$$

The frictional torque can be obtained by integrating equation (4.25) from r_i to r_o

$$T = \int_{r_i}^{r_o} \mu \frac{\Omega r}{h_r} (2\pi r) r dr = \frac{\pi \cdot \Omega \cdot \mu}{2h_r} (r_o^4 - r_i^4) \quad (4.26)$$

4.3 Results and discussion

When designing a bearing, the supporting force, speed limit and frictional torque are the key factors which should be considered. These performance parameters were investigated using both numerical and experimental methods and the results are shown in this section.

4.3.1 Supporting force of the bearing

The supporting force of the bearing, which comes from the Laplace pressure inside liquid ring, is directly related to the surface tension and curvature radius of the liquid/air interface. Because the temperature and the liquid composition used for all the tests in this chapter were the same, the surface tension was considered constant. Thus the static supporting force is only a function of the curvature radius of the liquid/air interface which is governed by the contact angle of the liquid ring, the misalignment of the patterns and the gap height between the rotor and the stator. Figure 4.10 shows both the theoretical and experimental results for the static supporting force as a function of the gap height.

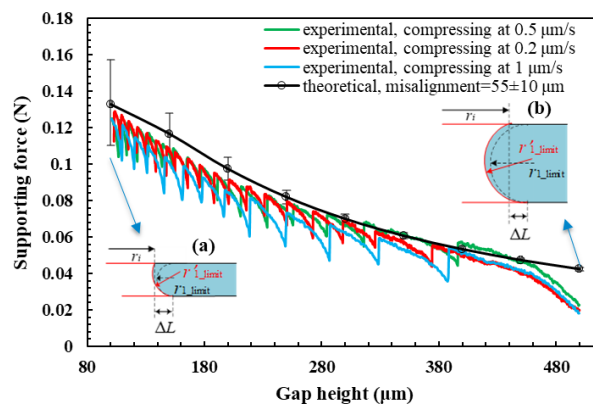


Figure 4.10. The supporting force of the bearing as a function of the gap height. Inserts: Schematic curvature radii in the cross-sectional plane.

In the experiments, first, 140 μL liquid was injected onto the hydrophilic strip on the stator and a liquid ring formed there. Then, the rotor which was attached to the main shaft of the rheometer moved down to compress the liquid ring. Three different approaching speeds of the rotor have been tested which are 0.2, 0.5 and 1 $\mu\text{m/s}$. Because liquid is incompressible, the height decrease of the liquid ring due to the movement of the rotor has to be compensated by an increase in the concave meniscus. Therefore, the liquid/air interface penetrates out further and leads to larger contact angles of the liquid ring. Larger contact angles and smaller gap heights together lead to smaller curvature radii thus a higher Laplace pressure inside the liquid ring. This explains why the measured supporting force shown in figure 4.10 increases as the gap height decreases. When the rotor moves down to the location where the contact angle of the liquid ring reaches the advancing contact angle of the superhydrophobic surface, the contact line slips and a small liquid droplet escapes from the liquid ring which causes a sudden drop to the

supporting force as shown in figure 4.10. After that, the remaining liquid rapidly rebuilds a liquid ring due to the surface tension. The newly formed liquid ring has less liquid and smaller contact angles thus a smaller supporting force than before it was broken. As the rotor moves down continuously, the pressure in the liquid ring builds up again. When the contact angle of the liquid ring reaches the limit again, another smaller liquid droplet escapes and the supporting force experiences another sudden drop. As the gap height decreases, the size of the meniscus decreases which means it takes less time to fill the meniscus. Thus, the collapse of the liquid ring happens more often. This is also reflected in figure 4.10 by the more frequent step changes in supporting force that occur in the small gap height region than in the large gap height region. The results also show that the effect of compression speed is very small. For the theoretical results, the compressing process and the escaping of the liquid droplets were not considered, only the maximum static supporting force at different gap heights was calculated. At a certain gap height, the static supporting force of the bearing reaches its maximum value when the inner contact angle of the liquid ring reaches the advancing contact angle of the superhydrophobic surface. It is shown that a misalignment of $55 \pm 10 \mu\text{m}$ (which is a reasonable value) between the patterns on the rotor and those on the stator would give a good agreement to the theoretical and experimental results. However, as the radial misalignment remains constant, the error in the supporting force increases as the gap height decreases. This is because when the misalignment is much smaller than the gap height (as shown in figure 4.10 insert b), the effect of the misalignment on the curvature radius is small. When misalignment is comparable to the gap height (as shown in figure 4.10 insert (a)), the effect of the misalignment on the curvature radius becomes significant.

As has been discussed, the supporting force of the bearing results from the Laplace pressure inside the liquid ring (F_{Laplace}) and the surface tension acting on the three-phase contact line (F_{γ}). Figure 4.11 compares these two contributions to the supporting force of the bearing without misalignment. As we can see, F_{Laplace} increases as the gap height decreases while F_{γ} does not vary with the gap height. F_{γ} is very small compared with F_{Laplace} . At the same gap height, F_{Laplace} increases with the advancing contact angle of the superhydrophobic surface, while the magnitude of F_{γ} decreases with the advancing contact angle. Because F_{γ} has a negative contribution to the supporting force, the supporting force is expected to increase with the advancing contact angle. The results shown later prove this expectation.

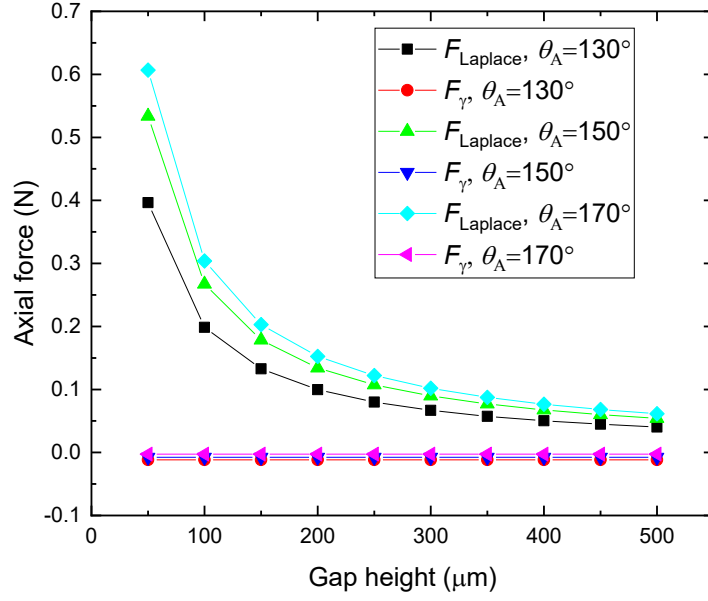
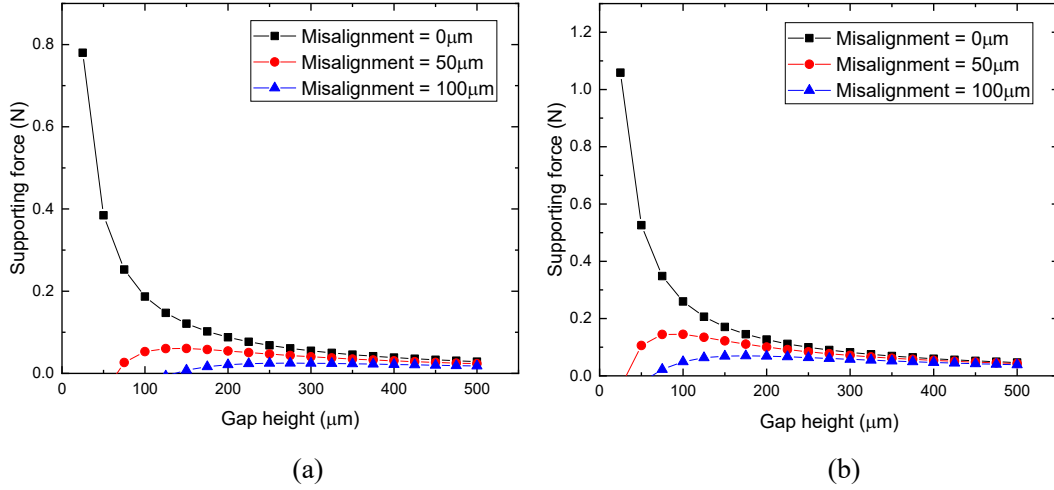
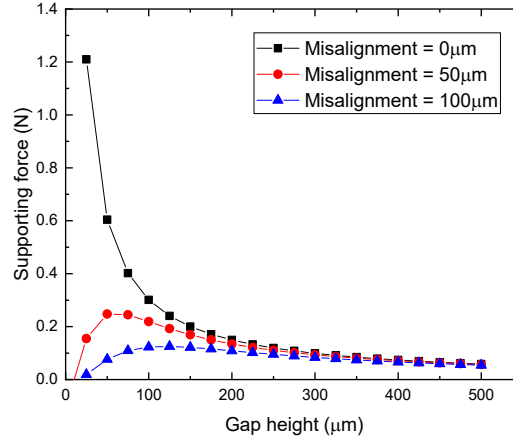


Figure 4.11. Contributions from the Laplace pressure and the surface tension on the three-phase contact line to the supporting force of the bearing without misalignment.

Using the theoretical model, the effects on the supporting force caused by the misalignment of the patterns and the advancing contact angle on the superhydrophobic surface have been studied and the results for the effect of misalignment are shown in figure 4.12.





(c)

Figure 4.12. Supporting force as a function of gap height for different misalignments at different advancing contact angle on the superhydrophobic surface. (a) Advancing contact angle equals 130° . (b) Advancing contact angle equals 150° . (c) Advancing contact angle equals 170° .

As shown in figure 4.12, for the bearing with no misalignment, the maximum supporting force increases monotonically as the gap height decreases. Moreover, the increasing rate gets larger when the gap height gets smaller. While for the bearing with a misalignment, the maximum supporting force increases as the gap height decreases and then starts to decrease below a critical gap height. In real application, a misalignment is inevitable and the load on the rotor is usually dynamic. As shown in figure 4.12, for bearing with a misalignment, the maximum supporting force of the bearing has a maximum value. Here we define the maximum value of the maximum supporting force as the global maximum supporting force of the bearing. It is the maximum supporting force that a bearing with a misalignment can give among all gap heights and contact angles. When the bearing works above the critical gap height and load shows a sudden increase, the gap height of the bearing would decrease and the supporting force of the bearing would increase to balance the impulse load. If the bearing works below the critical gap height and the load shows a sudden increase, the gap height of the bearing would decrease. However, as the gap height of the bearing decreases, the supporting force of the bearing decreases and the bearing collapses. Thus, when designing a liquid ring bearing, the working gap height of the bearing should be larger than the critical gap height.

Figure 4.13 compares the effect of the advancing contact angle of the superhydrophobic surface on the maximum supporting force of a bearing at different gap height. As we can see, for all the misalignments, the supporting force of the bearing at a certain gap height increases with the advancing contact angle on the superhydrophobic surfaces. For the bearing with a misalignment, the critical gap height decreases while the global maximum supporting force increases as the advancing contact angle on the superhydrophobic surface increases. As the misalignment increases (figure 4.13 (a) to (c)), the effect of the hydrophobicity of the superhydrophobic surfaces on the maximum static supporting force of the

bearing increases. Which means when designing the bearing, the superhydrophobic surface should be as hydrophobic as possible, it can to some degree compensate the negative effect of the misalignment.

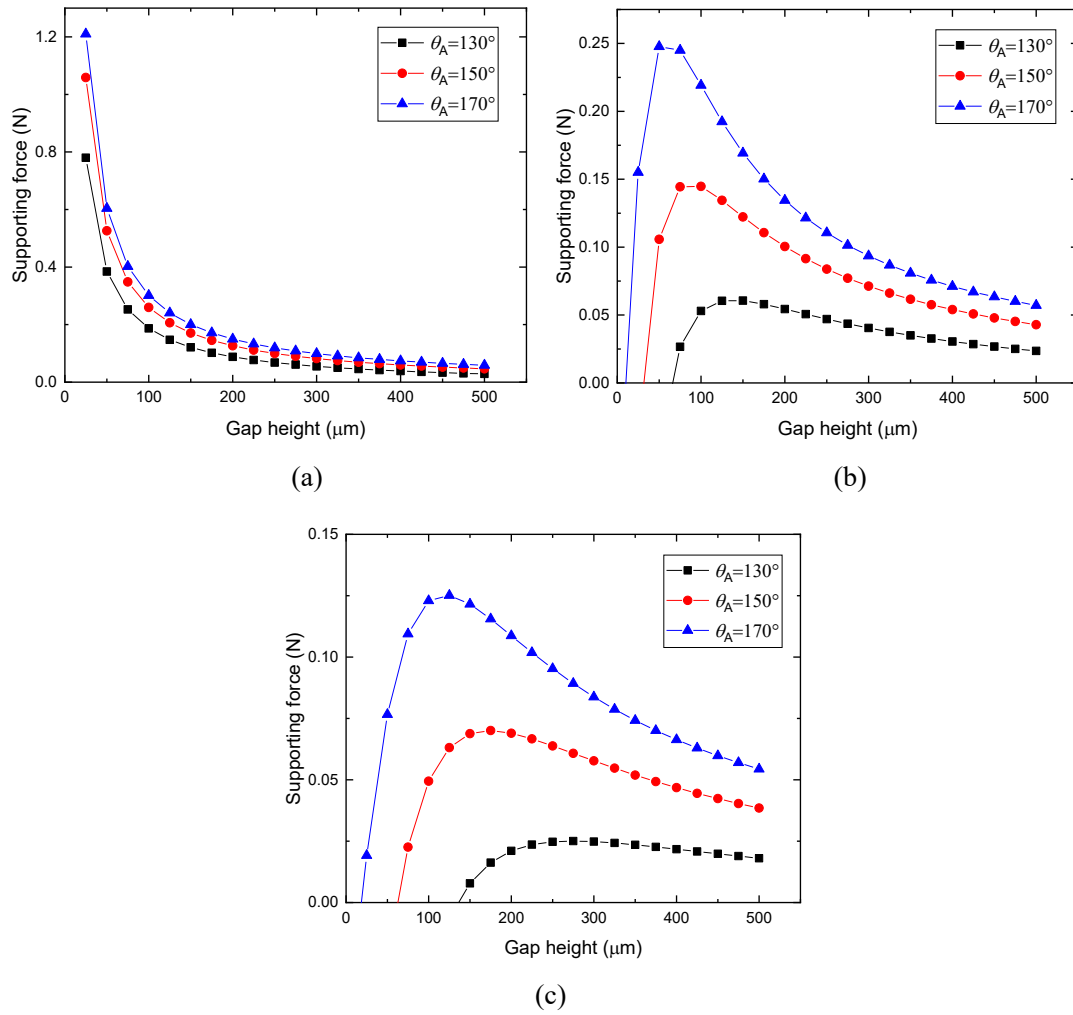


Figure 4.13. Supporting force as a function of gap height for different advancing contact angle on the superhydrophobic surface at different misalignments. (a) No misalignment. (b) Misalignment of 50 μm. (c) Misalignment of 100 μm.

As has discussed, the bearing should work at a gap height above the critical gap height and the maximum load on the rotor should be smaller than the global maximum supporting force of the bearing. Thus, these two factors are the two key limiting conditions when designing such a bearing. Figure 4.14 shows the critical gap height and the global maximum supporting force of the bearing with different misalignments. As shown in figure 4.14 (a), the critical gap height of the bearing increases linearly with the misalignment of the bearing with the same the superhydrophobic surface. The global maximum supporting force is shown in figure 4.14 (b). We can see that the bearing with smaller misalignment can work at a smaller gap height and provide a higher global maximum supporting force. The effect of the hydrophobicity of the superhydrophobic surface on the critical gap height and the maximum global supporting force can also be obtained from figure 4.14. It is shown that the critical gap height decreases

and the global maximum supporting force increases with the hydrophobicity of the superhydrophobic surface.

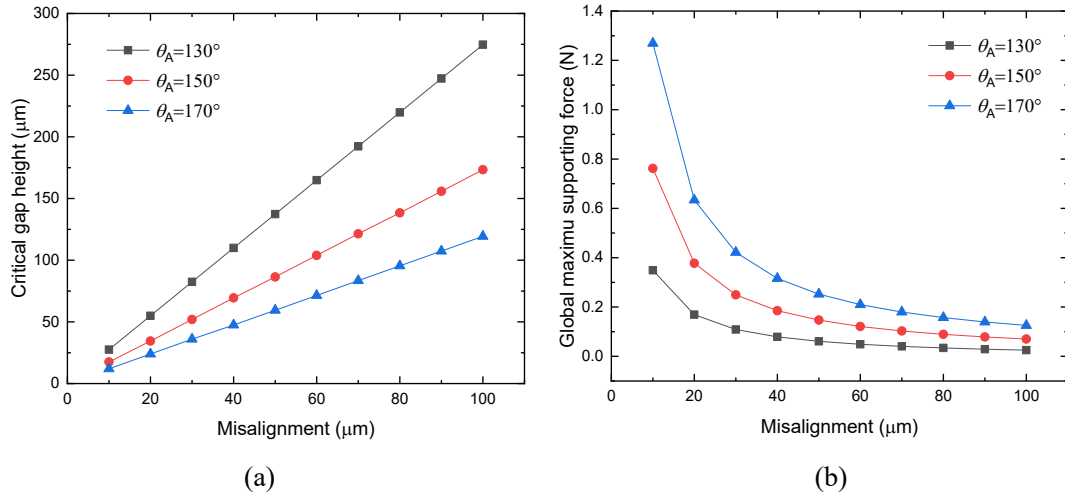


Figure 4.14. Critical gap height and supporting force of the bearing for different misalignments.

4.3.2 Profile of the outer liquid/air interface

Figure 4.15 shows the simulated outer meniscus shapes of the liquid ring at three different rotational speeds, which are 0, 500 and 1000 rpm, using the method in figure 4.7. The heights of the two liquid rings are 200 and 400 μm . The supporting force of the bearing is 0.1 and 0.026 N for the 200 and 400 μm gap heights respectively (and these remain constant with different rotational speeds). When the bearing is static, the profile only has a slight deformation (compared to perfect circularity) due to the gravity. As the rotor turns, the liquid close to the rotor has larger azimuthal momentum compared to that towards the lower stationary surface and thus experience a greater centrifugal force. Therefore, the upper part of the meniscus deforms more and the contact angle on the rotor becomes larger. For the bearing with a gap height of 200 μm , the upper (lower) outer contact angles of the liquid ring are 139.7° (134.7°), 144.4° (136.2°) and 160.6° (141.6°) for rotational speeds of 0, 500 and 1000 rpm, respectively. For the bearing with a gap height of 400 μm , the upper (lower) outer contact angles of the liquid ring are 125.0° (120.1°), 132.7° (122.1°) and 159.6° (128.4°) for rotational speeds of 0, 500 and 1000 rpm, respectively. As the rotational speed increases further, the contact angle on the rotor keeps increasing. When it reaches the advancing contact angle on the superhydrophobic surface, the contact line slips and the liquid ring collapses. This implies that the maximum dynamic supporting force of the bearing decreases with the rotational speed of the bearing. It is because a bigger portion of the Laplace pressure is providing centripetal force to the liquid ring instead of contributing to the supporting force when the rotational speed increases.

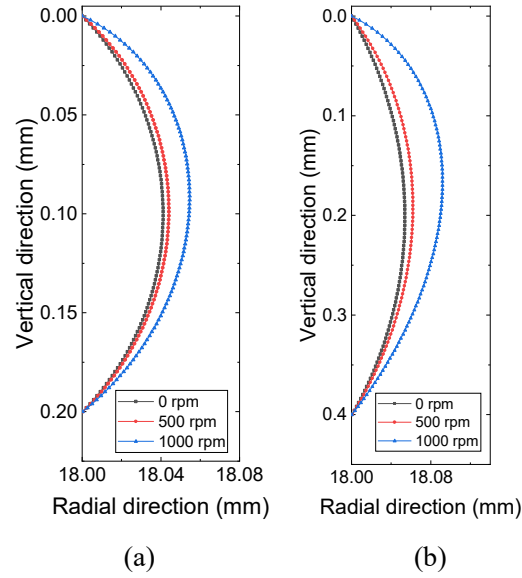


Figure 4.15. Profile of the outer liquid/air interface at different rotational speeds: 0, 500 and 1000 rpm for two gap heights: (a) 200 and (b) 400 μm .

The effect of the liquid ring width on the profile of the outer liquid/air interface has also been investigated and the results are shown in figure 4.16. The load on the bearing are 0.046, 0.10 and 0.146 N for liquid ring with a width of 1, 2 and 3 mm, respectively. As we can see from figure 4.16 (a), the profiles of the outer liquid/air interface for liquid rings with different widths are almost the same. When the rotor rotates, part of the Laplace pressure is going to provide centripetal force for the liquid in the ring. Thus, the outer liquid/air profile deforms. As there is more liquid in the ring with a bigger width, a bigger portion of the Laplace pressure is needed to hold the liquid in the liquid ring. As a result, the liquid ring with a bigger width shows a more severe deformation on the outer liquid/air interface as shown in figure 4.16 (b) and (c).

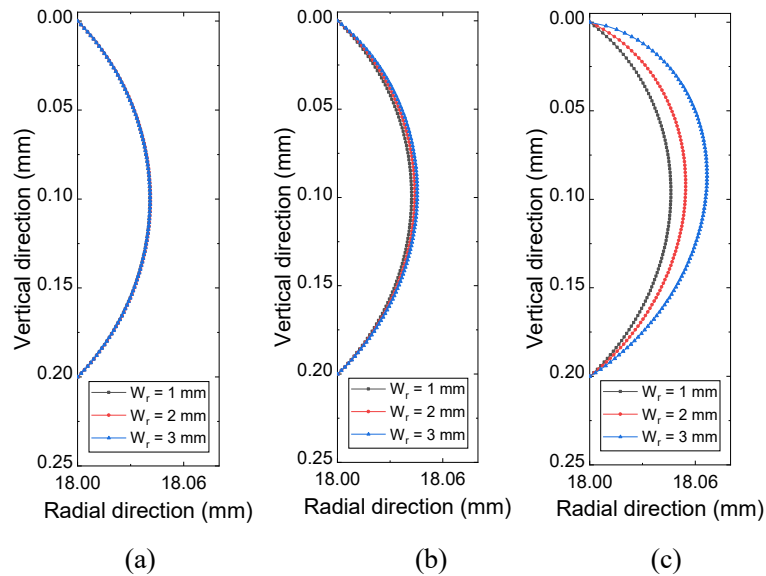


Figure 4.16. Profile of the outer liquid/air interface with different liquid ring width: 1, 2 and 3 mm for three different rotational speeds: (a) 0, (b) 500 and (c) 1000 rpm. The gap height of the bearing is all 200 μm .

4.3.3 The maximum dynamic supporting force of the bearing

The maximum dynamic supporting force of the bearing has been investigated using the method in figure 4.9 and the results are shown in figure 4.17. Note that no misalignment is considered here. It is shown that supporting forces of the bearing without misalignment calculated here agree well with the results obtained using equation (4.18). We can see that for all bearings with different hydrophobicity on the superhydrophobic surfaces, the maximum dynamic supporting force of the bearing decreases with the rotational speed. Therefore, the rotational speed should be considered when designing the maximum supporting force of a liquid ring bearing. The difference of the maximum dynamic supporting force between different rotational speeds is relatively constant among different gap heights.

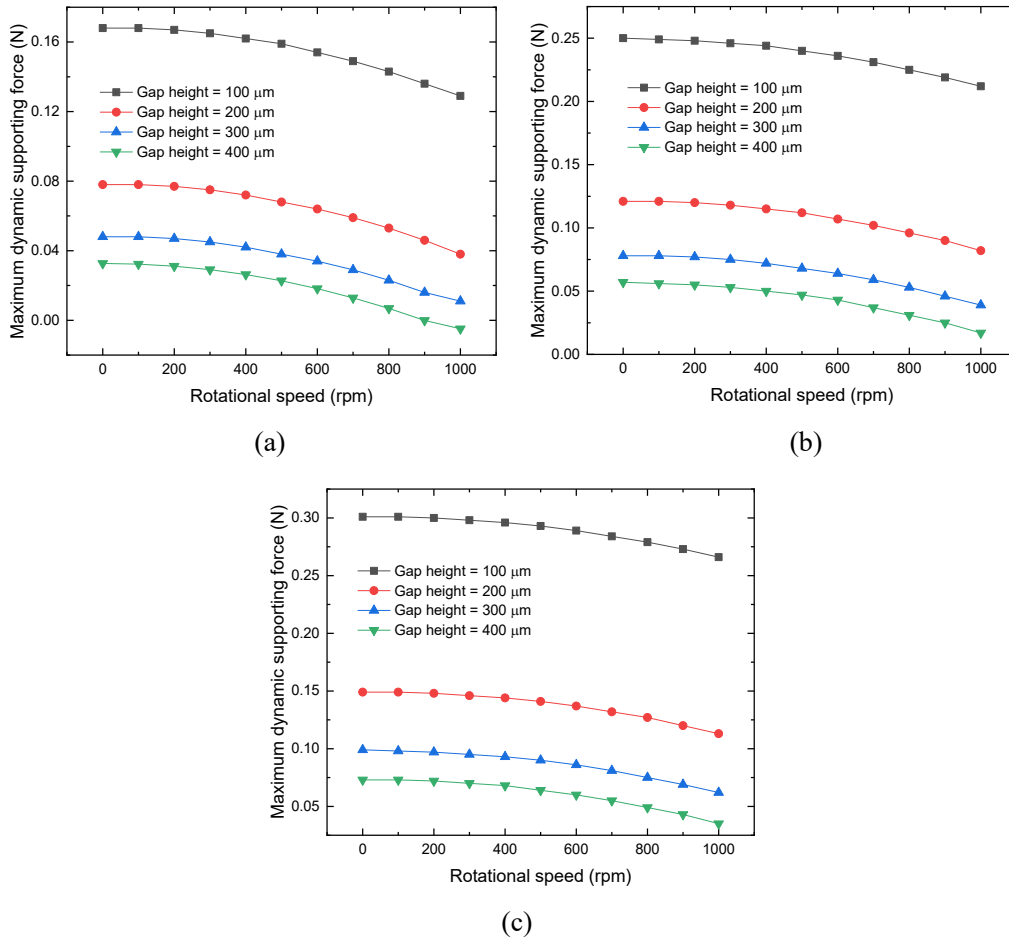


Figure 4.17. Maximum dynamic supporting force as a function of the rotational speed for the superhydrophobic surface with an advancing contact angle of (a) 130°, (b) 150° and (c) 170°.

The effect of liquid ring width on the maximum dynamic supporting force of the bearing is shown in figure 4.18. As has been discussed, the maximum supporting force of the bearing decreases with the

rotational speed as part of the Laplace pressure is going to provide the centripetal force to the liquid in the ring. For a liquid ring with a bigger width, the amount of liquid in the liquid ring is more and thus a larger portion of the Laplace pressure is going to provide the centripetal force. As a result, the maximum dynamic supporting force of the bearing decreases faster with the rotational speed which agrees with the results shown in figure 4.18.

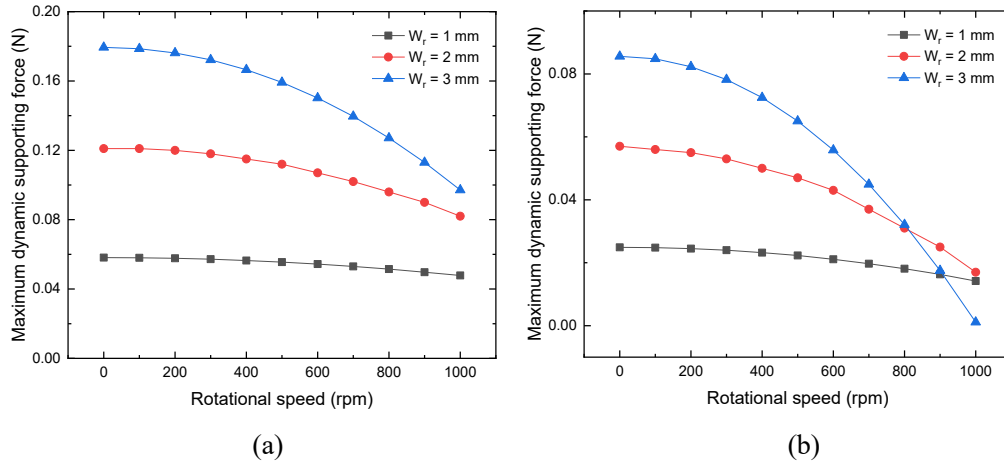


Figure 4.18. Maximum dynamic supporting force as a function of the rotational speed for bearings with different liquid ring widths. The gap heights of the bearing are (a) 200 and (b) 400 μ m. The advancing contact angle on the superhydrophobic surfaces is 150° for both (a) and (b).

4.3.4 Bearing torque: comparison between experimental results and predictions

The torque of the bearings for different widths of the trapped liquid ring (1, 2 and 3 mm) were measured under different gap heights. The experimental results are compared with the theoretical predictions based on the laminar assumption in figure 4.19. At small Re , the experimental results agree well with the theoretical predictions for all the tests. When the Re becomes larger, the experimental data shows strong nonlinearity and increases much more rapidly than the theoretical data. Moreover, the difference between the experimental and the theoretical results decreases as the width to height aspect ratio of the liquid ring increases. For example, at the gap height of 400 μ m the measured torque of the bearing decreases from 3.65 times the theoretical torque to 2.69 times as the width of liquid ring increases from 1 to 3 mm. It can also be seen that, for the same liquid ring width of 2 mm, the measured torque of the bearing decreases from 3.02 times the theoretical torque to 1.1 times as the height of liquid ring decreases from 400 to 100 μ m.

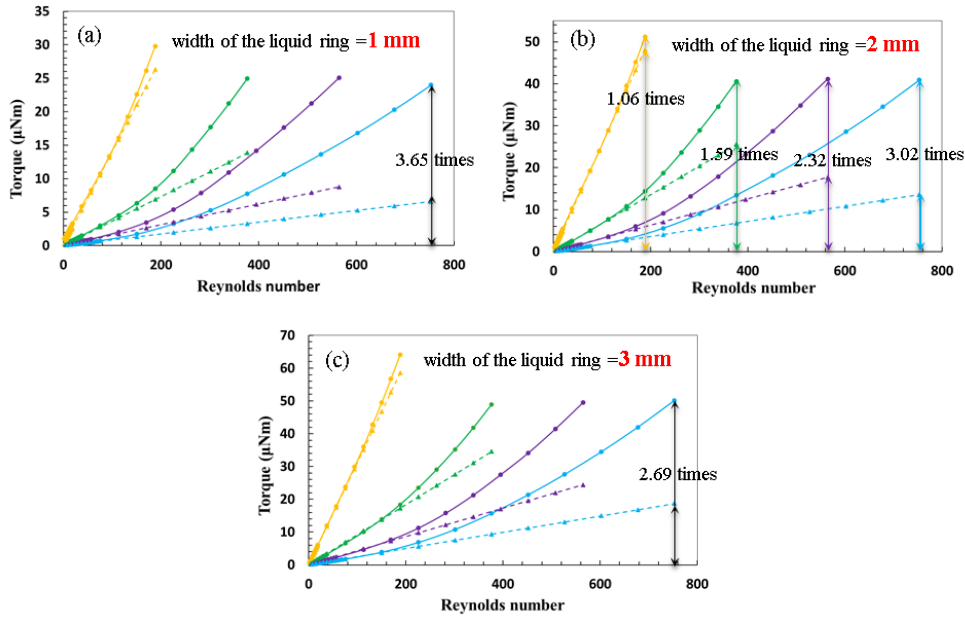


Figure 4.19. The torque of the bearing as a function of Re for different gap heights. There are four pairs of curves in every graph. Each pair contains a solid curve which represents the experimental data and a dashed curve which represents the theoretical data. From top to bottom, the four pairs of curves representing 4 gap heights which are yellow (—) for 100 μm , green (—) for 200 μm , purple (—) for 300 μm and blue (—) for 400 μm . For certain conditions, the ration of the experimental torque to the measured torque is labelled with vertical arrows.

As discussed above, the experimental data shows a strong nonlinearity at high Re s. Thus, a critical Re is defined here to show when the nonlinearity occurs. First, three polynomial curves were fitted to the measured torque and to its upper and lower limits, denoted $f_{exp}(Re)$, $f_{up}(Re)$ and $f_{low}(Re)$ respectively. The curves $f_{up}(Re)$ and $f_{low}(Re)$ form a band (defined by the experimental error in the measurements), within which the real torque of the bearing lies. Then, the theoretical results (indicated as $f_{theo}(Re)$) were compared to the band. The Re at which the relative difference $\frac{|f_{low}(Re) - f_{theo}(Re)|}{f_{theo}(Re)}$ exceeds 1% is defined as the critical Re (shown with red dots in figure 4.20). Using this method, the critical Re s for all the tests were obtained and they were all within the range of 144 to 169.

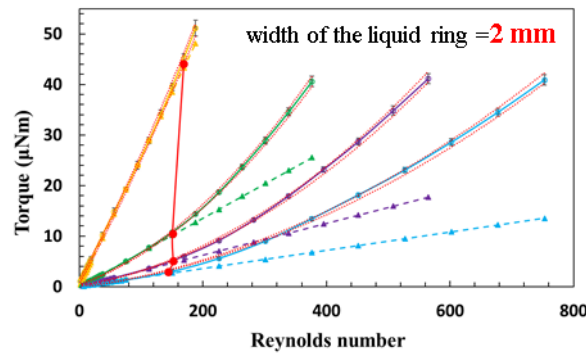


Figure 4.20. Torque of the bearing as a function of Re . There are four pairs of curves in this graph representing the same data as in figure 4.19 (b). The two red dotted lines around each curve of the experimental data are the

fitted lines using the upper and lower limit of the experimental data. The red solid curve represents the critical Res.

The nonlinearity of the torque could result from many factors, such as the capillary force induced by the roughness on the strip edges or potential vortex structures in the liquid ring flow. The capillary force has been shown to increase the startup torque of the bearing, however this effect has not been captured by the rheometer in this chapter. It could be that the startup torque of the bearing is too small to be captured by the rheometer. In order to investigate the influence of the roughness of the strip edges, some artificial textures were made on the strip edges (shown in figure 4.21 (a)) for both the rotor and the stator. The depth of the textures ($D_{texture}$) are 0.25 and 0.5 mm respectively and the results are shown in figure 4.21 (b). The gap height and the width of the liquid ring are 300 μm and 2 mm respectively. The results for the bearing with no artificial textures and theoretical results are the same as those in figure 4.20. The textures have two effects on the torque of the bearing. First, a capillary force caused by the contact angle difference between the two liquid/air interfaces of each radially aligned texture face will form to resist the rotation. Its magnitude is affected by the rotational misalignment of the texture features on the rotor and the stator. It is this component that is responsible for the differences between the measured torques at the low Re region, which are nearly constant with changing Re. The second effect of the textures is that they will cause a disturbance to the flow and increase the strength of the vortices in the liquid ring at the large Re region. This causes the torque of the bearing to increase much more rapidly with Re as shown in figure 4.21 (b). The transition points of the torques which are circled in figure 4.21 (b) are due to the splashing of the liquid in the liquid ring, which shows that the textures lead to an earlier collapse of the liquid ring. The fact that the experimental results for the non-textured ring are not offset from the theoretical results at low speeds suggest that the nonlinearity is not caused by capillary forces induced by the roughness of the ring edges.

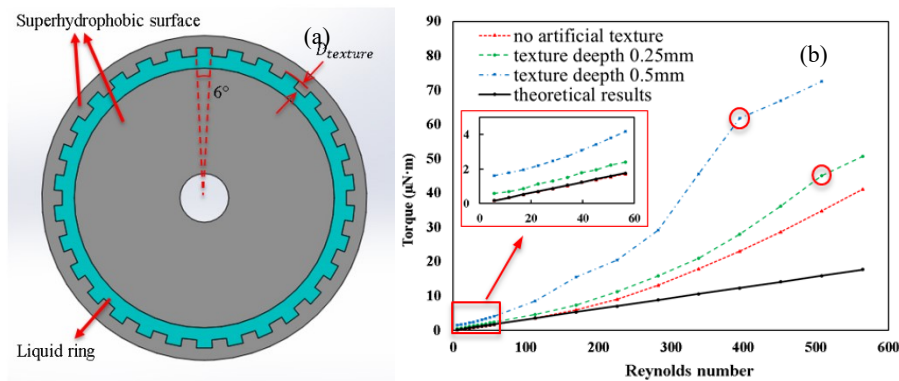


Figure 4.21. (a) Geometry of the artificial textures on the outer edge of the liquid ring. (b) Torque of the bearing with artificial textures on the edges of the superhydrophobic strips.

The concave meniscus can also have an influence on the frictional torque of the bearing by impacting on the flow patterns inside the liquid ring. When the rotor turns, the liquid in the rectangular region between the hydrophilic strips is sheared by the rotor and the stator and thus has a linear angular velocity profile along vertical direction. However, the liquid in the outer concave meniscus is not being sheared directly. The angular momentum of the liquid in this region comes from the liquid lying further inward of the liquid ring. Thus the liquid lying further inward would have larger centrifugal acceleration and tends to flow outwards. Such a trend is unstable. At small Re numbers, this trend can be compensated by the viscous radial drag force. Above a critical Re number, the drag force can no longer compensate the centrifugal force and the instability is triggered. Thus a vortex, similar to the Taylor vortex in the Taylor Couette flow, should form near the outer meniscus of the liquid ring (as shown in figure 4.22). This vortex would increase the energy dissipation in the liquid ring and leads to an increase of the frictional torque. When the width to height aspect ratio of the liquid ring is larger (figure 4.22 (b)), the proportion of the cross sectional area of the liquid ring affected by the vortex is smaller, thus the difference between the measured torque and the laminar prediction become smaller. This effect can be observed in figure 4.19 (*i.e.* the discrepancy between measured and theoretical results increases with aspect ratio), which suggests that vortices are playing a role at high Re .

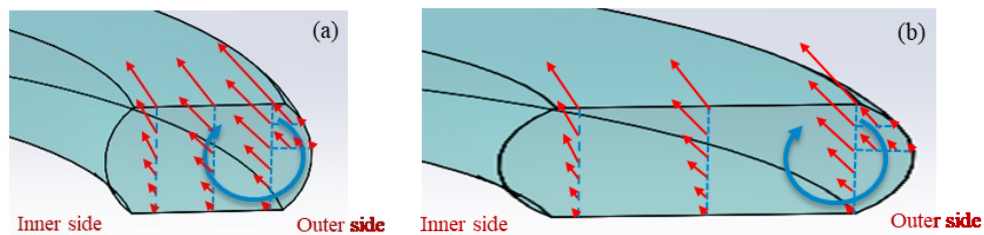


Figure 4.22. Schematic diagram showing the vortices induced by the outer menisci. The width of the liquid ring in (b) is twice that in (a) and hence the unstable region in (b) affects a smaller fraction of the liquid flow.

4.4 Other possible design of the bearing

As the supporting force of such bearings comes from the Laplace pressure built up by the curved liquid/air interface, the curvature radius of the interface is the key point when designing the bearings. With the same alternate superhydrophobic and hydrophilic pattern properties, the geometrical shape of the bearing can have a strong effect on the maximum curvature of the interfaces, thus affect the supporting force of the bearing. In this section, three other possible different configurations of liquid ring bearings have been proposed and evaluated briefly. The main configurations of these bearings are the same as the plane model studied previously in this chapter, which consist one rotor (upper plate), one stator (lower plate) and liquid rings confined between the rotor and the stator (see figure 4.1). The

geometrical shape of the hydrophilic strips which confines the liquid ring are different. These three configurations include the concave model, the convex model and the wavy model.

4.4.1 The concave model

For the concave model, the critical condition is the same as that for the plane model discussed previously, which is the inner contact angle of the liquid ring reaches the advancing contact angle on the superhydrophobic surface.

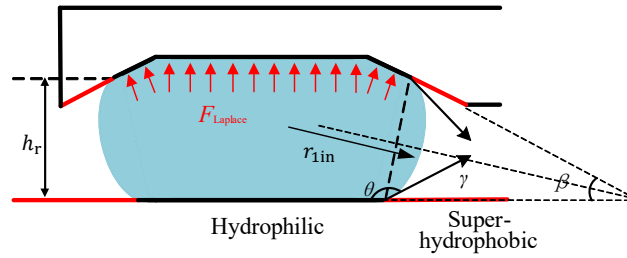


Figure 4.23. Stress analysis of the concave liquid ring bearing.

From figure 4.23 it can be deduced through some geometrical reasoning that the curvature radius of the inner liquid/air interface in the vertical plane (r_{1in}) is

$$r_{1in} = \frac{-h_r}{2\cos\frac{\beta}{2}\cos(\theta_A - \frac{\beta}{2})} \quad (4.27)$$

where h_r is the gap height of the bearing, β is the slant angle of the concave model and θ_A is the advancing contact angle on the superhydrophobic surfaces.

The curvature radius on the horizontal plane on the inner liquid/air interface is $r_{2in} = -r_i$. So the Laplace pressure can be obtained as

$$\Delta P = \frac{\gamma}{r_{1in}} + \frac{\gamma}{r_{2in}} = -\frac{2\gamma\cos\frac{\beta}{2}\cos(\theta_A - \frac{\beta}{2})}{h_r} - \frac{\gamma}{r_i} \quad (4.28)$$

Then the contribution of the Laplace pressure to the supporting force is

$$F_{\Delta P} = \Delta P \cdot \pi(r_o^2 - r_i^2) \quad (4.29)$$

The vertical component of the surface tension is

$$F_Y = \gamma \cdot \cos(\beta + \theta_A - 90^\circ) \cdot 2\pi(r_i + r_o) \quad (4.30)$$

Thus, the total supporting force is:

$$F = F_{\Delta P} - F_{\gamma}$$

$$= \left(-\frac{2\gamma \cos \frac{\beta}{2} \cos(\theta_A - \frac{\beta}{2})}{h_r} - \frac{\gamma}{r_i} \right) \cdot \pi(r_o^2 - r_i^2) - \gamma \cdot \cos(\beta + \theta_A - 90^\circ) \quad (4.31)$$

$$\cdot 2\pi(r_i + r_o)$$

The maximum static supporting force of the concave bearing with different slant angles are investigated with equation (4.31) and the results are shown in figure 4.24. Note here that the concave bearing becomes the plane bearing when the slant angle is 0° . The supporting force of the plane bearing obtained with equation (4.31) is the same as that obtained with equation (4.18). As we can see from figure 4.24 (a), the supporting force of the concave bearing shows the same trend as the plane bearing which increases as the gap height decreases. The supporting force of a concave bearing is smaller than that of a plane bearing at the same gap height. Moreover, it can be seen from figure 4.24 (b) that the supporting force of the concave bearing increases as the advancing contact angle on the superhydrophobic surface increases. With the same advancing contact angle on the superhydrophobic surface, the supporting force of the concave bearing decreases with the slant angle.

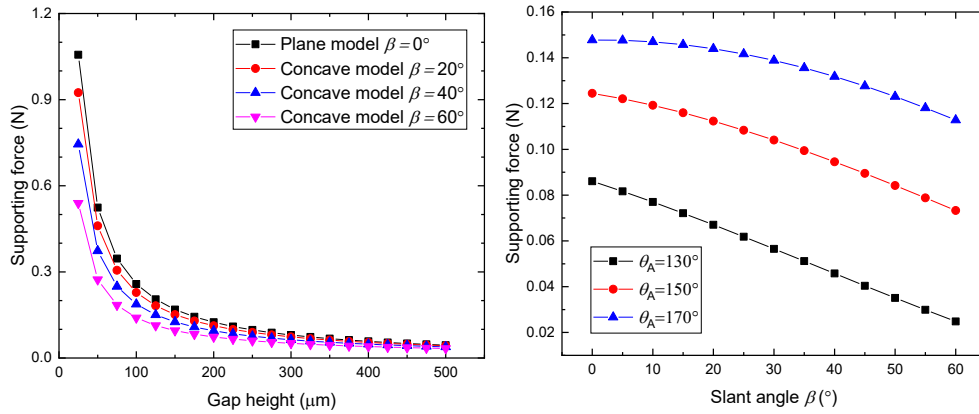


Figure 4.24. Supporting force of the concave bearing (Gap height = 200 μm). (a) Supporting force at different gap height for concave bearings with different slant angles. (b) Supporting force of the concave bearing as a function of the slant angle for different advancing contact angle on the superhydrophobic surface.

4.4.2 The convex model

The critical condition of the convex model is also the same as that for the plane model, which is the inner contact angle of the liquid ring reaches the advancing contact angle on the superhydrophobic surface.

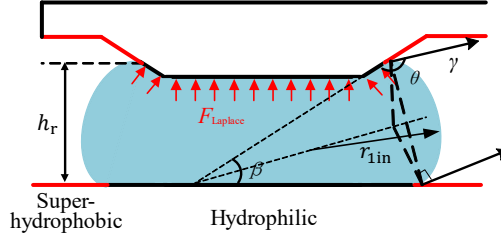


Figure 4.25. Stress analysis of the convex water ring bearing.

Similarly, it can be deduced from figure 4.25 through some geometrical reasoning that the curvature radius of the inner liquid/air interface in the vertical plane (r_{1in}) is

$$r_{1in} = \frac{-h_r}{2\cos\frac{\beta}{2}\cos(\theta_A + \frac{\beta}{2})} \quad (4.32)$$

where h_r is the gap height of the bearing, β is the slant angle of the concave model and θ_A is the advancing contact angle on the superhydrophobic surfaces.

The curvature radius on the horizontal plane on the inner liquid/air interface is also $r_{2in} = -r_i$. So the Laplace pressure can be obtained as

$$\Delta P = \frac{\gamma}{r_1} + \frac{\gamma}{r_2} = -\frac{2\gamma\cos\frac{\beta}{2}\cos(\theta_A + \frac{\beta}{2})}{h_r} - \frac{\gamma}{r_i} \quad (4.33)$$

Then the contribution of the Laplace pressure to the supporting force is

$$F_{\Delta P} = \Delta P \cdot \pi(r_o^2 - r_i^2) \quad (4.34)$$

The vertical component of the surface tension is

$$F_\gamma = \gamma \cdot \cos(\theta_A - \beta - 90^\circ) \cdot 2\pi(r_i + r_o) \quad (4.35)$$

Thus the total supporting force is

$$\begin{aligned} F &= F_{\Delta P} - F_\gamma \\ &= \left(-\frac{2\gamma\cos\frac{\beta}{2}\cos(\theta_A + \frac{\beta}{2})}{h_r} - \frac{\gamma}{r_i} \right) \cdot \pi(r_o^2 - r_i^2) - \gamma \cdot \cos(\theta_A - \beta - 90^\circ) \cdot 2\pi(r_i + r_o) \end{aligned} \quad (4.36)$$

The maximum static supporting force of the convex bearing with different slant angles are investigated with equation (4.36) and the results are shown in figure 4.26. Similarly, the concave bearing becomes the plane bearing when the slant angle is 0° . The supporting force of the plane bearing obtained with equation (4.31) is the same as that obtained with equation (4.36). As we can see from figure 4.26 (a),

the supporting force of the concave bearing shows the same trend as the plane bearing which increases as the gap height decreases. The effect of the slant angle on the supporting force is not monotonous. As shown in figure 4.26 (b), for a certain advancing contact angle on the superhydrophobic surface, the supporting force of the convex model increases first and then decreases with slant angle. The critical slant angle which shows the maximum supporting force varies with the hydrophobicity of the superhydrophobic surface. It is shown that the critical slant angle decreases as the hydrophobicity of the superhydrophobic surface increases. It can be concluded from the results in figure 4.26 that when the advancing contact angle on the superhydrophobic surface is relatively small, the convex model can provide a higher supporting force than the plane model. When the advancing contact angle is big, the plane model provides a higher supporting force.

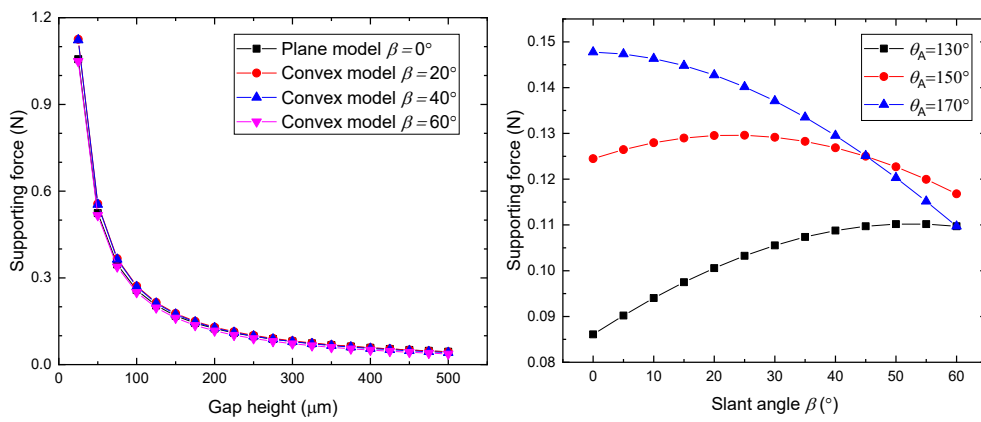


Figure 4.26. Supporting force of the convex bearing (Gap height = 200 μm). (a) Supporting force at different gap height for convex bearings with different slant angles. (b) Supporting force of the convex bearing as a function of the slant angle for different advancing contact angle on the superhydrophobic surface.

4.4.3 The wavy model

To calculate the supporting force of the bearing, first, the force vertical to the contact surface is calculated. Then the vertical component of this force which is the supporting force of the bearing is obtained.

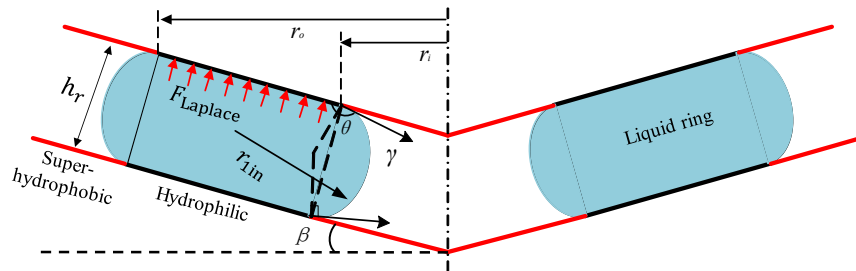


Figure 4.27. Stress analysis of the wavy water ring bearing.

From figure 4.27 it can be deduced that in each single ring, r_{1in} on the inner side is $r_{1in} = \frac{h_r}{2\cos(180^\circ - \theta_A)}$, while $r_2 = -r_1$. So the Laplace pressure is

$$\Delta P = \frac{\gamma}{r_1} + \frac{\gamma}{r_2} = \frac{2\gamma\cos(180^\circ - \theta_A)}{h_r} - \frac{\gamma}{r_i} \quad (4.37)$$

The supporting force provided by the Laplace pressure is

$$F_{\Delta P} = \Delta P \cdot \pi \left(\frac{r_o^2}{\cos(\beta)} - \frac{r_i^2}{\cos(\beta)} \right) \quad (4.38)$$

where β is the slant angle of the concave model.

The component of the surface tension vertical to the contact surface of the rotor is

$$F_Y = \gamma \cdot \cos(\theta_A - 90^\circ) \cdot 2\pi \left(\frac{r_o}{\cos(\beta)} + \frac{r_i}{\cos(\beta)} \right) \quad (4.39)$$

Thus, the total supporting force vertical to the contact surface of the rotor is

$$F' = F_{\Delta P} - F_Y \quad (4.40)$$

Finally, the total vertical supporting force is

$$\begin{aligned} F &= F' \cdot \cos(\beta) \\ &= \left[\left(\frac{2\gamma\cos(180^\circ - \theta_A)}{h_r} - \frac{\gamma}{r_i} \right) \cdot \pi \left(\frac{r_o^2}{\cos(\beta)} - \frac{r_i^2}{\cos(\beta)} \right) - \gamma \cdot \cos(\theta_A - 90^\circ) \right. \\ &\quad \left. \cdot 2\pi \left(\frac{r_o}{\cos(\beta)} + \frac{r_i}{\cos(\beta)} \right) \right] \cdot \cos(\beta) \end{aligned} \quad (4.41)$$

The maximum static supporting force of the wavy bearing with different slant angles are investigated with equation (4.41) and the results are shown in figure 4.28. Again, the wavy bearing becomes the plane bearing when the slant angle is 0° . The supporting force of the plane bearing obtained with equation (4.31) is the same as that obtained with equation (4.41). As we can see from figure 4.28(a) and (b), the supporting force of the wavy bearing is almost the same as that of the plane bearing. However, as shown in figure 4.27, the width of the liquid ring in the direction parallel to the gap, to which torque of the bearing is related, is longer than that of a plane bearing. Thus, the supporting force per unit width of the liquid ring is compared in figure 4.28 (c). It is shown that the supporting force of a wavy bearing per unit width parallel

to the gap decreases with slant angle. This means wavy bearings with the same size in the horizontal plane have the same supporting force but the bearing a bigger slant angle has higher frictional torque. It is also harder to make a wavy bearing than to make a plane bearing. An advantage of the wavy bearing is that it has a bigger horizontal force component which serves as the restoring force when the bearing has a misalignment.

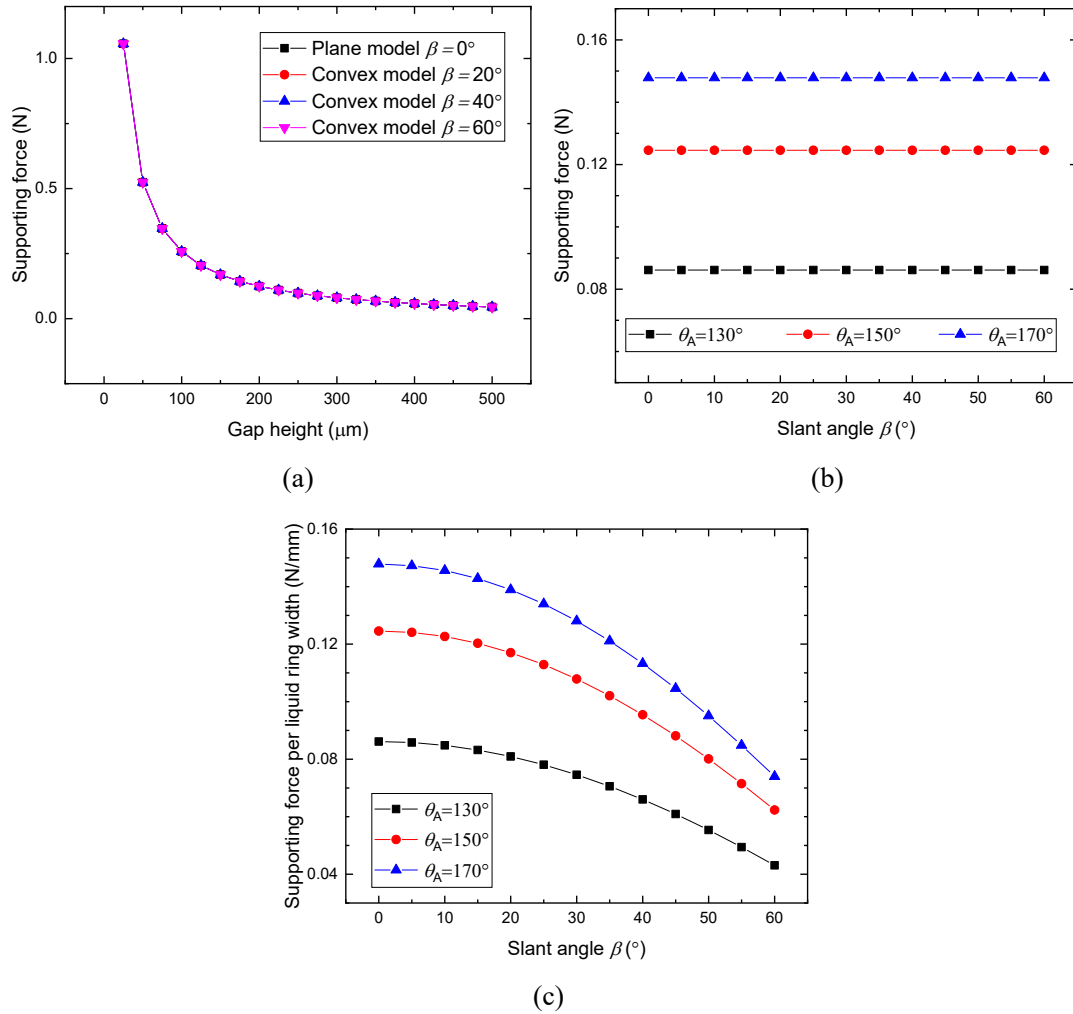


Figure 4.28. Supporting force of the wavy bearing (Gap height = 200 μm). (a) Supporting force at different gap height for wavy bearings with different slant angles. (b) Supporting force of the wavy bearing as a function of the slant angle for different advancing contact angle on the superhydrophobic surface. (c) Supporting force per unit width parallel to the gap of the wavy bearing as a function of the slant angle for different advancing angle on the superhydrophobic surface.

In conclusion, although, the convex bearing can provide a slightly higher supporting force under certain slant angle and hydrophobicity on the superhydrophobic surface, the real gap heights (the closet points between the rotor and the stator) of the concave and the convex bearing are smaller than a plane bearing which makes their rotor and stator more likely to contact when the bearing is working. The wavy bearing provides the same supporting force as the plane bearing with the same size in the horizontal plane.

However, it has a bigger width parallel to the gap which results in a higher frictional torque. Moreover, these bearings are technically harder to make than the plane bearing.

4.5 Conclusions

The performance of a novel liquid ring bearing has been investigated theoretically and experimentally. The results show that the supporting force of such a bearing can be increased by reducing the misalignment of the patterns on the rotor and the stator or increasing the hydrophobicity of the superhydrophobic surface. Due to the effect of the concave meniscus, vortex structures are expected to form in the liquid ring flow at relatively large Re s. These vortices increase the energy dissipation in the flow and lead to a strong nonlinearity in the torque vs. speed characteristics of the bearing. However, this nonlinear increase of the torque can be reduced by the increasing the width to height ratio of the liquid ring. A liquid ring with bigger width deforms severer than one with smaller width when the bearing is rotating and thus can only work under a smaller rotational speed. Therefore, when designing such a liquid ring bearing, the width of the liquid ring needs to be optimised considering the working speed of the bearing.

Chapter 5. Liquid ring sealed air bearing

A thrust bearing consisting of an air cushion formed within a liquid ring has been developed, which takes advantage of the Laplace pressure induced by the liquid/air surface tension. As forces induced by Laplace pressure and surface tension scales down much more slowly than gravity and inertial forces, such a bearing has great potential when scaled down to the micro-scale. The liquid ring between the rotor and the stator of the bearing is anchored there by alternating hydrophilic and superhydrophobic patterns. An important discovery is that the performance of this bearing is greatly enhanced by the sealed cushion of air within the ring. This air cushion and thin liquid ring arrangement mean that the solid/solid contact of the bearing is replaced by solid/air and solid/liquid contact which significantly reduces the friction and wear. The factors which affects the performance of the bearing have been studied both experimentally and numerically providing results that can be used to optimise the design of this new type of bearing.

5.1 Introduction

Governed by the scaling laws, the magnitudes of different types of forces vary differently with length scale [192, 193]. As a result, forces induced by surface tension which, under most circumstances are negligible compared to gravity and inertial forces at the macroscale, dominate at the micrometer and lower scales [103, 194]. Two typical forces which behave in this way are the force induced by surface tension acting on the contact line of a liquid/gas interface and the force due to Laplace pressure acting on the surface enclosed in a liquid/air interface [195]. As length decreases, these scale linearly [103] and hence decrease more slowly than body force and weight. Because of this, these two forces have been utilized in many small scale mechanical manipulators, such as self-assembly [196, 197], actuation [198, 199], lubrication [19-21, 142], grasp and release [200, 201]. A practical example is the liquid bridge [195, 202, 203] spanning the gap between two solid surfaces. This shows either an attractive or a repulsive axial force depending on its volume, the gap height, and the contact angles on the solid surfaces [204, 205]. To take advantage of the repulsive case, liquid bridge thrust bearings have been developed [19-21, 142]. Such bearings contain two plates which serve as a rotor and a stator. The confronting faces of the two plates were coated with alternating hydrophobic and hydrophilic patterns which anchor liquid bridges on the hydrophilic area. Thrust bearings with different shapes and distributions of liquid bridges have been studied, including a single liquid column [19, 142], a liquid column with surrounding droplets [21], and concentric liquid rings [20, 206]. Liquid bridges located at different positions provide different functions such as load support, lateral force resistance and tilting resistance, however, they all operate under the same fundamental mechanisms. When compressed, Laplace pressure builds up inside those liquid bridges which provide a repulsive force to support the load on the rotor. Thus, the solid/solid contact between the rotor and stator is replaced by liquid/solid

contact which reduces frictional torque and wear. The annularly scattered satellite droplets provide a resisting moment when the rotor tilts. The capillary force which acts on the contact line has a resultant horizontal component when there is a misalignment between the upper and lower patterns which balances the lateral force applied to the rotor. For these bearings, the supporting force originates from the Laplace pressure inside water droplet/ring. Thus for a given gap height, the maximum supporting force increases linearly with the wetted area inside the liquid bridges. However, the frictional torque exerted on the rotor also increases with the wetted area [206].

Another effective technique of lubrication at the millimeter and micrometer scales is the air levitated bearing [81, 122, 123]. The rotor of this bearing is levitated by pressurised air flow and thus the solid/solid contact is replaced by air/solid contact which dramatically reduces the friction and wear. However, these bearings need a continuous air supply and a complex control system.

In this chapter, an air levitated thrust bearing has been designed without need for a continuous supply of air. It is shown for the first time that an air cushion between rotor and stator can be maintained by a liquid ring, in this case water. In contrast to liquid bridge lubricated bearings in which the supporting force results from the wetted area, the supporting force of the liquid ring sealed air bearing results mainly from the sealed air cushion. Consequently, the latter has much higher supporting force and smaller frictional torque for the same rotor diameter. The variation of the supporting force, the stiffness and the frictional torque of the bearing as a function of the gap height and the rotational speed were investigated both experimentally and numerically. Effects of misalignment, air diffusion and liquid evaporation on the performance of the bearing were also assessed and discussed. The validated results can be used to design such bearings at smaller scales.

5.2 Experimental and Numerical Methods

5.1.1 Design and experimental methods

Taking advantage of the Laplace pressure at millimeter and micrometer scales, thrust bearings lubricated by liquid droplets, bridges and rings have been invented and investigated. Inspired by these, we report on a new design of air bearing, sealed by a liquid ring, which provides increased load capacity and decreased frictional torque. The liquid ring sealed air bearing developed here consists of a rotor, a stator, an air cushion and a liquid ring (shown in figure 5.1). The rotor and stator of the bearing are two aluminium parallel plates with a radius of $R = 20$ mm. Similar method to the one used in chapter 4 is adopted here to make the bearing. The inward facing surfaces of the plates were coated with Ultra-Ever Dry top coat (Ultra Tech International) with annular shaped tapes (characterised by a width of 2 mm and an inner diameter of 16mm) pasted concentrically on the plates. Tapes were removed later when the coating was dry thus leaving annular hydrophilic patterns (the hydrophilic plate surface protected by the tapes from superhydrophobic coating) alternating with coated superhydrophobic patterns. The

inner and outer radii of the hydrophilic strip are $R_{in} = 16 \text{ mm}$ and $R_{out} = 18 \text{ mm}$ giving a strip width of 2 mm. The same rheometer (DHR-1, TA Instrument, USA) used in chapter 4 was used here to measure the supporting force and the frictional torque of the bearing. The rotor and the stator were attached to the main axle and the base of the rheometer respectively. In the experiments, the temperature (T) was set to 25°C. The static supporting force was defined as the supporting force measured when the bearing was being compressed without rotating. To measure this, a known volume of liquid was first injected onto the hydrophilic strip of the stator. The liquid was trapped there by the surface free energy barrier at the boundary of the alternating hydrophilic and superhydrophobic patterns. Then, the rotor moved down gradually with the main axle of the rheometer to compress the liquid. During this movement, the force exerted on the axle (*i.e.* the supporting force of the bearing) was recorded at 0.2-micron intervals. When the liquid ring and the air cushion were compressed, the Laplace pressure, (*i.e.* the pressure difference across a curved liquid/air interface), started to build up inside the liquid ring and the air cushion. The Laplace pressure is directly proportional to the surface tension and the average curvature of the liquid/air interface and provides a force which supports the load on the rotor. The frictional torque and the dynamic supporting force of the bearing were measured simultaneously. The rotor was moved down and stopped at certain gap heights where the air cushion was compressed to give different supporting forces. Then, the rotational speed of the rotor was increased and measurements were taken at different speeds. Allowing 10 s for the rotor to stabilize, the frictional torque of the bearing was measured for 5 s at a rate of 2 Hz.

There are many factors that influence the performance of the bearing. In this chapter, effects of misalignment between the patterns on the rotor and the stator, the liquid evaporation from the liquid ring and the air diffusion through the liquid ring have all been investigated.

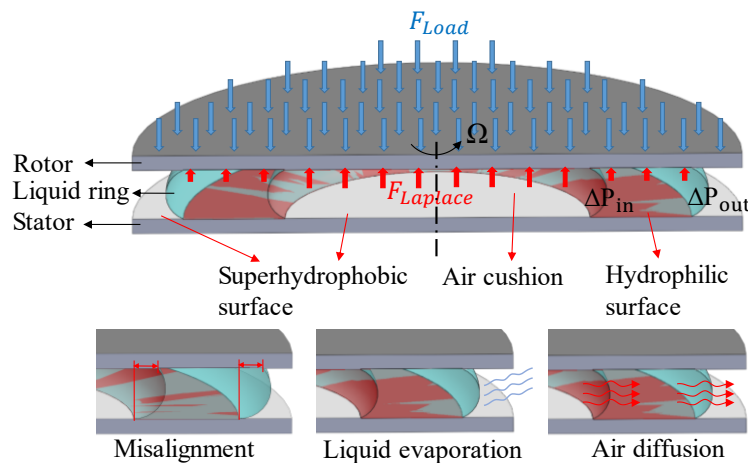


Figure 5.1. Schematic diagram of the liquid ring sealed air bearing.

5.1.2 Theoretical model for the maximum static supporting force

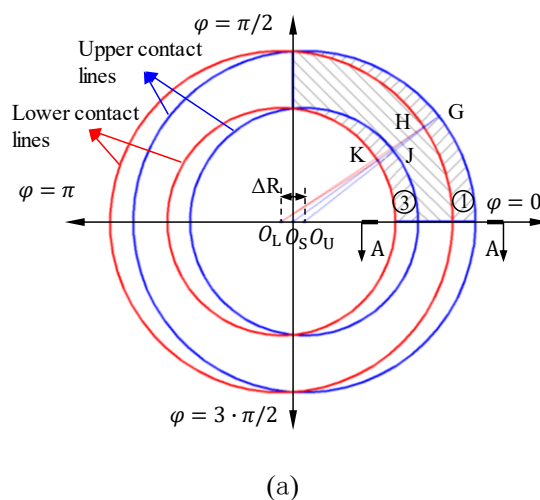
The gap height of the bearing studied in this chapter ranged from 100 to 500 μm . At such small range of gap heights, the effect of gravitational acceleration could be neglected. Thus, the cross section of the liquid/air interface can be well approximated by an arc of constant radius. It should be noted here that there is a potential misalignment between the patterns on rotor and the stator (shown in figure 5.2 (b) as ΔR) and this turns out to be an important factor affecting the supporting force of the bearing. Thus, it is taken into account in the numerical model derived below. The supporting force of the bearing ($F_{\text{Supporting}}$) results from the vertical component of the capillary force ($F_{\text{Capillary}}$) acting on the contact line of the liquid ring and the vertical force induced by the Laplace pressure (F_{Laplace}) inside the liquid ring (F_{LaplaceR}) and the air cushion (F_{LaplaceA}). The former is attractive and the latter is repulsive. Thus the supporting force is

$$F_{\text{Supporting}} = F_{\text{Laplace}} - F_{\text{Capillary}} = F_{\text{LaplaceR}} + F_{\text{LaplaceA}} - F_{\text{Capillary}} \quad (5.1)$$

$F_{\text{Capillary}}$ is calculated using the following equation:

$$F_{\text{Capillary}} = \int_0^{2\pi} \gamma \cdot \cos(\theta_{\text{in}}) \cdot R_{\text{in}} \cdot d\varphi + \int_0^{2\pi} \gamma \cdot \cos(\theta_{\text{out}} - \pi/2) \cdot R_{\text{out}} \cdot d\varphi \quad (5.2)$$

where γ is the surface tension of the liquid/air interface, θ_{in} and θ_{out} are the inner and outer local contact angles of the liquid ring (shown in figure 2 (b)) which vary with φ (*i.e.* the circumferential angle in the coordinate system in Figure 5.2 (a)). O_{U} and O_{L} are the centre points of the upper and lower coating patterns respectively. The origin of the coordinate system is O_{s} which is the midpoint between O_{U} and O_{L} . Points G, H, J, K and O_{s} are on the same straight line in figure 5.2 (a). Points G and J interact with the outer and inner contact line on rotator while points H and K interact with the outer and inner contact line on stator.





F_{Laplace} is calculated using the following equation:

where ΔP_{in} and ΔP_{out} are the Laplace pressures crossing the inner and outer menisci of the liquid ring. These are calculated using the following equations [207]:

$$\Delta P_{\text{out}} = \gamma/r_{\text{out}} = \gamma \cdot (1/r_{1\text{out}} + 1/r_{2\text{out}}) \quad (5.5)$$

$$r_{\text{lin}} = \frac{\sqrt{(\Delta R)^2 + h^2}}{2 \cdot \sin(\arctan\left(\frac{h}{\Delta R}\right) - \theta_{\text{inmin}})} \quad (5.6)$$

$$r_{1\text{out}} = \frac{-\sqrt{(\Delta R)^2 + h^2}}{2\sin(\theta_{\text{outmax}} + \arctan(\frac{h}{\Delta R}))} \quad (5.7)$$

where ΔR is the misalignment of the patterns on the rotor and stator, h is the gap height. As h is smaller than 500 μm , the effect of gravity can be neglected.

The inner and outer curvature radii of the liquid ring on the horizontal plane are $r_{2in} = R_{in} + \Delta r_{2in}$ and $r_{2out} = R_{out} + \Delta r_{2out}$, where Δr_{2in} and Δr_{2out} are represented with two red solid lines in figure 5.2 (b). As has discussed in chapter 4, because h is much smaller than the radius of the liquid ring, Δr_{2in} and Δr_{2out} are small enough to be neglected. Therefore, r_{2in} and r_{2out} are approximated to be R_{in} and R_{out} . Substituting equations (2) to (7) into (1), the static supporting force of the bearing is obtained as:

$$F_{\text{Supporting}} = \left\{ \pi \cdot R_{in}^2 \cdot \gamma \cdot \left[\frac{2 \cdot \sin \left(\arctan \left(\frac{h}{\Delta R} \right) - \theta_{inmin} \right)}{\sqrt{(\Delta R)^2 + h^2}} + 1/R_{in} \right] + \pi \cdot R_{out}^2 \cdot \gamma \cdot \left[\frac{2 \sin \left(\theta_{outmax} + \arctan \left(\frac{h}{\Delta R} \right) \right)}{-\sqrt{(\Delta R)^2 + h^2}} + 1/R_{out} \right] \right\} - \int_0^{2\pi} \gamma_{LA} \cdot \cos(\theta_{in}) \cdot R_{in} \cdot d\varphi - \int_0^{2\pi} \gamma_{LA} \cdot \cos(\theta_{out} - \pi/2) \cdot R_{out} \cdot d\varphi \quad (5.8)$$

It should be noted here that the pressure inside the air cushion and the liquid ring is constant. Thus, although θ_{in} and θ_{out} vary with φ , r_{in} and r_{out} must be constant in the circumferential direction (*i.e.* for different φ). Hence, because r_{2in} and r_{2out} are approximated to be R_{in} and R_{out} , which are constant, r_{1in} and r_{1out} should also be constant at different φ .

To calculate the contribution of the capillary force to the supporting force of the bearing, θ_{in} and θ_{out} were determined as functions of φ . Before this, the local misalignment of the inner ($\Delta R_{in}'$) and outer ($\Delta R_{out}'$) contact lines in the O_S coordinate system (shown in Figure 5.2 (a)) are calculated:

$$\Delta R_{in}' = JO_S - KO_S \quad (5.9)$$

$$\Delta R_{out}' = GO_S - HO_S \quad (5.10)$$

As the deductions of GO_S , HO_S , JO_S and KO_S are similar, here the deduction of GO_S is presented. As shown in figure 5.2 (a), according to the cosine law in the triangle $GO_S O_U$:

$$\cos(\varphi) = \frac{O_S O_U^2 + GO_S^2 - GO_U^2}{2 O_S O_U \cdot GO_S} \quad (5.11)$$

where $O_S O_U = \Delta R/2$. Through equation (5.11), GO_S can be obtained:

$$GO_S = \cos(\varphi) \cdot \Delta R/2 + \sqrt{[\cos(\varphi)]^2 \cdot \frac{\Delta R^2}{4} + R_{out}^2 - \frac{\Delta R^2}{4}} \quad (5.12)$$

Similarly, JO_S , KO_S and HO_S can be obtained:

$$JO_S = \cos(\varphi) \cdot \Delta R/2 + \sqrt{[\cos(\varphi)]^2 \cdot \frac{\Delta R^2}{4} + R_{in}^2 - \frac{\Delta R^2}{4}} \quad (5.13)$$

$$KO_S = \cos(\pi - \varphi) \cdot \Delta R/2 + \sqrt{[\cos(\pi - \varphi)]^2 \cdot \frac{\Delta R^2}{4} + R_{in}^2 - \frac{\Delta R^2}{4}} \quad (5.14)$$

$$HO_S = \cos(\pi - \varphi) \cdot \Delta R/2 + \sqrt{[\cos(\pi - \varphi)]^2 \cdot \frac{\Delta R^2}{4} + R_{out}^2 - \frac{\Delta R^2}{4}} \quad (5.15)$$

As expected, $\Delta R_{in}'$ and $\Delta R_{out}'$ decrease from ΔR at $\varphi = 0^\circ$ to 0 at $\varphi = 90^\circ$. Next, similar to what was done in chapter 4, through geometric reasoning, the equations for θ_{in} and θ_{out} are obtained as:

$$\theta_{in} = \tan^{-1}\left(\frac{h}{\Delta R_{in}'}\right) + \cos^{-1}\left(\frac{\sqrt{\Delta R_{in}'^2 + h^2}}{2 \cdot r_{1in}}\right) - \frac{\pi}{2} \quad (5.16)$$

$$\theta_{out} = \frac{3 \cdot \pi}{2} - \tan^{-1}\left(\frac{h}{\Delta R_{out}'}\right) - \cos^{-1}\left(\frac{\sqrt{\Delta R_{out}'^2 + h^2}}{2 \cdot r_{1out}}\right) \quad (5.17)$$

When considering the maximum supporting force of the bearing, the critical values of the inner and outer contact angles, which are the receding contact angle on the hydrophilic surface (θ_{phiR}) and the advancing contact angle on the superhydrophilic surface (θ_{phiA}), are applied to θ_{inmin} and θ_{outmax} respectively. Using the equations above, the maximum supporting force of the bearing at a certain gap height can be obtained.

5.1.3 Theoretical model for the stiffness of the bearing

The model for the stiffness of the bearing simulates the supporting force, $F_{Supporting}$, as a function of gap height, h_r , when the bearing is being compressed. Initially, the air cushion between rotor and stator is sealed but not compressed and the supporting force of the bearing was very small. It is assumed that the inner liquid/air interface is not curved and the initial value of θ_{inmin} was $\theta_{inmin_init} = \frac{\pi}{2} + \arctan(\Delta R/h_r)$. As the initial supporting force of the bearing is known and the inner liquid/air interface is assumed to be flat, the Laplace pressure is all from the outer liquid air interface. Thus, the outer contact angle of the liquid ring can be calculated. Through integration, the initial volume of the air cushion (V_{air_init}) and the liquid ring (V_{ring_init}) are obtained (see the method reported in the Appendix B and C). Using the ideal gas state equation the initial molar mass of air (n_{init}) inside the air cushion can be also obtained as:

$$P_{\text{air_init}} \cdot V_{\text{air_init}} = n_{\text{init}} \cdot R_{\text{gas}} \cdot T \quad (5.18)$$

where n_{init} is the initial molar mass of the air inside the air cushion, and R_{gas} is the ideal gas constant.

Next, the gap height decreased by a small value and the equilibrium state at the new gap height was calculated. An iterative loop is used to calculate the new equilibrium state. In this loop, first θ_{inmin} is assigned a value. Then according to the volume conservation of the liquid ring, θ_{outmax} is obtained. A liquid evaporation model (discussed later in this section) which excludes the liquid evaporated during the compressing process is included here. With θ_{inmin} and θ_{outmax} , the Laplace pressure and the volume of the air cushion after compression are obtained. Then, using equation (5.4) and (5.5), the pressure inside the air cushion (P_{air}) is obtained. Moreover, P_{air} is also calculated using the ideal gas state equation. An air diffusion model (discussed later in this section) is used here to exclude the diffusion of air through the liquid ring into the environment. When the two values of P_{air} , calculated using the above two methods, become equal, the loop ends and the equilibrium state is obtained. After this, the supporting force of the bearing at the new gap height is obtained. It should be noted that as the contact angle varies, the contact line moves slightly. This effect is taken into account by the wettability transition model which will be discussed later. When θ_{inmin} reaches θ_{phiR} , it stops decreasing and the inner contact line starts to slip which results in a larger R_{in} . When θ_{outmax} reaches θ_{phiA} , the liquid ring collapses.

A flowchart showing the workflow and the pseudo-code used to determine the stiffness of the bearing is shown in figure 5.3. In the following sub-sections, the details of the water evaporation, air diffusion and slip models, specifically identified as main items contributing to in the flow chart, will be discussed in more detail.

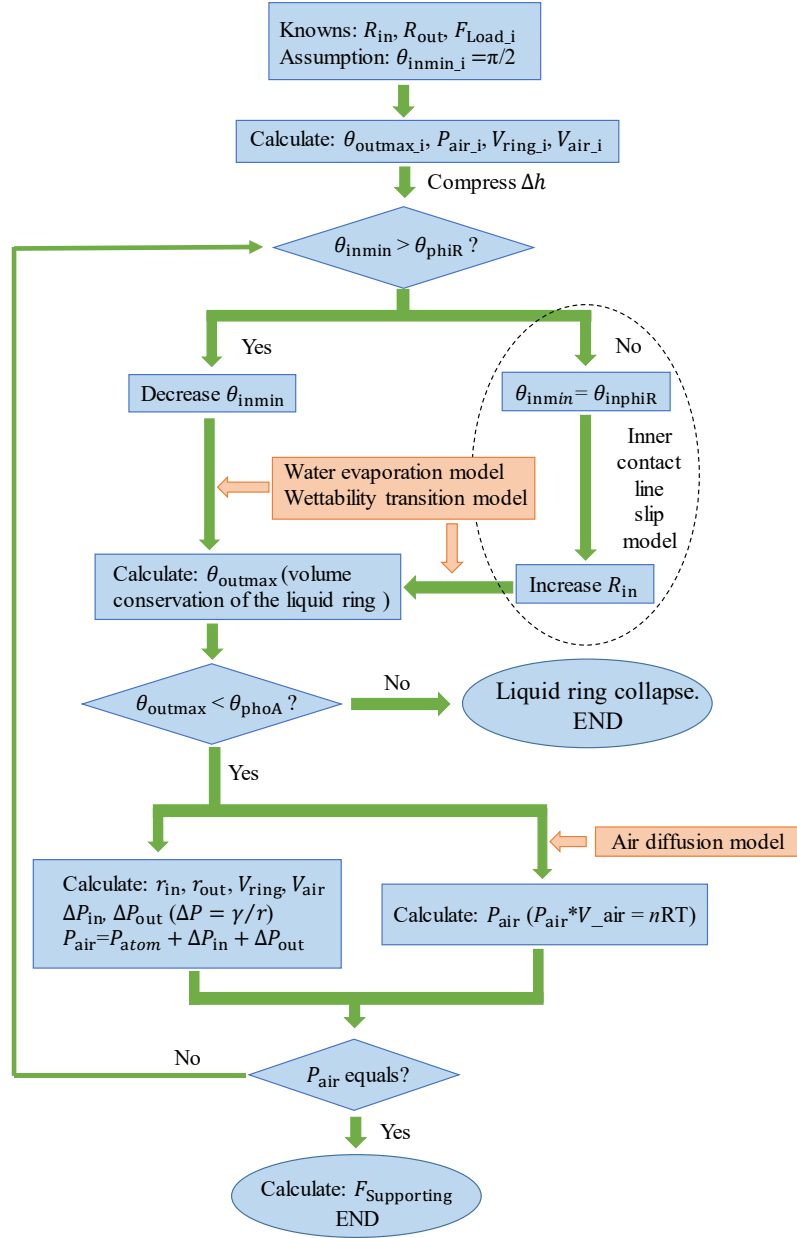


Figure 5.3. Flow chart of theoretical model for the stiffness of the bearing.

5.1.4 Liquid evaporation model

As the bearing tested in this chapter is open to the environment, the liquid in the liquid ring evaporates during the experiments which reduces the supporting force of the bearing. A liquid ring evaporation model is built to take this influence into account. In this model the liquid/air interface was assumed to be flat and without misalignment. The amount of liquid evaporated per second (L_e) is calculated using the following equation [208]:

$$L_e = \alpha \cdot A \cdot (X_s - X)/3600 \quad (5.19)$$

where $\alpha = (25 + 19 \cdot v)$ is the liquid evaporation coefficient, v is the air flow velocity around the bearing, A is the area of the liquid/air interface from which the liquid evaporates, X_s and X are the maximum and the actual humidity ratio (defined as the ratio between the mass of liquid vapour to the mass of the dry air) of the surrounding environment. In the experiment, the humidity measured was relative humidity (RH) and it was transformed to provide actual humidity values to be used to compute the current evaporation rates.

5.1.5 Air diffusion model

When the bearing was compressed, the pressure inside the air cushion was higher than the atmospheric pressure. Thus the air was diffusing through the liquid ring into the atmosphere gradually. This will cause a decrease to the supporting force of the bearing. Here this effect is evaluated using an air diffusion model. In this model the menisci of the liquid ring are also assumed as in the first approximation to be flat and without misalignment. The diffusion of gas i in the liquid ring is governed by Fick's First Law of diffusion:

$$\frac{\partial C_j}{\partial t} = D_j \cdot \nabla^2 C_j \quad (5.20)$$

where $C_j = K_{Hj} \cdot P_j$ is the concentration of gas j in the liquid ring, K_{Hj} and P_j are Henry's constant and the partial pressure of gas j respectively, t is time and D_j is the diffusion coefficient of gas j in liquid (water). The equations were solved using the Crank-Nicholson [209] finite difference method, where 100 segments were used in the simulation domain to obtained accurate results.

The molar mass of gas j diffused through the liquid ring (Δn_j) at time t is:

$$\Delta n_j = \int_{\varphi=0}^{\varphi=2\pi} \int_{y=0}^{y=h} \int_0^t D_j \cdot \nabla C_j \cdot d\varphi \cdot dy \cdot dt \quad (5.21)$$

Using equation (5.21) the molar mass of O_2 and N_2 , which are the two major components of air, diffused through the liquid ring were calculated.

5.1.6 Pressurized liquid ring test

To further verify the results obtained with the air diffusion and liquid evaporation models, a pressurized liquid ring test was designed. Figure 5.4 shows the stator of the bearing used in this test. As we can see, there is an air hole in the middle of the stator and it is connected to the outer atmosphere through an air hole on the side surface. The air chamber and the outer atmosphere can be disconnected by sealing the air hole on the side surface of the stator. There is liquid hole between two superhydrophobic strips where the liquid ring is confined. This liquid hole can be connected to a liquid pool through a nozzle

on the side surface. The liquid pool is open to air and the pressure inside the liquid ring can be adjusted by the height of the liquid pool through gravity:

$$P_{\text{Ring}} = \rho \cdot g \cdot h_{\text{pool}} \quad (5.22)$$

where P_{Ring} is the pressure inside the liquid ring, ρ is the density of the liquid, g is the gravitational acceleration and h_{pool} is the height of the liquid pool (from the free liquid surface of the liquid pool to the surface of the stator).

The free surface of the liquid pool is 2 cm^2 and the variation of the liquid level due to the change of the liquid ring volume is small enough to be neglected. This model is used to test the effect of air diffusion and liquid evaporation and the results are shown later in this chapter.

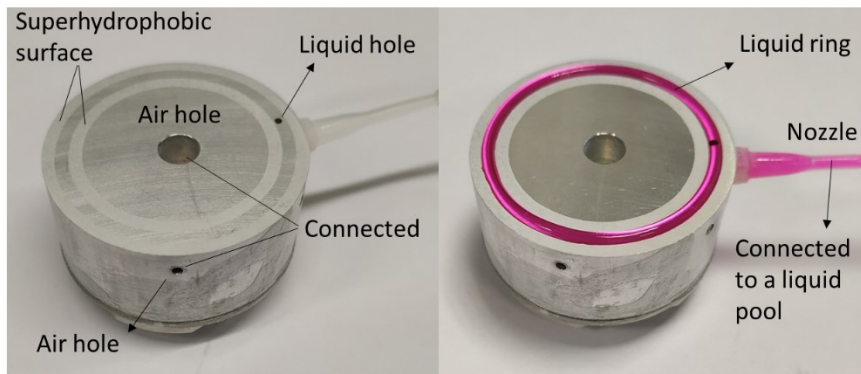


Figure 5.4. Models for pressurized liquid ring test. Left: stator without liquid ring. Right: stator with a liquid ring on it (the liquid is dyed red).

5.1.7 The wettability transition model

Due to the pinning effect of the energy barrier on the contact line, the contact angle at the boundary of the hydrophilic and superhydrophobic surfaces ranges from the contact angle on the hydrophilic surface to that on the superhydrophobic surface. This transition occurs within a band whose width is determined by the coated pattern on the bearing surfaces. Figure 5.5 (a) shows the variation of the contact angle of a liquid bridge confined by alternating hydrophilic and superhydrophobic patterns as used in this chapter. Here, the contact line moves slightly as the contact angle changes when the liquid bridge is squeezed. However, due to the limitation of the small gap, it is very difficult to obtain accurate contact angle measurements of the liquid bridge. Thus no quantitative results were obtained from figure 5.5 (a). Figure 5.5 (b) shows this transition schematically. Through SEM images (see in Figure 5.5 (c)), the width of the transition band for the patterns used in this chapter is obtained which is about 200 microns. A linear variation of the relative location of the contact line as a function of the contact angle in the wettability transition region is hypothesised. It is assumed that the contact angle was 90° at the nominal diameter ($R_{\text{in}} = 16 \text{ mm}$ and $R_{\text{out}} = 18 \text{ mm}$).

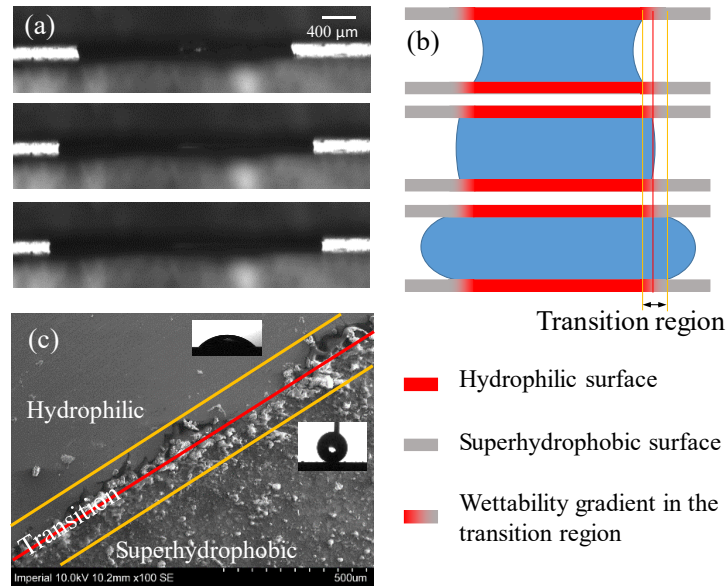


Figure 5.5. Transition band between the hydrophilic and superhydrophobic patterns. (a) A liquid bridge between two plates confined by alternating hydrophilic and superhydrophobic patterns. (b) Schematic diagram of the transition band. (c) SEM image of the transition band.

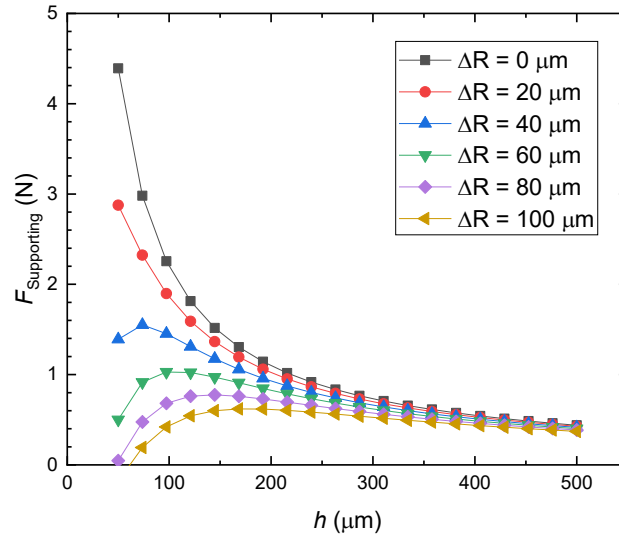
5.3 Results and discussion

5.3.1 The maximum static supporting force of the bearing

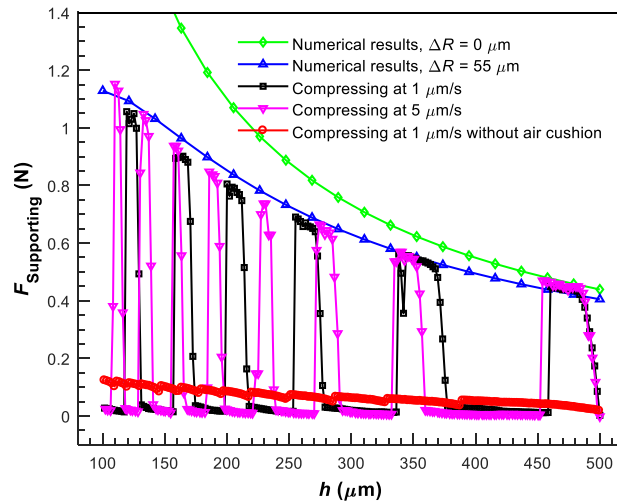
Figure 5.6 (a) shows the numerical results obtained for the maximum $F_{\text{Supporting}}$ of the bearing for different values of misalignment, ΔR . The advancing contact angle on the superhydrophobic surface (θ_{phoA}) and the receding contact angle on the hydrophilic surface (θ_{phiR}) are 160° and 45° , respectively. It is shown that as h decreases from 500 to 100 μm, the maximum $F_{\text{Supporting}}$ of the bearing with no ΔR increases all the way while those of the bearings with a ΔR starts to decrease at a critical gap height. For a given h , the maximum $F_{\text{Supporting}}$ of the bearing decreases with ΔR . Similar to the liquid ring bearing, a global maximum supporting force is defined for an air bearing with a misalignment. This global maximum supporting force is the maximum $F_{\text{Supporting}}$ a bearing can get at various h . When the bearing is working at a h bigger than the critical h and the load experiences a sudden increase, the gap height of the bearing will decrease and $F_{\text{Supporting}}$ will increase which will balance the sudden increase of the load. However, if the bearing works at a h smaller than the critical h and the load experience a sudden increase, h as well as $F_{\text{Supporting}}$ of the bearing will decrease and the bearing will collapse. Thus when designing a bearing, the working gap height should be larger than the critical gap height.

In Figure 5.6 (b), results containing the whole compressing process for two experiments with different compressing speeds are compared with the numerical results, which only show the maximum $F_{\text{Supporting}}$. The experiments started with a liquid ring and an air cushion sealed inside. During compression, the Laplace pressure builds up inside the liquid ring and the air cushion. $F_{\text{Supporting}}$

increases and reaches its maximum value when θ_{outmax} reached θ_{phoA} . After that, the liquid ring collapses and a droplet of liquid is expelled from the liquid ring due to the high pressure inside the air cushion. The remaining liquid between the rotor and the stator is not enough to instantaneously form a full liquid ring, but it spreads circumferentially along the hydrophilic strip as the rotor travels downwards to re-establish the full ring support as the system is compressed. During this period, $F_{\text{Supporting}}$ was measured to be around 0, until the moment the remaining liquid reforms an intact liquid ring and seals an air cushion within it. $F_{\text{Supporting}}$ increases again as the rotor continues downwards.



(a)



(b)

Figure 5.6. The static supporting force of the bearing. (a) Numerical results with different misalignments. (b) Experimental and simulated results.

The results show that the numerical model with a misalignment, ΔR , of 55 μm is in reasonable agreement with the experimental measurements. We could also see from the results that the $F_{\text{Supporting}}$

can be improved by reducing ΔR and this effect is more significant at smaller h_r . It is also evident that the effect of the compressing speed on $F_{\text{Supporting}}$ is very small. As a comparison, the experimental results for the liquid ring bearing without an air cushion (*i.e.* with an air hole in the stator) is presented in figure 5.6 (b). This shows that the air cushion dramatically increases the supporting force of the bearing. A detailed comparison of these two contributions are presented in the following part of this chapter.

Figure 5.7 shows the contribution of Laplace pressure inside the air chamber (F_{chamber}), Laplace pressure inside the liquid ring (F_{ring}) and the surface tension acting on the contact line of the liquid ring (F_{γ}) to the support force of the bearing. The θ_{phoA} and θ_{phiR} are 160° and 45° , respectively. No misalignment is considered in this figure. As we can see both contributions of the Laplace pressure inside the air chamber and the liquid ring increase as the gap height decreases. Among the three contributions, the Laplace pressure inside the air chamber contributes most to the supporting force while it doesn't contribute to the frictional torque of the bearing as the viscosity of air is small enough to be neglected. The surface tension acting on the contact lines of the liquid ring has a negative contribution but its magnitude is small and relatively constant.

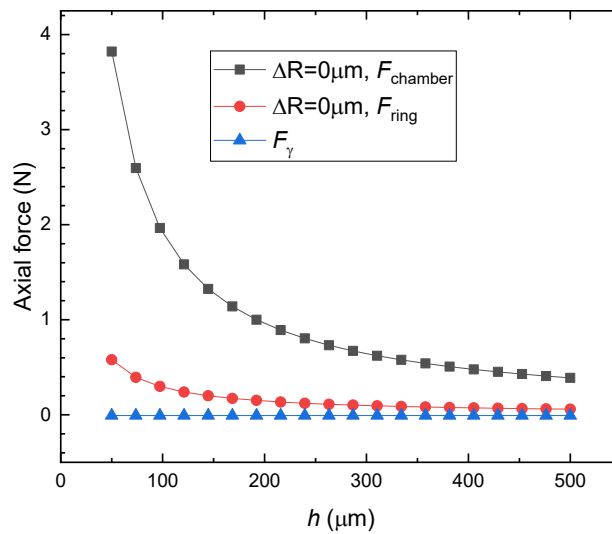


Figure 5.7. Different contributions to the supporting force of the air bearing.

Figure 5.8 shows the main contributions, which are the Laplace pressure inside the air chamber and the liquid ring, as a function of misalignment. The θ_{phiR} and θ_{phoA} are 45° and 160° , respectively. As we can see that the two forces show similar trends with h for different misalignment while the contribution from the air chamber is always higher than the contribution of the liquid ring. Both of the two forces increase all the way as h decreases for bearing without misalignment. When this is a misalignment,

these two forces start to decrease at a certain h as it decreases. The results shown in this figure is in agreement with the supporting force of the bearing shown in figure 5.6 (a).

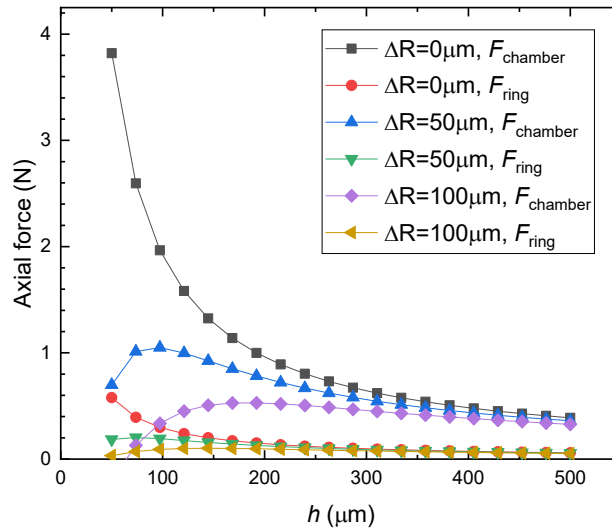


Figure 5.8. Contributions of the Laplace pressure inside the chamber and the liquid ring at different misalignment.

The effect of θ_{phiR} (*i.e.* receding contact angle on hydrophilic surface) on the maximum static supporting force of the bearing at different gap height is shown in figure 5.9. As we can see, for all the misalignments, the supporting force of the bearing at a certain gap height increases as θ_{phiR} decreases. For the bearing with a misalignment, the critical gap height decreases while the global maximum supporting force increases as θ_{phiR} decreases. As the misalignment increases (figure 5.9 (a) to (c)), the relative effect of the wettability of the hydrophilic surface on the maximum static supporting force of the bearing increases. Which means when designing the bearing, the hydrophilic surface should be as hydrophilic as possible, it can to some degree compensate the negative effect of the misalignment.

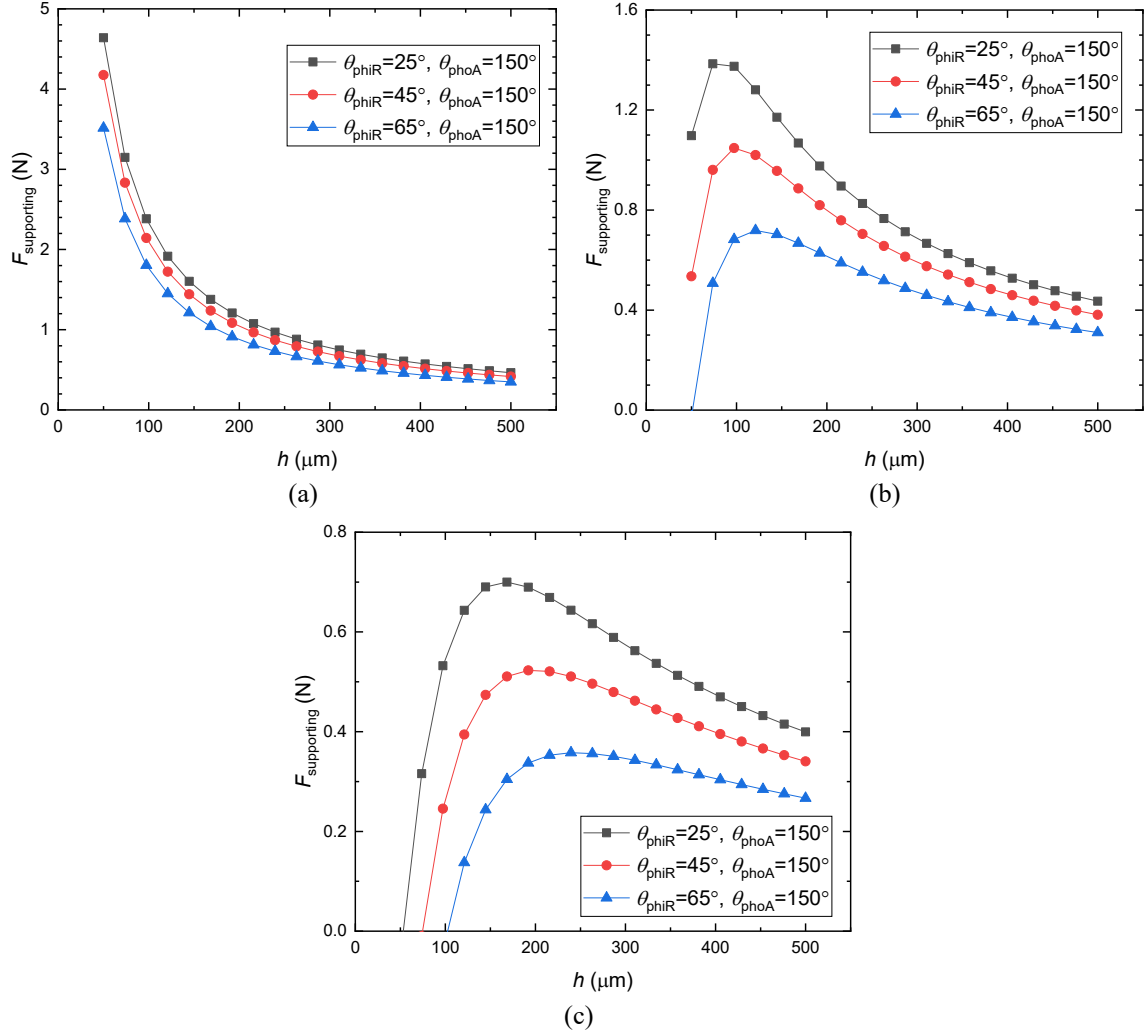


Figure 5.9. Supporting force as a function of gap height for different θ_{phiR} at different misalignments. (a) No misalignment. (b) Misalignment of 50 μm . (c) Misalignment of 100 μm .

Figure 5.10 shows the effect of θ_{phoA} (*i.e.* advancing contact angle on superhydrophobic surface) on the maximum static supporting force of the bearing at different gap height. As we can see when θ_{phoA} increases, it shows the same effect on the supporting force as θ_{phiR} decreases. For all the misalignments, the supporting force of the bearing at a certain gap height increases with θ_{phoA} . For the bearing with a misalignment, the critical gap height decreases while the global maximum supporting force increases with θ_{phoA} . As the misalignment increases (figure 5.10 (a) to (c)), the relative effect of the wettability of the hydrophobic surface on the maximum static supporting force of the bearing increases. This means when designing the bearing, the superhydrophobic surface should be as hydrophobic as possible.

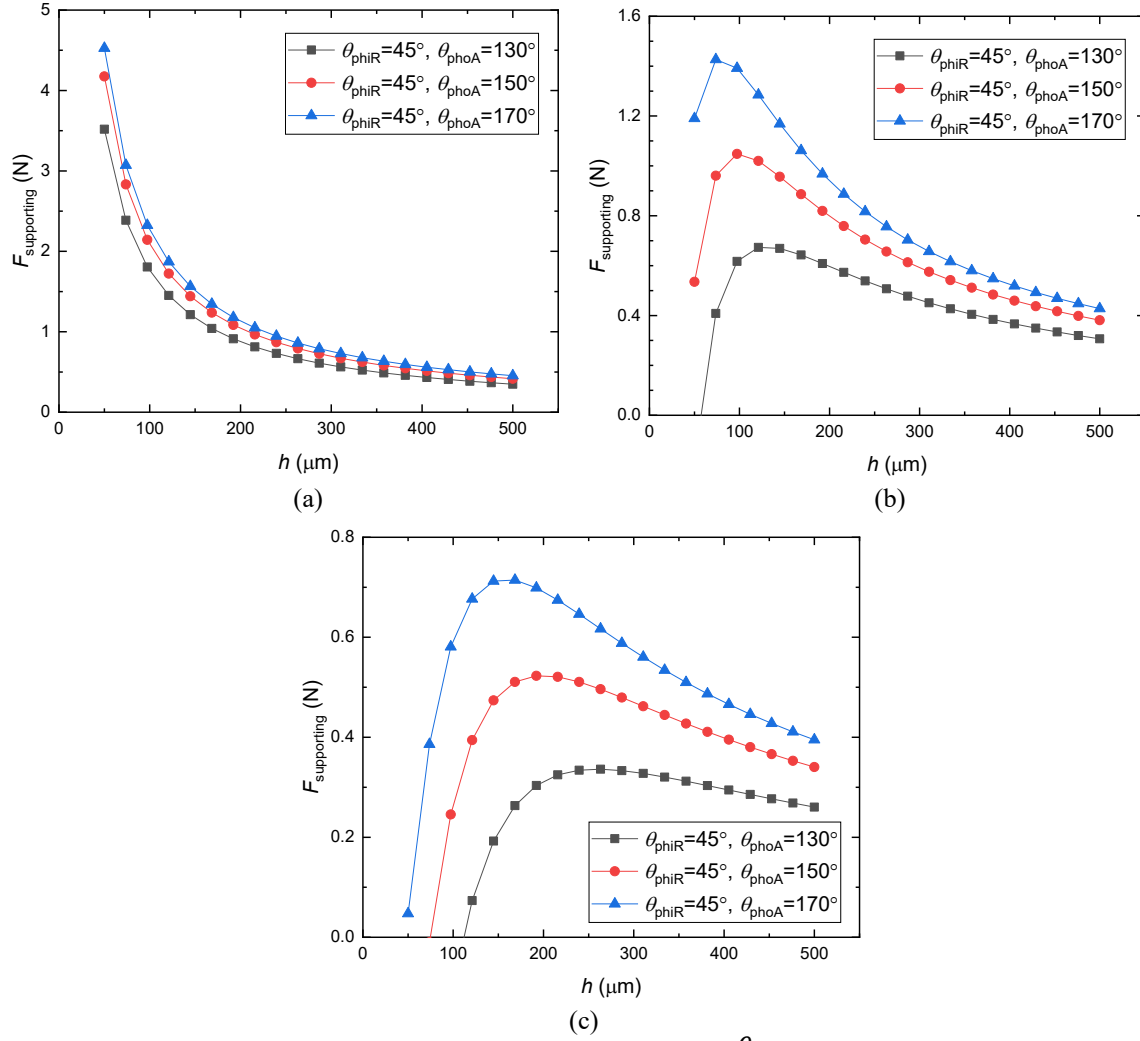


Figure 5.10. Supporting force as a function of gap height for different θ_{phoA} at different misalignments. (a) No misalignment. (b) Misalignment of 50 μm . (c) Misalignment of 100 μm .

Similar to the liquid ring bearing, when designing a liquid ring sealed air bearing, the working gap height should be above the critical gap height and the maximum load on the rotor should be smaller than the global maximum supporting force of the bearing. Thus, these two factors are the two key limiting conditions when designing such a bearing. figure 5.11 shows the effect of θ_{phiR} and θ_{phoA} on critical gap height and the global maximum supporting force of the bearing with different misalignments. As we can see, the effect of θ_{phiR} and θ_{phoA} are opposite. For a given misalignment, the critical gap height increases with θ_{phiR} while decrease with θ_{phoA} . The global maximum supporting force decreases with θ_{phiR} while increases with θ_{phoA} . For the same θ_{phiR} and θ_{phoA} , the critical gap height of the air bearing increases linearly while the global maximum supporting force decreases with the misalignment of the bearing. This is the same as that for a liquid ring bearing. From results shown above we can see that when designing an air bearing, the hydrophilic surface should be as hydrophilic as possible, the superhydrophobic surface should be as hydrophobic as possible and the misalignment should be as small as possible.

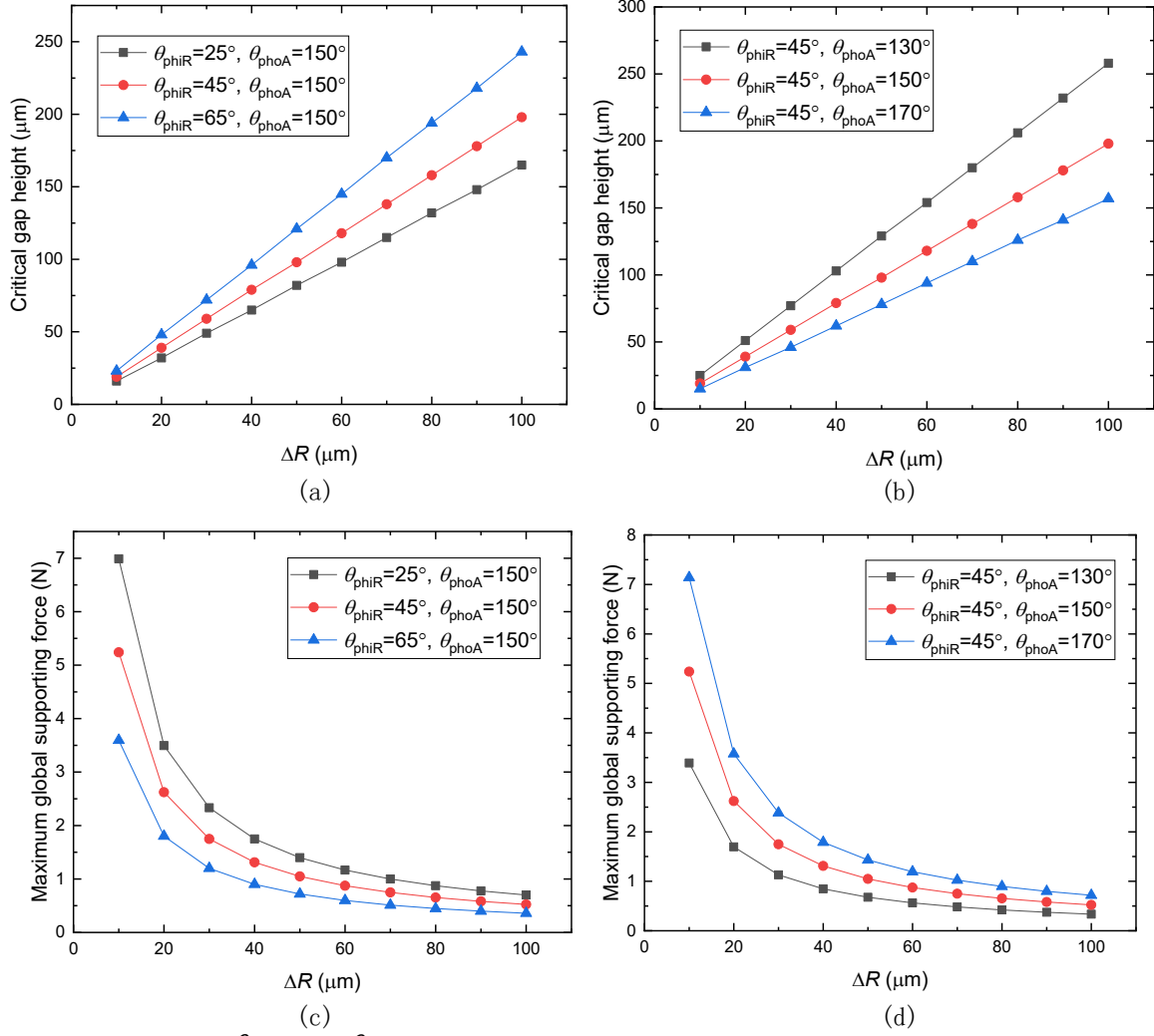


Figure 5.11. Effect of θ_{phiR} and θ_{phOA} on the critical gap height and the global maximum supporting force of the bearing. (a) and (b) Effect of θ_{phiR} and θ_{phOA} on the critical gap height. (c) and (d) Effect of θ_{phiR} and θ_{phOA} on the global maximum supporting force.

The effect of the width of the liquid ring (W_{ring}) on $F_{\text{Supporting}}$ has also been investigated numerically and the results are shown in figure 5.12. In this numerical model, R_{out} is the same in all cases and equal to 18 mm. Three different values of W_{ring} (1, 2 and 3 mm) were simulated. θ_{phiR} and θ_{phOA} were set to be 45° and 160° , respectively. And ΔR was set to be 0. It is shown that for the same h , $F_{\text{Supporting}}$ decreases slightly as W_{ring} increases. This is because, when compressed, the Laplace pressure inside the liquid ring is lower than that in the air cushion (since the former is controlled only by the outer liquid/air interface, while the latter is influenced by both the outer and inner liquid/air interfaces). Therefore, for the same R_{out} , a larger W_{ring} results in a reduced pressure in the air cushion and thus a smaller $F_{\text{Supporting}}$.

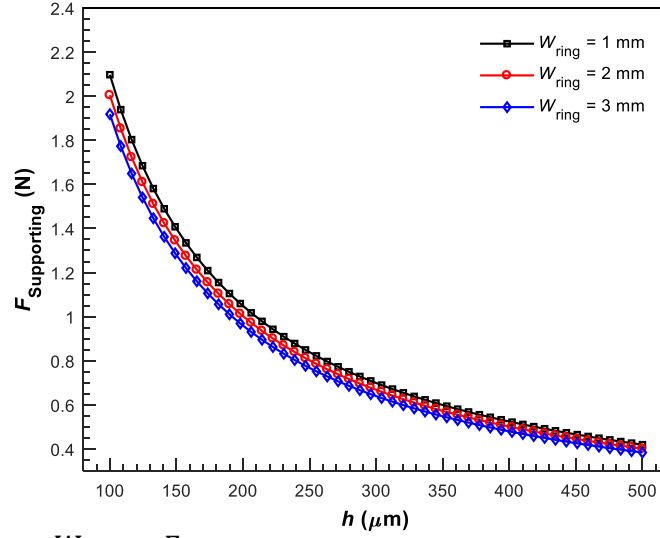


Figure 5.12. The effect of W_{ring} on $F_{\text{Supporting}}$.

5.3.2 The effect of air diffusion

The diffusion of the two major components of air, nitrogen and oxygen, through the liquid ring was investigated numerically. An example for the diffusion process of nitrogen is shown in figure 5.13. To exaggerate diffusion effects, the initial pressure inside the air cushion was assumed to be 1500 Pa which is higher than the largest pressure (~ 1400 Pa) obtained in any of the experiments. The initial concentration of air was assumed to be the saturation concentration at atmosphere pressure. These two assumptions give a higher concentration gradient at the inner liquid/air interface than the experiments, which results in a higher numerical diffusion rate of air through the liquid ring. The diffusion process was simulated for 300 s. Figure 5.13 shows how the concentration of nitrogen in the liquid ring ($W_{\text{ring}} = 2$ mm) changes with time. Through numerical integration the amount of nitrogen and oxygen that diffused through the liquid rings in 300 s were calculated. The resulting reduction in air cushion volume was $5.97, 3.95$ and $3.64 \times 10^{-8}\%$ for $W_{\text{ring}} = 1, 2$ and 3 mm respectively. The effect of such a small loss of air on the supporting force of the bearing can be considered negligible.

5.3.3 The effect of liquid evaporation

Several tests and simulations were conducted to investigate the effect of liquid evaporation on $F_{\text{Supporting}}$ and the results are shown in figure 5.14 (a). In these tests, h was kept constant and the rotor was rotating slowly at a speed of 0.01 rad/s. The supporting force of the bearing was recorded every 10 s. Six tests were conducted. Half of them were performed with the bearing exposed to air and the relative humidity of the environment was recorded. There was no air flow around the bearing during these experiments except the negligible flow rate induced by the rotation of the rotor. As we can see, $F_{\text{Supporting}}$ decreases as the liquid in the liquid ring evaporates.

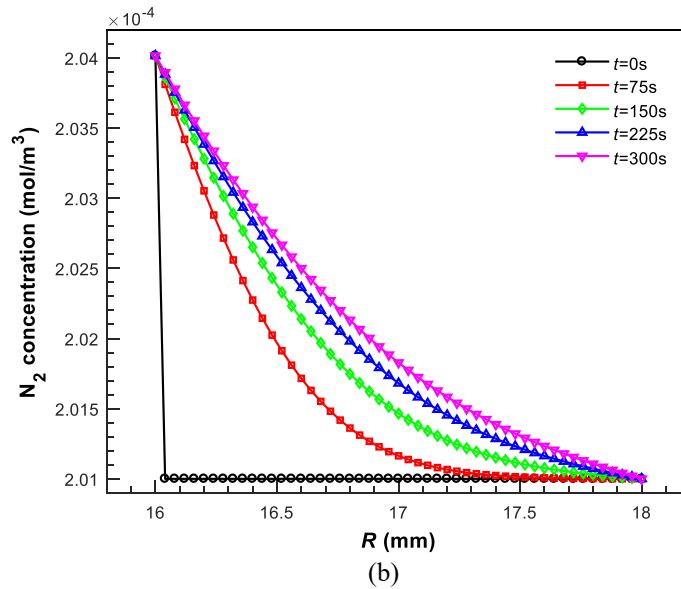
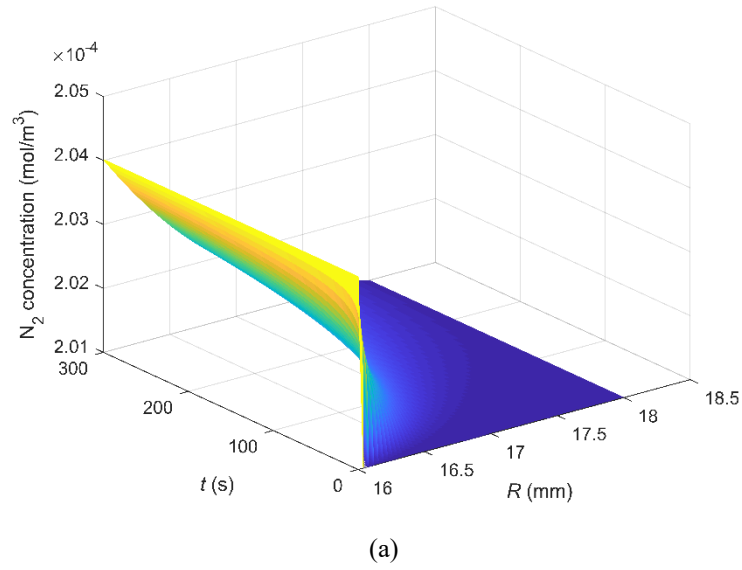


Figure 5.13. Concentration of nitrogen in the liquid ring, showing effect of diffusion. (a) 3D plot showing concentration of N_2 as a function of time and position along the liquid ring. (b) 2D plots showing snapshots in time.

As a comparison to these three tests, simulations were run under the same conditions but with a zero air flow velocity. It is shown that the numerical and experimental results agree well. The other half of the tests were conducted in a humidified environment. This was achieved by placing a liquid reservoir (i.e. the same liquid as that of the ring) next to the bearing and sealing them both inside a closed chamber. It is shown in figure 5.14 (a) that $F_{\text{Supporting}}$ remained approximately constant in these three humidified tests. No corresponding simulations to these three tests were conducted since at 100% relative humidity there would be no evaporation to drive diffusion in the numerical model.

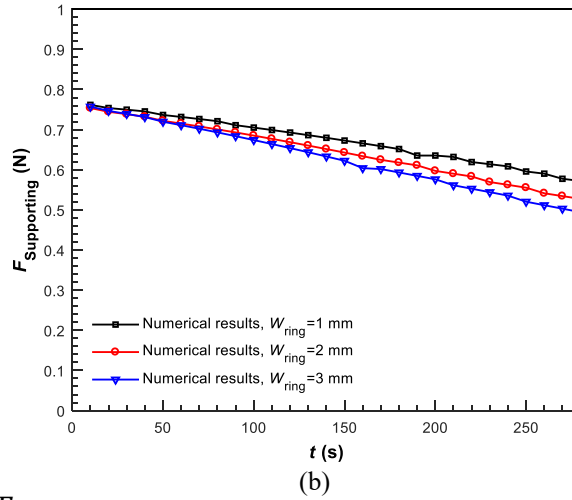
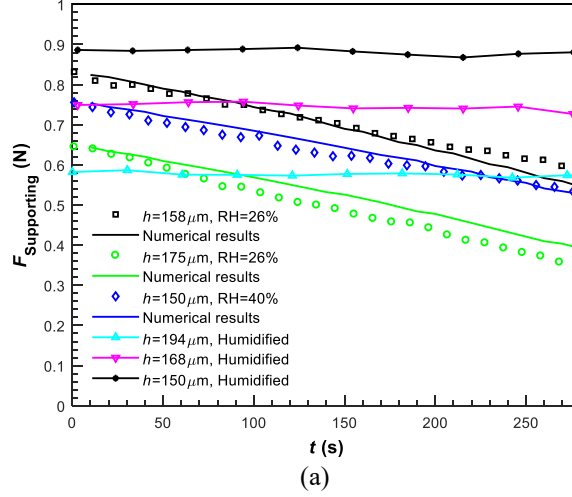


Figure 5.14. Variation in $F_{\text{Supporting}}$ over time (h constant) showing effect of evaporation. (a) Effect of RH on $F_{\text{Supporting}}$. (b) Effect of ring width W_{ring} on $F_{\text{Supporting}}$.

The effect of liquid evaporation on $F_{\text{Supporting}}$ of bearings with different widths W_{ring} was also investigated numerically and the results shown in figure 5.14 (b). In these three simulations, h was 150 μm , RH was 40% and outer radius was 18 mm. It is shown that the $F_{\text{Supporting}}$ of the bearing with a smaller W_{ring} decreases more slowly than that with a larger W_{ring} . The reason for this is that the liquid in the ring evaporates from the outer liquid/air interface. Under the same environmental conditions, the evaporation speeds remain the same, irrespective of ring width. However, a smaller W_{ring} leads to a larger air cushion inside the bearing. When the liquid evaporated from the liquid ring, the compressed air cushion expands to make up for the lost volume and the pressure inside the air cushion thus decreases. During this process, due to the compressibility of air, $F_{\text{Supporting}}$ for the bearing with a larger air cushion decreases more slowly.

In order to further verify the effect of air diffusion and liquid evaporation, a pressurised liquid ring test was conducted with the model shown in figure 5.4 and the results are shown in table 5.1 and figure 5.15.

Table 5.1. Pressurised liquid ring test results.

time (min)	gap height (μm)	height of the liquid pool (mm)	axial force (N)	state of the air hole	state of the liquid pool
0	210	219	0.11	open	connected
2	210	219	0.12	seal	connected
5	210	219	0.12	seal	connected
5	200	219	0.53	seal	connected
7	200	219	0.48	seal	connected
9	200	219	0.48	seal	connected
14	200	219	0.47	seal	connected
16	200	219	0.49	seal	disconnected
21	200	219	0.34	seal	disconnected
21	200	219	0.48	seal	connected
26	200	219	0.48	seal	connected
32	200	219	0.46	seal	connected
38	200	219	0.46	seal	connected
43	200	219	0.45	seal	connected
46	200	219	0.45	seal	connected
46	200	219	0.48	seal	disconnected
56	200	219	0.3	seal	disconnected
56	200	219	0.45	seal	connected
61	200	219	0.45	seal	connected
62	200	219	0.46	seal	connected
66	200	219	0.465	seal	connected
67	200	219	0.45	seal	connected
72	200	219	0.46	seal	connected
72	200	219	0.12	open	connected

At beginning (0 min), the air hole of the bearing was open to the atmosphere. Thus, the air chamber did contribute to the supporting force of the bearing. The liquid ring was connected to the liquid pool and the height of the liquid pool (free liquid surface to the surface of the stator) was 220 mm. As a result, the pressure in the liquid ring equals the pressure caused by the height of the liquid pool. The gap height of the bearing was 210 μm . For the following 5 minutes, the evaporated liquid in the liquid ring was compensated by the liquid pool whose height was constant. Thus, the supporting force of the bearing stayed relatively constant for 5 minutes. After that, the gap height of the bearing decreased and the air hole was sealed thus the supporting force of the bearing increased dramatically (air chamber is compressed and contributed to the supporting force of the bearing). Then the supporting force of the

bearing stayed relatively constant until 14 minute. During this period, the air hole was sealed and the liquid pool was connected. This proves that the air diffusion through the liquid ring is very slow. Otherwise, the supporting force would have decreased as there was no air supply to the air chamber. From 16 minute, the liquid pool was disconnected from the liquid ring. The liquid ring could not get liquid supply from the liquid pool. Thus, the supporting force of the bearing showed a dramatic decrease. This proves that the liquid evaporation has a strong effect on the supporting force. From 21 minute, the liquid pool was reconnected to the liquid ring and the supporting force of the bearing recovered. Again, this proves that little air has diffused through the liquid ring. After this the supporting force of the bearing stayed relatively constant until 46 minute as the air hole was sealed and the liquid pool was connected. Then the liquid pool was disconnected again and the supporting force of the bearing showed a dramatic decrease. When the liquid pool was reconnected at 56 minute, the supporting force recovered. Finally, at 72 minute, the air hole was opened to the atmosphere and the supporting force decreased to the value at the beginning on this test which proves the main contribution of the supporting force is from the air chamber.

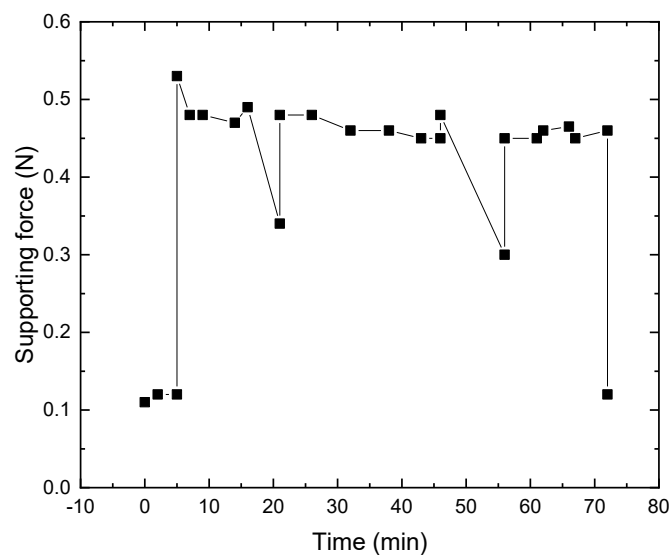


Figure 5.15. Pressurized liquid ring test results.

5.3.4 The stiffness of the bearing

The stiffness of the bearing was investigated numerically and the results validated against experimental data, as shown in figure 5.16.

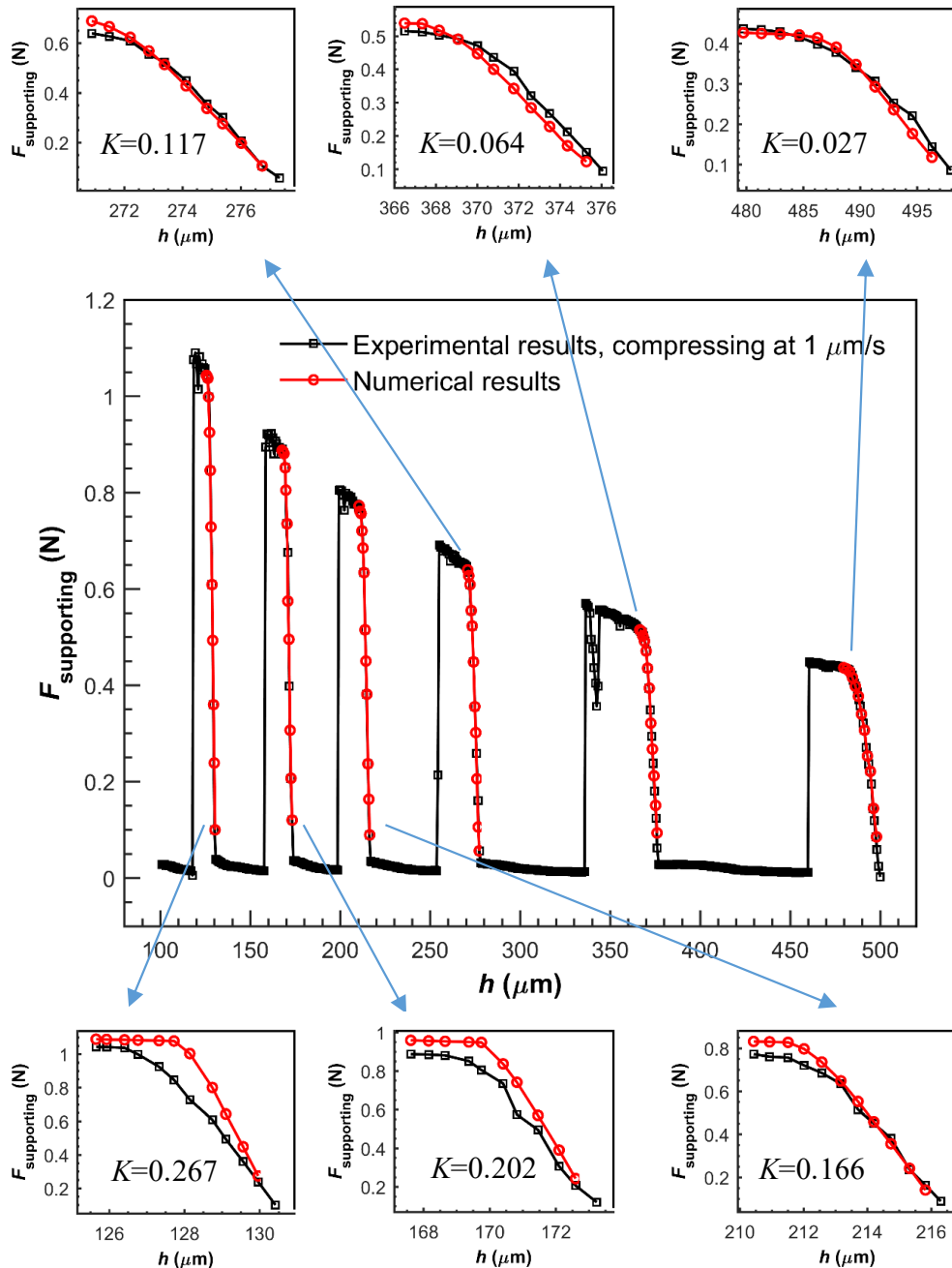


Figure 5.16. The stiffness of the bearing: experimental vs. modelling results. It should be noted here, the gap height of the bearing is decreasing as the bearing is being compressed. Thus, the results in this figure go from right to left in each individual plot.

The numerical model used the first experimental data point after the liquid ring was sealed as the initial condition and modelled the compression process before the liquid ring collapsed (individual events shown in figure 5.6 (b)). As we can see when h is larger than $200 \mu\text{m}$, the numerical results agree well

with the experimental results. When h is smaller than 200 μm , a difference between the numerical and experimental results appears. This is because, in the numerical model, the boundary of the hydrophilic and superhydrophobic rings was assumed to be smooth along the circumferential direction while there is in fact some roughness as can be seen from the SEM image in figure 5.5 (c). This roughness has an amplitude of about 200 μm and it shows an effect on $F_{\text{Supporting}}$ when h is comparable to the roughness. It is also shown in figure 5.16 that $F_{\text{Supporting}}$ increases almost linearly before it levels out as h decreases. Thus, a linear fitting was used to fit the linear section, $\Delta F_{\text{Supporting}} = -K \cdot \Delta h$, where K was defined as the stiffness coefficient of the bearing, which has a unit of $\text{N}/\mu\text{m}$, while $\Delta F_{\text{Supporting}}$ and Δh are the increase of the supporting force and the decrease of the gap height as the bearing is being compressed. We can see that K increases as h decreases, which is a desirable characteristic of a bearing. This is because the air cushion volume decreases as h decreases. Moreover, the percentage reduction in volume increases for the same Δh as h decreases and this causes a larger increase in pressure according to the compressibility of gas, and leads to a larger $\Delta F_{\text{Supporting}}$. This also suggests a way to modify the stiffness of the bearing by adding an extra air chamber to the air cushion of the bearing and the effect of such method has been discussed later.

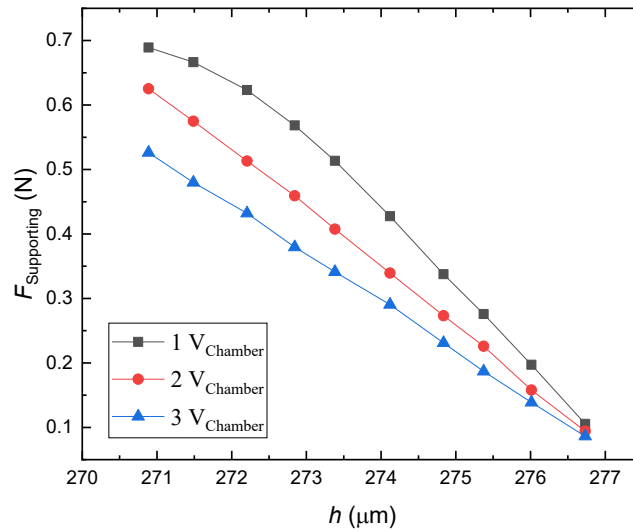


Figure 5.17. Effect of the volume of the air chamber on the stiffness of the bearing. Note here that the results go from right to left as the bearing is being compressed.

Figure 5.17 shows the effect of the volume of the air chamber (V_{Chamber}) on the stiffness of the bearing. In the figure, $n V_{\text{Chamber}}$ means the final volume of the air chamber to which the extra volume is added. We can see that the stiffness of the bearing decreases as the volume of the air chamber increases, which agrees with the results shown in 5.16.

The effect of surface wettability (denoted by θ_{phiR} and θ_{phoA}) on the stiffness has also been investigated and the results are shown in figure 5.18. As is shown in figure 5.18 (a), θ_{phoA} does not

affect the stiffness of the bearing at the initially stage with the same θ_{phiR} . Then for the case with the smallest θ_{phoA} , the stiffness of the bearing decreases slightly before the supporting force levels off. Figure 5.18 (b) shows the effect of θ_{phiR} on the stiffness of the bearing with the same θ_{phoA} . Similarly, θ_{phiR} does not show any effect on the stiffness of the bearing the initial stage. However, as the gap height decreases, the stiffness of the bearing decrease slightly for the largest θ_{phiR} . It is also shown that θ_{phiR} and θ_{phoA} also change the maximum supporting force of the bearing to which the curves level off. The results show that the maximum supporting force increases with θ_{phoA} while decrease with θ_{phiR} , which is in agreement with the results discussed in figure 5.10 and 5.11.

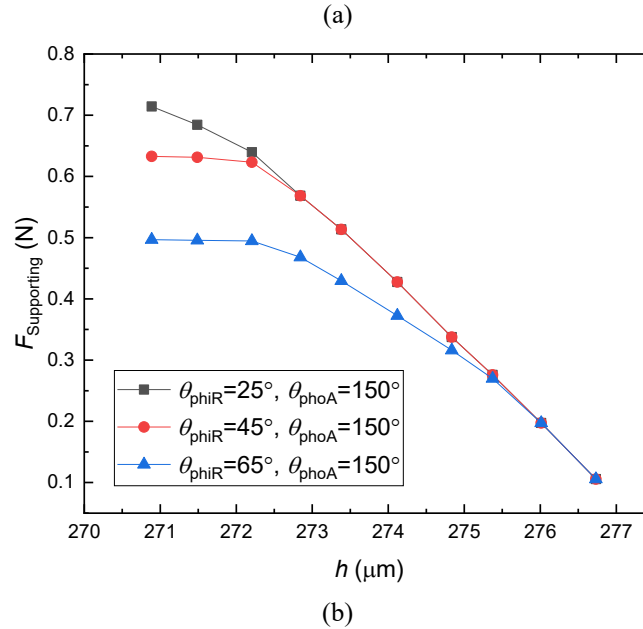
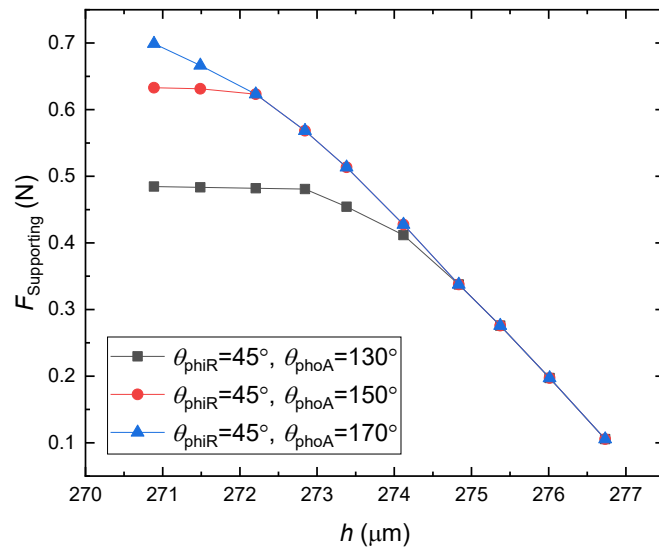


Figure 5.18. Effect of surface wettability on the stiffness of the bearing. (a) Effect of θ_{phoA} on the stiffness. (b) Effect of θ_{phiR} on the stiffness. Note here that the results go from right to left as the bearing is being compressed.

The effects of ΔR and W_{ring} on the stiffness of the bearing were investigated numerically and the results are shown in figure 5.19. As we can see from figure 19 (a), the effect of ΔR on the stiffness is negligible at the beginning of the compressing process. Then $F_{\text{Supporting}}$ for a bearing with a larger ΔR increases more slowly and reaches its maximum value earlier than that of a bearing with a smaller ΔR . This agrees with the result that the maximum static $F_{\text{Supporting}}$ decreases with ΔR . It is also shown in figure 5.19 (b) that the effect of W_{ring} on the stiffness of the bearing is small (K decreases slightly from 0.123 to 0.114 with W_{ring} increasing from 1 to 3 mm).

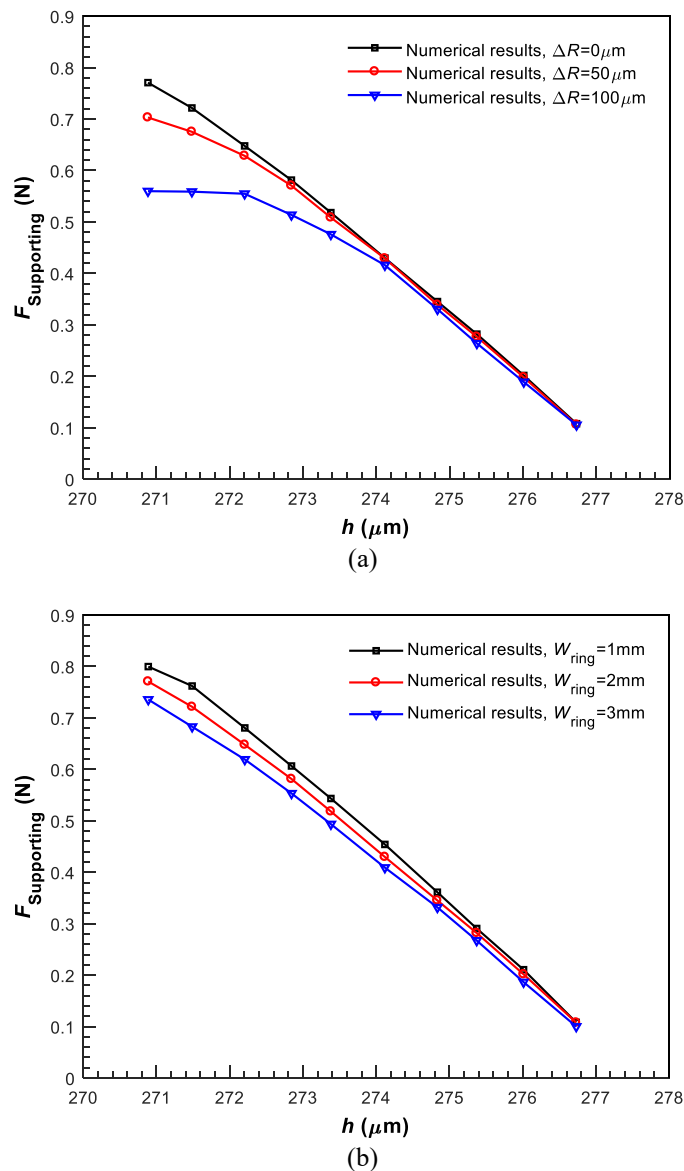


Figure 5.19. The stiffness of the bearing. (a) Effect of ΔR on stiffness. (b) Effect of W_{ring} on stiffness. Note here that the results go from right to left as the bearing is being compressed.

5.3.5 The dynamic supporting force of the bearing

Figure 20 shows the dynamic $F_{\text{Supporting}}$ and frictional torque of the bearing measured at different values of h . As the rotor rotates, the liquid ring deforms due to centrifugal acceleration. This deformation increases the volume of the air cushion and thus decrease $F_{\text{Supporting}}$. We can see from figure 5.20 (a) that the dynamic $F_{\text{Supporting}}$ decreases with the rotational speed. It should be noted here that the air diffusion and liquid evaporation also contribute to the decrease of the dynamic $F_{\text{Supporting}}$.

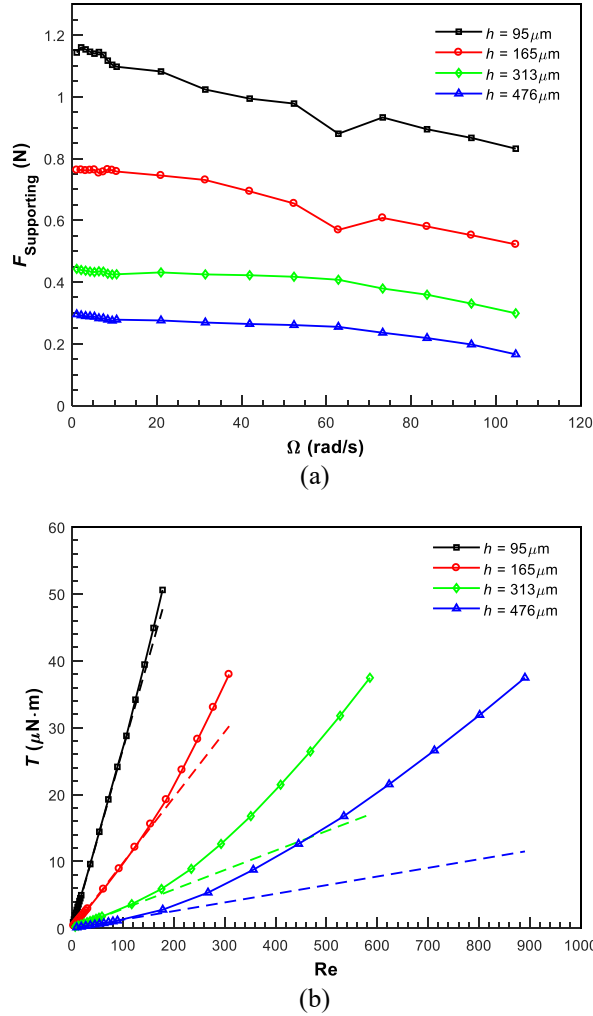


Figure 5.20. Experimental dynamic $F_{\text{Supporting}}$ and frictional torque of the bearing. The solid and dashed lines are the experimental and theoretical results (based on the Laminar assumption), respectively. (a) The dynamic $F_{\text{Supporting}}$ of the bearing at different h . (b) The frictional torque of the bearing at different h .

The measured frictional torque (T) of the bearing is plotted against Reynolds number ($Re = \frac{\rho \cdot h \cdot \Omega \cdot R_{\text{out}}}{\eta}$, where ρ is the density of the liquid, Ω is the rotational speed and η is the kinematic viscosity) in figure 5.20 (b) with solid lines. It is shown at the same Re , T increases as h decreases, while for the same h , T increases linearly at small Re . This linear increase agrees well with the theoretical results which assumes a laminar flow in the liquid ring. Based on the laminar assumption, the frictional torque can be

calculated with $T = \frac{\pi \cdot \Omega \cdot \eta}{2h_r} (r_o^4 - r_i^4)$ and the results are plotted in figure 5.20 (b) using dashed lines.

When Re gets larger, $Re > 150$, the system shows a strong nonlinearity. This is due to the energy dissipation caused by the vortex structures formed in the liquid ring flow at relatively large Re as discussed in Ref. [206].

5.4 Conclusions

A liquid ring sealed air bearing has been designed and the effects of different factors on its performance have been investigated both experimentally and numerically. The supporting force of the bearing results from the force induced by the Laplace pressure which dominates at micrometer scale and below. Separated by air and liquid ring, the bearing experiences very small friction and no wear. It was also shown that the air diffusion through the liquid ring is small and could be neglected during the experiments. This gives the bearing an advantage over the conventional air levitated bearings where continuous air supply is needed and an advantage over the liquid ring bearings which has much smaller supporting force and similar frictional torque for the same size and rotational speed.

It has been shown, through a systematic parametric study that the liquid evaporation causes a decrease to the supporting force of the bearing but this decreases at a slower rate when the environmental humidity is increased, which suggests that this problem could be handled by increasing the environmental humidity. Alternatively, ionic liquids with low vapour pressure could be used. The misalignment between the alternating hydrophilic and superhydrophobic rings on the rotor and the stator is an important factor which reduces the supporting force of the bearing, and this effect becomes significant when the misalignment is comparable to or smaller than the gap height. Thus, the misalignment should be avoided when constructing such a bearing. With the same outer diameter, the supporting force of the bearing decreases slightly as the width of the liquid ring increases while the frictional torque increases. Therefore, the width of the liquid ring should be as small as possible. However, it should be noted that reducing the width of the liquid ring may increase the vulnerability of the bearing to evaporation. The proposed model and the experimental results obtained in this chapter can be used to design new low cost and passive solutions using liquid ring sealed bearings for small system and devices (such as MEMS), for which the performance of the bearing is maximised.

Chapter 6 Conclusions and future work

6.1 Summary of the thesis achievements

As stated in Chapter 1, the exploration of surface tension and its dependence on curvature at the smallest of scales as well as its exploitation to design new bearing solutions at the micro-scale have been the principal aims of the thesis. First, I have set to investigate the curvature dependence of the surface tension and the Tolman length for both nanobubble and nanodroplet interfaces with MD simulations. Based on the understanding of the characteristics of surface tension, liquid ring and liquid ring sealed air bearings, which take advantage of the surface tension at micro-scale, have been designed. Numerical models, which can be used to predict and optimize the performance of the bearings have been built, thereby providing alternative lubricating methods for MEMS systems. A more detailed overview and breakdown of the key findings of the thesis is provided below.

The proposed aims of this project have been accomplished successfully by completing the following tasks:

- I. A literature review on the curvature dependence of the surface tension and the Tolman length and an overview of lubricating methods at the micro-scale have been conducted. It shows that the surface tension of liquid/gas interface with a curvature radius of molecular scale is still not well studied. The similarities between nanobubble and nanodroplet interfaces have not been thoroughly investigated and need to be researched. MD simulations which employ a mechanical framework for calculating the stress tensor and derive the surface tension are expected to be a way to address this question. The review also shows that current lubricating performance at the macro-scale is no longer efficient at the micro-scale and lower. The dominance of the surface tension at such scales must be explored and can provide a novel way of lubricating. Prototypes of such bearings have been designed; however, in my review I show that the factors affecting the performance of such bearings are yet to be well studied and the design of such microscopic devices can be greatly optimized.
- II. Following Tolman's deduction, a theoretical relationship between the surface tension and curvature has been deducted for cylindrical liquid/gas interfaces, as well as a mechanical way of calculating the surface tension through pressure tensors. MD models with alternate hydrophobic/hydrophilic patterns which introduce wettability steps to a solid wall have been developed. These patterns can be used to anchor the three-phase contact line and thus confine nanobubbles (nanodroplets) on hydrophobic (hydrophilic) areas. With this method, stable nanobubbles and nanodroplets were obtained in MD simulations which were then used to calculate the surface tension of the curved liquid/gas interface.

- III. With MD simulations on flat liquid/gas interfaces, a liquid/gas density ratio dependence of the surface tension and Tolman length was obtained. Such effect was then subtracted from the results for cylindrical liquid/gas interfaces. By doing this, the curvature dependence of the surface tension and Tolman length was obtained for both nanobubble and nanodroplet interfaces. It was shown that the curvature starts to have an effect on the surface tension and Tolman length when the curvature radius is smaller than 20 reduced LJ units. Moreover, the effect of curvature on the surface tension and Tolman length for nanobubble and nanodroplet interfaces are opposite in sign but have the same magnitude.
- IV. Using a patterned coating method, a prototype of liquid ring thrust bearings has been made. Theoretical predictions on the performance of the bearing, such as the maximum rotational speed, has been made and validated by experimental results. Results also suggest that the supporting force of such a bearing can be increased by reducing the misalignment of the patterns on the rotor and the stator or increasing the hydrophobicity of the superhydrophobic surface. The torque of the bearing was found to increase linearly with the rotational speed for Reynolds numbers smaller than 100 while it increases nonlinearly in higher Reynolds number region due to the extra energy dissipation caused by the formation of vortex structures.
- V. Based on the liquid ring thrust bearing, a liquid ring sealed air bearing has been developed. The supporting force of such an air bearing results from the force induced by the Laplace pressure which dominates at micrometer scale and below. Separated by air and liquid ring, the bearing experiences very small friction and no wear. Factors which affect the performance of the bearing, such as the hydrophobicity of the coating, the misalignment of the bearing and the height of the liquid ring have been studied theoretically and experimentally. A model which predicts the stiffness of the bearing has been built. In this model, factors like air diffusion, liquid evaporation and contact line slip have been included.
- VI. Results have shown that the air diffusion through the liquid ring is small and could be neglected during the experiments. The liquid evaporation causes a decrease to the supporting force of the bearing but this problem could be handled by increasing the environmental humidity. Alternatively, ionic liquids with low vapour pressure could be used. The misalignment of the bearing reduces the supporting force of the bearing; thus, it should be avoided when constructing such a bearing. The width of the liquid ring should be carefully chosen when designing such a bearing, because the supporting force of the bearing decreases slightly as the width of the liquid ring increases while the frictional torque increases. However, reducing the width of the liquid ring increases the vulnerability of the bearing to evaporation. The proposed model and the experimental results can be used to design new low cost and passive solutions using liquid ring sealed bearings for small system and devices (such as MEMS), for which the performance of the bearing is maximised.

6.2 Future work and research

Based on results obtained in this thesis, there are various areas that may require further investigation and the following tasks are potential routes to be considered for future work:

- I. It is shown from the results in chapter 3 that the curvature has opposite effect with the same magnitude on the surface tension of nanobubble and nanodroplet interfaces. It is known from the classical nucleation theory that the surface tension is a key factor affecting bubble (droplet) nucleation in bulk liquid (vapour). This suggests that there might be some interesting phenomena at the initial stage of these two phase-transition and this can be further investigated using MD simulations employing both simple mono-atomic systems but also more complex molecules. The effect of molecular structure on surface tension and Tolman length and its variation at the smallest scales is certainly something worth pursuing.
- II. It is shown in chapter 3 that alternate hydrophobic/hydrophilic patterns can anchor the three-phase contact line of nanobubbles and nanodroplets. These patterns may play an important role in the bubble or droplet nucleation process. It is therefore suggested that the effect of alternate hydrophobic/hydrophilic patterns on the phase-transition is investigated to explore its potential exploitation for the control of nucleation, which is particularly important for the safety of a number of engineering application where predicting boiling dynamics is a potential issue, including nuclear. The nucleation and control of droplet formation is also worth exploring to provide solutions for self-cleaning and anti-fog surfaces.
- III. I have shown in chapter 3 that the surface tension changes with the liquid/gas density ratio. It is also known that the surface tension changes with temperature, which is accompanied by a liquid/gas density ratio variation. Moreover, the kinetic component of the pressure tensor does not contribute to the surface tension (the kinetic components of the normal and tangential pressure tensors are identical). Thus, the origin of pressure dependence of the surface tension might be the variation of the liquid/gas density ratio and this needs further investigation.
- IV. We know from chapter 5 that each curved liquid gas interface will provide a pressure difference. Thus, a multi-liquid ring sealed air bearing can be designed. Through a proper design of the chamber volume between any two of the liquid rings, it is possible to make all the liquid/gas interface curved inwards. Each of these curved interface gives an increment to the pressure inside the air chamber which can largely increase the load capacity of the bearing. This design can be further investigated.
- V. When the liquid/gas interface of the bearing is curved outwards, it can form a negative pressure inside the air chamber. This can be utilised to design a bearing with the rotor suspended between two stators. Between the rotor and the lower stator there is a liquid ring

sealed air bearing with positive supporting pressure. Between the rotor and the upper stator, there is a liquid ring sealed air bearing with negative pressure, which also provides an upwards force to the rotor. This design can further increase the load capacity of the bearing and can be further investigated.

- VI. The numerical model obtained in chapter 5 has been validated with experimental results. It can be used to design a micro-scale bearing in the future. This bearing will have more advantages over other micro bearings as the size scales down; this effect must be explored to show both the real potential of the approach and the technological limitations of the applicability of the proposed technique.
- VII. Different liquids with smaller volatility and stronger surface tension can be tested on the bearing in the future. This will increase the load capacity and the durability of the bearing.

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List of Published Work

Published Articles

J. Wen, W. Zhang, L. Ren *et al.* *Controlling the number of vortices and torque in Taylor-Couette flow.* Journal of fluid mechanics, 2020

J. Wen, T. Reddyhoff, S. Hu *et al.* *Exploiting air cushion effects to optimize a superhydrophobic/hydrophilic patterned liquid ring sealed air bearing.* Tribology International, 2019

S. Hu, T. Reddyhoff, J. Wen *et al.* *Characterization and simulation of bi-Gaussian surfaces induced by material transfer and additive processes.* Tribology International, 2019

J. Wen, D. Dini and T. Reddyhoff. *Design and optimization of a liquid ring thrust bearing.* Tribology International, 2019

Articles Under Preparation in the Moment

J. Wen, E. Smith and D. Dini. *Molecular Droplets vs. Bubbles: effect of curvature on surface tension and Tolman length.* Journal of Colloid and Interface Science.

Presentations in Academic Conferences

J. Wen, D. Dini and T. Reddyhoff. *Liquid ring sealed air bearing.* International Tribology Congress. Sendai, JP, 17/Sep/2019 to 21/Sep/2019, Presentation.

J. Wen, D. Dini and T. Reddyhoff. *Design and optimization of a liquid ring thrust bearing.* 27th Mission of Tribology Research, London, UK, 6/Dec/2018 to 7/Dec/2018, Presentation.

J. Wen, D. Dini and T. Reddyhoff. *Design and optimization of a liquid ring thrust bearing.* 45th Leeds-Lyon Symposium on Tribology, Leeds, UK, 4/Sep/2018 to 7/Sep/2018, Presentation.

Appendix

Appendix A Deduction of the Tolman equations for cylindrical interfaces

For a cylindrical interface, the equations for surface tension based on pressure tensors can be deduced following the method similar to that for a spherical interface. The system can be simplified as a cylindrical drop of phase α immersed in phase β within a cylindrical coordinate system r, θ, z . The pressure tensor of the system is:

$$\mathbf{P} = P_N(\mathbf{e}_r\mathbf{e}_r) + P_T(\mathbf{e}_\theta\mathbf{e}_\theta) + P_z(\mathbf{e}_z\mathbf{e}_z) \quad (\text{A.1})$$

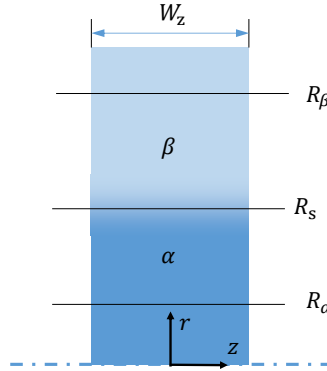


Figure A.1. Stress state of a strip in a longitudinal plane of a cylindrical interface.

Then, consider a longitudinal strip with a width of W_z in the z direction, stretching from R_α (in the bulk α region) to R_β (in the bulk β region) in the r direction, at a constant θ (shown in figure A.1). The surface of tension is at R_s in r direction. The force acting on one side of the strip can be expressed in two ways: as an integral of $P_T(r)$ over the strip, or, as a result of the pressure P_α acting on the surface between R_α and R_s , of the pressure P_β acting on the surface between R_s and R_β , and of the surface tension γ acting at R_s . The two expressions of the force and the momentum of the force about z axis equal each other:

$$\int_{R_\alpha}^{R_\beta} r^n W_z P_T dr = \int_{R_\alpha}^{R_s} r^n W_z P_\alpha dr + \int_{R_s}^{R_\beta} r^n W_z P_\beta dr - R_s^n W_z \gamma \quad (\text{A.2})$$

where $n = 0$ and 1 represent the force acting on the strip and its momentum about z axis, respectively. Here we define a pressure $P_{\alpha,\beta}(r; R_s)$ which equals P_α for r between R_α and R_s and P_β for r between R_s and R_β . Then equation (A.2) can be rewrote as:

$$\gamma = \int_{R_\alpha}^{R_\beta} \left(\frac{r}{R_s}\right)^n (P_{\alpha,\beta}(r; R_s) - P_T) dr \quad (\text{A.3})$$

At the same time, from the hydrostatic equilibrium condition of the system $\nabla \cdot \mathbf{P} = 0$ we have:

$$\int_{R_\alpha}^{R_\beta} \frac{d(r^m P_N)}{dr} dr = \int_{R_\alpha}^{R_\beta} r^{m-1} [(m-1)P_N + P_T] dr \quad (\text{A.4})$$

where m is an integer. Integrate the left side of equation (A.4):

$$R_\beta^m P_\beta - R_\alpha^m P_\alpha = \int_{R_\alpha}^{R_\beta} r^{m-1} [(m-1)P_N + P_T] dr \quad (\text{A.5})$$

In the meanwhile, form the integration of $mr^{m-1}P_{\alpha,\beta}(r; R_s)$:

$$\begin{aligned} \int_{R_\alpha}^{R_\beta} mr^{m-1}P_{\alpha,\beta}(r; R_s) dr &= \int_{R_\alpha}^{R_s} mr^{m-1}P_\alpha dr + \int_{R_s}^{R_\beta} mr^{m-1}P_\beta dr \\ &= R_\beta^m P_\beta - R_\alpha^m P_\alpha + (P_\alpha - P_\beta)R_s^m \end{aligned} \quad (\text{A.6})$$

Substitute equation (A.5) into (A.6):

$$(P_\alpha - P_\beta)R_s^m = \int_{R_\alpha}^{R_\beta} (mr^{m-1}P_{\alpha,\beta}(r; R_s) - r^{m-1}[(m-1)P_N + P_T]) dr \quad (\text{A.7})$$

At the surface of tension we have:

$$P_\alpha - P_\beta = \frac{\gamma}{R_s} \quad (\text{A.8})$$

Substitute equation (A.8) into (A.7):

$$\gamma = \int_{R_\alpha}^{R_\beta} \left(m \left(\frac{r}{R_s} \right)^{m-1} P_{\alpha,\beta}(r; R_s) - \left(\frac{r}{R_s} \right)^{m-1} [(m-1)P_N + P_T] \right) dr \quad (\text{A.9})$$

Equation (A.3) times 2 for $n = 1$ minus equation (A.9) for $m = 2$:

$$\gamma = \int_{R_\alpha}^{R_\beta} \frac{r}{R_s} (P_N - P_T) dr \quad (\text{A.10})$$

Equation (A.10) divided by equation (A.9) for $m = 0$:

$$R_s^2 = \frac{\int_{R_\alpha}^{R_\beta} r (P_N - P_T) dr}{\int_{R_\alpha}^{R_\beta} \frac{1}{r} (P_N - P_T) dr} \quad (\text{A.11})$$

Appendix B Volume of the liquid ring

The liquid ring is divided into 4 sections having the same volume ($V_{\text{ring}/4}$). Here $V_{\text{ring}/4}$ of the section between $\varphi = 0$ and $\varphi = \pi/2$ (see in figure 5.2 (a)) is calculated and the total volume of the liquid ring is $V_{\text{ring}} = 4 \cdot V_{\text{ring}/4}$. The section of the liquid ring again is divided into 2 sections: the outer meniscus (depicted as ① in figure 5.2 (a) and (b)), the rest body of the liquid ring (depicted as ② in figure 5.2 (b)). The volume of section ② (V_2) is calculated using the vertical column defined by the lower pattern (V_{column}) minus the volume (V_3) of the inner meniscus (depicted as ③ in figure 5.2 (a) and (b)). Thus the volume of the liquid ring is:

$$V_{\text{ring}} = 4 \cdot V_{\text{ring}/4} = 4 \cdot (V_1 + V_{\text{column}} - V_3) \quad (\text{B.1})$$

Here the calculation of the volume of section ① (V_1) was shown:

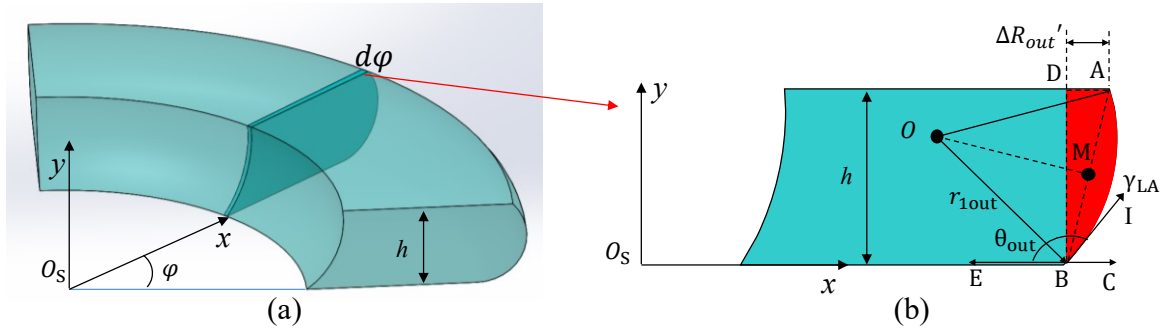


Figure B.1. The volume of section ①. (a) Coordinate system used for calculation. (b) Infinitesimal element of the liquid ring.

The O_S coordinate system is shown in figure B.1 (a). As discussed in the main text, the curvature radius of the outer meniscus on the cross sectional plane ($r_{1\text{out}}$) at different φ is constant and is calculated using equation (5.7). The local misalignment of the outer contact line ($\Delta R_{\text{out}}'$) is calculated using equation (5.10). The gap height (h) is known. Then the local outer contact angle θ_{out} is calculated:

$$\theta_{\text{out}} = 270^\circ - \arctan\left(\frac{h}{\Delta R_{\text{out}}'}\right) - \arccos\left(\frac{\sqrt{\Delta R_{\text{out}}'^2 + h^2}}{2 \cdot r_{1\text{out}}}\right) \quad (\text{B.2})$$

Then the coordinates of O were calculate:

$$x_O = R_{\text{out}} - \frac{\Delta R_{\text{out}}'}{2} - r_{1\text{out}} \cdot \cos\left(\theta_{\text{out}} - \frac{\pi}{2}\right) \quad (\text{B.3})$$

$$y_O = r_{1\text{out}} \cdot \sin\left(\theta_{\text{out}} - \frac{\pi}{2}\right) \quad (\text{B.4})$$

In the O_S coordinate system, the profile of the outer liquid/air interface was depicted:

$$(x - x_o)^2 + (y - y_o)^2 = r_{1out}^2 \quad (B.5)$$

Then volume of the annulus defined by the red area in figure B.1 (b) and the y axis as the axle of revolution can be calculated:

$$V = \int_0^h (\pi \cdot x^2 - \pi \cdot (R_{out} - \frac{\Delta R_{out}}{2})^2) dy \quad (B.6)$$

where x was calculated using the transformation of equation (B.5):

$$x = x_o + \sqrt{r_{1out}^2 - (y - y_o)^2} \quad (B.7)$$

Then the volume of section ① is:

$$V_1 = \int_0^{\frac{\pi}{2}} \frac{\int_0^h (\pi \cdot (x_o + \sqrt{r_{1out}^2 - (y - y_o)^2})^2 - \pi \cdot (R_{out} - \frac{\Delta R_{out}}{2})^2) dy}{2 \cdot \pi} d\varphi \quad (B.8)$$

To calculate the volume of section ② (V_2), first the volume of the vertical column defined by the lower pattern (V_{column}) is calculated:

$$V_{column} = \int_0^{2\pi} \frac{\pi \cdot (HO_S^2 - KO_S^2)}{2 \cdot \pi} d\varphi \quad (B.9)$$

where HO_S and KO_S are calculated with:

$$HO_S = \cos(\pi - \varphi) \cdot \Delta R/2 + \sqrt{[\cos(\pi - \varphi)]^2 \cdot \frac{\Delta R^2}{4} + R_{out}^2 - \frac{\Delta R^2}{4}} \quad (B.10)$$

$$KO_S = \cos(\pi - \varphi) \cdot \Delta R/2 + \sqrt{[\cos(\pi - \varphi)]^2 \cdot \frac{\Delta R^2}{4} + R_{in}^2 - \frac{\Delta R^2}{4}} \quad (B.11)$$

The calculation of the volume of the inner meniscus V_3 is similar to V_1 and is not presented here.

Appendix C Volume of the air cushion

As with the liquid ring, the air cushion is also divided into 4 sections each having the same volume ($V_{air/4}$). Here $V_{air/4}$ of the section between $\varphi = 0$ and $\varphi = \pi/2$ (shown in figure 5.2 (a)) is calculated and the total volume of the air cushion was $V_{air} = 4 \cdot V_{air/4}$. The section of the air cushion is calculated

using the vertical column defined by the lower inner contact line ($V_{\text{column_air}}$) plus the volume (V_3) of the inner meniscus (depicted as ③ in figure 5.2 (a) and (b)). Thus the volume of the air cushion is:

$$V_{\text{air}} = 4 \cdot V_{\text{air}/4} = 4 \cdot (V_{\text{column_air}} + V_3) \quad (\text{C.1})$$

The volume of the vertical column defined by the lower inner contact line ($V_{\text{column_air}}$) is calculated:

$$V_{\text{column_air}} = \int_0^{2\pi} \frac{\pi \cdot KO_S^2}{2 \cdot \pi} d\varphi \quad (\text{C.2})$$

where KO_S is calculated using equation (B.11). The calculation of the volume of the inner meniscus V_3 is similar to V_1 which is presented in appendix A.