

Contact Line Pinning Effects Influence the Determination of the Line Tension of Droplets Adsorbed on Substrates

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Abstract

The precise determination of the line tension of sessile droplets still represents a major challenge. At present the estimates of the line tension from contact angle measurements can differ by 4-5 orders of magnitude. Here we show that the pinning effect of the droplet contact line caused by the substrate inhomogeneities influences the apparent contact angle of the droplet, affecting the determination of the line tension via the corrected Young's equation. We introduce the contribution of pinning effects into the Gibbs free energy differential, and derive a modified version of the Young's equation. Using classical density functional theory we isolate the line tension and the pinning force contributions for substrates with different heterogeneity. The pinning effect leads to metastability of wetting states and influences the contact angle, hence introducing errors in the estimation of line tensions using the traditional analysis of contact angles, based on the modified Young's equation.

Introduction

The study of the three-phase contact line and the line tension in sessile droplets has attracted considerable interest¹⁻⁴ because of its relevance in a number of processes, such as nucleation,^{5,6} the stability of emulsions and foams⁷ and nanofluidics,⁸⁻¹⁰ and a wide range of applications related to contact line dynamics.¹¹⁻¹³ Despite its importance, there are not at present direct techniques for measuring the line tension, which is instead determined indirectly via contact angle measurements,¹⁴ attachment of particles at interface¹⁵ or surface pressure measurements.¹⁶ The contribution of the line tension to the excess free energy has been discussed theoretically and its impact on the droplet contact angle has been often included using the modified Young's equation,^{17,18}

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} - \frac{\tau}{r_p \gamma_{lv}} = \cos\theta_Y - \frac{\tau}{r_p \gamma_{lv}} \quad (1)$$

where r_p is the radius of the three phase line, θ represents the measured contact angle, θ_Y is the Young's contact angle, and γ_{sl} , γ_{sv} and γ_{lv} , are the solid-liquid, solid-vapor, and liquid-vapor surface

tensions, respectively.

It is known that the line tensions obtained from experiments and theories, including computer simulations may differ. In most theoretical studies, the estimates of the magnitude of the line tension vary from 10^{-12} to 10^{-10} J/m,^{19–23} whereas the experimental values of the line tension vary from 10^{-12} to over 10^{-5} J/m,^{1,24–28} sometimes 4-5 orders of magnitude larger than the estimated theoretical values. The differences depend on the systems under study and it has been argued recently that while at atomic scales the line tension is of the order of nN, mesoscopic contributions at nanometer length scales and gravitational effects at mm scales, can add significant contribution to the line tension.¹ Understanding the magnitude of the line tension is thus attracting great interest, in particular to rationalize the different values of line tensions reported in experimental and theoretical studies.

In this work, we discuss a possible contribution to the measured line tension force, which we attribute to the contact line pinning of droplets that sit on substrates featuring nanoscale heterogeneity. This notion provides a novel interpretation of possible causes behind the large variation of line tension values observed in experiments.

The paper is organized as follows. Firstly, we explicitly introduce the contribution of the pinning effect into the Gibbs free energy and derive a modified version of the Young’s equation. Then we use the normal and constrained lattice density functional theory (LDTF) to determine and separate the line tension and the pinning force for substrates with different heterogeneity. We finally discuss the possible origins of the deviations of measured and Young’s contact angles.

Theoretical Background

Let us start with a droplet adsorbed on a substrate, with a contact angle θ and a radius of the three phase line r_p . The volume V of the droplet and its liquid/vapor interfacial area A_{lv} can be written as^{29,30} $V = \frac{\pi r_p^3}{3 \sin^3 \theta} (1 - \cos \theta)^2 (2 + \cos \theta)$ and $A_{lv} = \frac{2\pi r_p^2}{(1 + \cos \theta)}$. The Gibbs free energy of the droplet, G , should include both interfacial free energies and the free energy of the three phase

contact line: $G = \gamma_{lv}A_{lv} + \gamma_{sl}A_{sl} + \gamma_{sv}A_{sv} + \tau L$, with $L = 2\pi r_p$ the length of three phase contact line the, A_{sl} the solid/liquid interfacial area, and A_{sv} the solid/vapor interfacial area. Using Young's equation $\cos\theta_Y = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$, we obtain $G = \gamma_{lv}\pi r_p^2 [\frac{2}{(1+\cos\theta)} - \cos\theta_Y] + \tau L$. For a droplet having a constant volume we get, $\frac{d\theta}{dr_p} = \frac{-\sin\theta(2+\cos\theta)}{r_p}$. At equilibrium, the free energy fulfils the condition: $\frac{dG}{dr_p} = \frac{\partial G}{\partial r_p} + \frac{\partial G}{\partial \theta} \frac{\partial \theta}{\partial r_p} = 0$. For flat and homogeneous substrates this condition gives the well known modified Young's equation, $\cos\theta = \cos\theta_Y - \frac{\tau}{r_p\gamma_{lv}}$. However, the situation is very different if the substrate is inhomogeneous, either physically rough or chemically heterogeneous. In these cases, there exists a pinning force that leads to metastability and stabilizes the droplet at certain contact angle, which may significantly deviate from the equilibrium contact angle. For the droplets pinned at a surface, as we consider here, a mean constraint force is required as a mechanical force in order to satisfy equation $\frac{dG}{dr_p}$ above. The mean constraint force that is here called the pinning force, f_p , which can be written as $\frac{dG}{dr_p} = \frac{\partial G}{\partial r_p} + \frac{\partial G}{\partial \theta} \frac{\partial \theta}{\partial r_p} = -f_p$, rather than $\frac{dG}{dr_p} = 0$ mentioned above. Minimizing the Gibbs free energy for the constrained system gives the following equation,

$$\cos\theta = \cos\theta_Y - \frac{\tau}{r_p\gamma_{lv}} - \frac{\tilde{f}_p}{\gamma_{lv}} \quad (2)$$

where $\tilde{f}_p = \frac{f_p}{2\pi r_p}$ is the pinning force per unit length of the contact line. This equation explicitly includes both the line tension and the pinning effects of contact line, and its definition allows to explore the impact of pinning on the measured contact angle.

In fact, the pinning force f_p can be interpreted as a result of Lagrange multiplier. Under contact line pinning $r_p=r_p^C$ with r_p^C the target radius of contact line, the Lagrange constraint ($r_p - r_p^C = 0$) needs to add into $G = \gamma_{lv}A_{lv} + \gamma_{sl}A_{sl} + \gamma_{sv}A_{sv} + \tau L$ to stabilize the pinning radius. Minimizing the modified grand potential $G^C = G + \lambda(r_p - r_p^C)$ with respect to pinning radius exactly gives $\frac{dG^C}{dr_p} = \frac{dG}{dr_p} + \lambda = 0$. Through defining $\lambda \equiv f_p$, we also have $\frac{dG}{dr_p} = -f_p$ as shown above. Therefore, f_p represents the pinning force for stabilizing the given contact line.

Lattice Density Functional Theory (LDTF) Calculations

Following Eqn. 2, two steps are required to calculate and separate the line tension and pinning force contributions. Firstly, we focus on droplets sitting on homogeneous and flat substrates, for which the pinning effect vanishes, and determine the line tension by decomposing the grand free energy into volume, interface and line contributions.³¹ Secondly, we calculate the contact angle of droplets on different inhomogeneous substrates, where the contact line pinning is present, and we use Eqn. 2 to derive the line tension and the pinning force contributions separately.

For nanodroplets studied here, we need to ensure that the droplets are in equilibrium with their surrounding vapor phase, and the non-equilibrium effect, especially, the evaporation effect is needed to completely remove.³² Therefore, in this work the nanodroplets are modeled as part of the critical nuclei for homogeneous nucleation at the given temperature and chemical potential, which has advantages of free of non-equilibrium effect. For this purpose, we employed normal and constrained LDTF³³ (see also the supporting information), which was developed to study nucleation in vapor-liquid transitions in an open system, to determine the droplets adsorbed at homogeneous and inhomogeneous substrates. We adopted periodic boundaries in the x- and y-directions, and a mirror boundary condition for the z-direction. The fluid-solid interaction ϵ_{sf} varies from 0.3 to 0.55, hence targeting both hydrophilic ($\theta_Y < \frac{\pi}{2}$ for $\epsilon_{sf} > 0.5$) and hydrophobic ($\theta_Y > \frac{\pi}{2}$ for $\epsilon_{sf} < 0.5$) substrates. As usual, all variables were reported here in the dimensionless units, e.g., temperature and chemical potential are reduced by the energy parameter of the fluid-fluid interactions ϵ_{ff} , while the length is reduced by the molecular diameter σ of the fluid.

The line tensions for droplets on the flat and smooth substrates were determined following the procedure proposed in our previous work.³¹ For the homogeneous and flat substrate the pinning effect vanishes (Fig. 1) and Eqn. 2 reduces to Eqn. 1. In this case, the droplet equilibrates with its surrounding with a global free energy minimum, and its grand free energy can be divided into volume, interface and line contributions, namely $\Delta\Omega = V(\omega_l - \omega_v) + A_{sl}(\gamma_{sl} - \gamma_{sv}) + A_{lv}\gamma_{lv} + \tau L$ with V being the volume of the droplet, and ω_i the bulk free energy density for the liquid or vapor phases. Once the grand free energy and its volume and interface contributions have been

determined, the line tension can be extracted. To eliminate the non-equilibrium effect and the lattice effect (see the supporting information), we used the critical nuclei at the given chemical potential and the given temperature of $T = 1.2$ to model the droplets (the critical nuclei produced from our constrained LDFT is in thermodynamic equilibrium with surrounding supersaturated vapor). We used the normal and constraint LDFT methods to determine $\omega_l - \omega_v$, $\gamma_{sl} - \gamma_{sv}$ and γ_v sequentially in carefully chosen systems (see Figs. 1a, b, c, d). More details on the approach used to calculate these thermodynamic properties can be found in our previous work.³¹ The line tension was determined by subtracting the interface and volume contributions from the grand free energy of the nanodroplet (Fig 1e). The calculated line tensions agree with those of our previous study.³¹ We obtain negative line tensions, and the ratio $\frac{\tau}{\gamma_v} < 1$ indicating that the line tension effects ($\frac{\tau}{r_p \gamma_v}$) can be safely ignored, since the size of the droplet is far greater than the molecular diameter (or $r_p \gg \sigma = 1$). Taking $r_p = 0.37\text{nm}$ and $\varepsilon_{ff} = 7.9226 \times 10^{-21}\text{J}$ ³⁴, we obtain line tensions of the order 10^{-11}N . This result is similar to those obtained in previous theoretical predictions²⁶ and in some experimental results.³⁵ In most cases the effect of the line tension becomes sufficiently small when compared to the pinning effect, and then the impact of the former can be neglected.

Following previous studies on flat surfaces, we investigated the impact of roughness by constructing two kinds of rough substrates: one was decorated with a cuboid-shaped protrusion in order to pin a cylindrical cap-shaped droplet with a radius of r_p (Fig. 2a and Fig. 2b). The droplet is periodic along the axis of the cylindrical cap, and thus the droplet contact line has zero curvature along the direction of contact line, meaning that according to Eqn. 1 the contact angle should not be influenced by the line tension and therefore the pinning force can be simply determined with Eqn. 2. The second substrate consisted of a cylindrical protrusion or a cylindrical pore in order to pin spherical cup-shaped droplets (see Fig. 3a-c). By comparing the contact angles of the cylindrical cap-shaped (Fig. 2a) and spherical cap-shaped droplets (Fig. 3a) of similar radius of curvature, with and without the effect of line tension we extracted the force contributions arising from the line tension and pinning.

For the rough substrate with a cuboid-shaped protrusion, we simulated the droplets at the chem-

ical potential of $\mu = -2.98$ (in comparison to $\mu_0 = -3.0$ for the liquid-vapor coexistence), which has radius of curvature of $R = 19.71$. This chemical potential corresponds to that of the homogeneous critical nucleus (Fig. 2b). For the present analysis, r_p is always defined by the length of the cuboid side that pins the droplet, again note that cylindrical droplet is periodic along the cylinder axis (see Fig. 2a). We show in Figure 2c the dependence of the contact angle with the size of the cuboid and the substrate wettability ε_{sf} . Increasing the size of the cuboid shaped protrusion, r_p , results in an increase of $\cos \theta$ for the pinned droplets. The required forces for pinning the droplet were determined using Eqn. 2 (in this case the effect of line tension vanishes) and are reported in Fig. 2d. The pinning force acting on the contact line and prevents its lateral motion, and increases to counter-balance the increasing deviation of the contact angle from Young's contact angle. Note that for cylindrical droplets a contact angle dependence of droplet size was observed, which was attributed to Tolman length of the curved liquid-vapor interface and a generalized line tension.³⁶ However, in this work the droplet curvature radius keeps unchanged at the given temperature and chemical potential, and such a size effect is not operative.

However, if one improperly ascribes the contact angle deviation from θ_Y to the contribution from the line tension and employ the modified Young equation (Eqn. 1), for which the pinning force is not included, to determine the line tension, we obtain a line tension that is several orders of magnitude larger (see Fig. 2e) than the actual value, $\tau/\gamma_v \sim -1$ (see Fig. 1e), assuming that the line tension does not change with respect to the flat surface case. Because Eqn. 1 leads to $\tau/r_p = (\cos\theta - \cos\theta_Y)\gamma_v = \text{const}$, namely, the obtained line tension increases linearly with the droplet size r_p . Therefore, the use of the modified Young's equation could lead to incorrect estimates of the line tension, and unreasonable large line tension would be obtained for large droplets (see detailed discussion in the supporting information). The results presented above show that we need to consider the effects of contact line pinning to explain the variations of contact angle.

We also investigated droplets pinned on the top of cylinders or cylindrical pores (Fig. 3b,c). As we discussed in our previous work on nanobubbles,^{37,38} both the larger and the smaller droplet-

s have the same radius of the curvature, which is equal to the radius of the critical nucleus in homogeneous nucleation. The larger droplet that corresponds to the critical nucleus for the vapor-to-liquid phase transition from the pinning state is thermodynamically unstable ³⁸ (Fig. 3b), while the smaller one is in the stable equilibrium state since it is stabilised by the pinning of the contact line ³⁷ (Fig. 3c). We show in Fig 3d that the cosine of the contact angle increases with the length of the three phase line, r_p , for unstable droplets, while it decreases with increasing r_p for the stable droplet, regardless of the fluid-solid interaction, and therefore regardless of the Young's contact angle. In general, as the contact line of a droplet is pinned by the substrate roughness, the contact angle of the droplet is independent on the Young's contact angle ³⁷ and it changes with the radius of the three phase contact line and the radius of the critical nucleus at the given thermodynamic condition, namely $\sin \theta = \frac{r_p}{R}$.

We used Eqn. 2 to calculate the pinning force (see Fig. 3e), by neglecting the line tension effects. This is expected to be a good approximation since for the nanodroplets we studied here $1/r_p < 0.2$ and the line tension effects decrease sharply with the increase of droplet size (for microdroplets in most experimental measures $1/r_p \ll 1$). If we included the line tension and assumed that the line tension does not change in going from the system in Fig. 1 and the cylindrical protrusion/cavity, the change obtained for pinning force are below 10 percent. As the radius of the cylindrical protrusion deviates from the radius corresponding to Young's contact angle, the pinning force increases gradually. This result shows that we need to include the effects of substrate inhomogeneity in the pinning force in order to interpret the deviations between the actual contact angle and Young's contact angle. Note that if we determine the line tension by employing the modified Young's equation (Eqn.1) and the contact angles in Fig.3, we would obtain line tensions that are much larger, by one order of magnitude, than the line tension calculated using the flat substrates (see Fig. 3f). Therefore, we conclude that pinning effects may introduce deviations in the line tension estimates, when the latter relies on the measurement/calculation of contact angles. This observation could help to interpret deviations between experimental data, as well as between experiments and theory.

Pinning effect controls contact angle behaviors

We have shown that the line tension and pinning effects influence the contact angles of droplets. We found that when the line tension effects vanish for large droplet sizes ($r_p \gg \sigma$), the pinning force dominates the variation of contact angle with droplet size. Here, based on our findings, we discuss the behavior of the contact angle (advancing and receding contact angles and hysteresis) in terms of the pinning force, as well as determining the required force for sliding a droplet.

As shown in Eqn. 2, sessile droplets can feature metastable states when the pinning force is present. These states result in different contact angles. Thus, our results support that contact angle behaviors is a function of the pinning effect that need to be overcome for contact lines to move from one metastable state to another. For the metastable states, the use of Eqn.1, which assumes one thermodynamic contact angle θ_Y , leads to an incorrect conclusion, namely, interfacial free energies alone determine wettability. Instead, the pinning effect should be taken into account, and it is $\frac{dG}{dr_p} = -f_p$ but not $\frac{dG}{dr_p} = 0$. Hence, droplets always have a range of contact angles, due to the pinning effect that leads to strong metastabilities, ranging from the advancing contact angle, θ_A to the receding contact angle, θ_R , i.e. the maximal and minimal values of the contact angles obtained. In such a case, the required pinning force that drives the drop to deviate from θ_Y can be determined from Eqn. 2 as

$$\tilde{f}_p = (\cos\theta_Y - \cos\theta)\gamma_v - \tau/r_p. \quad (3)$$

For large droplets, the contribution of the line tension, τ/r_p , can be neglected safely since the line tension should be a constant value that is related to an intrinsic material property (just as the surface tension, *i.e.*, the ratio of surface energy per unit area, is not a function of the area, for large droplets with a $r_p > 100$ nm and beyond.). Thus, for droplets on heterogeneous substrates where the pinning force acts, the required pinning forces $\tilde{f}_p^A$ and $\tilde{f}_p^R$, which correspond to the contact angle of θ_A and θ_R , respectively, can be determined from $\tilde{f}_p^A = (\cos\theta_Y - \cos\theta_A)\gamma_v$ and $\tilde{f}_p^R = (\cos\theta_Y - \cos\theta_R)\gamma_v$.³⁹

The determination of the forces associated to the sliding of a drop on a surface, using the line energy or the force approach, provide results that are conceptually contradictory.³⁹ The energy

argument dictates that the external force for sliding the droplet should be a constant value and therefore independent of the droplet size. The force argument indicates that the sliding force should be proportional to the drop size, $f_{ext} \propto r_p$.

The force approach takes into account the pinning effect, as indicated in Eqn. 3. Hence in order to slide a droplet an external force should be applied to counterbalance the total pinning force, $f_{ext}/l = \tilde{f}_p^A - \tilde{f}_p^R = (\cos\theta_R - \cos\theta_A)\gamma_v$, where we assumed that $l = l_A = l_R$, where l_A and l_R represent the effective lengths for the advancing and receding lengths. This equation agrees with the force per unit length associated to keeping a drop fixed on a tilted surface. This equation was developed by Furmidge⁴⁰ and Dussan,⁴¹ $f_{||}/w = \gamma_v(\cos\theta_R - \cos\theta_A)$, where $f_{||}$ is the lateral force which is needed to slide along the surface, and w is the width of the droplet.

We discuss now the reliability of the energy approach. We consider,

$$\tau/r_p = (\cos\theta_Y - \cos\theta)\gamma_v, \quad (4)$$

which follows from From Eqn. 1 upon minimization. The external force for sliding the droplet is $f_{ext}/l = (\cos\theta_R - \cos\theta_A)\gamma_v = (\tau_A - \tau_R)/l$. Hence, the lateral force for sliding the droplet $f_{ext} = \tau_A - \tau_R$ should be a constant irrespective of drop size,³⁹ as the line energy per unit length (line tension) should not be a function of the length. Here τ_A and τ_R represent the line tension for the maximal advancing and minimal receding contact angles that is determined from Eqn. 4. The main flaw of the energy approach lies in the breakdown of Eqn. 4 (or Eqn. 1) as the pinning effect takes place. From Eqn. 2, the line tension can be determined with $\tau/r_p = (\cos\theta_Y - \cos\theta)\gamma_v - \tilde{f}_p$. On the one hand, this equation should be used with care: except for very small droplets (nanodroplets), the line tension should not be a function of the length.⁴² On the other hand, this equation also indicates that, Eqn.4 holds only for droplets on flat and homogeneous substrates, on which the variation of contact angle shows a linear behavior in $1/r_p$.³¹ However, for droplets on substrates having either chemical or physical inhomogeneity, Eqn. 1 leads to an incorrect estimate of the line tension. For the same reason, f_{ext} in the energy approach gives a incorrect estimate of the required force, as the

same approximate equation (Eqn. 4) is used for obtaining $f_{ext} = \tau_A - \tau_R = \text{const.}$

Conclusions

In summary, we showed that the contact line pinning caused by the surface inhomogeneities induces the appearance of many apparent contact angles corresponding to local minima in the free energy, which influence the dependence of the contact angle with droplet size. For sessile droplets adsorbed on inhomogeneous substrates the estimates of line tensions and sliding forces using the approaches based on interfacial free energies, only, will give incorrect results. By explicitly introducing the contribution of the pinning effect into the Gibbs free energy equation, we derived a modified version of the Young's equation, which makes it possible to isolate the line tension and the pinning force effects arising from the adsorption of droplets on heterogeneous substrates. These results indicate that the calculation of the line tension measurements using the corrected Young's equation, should be exercised with care. The pinning effect can potentially lead to a large overestimation of the line tension if standard equations are employed.

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Figure 1: The procedure for determining the line tension of droplets on homogeneous substrates. (a) The volume contribution of the grand free energy $\Omega = V_l \omega_l$ or $V_v \omega_v$. (b) using $\Omega = V_l \omega_l + A_{ls} \gamma_{ls}$ or $V_v \omega_v + A_{vs} \gamma_{vs}$ to calculate the liquid/solid and vapor/solid surface tension by deducing the volume contribution. (c) using $\Delta\Omega = V_l \omega_l + V_v \omega_v + A_{lv} \gamma_{lv}$ to calculate the vapor/liquid surface tension by subtracting the volume contribution. (d) using $\Delta\Omega = V_l \omega_l + V_v \omega_v + A_{lv} \gamma_{lv} + \tau L$ to calculate the line tension by subtracting the volume and interface contributions. (e) The obtained line tension dependence on the fluid-solid interaction, ϵ_{sf} , which represents the substrate hydrophobicity. $\epsilon_{sf} = 0.3, 0.4, 0.5$, and 0.55 correspond, respectively, to the Young's contact angle of 138° , 113° , 92° , and 82° .

Figure 2: (a) The substrate coated with cuboid shaped protrusion for pinning cylindrical cap-shaped droplets. The radius R of the droplet is the critical nucleus of the bulk liquid phase at a given chemical potential of $\mu=-2.98$, and r_p is the pinning radius of the cylindrical cap. (b) The snapshot of the cylindrical cap-shaped droplet on a cuboid shaped protrusion. (c) The contact angle of the droplet changed with the radius of the substrate protrusion. (d) The obtained pinning force from Eqn. 2. (e) Using the modified Young's equation (Eqn. 1) results in unreasonable large line tensions even though the line tension did not exist under the given condition.

Figure 3: (a) The substrate with a cylindrical protrusion for pinning spherical cap-shaped droplets. The radius R of the droplet is the critical nucleus at the given chemical potential μ , and r_p is the pinning radius of the cylindrical pattern. (b, c) Snapshots for the droplet in (b) unstable equilibrium state and in (c) the stable equilibrium state. (d) The cosine of the contact angle as a function of $1/r_p$. (e) The variation of τ/γ_v as a function of $1/r_p$, in which $\tilde{f}_p/\gamma_v$ was obtained from Eqn. 2 by deducting the influence of the line tension. (f) Through the modified Young's equation (Eqn. 1), we derived a much larger τ/γ_v as a function of $1/r_p$.

Graphical TOC Entry

