Curvature Capillary Migration of Microspheres

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We address the question: How does capillarity propel microspheres along curvature gradients? For a particle on a fluid interface, there are two conditions that can apply at the three phase contact line: Either the contact line adopts an equilibrium contact angle, or it can be pinned by kinetic trapping, e.g. at chemical heterogeneities, asperities or other pinning sites on the particle surface. We formulate the curvature capillary energy for both scenarios. For particles with equilibrium contact angles, we find that the capillary energy is negligible, with the first contribution bounded to fourth order in the deviatoric curvature. For pinned contact lines, we find curvature capillary energies that are finite, with a functional form investigated previously by us for disks and microcylinders on curved interfaces. In experiments, we show microsphere migration along deterministic trajectories toward regions of maximum deviatoric curvature with curvature capillary energies ranging from $6 \times 10^3$ to $5 \times 10^6 \, k_B T$. These data agree with the curvature capillary energy for the case of pinned contact lines. The underlying physics of this migration is a coupling of the interface deviatoric curvature with the quadrupolar mode of nanometric disturbances in the interface owing to the particle's contact line undulations. This work is an example of the major implications of nanometric roughness and contact line pinning for colloidal dynamics.

I. INTRODUCTION

Capillary interactions are ubiquitous between particles on fluid interfaces. They trap particles at the interface [1] and determine their ensuing organization [2–4], allowing particles to be widely exploited in technological applications such as stabilization of foams and emulsions [5], and in settings as diverse as the food [6], pharmaceutical [7], mineral recovery [8], and petroleum industries [9]. For microparticles of radius $a$ at planar interfaces of tension $\gamma$, gravity is irrelevant, as the Bond number $Bo = \frac{\Delta \rho g a^2}{\gamma} \ll 1$, where $g$ is the gravitational acceleration constant, and $\Delta \rho$ is the density difference between the subphase fluids. In this limit, particles with undulated contact lines distort the interface around them; the resulting deformation fields depend on the relative position of the particles, yielding decreasing capillary energy as particles approach [10].

In this research we are interested in the behavior of isolated microparticles trapped on curved interfaces. In experiment, microparticles migrate along curvature gradients to sites of high curvature, as has now been observed for microcylinders [2], microspheres [11] and microdisks [12]. Theoretically, the curvature capillary energy driving this migration is simply the sum of the surface energies and pressure work for particles at the interface. When particles attach to their host interfaces, they change the interface shape owing to the boundary condition at the contact line where the interface meets the particle. There are two limits for this boundary condition. The interface can intersect the particle with an equilibrium contact angle $\theta_0$, determined by the balance of surface energies according to Young’s equation [13]. Alternatively, the contact line can be pinned by kinetic trapping at heterogeneities, roughness or other pinning sites on the particle surface [10] [14] [18]. In principle, the disturbance created by the particle in the interface and the related energy can depend on the local curvature field. Analysis for microspheres with equilibrium contact angles suggests that the curvature capillary energy is a quadratic function of the local curvature field [11] [19–21]. However, for particles with undulated, pinned contact lines, this dependency is linear [2] [12] [22]. In this report, we study the capillary migration of spheres on curved interfaces. We present an expression for curvature capillary energy for disks with pinned contact lines derived previously by our group which applies to spheres with pinned contact lines in the limit of weak undulations [12]. We recapitulate the derivation of the curvature capillary energy for spheres with equilibrium contact angles derived previously in the literature [19] [20]. We find, however, that the quadratic term for the capillary curvature energy has prefactor zero. We identify the source of the discrepancy between our result and that published previously. We predict that spheres migrate by capillarity on curved interfaces if their contact lines are pinned, and that spheres with equilibrium contact lines would migrate with energies several orders of magnitude weaker than is observed in experiment.

We perform experiments in which we record the trajectories of polystyrene microspheres at hexadecane-water interfaces with well defined curvature fields. We compare the energy dissipated by particle migration to the curvature capillary energy expressions, and find that the spheres migrate in agreement with the expression for pinned contact lines.

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\[ E_1 = \gamma \iint_D (1 + \frac{\nabla h_0 \cdot \nabla h_0}{2}) dA, \]

where \( h_0 \) is the Monge representation of the host interface height prior to particle deposition, \( D \) denotes the entire interfacial domain, and \( dA = dxdy \). In writing the above expression we have already utilized the small gradient approximation, i.e. \( |\nabla h_0| \ll 1 \). Upon attaching to the host interface, the particle creates a disturbance to satisfy its boundary condition on the three phase contact line. The free energy of the system in this case is,

\[ E_2 = \gamma_1 A_1 + \gamma_2 A_2 + \gamma \iint_{D-P} (1 + \frac{\nabla h \cdot \nabla h}{2}) dA, \]

where \( h \) is the interface height after the particle is adsorbed, \( \gamma_1 A_1 \) and \( \gamma_2 A_2 \) are the product of the surface energies and wetted areas for the solid in contact with the upper and lower fluids, respectively and \( P \) denotes the domain under the particle. The capillary energy associated with adsorption of a particle to an interface can be found simply via subtraction of the two energies,

\[ E = E_2 - E_1 = \gamma_1 A_1 + \gamma_2 A_2 + \gamma \iint_{D-P} (\frac{\nabla h \cdot \nabla h}{2} + \nabla h_0 \cdot \nabla h_0) dA - \iint_P (1 + \frac{\nabla h_0 \cdot \nabla h_0}{2}) dA, \]

FIG. 1. Schematic representation of a sphere trapped at a curved interface and its mapping to a tangent plane.

II. THEORY

Here we give a concise derivation of the capillary energy of a sphere trapped on a curved fluid interface. Without loss of generality, we focus on interfaces with zero mean curvature as the role of finite mean curvature gradient has been addressed in the literature [12, 20].

We first consider the free energy of the interface prior to the particle attachment which can be written as,

\[ E = \frac{1}{2} \int_0^2 \left( \nabla h_0 \cdot \nabla h_0 \right) dA = \frac{1}{2} \int_{\partial(D-P)} [\nabla h_0 \cdot \nabla h_0] dA, \]

\[ \partial(D-P) \]

\[ \int \left( \frac{1}{2} \nabla h_0 \cdot \nabla h_0 \right) dA, \]

\[ \frac{1}{2} \nabla h_0 \cdot \nabla h_0 \]

FIG. 2. Schematic representation of (a) a pinned undulated contact line and (b) an equilibrium wetting boundary condition with a contact angel \( \theta_c \).

where \( \eta \) is the disturbance field defined as \( \eta = h - h_0 \). In the above expression, the first term in the bracket is due to the disturbance created by the particle owing to the boundary condition at the three phase contact line and the second term is the area of the hole under the particle. We integrate the first integral by parts and then apply the divergence theorem to have,

\[ \iint_{D-P} [\nabla h_0 \cdot \nabla h_0] dA = \iint_{\partial(D-P)} \left[ \frac{1}{2} \nabla h_0 \cdot \nabla h_0 \right] dA, \]

\[ \nabla h_0 \cdot \nabla h_0 \]

\[ \frac{1}{2} \nabla h_0 \cdot \nabla h_0 \]

where \( \partial(D-P) \) denotes the contours enclosing the domain \( D - P \). There are two contours enclosing this domain: one, not shown, infinitely far from the particle, with outward pointing vector in the radial direction, and the other enclosing the region \( P \) with outward-pointing unit normal vector \( \mathbf{m} \) (see Fig. 1). Consequently the curvature capillary energy of the system can be expressed as,

\[ E = E_2 - E_1 = \gamma_1 A_1 + \gamma_2 A_2 + \gamma \iint_{D-P} [\nabla h_0 \cdot \nabla h_0] dA - \iint_P (1 + \frac{\nabla h_0 \cdot \nabla h_0}{2}) dA, \]

\[ \frac{1}{2} \nabla h_0 \cdot \nabla h_0 \]

\[ \frac{1}{2} \nabla h_0 \cdot \nabla h_0 \]

where \( (x, y) \) coordinate is tangent to the host interface, oriented along the principle curvatures \( c_1 \) and \( c_2 \), and \( \Delta c_0 \) is the deviatoric curvature of the host interface defined as,

\[ \Delta c_0 = c_1 - c_2, \]

we adopt a convention such that \( c_1 \) is always positive. To evaluate the integrals in Eq. (5), we must define the boundary condition at the three phase contact line, determine the associated disturbance field \( \eta \), and evaluate the corresponding curvature capillary energy. We discuss two distinct scenarios for this energy (see Fig. 2).
A. Pinned contact line

The curvature capillary energy \( E \), for a particle with nearly circular cross section and a pinned contact line trapped on a host interface with arbitrary mean curvature \( H_0 \) and deviatoric curvature \( \Delta c_0 \) was derived previously [12]. The height of the pinned contact line contour can be decomposed into a multipole expansion with quadrupolar mode of amplitude \( h_p \). The associated curvature capillary energy is,

\[
E = E_0 - \gamma \pi a^2 \left( \frac{h_p \Delta c_0}{2} + \frac{3a^2 H_0^2}{4} \right),
\]

the first term \( E_0 \) is independent of the local curvature. The second term predicts that a particle will move to sites of high deviatoric curvature, while the third predicts particle migration along gradients of mean curvature. To understand the relevant importance of these terms, we consider \( \frac{\partial^2 h^2}{H_0^2 \Delta c_0} \sim \frac{a}{r_0} \frac{a \Delta p}{\Delta c_0} \) where \( \Delta p \) is the pressure jump across the interface (see Appendix. B for non-dimensionalization scheme). This ratio suggests that, for sufficiently small pressure jump across the interface, the effect of mean curvature can be neglected. Below, we explore this regime in experiment.

B. Equilibrium wetting

For a spherical particle with an equilibrium wetting condition, the fluid interface deforms until it satisfies the equilibrium contact angle at every point on the contact line. The contact line shape is not known \textit{a priori} and must be determined as a part of analysis, as was originally done by Wirger [19]. Here we use an asymptotic approach to find the location of this contour and to bound our evaluation of the curvature capillary energy in terms of the small parameter in this problem \( \lambda = a \Delta c_0 \). The details for the derivation of the contact line is given in Appendix A. The shape of contact line can be deduced from geometrical relationships (see Fig. 3) to be,

\[
\cos \theta = \cos \theta_0 + \frac{h(r \in \rho)}{a}, \quad (9)
\]

\[
\sin \theta = \frac{\rho}{a}, \quad (10)
\]

In this expression, \( \rho(\phi) \) is the contour of the contact line projected into a plane, which obeys,

\[
\rho = a \sqrt{1 - \cos^2 \theta}, \quad (11)
\]

By substituting Eq. [9] and [10] in this expression and assuming \( h(r \in \rho) \sim O(\lambda) \ll 1 \), the radial location of contact line projected into the \( x - y \) plane is,

\[
\rho = r_0 - h(r) \cot \theta_0 - \frac{1}{2} \frac{h^2(r)}{r_0^2} (\cot^2 \theta_0 + 1) + \ldots |_{r \in \rho}, \quad (12)
\]

The curvature capillary energy at a particle with an equilibrium wetting angle \( \theta_0 \) accounts for the deformation due to the particle. \( \theta \) is the polar angle of the deformed contact line, and \( \rho \) is its radial position. (b) Schematic view of the contact lines in \( x - y \) plane in flat (in blue) and curved interfaces (in red).

The height of interface must satisfy the Young-Laplace equation which at small slopes reduces to the Laplacian:

\[
\nabla^2 h = 0. \quad (17)
\]

Using Eq. [16] and requiring the interface to tend to the host surface far from the particle,

\[
\lim_{r \to \infty} h(r, \phi) = h_0, \quad (18)
\]

the leading order interface shape is,

\[
h(r, \phi) = \frac{\Delta c_0 \cos 2\phi}{4} \left( r^2 + \frac{r_0^4}{3r^2} \right), \quad (19)
\]

with first correction as given in Appendix A, which we will use to bound the leading order contribution to the curvature capillary energy. The corresponding disturbance to the interface is,

\[
\eta = h - h_0 = \frac{\Delta c_0 \cos 2\phi r_0^4}{12} r^2. \quad (20)
\]
With this information, we determine the curvature capillary energy Eq. [5]. To do so, we evaluate:

(i) the self-energy of the disturbance created in the host interface, the sum of the following two contour integrals:

\[
\oint \rho \frac{\Delta c^2 \cos^2 2\phi}{144} d\phi = \frac{\pi \Delta c^2 \rho^4}{144} \quad (21)
\]

\[
\oint \rho \frac{\eta \nabla \eta \cdot m ds = 0}{r \to \infty} \quad (22)
\]

(ii) the interaction of the disturbance and the host interface, given by the sum of the following two contour integrals:

\[
\oint \rho \frac{\eta \nabla h_0 \cdot m ds = r_0^4 \theta_2^2}{2} \oint \theta_2^2 d\phi = \frac{-\pi \Delta c^2 \rho^4}{24}, \quad (23)
\]

\[
\oint \rho \frac{\eta \nabla h_0 \cdot m ds = r_0^4 \theta_2^2}{2} \oint \theta_2^2 d\phi = \frac{\pi \Delta c^2 \rho^4}{24}, \quad (24)
\]

These terms are equal and opposite, and hence sum to zero. Thus, the net contribution of the particle induced disturbance is,

\[
\oint \rho \frac{\eta \nabla \eta + \eta \nabla h_0 \cdot m ds = \frac{\pi \Delta c^2 \rho^4}{144}}{d (D-P)} \quad (25)
\]

(iii) Finally, we calculate the energy decrease owing to the area of the hole under the particle as,

\[
\oint \rho \frac{\theta_2^2}{2} \oint \theta_2^2 dS = -\pi \rho^4 - \frac{\pi \Delta c^2 \rho^4}{144} \quad (26)
\]

The second term in the above expression is equal and opposite to the term in Eq. [25]. Summing these contributions, the net curvature capillary energy to order \( \lambda^2 \) is identically zero, i.e.,

\[
\frac{E}{\gamma \pi r_0^2} = (\gamma_1 + \gamma_2) - 1 + O(\lambda^4), \quad (27)
\]

where the first constant term in the above is the non-dimensional trapping energy governed by Pieranski[1].

The above expression is exact up to the \( \lambda^4 \) term; the determination of this bound is described in Appendix A. The absence of any coupling to deviatoric curvature differs significantly from prior theory in the literature for this problem. The origin of the discrepancy is an inappropriate treatment of the contour integral given in Eq. [24] which was assumed to be zero in prior work.

III. EXPERIMENTS

We study migrations of polystyrene colloidal spheres (Polysciences, Inc.) with mean diameter of 2a = 10 \( \mu \)m.

Fig. 4(b) illustrates an SEM image of a microsphere revealing qualitatively the surface roughness of the particle. AFM measurement (Bruker Icon) indicates that the root mean squared roughness of the particles is \( \sim 15 - 21 \) nm (see Fig. 4(c)).

We impose a curvature field to the host interface using a technique reported previously [2] which we recapitulate briefly. A curved oil-water interface is formed around a micropost which is either circular or square in cross section (see the schematic in Fig. 4(a)). The interface pins to the edge of the post, and has a height \( H_m \) at the post’s edge. The post is centered within a confining ring located several capillary lengths away \( r_{ring} \) = 5.5, where \( r_{ring} \) is the radius of the outer ring. By adjusting the volume of water, the slope of the interface at the post’s edge is adjusted to be \( \psi \sim 15 - 18^\circ \). This system is gently covered in hexadecane in order to prevent evaporation and to protect the interface from stray convection. The interface height in a region sufficiently close to the circular post is well approximated by \( h_0 = H_m - R_m \tan \psi \ln(\frac{L}{r_{ring}}) \), where \( L \) is the distance to the center of the post. This interface has zero mean curvature \( H_0 = (c_1 + c_2)/2 = 0 \), and finite deviatoric curvature \( \Delta c_0 = c_1 - c_2 \) varying with the radial position.

Owing to the finite volume of fluid, there is a weak but negligible pressure drop across the interface as we confirm in numerical simulations described in Appendix B.

A dilute suspension of microspheres in hexadecane is prepared. A drop of this suspension is carefully dropped on top of the oil phase. The particles then gently sediment under gravity. Once attached to the interface, they migrate uphill in a deterministic path along deviatoric
curvature gradients. We only focus on isolated particles far from neighbors (distances greater than 10-15 radii) and the micropost ($L > R_m + 10a$) to rule out the pair capillary and hydrodynamic interactions 23. The capillary energy was estimated by evaluating the total dissipation according to the appropriate drag formula (Stokes’ law) along particle trajectories.

IV. RESULTS AND DISCUSSIONS

In Fig. 5(a), we illustrate the time stamped images of trajectories for migrating spheres for constant time increment ($\Delta t = 1$ s). These images reveal that the spheres are propelled faster in the region closer to the post where the magnitude of deviatoric curvature is greater. Note that the size of the spheres are so small that the inertial effects can be neglected ($Re \sim 10^{-3}$) within the entire trajectory. These trajectories are nearly radial, as the corresponding curvature field around the cylindrical post has no dependency on the azimuthal angle $\phi$. Fig. 5(b) shows the radial distance of the four microspheres from the center of the post, $L$, as a function of time remaining until contact, $t - t_c$, where $t_c$ is the time in which the sphere reached the edge of the post. Qualitatively, these trajectories are remarkably similar to those reported previously for microdisks with pinned contact lines migrating in curvature fields. To investigate this quantitatively, we compare energy dissipated along the particle trajectory to theory.

To do so, we note that, in the limit of zero inertia, and neglecting potential energy differences, the curvature capillary energy expended to drive the particles is balanced by viscous dissipation. The total energy dissipated along the trajectories can be extracted from the trajectories according to $\Delta E = \int_{L_0}^L F_{\text{drag}} dL'$ where $L_0$ is the reference point and $L$ is an arbitrary point along the trajectory. We used the Stokes’ drag formula for a sphere equally immersed in the subphase fluids, $F_{\text{drag}} = 6\pi \mu U a$, where $\mu$ is the average viscosity of oil and water evaluated at the temperature of the environment. The curvature capillary energy found over the trajectories beginning at $a\Delta c_0 = 6 \times 10^{-3}$ and ending ten particle radii from the micropost was plotted against $a\Delta c_0$ as open symbols in Fig. 6; this range of $a\Delta c_0$ was selected because all trajectories captured in experiment spanned this region. The relationship is linear and the total energy difference along a typical trajectory is thousands of times greater than thermal unit energy $k_B T$. The curvature capillary energy is presented normalized by $\gamma \pi a^2 = 8.8 \times 10^8 k_B T$; the energy for the segment of the particle paths shown in Fig. 6; this is in the range of $6,000 - 50,000 k_B T$. This magnitude indicates that the equilibrium wetting boundary condition cannot be responsible for the migration of the spheres in our experiment, as according to Eq. 27 for a typical microsphere $a = 5 \mu m$ with equilibrium contact angle of $\theta = 90^\circ$, the curvature capillary energy is of magnitude $\Delta E \sim \gamma \pi a^2 \sin \theta a \lambda^2 \sim 10k_B T$. Moreover the relationship between $\Delta E$ and $\gamma_0 \Delta c_0$ would be highly non-linear. Hence, we conclude that the equilibrium contact angle boundary condition does not apply to our microspheres. Rather, the microspheres migrate with pinned contact lines.

We propose that this curvature migration is an assay for nanometric corrugations of the contact line in a trapped state. The magnitude of the quadrupolar mode $h_p$ for the contact line undulations can be inferred from the trajectories in Fig. 5. While 7 of 10 of the reported trajectories have $h_p$ similar in scale to the particle roughness (between $20-40 nm$), magnitudes for the remaining
FIG. 7. (a) Time-stamped trajectories of microspheres around a square post illustrating that the microspheres follow complex trajectories as defined by the deviatoric curvature field (the scale bar is 100 µm). Numerically evaluated curvature gradient around (b) a square post and (c) a corner of the square post. The arrows scaled with the magnitude of deviatoric curvature gradient.

trajectories were larger, with \( h_p \) as high as 130 nm for one trajectory. These results indicate that similar particles have differing pinning states at the interface, with significant consequences for their ensuing dynamics. The role of gravity for particles on curved interfaces has been addressed previously [11, 12]. Because the Bond number is negligible, particle weight plays no role in the deformation of the interface, and the analyses above are valid. For weak enough curvature gradients, however, particles cannot overcome potential energy barriers and thus can attain an equilibrium height.

This form for the curvature capillary energy has been invoked previously to study curvature capillary migration of cylindrical microparticles which followed complex trajectories on interfaces around square microposts with associated complex curvature fields [2]. If the spheres indeed have identical physics, they, too, should migrate along complex contours in such a curvature field. We have studied trajectories of spheres in this setting (see Fig.7(a), in which isolated particles migrate to corners, as does a pair of dimerized particles at the lower right hand corner). To compare particle trajectories to local curvatures, the curvature field around the square micropost was determined using a Galerkin finite element method, as discussed in Appendix. Vectors indicating the magnitude and direction of gradients in deviatoric curvature are indicated in Fig. 7(b) and (c). The spheres migrate from their initial point of attachment along paths defined indeed by these vectors. The ability of the sphere to trace this complex trajectory confirms the underlying physics of microparticles with pinned contact lines is similar regardless of details of the particle shape, and is consistent with the concept that the particle quadrupolar mode couples to the underlying saddle shaped surface.

V. CONCLUSION

We study microparticle migration owing to curvature capillary energy in theory and experiment. We show that for equilibrium contact angles, the curvature capillary energy is very weak, with leading order contributions of fourth order in deviatoric curvature or higher, in contradiction to the accepted form in the literature. This leading order contribution would amount to roughly \( 10 k_B T \) in our experiments. In experiment, microspheres migrate along deterministic trajectories defined by curvature gradients. We find that the corresponding capillary curvature energy propelling the particles ranges from \( 6,000 - 50,000 k_B T \). We compare these observations to arguments derived previously for particles with pinned contact lines, in which the quadrupolar mode of the particle contact line undulation couples with the curvature field to yield an energy linear in the deviatoric curvature. The data indeed obey this form, allowing the magnitude of the particle induced quadrupole to be inferred. In many cases, it is comparable to particle roughness as determined by AFM. However, significantly larger magnitudes are also found, suggesting that similar particles can have different pinned states at the interface. These results imply that contact line pinning occurs for microparticles at these curved fluid interfaces with dramatic implications in their dynamics at interfaces.

VI. APPENDIX A

In this section, we provide a detailed derivation for the interface shape when a particle of radius \( a \) which attains an equilibrium contact angle is placed on a host interface which is a symmetric saddle with zero mean curvature. We pose a perturbation analysis with small parameter \( \lambda = a \Delta \sigma_0 \ll 1 \), where \( \Delta \sigma_0 \) is the deviatoric curvature of the host interface. We expand the non-dimensional height of the interface as a power series to yield,

\[
h^* = \frac{h}{r_0} = h^0 + h^1 \lambda + h^2 \lambda^2 + O(\lambda^3),
\]
where we adopt as a characteristic length \( r_0 = a \sin \theta_0 \) and \( \theta_0 \) is the equilibrium contact angle. Far from the particle, the interface height approaches to shape of the host interface. Since the host interface has zero mean curvature, the leading order term is identically zero, i.e. \( h^0 = 0 \). We non-dimensionalize the radial polar coordinate from the center of the particle,

\[
r^* = \frac{r}{r_0} \tag{29}
\]

The equilibrium wetting boundary condition is dictated by Young’s equation,

\[
n_P \cdot n_I = \cos \theta_0 |_{r \in \rho}, \tag{30}
\]

where \( n_P \) is the unit normal to the particle and \( n_I \) is the unit normal to the interface which can be determined as,

\[
n_P = e_R = \sin \theta e_r + \cos \theta e_z \tag{31}
\]

\[
n_I = \frac{e_z - \nabla_s h}{\sqrt{1 + (\nabla_s h)^2}} \tag{32}
\]

where \((R, \phi, \theta)\) and \((r, \phi, z)\) are spherical and cylindrical coordinates located at the particle center of mass, respectively. The operator \( \nabla_s \) is the surface gradient defined as,

\[
\nabla_s = (I - e_z e_z) \cdot \nabla,
\]

and \( I \) is the unit tensor. By replacing Eq. 9 and 10 in Eq. 31 and 32, Eq. 30 reduces to,

\[
n_P \cdot n_I |_{r \in \rho} = \frac{\cos \theta_0 + \frac{h(r)}{r_0} - \frac{\rho}{r} e_r \cdot \nabla_s h(r)}{\sqrt{1 + (\nabla_s h)^2}} |_{r \in \rho},
\]

\[
= \frac{\cos \theta_0 + \sin \theta_0 \left[ \frac{h(r)}{r_0} - \frac{\rho}{r} e_r \cdot \nabla_s h(r) \right]}{\sqrt{1 + (\nabla_s h)^2}} |_{r \in \rho},
\]

\[
= \cos \theta_0 \left[ 1 - \frac{1}{2} \left( \frac{\partial h(r)}{\partial r} \right)^2 + \left( \frac{\partial h(r)}{\partial \phi} \right)^2 \right] |_{r \in \rho},
\]

\[
+ \sin \theta_0 \frac{h(r)}{r_0} \left( 1 - \cot \theta_0 \frac{\partial h(r)}{r_0} \right) \frac{\partial h(r)}{\partial r} |_{r \in \rho}, \tag{34}
\]

where we have utilized the small gradient approximation \(|\nabla_s h(r \in \rho)| \ll 1\). Finally, the boundary condition (in dimensional form) at particle contact line can be written as,

\[
\frac{1}{2} \left( \frac{\partial h}{\partial r} \right)^2 + \left( \frac{\partial h}{\partial \phi} \right)^2 = \sin \theta_0 \frac{h}{r_0} \left( 1 - \cot \theta_0 \frac{h}{r_0} \right) \frac{\partial h}{\partial r}, \tag{35}
\]

By recasting this expression in dimensionless form and substituting it in Eq. 28, we can collect terms of similar power in \( \lambda \). One can show,

\[
\frac{\partial h^1}{\partial r^*} = h^1 |_{r^* = 1}, \tag{36}
\]

\[
h^2 - \frac{\partial h^2}{\partial r^*} |_{r^* = 1} = \frac{1}{6} - \frac{5}{18} \cos 4\phi, \tag{37}
\]

Given this boundary condition the particle-induced disturbance and associated energy field can be determined. The disturbance created by the particle obeys Eq. 36 and 37 as well as the Laplacian,

\[
\nabla^2 h^* = 0, \tag{38}
\]

To apply the boundary condition, we introduce a vertical shift factor \( \omega_0 = \frac{h^0}{r_0} \) to the particle center of mass and therefore we have,

\[
h^1 = \frac{\cos 2\phi}{4} (r^*^2 + \frac{1}{3r^*^2}) \tag{39}
\]

\[
h^2 = -\frac{\cos 4\phi}{18r^*^4} \tag{40}
\]

This is the solution to the shape of the interface up to \( \lambda^2 \). Owing to the orthogonality of \( \cos n\theta \), there is no coupling between \( h^1 \) and \( h^2 \) and therefore there would not be a term in energy expression in Eq. 5 of order \( \lambda^3 \). In the text, we evaluate the \( \lambda^2 \) term and find its prefactor to be identically zero. Hence, the leading order contribution to the curvature capillary energy for spherical particles with equilibrium contact lines is order \( \lambda^4 \).

### VII. APPENDIX B

In this section we discuss the numerical method used to calculate the height of interface around the square post. The height of interface in this case can be governed via the linearized Young-Laplace equation according to,

\[
\gamma \nabla^2 h = \Delta \rho gh + \Delta p, \tag{41}
\]

where \( \Delta \rho \) is the density difference of subphase fluids and \( \Delta p \) is the pressure jump across the interface. We scaled the variables as follows,

\[
\tilde{h} = \frac{h}{\Delta \rho g}, \quad \tilde{\nabla} = \left( \frac{\gamma}{\Delta \rho g} \right)^{\frac{1}{2}} \nabla. \tag{42}
\]

Eq. 41 can be rewritten as,

\[
\tilde{\nabla}^2 \tilde{h} - \tilde{h} = \pm 1, \tag{43}
\]

where \( \pm 1 \) on the right hand side stands for negative and positive pressure jumps across the interface. To obtain the discretized form of Eq. 43 in the weak form to implement the finite element algorithm for solution, we first multiply both sides of the Eq. 43 by a weighting function \( \varphi_i \) and then integrate over the area of element,

\[
\iint \varphi_i \tilde{\nabla}^2 \tilde{h} dA - \iint \tilde{\nabla} \varphi_i \tilde{h} dA = \pm \iint \varphi_i dA. \tag{44}
\]

Having utilized integration by parts and the divergence theorem, one can show,

\[
\iint \tilde{\nabla} \varphi_i \cdot \tilde{\nabla} \tilde{h} dA - \iint \tilde{\nabla} \varphi_i \cdot \tilde{h} dA - \iint \varphi_i \tilde{h} dA = \pm \iint \varphi_i dA, \tag{45}
\]
where \( \mathbf{m} \) is the unit normal vector of the enclosing contours which are pointing outward from the domain of interest. In the above expression, the first term only applies to the boundaries and therefore we neglect it since we have Dirichlet boundary conditions in our problem. Utilizing the Galerkin method \([24]\), the non-dimensionalized height \( \tilde{h} \) were approximated by a piecewise quadratic polynomial function where \( \varphi_i = 1 \) at vertex \( i \) and \( \varphi_i = 0 \) at all other vertices. Thus, the non-dimensional height can be approximated as \( \tilde{h} = \sum_{j=1}^{N} \varphi_j \tilde{h}_j \), where \( N \) is the total number of vertices in the mesh and \( \tilde{h}_j \) is the value of the height at the \( j \)th vertex. Since the problem is 2D, we generated a triangular structured mesh by discretizing the domain. This was done in such a way that more nodes were available in the transition region (sharp corner) to capture the rapid change in height. The pressure jump was not known \textit{a priori}; it is found from the slope condition at the middle of the square post. To do so, we solve the entire problem in an iterative manner. We guess a value for the pressure jump across the interface, solve the problem by applying the Dirichlet boundary conditions at the post and the outer ring, and subsequently calculate the slope at the middle of the square post. The slope is compared to the measured value in the experiment with \( \psi = 15^\circ \). The new pressure jump is estimated according to the following,

\[
\Delta p_{\text{new}} = -\frac{\tan \psi}{\frac{\partial \varphi}{\partial \gamma}}_{\text{midplane}} \sqrt{\gamma \Delta \rho g}, \tag{46}
\]

We follow this procedure until we reach the convergence and the difference between two consecutive iterations becomes less than 1\%. The pressure jump we found is \( \Delta p = -0.2170 \frac{N}{\text{m}^2} \). The solution was also tested against the number of triangular meshes to confirm that the final result is independent of number of meshes in the domain of interest. Furthermore, to evaluate the principle curvatures, we evaluated higher order partial derivatives in each individual mesh according to,

\[
h_{xx} = \sum_{i=1}^{3} h_i \frac{\partial^2 \varphi_i}{\partial x^2} \tag{47}
\]

Thereafter, we calculate the principle curvature according to appropriate relations. The resulting deviatoric and mean curvature fields are shown in Fig. 8 the deviatoric curvature diverges near the corners, spanning values ranging from 400 \( m^{-1} \) to 3000 \( m^{-1} \) whereas mean curvature varies from 3 \( m^{-1} \) to 5 \( m^{-1} \). It is therefore safe to ignore capillary energies owing to mean curvature gradients.

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\[\text{Fig. 8. Numerical solution of the curvature field via finite element analysis around a square post. (a) Deviatoric curvature and (b) mean curvature. The magnitudes of the deviatoric and mean curvatures are in m}^{-1}.\]
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