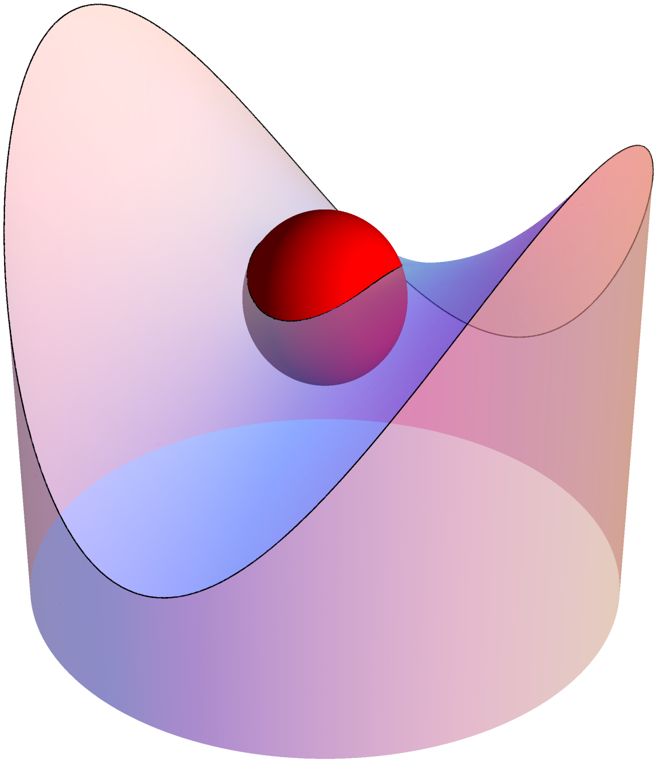
Spherical colloidal particle floating at a fluid interface shaped as a uniform saddle, with equilibrium wetting conditions at the Young angle.



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Comment on "Curvature Capillary Migration of Microspheres" by Nima Sharifi-Mood, Iris B. Liu and Kathleen J. Stebe, Soft Matter, 2015, 11, 6768

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In a recent paper, Nima Sharifi-Mood *et al.* analyze the capillary insertion energy of a spherical colloid at the interface between a liquid and a vapor phase with equilibrium wetting conditions. They claim that, contrary to what previously found, the insertion energy would be zero up to corrections of order four in the deviatoric curvature of the interface. I show that this conclusion is incorrect and comes from the failure of the small angle approximation far from the colloid. Once this approximation is lifted, I recover the leading quadratic contribution first derived by Würger [A. Würger, *Phys. Rev. E*, 2006, **74**, 041402]. This same approximation was employed by Lu Yao *et al.* [Lu Yao *et al.*, *J. Colloid Interface Sci.*, 2014, **449**, 436] in the case of pinned contact lines. The resulting expression, that is used by Nima Sharifi-Mood *et al.* to analyze their experimental data, is off by a factor of two and misses a term quadratic in the deviatoric curvature.

In Ref.[1], the authors derive the capillary insertion energy of a colloidal particle at a liquid-vapor interface with equilibrium wetting conditions at the Young angle θ_0 (here and in the following, I shall use the notations of Ref.[1]). This problem had been first analyzed by Würger[2], who found that, at leading order, the insertion energy is proportional to the square of the deviatoric curvature Δc_0. This result was confirmed by analytic and *exact* numerical calculations of the force on a spherical colloid floating at a surface of *arbitrary shape*[3,4], and found in agreement with experimental data[3]. In Ref.[1] it is claimed that such a quadratic contribution to the insertion energy would be zero. I show here that this conclusion is incorrect and comes from the failure of the small angle approximation far from the colloid. Once this approximation is lifted, I recover the results of Refs.[2–4]. This same approximation was employed by Lu Yao *et al.*[5] for pinned contact lines. The resulting insertion energy, used in the analysis of the experimental data of Ref.[1], is off by a factor of two and misses a term quadratic in Δc_0.

All the calculations in Ref.[1] are performed within the small angle approximation $|\nabla h| \ll 1$. However, for $r \to \infty$, the slope ∇h linearly diverges[6] [see Eq. (19) of Ref.[1]]. It is therefore necessary, namely when considering contour integrals at infinity, to lift this approximation. In particular, Eq. (3) of Ref.[1] must be replaced by $E = \gamma_1 A_1 + \gamma_2 A_2 - \gamma_1 A_s + \gamma I$, with

$$I = \oiint_{D-P} \sqrt{1+(\nabla h)^2}\, dA - \oiint_{D} \sqrt{1+(\nabla h_0)^2}\, dA\,. \tag{1}$$

Using the development $\sqrt{1+x} = \sqrt{1+x_0} + (x-x_0)/\left(2\sqrt{1+x_0}\right) - (x-x_0)^2/\left[8\,(1+x_0)^{3/2}\right] + \mathscr{O}\,(x-x_0)^3$, with $x = (\nabla h)^2$ and $x_0 = (\nabla h_0)^2$, and setting $h = h_0 + \eta$, Eq. (1) becomes, to second order in $\nabla\eta$, for $|\nabla\eta| \ll 1$ but $|\nabla h_0|$ *arbitrary*, $I = I_0 + I_1 + I_2$, with

$$I_0 = -\oiint_{P} \sqrt{1+(\nabla h_0)^2}\, dA\,, \tag{2}$$

$$I_1 = \oiint_{D-P} \frac{\nabla h_0 \cdot \nabla\eta}{\sqrt{1+(\nabla h_0)^2}}\, dA\,, \tag{3}$$

$$I_2 = \frac{1}{2}\oiint_{D-P} \left[\frac{(\nabla\eta)^2}{\sqrt{1+(\nabla h_0)^2}} - \frac{(\nabla\eta\cdot\nabla h_0)^2}{\left[1+(\nabla h_0)^2\right]^{3/2}}\right] dA\,. \tag{4}$$

Moreover, note that the *exact* nonlinear equation satisfied by h_0, obtained by minimizing the second integral at the right-hand side of Eq. (1) with respect to arbitrary variations of h_0, is

$$\nabla \cdot \left[\frac{\nabla h_0}{\sqrt{1+(\nabla h_0)^2}}\right] = 0\,. \tag{5}$$

This same equation is also satisfied by h inside the domain $D-P$.

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At first order, for $|\boldsymbol{\nabla}\eta| \ll 1$ but $|\boldsymbol{\nabla}h_0|$ *arbitrary*, one then finds

$$\boldsymbol{\nabla}\cdot\left[\frac{\boldsymbol{\nabla}\eta}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}-\frac{(\boldsymbol{\nabla}\eta\cdot\boldsymbol{\nabla}h_0)\,\boldsymbol{\nabla}h_0}{\left[1+(\boldsymbol{\nabla}h_0)^2\right]^{3/2}}\right]=0\,. \tag{6}$$

Let us first analyze the term (3) linear in $\boldsymbol{\nabla}\eta$. Using

$$\frac{\boldsymbol{\nabla}h_0\cdot\boldsymbol{\nabla}\eta}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}=\boldsymbol{\nabla}\cdot\left[\frac{\eta\,\boldsymbol{\nabla}h_0}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}\right]-\eta\,\boldsymbol{\nabla}\cdot\left[\frac{\boldsymbol{\nabla}h_0}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}\right] \tag{7}$$

and the equilibrium condition (5) we have, by Green theorem,

$$I_1=\oint_{\partial(D-P)}\frac{\eta\,\boldsymbol{\nabla}h_0\cdot\boldsymbol{m}}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}ds\simeq-\frac{\pi\Delta c_0^2r_0^4}{24}\,. \tag{8}$$

The integral in Eq. (8) replaces the sum of Eqs. (23) and (24) of Ref.[1]. It has two contributions: the first one is the integral on the contour of P. To lowest order in Δc_0 it coincides with Eq. (23) of Ref.[1] since, close to the colloid, $|\boldsymbol{\nabla}h_0| \ll 1$. The second contribution is a line integral on a circle of radius $r\to\infty$. This contribution is *zero* even if, for $r\to\infty$, $|\boldsymbol{\nabla}h_0|$ diverges:

$$\oint_{r\to\infty}\frac{\eta\,\boldsymbol{\nabla}h_0\cdot\boldsymbol{m}}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}ds=\lim_{r\to\infty}\frac{r_0^4\,\Delta c_0}{12r}\int_0^{2\pi}\cos(2\phi)\,\hat{\boldsymbol{u}}\cdot\boldsymbol{m}\,d\phi=0\,, \tag{9}$$

where $\hat{\boldsymbol{u}}=\boldsymbol{\nabla}h_0/|\boldsymbol{\nabla}h_0|$ is a *unit* vector, such that $|\hat{\boldsymbol{u}}\cdot\boldsymbol{m}|\le 1$[7]. Eq. (9) replaces Eq. (24) of Ref.[1], which is incorrect because of the small angle approximation $|\boldsymbol{\nabla}h_0| \ll 1$.

The remaining terms (2) and (4) give the same contributions as in Ref.[1]. Indeed, using

$$\frac{(\boldsymbol{\nabla}\eta)^2}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}-\frac{(\boldsymbol{\nabla}\eta\cdot\boldsymbol{\nabla}h_0)^2}{\left[1+(\boldsymbol{\nabla}h_0)^2\right]^{3/2}}=$$
$$\boldsymbol{\nabla}\cdot\left[\frac{\eta\,\boldsymbol{\nabla}\eta}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}-\frac{\eta\,(\boldsymbol{\nabla}\eta\cdot\boldsymbol{\nabla}h_0)\,\boldsymbol{\nabla}h_0}{\left[1+(\boldsymbol{\nabla}h_0)^2\right]^{3/2}}\right]$$
$$-\,\eta\boldsymbol{\nabla}\cdot\left[\frac{\boldsymbol{\nabla}\eta}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}-\frac{(\boldsymbol{\nabla}\eta\cdot\boldsymbol{\nabla}h_0)\,\boldsymbol{\nabla}h_0}{\left[1+(\boldsymbol{\nabla}h_0)^2\right]^{3/2}}\right] \tag{10}$$

and the equilibrium condition (6), Eq. (4) becomes, by Green theorem

$$I_2=\frac{1}{2}\oint_{\partial(D-P)}\left[\frac{\eta\,\boldsymbol{\nabla}\eta\cdot\boldsymbol{m}}{\sqrt{1+(\boldsymbol{\nabla}h_0)^2}}-\frac{\eta\,(\boldsymbol{\nabla}\eta\cdot\boldsymbol{\nabla}h_0)\,\boldsymbol{\nabla}h_0\cdot\boldsymbol{m}}{\left[1+(\boldsymbol{\nabla}h_0)^2\right]^{3/2}}\right]ds\,. \tag{11}$$

As before, the contribution on the circle $r\to\infty$ is zero. On the boundary of P, since $|\boldsymbol{\nabla}h_0| \ll 1$, the dominant contribution is

$$I_2\simeq\oint_\rho\frac{\eta}{2}\boldsymbol{\nabla}\eta\cdot\boldsymbol{m}\,ds\simeq\frac{\pi\Delta c_0^2r_0^4}{144}\,, \tag{12}$$

which coincides with Eqs. (21) of Ref.[1]. Finally, since inside P $|\boldsymbol{\nabla}h_0| \ll 1$, Eq. (2) becomes

$$I_0\simeq-\oiint_P\left(1+\frac{\boldsymbol{\nabla}h_0\cdot\boldsymbol{\nabla}h_0}{2}\right)dA\simeq-\pi r_0^2-\frac{\pi\Delta c_0^2r_0^4}{144}\,, \tag{13}$$

which coincides with Eq. (26) of Ref.[1]. Then, from Eqs. (13), (8), and (12), at quadratic order in Δc_0 Eq. (1) becomes $I\simeq-\pi r_0^2-\pi\Delta c_0^2r_0^4/24$ and Eq. (31) of Ref.[1] is therefore replaced by

$$\frac{E}{\gamma\pi r_0^2}=E_p-\frac{\Delta c_0^2r_0^2}{24}\,, \tag{14}$$

as originally found by Würger[2] and analytically and numerically confirmed in Refs.[3,4]. Note that in Refs.[3,4] the calculation of the force does not require the knowledge of the profile at infinity, thus avoiding the subtleties of the small angle approximation.

The quadratic dependence on Δc_0 of Eq. (14) cannot explain the linear dependence observed in Ref.[1]. However, in Ref.[1] the interpretation of the experimental data in terms of pinned contact lines relies on the analysis of Ref.[5], where the same small angle approximation at infinity was used. Then, following the lines of the previous analysis, it is easy to show that Eq. (8) of Ref.[1] must be replaced by[8]

$$E=E_0-\gamma\pi a^2\left(h_p\Delta c_0-\frac{1}{8}a^2\Delta c_0^2-\frac{a^2H_0^2}{4}\right)\,. \tag{15}$$

Eq. (15) implies that the values of h_p deduced in Ref.[1] must be halved, while the quadratic correction is almost negligible but consistent with the experimental data shown in Fig. 7 of Ref.[1]. For instance, for the black solid line, the quadratic correction on the last point lifts the fit by $\simeq 1.5\times10^{-5}$, thus improving the fit with respect to the linear approximation.

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Notes and references

1 N. Sharifi-Mood, I. B. Liu and K. J. Stebe, *Soft Matter*, 2015, **xx**, xxxx.

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3 C. Blanc, D. Fedorenko, M. Gross, M. In, M. Abkarian, M. A. Gharbi, J.-B. Fournier, P. Galatola and M. Nobili, *Phys. Rev. Lett.*, 2013, **111**, 058302.

4 P. Galatola and J.-B. Fournier, *Soft Matter*, 2014, **10**, 2197.

5 L. Yao, N. Sharifi-Mood, I. B. Liu and K. J. Stebe, *J. Colloid Interface Sci.*, 2015, **449**, 436.

6 Altough Eq. (19) of Ref.[1] is computed within the small angle approximation, the slope $\boldsymbol{\nabla}h$ diverges also when taking into account the full nonlinear equilibrium equation.

7 In Eq. (9) I used for η the small angle approximation (20) of Ref.[1]. Actually, for $|\boldsymbol{\nabla}h_0| \gg 1$, η must be solution of Eq. (6). However, since the reference plane can be tilted such that *locally* $|\boldsymbol{\nabla}h_0| \ll 1$, the true solution η for $r\to\infty$ cannot go to zero slower than its small angle approximation, and therefore Eq. (9) remains true.

8 The inessential correction in the constant term is due to the fact that in Ref.[5] the terms in Eqs. (2) and (3) proportional to Δp must be changed of sign to be consistent with Eq. (5).