Geometry-Dependent Electrostatics near Contact Lines

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Long-ranged electrostatic interactions in electrolytes modify contact angles on charged substrates in a scale and geometry-dependent manner. For angles measured at scales smaller than the typical Debye screening length, the wetting geometry near the contact line must be explicitly considered. Using variational and asymptotic methods, we derive new transcendental equations for the contact angle as functions of the electrostatic potential only at the three phase contact line. Analytic expressions are found in certain limits and compared with predictions for contact angles measured with lower resolution. An estimate for electrostatic contributions to line tension is also given.

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Modern microfluidic and patterning applications call for directed fluid flow and wetting on treated surfaces that often exhibit complex surface chemistry [1–3]. Mechanisms of differential wetting of small droplets of electrolytes have also been exploited as electrically activated switches and micropumps [4]. In such systems, the effects of surface ionization have been found to be important [1,5–7]. Consequently, one often considers two immiscible fluids of dielectric constants $\epsilon_0, \epsilon_1$ that partially wet an ionizable, rigid substrate, as shown in Fig. 1. The two liquids, depending on their individual pKa’s, will differentially hydrolyze/ionize substrates such as glass. Ionizable surfactants may also be adsorbed, imparting a fixed, relatively uniform surface charge $\sigma_m$ at the fluid-fluid interface. Microscopically, surface tensions $\gamma$ arise from mismatches in short-ranged molecular interactions (e.g., van der Waals) among the various species. Electrostatic double layers can also contribute to surface energies. The application of the classical Young-Dupré (YD) equation [8], $\gamma_{01} \cos \alpha^* = \gamma_0 - \gamma_{1*}$, with electrostatically modified surface tensions (e.g., $\gamma_{1*} = \gamma_{1} + \frac{1}{2} \sigma_1 \varphi_1$, where $\sigma_1$ and $\varphi_1$ are surface charges and potentials in, say, liquid 1 far from the contact point $P$) is accurate provided the apparent contact angle $\alpha^*$ is measured at $P^*$ well beyond the range $\kappa^{-1}$ of these electric double layers. Hydrolysis of pure water gives $\kappa^{-1} \sim 1 \ \mu$m, while in organic mixtures, with fewer mobile ions, the screening length can be even longer. However, even for screening lengths $\kappa^{-1}$ much smaller than the resolution of say, optical goniometry measurements, they may be within the resolution (nanometers) of emerging measurement techniques using atomic-force microscopy (AFM) [9]. If contact angles can be measured at $P$, within the ionic double layers, the simple YD equation will not be appropriate.

Previous theories that consider surface energy modifications [1,5–7,10,11] have either assumed microscopic-long interactions or infinite-system surface free energy changes (i.e., $\gamma \rightarrow \gamma + \frac{1}{2} \sigma_1 \varphi$). In this Letter, we explicitly consider the effects of the wedgelike geometry on the intrinsic electrostatics near the contact line. We derive formulas for the angle (measured within both double layers, but outside the length scale of other microscopic interactions) at the true three phase contact line in the presence of long-ranged electrostatic interactions. Rich features arise in this most simple and classic problem when geometry is self-consistently incorporated. Our results are summarized by Eqs. (3), (11), and (16).

The “mechanical” free energy of an axisymmetric liquid droplet of footprint radius $R$ (cf. Figs. 1a and 1b) in contact with a flat, solid substrate is $G_{\text{mech}} = (\gamma_{1*} - \gamma_{0*}) \int d\alpha + \gamma_{01} \oint dS_{01} + G_{\text{body}}$, where $\gamma$ are the surface tensions sans electrostatic interactions, $d\alpha$ is the in-plane surface element, and $S$ is the liquid-liquid surface element. The $G_{\text{body}}$ term may include gravitational energy, $(\rho_1 - \rho_0)g/2 \int h^2(r) \ d\alpha$, and/or Lagrange multipliers to, e.g., fix droplet volumes of incompressible liquids. The electrostatic free energy for a specified surface charge

![FIG. 1.](image)

(a) Two liquids with dielectric constants $\epsilon_0, \epsilon_1$ wet a charged substrate. (b) The substrate is ionized and acquires fixed charge densities of $\sigma_0, \sigma_1$. Charged surfactants can also impart a surface charge $\sigma_m$ at the fluid-fluid interface. (c) In order to satisfy electrostatic boundary conditions, the double layers in each fluid must deform near the contact point $P$. 

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ensemble written as a functional of the local electrostatic potential \( \varphi \) is [12]

\[
G_{el} = \int \sigma(S) \varphi(S) dS - \int dr dz \left[ \frac{e(r,z)}{8\pi} |\nabla \varphi|^2 + U[\varphi] \right],
\]

(1)

where \( U[\varphi(r)] = \sum_i e_i v_i c_i \exp[-v_i \varphi(r)] - 1 \) is a term summing the interactions among mobile charged species \( i \), each with valency \( v_i \) and bulk concentration \( c_i \). We have expressed all energy and length quantities in terms of \( k_B T \) and the Bjerrum length \( \ell_B = e^2/k_B T \). Variation of \( G_{el}[\varphi(r), \nabla \varphi(r), h(r), \nabla h(r)] \) with respect to \( \varphi(r) \) for a fixed droplet height function \( h(r) \) yields the Poisson-Boltzmann equation with appropriate boundary conditions. Similarly, a variation of \( G_T = G_{mech} + G_{el} \) with respect to the droplet height \( h(r) \) determines the complete shape of the electrolyte droplet via

\[
\gamma_{01} \partial_{rr}^2 h_{\perp}(r) = \left[ \frac{e}{8\pi} |\nabla \varphi|^2 + U[\varphi] \right]_0,
\]

(2)

where \( h_{\perp} \) is the normal deformation relative to a surface of constant slope. Further minimizing the boundary terms in \( G_T \) (which are independent of \( U[\varphi] \)) with respect to the position of the contact point, \( \delta G_T(z = 0)/\delta R = 0 \), yields

\[
\gamma_{01} \cos \alpha = (\gamma_{03} - \gamma_{13}) + (\sigma_0 - \sigma_1) \varphi(P, \alpha).
\]

(3)

The liquid-liquid surface tension \( \gamma_{01} \) may also change due to electrocapillarity, but this variation can be independently measured, e.g., pendant drop methods.

The first two terms arise from setting the variations in the boundary terms of \( G_{mech} \) to zero and reproduce the Young-Dupré equation. The last term in (3) is a new generalization of the YD equation and arises from minimizing the boundary terms of \( G_{el} \). The additional term depends only on the jump in the solid surface charge and the electrostatic potential \( \varphi(P) \) at the three phase contact line \( P \). This potential is found by solving the Poisson-Boltzmann equation \( \nabla^2 \varphi(r) = U[\varphi(r)] \) in the appropriate geometry, subject to boundary conditions. Therefore, \( \varphi(P) \) will depend parametrically on the droplet shape (and hence the contact angle \( \alpha \)) near \( P \). Equation (3) is exact provided the electrostatic energy is given by \( G_{el} \), and gives an implicit formula for predicting the contact angle \( \alpha \).

In the following, we compute \( \varphi(P, \alpha) \) in the linearized limit \( (U[\varphi] = \kappa^2 \varphi^2/2) \), valid for \( \varphi(r)/k_B T \ll 1 \), by solving the Debye-Hückel equation in each of the two fluid domains depicted in Fig. 1:

\[
\Delta \varphi_j = \kappa_j^2 \varphi_j(r, \theta), \quad \text{in fluid } j = 0, 1.
\]

(4)

The screening lengths \( \kappa_j^{-1} = (4\pi \varepsilon \sum_i v_i^2 c_i \varepsilon_i)^{-1/2} \) are assumed much smaller than the dimensions of the droplet. Furthermore, neglecting gravity, (2) shows that \( h_{\perp}(r) \) varies (relative to a perfect wedge) over a length \( L_h \sim \sqrt{\gamma_{01}/\kappa^2 \varphi^2(P)} \). If \( L_h \gg \kappa^{-1} \), the wedge is distorted only in the region where \( \varphi = 0 \), sufficiently beyond the contact point \( P \) to be appreciably influenced by electrostatic interactions. In this case, \( \varphi(P) \) can be computed using a perfect wedge geometry. The boundary conditions associated with (4) in 2D wedge domains are  

\[
e_0 \partial_\theta \varphi_0(r, \theta) = -4\pi r \sigma_0, \quad \varphi_0(r, \alpha) = \varphi_1(r, \alpha), \quad e_0 \partial_\theta \varphi_1(r, \theta) = -4\pi r \sigma_1, \quad \varphi_1(r, \alpha) = \varphi_0(r, \alpha),
\]

and

\[
e_0 \partial_\theta \varphi_0(r, \alpha) - e_1 \partial_\theta \varphi_1(r, \alpha) = 4\pi r \sigma_m.
\]

(5)

The linear problem defined above is related to the classic problem of wave scattering from a wedge, which remains a substantial mathematical and computational challenge [13]. The problem is best attacked using the Lebedev-Kantorovich integral transform

\[
f_j(x, \theta) = \int_0^\infty \varphi_j(r, \theta) K_{ik}(k_j r) \frac{dr}{r} = \mathcal{L}_k \varphi_j,
\]

(6)

and its inverse

\[
\varphi_j(r, \theta) = \frac{2}{\pi^2} \int_0^\infty f(x, \theta) K_{ik}(k_j r) x \sin(\pi x) dx
\]

\[
= \mathcal{L}_k^{-1} f_j.
\]

(7)

The potential \( \varphi(\kappa r \to 0) \) can be easily expressed in terms of its transform \( f(x, \theta) \). We will henceforth scale distance as \( \xi = k_0 r \) and reinsert \( k_0 \) back into the final, quoted results. Asymptotic analysis of the integral representation \( K_{ik}(\xi) = (1/2) \int_{-\infty}^{\infty} \exp[-\xi \cosh(x) + i\pi x] dx \) yields

\[
\lim_{\xi \to 0} K_{ik}(\xi) \sim \sinh(x)/x \times \pi \delta(x), \quad \lim_{\xi \to \infty} \sinh(x)/x = \pi \delta(x), \quad \text{implies}
\]

\[
\lim \varphi(\xi, \theta) = \lim_{x \to 0} [x^2 f(x, \theta)].
\]

(8)

We can find analytic expressions for \( \varphi(r, \theta) \) in two limiting cases that illustrate the full range of behaviors: \( k_0 = k_1 \), and \( k_1 \gg k_0 \). In the former case of nearly identical screening lengths, unequal dielectric constants \( \varepsilon_0 \neq \varepsilon_1 \) provide a nontrivial electric field jump across \( \theta = \alpha \). In the latter case, we will choose a small screening length (e.g., high salt) in region 1 without loss of generality. In both cases, the potential can be expanded in the power series \( \varphi_j(r, \theta) = \sum_{n=0}^{\infty} \mu^{(1)}(n)(e) \varphi_j^{(n)}(r, \theta) \), where \( e \) is a small parameter that depends on the ratio of screening lengths and the relevant regime:

\[
k_1 = k_0 \text{ limit}.
\]

In this limit, \( \mu^{(1)}(e) = e^\alpha \) and \( e^{(1)}(k_1/k_0)^2 = 1 \). At each order \( e^n \) the governing equations are \( \Delta \varphi_0 = \varphi_0 \) for \( \theta \geq \alpha \), and \( \Delta \varphi_1 = \varphi_1 + \varphi_1^{(n-1)} \) for \( \theta \leq \alpha \). Upon applying \( \mathcal{L}_1 \) to the nth order Debye-Hückel equations, \( \partial_{\theta} f_0(n) = x^2 f_0(n) \) and \( \partial_{\theta} f_1(n) = x^2 f_1(n) \) yields \( \varphi^{(n-1)}(x, \theta) = g^{(n-1)}(x, \theta) \), where \( g^{(n-1)}(x, \theta) = \mathcal{L}_1 \times \varphi^{(n-1)}(x, \theta) \). Similarly, the transformed boundary conditions at each order become \( \partial_{\theta} f_0(n) = (2\pi^2 \sigma_0/e_0) \text{sech}(\pi x/2) \delta_{n,0}, \partial_{\theta} f_1(n) = (2\pi^2 \sigma_1/e_1) \text{sech}(\pi x/2) \delta_{n,0}, \) and \( e_0 \partial_{\theta} f_0(n) - e_1 \partial_{\theta} f_1(n) = -\pi r \sigma_m \). Since \( f_1^{(n)}(x, \theta) \) obeys a homogeneous equation, it is determined explicitly. The equations for \( f_1^{(n=0)}(x, \theta) \) can be solved with the appropriate Green
function $G(x, \theta, \theta') = -\text{ch}x \theta - \text{ch}(\theta - \alpha)/(x \text{sh} \alpha)$, $\partial_\theta G(x, \theta, \theta' = 0, \alpha) = 0$, where $\theta_0(\theta', \theta)$ is the smaller (larger) of $\theta, \theta'$, and sh and ch are the hyperbolic sine and cosine functions. We obtain after some algebra, an integral equation for $f_1(x, \theta)$. The first iteration of this integral equation yields

$$e f_1^{(1)}(x, \theta) = e \int_0^\infty d\theta' \int_0^\alpha d\theta' H(\theta, \theta'; x, x') f_1^{(0)}(x', \theta'),$$

where

$$H(\theta, \theta'; x, x') = \frac{(e_1/4)G(\theta, \theta'; x)(x^2 - x'^2)x' \text{sh} x \text{sh} \alpha}{[e_1 \text{sh} \alpha + e_0 \text{ch} \theta \text{th} (\pi - \alpha)] \text{sh} \frac{x}{2}(x + x') \text{sh} \frac{x}{2}(x - x').}$$

Upon integrating (9) over $\theta'$, and using $f_1(x, \theta) = f_1^{(0)}(x, \theta) + e f_1^{(1)}(x, \theta)$ in (8), we find $\varphi(P; \alpha)$ up to $O(\varepsilon)$:

$$\varphi(P; \alpha) \sim -\frac{2\pi^2}{\varepsilon_1 \alpha + e_0(\pi - \alpha)} \left[\sigma_0 + \sigma_1 + \sigma_m\right] + O(\varepsilon^2).$$

The first (zeroth order) term arises from the limit $\varepsilon \to 0$, while the $O(\varepsilon)$ terms can be expressed as single $\alpha$-dependent integrals $S_i(\alpha; \lambda)$. The functions $S_i$ are plotted vs $\alpha$ in Fig. 2 for various dielectric mismatches $\varepsilon_0/\varepsilon_1 \equiv \lambda$. The term that remains when $\varepsilon_0 = \varepsilon_1$ and that multiplies all higher order terms in $\varepsilon$ is an effective angular average over the dielectrics $\varepsilon_0, \varepsilon_1$. This dominant term is qualitatively different from that arising from simple surface tension renormalization $\gamma \to \gamma + \frac{1}{2}\sigma_1 \varphi = \gamma + 2\pi \sigma^2/\varepsilon_k \lambda$. The higher order terms $S_i$ are determined with $\varepsilon_1$ relative to $\varepsilon_1$ and thus have their major effect when $\alpha = \pi$ as more of the volume is occupied by electrolyte of inverse screening length $\kappa$. For larger $\alpha = \pi$, $S_i$ varies more significantly over a smaller range of angles $\alpha$, reflecting the importance of the charged surface on the lower dielectric slice. The effects of the liquid-liquid surface

$$\partial_{\theta} f_1(x, \alpha) - \frac{e_0}{e_1} L_e L_1^{-1} \partial_{\theta} f_0^{(0)}(x', \alpha) = \left(\frac{2\pi^2\sigma_0}{\varepsilon_1 \kappa_0 \text{ch}(\pi \alpha/2)}\right).$$

Upon expanding $K_{ik}(\xi)$ about its dominant contribution at small $\xi$ in the operator $L_1^{-1}$ and performing the integration over $\xi$,

$$L_e L_1^{-1} \partial_{\theta} f_0^{(0)}(x', \alpha) = \frac{\pi \sigma_0}{\varepsilon_1 \kappa_0} \sum_{n=0}^\infty \frac{e^{2n}}{n!} \text{Im} \int_0^\infty x' \Gamma[n + \frac{1}{2}(x + x')] \Gamma[n + \frac{1}{2}(x - x')] e^{-ix' \text{Im} \text{ch} x'/2} \text{ch}(\pi \alpha/2) \text{ch}(\pi \alpha - x) \text{ch}(n + 1 - ix') dx'.$$

The contour integral in (14) can be performed exactly to find the two lowest order terms in $\varepsilon$ [for $n = 0, \mu^{(1)}(\varepsilon) = e^{\pi/(2\pi - 2\alpha)}$ and $\mu^{(2)}(\varepsilon) = e$] that must be considered. Using (8), our final result is

$$\varphi(P; \frac{e}{\alpha} \sim 0) \sim \frac{2\pi^2[\sigma_0 T_0(\alpha; \varepsilon) + \sigma_m \varepsilon]}{\alpha e_1 \kappa_0} + O(e^\xi/(\pi - \alpha)),$$

where

$$T_0(\alpha; \varepsilon) = \frac{\pi \Gamma^2(\frac{\pi}{4\pi - \alpha}) e^{\pi/(2\pi - 2\alpha)}}{4(\pi - \alpha)^2 \cos(\frac{\pi}{4\pi - \alpha}) \Gamma^2(3\pi - 2\alpha)/2\pi \cos \alpha} = e_0 = 20, e_1 = 80, \sigma_0 - \sigma_1 = 0.1, \sigma_0, \sigma_1 \sim O(1),$$

is plotted in Fig. 3 for various values of $\alpha$. The $\kappa_0/\kappa_1 \to 0$ analysis fails for small $\alpha$, when the fully screened approximation breaks down as the interface

charge are symmetric with the interchange $\alpha \to \pi - \alpha$, $\varepsilon_0, \kappa_0, \sigma_0 \to \varepsilon_1, \kappa_1, \sigma_1$ as expected.

$$\kappa_0/\kappa_1 \to 0 \text{ limit.}$$

In the limit $\kappa_1 \gg 1$, Eq. (4) becomes $\Delta \varphi = \varphi_0$ and $\Delta \varphi_1 = e^{-2}\varphi_1$, with $\varepsilon \equiv \kappa_0/\kappa_1$. Because of the strong screening in region 1, the potential at the surface under liquid 1, away from $P$, vanishes as $-\sigma_1(\varepsilon_0/\kappa_1)^{-1}$. The first iteration makes the approximation $\varphi_1^{(1)}(\theta, \varepsilon) = f_0^{(0)} \equiv 0$. However, as a result of continuity of the potential at $\theta = \alpha$, and finite $\kappa_0$ and $\sigma_0$,

$$f_0^{(0)}(x, \theta) = \frac{2\pi^2\varepsilon_1 \kappa_0 e}{e_0 \kappa_0 x} \text{ch}(\pi \alpha - \varepsilon_0 \varepsilon_1 \kappa_0 \text{ch}(\pi \alpha/2)).$$

Thus, $\varphi_0(\theta > \alpha) = L_1^{-1} f_0^{(0)} \neq 0$. The first nonzero term in $\varphi(P)$ arises from using (12) in the transformed jump condition (5) at $\theta = \alpha$:

$$f_0^{(0)}(x, \theta) = \frac{2\pi^2 e_0}{e_1 \kappa_0 x} \text{ch}(\pi \alpha - \varepsilon_0 \varepsilon_1 \kappa_0 \text{ch}(\pi \alpha/2)).$$

The contour integral in (14) can be performed exactly to find the two lowest order terms in $\varepsilon$ for $n = 0, \mu^{(1)}(\varepsilon) = e^{\pi/(2\pi - 2\alpha)}$ and $\mu^{(2)}(\varepsilon) = e$ that must be considered. Using (8), our final result is

$$\varphi(P; \frac{e}{\alpha} \to 0) \sim \frac{2\pi^2[\sigma_0 T_0(\alpha; \varepsilon) + \sigma_m \varepsilon]}{\alpha e_1 \kappa_0} + O(e^\xi/(\pi - \alpha)),$$

where

$$T_0(\alpha; \varepsilon) = \frac{\pi \Gamma^2(\frac{\pi}{4\pi - \alpha}) e^{\pi/(2\pi - 2\alpha)}}{4(\pi - \alpha)^2 \cos(\frac{\pi}{4\pi - \alpha}) \Gamma^2(3\pi - 2\alpha)/2\pi \cos \alpha} = e_0 = 20, e_1 = 80, \sigma_0 - \sigma_1 = 0.1, \sigma_0, \sigma_1 \sim O(1),$$

is plotted in Fig. 3 for various values of $\alpha$. The $\kappa_0/\kappa_1 \to 0$ analysis fails for small $\alpha$, when the fully screened approximation breaks down as the interface

charge are symmetric with the interchange $\alpha \to \pi - \alpha$, $\varepsilon_0, \kappa_0, \sigma_0 \to \varepsilon_1, \kappa_1, \sigma_1$ as expected.
The zeroth order correction to the surface energy varies from \(-0.5 \times 0.4 k_B T / \ell_B^2\) as \(\alpha\) varies from 0 to \(\pi\). Since one \(k_B T / \ell_B^2 \approx 8\) dyn/cm, the implicit \(\alpha\) dependence should be observable as long as the contact angle can be measured at a distance within 50 nm of \(\alpha\). Such measurements are possible using AFM techniques [9]. Our results also imply that dramatic effects on wettability \((\alpha = 0, \pi)\) can be induced by small changes in the physical parameters. Geometry-dependent electrostatics may also be an origin for the discrepancy between standard theory and measurements performed at low salt concentrations when screening lengths are long [7]. Furthermore, the true contact angle at \(P\) may be better correlated with dynamic contact angles of moving droplets.

In our strictly 2D analyses, the only bounded solution when \(\kappa_0 = \sigma_0 = 0\) (e.g., air) is \(\varphi(P; \alpha) = 0\). However, an asymptotic analysis for the large radius \((R \gg L, \kappa^{-1})\) limit is possible. The correction term to the YD equation resulting from such an analysis is proportional to \(\tau \propto \sigma_1^2 / \kappa^2 R\) times an \(\alpha\)-dependent factor, and defines the line tension [9,11,14] arising from electrostatics. These electrostatic forces giving rise to line tension may be sufficiently long ranged to be experimentally determined through a measurement of \(\alpha\). Ionic strength may thus provide a controllable parameter with which to measure the elusive, and controversial, line tension of wetting [9,14].

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