# Effective potential for adsorption

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A solution is proposed to the standing problem of the derivation of a wall-interface potential $V(\Gamma)$ as a function of the adsorption $\Gamma$. A stringent upper bound to $V(\Gamma)$ is obtained in the course of minimizing the surface free-energy functional $\bar{\gamma}[m]$, keeping $\Gamma$ constant, within the space of continuous and differentiable profiles $m(z)$. Comparison of $V(\Gamma)$ with available alternative potentials $\tilde{V}(l)$, $l$ being the wall-interface separation, indicates potentially important implications for critical wetting theory in three dimensions. The availability of $V(\Gamma)$, furthermore, leads to improved interface displacement models of three-phase contact lines.

A standing problem in the statistical mechanics of adsorption and wetting is the derivation of an effective wall-interface potential $V$ as a function of the *surface* order parameter, i.e., the coverage or *adsorption* $\Gamma$. Although $\Gamma$ is the natural (and experimentally measured) quantity to consider, practical considerations and the difficulties involved in deriving $V(\Gamma)$ have led wetting theorists to study $\tilde{V}(l)$, $l$ being the distance of the interface from the wall, i.e., the wetting-layer thickness.[1] Unlike $\Gamma$, $l$ is not well defined in general, and loses meaning when the adsorption is small.[2] Usually one is interested in the limit of large adsorption, and at bulk two-phase coexistence $l$ is then well defined via

$$|\Gamma| \approx 2m_0 l \quad \text{for } l \to \infty \ , \tag{1}$$

where $m_0$ is the absolute value of the *bulk* order parameter. Thus, in the limit of large $l$, $V(\Gamma)$ can be compared unambiguously with existing forms of $\tilde{V}(l)$.

It has been argued that the precise form of $\tilde{V}(l)$ at large $l$ is essential to the *critical* wetting behavior in a three-dimensional system with short-range forces.[1] Renormalization-group theory based on $\tilde{V}(l)$ predicts *nonuniversality* for critical wetting in $d=3$, but Monte Carlo simulations disagree. (See Ref. 1 for a list of pertinent references.) A careful derivation of $V(\Gamma)$ is therefore of crucial importance for critical wetting theory.

The derivation we give is interesting also from a mathematical standpoint. The reason why previous attempts to derive $V(\Gamma)$ have been discontinued is that the usual approach of functional minimization with an integral constraint fails if one assumes regular trial functions. We show that this approach becomes successful if one slightly extends the space of trial functions, and allows the order-parameter profile $m(z)$, $z \in [0,\infty)$ being the distance from the wall, to exhibit a discontinuous second derivative at *one* point $\hat{z}$. Such singularity is weaker than that which has been allowed in alternative derivations of $\tilde{V}(l)$.[1,3]

The variational problem to be solved consists of the minimization of the *mean-field* surface free-energy functional

$$\bar{\gamma}[m] = \int_0^\infty dz \left\{ \frac{c^2}{4} \left[ \frac{dm}{dz} \right]^2 + f(m) \right\} - h_1 m_1 - g \frac{m_1^2}{2} \ , \tag{2}$$

subject to the integral constraint

$$\bar{\Gamma}[m] \equiv -\frac{\partial \bar{\gamma}[m]}{\partial h} = \int_0^\infty dz \{ m(z) - m_b \} = \Gamma \ , \tag{3}$$

and the boundary condition

$$m(z) \to m_b \quad \text{for } z \to \infty \ , \tag{4}$$

where $m_b$ is the bulk order parameter. At bulk coexistence, $|m_b| = m_0$. The Landau bulk free-energy density is

$$f(m) = (m^2 - m_b^2)(m^2 + m_b^2 - 2m_0^2) - h(m - m_b) \ , \tag{5}$$

where $h$ is the bulk field ($h=0$ at bulk coexistence). The couplings $h_1$ and $g$ are, respectively, the surface field that induces wetting and the surface coupling enhancement,[4] and $m_1 \equiv m(z=0)$.

Minimization of Eq. (2) under constraint (3) leads to the Euler-Lagrange equation

$$\frac{c^2}{2} \frac{d^2 m}{dz^2} = \frac{df}{dm} + \lambda \ , \tag{6}$$

where $\lambda$ is the Lagrange multiplier. The useful first integral of this equation features an integration constant $\alpha$, which, like $\lambda$, can be chosen *piecewise* constant so that (4) is satisfied, with $m(z)$ and $dm/dz$ continuous on $[0,\infty)$, and $d^2m/dz^2$ discontinuous in at most one point $\hat{z}$. The need for allowing the latter discontinuity follows from the impossibility to satisfy (4) and (6) simultaneously for $\lambda \neq 0$. Furthermore, the restriction to a *single* singularity implies that for $z > \hat{z}$, we must take $\lambda = 0$ in Eq. (6), to allow for (4), and the choice of $\alpha$ is then trivial for that $z$ interval. For the interval $[0,\hat{z})$, however, the choice of $\alpha$ is not unique, and further minimization with respect to $\alpha$ may be required. Presently, we limit ourselves to the particular choice that minimizes $|m(\hat{z}) - m_b|$, and thus obtain an upper bound to $V(\Gamma)$. For $\lambda > 0$ this procedure amounts to requiring

 

$$m = m_b \quad \text{and} \quad \frac{dm}{dz} = 0 \quad \text{at } z = \hat{z} \,, \tag{7}$$

and, consequently, $m(z) = m_b$ for $z \geq \hat{z}$. An advantage of this simple condition is that analytical calculation of the free energy is tractable. For $\lambda < 0$ a different requirement applies, which will be discussed elsewhere.

Finally, subsequent minimization of the surface free energy with respect to $m_1$ leads to the boundary condition at the wall

$$h_1 + g m_1 = c[f(m_1) + \lambda(m_1 - m_b)]^{1/2} \,. \tag{8}$$

This condition is to be satisfied in general. Exceptions may be found when boundary minima occur, in mean-field theories with a bounded order parameter ($|m| \leq 1$).[5]

In the following we restrict attention to first-order and critical wetting transitions occurring at $h = 0$. We fix the bulk phase so that $m_b = -m_0$. The potential $V(\Gamma)$ is given by $\bar{\gamma}[\tilde{m}]$, with $\tilde{m}(z)$ the profile that minimizes $\bar{\gamma}[m]$ subject to the constraint $\bar{\Gamma}[\tilde{m}] = \Gamma$. A simple but useful upper bound $V^*(\Gamma)$ is obtained for the *regular* trial profile $m^*(z)$ which satisfies (3), (4), and

$$\frac{c^2}{4}\left[\frac{dm^*}{dz}\right]^2 = f(m^*) \,. \tag{9}$$

It follows that $m_1^*$ is uniquely determined and satisfies $-m_0 \leq m_1^* \leq m_0$ for $\Gamma \geq 0$ and $m_1^* \leq -m_0$ for $\Gamma \leq 0$. Note that $m_1^*$ is *not* determined by a boundary condition at the wall. Although $V^*(\Gamma)$ is a reasonable approximation and has been used, in the alternative form $\tilde{V}^*(l)$, for studying critical wetting,[6] it is qualitatively deficient at first-order wetting. It fails to reproduce the global minimum at $\Gamma = \infty$, associated with the macroscopically thick wetting layer, which coexists with the thin film, for which $\Gamma = \Gamma_1$. The $V(\Gamma)$ we seek must, of course, satisfy $V(\Gamma_1) = V(\infty)$.

The numerically computed upper bound to $V(\Gamma)$ at a first-order wetting transition is shown in Fig. 1. Analytic calculation of the asymptotic part for large $\Gamma$ gives

$$[V(\Gamma) - V(\infty)]/\gamma_0 = 6(x-1)\exp(-2\Gamma/c) - 6(x-1)^2(2\Gamma/c)\exp(-4\Gamma/c) + \mathcal{O}[\exp(-4\Gamma/c)] \,. \tag{10}$$

The quantity $\gamma_0$ ($= 4cm_0^3/3$) is the liquid-vapor surface tension, and $x \equiv m_1^{(0)}/m_0$, where $m_1^{(0)}$ is the value of $m_1$ that solves Eq. (8) with $\lambda = 0$, in the domain $m_1 > m_0$.

The computed approximation to $V(\Gamma)$ is exact at $\Gamma = \Gamma_1$ (first minimum), $\Gamma_2$ (local maximum), and $\infty$ (second minimum), where it reproduces the extrema of $\bar{\gamma}[m]$ *without* constraint on the adsorption. In the intervals $0 < \Gamma < \Gamma_1$ and $\Gamma_2 < \Gamma < \infty$, $V(\Gamma)$ has been computed with $\lambda > 0$ and using (7). For the remaining intervals computation with $\lambda < 0$ applies, but has been postponed, because in those intervals the simple upper bound $V^*(\Gamma)$ is a very reasonable approximation.

In the following we turn to the important case of critical wetting. Presently we restrict attention to the derivation of $V(\Gamma)$ *at* the transition, and postpone a discussion

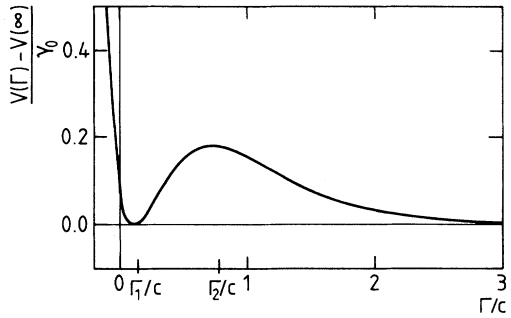


FIG. 1. Effective potential $[V(\Gamma) - V(\infty)]/\gamma_0$ vs $\Gamma/c$ at a first-order wetting transition, computed at the following system parameters: $m_0 = 0.2$, $h_1/c = 0.681 m_0^2$, and $g = 0$. Singularities occur at $\Gamma = 0$, $\Gamma_1$, and $\Gamma_2$, where the simple upper bound $V^*(\Gamma)$, shown for $\Gamma \leq 0$ and $\Gamma_1 \leq \Gamma \leq \Gamma_2$, coincides with the stringent upper bound, shown for $0 \leq \Gamma \leq \Gamma_1$ and $\Gamma \geq \Gamma_2$.

of the partial wetting regime preceding the transition. The numerically computed upper bound to $V(\Gamma)$ at a critical wetting transition is shown in Fig. 2. For $\Gamma > 0$ the result is presented of the computation with $\lambda > 0$ and using (7). For $\Gamma < 0$ the simple upper bound $V^*(\Gamma)$ is shown. Analytic calculation of the important asymptotic part for large $\Gamma$ gives

$$[V(\Gamma) - V(\infty)]/\gamma_0 = 6\left[\frac{g + 2m_0 c}{g - 2m_0 c}\right]\exp(-4\Gamma/c) + o[\exp(-4\Gamma/c)] \,, \tag{11}$$

where $o(y)$ means smaller than of order $y$. We remark that this leading term vanishes, as it should, at tricritical wetting. The potential we have derived constitutes, as expected, a significant improvement over the simple upper bound $V^*(\Gamma)$. Much more interesting is the comparison with the alternative potential $\tilde{V}(l)$ obtained by Fisher and Jin.[1] Our provisional comparative computation indicates

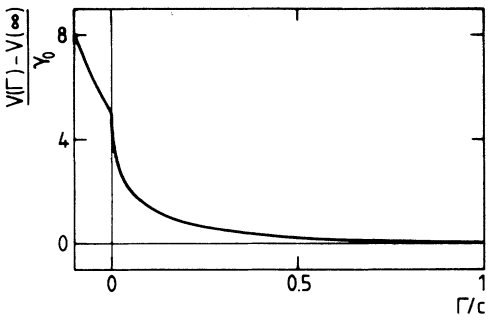


FIG. 2. Effective potential $[V(\Gamma) - V(\infty)]/\gamma_0$ vs $\Gamma/c$ at a critical wetting transition, computed at the following system parameters: $m_0 = 0.2$, $h_1/c = 4m_0^2$, and $g/c = -4m_0$. A singularity occurs at $\Gamma = 0$, where the simple upper bound $V^*(\Gamma)$, shown for $\Gamma \leq 0$, coincides with the stringent upper bound, shown for $\Gamma \geq 0$.

that the difference between Fisher and Jin's result and ours is small compared to the amount that both results gain over the simple upper bound. To be specific, at a fixed value of the adsorption $\Gamma$, our approach gives a slightly lower value for the surface free energy than that which we obtain following Fisher and Jin.[7] Conversely, at a fixed value for the zero-crossing point $l$, for which $m(l)=0$ (providing such a point exists), our result is slightly higher.[8] This is quite satisfactory, since Fisher and Jin's procedure was to minimize at fixed $l$, whereas ours is to minimize at fixed $\Gamma$. Clearly, we have obtained a stringent upper bound to the optimal effective potential.

The potential we have derived is likely to play an important role also in the context of interface displacement models for three-phase equilibria.[9] Near a solid-liquid-vapor contact line, for example, the adsorption is small and the concept of a wetting layer thickness $l$ breaks down, because the density or composition of the layer varies strongly on the length scale of its microscopic thickness. The adsorption $\Gamma$, however, remains well-defined and the adsorption profile $\Gamma(x)$, where $x$ is a coordinate along the solid substrate surface, perpendicular to the three-phase contact line, is the appropriate function to be used instead of the displacement profile $l(x)$. In particular, the expression for the line tension of the three-phase line then involves the following functional:

$$\bar{\tau}[\Gamma]=\int_{-\infty}^{\infty} dx \left\{ \frac{\sigma_0}{2} \left[ \frac{d\Gamma}{dx} \right]^2 + V(\Gamma(x)) \right\}, \tag{12}$$

where $\sigma_0$ is a function of $\gamma_0$ and $m_0$. The use of $V(\Gamma)$ should thus permit a better comparison between interface displacement models[9,10] and more microscopic mean-field approaches[11,12] for calculating, e.g., the line tension near wetting phase transitions.

Details and further developments will be reported elsewhere.

*Note added in proof.* For derivations of $\tilde{V}(l)$ and $V(\Gamma)$ within density-functional theory for inhomogeneous fluids with van der Waals forces, see S. Dietrich and M. Napiórkowsky, Phys. Rev. A **43**, 1861 (1991).

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[8]The computation was done at critical wetting for the following system parameters: $m_0=0.2$, $h_1/c=4m_0^2$, $g/c=-4m_0$, and $l/c=2.3495$. For $[\tilde{V}(l)-\tilde{V}(\infty)]/\gamma_0$ we obtained 0.0573 (simple upper bound, following Ref. 6), 0.0313 (following Ref. 1), and 0.0335 (our method).

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