# Fluid Adsorption at the Base of a Cylinder

Andrew O. Parry
*Department of Mathematics, Imperial College London, London SW7 2BZ, United Kingdom*

Carlos Rascón
*GISC, Departamento de Matemáticas, Universidad Carlos III de Madrid, 28911 Leganés, Madrid, Spain*

(Received 11 August 2011; published 8 November 2011)

We consider the adsorption of fluid at a cylinder protruding from a flat substrate. For small contact angles $\theta$, a liquid drop condenses at the base, the size of which is determined by macroscopic arguments. The adsorption exhibits scaling behavior related to a number of phase transitions and, for systems with short-ranged forces, shows a remarkable property: for small $\theta$, the height and width of the drop are near identical to expressions for the thickness and parallel correlation length for microscopic wetting films. The only difference is that the bulk correlation length is replaced by the cylinder radius. This geometrical *amplification* of the microscopic lengths occurs for second-order, first-order, and complete wetting transitions, and is specific to three dimensions. Similar phenomena occurs for long-ranged forces, and shows crossover scaling behavior.

DOI: 10.1103/PhysRevLett.107.206104 PACS numbers: 68.08.Bc, 05.70.Np

Fluid adsorption and the micro-fluidics of droplet spreading on structured substrates has received enormous attention recently [1–4]. One particularly interesting surface topography is a flat wall patterned with vertical rods, which leads to superhydrophobicity, in which a liquid drop is suspended by the tips of rods [5–8]. In this Letter, we point out that fluid adsorption in this geometry also shows scaling behavior, and a remarkable connection between macroscopic capillarity and microscopic theories of wetting transitions. To see this, consider a structured substrate in which a cylinder of radius $R$ protrudes normally from a planar wall. We assume that cylinder and wall are made of the same material, and are in contact with a bulk vapor at temperature $T$ (below its bulk critical point) and pressure $p$ close to saturation $p_{\rm sat}$. Gravity is neglected. At the wall, but far from the cylinder base, one finds a microscopic adsorbed layer characterized by a thickness $\ell_\pi$, a parallel correlation length $\xi_\parallel$, and an interfacial roughness $\xi_\perp$ [3,9,10]. A slightly thinner wetting layer coats the cylinder far above the wall [11]. In addition to this, a macroscopic liquid drop condenses at the foot of the cylinder, the size of which depends on $R$, $\theta$ and the undersaturation $\delta p = p_{\rm sat} - p$. Let us determine the drop size using macroscopic arguments. Let $\ell(r)$ denote the drop height at radial distance $r$ from the cylinder center. The height at contact is $\ell_0 \equiv \ell(R)$, while $R_\parallel$ is the lateral width, where $\ell(R_\parallel) = 0$ (see Fig. 1). To begin, we assume we are at two-phase coexistence, $p = p_{\rm sat}^-$. The macroscopic excess free-energy is the sum of the surface tension and line tension contributions which, on using Young's equation and ignoring constant terms, reduces to

$$F[\ell] = \sigma A - \pi(2R\ell_0 + R_\parallel^2)\sigma\cos\theta + 2\pi\tau R_\parallel. \qquad (1)$$

Here, $A = 2\pi\int_R^{R_\parallel} dr r\sqrt{1+\ell'(r)^2}$ is the area of the liquid-vapor interface, $\sigma$ is its interfacial tension, and $\tau$ is the line tension. Minimization of $F[\ell]$ leads to a simple Euler-Lagrange equation, which can be integrated to get the drop shape. For the width and height, we find

$$R_\parallel = -\frac{\tau\cos\theta}{\sigma\sin^2\theta} + \sqrt{\frac{\tau^2}{\sigma^2\sin^4\theta} + R^2\cot^2\theta} \qquad (2)$$

and

$$\ell_0 = R\cos\theta\ln\left(\frac{R_\parallel + \sqrt{R_\parallel^2 - R^2\cos^2\theta}}{R(1+\sin\theta)}\right), \qquad (3)$$

respectively. These macroscopic results are only valid for $0 < \theta < \pi/4$, where the bounds correspond to different phase transitions. As $\theta$ is increased to $\pi/4$, the droplet vanishes indicating that the adsorption is *microscopic* for larger contact angles. The vanishing of the macroscopic droplet is to be expected since $\theta = \pi/4$ is the filling

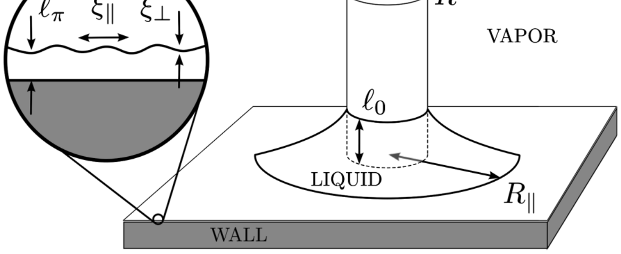

FIG. 1. Schematic illustration of a macroscopic drop of liquid at the base of the cylinder. Symbols are described in the text.

phase boundary of a right-angle linear wedge [12,13]—a geometry obtained in the limit of infinite cylinder radius. For $\theta > \pi/4$, one must improve on (1) and adopt a more microscopic approach, similar to studies of wedge filling, which allow for intermolecular forces and interfacial fluctuations [14]. Near the filling phase boundary, we anticipate crossover scaling behavior between these microscopic and macroscopic regimes. For example, for systems with short-ranged forces, we expect that, exactly at $\theta = \pi/4$, the droplet size scales as $\ell_0 \approx R_\parallel - R \approx (k_B T R/\sigma)^{1/3}$, where the power-law is determined by the wandering exponent for continuous filling transitions [14]. This scaling arises because the dominant correlation length (which would diverge in an infinitely long wedge) is limited by the cylinder circumference. Ising model simulations could test this using a "cylinder" of square cross section, similar to studies of interfacial behavior in double wedges and bipyramids [15,16].

The limit which is far more surprising corresponds to the approach to a wetting transition. Suppose that $\theta < \pi/4$ and the temperature is increased toward the wetting temperature $T_w$, at which $\theta = 0$. The behavior of the drop in this limit is intimately connected, far more than one may initially suspect, with the critical singularities of the underlying microscopic transition. Let us begin by focussing on systems with short-ranged intermolecular forces:

*Second-order (critical) wetting.*—In this case, $\ell_\pi$ and $\xi_\parallel$ diverge continuously as $T \to T_w$, while the line tension is negative and vanishes. At mean-field level, microscopically based calculations show that $\theta \propto (T_w - T)$ and the length scales diverge as

$$\xi_\parallel \approx \frac{\xi_b}{\theta}, \qquad \ell_\pi \approx -\xi_b \ln\theta, \tag{4}$$

where $\xi_b$ is the bulk correlation of the liquid wetting film [10,17]. Similarly, for the line tension, one finds $\tau \approx -\theta\sigma\xi_b$ [18]. For this transition, the upper critical dimension is $d_u = 3$, and while there are long-standing renormalization group predictions for the strongly nonuniversal critical behavior (for example, concerning the vanishing of $\theta$), the dependences of $\ell_\pi$, $\xi_\parallel$ and $\tau$ on $\theta$ are hardly altered [19,20]. Substituting for $\tau$ into (2) shows that the line tension does not influence the growth of the droplet as $T \to T_w$, whose size diverges *continuously* as

$$R_\parallel \approx \frac{R}{\theta}, \qquad \ell_0 \approx -R\ln\theta. \tag{5}$$

These are strikingly similar to the microscopic predictions for the wetting transition itself, but with the cylinder radius replacing the bulk correlation length.

*First-order wetting transitions.*—At a first-order wetting transition, the length scales $\ell_\pi$ and $\xi_\parallel$ remain finite as $T \to T_w$. The line tension is negative far from the transition, but becomes positive on approaching $T_w$ and, for systems with short-ranged forces, remains finite at $T_w$ [18]. From (2), it follows that, provided the condition

$$R \gg \frac{|\tau|}{\sigma\theta} \tag{6}$$

is met, the droplet grows initially according to the Eq. (5) and the line tension is unimportant. Obviously, for fixed $\theta > 0$, one may always imagine that $R$ is large enough so that this criterion (6) is fulfilled. For fixed $R$ and $\theta \to 0$, however, the criterion fails, which indicates crossover to another behavior. In this limit, the line tension controls the behavior of the drop, which saturates to a *finite* size at $T_w$—consistent with the first-order nature of the transition. The width of the drop at $T = T_w$ is given by

$$R_\parallel = \frac{\sigma R^2}{2\tau} + \cdots, \tag{7}$$

where the ellipses denote negligible terms, independent of the cylinder radius $R$. The significance of this result is, once again, the similarity it bares to the parallel correlation length at first-order wetting. This can be calculated from an effective interfacial Hamiltonian approach using a binding potential $W(\ell)$ which determines the length scales from $W'(\ell_\pi) = 0$ and $\xi_\parallel = \sqrt{\sigma/W''(\ell_\pi)}$ [10]. The expression for the line tension is a given by [18]

$$\tau = \sqrt{2\sigma}\int_{\ell_\pi}^{\infty} d\ell \left(\sqrt{\frac{\sigma}{2}\theta^2 + W(\ell)} - \sqrt{\frac{\sigma}{2}}\theta\right). \tag{8}$$

For first-order wetting, $W(\ell)$ has a potential barrier between the bound and wet phases. For systems with short-ranged forces, and exactly at $T_w$, this factorizes as

$$W(\ell) = ce^{-\kappa\ell}(e^{-\kappa\ell} - e^{-\kappa\ell_\pi})^2 + \cdots, \tag{9}$$

where $\ell_\pi$ is the finite thickness of the wetting layer at the transition. The ellipses denote higher-order exponentially decaying terms. These are unimportant if the transition is weakly first-order, corresponding to large $\ell_\pi$ and $\xi_\parallel$, for which the effective Hamiltonian approach is valid. Using this potential, we find the relation

$$\xi_\parallel = \frac{4\sigma\xi_b^2}{3\tau}. \tag{10}$$

Once again, comparison with the result (7) reveals that, for large cylinders, the geometry *amplifies* the underlying microscopic wetting length, replacing $\xi_b$ with (a simple multiple of) the cylinder radius.

The unexpected connection between short-ranged microscopic wetting and macroscopic capillarity extends to the complete wetting occurring for $T > T_w$ (for which $\theta = 0$). Close to coexistence, a thick wetting layer of liquid intrudes between the planar wall and the bulk vapour, and is similarly characterized by a thickness $\ell_\pi$ and parallel correlation length $\xi_\parallel$ [10]. Again, for systems with short-ranged forces, the upper critical dimension is $d_u^{\rm co} = 3$, and the mean-field predictions

$$\xi_{\parallel} \approx \sqrt{\frac{\xi_b \sigma}{\delta p}}, \qquad \ell_\pi \approx -\xi_b \ln \delta p \tag{11}$$

are accurate [20]. For example, only the amplitude of the logarithmic divergence is slightly altered. Now, compare these results with the macroscopic theory for the droplet near the cylinder, but with conditions of complete wetting. We suppose that the bulk vapor is at pressure $p < p_{\rm sat}$, and wish to determine how the height $\ell_0$ and lateral radius $R_{\parallel}$ grow as the undersaturation $\delta p$ is reduced. Recalling that the contact angle is zero, and that a line tension is no longer defined, the macroscopic free-energy reads

$$F[\ell] = \sigma A + \delta p V - \pi\sigma(2R\ell_0 + R_{\parallel}^2), \tag{12}$$

where $V$ is the drop volume. Upon minimization, we find that, for small undersaturations $\delta p < 1/R$, the dimensions of the drop are given by

$$R_{\parallel} \approx \sqrt{\frac{2\sigma R}{\delta p}}, \qquad \ell_0 \approx -\frac{R}{2} \ln \delta p \tag{13}$$

and, similarly, correspond to a geometrical amplification of the underlying complete wetting length scales.

The unexpected connection between the size of the drop, induced by the protruding cylinder geometry, and the length scales for the underlying microscopic wetting layer is the main result of our paper, and is summarized in Table I. This connection is somewhat similar to that between adsorptions at apexes, wedge filling and wetting transitions [21–23]. However, in that case, the comparison is between microscopic descriptions of phase transitions in different geometries. The origin of the present connection is more obscure to us, given the quite different natures of the macroscpic and microscopic calculations. The microscopic description of the length scales $\ell_\pi$ and $\xi_{\parallel}$ requires a specific binding potential function $W(\ell)$ (or equivalently a disjoining pressure) for each of the transitions. Yet, within the macroscopic approach, there is no mention of a binding potential. Some further remarks are made below:

(I) While the cylinder amplifies the length scales $\ell_\pi$ and $R_{\parallel}$, it does not affect the interfacial roughness. For planar wetting films, the roughness $\xi_{\perp}$ describes the r.m.s. fluctuations in the interfacial height about $\ell_\pi$. Within effective Hamiltonian theory, this is determined by

$$\xi_{\perp}^2 = \frac{k_B T}{2\pi\sigma} \int_0^{\Lambda} dq \frac{q}{\xi_{\parallel}^{-2} + q^2} \tag{14}$$

corresponding to the inverse of the Fourier transformed height-height correlation function [24]. Here, $\Lambda$ is a momentum cutoff of the order of $1/\xi_b$. For example, for critical wetting with short-ranged forces, this leads to

$$\xi_{\perp}^2 \approx \frac{k_B T}{2\pi\sigma} \ln \theta^{-1}, \tag{15}$$

where we have again expressed the result in terms of the contact angle. Now, reconsider the macroscopic description for the droplet (for critical wetting) and determine the analogous r.m.s. roughness $w$ for the height at contact with the cylinder. One can do this by partially minimizing the free-energy (1) keeping the height at the cylinder fixed at an arbitrary value $\ell$. For small $\theta$, this constrained free-energy has the form

$$\frac{f(\ell)}{\pi\sigma} = -2R\ell + \theta\ell X(\ell) + \frac{\theta^2}{2} X(\ell)^2, \tag{16}$$

where $X$ is defined implicitly from $\ell = \theta X \ln(X/R)$. The minimum of this potential recovers the asympotic result $\ell_0 = -R \ln\theta$, while the curvature determines the roughness of the drop from

$$w^2 = \frac{k_B T}{f''(\ell_0)}. \tag{17}$$

From the potential (16), it follows that the droplet roughness $w$ is the *same* as the *microscopic roughness* $\xi_{\perp}$, given by (15). The equivalence of the roughnesses is all the more surprising given that, in the calculation for the drop, there is no momentum cutoff.

TABLE I. Comparison of derived expressions for the droplet width $R_{\parallel}$ and parallel correlation length $\xi_{\parallel}$ for the cases of critical wetting, complete wetting, and first-order wetting in systems with short-ranged forces.

| | Critical | Complete | First-Order |
|---|---|---|---|
| $\xi_{\parallel}$ | $\frac{\xi_b}{\theta}$ | $\sqrt{\frac{\xi_b\sigma}{\delta p}}$ | $\frac{4\sigma\xi_b^2}{3\tau}$ |
| $R_{\parallel}$ | $\frac{R}{\theta}$ | $\sqrt{\frac{2R\sigma}{\delta p}}$ | $\frac{\sigma R^2}{2\tau}$ |

(II) We have shown that the connection between the droplet size and microscopic wetting is specific to three-dimensions. We illustrate this for critical wetting. For $d > 3$, the cylinder does not induce the condensation of a macroscopic drop, since its width $R_{\parallel} \approx \xi_b/\theta$ is the same size as $\xi_{\parallel}$. For $d < 3$, on the other hand, the width scales as $R_{\parallel} \approx R\theta^{1/(2-d)}$ which is much larger than the parallel correlation length $\xi \approx \xi_b \theta^{2/(1-d)}$. It follows that the cylinder has a marginal perturbative influence on the microscopic wetting layer in three dimensions, affecting the amplitude but not the power-law dependence on $\theta$. It is perhaps coincidental that this is also the marginal (upper critical) dimension for the wetting transition itself.

(III) Similar phenomena occurs in the presence of long-ranged (dispersion type) intermolecular forces. This is discussed in detail elsewhere [25] but is illustrated here for the case of critical wetting. Provided the condition (6) is met, the dimensions of the drop are the same as for systems with short-ranged forces, given by (4). In this regime, the line tension and the range of the intermolecular forces do not matter. However, as the wetting transition is approached, the singularity of the line tension,

$\tau \approx -\theta^{(p-1)/(p+1)}$, is all important and determines the droplet size (here $p = 2$ and $p = 3$ correspond to nonretarded and retarded dispersion forces, respectively). In this asymptotic regime, the width is *independent* of the cylinder radius, and scales instead with the parallel correlation, $R_\parallel \approx \xi_\parallel \approx (T_w - T)^{-(p+3)/2}$. The crossover between these regimes shows scaling behavior described by

$$R_\parallel = \xi_\parallel \phi(R/\ell_\pi), \tag{18}$$

where $\phi(x) = 1 + \sqrt{1 + x^2}$ is a scaling function (ignoring trivial metric factors). Note that the argument of the scaling function is a ratio of relevant length scales, and is similar to other finite-size scaling for wetting transition in confined geometries [26]. The condition $R/\ell_\pi \gg 1$ is precisely equivalent to the criterion (6).

Finally, we believe that our predictions can be tested using more microscopic density-functional theories, in simulations, and in the laboratory. Experiments using molecular fluids should be possible for complete wetting, similar to recent studies of adsorption in wedges and grooves [27,28]. It would also be very interesting to study this in colloid-polymer mixture which are effectively short-ranged [29]. Even for critical wetting, where there is a paucity of solid-fluid interfaces that exhibit the transition, one could use a binary-liquid mixture [30], and equivalently introduce a vertical needle into the wetting layer. For first-order wetting one may also envisage using the prediction (7) to measure the line tension close to the wetting transition [31]. We stress that, in all these experimental scenarios, gravity can be safely neglected below the scale of the capillary length.

C. R. acknowledges support from grants MODELICO (Comunidad de Madrid) and FIS2010-22047-C05-04 (Ministerio de Educación y Ciencia).

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