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## LETTER TO THE EDITOR

# Macroscopic shape of critical droplets in first-order wetting transitions

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**Abstract.** In a first-order wetting transition the decay of a metastable non-wet state occurs by nucleation and growth of supercritical droplets on the wall of the system. Based on an effective interface model for the wetting fluid the shape of the critical droplet is calculated outside a microscopic region near the wall for a class of long-range interface potentials. The solution has a surprisingly simple form if the dimension of the system coincides with the boundary dimension between the so-called strong and weak fluctuation regimes.

When a finite amount of liquid is brought into contact with a solid wall the liquid forms a drop under the action of the surface tensions between the vapour, liquid and solid phases. The calculation of the droplet shape in thermal equilibrium is an old problem considered already by Laplace [1]. More recently, the profile of droplets on a wall has been derived by different techniques including phenomenological methods [2], Monte Carlo simulations [3], random walks [4] and methods using conformal invariance [5].

Droplets on a wall may also appear as critical droplets in the metastable region of a first-order wetting transition. Such a transition occurs at bulk coexistence of two fluids in the presence of a wall which prefers one of the fluid phases [6]. Below the transition temperature  $T_w$  the wall is in a non-wet state whereas above  $T_w$  it is covered by a macroscopic wetting layer. If the system is overheated from below to above  $T_w$  the non-wet state becomes metastable and decays via nucleation and growth of supercritical droplets on the wall. As in homogeneous nucleation in the bulk the critical droplet plays an essential role in the nucleation process determining, for example, the lifetime of the metastable state [7].

The critical droplet in first-order wetting transitions can be determined [8] from the effective interface Hamiltonian [9]

$$H[f] = \iint d^{d-1}x \left[ \frac{\gamma}{2} (\nabla f)^2 + V(f) \right] \quad (1)$$

where  $f(x)$  is the local thickness of the fluid covering the wall. The first term in  $H$  derives from the capillary energy of the interface between the two fluids with  $\gamma$  being its surface tension.  $V(f)$  is an effective potential of the form shown in figure 1, where the repulsive core simulates the wall and the two minima at  $f=f_0$  and  $f=\infty$  represent

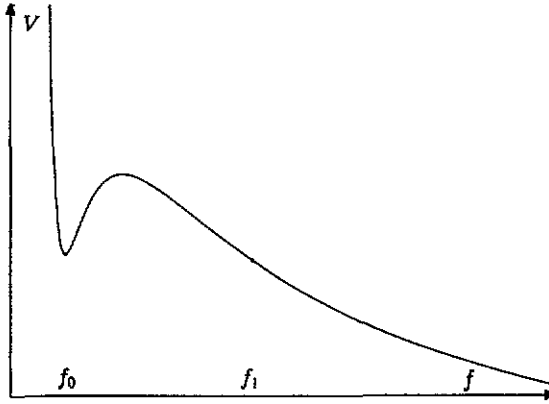


Figure 1. The interface potential  $V(f)$  with a metastable minimum at  $f=f_0$  and a stable one at  $f=\infty$ , shown for the example  $V(f)=Af^{1-\sigma}-Bf^{-\sigma}+Cf^{-1-\sigma}$  [9] with  $\sigma=3$ .

the non-wet and the wet states of the wall. By variation of temperature the relative height of the two minima can be changed and in a mean-field description the transition occurs at equal height of the minima.

Figure 1 describes the situation at some temperature  $T > T_w$  where the non-wet state of the wall is metastable. Then, under the assumption of rotational symmetry around the normal of the wall the profile of the critical droplet follows from the equation  $\delta H/\delta f(r)=0$ , i.e.

$$f''(r) + \frac{d-2}{r}f'(r) = \gamma^{-1} \partial V(f)/\partial f(r) \quad (2)$$

with the boundary conditions  $f'(r=0)=0$ ,  $f(r=\infty)=f_0$  [8]. A standard procedure [10] to solve this equation is to consider it as an equation of motion for a fictitious classical particle with 'position'  $f$  at 'time'  $r$  which moves under the influence of a potential  $-V(f)$  and a 'time'-dependent friction term. The boundary conditions then mean that the particle starts with zero velocity at a position  $f(r=0) \equiv f_1$  which needs to be determined such that for  $r \rightarrow \infty$  the particle comes to rest at  $f=f_0$ . Thus  $f_1$  is the maximum value of the particle trajectory and corresponds to the centre height of the critical droplet. Figure 2 shows the droplet profile in  $d=3$  for the potential shown in figure 1. It is convex up to a turning point and then approaches the value  $f=f_0$  in a smooth way.

From figure 1 and the mechanical analogy described above it follows that the droplet becomes large close to the wetting point  $T_w$  where the difference between the two minima of  $V(f)$  measured by the spreading coefficient  $S \equiv V(f_0) - V(\infty)$  [6] vanishes. Then  $f_1$  moves out to larger values of  $f$ , which is most easily seen in  $d=2$ , where energy conservation for the motion of the fictitious classical particle enforces  $V(f_0) = V(f_1)$ . The effect is qualitatively the same for  $d > 2$ , since then  $f_1^{(d>2)} > f_1^{(d=2)}$  [8]. On the other hand the turning point in the droplet profile in the limit  $S \rightarrow 0$  is given by the position of the local maximum of  $V(f)$  at  $f=f_2$  in figure 1. Consequently, with  $S \rightarrow 0$  we have  $f_2/f_1 \rightarrow 0$  and the non-convex part of the droplet profile is localized in a microscopic regime near the wall. Therefore the macroscopic droplet shape does not depend on the local structure of  $V(f)$  near the wall but only on the asymptotic part of  $V(f)$  for  $f \rightarrow \infty$ . For this part we assume  $V(f) = Af^{1-\sigma}$  with a Hamaker constant  $A$  and an

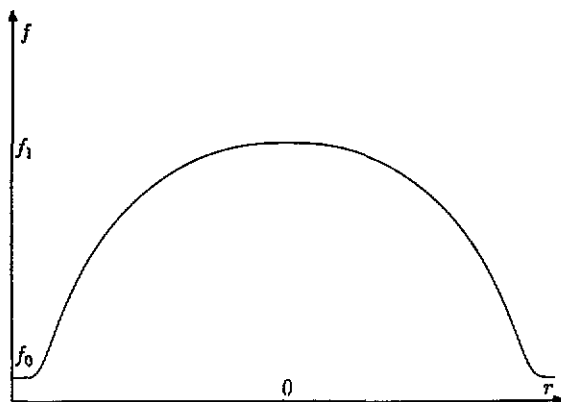


Figure 2. The profile of the critical droplet at  $d=3$  for the potential shown in figure 1.

exponent  $\sigma > 1$  which derives from the molecular interactions of the form  $W(r) \sim r^{-(d+\sigma)}$  [6]. Thus for the macroscopic critical droplet, equation (2) can be replaced by

$$f''(r) + \frac{d-2}{r} f'(r) = \frac{(1-\sigma)}{\gamma} A f^{-\sigma} \tag{3}$$

with new boundary conditions

$$f'(0) = 0 \quad f(R) = 0. \tag{4}$$

The latter condition means that the macroscopic droplet profile has been extrapolated down to  $f=0$ . The corresponding value  $r(f=0) \equiv R$  defines the critical radius of the droplet.

At  $d=2$  the friction term in (3) vanishes and energy conservation for the fictitious particle yields a first integral for our problem. The second integration can be performed analytically for  $\sigma=3$  and yields an elliptical droplet profile (see below). For  $d \geq 2$  we use the fact that the differential equation (3) is of a generalized homogeneous form. With the standard transformation [11]

$$r = R \exp \xi \quad f(r) = \exp(2\xi/(\sigma+1)) \eta(\xi) \tag{5}$$

equation (3) changes into the differential equation

$$\eta''(\xi) + (d-d_0(\sigma))\eta'(\xi) = \frac{(1-\sigma)}{\gamma} AR^2 \eta^{-\sigma} - \frac{2}{\sigma+1} \left( d-d_0(\sigma) - \frac{2}{\sigma+1} \right) \eta \tag{6}$$

where  $d_0(\sigma) \equiv (3\sigma-1)/(\sigma+1)$ . The boundary conditions (4) transform into

$$\eta(0) = 0 \quad \eta'(-\infty) = -\frac{2}{\sigma+1} \eta(-\infty). \tag{7}$$

The friction term in (6) now vanishes at  $d=d_0(\sigma)$  leading to the equation

$$\eta'' = \frac{\partial}{\partial \eta} \left[ \frac{A}{\gamma} R^2 \eta^{1-\sigma} + \frac{2}{(\sigma+1)^2} \eta^2 \right]. \quad (8)$$

This has the first integral

$$\frac{1}{2} \eta'^2 = \frac{A}{\gamma} R^2 \eta^{1-\sigma} + \frac{2}{(\sigma+1)^2} \eta^2 \quad (9)$$

where the boundary conditions (7) have been used and the fact that a finite value of  $f(0)$  requires  $\eta(-\infty) = \infty$ . Separation of variables leads to the second integral

$$-\frac{1}{\sqrt{2}} \int_0^n dy \left[ \frac{AR^2}{\gamma} y^{1-\sigma} + \frac{2}{(\sigma+1)^2} y^2 \right]^{-1/2} = \ln \left( \frac{r}{R} \right) \quad (10)$$

which can be performed exactly for all values of  $\sigma$ . In terms of the old variables (5) we finally obtain

$$\left( \frac{f}{F} \right)^{(\sigma+1)/2} + \left( \frac{r}{R} \right)^2 = 1 \quad (11)$$

for the droplet profile where  $F \equiv [AR^2(\sigma+1)^2/(8\gamma)]^{1/(\sigma+1)}$  is the central height of the droplet. We mention that close to the wetting transition point the droplet height and radius diverge according to  $F \sim S^{-2/(\sigma+1)}$ ,  $R \sim S^{-1}$  [12]. Equation (11) explicitly shows how the macroscopic shape of the droplet depends on the range of molecular interactions via the exponent  $\sigma$  and that for  $\sigma=3$  the droplet has exactly the shape of an ellipsoid, as stated before.

The simple expression (11) for the droplet profile is valid only in dimension  $d=d_0(\sigma)$  which is just the boundary dimension between the weak and strong fluctuation regimes for wetting, and has also been conjectured to be the lower critical dimension for first-order wetting transitions [13]. More recent renormalization group studies, however, seem to allow the existence of first-order wetting transitions below  $d_0(\sigma)$  in some range of  $\sigma$  [14].

Finally, for the case of short-range forces  $V(f) = A \exp -\beta f$  [9] the substitutions  $r = R \exp \xi$ ,  $\beta f(r) = 2\xi + \eta(\xi)$  transform the droplet equation into  $\eta'' + (d-3)\eta' + 2(d-3) = -(AR^2\beta^2/\gamma) \exp(-\eta)$ . At  $d=d_0(\infty)=3$  this again can be solved by quadrature, however, with no simple analytical result for the droplet profile.

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