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ADDENDUM

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Abstract. In a first-order wetting transition it is possible to overheat a microscopic layer from below to above the wetting temperature T_w, and to undercool a macroscopic layer from above to below T_w. In both cases the transition to stable equilibrium occurs by formation and growth of supercritical nuclei. The critical nuclei for overheating are droplets on the wall of the system and for undercooling they are dents in the macroscopic layer. A recent calculation of the critical droplet in a special dimension d_0 is now supplemented by the calculation of the critical dent for dewetting. Although the analytic expressions for the profiles are closely related, the nuclei above T_w are finite whereas they are infinitely large below T_w. The latter is to be expected since the system is infinitesimally close to coexistence of wet and non-wet states at all temperatures $T<T_w$.

In a recent note [1] we determined the macroscopic shape of a critcal droplet on a wall for a first-order wetting transition in the boundary dimension d_0 between the weak and strong fluctuation regimes. The calculation was based on the model Hamiltonian [2]

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

where $f(x)$ is the local thickness of the wetting layer on the $(d-1)$–dimensional wall, γ is the surface tension of the wetting fluid, and $V(f)$ is an effective potential of the form shown in figure 1. The regions $T<T_w$ and $T>T_w$ correspond to $V(f_0)<0$ and $V(f_0)>0$, respectively.

Assuming rotational symmetry, the macroscopic shapes of the critical nuclei are determined by the saddle point equation

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

where the asymptotic form $V(f)=Af^{1-\sigma}$ for $f\gg f_0$ has been used. In terms of the radial size R of the nuclei at the wall, the boundary conditions are $f(R)=0, f'(0)=0$ for the critical droplet and $f(R)=0, f'(\infty)=0$ for the critical dent.

In [1] we have presented the solution for the critical droplet in dimension $d=d_0(\sigma)\equiv(3\sigma-1)/(\sigma+1)$ for $\sigma>3$, corresponding to $d>2$. Using the same methods we now have derived the shape of the critical dent (see figure 2), again in dimension $d_0(\sigma)>2$. Both results can be summarized in the surprisingly simple form

$$\left(\frac{r}{R}\right)^2\pm\left(\frac{f}{F}\right)^{(\sigma+1)/2}=1 \tag{3}$$

with $F\equiv[AR^2(\sigma+1)^2/(8\gamma)]^{1/(\sigma+1)}$. The upper sign in (3) corresponds to the critical

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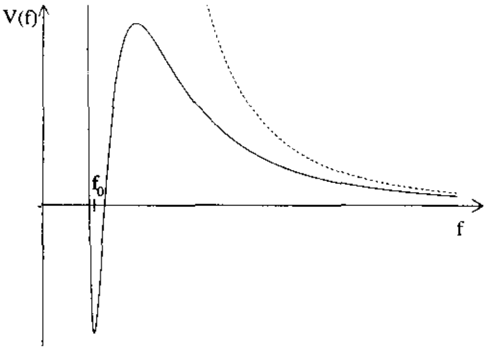

Figure 1. The interface potential $V(f)$ with a stable minimum at $f=f_0$ and a metastable one at $f=\infty$, shown for the example $V(f)=Af^{1-\sigma}-Bf^{-\sigma}+Cf^{-1-\sigma}$ [2] with $\sigma=4$. The dashed line indicates the asymptotic part of the potential $V(f)=Af^{1-\sigma}$.

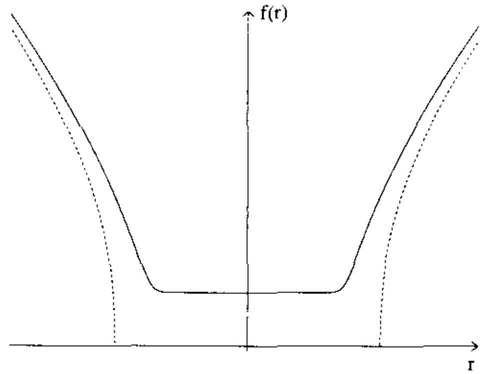

Figure 2. The profile of the critical dent in $d=d_0$ ($\sigma=4$) for the full potential of figure 1. Note that the minimum of the profile is slightly above the equilibrium value f_0. The dashed line indicates the macroscopic profile given by equation (3).

droplet where F measures its size orthogonal to the wall. With the lower sign equation (3) describes the critical dent where $F=f(\sqrt{2}R)$.

For both types of critical nuclei, R and consequently also F, diverge in the limit $T\rightarrow T_w$. This follows from the interpretation of the saddle point equation with the full potential $V(f)$ as an equation of motion for a particle with position f moving in time r in the potential $-V(f)$ [3]. When T_w is approached the particle stays an increasingly long time close to $f=F$ for the droplet and close to $f=f_0$ for the dent.

In conclusion, the size of the critical droplet is finite above T_w and diverges for $T\rightarrow T_w$ whereas the critical dent is infinitely large for all $T\leqslant T_w$. This is to be expected since in the region $T<T_w$ the system is infinitesimally close to a first-order coexistence line between wet and non-wet surface states. Correspondingly, the excess free energy of the critical droplet $E\equiv H[f]-H[f_0]$ goes to infinity as T approaches T_w from above. On the other hand the excess free energy for the critical dent $E\equiv H[f]$ is infinite at any temperature $T\leqslant T_w$. As pointed out recently [4], we expect this to be the case for all d and σ for which a first-order wetting transition exists. This expectation is supported by the recently observed [5] unusually long lifetime of undercooled wetting films.

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