# Absence of Critical Wetting in Systems with Long-Range Forces

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Study of a solid-on-solid model within the Migdal approximation leads the authors to conclude that the phenomenon of critical wetting cannot occur in the presence of long-range, van der Waals forces.

The wetting transition has been the subject of much attention recently.[1-12] It occurs in many different physical systems including the particularly simple one of a gas enclosed in a cell. In general there will be a film of liquid on the walls of the cell, and the behavior of interest concerns the thickness $l$ of this film as the pressure of the bulk gas is increased and approaches that of bulk gas-liquid coexistence. If $l$ increases without limit as coexistence is approached, the walls of the cell are said to be wet, whereas if $l$ remains finite at coexistence, they are said to be not wet or partially wet. The transition which occurs with changing temperature between these two behaviors *at* coexistence is the wetting transition. It can be first order or continuous.[3-7]

It is the latter case, denoted critical wetting, which has received most of the theoretical attention. In particular the divergence of $l$ as the critical wetting temperature is approached and the concomitant thermodynamic singularities have been calculated for the case in which all interactions within the system are of short range.[8,9] In most physical systems, however, the interactions are of the long-range van der Waals nature. It is of interest, therefore, to determine the effect of such forces on critical wetting behavior. *In this note we present strong evidence that critical wetting cannot take place in the presence of such forces.*

That long-range forces could significantly alter wetting behavior was suggested by Pandit, Schick, and Wortis.[1] They argued that the surface free energy of a system with a liquid film of thickness $l$ consists of two terms,

$$f(T,l) = V(l) - TS(l), \qquad (1)$$

with $f(T,l)$ minimized by the equilibrium $l(T)$ (note that Boltzmann's constant is set to unity). The first term is an energy which, for large $l$, must increase monotonically with $l$ if critical wetting is to be possible. This term favors a finite $l(T)$. The second term contains the entropy which increases with $l$ because of the larger number of surface fluctuations that are permitted. This favors an infinite $l(T)$, and the competition between the two brings about the wetting transition. Pandit, Schick, and Wortis argued that below the roughening temperature[13] $T_R$ of the high-density bulk phase, the entropy $S(l)$ would approach its limiting value exponentially with $l$. This form has been confirmed by field-theoretic models of wetting.[8,9] Such a dependence could dominate a short-range interaction and lead to wetting, but it could not overcome a long-range interaction so that wetting would be prevented by such forces. They further surmised that above $T_R$ the approach of the entropy to its asymptotic value would change from exponential to power law, a form that could bring about critical wetting. Our results indicate that this is not correct.

We have investigated the phenomenon of critical wetting within the context of a two-dimensional solid-on-solid model which represents the interface between the liquid film and bulk gas.[14] The Hamiltonian of the model is

$$H = \sum_{\langle ij \rangle} |h_i - h_j| + \sum_i V(h_i), \qquad (2)$$

where the $h_i$ are nonnegative integers and the first sum is over nearest-neighbor pairs on a triangular lattice. It should be noted that $V(h_i)$ is the interaction between the substrate and an *interface* a distance $h_i$ above it at site $i$. This in-

teraction can be related to the difference between *attractive* adatom-substrate and adatom-adatom potentials. In particular, when the former dominates (strong substrate), $V(h_i)$ is repulsive; when the latter dominates (intermediate substrate), $V(h_i)$ is attractive. It is the latter case which we are primarily concerned with. We have employed real-space renormalization-group methods within a simple Migdal approximation as described elsewhere.[10] The roughening temperature, as defined below, is $T_R \simeq 1.9$.

We first discuss our results at bulk gas-liquid coexistence for short-range interactions of the form

$$V_{SR}(h) = \begin{cases} A[1 - \exp(-h/\lambda)] + B, & h > 0, \\ 0, & h = 0. \end{cases} \tag{3}$$

When $A$ is negative, a wetting transition occurs only for $A + B > 0$; otherwise the system is wet already at zero temperature. The transition in this case is always first order, as expected for such an interaction with a potential barrier.[15] Critical wetting, if it occurs at all, can occur only with $A$ positive. In this case the value of $B$ does not affect the results qualitatively, and so we report them for $B = 0$. For values of $A$ that are smaller than a value $A_T(\lambda)$, we observe critical wetting, while for $A$ greater than this value we find a first-order wetting transition. Figure 1 shows three cases with $\lambda = 0.5$. Critical wetting occurs with $A = 0.25$ and first-order wetting for $A = 1$ and 2. The dependence of the average height
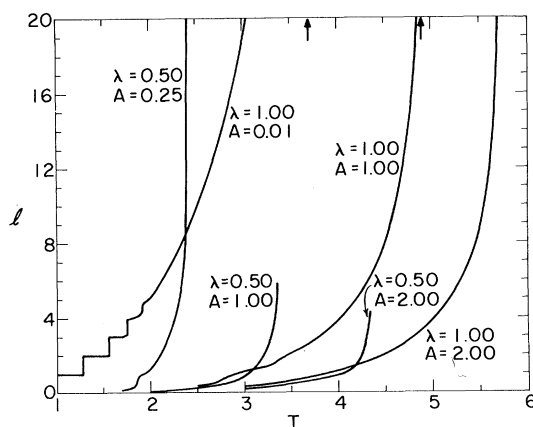


FIG. 1. Film thickness vs temperature shown for the short-range potential of Eq. (3) with amplitude $A$ and range $\lambda$. Four examples of critical wetting are shown. Arrows indicate the wetting temperature (assuming logarithmic divergence of $l$) where it is not obvious. In the two first-order transitions the jump in $l$ is deleted.

$\langle h_i \rangle \equiv l$ on temperature for $A \lesssim A_T(\lambda)$ is, from our data, well fitted by $l \sim - \ln(T_W - T)$, where $T_W$ is the critical-wetting temperature. This form is predicted by almost all theoretical work.[8,9,11] For $A \ll A_T(\lambda)$, a case shown in Fig. 1 with $\lambda = 1$, we find that the parameters in a fit to our data are ill determined because the amplitude of the singularity increases with decreasing $A$. Thus the asymptotic behavior sets in at values of $l$ which are quite large and thus difficult to handle computationally. Figure 1 also shows first-order layering transitions occurring at low temperatures in a system which undergoes critical wetting. We find that the critical-wetting temperature decreases with decreasing potential strength $A$, but that it is always greater than some temperature which depends on the range of the potential. This condition, which can be written

$$\xi(T_W) > \lambda \tag{4}$$

with $\xi$ a monotonically increasing function of $T$, is also obtained within mean-field theory.[5-7]

We now consider long-range interactions of the form

$$V_{LR}(h) = \begin{cases} -A/h^\sigma + B, & h > 0, \\ 0, & h = 0. \end{cases} \tag{5}$$

Two cases with an obvious physical interpretation are $\sigma = 2$ and $\sigma = -1$. A system with van der Waals interactions which is at gas-liquid (solid) coexistence corresponds to $\sigma = 2$, because $V_{LR}$ is the energy of an entire column of height $h$. The case $\sigma = -1$ refers to a system off coexistence in which the net result of the interparticle interactions is a hard wall only. When $A$ is negative, the wetting transition occurs only for $B > 0$ and is then always first order as expected, just as for short-range potentials.[15] As above, we report results only for $B = 0$ as the value of $B$ does not affect our results qualitatively. As in the case of short-range interactions, the behavior of $l$ with $T$ depends upon the potential strength $A$, being a continuous function of $T$ for small $A$ while exhibiting a finite jump for large $A$. The crucial difference is that with long-range forces we find that the thickness $l$ is finite for all $T$ and thus there is no wetting, critical or first order. In particular, for sufficiently large $l$, the thickness varies as

$$l = - \xi(T) \ln A / T + (\sigma + 1) \xi(T) \ln(- \ln A / T), \tag{6}$$

where $\xi(T)$, the same function as appears in Eq. (4), is almost linear in $T$ but is independent of the power $\sigma$. The dependence on $\ln A$ is shown in

Fig. 2 together with the function $\xi(T)$. The assumption of a free energy as a function of film thickness of the form of Eq. (1), with $S(l)$ depending exponentially on $l$ with range $\xi(T)$ also for $T > T_R$, immediately leads to Eq. (4) for short-range potentials and to Eq. (6) for long-range potentials. We note that the behavior of $l$ embodied in the latter equation is consistent with the mean-field-theory results for a chemical potential term $V_{LR}(h) = -|\Delta\mu|h$ [i.e., $\sigma = -1$ in Eq. (5)], which is $l \simeq -\xi_B \ln|\Delta\mu|$. Here $\xi_B$ is the bulk correlation length and sets the scale of the intrinsic width of the interface. In the solid-on-solid model in which unit deviations of the interface $h_i - h_j$ cost a fixed energy, the width depends linearly on the temperature. Because our result shows that fluctuations of the interface are not sufficient to bring about wetting when in competition with a long-range attractive force, one would expect mean-field theory, which ignores such fluctuations, to predict a similar effect for any algebraic attraction. The results of two such calculations are ambiguous, however, with one study[7] suggesting a conclusion in agreement with ours and another in explicit disagreement.[5]

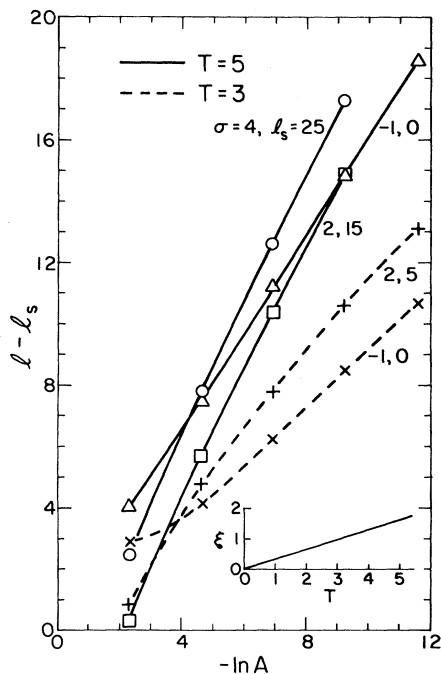That long-range forces can prevent wetting



FIG. 2. Film thickness as a function of amplitude $A$ of the long-range potential of Eq. (5) which varies algebraically with power $-\sigma$. Data points are calculated, while solid and dashed lines are from Eq. (6) with $\xi$ given in the inset.

should not, in itself, be surprising. The well-known correspondence between the statistical mechanics of the one-dimensional interface of a two-dimensional bulk and the quantum mechanics of a particle in a well[14] combined with the observation that potential wells $V(z)$ which fall off more slowly than $z^{-2}$ have an infinite number of bound states[16] shows that wetting is prevented by such potentials. Wetting does occur for algebraic potentials which fall off more rapidly.[12] What is surprising is that in three bulk dimensions critical wetting is prevented by an algebraic potential of *any* power. Presumably this stems from the fact that fluctuations in the two-dimensional interface are much weaker than those in the one-dimensional interface, so that the former is more easily bound to the substrate.

It is clearly necessary that our Migdal approximation adequately describe the effects of such fluctuations. As these fluctuations bring about the roughening transition in the infinitely thick film, we have checked that the method is adequate to describe the effects of roughening for our purposes. There is no fixed line to describe the roughening transition within the Migdal approximation[17] but only an approximate one to which renormalization flows are initially attracted. These flows are essentially stationary for a large number of renormalization steps which depend on the temperature, but eventually they go to a trivial sink. We have verified that, for the temperatures $T > T_R$ reported above, the trivial fixed point does not influence our results because the calculation of the thermodynamic functions to machine accuracy converges while the flows are still essentially stationary at the pseudo fixed line. In fact, the lowest temperature for which the trivial fixed point does not influence the thermodynamic functions to within machine accuracy is taken to be the definition of $T_R$ within the Migdal approximation. It is a definition rather insensitive to the criterion of machine accuracy.

The results above for $T > T_R$ are also obtained from a low-temperature series expansion,[15] again indicating that roughening plays no role in wetting phenomena. At low temperatures the increase in the film thickness proceeds by a series of first-order layer transitions.[1] The location of these transitions as a function of interaction strength (or chemical potential) is obtained by equating the free energies obtained from formal expansions around layers $h$ and $h + 1$ up to the order at which they first differ as a result of the presence of the hard-wall part of the substrate

potential. For short-range potentials we find, just as at high temperatures, a divergence of the thickness $l$ with temperature provided that Eq. (4) is satisfied now with $\xi(T)$ given by $T/q$ to lowest order, where $q$ is the coordination number of the two-dimensional lattice. For long-range potentials we find, again as at high temperatures, no divergence of $l$ with temperature and a dependence of $l$ on $T$ as given in Eq. (6) with $\xi(T) = T/q$.

In conclusion, we find that the solid-on-solid model system of Eq. (2) does not exhibit critical wetting at any temperature when the forces in the system are of long range. We expect that this conclusion is applicable to adsorption systems at two-phase coexistence[18] except at isolated critical points. It most likely applies to binary liquid mixtures as well, although the fact that the "substrate" in this case itself is rough could conceivably affect results. We are currently investigating such systems.

The calculations reported above were carried out on a VAX 11/780 with use of double-precision arithmetic. A cutoff $h_{max}$ was introduced to restrict the variables $h_i$ of the solid-on-solid model to the range $0 \leq h_i < h_{max}$. This produces a finite Hamiltonian space, invariant under Migdal renormalization, of $\frac{1}{2}h_{max}(h_{max}+1)$ nearest-neighbor couplings. The film thickness $l$ was obtained by numerical differentiation of the free energy. Calculations were repeated for increasing values of $h_{max}$ unitl, to the required accuracy, $l$ was independent of this cutoff. This usually occurred for $h_{max} \lesssim 3l$.

During the preparation of this manuscript, we received a preprint by Brézin, Halperin, and Leibler.[19] Although they do not explicitly treat fluctuations in the presence of long-range forces, they suggest that such forces will suppress wetting. This agrees with our work in which the fluctuations are treated within the presence of the potential.

We are pleased to acknowledge instructive conversations with A. N. Berker, C. Ebner, and M. Wortis. This work was supported in part by the National Science Foundation under Grant No. DMR-79-20785.

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