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Surface melting and the surface phase diagram

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We solve a spin-1 model at zero temperature which exhibits the analogue of surface melting as its triple point is approached, and study the effect of this phenomenon on the surface phase diagram of the system enclosed by walls. We note that when a thick film of the "solid" phase can adsorb on the walls, it is reasonable that it will do so all the way to the triple point. In this case, the surface phase diagram exhibits two distinct series of layering transitions in the region of the bulk "gas" phase. One of these is the well-known series by which the solid grows; the other is seen to be intimately related to the layering transitions associated with surface melting and is, therefore, the direct effect of such melting on the surface diagram. A single series of layering transitions appears in the region of the bulk "liquid" phase, and none in the solid. Effects of finite temperature and roughening are discussed and a schematic phase diagram proposed for the finite-temperature system, one which may be applicable to CF_4 and C_2H_4 adsorbed on graphite. When a thick film of the solid cannot adsorb on the walls, surface melting does not affect the surface phase diagram off of coexistence.

I. INTRODUCTION

Surface melting, the melting of a solid from its surface inward, is a particular case of interfacial wetting, one in which a film of liquid is nucleated at the solid/gas interface and grows in thickness without limit as the triple point is approached.[1] Simply because it is a wetting phenomenon, much is known about it.[2] In particular, it is possible for the melting of the solid, proceeding from the gas solid interface, to take place via a series of layer transitions.[2] The surface phase diagram will reflect this in the presence of a series of singularities along the bulk gas/solid coexistence line. If the system is now enclosed by a wall upon which a thick film of solid can be grown, we further expect that layer melting transitions *at* bulk gas/solid coexistence will be manifest in the region of the surface phase diagram *off* this coexistence corresponding to the bulk gas phase. Thus, a series of transition lines at which layers of adsorbed liquid appear as the bulk gas/liquid transition is approached may be evident. This series of transitions is distinct from the well studied series[2–5] by which the adsorbed solid grows as the bulk gas/solid transition is neared. The relation between these two series of transitions in the surface phase diagram is not obvious.

Clearly, in order to observe effects of surface melting off of coexistence, it must be possible to grow a thick film of solid upon the walls; that is, the solid must wet the wall/gas interface over some interval of temperature up to T_t, the triple temperature.[6] We shall assume this to be the case, and also that the liquid wets the wall/gas interface throughout an interval of temperature above T_t. For the former to occur, it is not sufficient that the solid be attracted to the substrate more strongly than the liquid. This is because the interfacial tension between solid and gas may be sufficiently larger than that between liquid and gas so as to favor the presence of a thick liquid film even at temperatures somewhat below T_t. As a consequence, the solid no longer wets the substrate near the triple temperature.[7]

This scenario does not occur, however, if the bulk system undergoes surface melting, as postulated, and if the solid wets the wall/*liquid* interface. In this case, a compound film is formed between the wall and gas as T_t is approached. The film consists of a thick layer of liquid on top of a thick layer of solid; thus the sequence is wall/solid/liquid/gas.[7] The validity of these statements is easily seen as follows. The assumption that the system undergoes surface melting implies that at the triple point,

$$\sigma_{sg}=\sigma_{sl}+\sigma_{lg} \ , \tag{1}$$

where the term on the left is the surface tension between solid and gas phases, and the two on the right are the surface tensions between solid and liquid, and between liquid and gas. The additional assumption that the solid wets the wall/liquid interface implies that

$$\sigma_{wl}=\sigma_{ws}+\sigma_{sl} \ , \tag{2}$$

where the subscript w stands for "wall." We now suppose that, contrary to the desired result, the solid wets the wall/gas interface far from the triple point but undergoes a dewetting transition to a thick but finite film of liquid as T_t is approached. It does so in order to take advantage of the lower surface energy of the liquid which is expressed in the inequality

$$\sigma_{ws}+\sigma_{sg}>\sigma_{wl}+\sigma_{lg} \ . \tag{3}$$

It is understood that the surface energies on the right are continuations below T_t of the thermodynamic functions defined at and above T_t. Upon substitution of Eq. (1) (surface melting) into inequality (3) and cancellation of the common factor of σ_{lg}, we arrive at the inequality

$$\sigma_{ws}+\sigma_{sl}>\sigma_{wl} \ ,$$

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which violates the assumption that the solid wets the wall/liquid interface, Eq. (2). Thus, the supposition that the solid undergoes a dewetting transition is false. Furthermore, at the triple point,

$$\sigma_{wg} = \sigma_{ws} + \sigma_{sg} \ ,$$

because the solid wets the wall/gas interface all the way to T_t. This becomes, with the assumption of surface melting Eq. (1),

$$\sigma_{wg} = \sigma_{ws} + \sigma_{sl} + \sigma_{lg} \ ,$$

which shows that the film is compound as stated.

We note that both of the assumptions embodied in Eqs. (1) and (2) are reasonable. First, in a one-density theory, one expects surface melting to occur whenever the density of the liquid is intermediate between that of solid and vapor,[2,8] a situation encountered in almost all cases (the notable exception being the system of water). Second, a necessary condition in such theories that the solid wet the wall/liquid interface is identical to the condition that the solid wet the wall/gas interface.[9] In sum, if we have a system in which the solid wets the wall/gas interface below the triple temperature, it is reasonable that it will continue to do so all the way to the triple temperature.[10] Above this temperature, the solid will wet the wall/liquid interface. As a consequence, in the bulk liquid phase, we also expect, in the absence of roughening,[3,4] a series of layer transitions in which the solid grows as the bulk solid/liquid coexistence line is approached.[11] In the next section, we will determine the surface phase diagram of a model system which has a triple point and which undergoes the analog of a surface melting transition. It has the further advantage of being exactly solvable. It is a Blume-Emery-Griffiths model subject to surface fields, and at zero temperature. The phase diagram, Fig. 1, displays two series of layer transitions in the bulk "gas" phase, and one series of layer transitions in the bulk "liquid" phase. In the final section, we briefly discuss the effects of temperature and of roughening and propose a plausible phase diagram. We believe that it has application to the systems of CF_4 adsorbed on graphite[12] and to C_2H_4 adsorbed on graphite.[13]

II. CALCULATIONS ON THE MODEL SYSTEM

We consider a spin-1 system on a cubic lattice of unit lattice constant which is governed by the Blume-Emery-Griffiths Hamiltonian[14]

$$\mathcal{H} = -\tfrac{1}{2}\sum_{i,j}\left[J_{ij}S_iS_j + K_{ij}S_i^2S_j^2 + C_{ij}(S_iS_j^2 + S_i^2S_j)\right] - \sum_i (HS_i - \Delta S_i^2) \ ,$$

where each spin variable $S_i = +1, -1, 0$. This model, with ferromagnetic interactions, has three ground states in which the spins are in one of the three configurations, and these three states meet at a triple point. Phase transitions between these states occur at zero temperature by varying the two bulk fields H and Δ just as those between the three phases in bulk helium at zero temperature occur by varying the single field of pressure. The additional freedom of a second field, however, permits the existence of a triple point in the model system. We will arrange the interactions so that the $+, -$, and 0 phases will play roles analogous to solid, liquid, and gas respectively.

The bulk phase diagram at zero temperature is easily obtained. Let

$$J_n \equiv \sum_{j \subset n} J_{ij} \ ,$$

where the sum is over all sites j in the plane with z coordinates which differ from the z coordinate of the site i by n, with n a positive or negative integer. Similar definitions apply to K_n and C_n. The energy per spin of the three ground states with all spins in configuration $+1, -1, 0$ are then

$$e_+(H,\Delta) = -\tfrac{1}{2} \sum_{-\infty < n < \infty} (J_n + K_n + 2C_n) - H + \Delta \ ,$$

$$e_-(H,\Delta) = -\tfrac{1}{2} \sum_{-\infty < n < \infty} (J_n + K_n - 2C_n) + H + \Delta \ ,$$

$$e_0(H,\Delta) = 0 \ .$$

Equating these three energies pairwise, we obtain the phase boundary between the + and 0 phases

$$H_{+0} = \Delta - \tfrac{1}{2} \sum_{-\infty < n < \infty} (J_n + K_n + 2C_n) \ ,$$

between the − and 0 phases

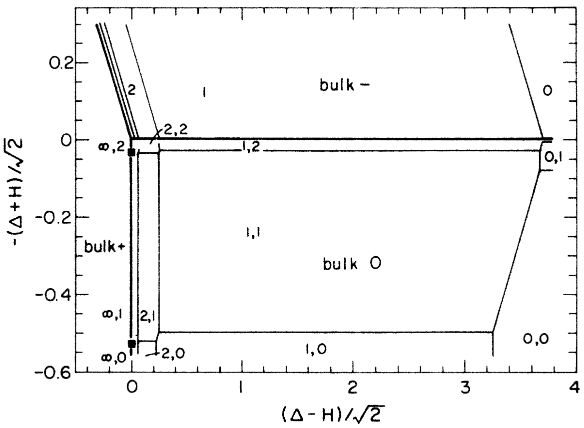

FIG. 1. Calculated surface phase diagram of the model system at zero temperature in the space of the two chemical potentials Δ and H which, for simplicity, have been measured with respect to their triple-point values. Bold lines indicate first-order boundaries between bulk $+, -$, and 0 phases. Surface phases in the bulk 0 regime are compound films denoted by two integers; the first is the number of layers of + phase adsorbed on the wall, the second is the number of layers of − phase adsorbed on top of the + layers. Solid squares on the +/0 boundary indicate the layer transitions associated with surface melting which separate, for example, regions of one layer of − at the +/0 interface (denoted ∞,1) from two such layers (∞,2). Surface phases in the bulk − regime are specified by one integer; the number of + layers adsorbed on the wall. Note that the + phase wets the wall/− interface.

$$H_{-0}=-\Delta+\tfrac{1}{2}\sum_{-\infty<n<\infty}(J_n+K_n-2C_n)\ ,$$

and between the + and − phase

$$H_{+-}=-\tfrac{1}{2}\sum_{-\infty<n<\infty}2C_n\ . \tag{4}$$

Thus the triple point is located at

$$H_t=-\tfrac{1}{2}\sum_{-\infty<n<\infty}2C_n\ ,$$

$$\Delta_t=\tfrac{1}{2}\sum_{-\infty<n<\infty}(J_n+K_n)\ .$$

The interfacial tensions between these bulk phases are easily calculated. To obtain the interfacial tension σ_{+-} between the bulk + and − phases, we calculate the excess surface energy per unit area, $\Omega_{+-}(l_0)$ of a configuration consisting of a slab of the 0 phase, of thickness l_0, between semi-infinite amounts of + and − phases. The interfacial tension is the minimum of this excess surface energy. The calculation is carried out for H and Δ on the +/− phase boundary given by Eq. (4). We find directly

$$\Omega_{+-}(l_0)=-l_0e_+ +2\sum_1^{\infty}nJ_n-\sum_1^{l_0}n(J_n-K_n)-l_0\sum_{l_0+1}^{\infty}(J_n-K_n),\quad l_0>0\ ,$$

$$=2\sum_1^{\infty}nJ_n,\quad l_0=0\ .$$

We will choose interactions such that

$$J_n-K_n<0 \tag{5}$$

for all n, which is sufficient to guarantee that $l_0=0$, so that

$$\sigma_{+-}=\Omega_{+-}(0)$$

$$=2\sum_1^{\infty}nJ_n\ .$$

Similarly, the excess surface energy of semi-infinite amounts of the − and 0 phases separated by a slab of thickness l_+ along their phase boundary is

$$\Omega_{-0}(l_+)=l_+e_+ +\tfrac{1}{2}\sum_1^{\infty}n(J_n+K_n-2C_n)+2l_+\sum_{l_++1}^{\infty}(J_n+C_n)+2\sum_1^{l_+}n(J_n+C_n)\quad l_+>1$$

$$=\tfrac{1}{2}\sum_1^{\infty}n(J_n+K_n-2C_n)\quad l_+=0\ .$$

We will choose interactions such that

$$J_n+C_n>0\ , \tag{6}$$

for all n which guarantees that $l_+=0$ so that

$$\sigma_{-0}=\Omega_{-0}(0)$$

$$=\tfrac{1}{2}\sum_1^{\infty}n(J_n+K_n-2C_n)\ .$$

Stability of this interface is guaranteed by choosing

$$J_n+K_n-2C_n>0\ ,$$

for all n. Finally, we consider the excess surface energy per unit area between semi-infinite amounts of + and 0 phases separated by a slab of − phase of width l_-;

$$\Omega_{+0}(l_-)=l_-e_-+\sigma_{+-}+\sigma_{-0}-2\sum_{l_-+1}^{\infty}(n-l_-)(J_n-C_n)\ .$$

We want to arrange that the − phase wets the interface between + and 0 phases as the triple point is approached along the +/0 coexistence boundary. This is the analog of surface melting in which the +, −, and 0 phases play the roles of solid, liquid, and gas respectively. To bring this about, it is sufficient to choose

$$J_n-C_n<0 \tag{7}$$

for all n. In this case, the value of l_- which minimizes the excess surface energy increases without limit as the triple point is approached [and $e_-(H,\Delta)$ decreases]. At the triple point,

$$\sigma_{+0}(H_t,\Delta_t)=\Omega_{+0}(\infty)$$

$$=\sigma_{+-}(H_t,\Delta_t)+\sigma_{-0}(H_t,\Delta_t)\ .$$

Now that all interfacial tensions have been obtained, it is necessary to calculate the surface tensions between the wall and the various bulk phases. The interactions with the wall, which is taken to be in the plane $z=0$, are given by the surface Hamiltonian

$$\mathcal{H}_s=-\sum_1^{\infty}(h_nS_n-\delta_nS_n^2)\ ,$$

where n is the z coordinate of a lattice site. Note that there are two surface fields just as there must be in the system of liquid, solid, and gas. One field, δ, differentiates between the gas and the other two phases. This is like a field which couples to the density. The other field, h, differentiates between the solid and liquid. Again there is such a field in the physical system as evidenced by the fact that the surface energies of ice and water, for example, against a wall are not expected to be identical even when they have the same density. As we want to arrange that both the "solid" and "liquid" phases wet the wall/"gas" interface, the field δ will be negative. As we want the "solid" to wet the wall/"liquid" interface, the field h will be positive.

We first consider the excess surface energy between the wall and the + phase. We shall require that no amount of the 0 or − phase intrude between the + phase and the wall. For the first, it is sufficient to require that

$$h_n>\delta_n\ ,$$

for all n, and for the second that

$$h_n > \sum_{n}^{\infty} (C_m - J_m) ,$$

for all n, which with Eq. (7), implies

$$h_n > 0 , \tag{8}$$

for all n. This is as we expected. The surface energy is

$$\sigma_{w+} = \sum_{1}^{\infty} \left[\frac{n}{2}(J_n + K_n + 2C_n) - h_n + \delta_n \right] .$$

Next we consider the interface between the wall and the $-$ phase. We shall require that no amount of 0 phase intrude, for which

$$-\delta_n > h_n , \tag{9}$$

for all n is sufficient. We also require that the $+$ phase wet the wall/$-$ interface. The excess surface energy per unit area of a slab of $+$ phase of thickness l_+ situated between the wall and bulk $-$ phase is

$$\Omega_{w-}(l_+) = l_+(e_+ - e_-) + \sigma_{w+} + \sigma_{+-} - 2 \sum_{l_+ + 1}^{\infty} [(n - l_+)(J_n + C_n) - h_n] . \tag{10}$$

In order that the $+$ phase wet the wall/$-$ interface, it is sufficient to require

$$h_n > \sum_{n}^{\infty} (J_m + C_m) , \tag{11}$$

for all n, which, with the inequality (6), is more stringent than inequality (8).

Finally, we calculate the interfacial energy which is of most interest, that between the wall and the 0 phase. In general there will be a compound film which consists of l_+ layers of $+$ phase next to the wall, then l_- layers of $-$ phase on top of that, and then the bulk 0 phase. The energy of the compound film is found to be

$$\Omega_{w0}(l_+, l_-) = l_+ e_+ + l_- e_- + \sigma_{w+} + \sigma_{+-} + \sigma_{-0} - 2 \sum_{l_+ + 1}^{\infty} [(n - l_+)(J_n + C_n) - h_n] - 2 \sum_{l_- + 1}^{\infty} (n - l_-)(J_n - C_n) + \sum_{l_+ + l_- + 1}^{\infty} [(n - l_+ - l_-)(J_n - K_n) - h_n - \delta_n] . \tag{12}$$

In order to ensure that the $-$ phase wets the wall/0 interface far from the triple point where $l_+ = 0$, it suffices to require

$$0 > \delta_n + h_n + \sum_{n}^{\infty} (J_m + K_m - 2C_m) ,$$

for all n. Similarly, to ensure that the $+$ phase wets the wall/0 interface far from the triple point where $l_- = 0$,

$$0 > \delta_n - h_n + \sum_{n}^{\infty} (J_m + K_m + 2C_m)$$

is sufficient. As noted previously, this does not guarantee that the $+$ phase wets the wall/0 interface up to the triple point; this requires that the $+$ phase wet the wall/$-$ interface above the triple point, which is guaranteed by the inequality (11).

The surface phase diagram is now obtained by minimizing the excess surface energy $\Omega_{w-}(l_+)$ of Eq. (10) with respect to l_+ when the bulk is in the $-$ phase, and $\Omega_{w0}(l_+, l_-)$ of Eq. (12) with respect to both l_+ and l_- when the system is in the bulk 0 phase. With the interactions chosen as noted above, the surface energy between the wall and 0 phase at the triple point is given by

$$\sigma_{w0}(H_t, \Delta_t) = \Omega_{w0}(l_+ \to \infty, l_- \to \infty) = \sigma_{w+}(H_t, \Delta_t) + \sigma_{+-}(H_t, \Delta_t) + \sigma_{-0}(H_t, \Delta_t) ,$$

which shows that a compound film of $-$ phase on top of $+$ phase is adsorbed on the wall below the bulk 0 phase.

The interactions we have chosen are long-ranged and of the form

$$J_{ij} = J / r_{ij}^6 ,$$
$$K_{ij} = K / r_{ij}^6 ,$$
$$C_{ij} = C / r_{ij}^6 ,$$

where r_{ij} is the distance between the sites i and j. With such a choice, $J_n = JF_n$, $K_n = KF_n$, and $C_n = CF_n$, with

$$F_n \equiv \sum_{j \subset n} 1 / r_{ij}^6 ,$$

where the sum is over all sites j whose z coordinates differ from the z coordinate of the site i by n, an integer. We have taken $J = 1$, $K = 1.5$, and $C = 1.2$, so that the inequalities (5), (6), and (7) are satisfied. For the interactions with the wall, we have chosen $h_n = hG_n$, and $\delta_n = \delta G_n$, with $h = 3.6$, $\delta = -3.76$ and

$$G_n \equiv \sum_{m=n}^{\infty} F_m .$$

Inequalities (8) and (9) are fulfilled.

The surface phase diagram, obtained numerically, is shown in Fig. 1 in the space of the two chemical potentials Δ and H. The heavy lines denote the bulk phase boundaries. In the region of the phase diagram occupied by the bulk $-$ phase, the surface phases are denoted by a single integer which gives the number of layers of $+$ phase between the wall and the bulk $-$ phase. These phases are separated by a series of layer transitions. The number of layers increases as the $+/-$ phase boundary is approached because the $+$ phase wets the wall interface. (Of course only a few of these layer transitions can be shown in the figure.) In the region of the bulk 0 phase, the surface phases are denoted by a pair of integers needed to describe the compound film; the first gives the number of layers of $+$ phase adsorbed at the wall, the second gives the number of layers of $-$ phase adsorbed on top of the layers of $+$ phase. There are two distinct series of layering transitions; lines from the two series cross by producing two triple points.

At the lower right of the figure, the values of the chemical potentials are such that the wall has no layers of $+$ or $-$ phase adsorbed on it. As one proceeds toward the $+/0$ phase boundary at the left, the number of $+$ layers increases without limit because the $+$ phase wets the wall/0 interface; as one proceeds toward the $-/0$ interface, the number of $-$ layers increase without limit because the $-$ phase wets the wall/0 interface. If such a path is parallel to the $+/0$ phase boundary, one finds the number of $-$ layers growing on top of a fixed number of $+$ layers via a series of layering transitions. There are an infinite number of such paths in which the $-$ phase grows on top of one $+$ layer, on top of two $+$ layers etc. In this way we see that the surface melting transitions are the limit of such a series in which the $-$ phase grows on top of an infinite number of $+$ layers. Paths which are analogous to constant-density trajectories are those in which the sum of the two integers is constant. Along such a path, one could see a thick film of $+$ phase, say 20,0, melt to a thick film of $-$ phase via the sequence 19,1;18,2;. . . 1,19;0,20. This is the analog of surface melting but necessarily limited to a finite number of layers because the system is off of coexistence.

In contrast to the phase diagram of Fig. 1, we show in Fig. 2, the results for the case in which the bulk interactions are unchanged, but the surface fields have been weakened so that the $+$ phase no longer wets the wall/$-$ interface; i.e., inequality (11) is violated. The surface fields are of the same form as before but $h = 2.0$ and $\delta = -3.5$. The result is that the solid, which wet the wall/0 interface far from the triple point undergoes a "dewetting" transition as the triple point is approached. Similar phase diagrams have been predicted in previous studies,[15] while that of Fig. 1 has not. Note that the transitions (denoted by squares) associated with surface melting at $+/0$ coexistence no longer influence the surface phase diagram off of coexistence.

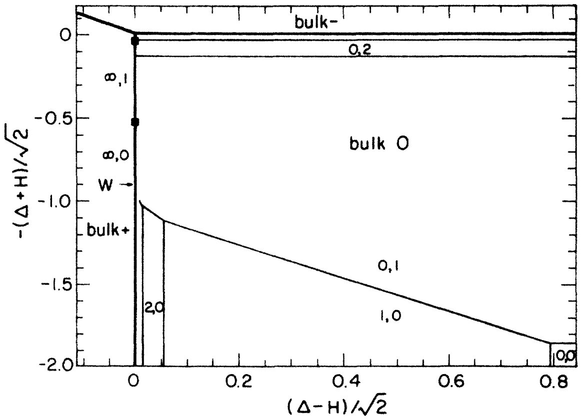

FIG. 2. Same as in Fig. 1 except that the surface interactions have been changed so that the $+$ phase no longer wets the wall/$-$ interface. Consequently, the $+$ phase no longer wets the wall/0 interface either, sufficiently close to the triple point, but undergoes a dewetting transition at the value of the bulk field marked W.

III. EFFECTS OF TEMPERATURE AND OF ROUGHENING

We now consider what the effects of temperature and of roughening will be on the phase diagram found in the previous section. The principal effect of temperature is that surface phases of the same symmetry are now connected by thermodynamic paths which do not cross a phase boundary just as the bulk phases of the same symmetry are connected. This means that the layering transitions end in critical points.[16] The effect is shown in Fig. 3 which is a schematic phase diagram in the plane of temperature and one chemical potential for a fixed ratio of the two chemical potentials Δ and H. Such a cut is more like the situation in the one-component liquid-gas-solid system which has only a single chemical potential. As in Fig. 1, only a small number of the transitions can be

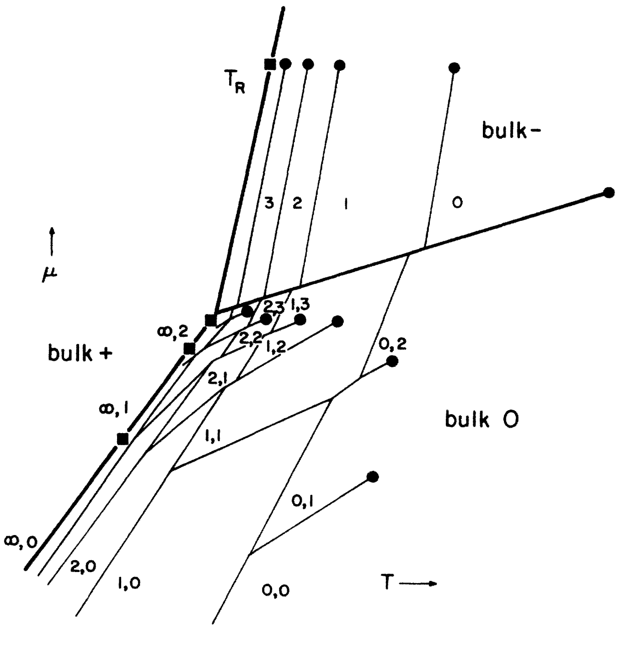

FIG. 3. Schematic phase diagram of the model system in which the ratio of the two chemical potentials are fixed. The diagram is in the plane of one them, denoted μ, and temperature. Dots are critical points. Solid squares on the $+/0$ boundary again denote layering transitions associated with surface melting; the square on the $+/-$ boundary is a roughening temperature of the $+/-$ interface. Critical points in the 0 phase are drawn as if the triple point were the roughening temperature of the $-/0$ interface.

shown for clarity. The effects of roughening, which depend upon the relative temperatures of wetting and roughening transitions and of the triple point, are clear from earlier work.[2–4,7] We discuss only a few of the possibilities here. If we identify the $-,+$ and 0 phases as liquid, solid, and gas respectively, then the liquid/gas $(-/0)$ interface is always rough. As a consequence, an infinite number of the layer transitions, those in which the surface liquid grows via condensation of the vapor, do not occur. Instead, such growth proceeds smoothly, unaccompanied by thermodynamic singularities. There is no reason to believe that *no* such liquid-layer transitions occur, particularly in light of the fact that the fluctuations of liquid interfaces in the presence of gravity are never large,[17] however the number of such transitions is presumably small. The effect on surface melting is that this process also occurs smoothly for the most part with only a small number of singularities due to layer transitions. If the solid/gas interface is smooth (i.e., not rough), then the series of layer transitions by which the solid grows and melts will be unaffected in the region of the phase diagram in which the bulk is gas. Consequently, the appearance of liquid due primarily to the melting of solid (which would be encountered along a path of constant density) would in general proceed by layer transitions, while the appearance of liquid due principally to the condensation of gas would not. A schematic phase diagram would look much like that of Fig. 3; the difference would be that the surface-liquid condensation transitions which are not shown in Fig. 3 for reasons of clarity would no longer exist even in principle. We note that this phase diagram is similar in many respects to those observed in CF_4 and C_2H_4 adsorbed on graphite.[12,13] Finally, if the solid/gas interface is rough, the solid grows and melts without singular behavior in thermodynamic quantities. This is the behavior observed in a recent experiment on surface melting.[18]

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[1] Recent experimetal work on surface melting can be found in W. M. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985); Da-Ming Zhu and J. G. Dash, *ibid.* **57**, 2959 (1986); M. Bienfait, Europhysics Lett. **4**, 79 (1987).

[2] Two excellent reviews on wetting are provided by D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, 1986); S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, London, 1988), Vol. 12. See, in particular, Sec. VIII A of the latter.

[3] M. J. de Oliveira and R. B. Griffiths, Surf. Sci. **71**, 687 (1978).

[4] R. Pandit M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

[5] An example of interfacial wetting which proceeds by a series of layer transitions is provided by P. Upton and J. Yeomans, J. Phys. A **20**, 2989 (1987). Note that this paper considers the special case in which the interface is between two phases related by symmetry. This is not the case with which we are concerned.

[6] Although this is not possible in principle, it occurs, for all practical purposes, in some experimental systems. For the principle, see D. A. Huse, Phys. Rev. B **29**, 6985 (1984); F. T. Gittes and M. Schick, *ibid.* **30**, 209 (1984). For relevant experiments, see M. Bienfait, Surf. Sci. **162**, 411 (1985), and the reviews cited in Ref. 2.

[7] This point was made by R. Pandit and M. E. Fisher, Phys. Rev. Lett. **51**, 1772 (1983) who also provide a general discussion of wetting near triple points.

[8] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982), Ch. 8.

[9] We assume that the density of the solid phase is the largest of the three phases. The necessary condition is that the Hamaker constant have a certain sign. With the densities as assumed, this sign is independent of whether the bulk phase in contact with the wall is liquid or gas. See, for example, S. Dietrich and M. Schick, Phys. Rev. B **33**, 4952 (1986), Eq. (2.15).

[10] However, a dewetting transition extremely close to the triple temperature in the system of CH_4 adsorbed on graphite has been reported by M. J. Lysek, M. S. Pettersen, and D. L. Goodstein, Phys. Lett. A **115**, 340 (1986).

[11] Such layer transitions have been seen in liquid He as the solid-liquid coexistence is approached, but this system lacks a triple point; S. W. Van Sciver and O. E. Vilches, Phys. Rev. B **18**, 285 (1978); K. Carneiro, L. Passell, W. Thomlinson, and H. Taub, *ibid.* **24**, 1170 (1981); S. Ramesh, Q. Zhang, G. Torzu, and J. D. Maynard, Phys. Rev. Lett. **52**, 2375 (1984).

[12] H. S. Nham, M. Drir, and G. B. Hess, Phys. Rev. B **35**, 3675 (1987).

[13] H. K. Kim, Y. P. Feng, Q. M. Zhang, and M. H. W. Chan, Phys. Rev. B **37**, 3511 (1988).

[14] M. Blume, V. Emery, and R. B. Griffiths, Phys. Rev. A **4**, 1071 (1971); see also D. Mukamel and M. Blume, *ibid.* **10**, 610 (1974).

[15] C. Ebner, Phys. Rev. B **28**, 2890 (1983), and Fig. 4(c) in Ref. 7.

[16] Note that there is a difference in principle here between our model system, in which all phases have the same symmetry, and in the liquid-gas-solid system in which the solid phase differs in symmetry from the other two. The consequence is that, while all transition lines in the model system end in critical points, the transition line separating the surface phase with no layers of adsorbed solid from that with one layer of solid, a transition which can be first order or continuous of the Kosterlitz-Thouless kind, (see D. R. Nelson in *Phase Transitions and Critical Phenomena,* op. cit. Vol. 7) does not end in a critical point. Similarity, the transition line separating one adsorbed layer from two, a transition which can be first order or continuous of the Ising kind, reflecting the two

possible stackings of the close-packed second layer upon the first, does not end in a critical point. The symmetry of the two possible stackings is, for layers beyond the third, broken due to interactions with lower layers. Therefore transition lines involving these layers cannot be continuous, but can be first order and end in critical points.

[17] A. Braslau, M. Deutsch, P. S. Pershan, A. H. Weiss, J. Als-Nielsen, and J. Bohr, Phys. Rev. Lett. **54**, 114 (1985), and references therein.

[18] Da-Ming Zhu and J. G. Dash, op. cit.