

Surface melting away from equilibrium

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A solid-vapor interface is theoretically studied in the vicinity of the triple point, where the liquid phase coexists with the solid and the vapor. We find that surface melting also occurs if the solid-vapor interface moves with constant velocity v as a result of slow evaporation of the crystal. In fact, the thickness of the liquidlike surface layer is found to increase with increasing v . For materials with a low vapor pressure such as Pb, this dynamically induced thickening of the liquidlike surface layer is, however, estimated to be very small. This implies that the interfacial structure observed in recent experiments should closely resemble the equilibrium structure.

I. INTRODUCTION

Melting of a solid phase is a ubiquitous phase transformation that occurs for any material at sufficiently high temperature. It is well established that this process represents a first-order phase transition at which *bulk* quantities change in an abrupt or discontinuous way.¹ The physical mechanism underlying this transition is still not fully understood from a microscopic point of view but recent experimental and theoretical work tends to confirm the old idea²⁻⁴ that the melting process is typically initiated at the *surface* of the crystal.

On the theoretical side, the idea of surface melting has been developed into a consistent framework: surface melting is now viewed as an interfacial phase transition which has the same characteristic features as wetting in fluid systems and surface-induced disorder in binary alloys.⁵⁻⁷ This implies that surface melting leads to a variety of *surface critical phenomena* even though the bulk crystal undergoes a discontinuous phase transition.

As far as experiments are concerned, surface melting has been clearly demonstrated for the (110) surface of Pb by ion scattering,^{8,10} by LEED,^{11,12} by x-ray reflectivity,¹³ and by spin-polarized LEED.¹⁴ Likewise, experimental evidence for surface melting has recently been obtained for Ar films (Ref. 15), O₂ films on graphite (Ref. 16), methane films on MgO (Ref. 17), Ne films (Ref. 18), and for the (111) surface of Ge (Ref. 19).

It is now generally accepted that surface melting occurs in *thermal* equilibrium, i.e., when both bulk phases and the interfacial region have the same temperature. As far as *chemical* equilibrium is concerned, one may distinguish two limiting cases. First, one may consider *partial chemical equilibrium* and assume that the exchange of material between the crystal and the vapor phase is so slow that it can be ignored on experimentally relevant time scales. One is then led to study a semi-infinite crystal bounded by a surface.^{20,21} On the other hand, one may assume that the transport of particles through the vapor-crystal interface is sufficiently fast to

achieve *full chemical equilibrium* throughout the whole system. In the latter case, surface melting is restricted to a thermodynamic path along the solid-vapor coexistence curve.^{6,7,22}

In this paper, we will consider a more realistic situation *away from chemical equilibrium*. Indeed, scattering experiments on surface melting are typically performed in ultrahigh vacuum, i.e., at large undersaturation, in order to reduce the scattering from the vapor phase. In these experiments, the crystal slowly evaporates. Therefore, we will study theoretical models for surface melting in which the crystal-vapor interface moves at constant velocity towards the bulk of the crystal.

The two situations of surface melting with and without chemical equilibrium are visualized in Fig. 1 as paths in a p - T diagram. The latter case is characterized by a pressure difference Δp from the pressure of the sublimation line.

Our paper is organized as follows. In Sec. II, we study the interfacial structure within a Landau-type model for

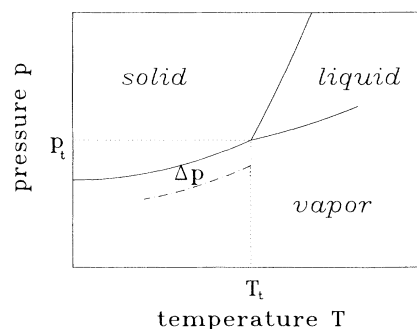


FIG. 1. p - T diagram and possible paths for surface melting. Idealized situation with chemical equilibrium on the sublimation line (solid line) and experimental situation without chemical equilibrium away from the sublimation line (dashed line). The latter case can be characterized by a pressure difference Δp .

solid, the mobility is several orders of magnitude smaller than in the liquid. We model the functional dependence of Γ on M as a piecewise constant function given by

$$\Gamma(M) = \begin{cases} \Gamma_V & \text{for } M < M_{VL} , \\ \Gamma_L & \text{for } M_{VL} < M < M_{LS} , \\ \Gamma_S & \text{for } M_{LS} < M . \end{cases} \quad (2.7)$$

In Appendix A, the various parameters entering the Landau theory are estimated. In particular, the mobility is expressed in terms of measurable *static* quantities.

We are primarily interested in steady-state situations where the interface moves with a constant velocity v . Therefore we are looking for solutions

$$M(z, t) = m(z - vt) \equiv m(x) \quad (2.8)$$

with boundary conditions

$$m(x \rightarrow -\infty) = M_V = 0 \quad \text{and} \quad m(x \rightarrow \infty) = M_S . \quad (2.9)$$

As frequently stated by many authors, see, e.g., Refs. 24 and 25, the partial differential equation as given by (2.6) reduces to an ordinary differential equation which then describes a fictitious "particle" in order parameter space, moving in a "potential" $U(M)$ with "mass" g and "friction" $v/\Gamma(M)$. The coordinate x plays a role of "time."

With our assumptions for $U(M)$ and $\Gamma(M)$, the steady-state equation for $m(x)$ can easily be solved. For each quadratic piece of $f(M) = -U(M)$, we get a linear second-order differential equation which can be solved by exponentials $\sim \exp(z/l_\alpha^\pm)$ with $\alpha = V, L, S$. The corresponding decay lengths are v dependent and given by

$$1/l_\alpha^\pm = [-v \pm \sqrt{v^2 + (2\Gamma_\alpha g)^2/a_\alpha^2}] / 2g\Gamma_\alpha . \quad (2.10)$$

For small v , these length scales have the asymptotic behavior

$$l_\alpha^\pm \approx \pm a_\alpha + (a_\alpha^2 / 2g\Gamma_\alpha) v . \quad (2.11)$$

These experimental solutions are then matched at $x=0$ and $x=l$ where l denotes the thickness of the quasiliquid layer. This leads to the two matching conditions

$$0 = H - (B/l_1)e^{-l/l_1} - (C/l_2)e^{-l/l_2} , \quad (2.12)$$

$$0 = H/l_1 - (D/l_1)e^{-l/l_1} - (C/l_2 l_L^-)e^{-l/l_2} , \quad (2.13)$$

which determine the thickness l and the velocity v . The two length scales l_1 and l_2 are defined by

$$l_1 \equiv l_L^+ = a_L + O(v) , \quad (2.14)$$

$$l_2 \equiv l_L^- l_L^+ / (l_L^- - l_L^+) = \frac{1}{2} a_L + O(v) , \quad (2.15)$$

The parameter H is given by

$$H = M_{VL} / l_V^+ + (M_L - M_{VL}) l_L^- . \quad (2.16)$$

For $v=0$, this parameter measures the distance from three phase coexistence: $H \sim \Delta p_L$ for small Δp_L . The other coefficients in (2.12) and (2.13) are

$$B/l_1 = (M_{LS} - M_L) / l_2 , \quad (2.17)$$

$$C/l_2 = M_{VL} / l_V^+ + (M_L - M_{VL}) / l_L^+ , \quad (2.18)$$

and

$$D/l_1 = (M_{LS} - M_S) / l_2 l_S^- . \quad (2.19)$$

With a little bit of algebra, one may eliminate the variable l from the matching conditions (2.12) and (2.13). As a result, one obtains an implicit equation for the velocity v alone which can be written as

$$Q(l_L^+) = Q(l_L^-) l_L^+ / l_L^- \quad (2.20)$$

with

$$Q(x) \equiv \frac{-(M_S - M_{LS}) / l_S^- - (M_{LS} - M_L) / x}{M_{VL} / l_V^+ + (M_L - M_{VL}) / x} . \quad (2.21)$$

By Eqs. (2.10) and (2.11), the variables l and v are determined as a function of Δp and Δp_L . In general, this functional dependence can be easily found from a numerical solution of these equations. In order to get some insight into this solution, it is also useful to retain v as a parameter and to introduce an effective interface potential, which is obtained by integrating (2.12) with respect to l :

$$V(l) = Hl + B e^{-l/l_1} + C e^{-l/l_2} . \quad (2.22)$$

The thickness l of the quasiliquid layer in the steady state is then given by

$$\frac{\partial V(l)}{\partial l} = 0 . \quad (2.23)$$

This determines the layer thickness l provided the interface velocity v is known. In fact, the interface potential (2.22) and the condition (2.23) are even useful if v is treated as an unknown parameter since they directly show the connection to the equilibrium case with $v=0$.

Let us first discuss this case of surface melting at full chemical equilibrium, i.e., $\Delta p=0$ and $v=0$. Then, the coefficient H in (2.22) behaves as $H \sim T_T - T$, where T_T is the triple point temperature, and the decay lengths satisfy $l_1 = 2l_2 = a_L$. Moreover

$$l \approx l_1 |\ln[(T_T - T) / T_T]| \quad (2.24)$$

as the triple point temperature is approached from below.

In the dynamical situation with $\Delta p \neq 0$, the condition $H=0$ defines a characteristic temperature T_* , which, in general, is different from the triple point temperature T_T . Furthermore, $H \sim T_* - T$ for small $T_* - T$. Hence, l diverges logarithmically as in (2.24) but with T_T replaced by T_* . The prefactor l_1 , however, depends on v and will be enhanced. For small v , one finds immediately from (2.14) and (2.10) that

$$l_1 = a_L \left[1 + \frac{v a_L}{2g\Gamma_L} + O(v^2) \right] . \quad (2.25)$$

This means that nonequilibrium conditions enhance the thickness of a wetting layer.

For $T > T_*$, there is no steady-state solution. In this

case, the vapor-liquid and the liquid-solid interfaces move with different velocities v_{VL} and v_{LS} , respectively, with $v_{VL} < v_{LS}$.

In summary, nonequilibrium surface melting is similar to surface melting at full chemical equilibrium, but takes place at a different temperature $T_* \neq T_T$. For short-ranged forces, the growth law for the width of the quasiliquid layer is still logarithmic but the prefactor depends on the interface velocity v .

III. MULTICOMPONENT ORDER PARAMETER

Let us now include more order parameters, characterized by a set $\Xi = \{M_0, M_1, M_2, \dots\}$. More specifically, let M_0 be the mean density and M_1, M_2, \dots be crystallinity order parameters. The latter order parameters can be chosen to be the amplitudes of a density oscillation with a nonzero reciprocal lattice vector of the solid^{6,26,27} which then vanish in the liquid and vapor phase. We assume that the dynamics is not coupled and given by

$$\frac{\partial M_n}{\partial t} = -\Gamma_n(\Xi) \frac{\delta F}{\delta M_n} \quad (3.1)$$

for $n=0, 1, 2, \dots$, Γ_n denoting the mobility corresponding to M_n and F being the grand-canonical free energy functional now generalized to a multicomponent order parameter Ξ . In this section, we consider general functionals of the form

$$F\{\Xi(z)\} = \int_{-\infty}^{\infty} dz \left[\sum_n \frac{1}{2} g_n(\Xi(z)) \left(\frac{dM_n}{dz} \right)^2 + f(\Xi(z)) \right], \quad (3.2)$$

where the ‘‘mass tensor’’^{7,22} is diagonal and depends on Ξ . In multidimensional order parameter space, $f(\Xi)$ exhibits a three peak structure, too. Near the metastable liquid peak $\Xi_L = (M_{0L}, 0, 0, \dots)$, $f(\Xi)$ reads^{6,22}

$$f(\Xi) = \frac{1}{2} \left[\lambda_0 (M_0 - M_{0L})^2 + \sum_{n \neq 0} \lambda_n M_n^2 \right]. \quad (3.3)$$

We also remark that the quantities λ_n and $g_n(\Xi_L)$ can explicitly be related to the liquid structure factor.^{26,27} Clearly, for a concrete choice of the crystallinity order parameters, the different parameters λ_n, g_n, Γ_n are not independent from one another.

The discussion of the influence of dynamics is quite similar to Sec. II and we only quote the results. Let us define a correlation length ξ_n for the order parameter M_n in the liquid phase by

$$1/\xi_n(v) = \frac{-v + \sqrt{v^2 + 4g\Gamma_n^2(\Xi_L)\lambda_n}}{2\Gamma_n(\Xi_L)g_n(\Xi_L)}. \quad (3.4)$$

Then the width of the quasiliquid layer diverges for a certain temperature T_* as

$$l \approx l_1(v) |\ln[(T_* - T)/T_*]| \quad (3.5)$$

for small $T_* - T$ with a v dependent prefactor l_1 that is given by

$$l_1(v) = \max[\xi_0(v), \xi_1(v)/2, \xi_2(v)/2, \dots]. \quad (3.6)$$

Obviously, for a single order parameter, one recovers the results of Sec. II.

Another interesting quantity is the residual crystallinity $c_n \equiv M_n(-vt, t) = m_n(x=0)$ of the order parameter M_n at the quasiliquid-vapor interface. For the equilibrium situation, it is well known^{6,7,22,27,28} that c_n vanishes as a power law in $T_T - T$ with nonuniversal exponents β_{1n} for small $T_T - T$. In the generalization to the nonequilibrium situation, the exponents turn out to become v dependent. For small $T_* - T$ one finds

$$c_n \sim (T_* - T)^{\beta_{1n}(v)} \quad (3.7)$$

with

$$\beta_{1n}(v) = l_1(v) / \xi_n(v). \quad (3.8)$$

IV. INFLUENCE OF LONG-RANGED INTERPARTICLE FORCES

Finally, let us consider long-ranged algebraic tails $\Phi_{LR}(r)$ in the interparticle potential. If the tails are slowly varying compared to the lattice constant of the crystal, only the local mean density M_0 interacts via $\Phi_{LR}(r)$.^{22,29} More explicitly, the long-ranged term

$$F_{LR} = -\frac{1}{4} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' w(|z - z'|) [M_0(z) - M_0(z')]^2 \quad (4.1)$$

has to be added to F in (3.2). Here, $w(z)$ is the laterally integrated long-range tail

$$w(z) = \int d^2 r_{\parallel} \Phi_{LR}(\sqrt{r_{\parallel}^2 + z^2}). \quad (4.2)$$

Representing a ‘‘memory term,’’ F_{LR} complicates the steady-state equations of motion considerably.

Let us first focus on a single order parameter M_0 . Later on, we include crystallinity order parameters (M_1, M_2, \dots), too. To gain first insight into the interplay of dynamics and long-ranged forces, we further simplify our model (2.1), (2.2), (2.5), and (2.7) and take *constant* mobilities and potential curvatures for the three phases:

$$\Gamma(M_0) \equiv \Gamma \quad \text{and} \quad \lambda_V = \lambda_L = \lambda_S \equiv \lambda = g/a^2. \quad (4.3)$$

Then, by the technique described in Refs. 30 and 22, the steady-state equation can be solved exactly for *arbitrary* $w(z)$. For more details, see Appendix B. As a result, one obtains the steady-state solution $m_0(x)$ as given by

$$m_0(x) = \frac{M_L}{M_S} \hat{m}(x) + \frac{M_S - M_L}{M_S} \hat{m}(x - l) \quad (4.4)$$

with

$$\hat{m}(x) = \frac{\lambda M_S}{2\pi} \int_{-\infty}^x dy \int_{-\infty}^{\infty} dk \exp(-iky) \times \left[gk^2 + \frac{ikv}{\Gamma} + \lambda + \tilde{W}(k) \right]^{-1}, \quad (4.5)$$

where

$$\bar{W}(k) \equiv \sqrt{2\pi}[\bar{w}(k) - \bar{w}(0)] , \quad (4.6)$$

and $\bar{w}(k)$ denotes the Fourier transform of $w(z)$. The interface velocity v and the width of the liquid layer are determined by the matching conditions

$$\begin{aligned} m_0(0) &= M_{VL} = \frac{1}{2}M_L + \Delta p_L / \lambda M_L , \\ m_0(l) &= M_{LS} = \frac{1}{2}(M_S + M_L) + \frac{\Delta p - \Delta p_L}{\lambda(M_S - M_L)} . \end{aligned} \quad (4.7)$$

Combining Eqs. (4.4) and (4.7), one obtains that the wetting layer thickness l diverges if

$$\Delta p_L = (\Delta p_L)_0 = \frac{M_L^2}{(M_S - M_L)^2 + M_L^2} \Delta p . \quad (4.8)$$

We can now introduce a pressure difference $\Delta \bar{p}_L$ with respect to this pressure $(\Delta p_L)_0$, i.e.,

$$\Delta \bar{p}_L \equiv \Delta p_L - (\Delta p_L)_0 . \quad (4.9)$$

For positive $\Delta \bar{p}_L$ the thickness l of the quasiliquid layer is finite. By Eqs. (4.7), (4.4), and (4.5) the divergence law for l as $\Delta \bar{p}_L \rightarrow 0$ can be obtained studying the ‘‘wings’’ of the interfacial profile $\hat{m}(x)$, i.e., the asymptotic form of $\hat{m}(x)$ for large $|x|$. Clearly, these wings depend explicitly on the long-ranged potential, see (4.5). In the following, we assume a Lennard-Jones long-range tail in the interparticle potential

$$\Phi_l(r) \approx -\frac{\gamma}{r^6} \quad \text{for } r \rightarrow \infty . \quad (4.10)$$

Doing an asymptotic analysis of the integral in (4.5), it turns out that the divergence law for the layer thickness l as $\Delta \bar{p}_L \rightarrow 0$ is *independent* of v . As in the equilibrium case²² one finds

$$l \approx \left[\frac{2W}{\Delta \bar{p}_L} \right]^{1/3} \quad (4.11)$$

with a v independent Hamaker constant W given by

$$W = \frac{\gamma \pi (M_S - M_L) M_L}{12 M_S} . \quad (4.12)$$

As in the case of short-range forces, surface melting occurs at a characteristic temperature T_* , which is implicitly given by (4.8) and differs in general from the triple point temperature T_T . The Hamaker constant, on the other hand, does *not* depend on the dynamics, i.e., on the interface velocity v .

If one includes more than one order parameter, the calculations become more elaborate. However, one again finds a temperature T_* such that the thickness of the disordered layer diverges as

$$l \approx \left[\frac{2W}{A(T_* - T)} \right]^{1/3} \quad (4.13)$$

for small $T_* - T$. Here, A includes the temperature dependence of Δp . Accordingly, with the notation of

(3.4), the residual crystallinity of the order parameter M_n ($N > 1$) vanishes as a v -dependent stretched exponential such as T_* is approached from below:

$$c_n \equiv m_n(x=0) \approx \exp[-l/\xi_n(v)] . \quad (4.14)$$

V. DISCUSSION

The dynamically induced corrections to surface melting at full chemical equilibrium are of the order of $v a_L / g \Gamma_L$, see (2.25). The velocity scale

$$\bar{v}_L \equiv g \Gamma_L / a_L \quad (5.1)$$

can be viewed as the velocity scale by which a density perturbation propagates in the liquid. Primarily, the velocity scale \bar{v}_L is governed by the mobility Γ_L which is strongly temperature dependent.

An estimate of \bar{v}_L can be obtained in two ways. First, one can use the estimates in Appendix A where \bar{v}_L is expressed by static quantities. For lead, this leads to $\bar{v}_L = O(100 \text{ m/s})$. Second, an upper bound on the time scale corresponding to \bar{v}_L can be found using measurements of the diffusion constant D of the liquid phase near the triple point. This means

$$\bar{v}_L \geq D / a_L . \quad (5.2)$$

For lead, one obtains³¹ $D / a_L \approx 10 \text{ m/s}$ so that the order of magnitude is consistent in the two estimations.

Consequently, the resulting velocity scale \bar{v}_L is much larger than the interface velocity v which, for lead, is $\approx 5 \text{ \AA}$ per hour⁹ where one typically works with a very small pressure difference $\Delta p = 7 \times 10^{-7} \text{ Pa}$. This implies that the interfacial structure observed in recent scattering experiments resembles the structure in full chemical equilibrium. Indeed, this was anticipated in the interpretation of the data (see, e.g., Ref. 9), but a quantitative estimate was not available.

The dynamical influence may be detectable in materials with a relatively high vapor pressure, such as, e.g., ice. For experimental reasons, since one works with finite-size crystals v is limited by $\leq O(10^{-5} \text{ m/s})$. Therefore, the dynamical effect will be small in any case. However, at the onset of surface melting, merely a quasiliquid layer is present which has a perpendicular mobility between the solid and liquid bulk mobilities Γ_S, Γ_L . Since $\Gamma_S \approx 10^{-5} \Gamma_L$, dynamical effects may be detectable and more relevant at the onset of surface melting.

Let us finally make some remarks: First, the pressure difference Δp must not be too large. Otherwise, for $\Delta p > \Delta p_c$, the liquid is no longer metastable and surface melting will not take place. In Fig. 2, this corresponds to the situation where the liquid peak lies below the vapor and the solid peak. A crude estimate for Δp_c yields

$$\Delta p_c \approx \frac{1}{2} \sigma_{LV} / \xi , \quad (5.3)$$

where σ_{LV} is the liquid-vapor interfacial tension at the triple point and ξ is the corresponding interfacial width.

Second, we comment on limitations of the theory. Doing a steady-state analysis with one coordinate z , we have

neglected melting in the metastable bulk solid, yielding quasiliquid bubbles. This effect is pronounced if both Δp and T are large. Furthermore, we have neglected effects of dynamical roughening of the solid-vapor interface. Computer simulations should be used to obtain a more detailed picture of the interplay between roughness and surface melting.

APPENDIX A: PARAMETERS OF LANDAU THEORY

In this appendix, we will estimate the various parameters which enter the Landau model in Sec. II. We choose the "order parameter" M to represent the dimensionless mean particle density defined by

$$M \equiv (\rho - \rho_V) / \rho_L, \quad (\text{A1})$$

where ρ_V and ρ_L are the particle densities of the bulk vapor and the bulk liquid, respectively.

Now, consider two phase coexistence between the vapor and the liquid phase. Such a situation is described by the free energy (2.1) with

$$f(M) = \begin{cases} \frac{1}{2}gM^2/a_V^2 & \text{for } M < M_{VL}, \\ \frac{1}{2}g(M - M_L)^2/a_L^2 + \Delta p_L & \text{for } M_{VL} < M. \end{cases} \quad (\text{A2})$$

The parameters a_V and a_L are microscopic length scales of the order of the molecular size. The parameter g is a free energy scale. Indeed for $\Delta p = 0$, the tension or free energy, Σ_{VL} , of the liquid-vapor interface is given by

$$\Sigma_{VL} = \int_{-\infty}^{\infty} dz g \left[\frac{dM}{dz} \right]^2 = \frac{1}{2}gM_L^2 / (a_V + a_L). \quad (\text{A3})$$

Thus, we obtain the estimate

$$g = 2(a_V + a_L)\Sigma_{VL} / M_L^2 \simeq 4a_L\Sigma_{VL}. \quad (\text{A4})$$

In deriving the second step of Eq. (A4), we assumed $a_V \simeq a_L$ and, since $\rho_V \ll \rho_L$, $M_L \simeq 1$. Next, consider the system with $\Delta p_L \neq 0$. It then follows from (2.6)–(2.8) that the stationary profile, $m(x) = m(z - vt)$, satisfies

$$-v \frac{\partial m}{\partial x} = \begin{cases} g\Gamma_V \left[\frac{\partial^2 m}{\partial x^2} - m/a_V^2 \right] & \text{for } m < M_{VL}, \\ g\Gamma_L \left[\frac{\partial^2 m}{\partial x^2} - (m - M_L)/a_L^2 \right] & \text{for } m > M_{VL}. \end{cases} \quad (\text{A5})$$

Matching at $x = 0$ leads to

$$\begin{aligned} M_{VL} \{ -v/2g\Gamma_V + [(v/2g\Gamma_V)^2 + 1/a_V^2]^{1/2} \} \\ = (M_L - M_{VL}) \{ v/2g\Gamma_L + [(v/2g\Gamma_L)^2 + 1/a_L^2]^{1/2} \} \end{aligned} \quad (\text{A6})$$

which determines v as a function of the pressure Δp . This pressure enters (A6) only through M_{VL} with

$$M_{VL} \simeq \frac{a_V}{a_V + a_L} M_L + \frac{a_V a_L}{g M_L} \Delta p_L \quad (\text{A7})$$

for small Δp_L . Expansion of (A6) then leads to

$$v \simeq 2[(a_V + a_L)^2 \Gamma_V \Gamma_L / (a_V \Gamma_L + a_L \Gamma_V) M_L^2] \Delta p_L \quad (\text{A8})$$

for small Δp_L .

The relation as given by (A8) will now be compared with the corresponding relation as obtained from a simple model for interfacial growth.²³ In this model, the deposition rate, J_D , i.e., the number of molecules which arrive from the vapor phase at the interface per unit area and unit time is taken to be

$$J_D = c_{st} p / \sqrt{2\pi m T}, \quad (\text{A9})$$

where p is the vapor pressure, m the mass of the molecule (and the temperature T is measured in energy units). The sticking coefficient c_{st} is of order 1. The expression (A9) follows from the kinetic theory of an ideal gas. The evaporation rate, J_E , on the other hand, is taken to be

$$J_E = J_0 \exp(-\Delta E / T), \quad (\text{A10})$$

where ΔE represents the binding energy within the interface.

At two phase coexistence with $p = p^*$, one has $J_E = J_E^* = J_D^* = J_D$. Now, off the coexistence with $p = p^* - \Delta p_L$, one obtains the effective evaporation rate

$$J_E - J_D + J_E^* - J_D^* + c_{st} \Delta p_L / \sqrt{2\pi m T}, \quad (\text{A11})$$

where $J_E = J_E^*$ has been assumed. This implies that the interface velocity v is given by

$$v = [c_{st} / \sqrt{2\pi m T} (\rho_L - \rho_V)] \Delta p_L \quad (\text{A12})$$

within this model.

Now, consider the simplified case with $\Gamma \equiv \Gamma_V = \Gamma_L$. It then follows from (A8) and (A12) that

$$\begin{aligned} \Gamma &\simeq c_{st} (\rho_L - \rho_V) / \sqrt{2\pi m T} (a_V + a_L) \rho_L^2 \\ &\simeq c_{st} / 5a_L \rho_L \sqrt{m T}, \end{aligned} \quad (\text{A13})$$

where the choice (A1) has been used.

Finally, consider the velocity scale $\bar{v}_L = g\Gamma_L / a_L$ which determines the relative size of the correction term in (2.25). From (A4) and (A13), one now obtains the estimate

$$\bar{v}_L = g\Gamma_L / a_L \simeq \frac{4}{5} \Sigma_{VL} / \rho_L a_L \sqrt{m T}. \quad (\text{A14})$$

For Pb near the triple point, one has $m \simeq 3 \times 10^{-22}$ g, $T = T_T \simeq 8 \times 10^{-14}$ erg, $\rho_L \simeq 2 \times 10^{22}$ cm⁻³, $a_L \simeq 3 \times 10^{-8}$ cm, and $\Sigma_{VL} \simeq 300$ erg/cm². This leads to $\bar{v}_L = O(100$ m/s).

APPENDIX B

For the model of Sec. IV, including the long-ranged forces, the steady-state equation reads explicitly

$$g \frac{d^2 m_0}{dx^2} + \frac{v}{\Gamma} \frac{dm_0}{dx} - \lambda m_0 - \int_{-\infty}^{+\infty} dx' w(|x-x'|) [m_0(x') - m_0(x)] = -\lambda [M_L \Theta(x) + (M_S - M_L) \Theta(x-l)], \quad (\text{B1})$$

where $\Theta(x)$ denotes the step function. Note that we have transferred the nonlinearity of df/dm_0 in $m_0(x)$ to a merely x -dependent inhomogeneity. As a consequence, we have to require the matching conditions (4.7). Equation (B1) can straightforwardly be solved by Fourier transformation. Introducing the Fourier transform $\bar{m}_0(k)$ by

$$\bar{m}_0(k) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \exp(ikx) m_0(x), \quad (\text{B2})$$

one arrives at the following result:

$$\bar{m}_0(k) = \frac{\lambda}{\sqrt{2\pi}} \frac{M_L \left[\int_0^{\infty} dx' \exp(ikx') \right] + (M_S - M_L) \int_l^{\infty} dx' \exp(ikx')}{gk^2 + ikv/\Gamma + \lambda + \sqrt{2\pi} [\bar{w}(k) - \bar{w}(0)]}. \quad (\text{B3})$$

Doing the Fourier backtransform, one obtains directly (4.4).

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