

## Van der Waals Theory of Surface Melting.

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**Abstract.** – We introduce a multi-order parameter van der Waals theory for surface melting near the triple point  $T_t$  which is based on density functional techniques and includes long-range interparticle forces. As a result we establish that long-range attractive forces induce a stretched exponential decay as  $T \rightarrow T_t$  of the residual crystal order in the quasi-liquid interfacial layer. If these forces are weak, a crossover from logarithmic to power law growth in  $T_t - T$  of the interfacial width occurs.

It has been suggested long ago [1] that the melting of a solid might start at the surface, which is a natural defect in the crystalline order. Recent ion back-scattering experiments [2] on Pb and calorimetric studies [3] with adsorbed multilayer rare-gas films provide strong evidence for the idea of surface melting. These measurements may be interpreted by assuming that near the triple point temperature  $T_t$  some faces of a crystal in coexistence with its vapour are covered by a liquidlike layer whose thickness increases steadily as  $T_t$  is approached. Hence, surface melting may be viewed as an instance of interfacial wetting.

Although the theory of both wetting phenomena [4] and bulk freezing [5] has advanced considerably in the last few years, the molecular aspects of surface melting are still not well understood. The difficulty is to cope with the strong spatial density oscillation in a crystal lattice as well as the inhomogeneous decay of lattice translational order in the interface.

Qualitative features of the wetting layer may be explained within phenomenological Landau models [6-8], originally devised to deal with interface delocalization at geometric surfaces. A more detailed picture of the interfacial profiles has been supplied by a numerical mean-field study of a discrete lattice model [9].

In this letter we present a van der Waals-type variational free energy for the solid (liquid)vapour interface which is derived from the density functional theory (DFT) of bulk freezing [5]. The strategy of DFT is based on the assumption that the short-distance structure of a bulk solid can be described by a hard-sphere reference fluid with the intermolecular attractive forces treated perturbatively. For the hard-sphere system, reliable approximations for the equation of state and for two-body density correlation functions are available. A noteworthy feature of our approach to surface melting is that only those microscopic input data are required which are supplied by the current DFT of bulk

freezing. The main additional assumption we have to make is that the interfacial profiles of the local mean density and of the crystalline order vary slowly over lattice distances. As an application, we consider the effects of the range of molecular forces on the residual crystal order in the quasi-liquid film and on the growth of its width.

Let us first outline the arguments leading to the van der Waals expression for the interfacial free energy. The grand canonical functional for an inhomogeneous system with local density  $\rho(\mathbf{r})$ , chemical potential  $\mu$  and volume  $V$  reads [10]

$$\Omega[\rho] = F_{\text{id}}[\rho] + F_{\text{exc}}[\rho] - \mu \int_V d^3r \rho(\mathbf{r}), \quad (1)$$

where  $F_{\text{id}}$  denotes the ideal gas term. We assume a pairwise potential  $\phi(r)$  which is divided into a short-range part,  $\phi_s(r)$ , and long-range tail  $\phi_l(r)$ . Besides a repulsive core,  $\phi_s(r)$  includes a short-range attractive part. The excess Helmholtz functional  $F_{\text{exc}}$  is then given by

$$F_{\text{exc}}[\rho] = F_s[\rho] + \frac{1}{2} \iint_V d^3r d^3r' \phi_l(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}'), \quad (2)$$

with  $\phi_l$  treated in mean-field fashion. Finally,  $F_s[\rho]$  may be written in the form

$$F_s[\rho] = k_B T \int_0^1 d\alpha (\alpha - 1) \iint_V d^3r d^3r' c(\mathbf{r}, \mathbf{r}'; [\alpha\rho]) \rho(\mathbf{r}) \rho(\mathbf{r}'), \quad (3)$$

where  $c(\mathbf{r}, \mathbf{r}'; [\rho])$  denotes the direct correlation function (d.c.f.) arising from the short-range repulsion and attraction combined in  $\phi_s(r)$ .

Consider now a semi-infinite crystal in coexistence with the vapour phase and with a planar interface perpendicular to the  $z$ -axis. For this geometry the local density may be written as  $\rho(\mathbf{r}, \Gamma(z)) = \rho_0(z) + \tilde{\rho}(\mathbf{r}, \Gamma(z))$  with  $\Gamma = \{\rho_0, \rho_1, \rho_2, \dots\}$ ;  $\rho_0(z)$  is the local mean density and  $\rho_i$ ,  $i \geq 1$ , are local crystal order parameters such as Fourier coefficients of  $\rho(\mathbf{r})$  or functions thereof. In the bulk phases we have

$$\begin{cases} \Gamma(z \rightarrow -\infty) \equiv \Gamma_S = \{\rho_S, \rho_{1S}, \dots\}, & \text{in the crystal,} \\ \Gamma(z \rightarrow \infty) \equiv \Gamma_G = \{\rho_G, 0, \dots\}, & \text{in the vapour.} \end{cases} \quad (4)$$

$\tilde{\rho}(\mathbf{r}, \Gamma_S)$  is defined such that its average over the unit cell vanishes.

To proceed, we now assume that the parameters  $\Gamma(z)$  vary slowly within the range of the d.c.f. in eq. (3). Therefore, we may perform a gradient expansion in  $F_s[\rho]$  with respect to  $\Gamma(z)$ . To leading order we obtain a free energy functional per unit area for the interface

$$\Sigma[\Gamma] = \int_{-\infty}^{\infty} dz \left[ \frac{1}{2} g_{ij}(\Gamma(z)) \frac{d\rho_i(z)}{dz} \frac{d\rho_j(z)}{dz} - v(\Gamma(z)) \right] - \frac{1}{4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dz dz' w(|z - z'|) [\rho_0(z) - \rho_0(z')]^2. \quad (5)$$

In (5), summation on  $i, j \geq 0$  is implied; the matrix  $g_{ij}(\Gamma)$  is given by

$$g_{ij}(\Gamma) = \frac{k_B T}{2V} \iint d^3r d^3r' (z - z')^2 c(\mathbf{r}, \mathbf{r}'; \Gamma) \frac{\partial c(\mathbf{r}, \Gamma)}{\partial \rho_i} \frac{\partial c(\mathbf{r}', \Gamma)}{\partial \rho_j}, \quad (6)$$

and the limit  $V \rightarrow \infty$  is understood. In (5),  $-v(I)$  denotes the grand canonical potential per unit volume of a system with spatially uniform parameters  $I$  and  $w(z)$  is the laterally integrated tail potential  $\hat{\phi}_1(r)$ .

Note that the gradient expansion is made only in  $F_s[\rho]$  but not in the mean-field term in (2). The latter is dominated by the profile  $\rho_0(z)$ , since the density deviation  $\tilde{\rho}(r, I(z))$  oscillates rapidly over distances where  $\hat{\phi}_1(r)$  remains practically constant.

The final input required to specify  $\Sigma$  is the d.c.f. in (6) for a crystal with uniform  $I$ . This quantity also enters crucially in  $v(I)$ , which yields the bulk phase diagram. The usual procedure is to treat  $\hat{\phi}_s$  perturbatively and to set

$$c(\mathbf{r}, \mathbf{r}'; I) \cong c_{\text{HS}}(\mathbf{r}, \mathbf{r}'; I) - \frac{1}{k_B T} \hat{\phi}_s(|\mathbf{r} - \mathbf{r}'|). \tag{7}$$

The first term,  $c_{\text{HS}}$ , may be constructed from the d.c.f. of a uniform hard-sphere fluid using the weighted density technique [11];  $\hat{\phi}_s(r)$  is the WCA-modification [12] of  $\phi_s(r)$  whereby short-distance hard-core effects are taken into account approximately.

The equilibrium profiles  $\bar{I}(z) = \{\bar{\rho}_0(z), \bar{\rho}_1(z), \dots\}$  are obtained from minimizing  $\Sigma[I]$  subject to the boundary conditions (4) with  $v(I_S) = v(I_G)$ . We note that the functional  $\Sigma[I]$  may be viewed as the mechanical action of a fictitious particle in  $I$ -space with metric  $g_{ij}(I)$  and where  $z$  plays the role of time. The particle moves in the potential  $v(I)$  and behaves as a polaron in  $\rho_0$ -direction.

In the subsequent discussion, approximations such as (7) are not required. Instead, we assume that the bulk system displays three phase coexistences at a triple point. Accordingly, on the sublimation curve in the vicinity of  $T_t$ , the potential exhibits a three-peak structure with two maxima of equal height at  $I_G$  and  $I_S$  and a lower maximum at  $I_L = \{\rho_L, 0, \dots\}$  rising with  $\tau \equiv (T_t - T)/T_t \rightarrow 0$  so that  $v(I_t) = v(I_L) = v(I_G)$  for  $\tau = 0$ ;  $\rho_L$  is the density of the bulk liquid at the triple point. In the dynamical terminology we look for solutions of the Euler equations  $\delta\Sigma/\delta\varphi_i(z) = 0$  which correspond to trajectories starting on top of the vapour peak and terminating on top of the solid peak.

In general, the Euler equations may have several solutions. For a simplified model with a single-crystal order parameter  $I = \{\rho_0, \rho_1\}$ , and with short-range forces only ( $w = 0$ ), we can show that the number of extremals,  $N_{\text{ext}}$ , is odd<sup>(1)</sup>. Furthermore, there is always a «melting» trajectory which visits the liquid peak and approaches its top as  $\tau \rightarrow 0$ . The other solutions (if they occur) qualify as «nonmelting» or «blocked melting». Of course, the physically realized trajectory is the one having minimal «action»  $\Sigma$ <sup>(2)</sup>.

In the case of long-range forces ( $w \neq 0$ ) we have no proof but numerical evidence that  $N_{\text{ext}} = \text{odd}$  remains true.

Let us focus attention on the melting trajectory. The analytic results listed below are based on the following approximation for  $v(I)$  in the vicinity of the liquid peak at  $I_L$ :

$$v(I) = -\frac{1}{2} \lambda_0 (\rho_0 - \rho_L)^2 - \frac{1}{2} \sum_{i=1}^D \lambda_i \rho_i^2 - a\tau, \tag{8}$$

with a finite but arbitrary number  $D$  of crystal order parameters. Furthermore, we assumed

<sup>(1)</sup> A proof of this statement and further details will be published elsewhere.

<sup>(2)</sup> It might be expected that the «blocked melting» solution is normally unstable. Indeed, we found numerically that this appears to be the case for physically reasonable potentials  $v(I)$ . However, we have no compelling argument to exclude in general substructures in  $v(I)$  which would render the blocked melting trajectory into a stable one, at least in some range of the thermodynamic parameters.

the metric tensor at  $\Gamma_L$  to be diagonal,  $g_{ij}(\Gamma_L) = g_{ii} \delta_{ij}$ . The attractive tail potential is taken as  $\phi_1(r) \sim r^{-n}$ ,  $n > 3$ , at large distances. The results for short-range forces ( $\phi_1 \equiv 0$ ) are given within brackets.

As in previous models [4, 6] the gross asymptotic features of the liquid layer such as its width  $l(\tau)$  or the surface excess specific heat  $C_s(\tau)$  are insensitive to the detailed form of the profiles  $F(z)$  and follow already from a crude sharp-kink approximation which yields  $l(\tau) = (2H/\tau)^{1/(n-3)} [-\ln \tau]$ , and  $C_s(\tau) \sim \tau^{-(n-2)/(n-3)}$ ,  $[\tau^{-1}]$ .  $H$  denotes the Hamaker constant.

Important information on the molecular structure of the wetting layer is provided by the temperature dependence of the residual crystal order  $\{\tilde{\rho}_1(\tau), \tilde{\rho}_2(\tau), \dots\}$  at the vapour/liquid interface. We obtain

$$\tilde{\rho}_i(\tau) \sim \exp[-\omega_i (2H)^{1/3} \cdot \tau^{-1/3}], \quad [\tau^{\omega/\bar{\omega}}], \quad (9)$$

where  $\omega_i = \sqrt{\lambda_i/g_{ii}}$  and  $\bar{\omega} = \text{Min}(\omega_0, 2\omega_1, \dots, 2\omega_n)$ .

The decay law (9) in the case of long-range forces agrees with numerical findings [9] and can be tested experimentally, for instance with X-ray surface-scattering.

The mean-density profile  $\rho_0(z)$  approaches its bulk vapour or solid value as  $|z|^{-(n-3)} \cdot (\exp[-\lambda|z|], \lambda: \text{nonuniversal})$ ; the order parameters  $\rho_i(z)$ ,  $i \geq 1$ , decay exponentially in  $z$  within the quasi-liquid film for both short- and long-range forces, whereas they approach the solid bulk in the same way as  $\rho_0(z)$ .

To obtain some insights into the global features of the melting trajectory, we adopt the strongly simplified model mentioned above [7] with a single order parameter  $\rho_1$ , which may denote the width of the density peaks in the crystal, for instance. The matrix  $g_{ij}$  is taken to

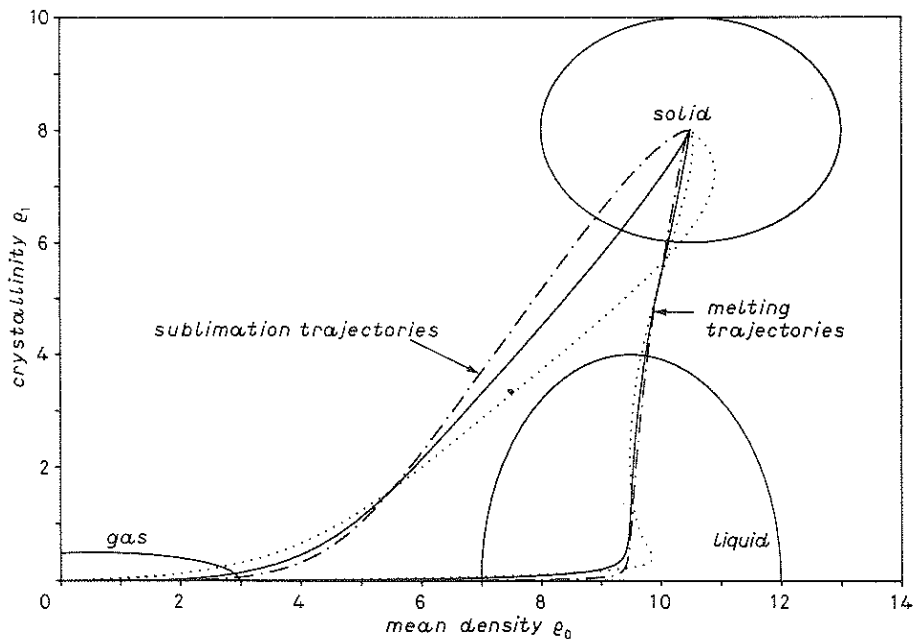


Fig. 1. - Melting ( $\tau = 0.0033$ ) and sublimation ( $\tau \rightarrow \infty$ ) trajectories in order parameter space in arbitrary units. The solid line is for a short-range potential ( $\alpha = 0$ ), whereas the dot-dashed and the dotted line correspond to a long-range attractive ( $\alpha = -1$ ) and repulsive ( $\alpha = 1$ ) potential. The ellipses are given by  $v(\Gamma) = -2$ . We choose  $g_{00} = 1$ ,  $g_{11} = 0.485$ ,  $a = 1$ ,  $\sigma = 1$ .

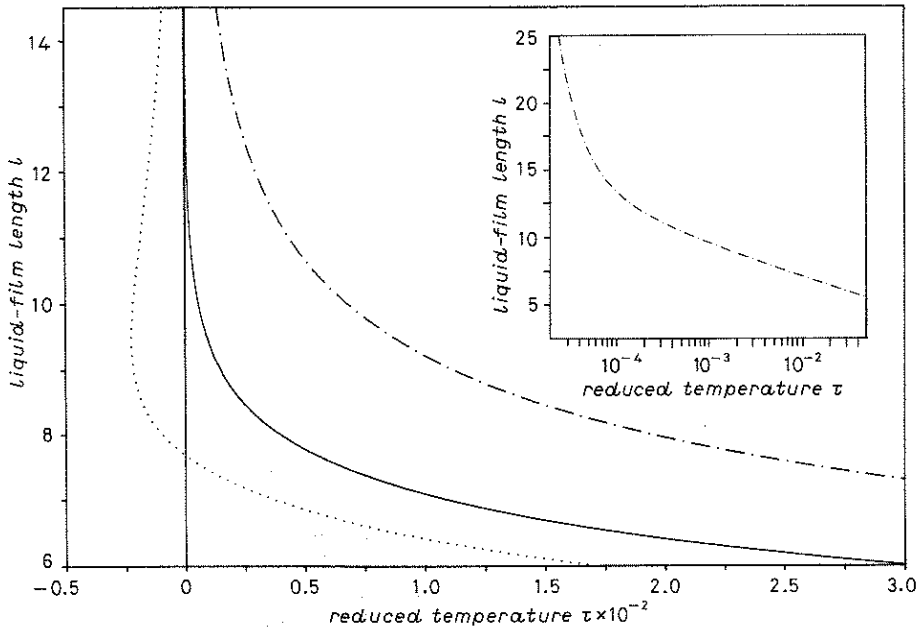


Fig. 2. – Width of the liquid film *vs.* reduced temperature  $\tau$  in arbitrary units for different kinds of potentials. The line type and the parameters are as in fig. 1. The dotted curve for  $\tau < 0$  corresponds formally to a nonequilibrium situation where the solid and the vapour are overheated. The inset shows the crossover from a logarithmic to an algebraic divergence law for a weak attractive long-range potential ( $\alpha = 0.05$ ).

be diagonal and constant; the potential  $v(\Gamma)$  is approximated by the truncated paraboloids

$$v(\Gamma) = \frac{1}{2} \max \{ -\lambda(\rho_0 - \rho_G)^2 - \lambda_G \rho_1^2; -2a\tau - \lambda(\rho_0 - \rho_L)^2 - \lambda_L \rho_1^2; -\lambda(\rho_0 - \rho_S)^2 - \lambda_S(\rho_1 - \rho_{1S})^2 \}, \quad (10)$$

with  $\lambda_G > \lambda_L > \lambda_S > 0$ . The curvatures in  $\rho_0$ -direction are chosen to be equal, since the qualitative behaviour of the trajectories is insensitive to  $\lambda$ . With expression (10) we adopted the model of Levi and Tosatti [7] for the contribution of the short-range forces. However, in contrast to ref. [7] we include long-range forces with  $w(z) = \alpha/(\sigma^2 + z^2)^2$ , corresponding to  $\phi_1(r) \sim r^{-6}$ . In the case of attractive forces we have  $\alpha < 0$ , but we may also consider repulsive tails by taking  $\alpha > 0$  although their occurrence is not immediately obvious. Results are given in fig. 1. For comparison, «sublimation» trajectories are also shown as obtained in the formal limit  $\tau \rightarrow \infty$ . Remarkably, the trajectory approaches the solid peak nonmonotonically if the tail potential is repulsive.

The «resting time» of the melting trajectory near the top of the liquid peak is a measure for the width of the interfacial layer, see fig. 2. If the strength of the Lennard-Jones potential  $\phi_1 \sim r^{-6}$  is weak (*e.g.*, as in metals) the numerical solution displays a crossover at some small finite  $\tau_0$  from  $l(\tau) \sim \ln(1/\tau)$  to  $l(\tau) \sim \tau^{-1/3}$  as  $\tau \rightarrow 0$ . This behaviour also induces a crossover in the residual crystallinity from a power law to a stretched exponential (9). The crossover in  $l(\tau)$  has apparently been observed in recent measurements [13] on Pb. In the case of a repulsive tail, the width of the interfacial layer remains finite as  $\tau \rightarrow 0$  (blocked melting).

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