

# Surface Melting: A Density Functional Approach

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A microscopic theory of surface melting is described and applied to Lennard-Jones systems. Our approach is based on density functional theory with the hard sphere fluid as a reference system. In particular we use a weighted density approximation which yields an accurate Lennard-Jones bulk phase diagram. Within a practically free minimization of the functional, we find surface melting of a Lennard-Jones crystal for different surface orientations. Furthermore the hard-sphere crystal-fluid interface and the hard-sphere crystal at a hard wall are explored with density functional theory. It is found that the crystal-fluid surface tension of hard spheres is extremely small and that the hard wall prefers to be covered by a hard-sphere-solid at solid-liquid coexistence.

## I. Introduction

How does a crystal melt if it is heated up slowly? One may conjecture that bulk melting may be initiated at point defects, vacancies, grain-boundaries or at the crystal *surface* which is a natural and omnipresent defect in the crystalline order. This is based on the common experience that liquids may easily be undercooled due to kinetic obstacles of nucleation but crystals can hardly be overheated. The idea that the crystalline surface plays a decisive role to initiate melting gains further support from the experimental observation that silver crystals (melting temperature 1234 K) coated by a thin film of gold (melting temperature 1337 K) can be substantially overheated [1].

Let us focus on an idealized *planar* and *equilibrium* situation of surface melting. A semi-infinite three-dimensional crystal in coexistence with its gas is heated up along the sublimation line until the temperature  $T$  approaches the triple point temperature  $T_T$  where the liquid phase becomes thermodynamically stable. The distance to the triple point

is conveniently measured by the reduced temperature distance

$$t \equiv \frac{T_T - T}{T_T} > 0 \quad (1)$$

The crystal is cut along a fixed plane with an area  $A$ , the position perpendicular to this plane is  $z$ . The structure of the solid-gas interface can be characterized by the parallel-integrated particle number density  $\rho^{\perp}(z)$  which is obtained from the full density  $\rho(\vec{r})$  via

$$\rho^{\perp}(z) = \frac{1}{A} \int dx dy \rho(\vec{r}) \quad (2)$$

Typically the parallel-integrated density for a solid-gas interface far away from the triple point consists of sharp peaks reflecting the periodic crystal lattice while it equals the gas bulk density in the gas phase. Between the two



phases there is a sharp interface typically involving only a few crystalline layers. As one approaches the triple point, two different situations can occur. In the first case, the *non-melting* case, there is no drastic change in the structure of the solid gas interface at  $T = T_T$ , i.e. the solid remains nonwet at its surface, even at  $T_T$ , and there is a sharp solid-gas interface. Apart from a broadening of the solid peaks due to the higher temperature, the parallel-integrated density across the solid-gas interface then is very similar to the one far from the triple point. In the second case, near  $T_T$ , a *quasiliquid layer* intervenes between the solid and the gas exhibiting a certain temperature-dependent width  $l$ . Surface melting is *complete*, if  $l$  diverges as  $t \rightarrow 0$ . Of course, the behaviour depends on the orientation of the crystalline plane. Surface melting is more likely in looser packed planes, since in denser packed planes the atoms are bound more tightly and disorder cannot be induced easily. Thus the following questions are relevant: Does the crystal melt from its surface or not? What is the detailed structure of the solid-quasiliquid-gas interface? If complete melting occurs, what is the divergence law for  $l(t)$  as  $t \rightarrow 0$ ?

The problem of surface melting originates from 1842, when Faraday [2] started investigations on melting and freezing of pieces of ice. In 1910, Tammann [3] pointed out that the surface has a decisive role to initiate bulk crystal melting. Later in 1942, Stranski [4] concretized this idea by macroscopic, qualitative considerations, including the dependence on the orientation of the solid plane. In the last decade, new powerful surface-sensitive experimental methods for studying microscopic aspects of surface structure were developed and thereby surface melting became a topical problem. Several recent experimental and theoretical results are reviewed in Refs. [5–7]. As an important example, the surface melting of ice which was controversial for a long time has recently been clarified. Ice is probably the material where surface melting has most practical applications ranging from charge transfer between ice crystallites in thunderstorm clouds and frost heaves to ice-skating. Reproducible X-ray scattering experiments by Lied et al. [8] strongly indicate that ice is an example of complete surface melting for every high-symmetry surface orientation.

As a simple model for rare gases, a system with a Lennard-Jones (LJ) pair-potential

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (3)$$

is often considered. There have been a number of computer simulations for the LJ system [7] but they are still inconclusive due to small system size. Among theoretical approaches we mention a lattice theory [9], a density functional theory [10] and combination of a density functional and van der Waals theory [11, 12]. Apart from the latter approach the theories suffer from an inadequate bulk phase diagram for the LJ system which is a necessary starting point for a quantitative theory of surface melting. In this paper, we propose

a density functional theory for surface melting which provides an accurate Lennard-Jones bulk phase diagram and improves the results of Ref. [12] substantially. In fcc crystals, surface melting is found to occur for the (100) and (110) orientations.

## II. Density Functional Theory

We start from the grand canonical free energy functional  $\Omega[\rho]$  of an inhomogeneous system with local density  $\rho(\vec{r})$ , temperature  $T$ , and chemical potential  $\mu$ . The basic variational principle establishes the existence of an excess free energy functional  $\mathfrak{F}_{\text{exc}}[\rho]$  such that the equilibrium density *minimizes* the grand canonical free energy functional,

$$\Omega[\rho] = \mathfrak{F}_{\text{exc}}[\rho] + \int d^3r \rho(\vec{r}) (V_{\text{ext}}(\vec{r}) - \mu - k_B T + k_B T \ln(\Lambda^3 \rho(\vec{r}))) \quad (4)$$

The minimum of  $\Omega[\rho]$  equals the real grand canonical free energy. In (4),  $\Lambda$  denotes the thermal wavelength and  $V_{\text{ext}}(\vec{r})$  is an external potential, e.g. a wall potential. In general, the explicit form of  $\mathfrak{F}_{\text{exc}}[\rho]$  is not known and one has to rely on approximations. One of the best schemes proposed to date is the weighted density approximation (WDA) [13],

$$\mathfrak{F}_{\text{exc}}[\rho] = \int d^3r \rho(\vec{r}) \Psi(\bar{\rho}(\vec{r})) \quad (5)$$

where  $\Psi(\rho)$  denotes the excess free energy per particle for any homogeneous density; the weighted density  $\bar{\rho}(\vec{r})$  is given implicitly by

$$\bar{\rho}(\vec{r}) = \int d^3r' \bar{w}(|\vec{r} - \vec{r}'|, \bar{\rho}(\vec{r}')) \rho(\vec{r}') \quad (6)$$

The weight function  $\bar{w}(r, \rho)$  is normalized and chosen in such a way that the known liquid structure factor  $S(k, \rho)$  is reproduced by the functional in the limit of a uniform density.

With the concrete form for the functional  $\Omega[\rho]$  specified, one calculates bulk phase diagrams by comparing the liquid free energy with that of a solid where the minimizing density consists of sharp peaks on a crystalline lattice. In practice, the width of Gaussian peaks and the lattice constant of the crystalline lattice are usually chosen as variational parameters describing the density distribution.

The WDA describes hard-sphere freezing and the results for the coexisting liquid and crystalline densities agree quite well with the simulational data. The LJ bulk phase diagram is accurately obtained if one treats the LJ-potential within hard-sphere perturbation theory [14]: The LJ potential is approximated by a sum of two Yukawa potentials [15] and split into a repulsive and an attractive part following the prescription of Weeks, Chandler and Anderson [16]. The repulsive core is approximated by an effective temperature-dependent hard sphere diameter  $d(T)$  obtained from the Barker-Henderson formula [17]. The attractive potential  $V_a(r)$  is treated in a mean field fashion:



$$\begin{aligned} \Omega[\rho] = & \Omega_{\text{WDA}}[\rho] + \int d^3 r \bar{\rho}(\vec{r}) [\Psi_{\text{LJ}}(\bar{\rho}(\vec{r})) - \Psi_{\text{HS}}(\bar{\rho}(\vec{r}))] \\ & + \frac{1}{2} \int d^3 r \int d^3 r' [\rho(\vec{r}) - \bar{\rho}(\vec{r})] [\rho(\vec{r}') \\ & - \bar{\rho}(\vec{r}')] V_a(|\vec{r} - \vec{r}'|) \Theta\left(\frac{d}{2} - |\vec{r} - \vec{r}'|\right), \end{aligned} \quad (7)$$

where  $\Omega_{\text{WDA}}$  is the WDA expression for hard spheres with diameter  $d$ . Here we have introduced another weighted density,

$$\bar{\rho}(\vec{r}) = \frac{24}{\pi d^3} \int d^3 r' \rho(\vec{r}') \left(1 - \frac{|\vec{r} - \vec{r}'|}{d}\right) \Theta(d - |\vec{r} - \vec{r}'|). \quad (8)$$

Therefore the last term in (7) vanishes in the homogeneous liquid.  $\Psi_{\text{HS}}(\rho)$  and  $\Psi_{\text{LJ}}(\rho)$  are the excess free energies per particle of the hard sphere and the LJ homogeneous liquid. For the former we take the analytic Percus-Yevick expression, for the latter quite accurate results are also available [18]. The unit step function  $\Theta(r)$  is introduced in (7) in order to avoid self-interaction effects in the solid.

The profile of the hard-sphere solid-fluid interface and its surface tension has been calculated within the WDA by Curtin [19]. He used two variational parameters for the interfacial density profile. This procedure was then also applied to LJ-solid-fluid interfaces [20].

In the present work we perform a *free* minimization [21] where we parameterize the solid density field in a periodically repeated slab by a large number  $N_g \approx 10^6$  of grid points and minimize the functional with respect to  $N_g$  variables. This does not give significantly different results for the bulk phase diagrams but it drastically affects the surface tensions. Thus, free minimization is required for calculating the structure of interfaces and investigating surface melting accurately.

### III. Solid-Fluid and Solid-Gas Interfaces

#### III.A. Hard Spheres

The *bulk phase diagram* of a hard-sphere system (with diameter  $d$ ) is temperature-independent and shows a strong first-order freezing transition from a fluid to a close-packed crystal. The corresponding liquid and solid densities ( $\rho_l = 0.94 d^{-3}$ ,  $\rho_s = 1.04 d^{-3}$ ) are known from computer simulation. With the Percus-Yevick expressions for  $S(k, \rho)$  and  $\Psi(\rho)$  and a constraint which avoids configurations of overlapping hard spheres [12], the results of the WDA,  $\rho_l = 0.89 d^{-3}$  and  $\rho_s = 1.02 d^{-3}$ , are close to the 'exact' values. Note that a free minimization has been performed in the space of periodic densities. However, there is practically no shift in the coexistence densities as compared to a Gaussian parameterization. We studied this density distribution in some detail [21]. The small anisotropy in the solid peak has the wrong qualitative behaviour in comparison with computer simulations. Hence the WDA is not able to reproduce such subtle features of the solid density distribution.

Next, let us discuss the structure of the hard-sphere *solid-liquid interface*. Unfortunately there are no computer simulation data neither for the interface structure nor for the surface tension. We have performed a density functional calculation in a finite slab with periodic boundary conditions. In order to avoid interaction with the periodically repeated interfaces, the width in  $z$  direction was chosen to be about  $25d$ . For the (100) orientation, free minimization of the WDA-functional yields a parallel-integrated density which is shown in Fig. 1. The lateral-integrated density profile is broader than and differs qualitatively from the restricted two-parameter *Ansatz* of Curtin [19]. Also the minimal lateral density  $\rho_m(z) \equiv \text{Min}_{(x,y)} \rho(\vec{r})$  is depicted which measures lateral ordering: it equals the bulk liquid density in the liquid phase and drops to very small values in the solid phase. The oscillation mismatch of  $\rho_m(z)$  with respect to  $\rho^\perp(z)$  in the interfacial region indicates that the interfacial profile is quite complex which cannot be parameterized by an *Ansatz* with few variational parameters. In fact, due to the free minimization, the resulting solid-liquid surface tension ( $\gamma_{\text{sl}} \leq 0.04 k_B T/d^2$ ) is much smaller than Curtin's result ( $\gamma_{\text{sl}} = 0.66 k_B T/d^2$ ). Thus the WDA predicts a very small surface tension which may be the reason why  $\gamma_{\text{sl}}$  is difficult to compute by simulations.

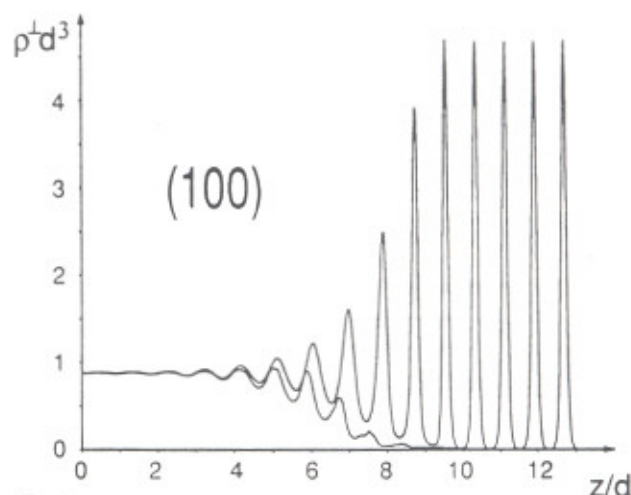


Fig. 1 Parallel-integrated density  $\rho^\perp(z)$  (upper curve) and minimal density  $\rho_m(z)$  (lower curve) versus  $z$  for a hard-sphere crystal-fluid interface in (100)-orientation, obtained within the WDA. The densities are in units of  $d^{-3}$ .

As a further example we also consider *hard-spheres at a hard wall*. Recent molecular dynamics simulations [22] indicate that a hard wall prefers to be covered by a crystal rather than by a liquid if the bulk density is in the liquid-solid coexistence region. We have calculated within WDA the surface tension of a wall-liquid system,  $\gamma_{\text{wl}}^*$ , and, for the first time, that of a wall-solid system,  $\gamma_{\text{ws}}$ , the densities being at coexistence [23]. It turns out that  $\gamma_{\text{wl}}^* = -2.92 k_B T/d^2$ ,  $\gamma_{\text{ws}} = -3.58 k_B T/d^2$  so that

$$\gamma_{\text{wl}}^* > \gamma_{\text{ws}} + \gamma_{\text{sl}} \quad (9)$$



implying that a hard wall prefers to be covered by the solid phase in accordance with the results of computer simulation. Therefore  $\gamma_{wl}^*$  is not a true thermodynamic surface tension but corresponds to a metastable situation. Thus the WDA describes complete wetting of a hard wall by a hard-sphere crystal correctly.

### III.B. Surface Melting of the Lennard-Jones System

Using the hard-sphere perturbation theory described in Chap. II and the WDA-functional for hard spheres, the resulting bulk phase diagram of the Lennard-Jones system is found to be in good agreement with results from computer simulations. For instance, the triple point temperature is at  $T_T = 0.75\epsilon/k_B$  in the WDA which compares well with the simulation result ( $T_T = 0.70\epsilon/k_B$ ) [24]. However, the theory suffers from the fact that the treatment of the attractive tail in perturbation theory is somewhat arbitrary.

The free minimization of the WDA-functional for a slab with periodic boundary conditions yields parallel-integrated density profiles displayed in Fig. 2. Two reduced temperatures  $t$  and the (100) and (110) surface orientations of the LJ fcc crystal have been investigated. As  $t \rightarrow 0$  both orientations exhibit surface melting. The first few crystalline layers become liquid-like and the width  $l(t)$  of the liquid film increases. For the LJ potential,  $l(t)$  diverges as  $-\ln t$  with a crossover to a power-law divergence  $\propto t^{-1/3}$  for very small  $t$  [11].

One also sees the influence of different surface orientations in Fig. 2. For the same reduced temperature  $t$ , the looser packed (110) plane is much more disordered than the (100) plane. The solid-liquid surface tension at the triple point is found to be  $\gamma_{sl}^{(100)} = 0.30\epsilon/\sigma^2$  for the (100) and  $\gamma_{sl}^{(110)} = 0.27\epsilon/\sigma^2$  for the (110) orientation. These values are in reasonable agreement with the simulation data:  $\gamma_{sl}^{(100)} = 0.34\epsilon/\sigma^2$  and  $\gamma_{sl}^{(110)} = 0.36\epsilon/\sigma^2$  [25]. However, there is a caveat in a direct comparison since the LJ-potential was truncated differently in the simulation and in our theory. For comparison, the two-parameter variational Ansatz of Curtin [20] yields  $\gamma_{sl}^{(111)} = 0.43\epsilon/\sigma^2$  and we find again that free minimization is mandatory in the study of interfacial properties.

The liquid-gas surface tension at the triple point is  $\gamma_{lg} = 0.44\epsilon/\sigma^2$  for the WDA; the simulation result is  $\gamma_{lg} \approx 0.8\epsilon/\sigma^2$  [26]. Thus  $\gamma_{lg}$  is only poorly reproduced by the density functional theory. However, one should also note that the simulation data have a rather large statistical error. An unexpected feature of the liquid-gas density profile at  $z/\sigma \approx 2$  in Fig. 2c is an oscillatory behaviour at the liquid side of the profile. This appears to be an intrinsic property of the free liquid-gas interface [27].

In conclusion, a weighted density functional approach has been proposed and applied to density profiles of interfaces in hard-sphere and Lennard-Jones systems. Free minimization is necessary to obtain the correct solid-liquid surface tension for hard spheres. Also surface melting and the corresponding orientation-dependent profile of the solid-gas interface of a Lennard-Jones system has been ob-

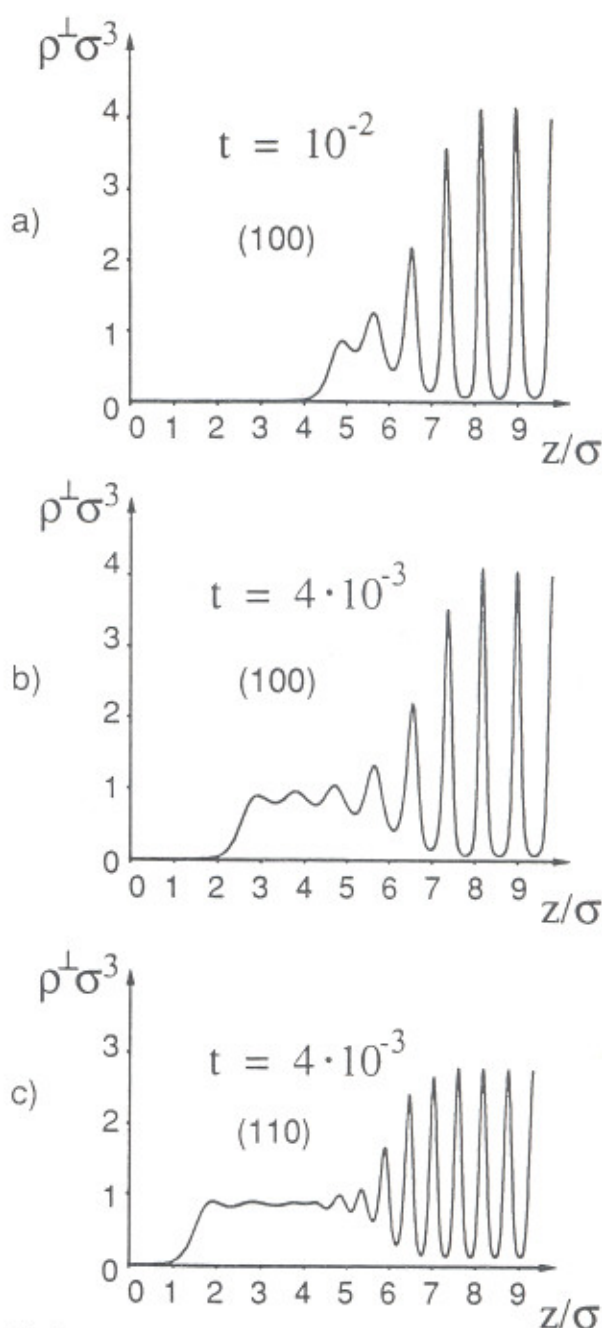


Fig. 2 Parallel-integrated density  $\rho^\perp(z)$  versus  $z$  for a LJ system obtained from hard-sphere perturbation theory of the WDA. a) Reduced temperature  $t = 10^{-2}$  and (100)-orientation; b)  $t = 4 \times 10^{-3}$  and (100)-orientation; c)  $t = 4 \times 10^{-3}$  and (110)-orientation

tained. The present theory can be generalized to address grain-boundary and edge melting of Lennard-Jones crystals. However, for such situations one needs a large system in two directions and the storage capacity required for a free minimization of the functional with a reasonable grid resolution is at the limits of present-day computers.

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