Multicomponent Order Parameter for Surface Melting

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A multicomponent order parameter for surface melting is introduced which depends both on the structure of the bulk crystal and on the orientation of the crystal surface. Each order-parameter component, \( \hat{M}(Q^f) \), corresponds to a reciprocal-lattice vector, \( Q^f \), of the two-dimensional lattice parallel to the surface. For complete surface melting, all order-parameter components with \( |Q^f| > |Q| \) vanish simultaneously but the associated critical behavior depends on the length of \( Q^f \). \( \hat{M}(Q^f) \) vanishes faster than \( \hat{M}(Q) \) if \( |Q^f| > |Q| \). For a surface of low symmetry, this implies a marked anisotropy of the melting process.

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Consider a crystal in equilibrium with its surrounding vapor. As the temperature, \( T \), is increased towards the triple-point temperature, \( T_t \), the bulk of the crystal remains almost unchanged up to \( T_t \) where it melts and, thus, undergoes a first-order phase transition. In contrast, surface quantities may exhibit continuous behavior characterized by critical exponents which can be observed over a whole \( T \) range below \( T_t \). This happens when the surface region starts to melt and, thus, to become disordered even though the bulk crystal remains in its ordered state. Then a thin liquidlike layer appears at the interface of the crystal and the vapor.

As one comes closer and closer to the triple point, the thickness of the disordered layer may continuously grow. Then the liquid-like phase will become more and more similar to the bulk liquid. This is the case of complete surface melting. On the other hand, no layer may appear at the crystal-vapor interface, or the thickness of this layer may remain finite as the triple point is approached even though the bulk crystal remains in its ordered state. Then a thin liquidlike layer appears at the interface of the crystal and the vapor.

As one comes closer and closer to the triple point, the thickness of the disordered layer may continuously grow. Then the liquid-like phase will become more and more similar to the bulk liquid. This is the case of complete surface melting. On the other hand, no layer may appear at the crystal-vapor interface, or the thickness of this layer may remain finite as the triple point is attained: This is the case of incomplete surface melting.

Much of the recent work on surface melting has focused on lead (Pb), for which it was first observed by ion scattering from the (110) surface. The same experimental technique has been used in order to investigate the dependence of surface melting on the surface orientation. More recently, the onset of surface melting for Pb(110) was also observed by low-energy electron diffraction (LEED). In addition, surface melting has been recently studied for Ar, O\(_2\), methane, and Ne. These systems seem to provide examples of complete surface melting. In contrast, incomplete surface melting has been observed for Pb(111) and for Ge(111).

In this paper, we introduce a multicomponent order parameter (OP) for surface melting. The choice of this OP depends both on the bulk structure of the crystal and on the orientation of the surface. The various OP components, \( m^{(j)}(z) = \hat{m}(Q^f_j,z) \), are labeled by the reciprocal-lattice vectors, \( Q^f_j \), and depend on the distance, \( z \), from the surface. The vectors \( Q^f_j \) are obtained by projecting the reciprocal-lattice vectors \( Q \) of the bulk crystal onto the surface plane, and are ordered according to their size:

\[
0 < |Q^f_j| \leq |Q^f_2| \leq |Q^f_3| \leq \cdots
\]

We will show below that the OP decay within the liquid-like layer is governed by the length scales

\[
a_{LJ} = a_{LO} |1 + (a_{LO} Q^f_j)^2|^{1/2} \leq a_{LO}.
\]

Here, \( a_{LO} \) is the bulk correlation length within the liquid phase which governs the exponential decay of the density fluctuations in the bulk liquid.

At the surface of the crystal (\( z = 0 \)), all OP components, \( m^{(j)}(0) \) with \( j \geq 1 \), vanish simultaneously for complete surface melting. The work presented here implies that \( m^{(j)}(0) \) vanishes faster than \( m^{(1)}(0) \) if \( |Q^f_j| > |Q^f_1| \). As an example, consider the (110) surface of Pb (or any other fcc lattice) which is characterized by two orthogonal vectors, \( Q^f_1 \) and \( Q^f_2 \), with \( |Q^f_1| = 2\pi/a \) and \( |Q^f_2| = \sqrt{2} \cdot 2\pi/a \) and bulk lattice parameter \( a \). Then, \( m^{(1)}(0) = \hat{m}(Q^f_1,0) \) should vanish faster than \( m^{(1)}(0) = \hat{m}(Q^f_2,0) \), and the process of surface melting becomes anisotropic. Such a behavior has indeed been observed for Pb(110): The (10) diffraction beam corresponding to \( Q^f_2 \) was observed to vanish faster than the (01) beam corresponding to \( Q^f_1 \).

Melting of Pb(110) seems to be governed by short-ranged forces. For such a system, we find the mean-field behavior

\[
m^{(1)}(0) \sim (T - T_c)^{\beta_{LJ}}
\]

with

\[
\beta_{LJ} = b_1 + (a_{LO} Q^f_1)^2 \frac{1}{2},
\]

and \( b = 1 \) or \( b = \frac{1}{2} \) if the particle densities within the bulk liquid and the bulk crystal are different or (nearly) equal, respectively. In general, interfacial fluctuations...
and long-ranged forces can affect the surface critical behavior as discussed at the end of this paper.

The bulk state of a crystal is characterized by its Bravais lattice, $|R|$, which is generated by three primitive lattice vectors, $\mathbf{r}_1, \mathbf{r}_2,$ and $\mathbf{r}_3$: $R = \mathbf{R}_1 \mathbf{r}_1 + \mathbf{R}_2 \mathbf{r}_2 + \mathbf{R}_3 \mathbf{r}_3$ with integer $\mathbf{R}_i$. The corresponding reciprocal lattice will be denoted by $\mathbf{Q} = \sum \mathbf{Q}_i \mathbf{r}_i$ with integer $\mathbf{Q}_i$. All bulk densities, $M_{C}(\mathbf{r})$, of the crystal depending on the spatial coordinate $\mathbf{r}$ are invariant with respect to arbitrary lattice translations and, thus, can be parametrized as

$$M_{C}(\mathbf{r}) = \sum_{\mathbf{Q}} M_{C}(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}).$$

(4)

Since $M_{C}(\mathbf{r})$ is real, $M_{C}(-\mathbf{Q}) = M_{C}^*(\mathbf{Q})$. The first term with $Q=0$ represents the overall particle density within the crystal.

Now consider a semi-infinite crystal bounded by a planar surface with coordinates $\mathbf{x} = (x_1, x_2)$ and $z$ parallel and perpendicular to the surface; the crystal is at $z > 0$ while $z < 0$ corresponds to the vapor. First, we decompose the crystalline state into lattice planes parallel to the surface. We choose the vector $\mathbf{q}_1$ of the reciprocal lattice to be perpendicular to these lattice planes. This implies $|\mathbf{q}_1| = 2\pi/d_{\perp}$, where $d_{\perp}$ is the separation of these planes. It then follows from $\mathbf{r}_1 \cdot \mathbf{q}_1 = 2\pi n_1$ that the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ of the direct lattice are parallel to the surface while the vectors $\mathbf{q}_1$ and $\mathbf{q}_3$ of the reciprocal lattice have, in general, both a parallel and a perpendicular component: $\mathbf{q}_i = \mathbf{q}^i_\parallel + \mathbf{q}^i_\perp$ for $i=1,2$. Thus, one has

$$Q^q = Q^q_\parallel + Q^q_\perp.$$

(5)

with

$$Q^q_\parallel = Q^q + Q^q_0, \quad Q^q_\perp = Q^q_\parallel + Q^q_0.$$

Deep in the crystalline phase, one must recover the form (4) for the bulk crystal which can be rewritten as

$$M_{C}(\mathbf{Q}, \mathbf{z}) = \sum_{\mathbf{Q}} M_{C}(\mathbf{Q}, \mathbf{z}) \exp(i\mathbf{Q} \cdot \mathbf{x}),$$

(6)

where $M_{C}(\mathbf{Q}, \mathbf{z})$ contains, in general, a phase factor, $\exp[iz(Q_1|q^1_\parallel + Q_2|q^2_\parallel)]$, arising from a shift of adjacent atomic layers parallel to the surface. Furthermore, any density, $M(\mathbf{x}, \mathbf{z})$, of the semi-infinite crystal is still invariant with respect to arbitrary lattice translations parallel to the surface, which implies

$$M(\mathbf{x}, \mathbf{z}) = \sum_{\mathbf{Q}} M(\mathbf{Q}, \mathbf{z}) \exp(i\mathbf{Q} \cdot \mathbf{x})$$

(7)

for all values of $\mathbf{z}$, where $\mathbf{Q}^q$ is again given by (5) and $\mathbf{Q}^q_\perp = 0$ is included. In the bulk of the crystal, (7) must be identical with (6) which implies

$$M(\mathbf{Q}, \mathbf{z}) = \tilde{M}(\mathbf{Q}, \mathbf{z}) \tilde{M}(\mathbf{Q}, \mathbf{z}),$$

(8)

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(8)

with $\tilde{M}(\mathbf{Q}, \mathbf{z}) \approx 1$ for large $\mathbf{z}$, where $\tilde{M}(\mathbf{Q}, \mathbf{z})$ describes the envelope of the profile $M(\mathbf{Q}, \mathbf{z})$. These envelopes vary smoothly with $\mathbf{z}$ even on atomic scales.

In order to focus on these smooth envelopes, we introduce averaged bulk variables $\tilde{M}(\mathbf{Q}) \equiv \langle \tilde{M}(\mathbf{Q}, \mathbf{z}) \rangle_z$, where $\langle \cdot \rangle_z$ represents a spatial average over the $\mathbf{z}$ coordinate. Then, we define the smoothed profiles

$$\tilde{M}(\mathbf{Q}, \mathbf{z}) \approx \tilde{M}(\mathbf{Q}, \mathbf{z}) \tilde{M}(\mathbf{Q}),$$

(9)

which will be taken as the components of the OP for surface melting. As in (1), we label the reciprocal lattice vectors, $\mathbf{Q} = \mathbf{Q}_j^0$, in such a way that $0 < |\mathbf{Q}_j^0| \leq |\mathbf{Q}_{j+1}^0| \leq \cdots$. Furthermore, we define the real OP component $m^{(j)}(\mathbf{z}) \equiv \tilde{M}(\mathbf{Q}^0 \cdot \mathbf{z})$, and the complex OP components $m^{(j)}(\mathbf{z}) \equiv m^{(j)}(\mathbf{Q}^0 \cdot \mathbf{z})$ for $j \geq 1$.

In terms of these variables, our Landau-type models have the generic form

$$F[\mathbf{m}] = F_{SC} \int_{-\infty}^{\infty} dz \left\{ \sum_{j \geq 0} \frac{1}{2} \left| \frac{dm^{(j)}}{dz} \right|^2 + f(\mathbf{m}) \right\},$$

(10)

with $\mathbf{m} = (m^{(0)}, m^{(1)}, \ldots)$ and a scale parameter $F_{SC}$. The function $f$ exhibits three local minima at $\mathbf{m} = \mathbf{m}_L$, $\mathbf{m}_A$, and $\mathbf{m}_C$ corresponding to the three bulk phases vapor (V), liquid (L), and crystal (C). When the triple point is approached along the C-V coexistence curve, one has $f(\mathbf{m}_L) < f(\mathbf{m}_V) < f(\mathbf{m}_C)$, where the caret indicates that the melt is metastable.

Close to the liquid phase with $\mathbf{m} = \mathbf{m}_L = (n_L, 0, \ldots)$ and $n_L \equiv m_L^{(0)}$, the function $f$ behaves as

$$f(\mathbf{m}) \approx \tilde{f}_L + \frac{1}{2} \left( m^{(0)} - n_L \right)^2 + \sum_{j \geq 1} \frac{1}{2} \left| m^{(j)} + n_L \right|^2 \left| a_{Lj} \right|^2.$$  

(11)

There are no mixed terms $-m^{(i)}m^{(j)}$ with $i \neq j$ since $f(\mathbf{m})$ must not change when the origin of the $z$ coordinate is shifted.

The physical meaning of the parameters introduced above is as follows. The parameter

$$H \equiv F_{SC} \tilde{f}_L - f(\mathbf{m}_L) \approx \Delta S(T - T_f)$$

(12)

represents an effective external pressure, where $\Delta S = S_{CV}^L - S_{CV}^A - S_{CV}^L - \delta F_{SC} \tilde{f}_L / \delta T$, and $S_{CV}^L = \delta F_{SC} \tilde{f}_L / \delta T$ are bulk entropies per unit volume at the triple point. The parameter $n_L \equiv m_L^{(0)}$ is the particle density within the liquid, and the parameters $a_{Lj}$ with $j \geq 0$ are length scales which govern the exponential tails, $m^{(j)}(\mathbf{z}) \exp(-\mathbf{z}/a_{Lj})$, of the OP's within the melt.

Now, we will show that these length scales satisfy the relation $a_{Lj} = a_{L0} \left( 1 + (a_{L0} / |Q^0|) \right)^{1/2}$ as given by (2). Thus, consider the (total) density $M(\mathbf{x}, \mathbf{z})$ within the bulk liquid. In general, this density is governed by the free-energy functional

$$F_L [M] = F_{SC} \int d^2 \mathbf{z} dz \left\{ \frac{1}{2} \left| \frac{dM}{dz} \right|^2 + \frac{1}{2} \left( V_1 M \right) \right\} + \frac{1}{2} \left( M / a_{L0} \right)^2,$$

(13)

with $V_1 = (\delta / \delta x_1, \delta / \delta x_2)$. As mentioned, $a_{L0}$ is the bulk correlation length within the liquid. The two coefficients in front of the two gradient terms must be identical since
the liquid is isotropic. Now, assume that
\[ M(x,z) = M_0 + m^{(l)}(z) \exp(iQ \cdot x) \]
which mimics one OP component of the crystalline state. When this form is inserted into (13), Eq. (2) follows by comparison with (10) and (11).

The thickening of the liquidlike layer at surface melting is most easily understood in terms of the effective interaction between the two interfaces bounding the layer. If one ignores the possible effects of interfacial fluctuations, this interaction is given by the direct interaction, \( V_{DI}(l) \), between planar interfaces. The Landau models defined above lead to a direct interaction which behaves as
\[ V_{DI}(l) = B_0 \exp(-l/a_{L0}) + C_0 \exp(-2l/a_{L0}) + \sum_{j \geq 1} C_j \exp(-2l/a_{Lj}) \] (14)

for large \( l \) with \( B_0 \sim (\eta_l - \eta_v)(\eta_C - \eta_l) \), where \( \eta_v, \eta_l, \) and \( \eta_C \) are the particle densities of the three phases. Within mean-field theory, the equilibrium value of the layer thickness, \( l \), follows from \(-\partial V_{DI}/\partial l = H = \Delta S(T_l - T) \) for small \( T_l - T \), with \( \Delta S = S^{L_1} - S^{C_1} \) as defined in (12).

Now, consider the case where \( V_{DI}(l) \) is positive for large \( l \). Then, \( l \) will continuously grow as \( H \) goes to zero. Two cases must be distinguished: case (i) with \( B_0 < 0 \) and \( n_c < n_l > 0 \), and case (ii) with \( n_c - n_l < 0 \). Case (i) is characterized by \( V_{DI}(l) = B_0 \exp(-l/a_{L0}) \) for large \( l \). Then, \( l = a_{L0} \ln[T_{so}/(T_l - T)] \) with \( T_{so} = B_0/a_{L0} \Delta S \), and the surface order parameters behave as
\[ m^{(l)}(0) \sim \exp(-l/a_{L0}) \sim (T_l - T)^{\beta_{L1}} \] (15)
with \( \beta_{L1} = a_{L0}/a_{Lj} \). This together with (2) leads to (3) and \( b = 1 \).

For case (ii) with \( n_c - n_l < 0 \), (14) implies \( V_{DI}(l) = C_0 \exp(-2l/a_{L0}) \). Now, \( l = \frac{1}{2} a_{L0} \ln[T_{so}/(T_l - T)] \) with \( T_{so} = 2a_{L0}a_{L} \Delta S \), and the critical exponents \( \beta_{L1} \) of the order parameters are given by \( \beta_{L1} = a_{L0}/2a_{Lj} \). Thus, one obtains (3) with \( b = \frac{1}{2} \). In real materials, \( n_c - n_l \) is not strictly satisfied but one often has \( n_c - n_L \ll n_C \). Then, the critical behavior associated with case (ii) will be visible only if \( l \) values.

In general, this crossover may be preceded by other crossovers arising from interfacial fluctuations or from long-range forces. First, consider the possible effects of interface fluctuations. The \( L-V \) interface is always rough, and its fluctuations are controlled by the interfacial tension, \( \Sigma_{LV} \). On the other hand, the \( C-L \) interface may be rough or smooth; its fluctuations are governed by the interfacial stiffness, \( \Sigma_{CL} \), which is finite and infinite for the rough and smooth state, respectively. For the direct interaction as given by (15), these fluctuations lead to a nontrivial renormalization which is governed by the length scale \( a_L \equiv (k_0 T/2\Sigma)_{1/2} \), with \( \Sigma = \Sigma_{LV} \Sigma_{CL} \).

Within linear renormalization-group schemes, the critical exponents \( \beta_{L1} \) are found to depend on the length scales \( a_{L0}, a_{Lj} \), and \( a_L \). The surface critical behavior is nonuniversal and rather complex; it simplifies only in the limit of sufficiently strong fluctuations where \( \beta_{L1} = 1 \) for \( j \geq 1 \).

It is not clear, however, if these fluctuation effects will be visible in experiments or computer simulations on surface melting. Indeed, similar effects are expected for wetting in fluids and surface-induced disorder in alloys, but computer simulations of lattice models have not produced, so far, any evidence for these effects.\(^{17,18}\)

On the other hand, all atoms or molecules interact via long-range van der Waals forces. These forces give a direct interaction \( V_{DI}(l) \) which behaves as \( V_{DI}(l) \sim -W/l^r \) for large \( l \), with \( r = 2 \) and \( r = 3 \) for nonretarded and retarded forces in three-dimensional systems.\(^{19}\) The parameter \( W \) is the so-called Hamaker constant. For such a direct interaction, thermally excited fluctuations can be ignored,\(^{20}\) and the equilibrium thickness follows from \(-\partial V_{DI}/\partial l = H \) which implies \( l \sim 1/(T_l - T)^{1/3} \) with \( \psi = 1/(1 + r) \). Since the van der Waals interaction is longer ranged than the exponential interaction in (15), it should govern the process of surface melting as soon as the disordered surface layer becomes sufficiently thick.\(^2\)

The influence of van der Waals forces has indeed been observed for the surface melting of Ar and Ne films\(^{8,12}\) and, quite recently, for the surface melting of Pb(110) very close to \( T_c \).\(^{21}\)

Once the thickening of the liquidlike layer is controlled by long-ranged forces, the critical behavior of the surface OP's \( m^{(l)}(z = 0) \) is also affected. If the tails of the OP profiles are still given by exponentials, the surface OP's vanish very rapidly as\(^{22}\)
\[ m^{(l)}(0) \sim \exp(-l/a_{Lj}) \sim \exp[-c/a_{Lj}(T_l - T)^{1/3}] \]

On the other hand, the OP profiles are expected to acquire small power-law tails in the presence of long-range forces which could give another crossover for the surface OP's back to power laws.

In summary, we introduce a multicomponent OP, \( m^{(l)}(z) = m(Q_j, z) \) with \( j \geq 0 \), for surface melting. The decay of these OP components within the liquidlike surface layer is governed by the length scales \( a_{Lj} = a_{L0}/[1 + (a_{L0}Q_j)^{21/2}] \) which depend both on the bulk structure and the surface orientation of the crystal and on the bulk correlation length \( a_{L0} \) of the melt. We predict that all surface OP's, \( m^{(l)}(0) \) with \( j \geq 1 \), vanish simultaneously for complete surface melting, and that \( m^{(l)}(0) \) vanishes faster than \( m^{(l)}(0) \) if \[ |Q|_{j+1} > |Q|_{j} \]. As explained, this is consistent with recent LEED measurements on Pb(110).\(^7\) The presence of strong multiple scattering makes it difficult to interpret the LEED data in a quantitative way. Therefore, the application of other experimental techniques such as totally reflected x rays is highly desirable in order to check the theoretical.
prediction (3) for the surface critical behavior.

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3This terminology emphasizes the close analogy of surface melting with wetting by fluids. Likewise, the crystal may also exhibit surface-melting transitions, or discontinuous premelting transitions.


6A review is by J. F. van der Veen, B. Pluis, and A. W. Denier van der Gon, in “Chemistry and Physics of Solid Surfaces” (to be published), Vol. VII.


9A review is by J. G. Dabs, in “Proceedings of the Solvay Conference on Surface Science” (Springer-Verlag, Berlin, to be published).


13If the vapor is undersaturated, the disordered surface layer should attain a stationary state which resembles the equilibrium state.


16The technical details will be presented elsewhere.


