SURFACE ROUGHENING AND QUASI-LIQUID LAYER

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The formation of a quasi-liquid layer on the crystal surface is studied. A model of roughening of the crystal—quasi-liquid-layer interface is proposed. The roughening temperature of this interface and the temperature above which the quasi-liquid layer exists are calculated. The possibilities for the appearance of surface roughening and quasi-liquid layer are discussed. The results are compared with the experimental data available.

1. Introduction

The problem concerning the appearance of a quasi-liquid layer on the crystal surface below the melting point was discussed back in 1949 by Stranski [1–3]. He considered the complete wetting of a crystal face by its own melt as a necessary condition for appearance of a quasi-liquid layer. Later this condition was used as a basis for phenomenological studies on the problem [4–6]. The appearance of a liquid-like layer on the crystal surface was ascertained by Broughton and Woodcock [7] and later by Broughton and Gilmer [8] by means of computer simulations using molecular dynamics method.

On the other hand, Burton and Cabrera [9], also Burton, Cabrera and Frank [10] found out a transition “atomic-smooth–atomic-rough” crystal surface, taking into account the cooperative interaction between atoms within the frames of the Ising model. Later the surface roughening was investigated considering crystal–vapour [11–16] as well as crystal–fluid interfaces [17–19]. It was found out that above the roughening temperature the interface width became divergent [14]; the step energy vanished [13]; normal crystal growth occurred [15]. Similar results were obtained when simulating surface roughening by means of Monte Carlo method [20–28]. The surface roughening has not yet been observed directly. The indirect experimental data [29] concerning this phenomenon showed that for some substances the roughening occurred below the melting point, the roughening temperatures being different for different crystal faces. There is a discrepancy between the experimental and the theoretical results – in particular, the theoretically predicted roughening temperatures are 2–4 times higher than the ones obtained experimentally.

Much indirect experimental proof for the existence of a quasi-liquid layer [32–44] is also available.

The question whether the surface roughening and the quasi-liquid layer are one and the same phenomenon or not, is controversial. They both are consequences of different theoretical models. Experimental data concerning the existence of quasi-liquid layer on a crystal surface and the structure of this surface were not available together. Only for the prismatic face of ice there was some information. The ellipsometric investigations of this face [44] show presence of liquid-like layer, while morphologic data [45,46] show the presence of singular crystal surface. Recently, Chernov and Yakovlev [55] have shown that the basal diphenyl face is covered with a quasi-liquid layer below the melting point. Since this basal plane is known to be atomically flat in contact with the melt [50], these findings support the distinction between the surface melting and surface roughening. According to Broughton and Gilmer [8] surface roughening is denoted by the presence of long-wave-length per-
turbations in the surface, while the liquid-like layer involves changes in the short-range order of atoms in the surface region. Broughton and Woodcock [7] regarded the surface roughening as preceding the appearance of the liquid-like layer, the latter not at all appearing in some cases. Investigating ice crystals, Lacmann and Stranski [4] presumed that a quasi-liquid layer is formed on atomically smooth surfaces. Chernov [49,52] considered that the presence of a quasi-liquid layer on a crystal face may facilitate the surface roughening.

The aim of the present paper is, assuming that surface roughening and quasi-liquid layer are different phenomena, to study the formation of a quasi-liquid layer on a crystal surface and the roughening of that crystal–layer interface.

2. Method and results

In order to investigate the conditions providing the existence of a thin melt (quasi-liquid) layer on the crystal surface, let us consider the change of the free energy $\Delta F$ due to the formation of such a layer. If the layer thickness $d$ is much smaller than the lateral sizes of the face, then $\Delta F$ can be expressed as follows [53]:

$$\Delta F = \frac{S}{a^2} \left[ \frac{d}{a} \Delta \mu + a^2 \Delta \sigma + \sum_{n=1}^{\infty} \epsilon_n \left( \frac{d}{a} \right)^n \right],$$

where $a$ is the average intermolecular distance and $S$ is the area of the crystal surface. The first term in eq. (1) is due to the difference between the chemical potential of the melt and that of the crystal:

$$\Delta \mu = \mu_m - \mu_v = \frac{L_m}{T_m} (T_m - T).$$

Here $L_m$ is the latent heat of melting and $T_m$ is the melting point of the crystal.

The second term in eq. (1) presents the energy gain $\Delta \sigma$ when covering the surface with a quasi-liquid layer:

$$\Delta \sigma = \sigma_m + \sigma_m - \sigma_v,$$

where $\sigma_m$, $\sigma_m$, and $\sigma_v$ are the surface energies of the crystal–melt, the melt–vapour and the crystal–vapour interfaces, respectively.

The long-range forces and the cooperative effects find expression in the third, fourth, etc., terms in eq. (1). The contribution of the thermal vibrations to the free energy of an isolated liquid layer is the following [53]:

$$\Delta F_1 = \frac{S}{a^2} \epsilon_1 \frac{d}{a},$$

where

$$\epsilon_1 = C k T.$$  

Here $C$ is a constant of order of unity. In the case of isolated liquid layer, the value of $C$ was calculated by Chernov and Simon [53]. When a crystal surface is covered by the layer, due to the penetration of phonon waves into the crystal, the value of $C$ is probably slightly lower than the value calculated by Chernov and Simon [53].

The dispersion interatomic forces contribute to the free energy by the following correction term [54]:

$$\Delta F_2 = \frac{S}{a^2} \epsilon_2 \frac{d^2}{a^2} \left( \epsilon_2 \sim 10^{-14} - 10^{-15} \text{ erg} \right).$$

According to Chernov’s estimate [53], at room temperature the ratio between eqs. (4) and (6) is $(1-10)d/a$. At higher temperatures all the terms, for which in eq. (1) $n$ is greater than one, can be neglected.

$$\Delta F = \frac{S}{a^2} \left[ \frac{d}{a} \Delta \mu + a^2 \Delta \sigma + \epsilon_1 \frac{d}{a} \right].$$

At equilibrium the free energy $\Delta F$ reaches a minimum. The equilibrium layer thickness is [53]:

$$d_{eq} = a \frac{\epsilon_1}{\Delta \mu}.$$

The quasi-liquid layer is stable when $\Delta F_{eq} \approx 0$, the necessary conditions for which being as follows:

$$\Delta \mu \approx (a^2 \Delta \sigma)^2 / 4 \epsilon_1,$$

$$\Delta \sigma < 0.$$  

According to eq. (10), the quasi-liquid layer can be formed only on a completely wetted by its own melt crystal surface.
Using eqs. (2), (5) and (9), one can obtain the following equation for the temperature \( T_q \), above which a quasi-liquid layer exists on a crystal surface:

\[
T_q(T_m - T_q) = AT_m^2, \tag{11}
\]

where

\[
A = (a^2 \Delta \sigma)^2/4CKT_mL_m. \tag{12}
\]

If the parameter \( A < 0.25 \), eq. (11) has two roots. However, only the greater is the temperature \( T_q \), because at low temperatures the correction terms with \( n > 1 \) in eq. (1) cannot be neglected and then eq. (11) is not correct. Above the temperature \( T_q \), the quasi-liquid layer is stable and its thickness \( d \) increases with the increase of the temperature.

Let us now consider the roughening of this crystal–quasi-liquid-layer interface. In order to determine the roughening temperature of the interface we used Jackson’s criterion [17], according to which an interface is rough when the \( \alpha \) factor,

\[
\alpha_{hkl} = \frac{L}{kT \nu}, \tag{14}
\]

satisfies the following inequality:

\[
\alpha_{hkl} \leq \alpha_{hkl}^R, \tag{15}
\]

where \( \xi \) is the number of the lateral neighbours of an atom from the crystal surface and \( \nu \) is the total number of the neighbours of an atom from the crystal. In the paper of Jackson [17] the value of the critical \( \alpha \) factor \( \alpha_{hkl}^R \) is equal to 2, while according to Bennema and Gilmer [18] it depends on the crystallographic type of the face.

In general, for a crystal–layer interface the latent heat \( L \) depends on the layer thickness \( d \). In turn, the equilibrium thickness of the layer increases with an increase of the temperature, becoming infinite at the melting point \( T_m \). In this way the temperature converting inequality (15) into equation is exactly the roughening temperature.

The latent heat \( L \) (per atom) can be obtained from the following thermodynamical formula:

\[
L = a^3 \frac{\partial}{\partial T} \left[-T \frac{\partial \Delta F}{\partial T}\right] = \frac{a^3}{S} \frac{\partial}{\partial d} \left[-T \frac{\partial \Delta F}{\partial T}\right]. \tag{16}
\]

Using eqs. (2), (5), (7) and (16) and neglecting the temperature dependence of the surface energies, the dependence of \( L \) on the layer thickness \( d \) becomes as follows:

\[
L = \frac{L_m T + CKT \frac{a^2}{d^2}}{T_m}. \tag{17}
\]

Substituting eq. (8) into eq. (17) leads to \( L = L_m \) for the present model. Thus from eqs. (14) and (15) one can obtain an expression for the roughening temperature:

\[
\frac{T_R}{T_m} = \frac{\alpha_{hkl}^m}{\alpha_{hkl}^R}. \tag{18}
\]

where \( \alpha_{hkl}^m \) is the \( \alpha \) factor for a crystal–melt interface at the melting point:

\[
\alpha_{hkl}^m = \frac{L_m \xi}{kT_m \nu}. \tag{19}
\]

3. Discussion

For the different substances and crystal faces the following cases are possible in general:

1. \( \Delta \sigma > 0 \). In this case the quasi-liquid layer does not exist up to the melting point (see eq. (10)). The roughening, if any, occurs on the crystal–vapour interface. Then the roughening temperature cannot be calculated according to eq. (18). Its theoretically predicted value is usually above the melting point.

2. \( \Delta \sigma < 0 \) and \( T_q < T_R \) (calculated according to (18)) \( < T_m \). The roughening temperature of the crystal–quasi-liquid-layer interface is below the melting point only when the crystal–melt interface is rough \((\alpha_{hkl}^m < \alpha_{hkl}^R)\). This condition is fulfilled for many substances (metals, etc.) [17]. In this case, increasing the temperature, a quasi-liquid layer appears on the crystal surface. An additional increase of the temperature leads to roughening of the crystal–layer interface.
(3) $\Delta \sigma < 0$ and the roughening temperature calculated according to (18) is lower than $T_u$. Below $T_u$ the quasi-liquid layer does not exist and the crystal–vapour interface is atomically smooth. At $T = T_u$ wetting of the crystal face occurs and the crystal–layer interface becomes rough.

(4) $\Delta \sigma < 0$ and $T_u < T_m < T_R$ (calculated according to (18)). The quasi-liquid layer exists on the atomically smooth crystal surface.

The results of the present paper can be used to set in conformity the theory and the experiment regarding the roughening temperatures of crystal–vapour interfaces. As an example, let us consider diphenyl crystals. The singularity–nonsingularity transition of these crystals was experimentally investigated in detail below the melting point (vapour growth) [51] as well as theoretically and experimentally at the melting point (crystal–melt interface) [50]. According to the experimental results, only the faces (001) and (110) are smooth at the melting point and as the calculation [50] showed, the corresponding $\alpha_{hkIZ}$ factors are greater than the critical ones. The other three faces (table 1) are rough, their $\alpha_{hkIZ}$ factors being lower than $\alpha_{hkIZ}^R$. Below the melting point only these faces become nonsingular [51]. It could be supposed that a quasi-liquid layer exists on these three faces and the experimentally observed singular–nonsingular transition might be related to roughening of the crystal–layer interface. The lower values of the experimentally obtained roughening temperatures in comparison to those calculated according to eq. (18) suggest that $T_R$ could be lower than $T_u$ (case 3).

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References


Table 1
Comparison between experimental and theoretical results for different faces of diphenyl

<table>
<thead>
<tr>
<th>Face ( hkI )</th>
<th>Crystal–melt interface [50]</th>
<th>Crystal–vapour interface [51]</th>
<th>( T_R / T_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>( \alpha_{h1z} = 2.6 )</td>
<td>Flat</td>
<td>2.0</td>
</tr>
<tr>
<td>(110)</td>
<td>( \alpha_{h1z} = 2.8 )</td>
<td>Flat</td>
<td>1.04</td>
</tr>
<tr>
<td>(111)</td>
<td>( \alpha_{h1z} = 3.4 )</td>
<td>Rough</td>
<td>0.96</td>
</tr>
<tr>
<td>(201)</td>
<td>( \alpha_{h1z} = 2.7 )</td>
<td>Rough</td>
<td>0.99</td>
</tr>
<tr>
<td>(100)</td>
<td>( \alpha_{h1z} = 3.0 )</td>
<td>Rough</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Present paper, eq. (18)
A. Trayanov, D. Nenow / Surface roughening and quasi-liquid layer