MORPHOLOGY AND SURFACE STRUCTURE OF SIMPLE CRYSTALS

J. P. VAN DER EERDEN

RIM Laboratory of Solid State Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Abstract. Two theoretical models for simple crystals, the Kossel model and the Lennard-Jones model, are compared, as far as their roughening behaviour is concerned. The predictions are shown to be in line with experiments on $^4$He crystals but not with experiments on naphtalene crystals. The tentative conclusion is that the shape of the growth unit may drastically change the character of the roughening transition.

1. Introduction

The atomic structure of a crystal reflects itself in several macroscopic phenomena. For crystal growth most prominent are the morphology and the growth rate. This, of course, has been realized long ago, starting with the work of Kepler and Hauy (for a short review see ref. (1)).

For general experimental conditions we are still far away from understanding or predicting crystal growth rates and forms on the basis of atomic and molecular properties. Therefore, we have to rely on the results of very simple models and compare these with carefully designed experiments in which the major model simplifications are reasonable approximations of reality. In his lecture Bennema shows how results from a simple model can be generalized for complex crystal structures.2)

The simplest possible model for crystal surfaces and crystal growth is the Kossel model3) also known as simple cubic solid on solid model. This model contains two possible bulk phases:

(i) a completely homogeneous mother phase
(ii) a crystalline phase with exact simple cubic symmetry.

These phases are separated by an infinitesimally thin interface which is essentially two dimensional (due to the solid on solid restriction). The external variables are temperature (scaled with an effective bond energy) and supersaturation.
Already this most simple model has posed many difficulties and is well understood only since the relationship with the planar spin model \(^4\) and the Coulomb gas model \(^8\) have been established. Indeed we now know that this model possesses a infinite order phase transition. The edge free energy \(\gamma\) is the order parameter which vanishes at and above \(T_R\). When \(T\) approaches \(T_R\) from below then \(\gamma\) tends to zero with a very weak (so called essential) singularity (usually \(\gamma\) is taken per growth unit).

In Section 2 we shortly summarize the Kossel model results and in Section 3 we discuss some of the available results on the more general Lennard-Jones model. Though these results are not yet beyond criticism we can find some essential trends. In Section 4 we compare experimental results on \(^4\)He crystals with the predictions of these models, concluding that in many respects there is a good correspondence. In Section 5 finally we introduce experimental results on naphtalene, and find striking disagreement. We shall argue that this disagreement may be due to the non-spherical shape of the (molecular) growth units. Therefore we would expect a similar disagreement for many molecular crystals.

2. The Kossel Crystal

The Kossel model has been studied in mean field approximation by Temkin.\(^9\) His results already indicated that a roughening transition might exist. The nature of the roughening transition has been studied in great detail with Monte Carlo simulations, for extensive reviews see ref. (10–12). Deeper understanding, however, arose only after the relation with the planar spin model was established.\(^4\)-\(^7\) More precise numerical evidence was given by Monte Carlo simulation of the Coulomb gas model.\(^8\),\(^13\)

The order parameter for the transition is the edge free energy \(\gamma\). It vanishes, when the temperature approaches \(T_R\) from below, as

\[
\gamma \sim \exp[-\alpha(T_R - T)^{-1/2}].
\]  

(1)

The total temperature dependence is given in Fig. 1.

The problem with this order parameter is that on one hand it is very difficult to measure, and that on the other hand rather accurate values are necessary to test Eq. (1). E.g. specific heat measurements do show a maximum\(^{13,14}\) (this maximum is not a singularity\(^{13}\)), but at a temperature which is about 10% below \(T_R\), whereas at \(T_R\) no measurable singularity is present.

However, indirect measurement is possible. In principle the facet size on an equilibrium form (\(\sim \gamma\)) contains the necessary information but this form is very difficult to achieve both in Monte Carlo simulations (see the lecture of Y. Saito\(^15\)) and in experiments (see, e.g., Uwaha\(^16\) for \(^4\)He and Ohachi\(^17\)) for
Ag$_2$S). It turns out to be easier to use growth rate data. Either one fits the
growth rate $R$ to a formula obtained in a two dimensional nucleation and
growth model.$^{10,16}$

$$ R \sim (\Delta \mu)^p \exp \left( -b\gamma^2/(kT \Delta \mu) \right), $$

(2)

where $p$ and $b$ are constants which are somewhat model dependent but
approximately are given by$^{10-12}$

$$ p \approx 1, $$

(3)

$$ b \approx \pi/3. $$

(4)

Or one measures the supersaturation $\Delta \mu^*$ at which kinetical roughening sets
in.$^{19}$ In the latter case one assumes that at $\Delta \mu = \Delta \mu^*$ the excess free energy of
the critical nucleus ($= \pi \gamma^2 / \Delta \mu$) equals the average thermal energy ($kT$). This
leads to

$$ \gamma^2 \approx kT \Delta \mu^*/\pi. $$

(5)

Comparison with help of Monte Carlo data (for a discussion in more
detail see ref. (19)) shows that the first method tends to overestimate $\gamma$ near $T_R$
whereas the second method underestimates $\gamma$ when $T$ is more than 20% below $T_R$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The temperature dependence of the edge free energy in the Kossel model. At
$T = T_R$ one has the essential singularity, given by Eq. (1), for $T \approx T_R$ one has $\gamma \approx 0$.}
\end{figure}
3. The Lennard-Jones Model

In the Lennard-Jones model the atoms are in principle free to move around in space but they interact with a Lennard-Jones type of interaction. In this model the three fundamental phases, solid, liquid and gas exist and can be studied. Also, in principle one might study the surface of a Lennard-Jones crystal in contact with its melt or with vapour. This has been done by Gilmer and Broughton.20 Such models could exhibit two types of surface phase transition.

First, at certain temperatures below the melting temperature $T_m$, a layer could be formed which resembles a kind of two dimensional melt (since the underlying crystal imposes still some long range correlation it may be more appropriate to call this layer a plastic crystal). This is what one usually describes as surface melting. The interface between this layer and the real rigid crystal might well be smooth if surface melting happens below $T_R$.

Second, it may happen that the surface becomes rough without a dramatic increase in the mobility of the atoms in the top layers. In this case we would have a roughening transition much like in the Kossel model (since the transition is governed by long-distance fluctuations).

However, already Gilmer and Broughton have noted that apparently in the Lennard-Jones model surface roughening and surface melting are strongly coupled and seem to occur simultaneously.

It should be noted that, to my knowledge, it is impossible at the moment to argue from first principles on the existence of a well defined (quasi) liquid layer separating a solid crystal from the vapour phase, as has been suggested in the early paper of Broughton and Woodcock on the subject.21 Indeed, Kroll and Meister have nicely shown that a macroscopic liquid film may cover an attractive solid substrate if the range of substrate-fluid interactions is longer than that of the fluid-fluid interactions.22 However no such rule can be given in the crystal growth case where these ranges are equal.

In Fig. 2 some data are shown which we obtained with Monte Carlo simulations of Lennard-Jones particles on a smooth substrate which consists out of almost similar particles.

The substrate is a (111) face of an fcc crystal. Its lattice parameter is adjusted for thermal expansion20 but thermal motion of its atoms is neglected. The data are of insufficient accuracy to locate the melting and roughening transitions very accurately. Therefore we took as a provisional estimate of the melting point the temperature where the second and third neighbour peak in the pair correlation function of the adsorbed particles merge. As a provisional roughening point we took the temperature where 10% of the adsorbate particles is in the second or higher layers. The minimum energies in the Lennard-Jones interactions are taken equal for the three
possible pairs (substrate-adsorbate, substrate-substrate and adsorbate-adsorbate), but the radius \( \sigma_a \) of the substrate particles could be larger than the radius \( \sigma_s \) of the adsorbate.

In correspondence with Kroll and Meister's rule \(^{22}\) our data shown that for \( \sigma_s > 1.1 \sigma_a \) a distinct liquid film can be formed in a certain temperature interval. However, when we approach the crystal growth case \( \sigma_s \rightarrow \sigma_a \) then the temperature interval narrows and when \( \sigma_a \approx \sigma_s \) surface melting and surface roughening have merged into a single process, as stated by Broughton and Gilmer. \(^{20}\) Hence, surface roughening in a Lennard-Jones system seems to be a multicritical transition and can not be expected to belong to the universality classes of either the two dimensional melting transition or the Kosterlitz-Thouless transition.

Because of this situation we are not able to predict the behaviour of the edge free energy near the expected transition. Also to measure the edge free energy in a Monte Carlo experiment turns out to be a difficult task, due to the fact that the direct determination of this excess quantity requires very good statistics. Nevertheless we can get some indication from the pressure tensor. Indeed if we would have a two-dimensional liquid strip along the \( X \)-axis, and if this strip is sufficiently wide to have bulk liquid behaviour in the centre, then
the interfacial free energy $\gamma$ of the two-dimensional liquid-vapour interface would be given by\(^{23}\)

$$2\gamma L = \langle p_{xx} - p_{yy} \rangle A$$

(6)

where $p_{xx}$ and $p_{yy}$ are diagonal components of the pressure tensor $p_{ij}$, $L$ and $A$ are the length and the area of the strip. Of course the relation above is not exact in the case where the bulk of the strip is not a real isotropic liquid but has some crystalline order. Most likely the right hand side of Eq. (2) is an underestimation of the interfacial energy, the error becoming the smaller the more the strip behaves as a liquid strip.

Consequently we measured $p_{xx} - p_{yy}$ in a Monte Carlo calculation of a strip of $24 \times 24$ atoms on a Lennard-Jones (111) substrate with $24 \times 48$ possible adsorption sites, using $4 \times 10^7$ Monte Carlo steps, neglecting the first $2 \times 10^7$ steps for averaging.

The result, shown in Fig. 3 indicates at least a smoothly temperature dependent edge free energy in the neighbourhood of the roughening point (which is, by definition, the temperature above which $\gamma$ vanishes). The nature

![Graph](image)

**Fig. 3.** Difference of normal and lateral pressure for a strip of Lennard-Jones particles on a crystalline substrate with the same interaction parameters. Equation (6) suggests that this should give an indication of the edge free energy.
of the transition can not be deduced from these data (already because of the only approximate validity of Eq. (6)).

In conclusion, we think that our data support the congestion that for a Lennard-Jones crystal surface (i) the edge free energy is temperature dependent near the roughening point and (ii) the surface melts at the same temperature.

In many experiments it will be difficult to distinguish between the two features. Scattering with α-particles on Pb showed surface melting below the bulk melting temperature but is insensitive to surface roughening. Ellipsometry which has been proposed by Kuroda and by Yakovlev and Chernov during this seminar, gives the same type of information. Measurements of the growth laws, as will be discussed in the rest of this paper give direct information only about the edge free energy, not about surface melting.

4. Roughening Experiments on $^4$He-Crystals

During the last five years a lot of morphological observations have been done on $^4$He crystals in contact with its superfluid melt. The advantage of this system, as compared with more conventional crystal growth systems, is that it relaxes very rapidly to equilibrium. Indeed capillary waves can be visualized in real time movies, showing that relaxation times are of the order of a second.

The experiments have established that several faces disappear at different temperatures, the (0001) face at 1.2 K, (1101) at 0.9 K and (1101) at 0.35 K.

A study of the equilibrium form around these transition temperatures shows that the curvature near the disappearing facets behaves, within experimental accuracy, in accordance with the predictions of the Kossel crystal. Recently one has studied the growth curves as well. Here the result was that below 1.2 K these curves for the (0001) plane could be fitted very well with a nucleation formula. This fit gives values of the edge free energy which support firmly the consequence of a Kossel model that the roughening transition is of the infinite order type.

In summary, the $^4$He crystal behaves similar to the theoretical models, at least as far as the character of the transition is concerned. Nonetheless it is as yet impossible to decide whether the system is more Kossel-like or more Lennard-Jones-like, since no direct data on the atomic surface structure are available to my knowledge. Another point which still needs further study is the unusual temperature dependence of the kinetical coefficient (growth rate divided by driving force), which in some cases increases with decreasing temperature.
5. **Naphtalene Crystals**

There are a lot of crystals where faces can be observed which do not seem to disappear. E.g. one has obtained the equilibrium shape of small lead and gold crystallites\(^{28}\) which show faces and rounded parts but no roughening transition below the melting point.

The same seems to happen with several organic crystals. Human and Jetten have investigated which faces should appear on biphenyl and naphtalene crystals, using the equivalent wetting condition to estimate effective bond energies.\(^{29}\) Though their results were in good agreement with theoretical estimations further analysis by Elwenspoek\(^{30}\) showed that in most solvents faces of naphtalene were more stable against roughening than expected. Moreover careful experiments have shown that equilibrium roughening was never observed, though kinetical roughening was easy for certain faces.

Consequently Elwenspoek decided to measure the critical value \(\Delta \mu^*\) for kinetical roughening. Surprisingly enough the value turned out to be virtually independent of temperature for naphtalene growing from a toluene (ideal!) solution over the range from \(-5^\circ\)C to \(80^\circ\)C. The fact that \(\Delta \mu^*/kT\) moreover is very small (0.014 for the (110) face and 0.0013 for (201)) is in obvious contradiction with the Kossel-model behaviour. Indeed such small values of \(\gamma\) (estimated with Eq. (5)) imply that one is at most 10\% below \(T_R\), such that the experimental temperature interval of 25\% of the absolute temperature should contain \(T_R\).

If we, tentatively, think about the consequences of this unexpected behaviour we first have to note that a constant edge free energy implies a vanishing edge entropy. Hence the steps on the naphtalene surfaces are very straight. In combination with the small edge energy (equal to the edge free energy in case of vanishing entropy) this means that the formation of a kink should be related to a very high energy. This high kink energy could arise from the anisotropy of the bond-strength on the surface. However the ratios of the solid-solid bonds, relevant for the (110) and (201) faces, suggest only a moderate anisotropy; the highest step energy at \(T=0\) K is only 1.5 times higher than the lowest one. In order to have a kink energy of the order of \(kT\) and an average edge energy of the order of 0.1 \(kT\) an anisotropy factor of 10 is necessary. This reasoning, almost inevitably leads to the conclusion that the structure of the solution near the kinks should be different from the average solution structure. If Chernovs suggestion of a quasi liquid or quasi plastic surface layer is valid\(^{26}\) then one would certainly expect further modifications near steps and kinks, if only due steric hindrance effects.
6. Conclusion

I have discussed the roughening of surfaces on theoretical simple crystal models, the Kossel and the Lennard-Jones model. The roughening process is characterized by a smoothly vanishing edge free energy when approaching the roughening temperature from below.

The experiments on $^4$He crystals are in line with these predictions, the experiments on napthalene are not.

In my view the crucial difference is the shape of the growth units. Both in the theoretical models and in the $^4$He experiments these are highly isotropic. In the napthalene case, however the molecules are highly anisotropic and this influences the solid-liquid interface so strongly that the basic assumption of the Kossel model (to have only two states for a given cell) is invalid.

REFERENCES

[15] SAITO, Y.: Monte Carlo studies of equilibrium crystal shapes, this seminar.
[16] UWABA, M.: Crystal shapes viewed as mechanical equilibrium of steps, this seminar.
DISCUSSION

Bennema

We published in our group two papers on—what now turns out kinetical—roughening of the weak side faces 201, in (110) faces of naphthalene and biphenyl growing from organic solution. We thought that these transitions could be interpreted as roughening transitions of the Kossel SOS model. Thanks to the very recent experiments of Elwen Spoek it now turns out that the transition at the surface is more complicated as explained by Van der Eerden.

A: Yes, indeed. One of our future tasks is to find out whether these organic crystals are exceptional or representatives of a large group.

Müller-Krumbhaar

Surface melting may (possibly) be understood as surface “wetting”. For the latter there are good first-principles calculations available: T.
Meister, D. Kroll (Phys. Rev. Lett., 1985). In the wetting problem the interplay with the roughening transition is fairly well understood.

A: However, if the “substrate” becomes identical to the “adsorbing film”, the situation is still not understood. Especially the role of the lateral inhomogeneity of the substrate may decisively change the structure and other properties of an adsorbed film.

Kirkpatrick

Can you comment on the kind of materials that should undergo surface roughening as opposed to surface melting?

A: I can, at the moment, not do much more than guess. My guess would be that isotropic growth units usually lead to a Kossel like behaviour whereas anisotropic growth units are more likely to produce a “quasi-liquid” layer.

Kuroda

I have a comment to surface-melting. We are doing ellipsometric study of surface melting of ice crystals. We’ve found that molten layer exists not far below the melting point of ice. There are 2 possible interface structures between molten layer and crystal: One is sharp interface and the other is diffuse one.

A: I do not dare to say which of the two possibilities is most likely. From a theoretical point of view this is because we do not have a general argument to decide whether \( T_R < T_m \text{ (surf)} \) or \( T_m \text{ (surf)} > T_R \) or even \( T_R = T_m \text{ (surf)} \).