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Kinetic roughening and step free energy in the solid-on-solid model and on naphthalene crystals

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Abstract. We describe a method to estimate the critical supersaturation σ_c above which a growing crystal face becomes kinetically rough. We discuss the relation of σ_c with the step free energy $kT\gamma$. The method is tested with computer simulations of the growth of the (001) face of a simple cubic crystal in the solid-on-solid (SOS) model. Near T_R , the roughening transition temperature, the results are in good agreement with other estimates of γ . The method is then applied to growth of (110) faces of naphthalene from melt and solution. We find that γ does not depend on the temperature, in contrast to γ found for the SOS model. The (110) face of naphthalene hence does not behave according to the infinite-order roughening transition of Kosterlitz-Thouless type. The classical method to model crystal growth from solution with SOS models turns out to be fundamentally incapable to describe surface roughening in the naphthalene case.

1. Introduction

The free energy per growth unit in a step on crystal faces, $kT\gamma$ (k and T are the Boltzmann constant and the absolute temperature, respectively), plays a key role in crystal growth. γ reflects the physical state of the surface: it is related to the density of steps and to the width of the surface.

It also controls the growth mechanism. At large γ , two-dimensional nucleation on a flat crystal face is very improbable and growth is possible only via screw dislocations emerging on the surface which serve as step sources (Burton *et al* 1951). At smaller γ , two-dimensional nucleation becomes more important and if $\gamma=0$ the nucleation barrier vanishes and direct incorporation of growth units is possible. The temperature at which γ vanishes is called the roughening transition temperature T_R . Above T_R , the crystal surface is rough on the microscopic scale. The surface width diverges and macroscopically the roughening transition manifests itself by rounding off of the crystal face in question. Usually (i.e. if geometrically possible) a rough crystal face disappears from the growth form since its growth rate is much larger than that of the flat faces.

Obviously it is of great interest to measure step free energies. In this paper we suggest the kinetic roughening as a measure of γ . Kinetic roughening is often observed on growing organic crystals. Faces which are smooth in equilibrium may become round if they grow at sufficiently large supersaturation.

In this paper we first discuss the relation of σ_c , above which the growth form changes from flat to round crystal faces, with the growth curve (the dependence of the growth rate R on the supersaturation) and with the free energy of steps. In § 3

we test the method on growth curves of the (001) face of a simple cubic crystal, measured with Monte Carlo simulations in the sos model (van der Kruk 1975). Sections 4 and 5 are devoted to the growth form and growth rate of naphthalene growing from melt and solution. Application of our method to estimate the edge free energy in this experimental system leads to a new insight into the roughening phenomena on this crystal.

2. Kinetic roughening

At low temperature, i.e. at $T < T_R$, where T_R is the roughening temperature above which the step free energy $kT\gamma$ vanishes, the growth of a crystal is hindered by the nucleation barrier. We assume a rectangular lattice with horizontal interaction parameters ϕ_x and ϕ_y ($|\phi_x| \geq |\phi_y|$). Let us approximate the shape of a nucleus by an ellipse with main half-axes a and b ($a > b$). We assume that

$$\delta = b/a \approx \phi_y/\phi_x$$

where a is parallel to the x direction. The free energy of an elliptical cluster characterised by a and δ is given by

$$g = 4aEkT\gamma - \pi a^2 \delta \Delta\mu / f_0 \quad (1)$$

where $\Delta\mu$ is the chemical potential difference between the growth units in the liquid and crystalline state, γ is the mean step free energy, $\frac{1}{2}(\gamma_x + \gamma_y)$, $E \equiv E((1 - \delta^2)^{1/2}, \pi/2)$ is the elliptic integral of second kind and f_0 is the surface of one growth unit. The magnitude of the critical nucleus is obtained from (1) by minimising g with respect to a : we then find

$$a^* = \frac{4E}{2\pi\delta} - \frac{\gamma}{\sigma} f_0 \quad (2)$$

where

$$\sigma = \frac{\Delta\mu}{kT}. \quad (3)$$

The often used shape factor is defined by

$$\xi = 2\sqrt{\pi} \frac{\sqrt{s}}{l}$$

where s and l are the surface and the perimeter of the nucleus, respectively. Note that for a circle, $\xi = 1$ and $E(0, \pi/2) = (\pi/2)$. ξ and E are related by

$$\xi = \frac{\pi\sqrt{\delta}}{2E}. \quad (4)$$

At a supersaturation σ a nucleus with long axis less than a^* will tend to dissolve while a larger nucleus will grow.

At equilibrium, $\sigma = 0$, there are nuclei present by thermal fluctuations. The mean long half-axis of these nuclei $\langle a \rangle$ is given by

$$\begin{aligned} \langle a \rangle &= \int_0^\infty a \, da \exp(-4aE\gamma) \left(\int_0^\infty da \exp(-4aE\gamma) \right)^{-1} \\ &= \frac{1}{4\gamma E}. \end{aligned} \quad (5)$$

If $\langle 2a \rangle$ is smaller than the linear dimensions of one growth unit, the number of single growth units on a flat surface is very small. At sufficiently small γ , $\langle 2a \rangle$ will be larger than one growth unit. Then the surface will be covered with nuclei with long axis $\langle 2a \rangle$. But if in a non-equilibrium situation with a certain σ so that $\langle a \rangle < a^*$ they will not grow. The nucleation barrier breaks down if thermal fluctuations serve for the creation of a vast number of critical nuclei. A criterion for this phenomenon could be (i) $a^* = \langle a \rangle$ or (ii) $g(a^*) = kT$. In both cases γ does not play an important role for growth: the crystal grows as if $\gamma = 0$, i.e. it grows as if $T > T_R$.

This situation we identify with kinetic roughening. The supersaturation at which $g(a^*) = kT$ is easily found to be

$$\sigma_c = \pi f_0 (\gamma / \xi)^2. \quad (6)$$

The first criterion, $a^* = \langle a \rangle$, leads to twice as large a critical value of the supersaturation.

The second mechanism, therefore, sets in at a smaller supersaturation than the first one—hence we expect it to be the more important one and we adopt (6) for the estimate of γ from a measurement of σ_c . If the supersaturation exceeds σ_c , the face becomes round and the growth rate depends linearly on the supersaturation. If kinetic roughening is observed, the growth curve (i.e. growth rate against supersaturation) consists of a non-linear part at $\sigma < \sigma_c$. We can estimate σ_c by extrapolating the growth curve down to zero growth rate.

On real crystals an independent check is the change of the growth form of the crystal. This method is of course not applicable to computer simulations due to the very limited size of the systems.

3. Computer simulation

The growth curves of the (001) face of a Kossel crystal have been measured by Gilmer and Bennema (1972a, b), de Haan *et al* (1974) and van der Kruk (1975). Part of the results of van der Kruk's measurements have been published in van der Eerden *et al* (1977). Here we use van der Kruk's raw data. The data had been obtained on a special purpose computer (SPC), which worked about 200 times faster than a general purpose computer like IBM 370/55. The hardware model represented 20×20 horizontal lattice sites of the Kossel crystal and pseudoperiodic boundary conditions are introduced. Further details can be found in the papers of de Haan *et al* (1974) and van der Eerden *et al* (1977). Some of the measured growth curves ($\delta = 1$) are shown in figure 1. It is clearly seen that at high σ , the curves all become linear in σ . Annoyingly, all curves show a sharp bending at $\Sigma \approx 0.05$ ($\Sigma =$ stick fraction) which introduces an uncertainty of $\pm 30\%$ for σ_c . The reason for this bending is unknown.

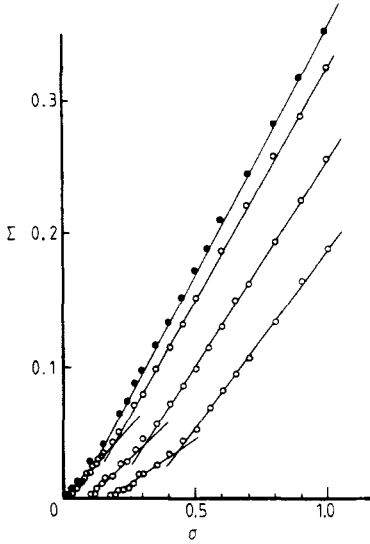


Figure 1. Stick fraction in the SOS model of finite size (20×20) as a function of supersaturation $\sigma = \Delta\mu/kT$ for various temperatures. From the bottom line up, $T = 0.89, 1.00, 1.14$ and 1.21 .

We show the resulting values for γ in figure 2 (using (6)). We included step free energies for a Kossel crystal with anisotropic interaction $\delta = 0.33$; for elliptical two-dimensional nuclei we have $\xi = 1.4$. Though the error bars of the individual points for isotropic and anisotropic interaction overlap, all $\delta = 0.33$ points lie systematically below the γ belonging to the isotropic case. Unquestionably, $T_R(\delta = 0.33) < T_R(\delta = 1)$. $\sigma_c(\delta = 0.33)$ has also been taken from van der Kruk's (1975) work (not shown in figure 1).

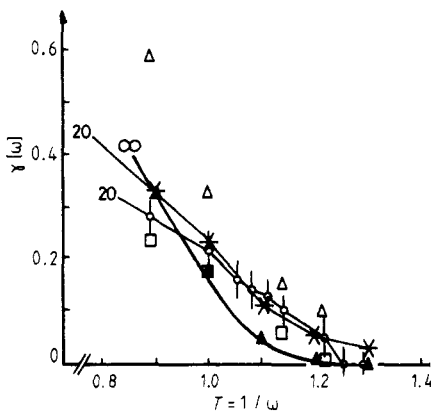


Figure 2. Step free energy as a function of temperature for the SOS model. Open triangles obtained from a fit of the growth curve with (7) (two-dimensional nucleation). Open points and open squares are obtained by the extrapolation method described here. The points are for $\delta = 1$ and the squares for $\delta = 0.33$. Asterisks and full triangles are measurements of Quirke and Jacucci (1984) for the finite SOS model (20×20) at $\delta = 1$ and their extrapolation for the infinite system.

Van der Kruk had fitted his growth curves using a formula derived from two-dimensional nucleation theory (see, e.g., van Leeuwen and van der Eerden 1977)

$$\Sigma \sim \sigma^{4/5} \exp - \frac{\pi}{2} \frac{\gamma^2}{\xi^2 \sigma}. \quad (7)$$

γ obtained by this method is considerably larger than that obtained by our method.

Our results may be compared with measurements of γ by Quirke and Jacucci (1984) for the finite system (20×20). Their results are included in figure 2 and it is seen that they are in excellent agreement with our ones. Note that the γ of Quirke and Jacucci is finite also at $T > T_R$. This results from the finite size of the system. γ as extrapolated to infinite system size is somewhat smaller than γ for finite systems and vanishes, as it should at $T \geq T_R$.

According to van Beijeren (1977), van der Eerden and Knops (1978) and Knops (1977), the sos model falls in the same universality class as the xy model (Kosterlitz and Thouless 1973, José *et al* 1977). The step free energy is then expected to vanish near T_R as

$$\gamma \sim \exp \left[- \left(\frac{T_R}{T_R - T} \right)^{1/2} \right] \quad (8)$$

approaching T_R from below. The points found from σ_c can be fitted by (8) which leads to T_R between 1.25 and 1.29. The estimates of T_R due to other authors using other methods range from $T_R = 1.24$ (Weeks 1979), 1.25 (Quirke and Jacucci 1984) and 1.30 (van der Eerden 1976).

Step energies E_S in the sos model have been measured by Swendsen (1977). We tried to reduce his results to free energies but the data are too inaccurate to serve as a serious test. An alternative comparison is provided by reducing the free energies shown in figure 2 to energies. Then only a differentiation is involved: $E_S = \gamma - T\sigma\gamma/\sigma T$. However the results of our procedure are much too inaccurate to serve for a reasonable comparison.

The poor results of our method at small T (large γ) has a simple reason. Here the mean diameter of a thermally activated two-dimensional nucleus becomes smaller than one growth unit. Then our argument breaks down. If we trust Quirke's and Jacucci's work, we have $\gamma = 0.18$ at $T = 1$ and consequently $\langle a \rangle = 0.88$. Thus, $T \sim 1$ constitutes the lower limit for the use of the kinetical roughening for the estimate of γ .

In de Haan's paper (de Haan *et al* 1974) the authors report difficulties in fitting their growth curves with the nucleation formula, for $T > 1.08$; 'good fits' are obtained at $T < 1.0$. It appears that the nucleation concept does not work near T_R —between $T = 1$ and T_R our method seems to be superior to nucleation theories.

4. Growth of (110) face of naphthalene

Naphthalene crystallises in the space group $P2_1/a$ with two molecules per unit cell. The cell dimensions are $a = 9.253 \text{ \AA}$, $b = 6.003 \text{ \AA}$, $c = 9.652 \text{ \AA}$ and $\beta = 123^\circ$ (Cruickshank 1957). Naphthalene and toluene form an ideal solution in the liquid state as can be inferred from solubility data, and toluene is not soluble in solid naphthalene. Growing from toluene solution the naphthalene crystals are platelets with large (001) and small elongated (110) and (20 $\bar{1}$) faces. Growing from toluene solution they have elongated (110) and (20 $\bar{1}$) faces. On growth forms, the (20 $\bar{1}$) face often disappears

due to the higher growth rate of this face compared to the (110) face. At increasing supersaturation first the $(20\bar{1})$ and then the (110) face become round. The crystals then resemble the shape of 'flying saucers'. An example is shown in figure 3. More illustrations of this phenomenon can be found in a previous publication (Jetten *et al* 1984). The crystals were observed in well thermostatted ($\Delta T \leq 0.02^\circ\text{C}$) cylindrical (~ 70 mm of diameter ~ 3 mm of height) double walled glass cells using polarisation microscopy. In the cells, crystals were nucleated, and subsequently all but one crystal were dissolved in a somewhat tedious procedure as described by Human *et al* (1981). Linear dimensions of the crystals were typically of the order of 1 mm.

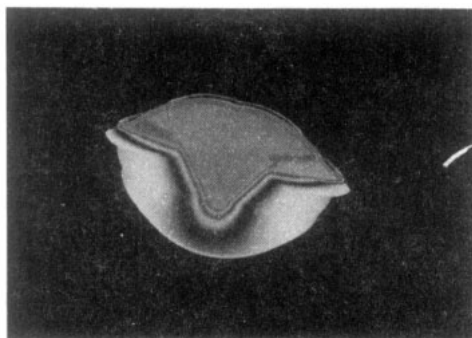


Figure 3. An example for a kinetically rough naphthalene crystal. $T^* = 16^\circ\text{C}$, $\sigma \sim 0.02$. The long axis of the crystal is approximately $100\ \mu\text{m}$.

The growth rates were measured in stagnant solutions on crystals lying on the (001) face by observing directly the rate of advance of the crystal surface. Toluene was purchased from Merck (Darmstadt, West Germany) (per analyse) and naphthalene from Janssen Chimica (Belgium). We checked the results using highly purified naphthalene (99.995%, a gift from the Organisation For Applied Scientific Research (TNO), Zeist, the Netherlands), without noting any significant change in growth rate and growth form.

A 'periodic bound chain' (PBC) analysis of naphthalene has been given by Hartman (1973). He found the following so-called F faces (which are faces with nearest neighbours in at least two crystallographic directions in a slice; these slices are candidates for faces having a roughening transition temperature greater than 0): (001), $(20\bar{1})$, (110), (200), (111), (010), (112). Of these only (001), (110) and $(20\bar{1})$ are observed on crystals growing from melt and toluene solution. This agrees very well with estimates of the Jackson α factors (Jackson 1967) of the F faces given by Jetten *et al*. In Jetten *et al* (1984) the critical Ising temperatures $T_c \approx T_R$ of the F faces are also calculated. The result is that the (001) face grows below T_R , the (110) and $(20\bar{1})$ approximately at T_R and the other faces above T_R (at $T \sim$ room temperature). The critical assumptions made in this analysis are, besides $T_R \sim T_c$, (i) the continuation of the crystal structure into the liquid (lattice gas model) and (ii) the equivalent wetting assumption. (ii) means that the coupling constant in the lattice gas model of a solute molecule with other molecules is ϕ_{ff} , irrespective of whether this other molecule is 'solid' or 'liquid'.

The (110) net (Bennema and van der Eerden 1986) has a distorted hexagonal structure with binding energies after Williams (1966) (in kcal) -3.66 , -1.03 and -0.82 . If we want to compare the (001) face of the Kossel crystal with the (110) face of

naphthalene, the anisotropy of $\delta = 0.33$ of the Kossel crystal constitutes a lower limit for the anisotropy of the (110) naphthalene face.

The measured growth curves as a function of $\sigma = \Delta\mu/RT^*$, where T^* = equilibrium temperature, are shown in figure 4. The linear extrapolation of the growth curves to zero growth rate according to

$$R = R_0(\sigma - \sigma_c) \quad \sigma > \sigma_c \quad (9)$$

is easily seen. The nucleation curve (7) does not satisfactorily fit to the experimental points. In figure 4 the growth rates have been normalised to a growth rate 1 at $\sigma = 3\%$. The reduction factor η is in $\mu\text{m s}^{-1}$: 35 at $T^* = 54^\circ\text{C}$, 2.5 at $T^* = 39^\circ\text{C}$, 1.2 at $T^* = 2^\circ\text{C}$ and 0.175 at $T^* = 10^\circ\text{C}$. This dramatic temperature dependence will be discussed elsewhere (Elwenspoek 1986). We concentrate here on σ_c and on the step free energy. We want to point out that the growth curves cannot be described by a spiral growth law (see, e.g., Bennema 1973)

$$R \sim \sigma^2 \tanh \sigma_1/\sigma \quad (10)$$

since the linear part of that curve extrapolates to $\sigma = 0$, in contrast to the curves presented in figures 1 and 4.

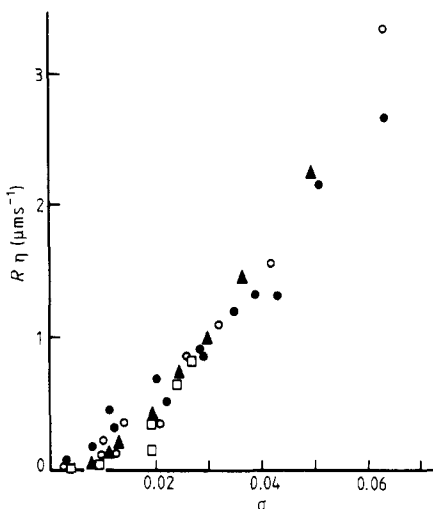


Figure 4. Growth curves of (110) faces of naphthalene. The growth rates have been reduced to a growth rate $R = 1$ at $\sigma = 0.03$. Equilibrium temperatures T^* and reduction factor η are as follows: full points: $T^* = 10^\circ\text{C}$, $\eta = 0.175$; open points $T^* = 25^\circ\text{C}$, $\eta = 1.2$; full triangles: $T^* = 39^\circ\text{C}$, $\eta = 2.5$; open squares $T^* = 54^\circ\text{C}$, $\eta = 35$.

The resulting σ_c are given in table 1 along with σ_c^m , the supersaturation above which the (110) faces become round. We included the results of Jetten *et al* (1984). Also given is γ , calculated with the help of (6). We took $\xi = 1.3$, corresponding to elliptic nuclei with anisotropy $\delta = 0.5$.

Obviously, σ_c and σ_c^m are very close, which gives great confidence in our method to employ the growth kinetics of the SOS model as an estimate for kinetical roughening.

Growing from the melt, naphthalene exhibits the same properties as growing from toluene solution at small supersaturation. The (001), (110) and (20 $\bar{1}$) faces are all

Table 1. Critical supersaturation of (110) faces of naphthalene crystals growing from a toluene solution. T^* is the equilibrium temperature. σ_c is taken from the growth curve and σ_c^m from the change of the growth form. The values labelled by (1) have been taken from Jetten *et al* (1984). γ was calculated using equation (6) with $\xi(\delta = 0.5) = 1.3$.

$T^*(^{\circ}\text{C})$	$\sigma_c(10^{-2})$	$\sigma_c^m(10^{-2})$	γ
-3		1.4	0.086
+2		1.3	0.083
10	1.1 ± 0.3	1.3 ⁽¹⁾	0.083
		1.4	0.076
25	1.5 ± 0.2		0.091
30		1.5 ⁽¹⁾	0.091
38		1.4 ⁽¹⁾	0.086
39	1.35 ± 0.2		0.085
50		1.4 ⁽¹⁾	0.086
54	1.35 ± 0.2		0.085
82		> 1.0	> 0.074

facetted: no face on the equilibrium form is rough at this highest accessible temperature. At $\sigma \approx 0.01$ we found rapidly growing facetted dendrites, which made observation at higher supersaturation impossible. If crystals are nucleated at high supersaturation, $\sigma > 0.03$, only the (001) face remains facetted. So we can state that $\sigma_c^m(82^{\circ}\text{C}) \geq 0.01$.

5. Discussion

The numerical value of γ of the (110) face of naphthalene is in a range comparable to that of the (001) face of a Kossel crystal in the sos model at a temperature near T_R , see figure 2. Clearly, the temperature dependence of γ is completely unexpected: $kT\gamma$ shows a tendency to increase with increasing temperature in place of no decrease. An increasing free energy implies negative entropy, as such a free energy makes no physical sense at all. However, the experimental uncertainty is so large that we do not take the observed trend too seriously and state that the step free energy of the (110) face on naphthalene is constant in the temperature range covered.

This is a great contrast to the properties of the Kossel crystal, as well for the isotropic as for the anisotropic one. $kT\gamma = \text{constant}$ could be explained by assuming that our experiments are carried out essentially at $T = 0$, far away from T_R . However the very small γ points to a roughening transition temperature not too far from the covered range of temperature. The estimate $\alpha_{110} = \alpha_{110}^R$ (Jetten *et al* 1984) also strongly suggests that we are near T_R . Moreover, we mention an observation of roughening of negative naphthalene crystals in equilibrium with the vapour phase: at $T \sim 70^{\circ}\text{C}$ the (110) faces are round (Pavlovskaya and Nenov 1972). Note that this contradicts our observations: for lattice gas models one would expect that $T_R^{\text{melt}} < T_R^{\text{vapour}}$ since the melt decreases all surface energies. A liquid layer covering the naphthalene crystal near T_M could resolve the discrepancy in part. Liquid layers have been observed on several crystals near T_M , among others on the (001) face of biphenyl (Chernov and Yakovlev 1985), a crystal with very similar properties as naphthalene (Human *et al* 1981). The remaining discrepancies between our work and that of Pavlovskaya and Nenov (1972) could be due to impurities (see, e.g., Pavlovskaya 1979), or due to the use of very small negative crystals in the experiments of Pavlovskaya and Nenov.

We believe therefore that T_R is not very far from T_M (but larger) and the question arises: 'Why does the step free energy on the (110) face not depend on temperature?' The weak temperature dependence of $kT\gamma$ leads us to think of a roughening transition of first order rather than of infinite order. In any case, the temperature dependence of $kT\gamma$ of naphthalene sharply contrasts the infinite-order transition expected for the roughening transition.

Obviously the nature of the crystal—solution (or melt)—interface is very much different from the interface models as described by cell models where, to every cell, there can be assigned the state 'fluid' or 'solid'. Maybe this idea is too simple, since 'fluid' and 'solid' describe states of macroscopic systems and not those of single molecules or atoms. However, abandoning these notions produces difficulties with the notion of steps on the surface and monomolecular growth spirals on crystals growing from solution have clearly been identified (Tsukamoto *et al* 1983). So we suggest that the (probably) different character of the roughening transition on a real organic crystal growing from solution and melt is connected with the state of the fluid near the growing crystal which cannot be described by a lattice gas model.

In a recent publication (Wolf *et al* 1985) measurements of the growth rate of the (0001) face of ^4He growing from the melt were reported. The authors fitted the growth curves with the two-dimensional nucleation formula (7) and found a $\gamma(T)$ which agrees very well with the infinite-order transition picture. Thus, the difficulties concerning naphthalene are perhaps due to the additional degrees of freedom (rotation) which become free at melting.

This idea is supported by experiments described elsewhere (Elwenspoek *et al* 1986) which show that σ_c becomes very large if naphthalene grows from solutions, the solvent of which does not consist of molecules containing benzene rings (acetone, hexane, etc). Similar observations on biphenyl and naphthalene crystals are due to Podolinsky and Drykin (1983).

However, even in the simplest model system the melt-crystal interface is poorly understood (see, e.g., Cerjan *et al* 1985), and up to date we have no satisfactory explanation for the peculiar properties of the crystal-solution interface of naphthalene.

6. Conclusion

We have proposed a method to derive step free energies on crystal faces which employs the critical supersaturation. Near the roughening transition temperature we could demonstrate that for the sos model the results are superior to a fit of the growth curve using two-dimensional nucleation theory. Our resulting step free energies are in excellent agreement with measurements in the finite sos model. We applied the method to naphthalene. We found that the (110) face of naphthalene behaves in a way which is much different from the Kossel crystal. The success of a PBC analysis, on the other hand, suggests that at low temperatures the Kossel crystal is a good model for crystal-liquid or crystal-gas interface. Near T_R , the lattice gas model is not an adequate description of a real face of a molecular crystal.

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