

LETTER TO THE EDITOR

Finite-size effects cannot explain experimental equilibrium crystal shape

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Abstract. Experiments on equilibrium metallic and helium crystals show an 'anomalous' mean-field behaviour of crystal shape near facet edges, in contradiction with existing microscopic theories. In this work, the possible finite-size, or $1/R$, origin of the observed behaviour is analysed. It is shown that these $1/R$ effects are negligible, even for very small crystals ($\sim 1 \mu\text{m}$). We conclude that, neither finite-size effects nor classical long-range step-step interaction can account for the observed experimental behaviour.

Since the work of Burton and Cabrera [1], the subject of the roughening transition and its related faceting phenomena has been a classical topic in surface physics. Despite the theoretical and experimental effort devoted to clarify the nature of this faceting transition, a controversial situation still exists about some fundamental questions. From a theoretical point of view, a wide class of interface models [2, 3] predicts the existence of a universal behaviour of the equilibrium crystal shape near the roughening transition. One of the most important predictions of these models is the existence of a universal behaviour of the equilibrium crystal shape (ECS) near a facet edge. The ECS, $Z(x)$, as a function of the distance, x , to the facet edge should behave as

$$Z \approx Z_0 - Bx^{3/2}. \quad (1)$$

This behaviour, characteristic of a Pokrovsky-Talapov transition [4], reflects the fact that the surface free energy has a dependence on the surface slope p as $\beta = \beta_0 + \beta_1|p| + \beta_2|p|^3$, where the $\beta_2 p^2$ term, characteristic of the classical phenomenological theories [5-7] is absent.

Recent experiments on equilibrium lead [8] and indium [9] crystals are in disagreement with the predictions which lead to the PT behaviour. They are in full agreement with the mean-field-like theories. This discrepancy between experiments and PT behaviour has been attributed to two very different physical origins. First, there is the possible existence of some effective interaction between steps (up to now of unknown origin) which could lead to the p^2 term observed experimentally [7]. On the other hand, it has been argued that finite-size, or $1/R$, effects could account for this discrepancy [8, 10]. In particular, Rottman and co-workers [8] have claimed that $1/R$ effects would produce a rounding effect near the facet edge. From the experiments on lead [8] and indium [9]

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crystals (with a typical size of 5–10 μm) it can be seen that the characteristic size of this $1/R$ -rounded region is about 3000 \AA in the x direction parallel to the facet plane, and about 300 \AA in the z direction normal to it. Within this region the PT behaviour would be modified by the rounding effect.

In this work, we study in detail the possible $1/R$ effects in the ECS, as well as their relevance in the analysis of the experimental profiles. As we will show, all the $1/R$ effects are too small to be observable in the usual type of experiment, where the spatial resolution is about 60 \AA [8, 9].

Below the roughening temperature, the physical picture of a crystal surface is based on the concept of 'steps' as linear defects on the surface. From a microscopical point of view, the equilibrium crystal shape of a finite crystal is determined by a given distribution of a finite number of steps. In order to study the possible finite-size corrections to the ECS, we must take into account the atomic structure (i.e. the step distribution) of the region adjacent to the facet. Let us consider the simple model of the crystal surface sketched in figure 1. In this model the crystal surface consists of a flat surface and a finite

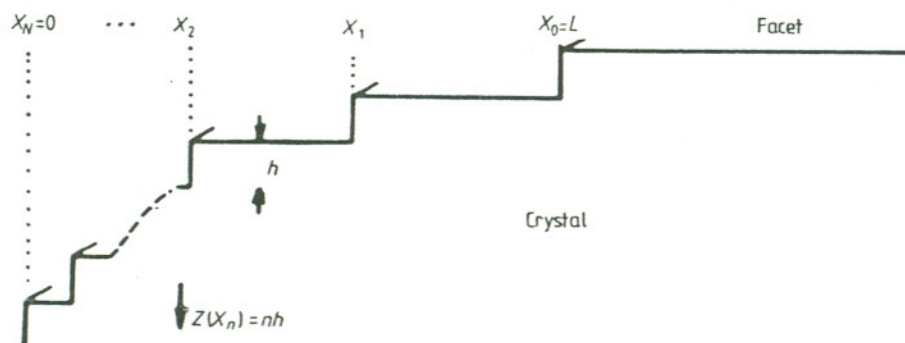


Figure 1. A microscopic model for a crystal surface near a facet edge.

number N of steps, of height h , located at $x_0 > x_1 > \dots > x_N$, and with the boundary conditions $x_0 = L$ and $x_N = 0$. We will assume that the characteristic size L is much smaller than the typical facet size. In this case, we can neglect the curvature of steps and we can consider them as parallel straight steps. It is well known that the interaction between two parallel steps, separated at a distance r , follows a general r^{-2} interaction law. This behaviour does not depend on the nature of the interaction (both elastic [11], dipole-dipole [12] and entropic (PT) [4] interactions lead to the same result). Then we can write the total energy E of our system as

$$E = \beta_1 N + (\gamma/2) \sum_{m \neq n} (x_m - x_n)^{-2} \quad (2)$$

where β_1 is the energy per step and γ is a constant ($\gamma > 0$).

The equilibrium positions of the steps will correspond to the minimum of the total energy, with the additional condition of constant number of steps N , and constant volume V of the crystal, i.e.

$$F = \beta_1 N + (\gamma/2) \sum_{m \neq n} (x_m - x_n)^{-2} + \lambda V = \text{minimum} \quad (3)$$

where λ is a Lagrange constant ($\lambda > 0$) and V is given by

$$V = \sum_{n=0}^N hx_n.$$

Taking the variational derivative of (3) we have

$$\Delta F = 0 = -\gamma \sum_{m \neq n} (x_m - x_n)^{-3} + \lambda h \quad (4)$$

or, taking $\xi_n = (\lambda h/\gamma)^{1/3} x_n$,

$$\sum_{\substack{n \neq 0 \\ n \neq m}}^N (\xi_m - \xi_n)^{-3} = 1. \quad (5)$$

Since this sum converges sufficiently quickly, we can take, as a first approximation, the nearest-neighbours contribution. In this case (5) reduces to the simple relation

$$d_1^{-3} = 1 \quad d_{m+1}^{-3} - d_m^{-3} = 1 \quad (6)$$

with $d_m = (\xi_{m-1} - \xi_m)$. The above equation has the solution $d_m = m^{-1/3}$, or in other words

$$x_0 - x_m = (\gamma/\lambda h)^{1/3} \sum_{n=1}^m d_n = (\gamma/\lambda h)^{1/3} \sum_{n=1}^m n^{-1/3}. \quad (7)$$

For $m \gg 1$ we can replace the sum in (7) by an integral obtaining

$$x_0 - x_m = (3/2)(\gamma/\lambda h)^{1/3} m^{2/3}. \quad (8)$$

Taking $Z(x_m) = mh$ (see figure 1), we obtain

$$Z = (2h/3)^{3/2} (\lambda/\gamma)^{1/2} (x_0 - x_m)^{3/2} \quad (9)$$

i.e. exactly the Pokrovsky-Talapov behaviour. It can be shown that corrections to (7) and (9) associated with 'long-range' interaction between steps have only the effect of a renormalisation of the coefficients γ , but the main result, i.e. the PT behaviour, remains unchanged.

As we can see from (7) and (8), the only difference in the ECS associated to the finite number of steps (or finite-size effects) is just the difference between $\sum_{n=1}^m n^{-1/3}$ and $\int_0^m n^{-1/3} dn$, which is non-negligible only for the first few steps. It is worth noting that our approach is rather general. In fact, the PT behaviour $Z \approx x^{3/2}$ is a general consequence of a r^{-2} step interaction law and does not depend on the details of the different microscopic theories. Moreover, the above analysis shows that the inhomogeneity in the step distribution, associated to the finite size of the crystal, produces no corrections to the PT behaviour. It means, in particular, that any macroscopical approach which would take into account the existence of this inhomogeneity (for example by including 'gradient terms' in the surface free energy) should give negligible corrections on a macroscopic scale.

J J Sáenz and N García (unpublished work) have recently studied the possible corrections to the ECS associated to the existence of gradient terms ($\approx K(\nabla p)^2$) in the surface free energy. However, an inhomogeneous distribution of steps (following a r^{-2} interaction law) gives a negligible, and negative (see [5]), square gradient contribution to the macroscopic surface free energy.

There is also another trivial finite-size effect connected to the finite initial slope given by

$$p_0 = h/(x_0 - x_1) = (\gamma/\lambda h)^{-1/3} h. \quad (10)$$

We can estimate the order of magnitude of p_0 just by noting that when $(x_0 - x_m) \approx R$ the slope will be $p = \partial Z/\partial x \approx 1$. Then from (9) and (10) we will have

$$p_0 \approx (h/R)^{1/3}. \quad (11)$$

Taking $h \approx 5 \text{ \AA}$ and a crystal size $R \approx 5 \text{ \mu m}$, we have $p_0 \approx 0.05$. It is clear that the size effects discussed above are very small on the macroscopic scale, and cannot be observable within the actual experimental resolution of about 60 \AA as reported in [8] and [9].

Now we turn to other possible finite-size effects from a macroscopical point of view. It is well known [13] that the presence of surface stress causes small crystals to have compensating volume stresses which should be included in the determination of the ECS. These elastic effects will produce corrections to the surface free energy of the order of $\beta_0^2/(\mathcal{E}R)$ where β_0 is the surface stress, \mathcal{E} is an elastic constant and R is the mean radius of the crystal. Other possible sources of $1/R$ effects, like the dependence of the free energy on the curvature of the crystal, are expected to be as much of the order of $\beta_0 h/R$ (notice that in general $\beta_0^2/(\mathcal{E}R) < \beta_0 h/R$). We will expect that corrections to PT behaviour become important when $1/R$ contributions are of the order of the PT term in surface free energy ($\approx \beta_3 |p|^3$), i.e. $\beta_3 p^3 < \beta_0 h/R$. It is easy to see that this condition implies a $1/R$ -rounding region, in the x direction, of the order of [10]

$$(x_0 - x_m) \approx (h^2 R)^{1/3} \quad (12)$$

which for typical experimental values gives a region of about 100 \AA , well below the approximate value of 3000 \AA proposed by Rottman and co-workers [8, 10]. Notice that the macroscopic discussion of $1/R$ effects gives essentially the same answer that we have obtained before. In fact, the condition given by (12), in terms of the surface slope, means that we would expect corrections to the PT behaviour for slopes $p < (h/R)^{1/3} \approx p_0$, i.e. in a region of the order of one or two surface steps.

All of these estimations show that $1/R$ effects are negligible on the macroscopic scale and do not significantly influence the ECS of even very small crystals (of the order of 1 \mu m in size). This means that any reasonable interpretation of experimental data on crystals larger than about 1 \mu m should be based on a surface free energy $\beta(p)$ defined for a crystal of 'infinite' size. From this point of view the non-zero mean-field term ($\beta_2 p^2$) obtained by fitting of experimental shapes of both Pb [7, 8] and In [9] crystals should reflect some characteristic interaction energy of the surfaces of infinite crystals. There is also evidence of the existence of a non-zero β_2 term in very large ($\approx 1 \text{ cm}$) helium crystals [14, 15]. Moreover, in He crystals the surface stiffness ($\tilde{\alpha} = \partial^2 \beta / \partial p^2$) even increases when $p \rightarrow 0$! (in clear contrast with the PT-predicted vanishing of $\tilde{\alpha}$). In this respect the experiments of Keshishev and Andreeva [16] seem to be specially relevant. First their data were obtained by measuring the spectrum of crystallisation waves [17] which removes all questions about the equilibrium character of the surface. Second, the temperature was well below the roughening temperature, where the 'critical region' in which the PT behaviour should be observable is sufficiently wide. In this case they also obtained a non-vanishing surface stiffness near $p = 0$.

We can conclude that the experimental data on both metallic and helium crystals do not show the PT critical behaviour ($\beta_2 = 0$) and support the mean-field-like picture ($\beta_2 > 0$). The main unresolved problem is: what is the physical sense of a non-zero β_2 ?

Even when finite-size corrections can lead to some effective β_2 term in the free energy, it is negligible in actual experiments. Then, we could think in terms of interactions between steps which could lead to a mean-field behaviour of the surface. Generally speaking we can write the surface free energy as

$$\beta \approx \beta_0 + \beta_1 |p| + \Delta\beta_{\text{int}} \quad (13)$$

where $\Delta\beta_{\text{int}}$ would be the contribution of the step-step interaction. This term can be expressed as

$$\Delta\beta_{\text{int}} = (1/2L) \sum_n U(nL) \quad p = h/L \quad (14)$$

where L is the distance between steps. Long-range interactions $U \approx x^{-m}$ give $\Delta\beta_{\text{int}} \approx p^{m+1}$. As commented before, all known interactions go as x^{-2} and give $\beta_2 = 0$. In order to obtain $\beta_2 \neq 0$ it is necessary that $U \approx x^{-1}$ and only nearest neighbours can interact to avoid divergency in (14). From a classical point of view it means that each step would create a field $\approx x^{-1}$. In this case the total energy of a solitary step, which includes the interaction of this field with point defects on the surfaces, should diverge at long distances. However, such a step cannot be considered as a linear defect on the surface, and the roughening transition, based on the concept of steps, would become unphysical. We have also considered the possible corrections to the surface energy, associated to the interactions between steps and a non-zero distribution of point defects, present always in a real crystal. Also, in this case there are not mean-field-like corrections and the critical PT behaviour is not modified.

To conclude, we have shown that finite-size effects cannot explain the experimental data on the equilibrium crystal shape. A mean-field term, $\approx p^2$, is needed to explain the experimental results both on metallic and He crystals. Experimentally, this term is not a small quantity and even dominates near the facet edge [7, 9]. We have shown that if the global picture of the roughening transition, based on the concept of steps as linear defects on the surface, is correct, the mean-field p^2 -term cannot come from a classical long-range interaction between steps. Therefore, in metal and helium crystals the physical interaction which leads to the dominant, mean-field, term in the surface energy is unknown and the existing theories with a leading $\approx p^3$ term give a clearly unrealistic surface behaviour. Further research in this direction will help us in the understanding of general surface phenomena.

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