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New Possibilities in Crystal Morphology¶

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Two new morphological phenomena are predicted in crystals: meniscus disappearance and meniscus fixation. Helium crystals are the most convenient objects for their observation.

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Since the discovery of the faceting of helium crystals, there have been many experimental and theoretical studies on the energy of elementary steps, the step–step interactions, and the surface energy anisotropy (for a review, see [1]). Most of the experimental results were obtained by dynamical methods, such as measurements of crystallization wave spectra [2, 3], the surface mobility near the roughening transition [4] in ^{4}He, and the spiral growth velocity [5] in ^{3}He. On the other hand, all these parameters can also be measured statically.

We begin with a discussion of the possibility of measuring the (free) energy of elementary steps β under static conditions. It seems that β could be derived directly from measurements of the facet's size. As was shown by Landau [6], the equilibrium facet size is proportional to β. However, this does not work in practice, because the corresponding relaxation times are extremely long: in contrast to a rough surface, the kinetic growth coefficient of a facet is zero at small driving forces. This means that, under stationary conditions, the facet is always metastable and its size is far from the equilibrium value. In this Letter, we propose a new method to measure β under static conditions not affected by this disadvantage. The more precise analysis also opens new experimental possibilities for studies of the surface energy anisotropy.

Consider a crystal with a horizontal (xy plane) facet in a cell with vertical (z axis) walls. There is some contact angle due to the difference ϵ of the crystal–wall and the liquid–wall energies. This results in bending of the crystal surface near the walls on a scale of capillary length of ~1 mm (Fig. 1a). We assume the cell is relatively large in the y direction (along the wall). One can then neglect the effects of shape distortion in the y direction. The equilibrium crystal shape $Z(x)$ corresponds to the minimum of the sum of the surface and the gravitational energies for a given crystal volume,

$$\int \frac{\alpha(\theta)}{\cos\theta}dx + \int \int_0^{Z(x)} (\varrho g z - \lambda)dzdx, \qquad (1)$$

where α is the crystal–liquid boundary energy, the angle θ is defined by $\tan\theta = \partial_x Z$, ϱ is the density difference of the crystal and liquid, and λ is the Lagrange multiple. The variational procedure gives

$$(\alpha + \alpha'')\cos\theta\partial_x\theta - \varrho g Z + \lambda = 0, \qquad (2)$$

where the prime denotes an angular derivative. At the cell wall $\theta = \theta_0$, where θ_0 is a solution of the equation $\alpha'\cos\theta_0 + \alpha\sin\theta_0 = \epsilon$. For a wall inclined by an angle ψ (Fig. 1), this boundary condition should be replaced by

$$\alpha'(\theta_0)\cos(\theta_0 + \psi) + \alpha(\theta_0)\sin(\theta_0 + \psi) = \epsilon(\psi). \qquad (3)$$

This would yield a continuous dependence $\theta_0(\psi)$ if α and ϵ were smooth functions. In fact, the reality is complicated by the α' discontinuity. At small θ, we have

$$\alpha(\theta) = \alpha_0\cos\theta + \frac{\beta}{h}|\sin\theta| + \frac{\gamma}{6}|\theta|^3, \qquad (4)$$

where h is the step height and the last term is due to the step–step interaction (electrostatics [7], elasticity [8], and thermal fluctuations [7, 9]). From (3) and (4), we find

$$\theta_0 = \pm\sqrt{\frac{2}{\gamma\cos\psi}\left(\pm\epsilon \mp \alpha_0\sin\psi - \frac{\beta}{h}\cos\psi\right)}. \qquad (5)$$

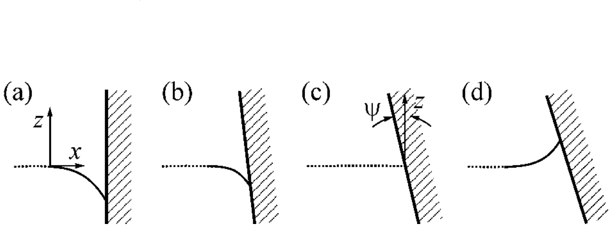

Fig. 1. Crystal shape evolution under the wall inclination: (a) $\psi = 0$, (b) $\psi < \psi_-$, (c) $\psi_- < \psi < \psi_+$, (d) $\psi > \psi_+$.

¶ The text was submitted by the authors in English.

These two cases are presented in Fig. 1b and 1d. However, in the interval $\psi_- < \psi < \psi_+$ defined by

$$(\alpha_0 \sin\psi_\pm - \epsilon(\psi_\pm))h = \pm\beta\cos\psi_\pm, \qquad (6)$$

solution (5) makes no sense. When the inclination approaches this interval both from smaller and bigger angles, the asymptotic expression $\theta_0 \propto |\psi - \psi_\pm|^{1/2}$ is valid. Inside the interval, the meniscus vanishes completely and the facet touches the wall (Fig. 1c). It is easy to show that this state is stable. Indeed, a change of the state would be possible only via formation of a "positive" (upward shift) or "negative" (downward shift) atomic terrace of macroscopic width $L \ll R$, where R is the characteristic size of the crystal. This requires an energy of

$$\delta E_\pm = \beta \pm \frac{\epsilon h}{\cos\psi} \mp \alpha_0 h \tan\psi + \frac{\varrho g}{2} h^2 L \mp \lambda h L$$

per unit length of the terrace, where +(–) corresponds to a "positive" ("negative") terrace. The last term is small with respect to the others, because $\lambda \sim \alpha_0/R$. We see that $\delta E_\pm > 0$ inside the interval (ψ_-, ψ_+).

If the crystal orientation dependence of ϵ can be neglected, from (6) we obtain

$$\beta = \alpha_0 h \tan\frac{\psi_+ - \psi_-}{2}.$$

Thus, we have a new means of finding the value of β, because α_0 is known with reasonable accuracy [10], and the angles $\psi_\pm$ can be measured directly. An important advantage of this method is that it avoids the problem of metastability. Indeed, the cases $\psi = \psi_\pm$ correspond to the wetting point of the wall by "negative" and "positive" terraces, respectively (i.e., $E_\pm \longrightarrow 0$). This means that the terraces can be formed without any macroscopic barriers.

Note that instead of tilting the cell wall, one can also control boundary condition (3) with an electric field [2].

Further, we consider a new possibility to measure $\alpha(\theta)$. The first integral of Eq. (2) is

$$\alpha' \sin\theta - \alpha\cos\theta = \frac{\varrho g}{2} Z^2 - \lambda Z + C, \qquad (7)$$

where C is a constant. Let $Z = 0$ at the level of the facet. Then, from (7) we have $C = -\alpha_0$. It is worth mentioning that condition (3) is valid for the juncture line between the curved surface and the facet. In this case, $\epsilon = \alpha_0$, and the boundary condition is satisfied if the juncture is smooth. Let us find the function $Z = Z(\theta)$ from (7):

$$Z_\pm = \frac{\lambda}{\varrho g} \pm \sqrt{\left(\frac{\lambda}{\varrho g}\right)^2 + \frac{2}{\varrho g}(\alpha_0 + \alpha' \sin\theta - \alpha\cos\theta)}.$$

An interesting situation arises in the case of asymmetric conditions. Suppose that Z has opposite signs at the right and left cell walls (Fig. 2). The only possibility to have the same level of the facet $Z = 0$ on both sides is to fix the Lagrange multiple $\lambda = 0$. Under this condition, the meniscus becomes rigidly determined, with no dependence on the crystal size. This shape fixation phenomenon exists for relatively large crystals when the facet is presented. The value of facet size does not contain essential information if $\lambda = 0$, but the small-angle asymptotic expression of the crystal profile

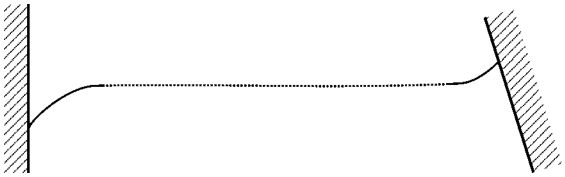

Fig. 2.

$$Z_\pm = \pm\frac{\varrho g}{18\gamma}|x|^3$$

gives the step–step interaction constant γ. In the general case, consider Eq. (7) as an ordinary differential equation for the function $\alpha(\theta)$. One can measure the function $Z = \pm Z_\pm(\theta)$ and put the data into Eq. (7). Integration over $\theta > 0$ yields

$$\alpha = \left(\alpha_0 - \frac{\varrho g}{2} Z^2\right)\cos\theta + \left(\tilde{C} + \varrho g \int\limits_{x(0)}^{x(\theta)} Z dx\right)\sin\theta.$$

Here, $\tilde{C}$ is just β/h, because there is no other singular term $\propto|\theta|$ at $\theta \longrightarrow 0$.

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