Pis'ma v ZhETF, vol. 83, iss. 9, pp. 485 – 486 © 2006 May 10

New possibilities in crystal morphology

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Submitted 6 April 2006

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

PACS: 67.80.–s

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

We start from the discussion on the possibility to measure the (free) energy of elementary steps β under static conditions. It seems, β could be derived directly from measurements of the facet size. As was shown by Landau [6], the equilibrium facet size is proportional to β. However, in practice this does not work 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. It means that under stationary conditions the facet is always metastable and its size is far from 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 opens also new experimental possibilities for studies of the surface energy anisotropy.

Consider a crystal with 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. It results in bending of the crystal surface near the walls on the scale of capillary length ~ 1 mm (Fig.1a). We assume the cell being large enough in y-direction (along the wall). Then one can neglect the effects of shape distortion in the y-direction. Equilibrium crystal shape $Z(x)$ corresponds to the minimum of the sum of the surface and the gravitational energies for a given crystal volume

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

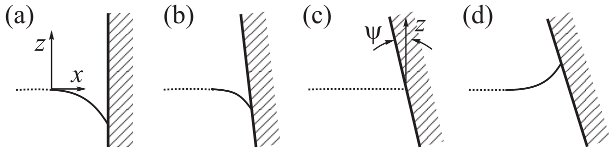

Fig.1. Crystal shape evolution under the wall inclination: (a) $\psi = 0$, (b) $\psi < \psi_-$, (c) $\psi_- < \psi < \psi_+$, (d) $\psi > \psi_+$

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

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

where the prime denotes 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 the wall inclined by an angle ψ (Fig.1) this boundary condition should be replaced by

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

It would give a continuous dependence $\theta_0(\psi)$ if α and ϵ were smooth functions. In fact, 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

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

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

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

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

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

per unit length of the terrace, where $+(-)$ corresponds to a "positive" ("negative") terraces respectively. 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 the new means of finding the value of β, because α_0 is known with reasonable accuracy [10], and angles $\psi_{\pm}$ can be measured directly. Important advantage of this method: it allows to avoid the problem of the metastability. Indeed, the cases $\psi = \psi_{\pm}$ correspond to the wetting point of the wall by "negative" and "positive" terraces respectively (t.e., $E_{\pm} \to 0$). It means that the terraces can be formed without any macroscopic barriers.

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

Further we consider a new possibility to measure $\alpha(\theta)$. The first integral of equation (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 $C = -\alpha_0$. Worthy to mention that the condition (3) is valid for the juncture line between 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

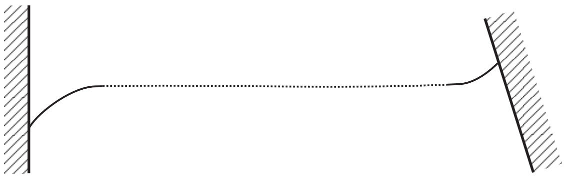

Fig.2

sides is to fix 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 large enough crystals when the facet is presented. The value of facet size does not contain essential information if $\lambda = 0$, but a small angle asymptotics of the crystal profile

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

gives the step-step interaction constant γ. In general case consider the 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). The integration over $\theta > 0$ gives

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

here $\tilde{C}$ is nothing but β/h, just because there is no other nonanalytic term $\propto |\theta|$ at $\theta \to 0$.

We thank A.F. Andreev and K.O. Keshishev for helpful discussions. The work is supported by RF President Program "Leading Scientific Schools" # 7018.2006.2 and 5763.2006.2 and Israel-Russia Grant # 06-02-72013.

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