Comment on "Electrically Induced Morphological Instabilities in Free Dendrite Growth"

In a recent Letter, Libbrecht and Tanusheva (LT) [1] described a new instability mechanism in dendritic growth which arises from electrically enhanced diffusion of polar molecules. They found, both theoretically and experimentally, that the tip velocity increases with the applied potential, and beyond the threshold potential they observed a runaway growth of thin needle crystals. Their basic idea is very interesting. In the presence of the external force, the usual diffusion equation and the continuity equation at the growing interface are modified:

$$\partial c/\partial t = D\nabla \cdot (\nabla c - c\mathbf{F}/kT), \tag{1}$$

$$v_n = D\mathbf{n} \cdot (\nabla c - c\mathbf{F}/kT)_{\text{int}}, \tag{2}$$

where $\mathbf{F} = \alpha\nabla(\mathbf{E} \cdot \mathbf{E}) = \alpha\nabla\Phi$, α is the electric polarizability, and the solute density c is measured in units of c_{solid}. However, LT used the equilibrium condition at the interface in the form $c_{\text{int}} = c_{\text{sat}} + d_0K$, where c_{sat} is the equilibrium concentration at the flat interface without external potential, d_0 is the capillary length, and K is the curvature of the interface. Our main objection concerns the above boundary condition which in the presence of the potential $\alpha\Phi$ also has to be modified to

$$c_{\text{int}} = (c_{\text{sat}} + d_0K)\exp(\alpha\Phi_{\text{int}}/kT). \tag{3}$$

Let us first look at a spherically symmetric solution which corresponds to a critical nucleus of radius R_c. In the absence of a flux, the concentration field is $c(r) = c_\infty\exp[\alpha\Phi(r)/kT]$, where c_∞ is the concentration far away from the nucleus. The modified chemical potential (which includes the $\alpha\Phi$ term) is constant along the system and equal to the usual chemical potential for the solute density c_∞ where $\Phi = 0$. On the other hand, the chemical potential of the solid phase, which is not affected by the force potential ($\Phi_{\text{solid}} = 0$), corresponds to the concentration ($c_{\text{sat}} + d_0/2R_c$). Thus, we find, for the critical nucleus, $c_{\text{sat}} + d_0/2R_c = c_\infty$, and we recover Eq. (3) for the equilibrium boundary condition at the interface. Contrary to the statement of LT, the critical radius remains unchanged in this approximation [2].

The best we have been able to do so far, looking at the dendritic growth problem defined by Eqs. (1)–(3), is to give a "naive" analytical treatment in the spirit of LT, but taking into account the modified boundary condition, Eq. (3). We replace the concentration c in the force terms of Eqs. (1)–(2) by its constant value c_∞ far away from the interface. This approximation requires one to also replace the exponential factor in Eq. (3) by $(1 + \alpha\Phi_{\text{int}}/kT)$, and allows us to map the problem onto the classical dendritic problem with a simple modification. Indeed,

introducing the field $u = c_\infty(1 + \alpha\Phi/kT) - c$, we eliminate the force term from the diffusion and continuity equations but the equilibrium boundary condition, Eq. (3), reads $u_{\text{int}} = \Delta_m - d_{0m}K$, where $\Delta_m = (c_\infty - c_{\text{sat}})(1 + \alpha\Phi_{\text{tip}}/kT)$ is the modified supersaturation and $d_{0m} = d_0(1 + \alpha\Phi_{\text{tip}}/kT)$ is the modified capillary length.

In the static approximation, used in [1], the Peclet number is $P = vR/2D \sim \Delta_m$. Since P and d_0 are modified in the same way, the selection condition for the stability parameter $\sigma(R) = d_{0m}/PR = \sigma^*$ remains unchanged even in the presence of the force potential, and the selected radius of the dendritic tip is the same as in the case of the absence of the potential, $R = R_0$. The dendrite tip velocity increases with the applied electrical potential but there is no sign of the runaway growth regime. What will be then a possible explanation of the observed phenomena? In the spirit of the used approximations, one possibility would be to give up the static condition and to use instead the usual steady-state Ivantsov relation $P = -\Delta_m/\ln\Delta_m$. In this case the potential $\alpha\Phi_{\text{tip}}$ remains present in the selection condition due to the logarithmic dependence of the Peclet number on Δ_m, and it leads to an equation for R which has qualitatively the same properties as LT's quadratic equation: two solutions merge and disappear for some critical value of the applied electrical potential.

The other possibility is to include in the consideration the neglected effect [2] which leads to further modification of Eq. (3). Then even in the static approximation the potential Φ_{tip} remains present in the solvability condition, and the runaway effect again reappears. However, this effect will be almost independent of the polarizability, and the physics involved is very much different compared to the original idea of [1]. We hope that further investigations will make clear which of the discussed scenarios is relevant to the experiments of [1].

Efim A. Brener and H. Müller-Krumbhaar
  Institut für Festkörperforschung
  Forschungszentrum Jülich
  52425 Jülich, Germany

[1] K. G. Libbrecht and V. M. Tanusheva, Phys. Rev. Lett. **81**, 176 (1998).
[2] Following LT we have assumed that the main effect is electrically enhanced diffusion of polar molecules. Equation (3) does not account for the change of the solid chemical potential, $\Phi_{\text{int}}/(8\pi c_{\text{solid}})$, due to the tensile stress which appears in the conducting solid phase and leads to the decrease of the critical radius.