Asymmetry of dynamics at the growing crystal-melt interface

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Dynamic light-scattering measurements on the b face of a salol crystal growing into the melt revealed simultaneous lateral translation dynamics on the crystal surface and slow relaxational dynamics in a thin boundary layer of melt adjacent to the crystal. Analysis of the translational dynamics shows that crystal growth is mediated by highly polygonized screw dislocations. An explanation is suggested for the relaxational dynamics based on the dynamics of nematic liquid crystals.

The interface between a growing crystal and its melt has long been a system of great practical interest. It is also an important example of a nonequilibrium dynamical system exhibiting dynamical transitions, morphological instabilities, and spontaneous pattern selection.[1] Recently, J. Bilgram and his co-workers at the Eidgenössische Technische Hochschule (ETH), Zurich have applied dynamic light-scattering spectroscopy to the crystal-melt interface of both ice and salol.[2-5] They observed slow relaxational dynamics of the ice-water interface, initially interpreted as time-dependent surface roughness[2] and subsequently described as "structure diffusion" in a fluid boundary layer[3,5] or modification of the thermal diffusion mode.[6] Their preliminary studies of salol indicated the presence of either relaxational or lateral translation dynamics, depending on the growth rate.[4] No interpretation of the translational dynamics was proposed.

In this Rapid Communication we report new observations on the salol-crystal–melt interface. Although our experimental procedure closely resembles that of the ETH group, we have exploited the optical anisotropy of crystalline salol to unambiguously separate scattering from the crystal surface and scattering from the thin boundary layer of the melt above it. We have established that isotropic slow relaxational dynamics in the fluid boundary layer and highly anisotropic translational dynamics on the crystal surface occur simultaneously. From the value of the lateral translation velocity v_L as a function of the growth velocity v_G, we have demonstrated that the translational motion detected on the crystal surface represents the lateral spreading of steps of highly polygonized screw dislocations.

Experiments were performed *in situ* during zone refining in the apparatus shown in Fig. 1. A temperature gradient was established between the upper and lower aluminum cylinders ($T_U = 43.5\,°C$, $T_L = 35.5\,°C$). The bores of the aluminum cylinders and the Plexiglas cylinder between them were filled with paraffin oil which provides both thermal contact and optical index matching. The temperature was measured by ten matched thermistors embedded in the Plexiglas cylinder at 5-mm vertical intervals.

The Pyrex growth tube, 35-cm-long by 16-mm-i.d., was suspended from a stepping-motor driven rotary stage which can be rotated to any orientation. Vertical motion of the stage was generated by a precision screw drive providing 27 growth speeds in the range 0.000 423 to 8.47 μm/s. Samples were prepared following the procedure of Bilgram, Dürig, Wächter, and Seiler.[7]

After mounting the tube in the stage, the distilled salol was melted by raising the stage until the molten region reached the top of the cylindrical seed. Slow downward motion was started and maintained until a clean, flat crystal-melt interface formed. The tube velocity was then set to the desired value. After several hours, a steady state was reached and the interface then remained stationary in the laboratory.

The position of the interface with respect to the thermistors was measured to within ±0.1 mm by a traveling microscope. The temperature at the center of the interface was determined by fitting the ten thermistor readings to the heat-flow equation including the latent heat generated at the surface and convective heat exchange with the 39.5 °C air circulating between the Plexiglas cylinder and the outer glass sleeve. The growth velocity v_G was equal (and opposite) to the downward tube velocity, corrected for any observed motion of the interface with respect to the laboratory frame.

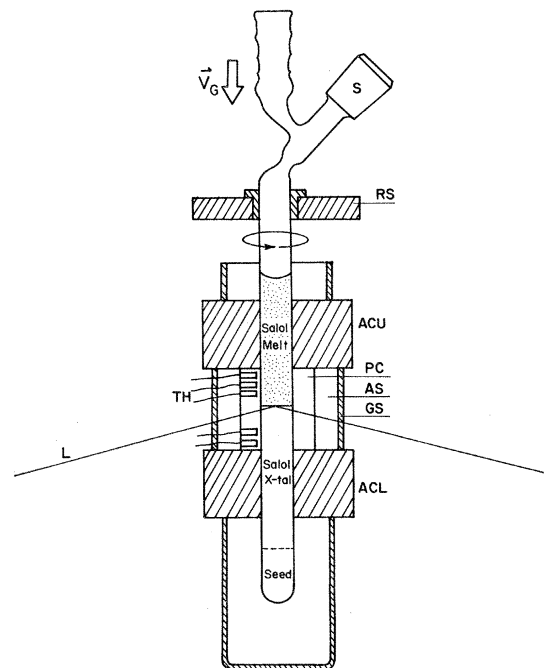Salol is a highly birefringent anisotropic crystal with

FIG. 1. Crystal growth apparatus. ACU—upper aluminum cylinder, $T = 43.5\,°C$; ACL—lower aluminum cylinder, $T = 35.5\,°C$; PC—Plexiglas cylinder; GS—glass sleeve; AS—air space (39.5 °C); RS—rotary stage; S—Teflon stopcock; L—incident laser beam; TH—thermistors.

orthorhombic unit-cell dimensions $a = 11.25$ Å, $b = 25.5$ Å, and $c = 8.10$ Å.[8] With this convention, the refractive indices at $\lambda = 4880$ Å were measured as $n_a = 1.663$, $n_b = 1.827$, and $n_c = 1.552$. The refractive index of the melt, $n_m = 1.598$, is intermediate between n_a and n_c.

In our scattering configuration, the incident laser beam is focused onto the interface from slightly below the horizontal, near grazing incidence, and scattered light is collected from below the horizontal as well. The optical path in the growth tube is thus entirely within the crystal. Since the refractive index along the vertical direction n_b is considerably larger than n_m, vertically polarized incident light is *always* totally internally reflected at the crystal-melt interface. For horizontally polarized incident light, the beam is transmitted through the interface when the a axis is in or near the plane of incidence. The change from total internal reflection to partial transmission as a function of polarization and crystal rotation provided the key to identifying the origin of the different types of scattering that we observed.

With vertically polarized incident light, the scattered light must come from the surface of the crystal and not from the melt above it. This scattering was observed to be highly anisotropic with respect to rotation of the crystal about the vertical b axis. It appeared only when v_G was increased to at least 0.1 μm/s, but persisted when v_G was subsequently decreased to the lowest accessible values. It was observed only when the scattering vector $\bar{q}$ was oriented in a particular direction relative to the crystallographic a and c axes to within $\sim \pm 2°$. The preferred direction was not permanent, but shifted on successive runs. Certain preferred directions occurred frequently, however, particularly $\langle 101 \rangle$ and $\langle 201 \rangle$.

The intensity autocorrelation function of this scattered light was sinusoidal and undamped. An example is shown in Fig. 2(a). For any particular orientation of $\bar{q}$, the frequency of the sinusoid was linear in $|q|$ and increased with increasing growth rate. The linear q dependence suggests that elastically scattered light beats with light that is Doppler shifted by $\Delta\omega = v_L q$, where v_L is a lateral velocity parallel to q on the interface, as suggested by Dürig and Bilgram.[4]

When horizontally polarized light was transmitted through the interface, strong isotropic scattering was observed at the interface at *all* growth velocities, which was considerably more intense than light scattering in the melt. Its intensity autocorrelation function was exponential with decay rate $\Gamma \propto q^2$, independent of growth rate or crystal orientation. An example is shown in Fig. 2(b). We also directed the incident laser beam into the growth tube from above the interface. When it passed entirely through the melt close to but not touching the interface, weak scattering characteristic of the melt was observed. If the incident beam touched the interface, however, strong scattering with a relaxational autocorrelation function reappeared, independent of polarization, identical to the scattering observed with the beam incident from below. Thus this scattering must arise from a thin boundary layer of melt adjacent to the interface.

The three principal mechanisms for growth of a plane-crystal surface into the adjacent melt are (a) surface nucleation, (b) screw dislocation mediated growth, and (c) continuous growth. In (a) and (b), growth occurs by steps spreading across the interface. These are source-limited mechanisms, since the growth velocity v_G depends on the number of growth steps on the crystal surface. If the crystal surface is microscopically rough, steps are not required and continuous growth is normal to the interface.[9] The kinetic
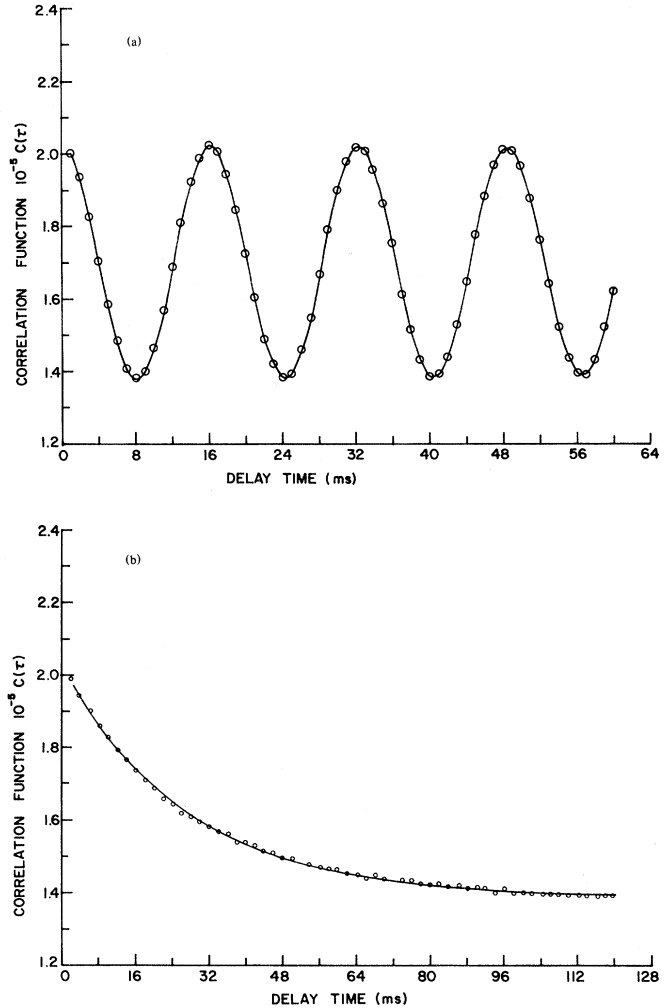

FIG. 2. (a) Correlation function of light scattered from the growing crystal surface observed in the geometry of Fig. 1 in VT polarization. ($\theta = 45°$; $v_G = 0.20$ μm/s). The circles are the experimental data. The solid line is a computer fit giving $\nu = 61.89$ Hz and $v_L = 21.8$ μm/s. (b) Correlation function of light scattered from the fluid boundary layer observed in the geometry of Fig. 1 in HT polarization. The circles are the experimental data. The solid line is a computer fit giving $\Gamma^{-1} = 26.9$ ms and $D = 0.76 \times 10^{-9}$ cm²/s.

equations for these three mechanisms which relate the growth velocity v_G to the interfacial undercooling ΔT are[10]

$$v_G = \mu_a \exp(-K/\Delta T) \ , \tag{1a}$$

$$v_G = \mu_b(\Delta T)^2 \ , \tag{1b}$$

$$v_G = \mu_c(\Delta T) \ , \tag{1c}$$

where the undercooling $\Delta T = T_M - T_I$, T_M is the melting temperature, and T_I is the interface temperature.

For strongly faceting crystals with large Jackson α factors[9] such as salol ($\alpha \sim 5$), the predicted lateral motion of steps across the smooth surface with velocity v_L is consistent with the observation of oscillatory correlation functions. Since the step edge is rough, for small ΔT a linear relation holds:[11]

$$v_L = \sigma \Delta T \ . \tag{2}$$

Combining Eq. (2) with Eq. (1a), we obtain, for nucleated

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layer growth,

$$v_L = K\sigma/\ln(\mu_a/v_G) \quad . \tag{3a}$$

Combining Eq. (2) with Eq. (1b) for screw dislocation growth,

$$v_L = \sigma\sqrt{v_G}/\sqrt{\mu_b} \quad . \tag{3b}$$

In attempting to fit our experimental data to Eqs. (1), (2), and (3), the temperature dependence of the viscosity was first divided out to isolate kinetmatic effects on the crystal surface.[12] Fits of v_G vs ΔT were not able to distinguish between mechanisms (a) and (b) due, in part, to the uncertainties in ΔT. Fits of v_L vs v_G following Eqs. (3) gave better agreement for the screw dislocation mechanism than for surface nucleation, as shown in Fig. 3. Further, a fit to $v_L = Cv_G^n$ gave $v_L = (62.34 \pm 1.81)v_G^{0.503 \pm 0.018}$ μm/s, with n very close to $\frac{1}{2}$, the value predicted by Eq. (3b). From Eq. (2), the lateral kinetic coefficient and melting temperature were $\sigma = (21.98 \pm 1.36)$ μm/s K, $T_M = (41.21 \pm 0.07)$ °C. Values for the normal kinetic coefficient μ_b were obtained from either Eq. (1b) or Eqs. (2) and (3b). The results were $\mu_b = 0.129$ and 0.124 μm/s K^2, respectively.

Screw dislocations produce spirals which spread across the crystal surface. The spirals can be either round or polygonized, depending on the crystal structure and driving force.[13] Very anisotropic crystals with high Jackson α factors tend to exhibit highly polygonized faceted growth spirals, consistent with the observed highly anisotropic light scattering. Geometrically, the relation

$$v_L/v_G = w/h \tag{4}$$

should hold, where w is the horizontal distance between the arms of the spiral and h is the height of the steps. Typically, $w/h \sim 10^2$–10^3 for solution growth, $\sim 10^3$–10^4 for vapor growth.[13] From our measured values of v_L and v_G, $w/h \sim 600$ for the smallest v_G, $w/h \sim 100$ for the highest v_G. Most often, h corresponds to one lattice constant, i.e.,
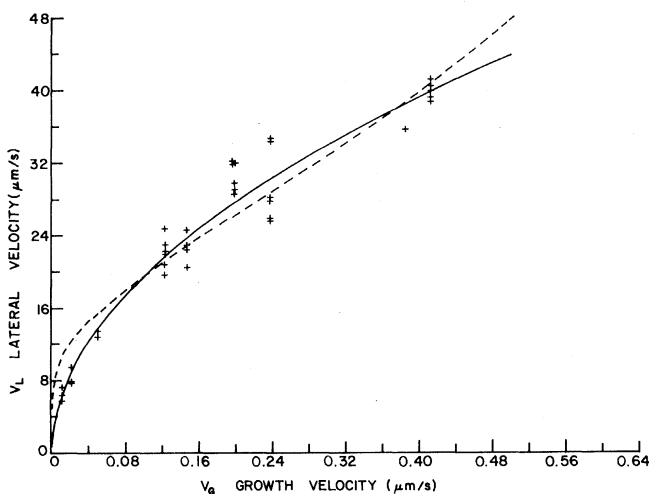

FIG. 3. Lateral velocity v_L vs growth velocity v_G. Crosses are experimental points. The solid line is the prediction of the screw dislocation model [Eq. (3b)]; the dashed line is the prediction of the surface nucleation model [Eq. (3a)].

the magnitude of the Burgers vector of the dislocation is one.[13] With $h = 25.5$ Å, at maximum undercooling ($\Delta T \sim 2$ K), $w \sim 2500$ Å, which comes close to satisfying the Bragg condition. We observed large changes in the intensity of scattering from the crystal surface which can be understood in terms of nearly constructive interference in scattering from successive steps.

Theoretically, the step width w is related to the radius r^* of a critical nucleus for two-dimensional nucleation by

$$w = sr^* \quad , \tag{5}$$

where $s = 5.4$ for polygonized spirals and $s = 19$ for rounded spirals.[13] $r^* = \beta v_m/\Delta S \Delta T$, where β is the edge free energy, v_m is the molar volume, and ΔS is the molar melting entropy. From our experimental results, we obtained a value for s of approximately 5, very close to the value expected for polygonized spirals. Thus we conclude that the observed translational dynamics on the crystal surface results from crystal growth mediated by highly polygonized screw dislocations with prominent $\langle 101 \rangle$ or $\langle 201 \rangle$ facets.

As discussed above, both scattering from the crystal surface with an oscillatory correlation function and scattering from the fluid boundary layer with a relaxational correlation function could be observed during steady-state crystal growth by changing the polarization of the incident light. The boundary-layer correlation functions always exhibited single exponential decay with decay rate $\Gamma = Dq^2$. We found values of D in the range

$$0.3 \times 10^{-9} \text{ cm}^2/\text{s} < D < 1.0 \times 10^{-9} \text{ cm}^2/\text{s} \quad ,$$

with no clear correlation to other experimental variables. This is four orders of magnitude smaller than the self-diffusion coefficient of the melt.[14]

The following properties of the relaxational scattering have now been established: (a) It originates in the fluid boundary layer and coexists with translational dynamics on the crystal surface. (b) It is much stronger than scattering from the bulk fluid. (c) The correlation function is, to within experimental error, described by single exponential relaxation. (d) The relaxation rate $\Gamma = Dq^2$. (e) $D \approx 10^{-9}$ cm^2/s, independent of growth rate.

To explain these observations, several mechanisms can be considered: (1) The corrugated surface model originally porposed by the ETH group is ruled out by (a) despite the remarkable agreement with the Gibbs-Thomson equation.[4] (2) Formation of clusters of precrystalline material near the interface would explain all the data. However, the observed values of D imply clusters of ~ 2000-Å radius, and (c) implies little or no variation in cluster size, both of which seem highly improbable. (3) Small-scale turbulence within the boundary layer. For this model, observations (c) and (d) are inconsistent since q^2 scaling implies a Gaussian (rather than Lorentzian) spectrum. (4) Structure within the boundary layer. Bilgram has concluded that for the ice-water interface the boundary layer is between 1.4 and 6 μm thick and has properties distinct from those of the bulk fluid phase. Indirect support is provided by computer simulation experiments by Landman, Cleveland, Brown, and Barnet which show that a stratified layer structure develops in the melt adjacent to the growing surface of a crystal.[15]

Recently, Mauger and Mills proposed light-scattering experiments similar to those reported here in a nematic liquid

crystal adjacent to a solid boundary which would induce orientational ordering of the molecules and increased light-scattering intensity.[16] We suggest that the growing salol crystal may similarly induce a layer of oriented salol molecules in the melt above it which resembles a nematic liquid crystal. Near the nematic-isotropic phase transition, liquid crystals possess slowly relaxing collective modes which scale with q^2.[17] Scattering from these modes is generally much stronger than scattering from the isotropic fluid.

Additional experiments will be necessary to thoroughly test this explanation. Indirect supporting evidence follows from the fact that materials with small Jackson α factors ($\alpha < 2$) crystallize with molecules in random orientations,[18] and the interface cannot exert an orientating force on the molecules in the boundary layer. Ice (in its basal plane) and salol have high α factors, and both exhibit strong boundary layer scattering.[19] Succinonitrile is a material with a small α factor in which we have seen no evidence for this kind of light scattering.

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