

Dynamic-light-scattering study of the solid-liquid interface in succinonitrile during growth

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The dynamic scattering of light by the crystal-melt interface of succinonitrile growing in a three-dimensional Bridgman setup is studied as a function of different control parameters. Strong scattering with an exponentially decaying autocorrelation function is observed during the solidification but not during the remelting. The angular dependence of the signal is characteristic of the diffusion of objects in the liquid. After pumping out gases dissolved in the liquid, we observe a striking decrease of the diffusion coefficient, up to two orders of magnitude. These results can be satisfactorily interpreted in the framework of the microbubble model recently proposed.

Recently, the mechanism of crystal growth has been the object of a renewed interest. In particular, the use of laser light scattering to study the dynamics of crystal growth has provided new possibilities for making *in situ* measurements of fluctuations at the nonequilibrium crystal-fluid interface. The correlation function of the scattered light, which is proportional to the spatial Fourier transform of the density-fluctuation autocorrelation function, gives interesting information about the temporal and morphological evolution of the interface.

Up to now, the main result provided by this method has concerned the structure of the fluid boundary layer adjacent to the crystal surface. The first experiment of this kind was performed by Bilgram, Guttinger, and Kanzig¹ in the ice-water system. The authors pointed out that strong light scattering with an exponentially decaying temporal autocorrelation function of the form $C(\tau) = B + A \exp(-2\Gamma\tau)$ was observed. They noted that $\Gamma = Dq^2$, with q the magnitude of the scattering wave vector. This suggested that the light is scattered by objects that diffuse in the liquid, the diffusive constant being D . The occurrence of such a scattering has been confirmed by other authors who have observed it in ice, salol, cyclohexanol, biphenyl, and naphthalene.²⁻⁷ Two principal models have been proposed to explain this diffusive process: the assumed existence of an interface layer, with thickness in the micrometer range, consisting of a mesomorphic phase intermediate between the solid and the liquid,^{3,8} and the gaseous microbubble model,⁵⁻⁷ which assigns the scattering to the nucleation of gas bubbles near the interface. At present, no agreement exists on the interpretation in favor of one model or the other.

It is therefore useful to systematically examine the considered type of scattering in new materials and to vary the experimental conditions of its observations. In the present paper we present results of this type relative to succinonitrile, a nonfacetting organic compound, which had not been previously investigated by the dynamical light-scattering technique. We were able to confirm the existence of a diffusive process just above the solid-liquid interface, and we performed several measurements sys-

tematically modifying the control parameters of the system during solidification or melting.

The experimental setup, represented in Fig. 1, is, in its principle, similar to the one described by Durig, Bilgram, and Kanzig.³ A glass growth tube, 30 cm long and 12 mm in internal diameter, is lowered at a constant velocity V_g in a thermal gradient established between two bronze cylinders, a typical set of values used being $T_{\max} = 76^\circ\text{C}$ and $T_{\min} = 53^\circ\text{C}$. Once a steady state is reached, the growth velocity of the crystal is V_g so that the crystal-liquid interface is at rest in the laboratory frame. The vertical motion is achieved with help of a synchronous motor and a precision endless screw providing growth speeds comprised between 0.08 and 1.7 $\mu\text{m/s}$. An optical

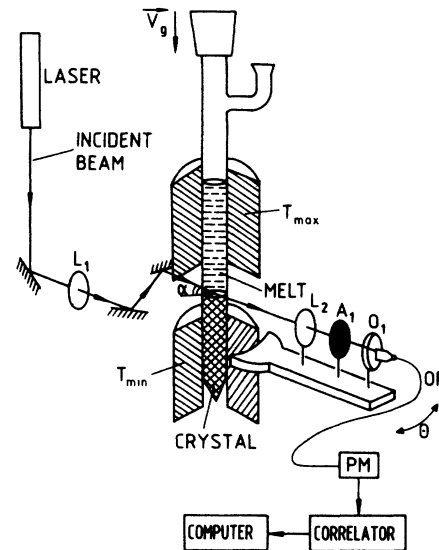


FIG. 1. Schematic representation of the crystal growth apparatus.

glass cylinder surrounds the growth tube at the level of the interface in order to decrease the lateral temperature gradient.

The interface is illuminated either from the solid side or from the liquid side by the ≈ 100 mW focused beam of an argon laser at 489 nm. The light is focused to a diameter of about $150 \mu\text{m}$ by a lens $L1$ ($f=20$ cm), and its direction controlled with the help of two mirrors which allow selection of the incidence angle α between the laser beam and the interface plane. The scattered light is detected from above the interface. The detection system can be rotated around the axis of the growth tube. The interface is imaged by means of a lens $L2$ ($f=15$ cm) on an aperture $A1$, the diameter of which is variable, and then focused by a microscope-objective ($26\times$) O_1 on an optical fiber OF having a core diameter of $5 \mu\text{m}$. This fiber carries the light to a photomultiplier, connected to a Brookhaven Instruments autocorrelator and a microcomputer.

We used Janssen Chimica succinonitrile with less than 1% impurities. Prior to using it in the experiment, we purified it by melting it and putting it under vacuum in a 1 m long tube. This tube was pulled in a zone refining apparatus with 16 zones. We passed the tube through the zone refiner nine times. The upper half of the obtained crystal was then melted and transferred into the growth tube under the vacuum. Without these precautions one would obtain, even at low growth rates, a perturbed interface unsuitable for the experiment. The physical constants for succinonitrile are melting temperature, $T_m=57^\circ\text{C}$;⁹ refractive index of the liquid, $n=1.417$;⁹ bulk viscosity of the liquid, $\eta=2.6$ cPoise.¹⁰

Most of the measurements were performed with the interface illuminated from the liquid side. Similarly, from Cummins *et al.*,⁵ we observe that the scattering by the interface onsets only a few hours after starting the crystal growth (between 2 and 4 h). The scattering is then very intense and can easily be seen by the eye. It is at least ten times stronger than the scattering by the liquid. In a first set of experiments we studied the sample as initially transferred to the growth tube. We measured the autocorrelation function of the scattered light for different growth rates and different scattering angles. In Fig. 2 we show a typical exponentially decaying correlation func-

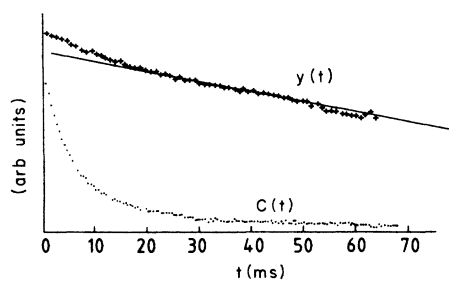


FIG. 2. Intensity correlation function of light scattered at the succinonitrile crystal-melt interface. The black circles represent the normalized correlation function $C(t)=\exp(-Dq^2t)$, the crosses represent $y(t)=\ln[C(t)]$. $\theta=50^\circ$, $V_g=0.50 \mu\text{m/s}$. Single exponential fit: $D=0.16\times 10^{-8} \text{ cm}^2/\text{s}$.

tion implying the same kind of process as observed in ice, salol, and other materials.²⁻⁷ This function can be fitted with a single exponential and we have a good fit of Γ versus q^2 giving $\Gamma=Dq^2$. However, from one experiment to another there is some dispersion in the obtained D values. The values obtained are $D=(2.25\pm 0.75)\times 10^{-9} \text{ cm}^2/\text{s}$.

In the framework of the microbubbles model,⁵ and using the Stokes-Einstein relation, $D=kT/6\pi\eta R$. We can deduce from D the bubbles radius R , in the range 600–1200 nm. In the framework of the alternate model of the interface layer, model one has a pair correlation function $g(r)$ and a correlation length ξ . We can calculate³ ξ , and we find that it is in the range 780–1560 nm.

Measurements were performed with different growth rates, from 0.08 to $1.67 \mu\text{m/s}$, all other parameters being equal. In all cases we observe similar characters for the scattered light with no significant variations in either the intensity, the single-exponential nature of the correlation function, or the calculated values of D . Similarly, as in the case of cyclohexanol⁶ and of salol,⁶ when growth was interrupted, the scattering only disappeared after a time of 4 to 7 h. Unlike the claim in Ref. 3 we do not observe any threshold in growth velocity for the onset of the scattering.

We also performed measurements during the remelting of the solid (by raising the growth tube). We could not detect any signal even several hours after the beginning of the melting. These measurements were performed at three different growth rates: 0.5, 0.75, and $1.67 \mu\text{m/s}$. In all cases, there was no difference between the signal in the liquid and the signal close to the interface, by contrast to the case of solidification. We also verified that, starting the growth of the crystal again after a few hours of melting, the scattered light consistently reappeared 3 or 4 h later. Measurements performed with the interface illuminated from the crystal side provided the same correlation function for the scattered light with the same diffusive coefficient D .

We also changed the temperature gradient. Measurements were performed with gradients of 16, 31, and 41°C/cm . We found no significant variations in the results. The only difference was that, with the gradient of 41°C/cm , it was easier to preserve a flat interface at high growth rates and, in this case, a less dispersed range of values was obtained for the diffusive coefficient D : $(2.5\pm 0.5)\times 10^{-9} \text{ cm}^2/\text{s}$.

A more striking result concerns the effect of pumping our dissolved gases after the crystallization (see Fig. 3). The pumping was performed outside the crystal growth apparatus. We melted the crystal, let it crystallize at room temperature, and then pumped out the dissolved gases. These operations were repeated several times. After one pumping, we observed no differences in either the intensity of the scattered light, the single exponential fit, or the diffusion coefficient D . After five pumping cycles, the intensity was found 3 or 4 times smaller than before the pumping and, more strikingly, the diffusion coefficient was found in the range 0.33×10^{-9} – $0.11\times 10^{-8} \text{ cm}^2/\text{s}$. After ten pumping cycles the intensity did not change further but the diffusion coefficient D was in

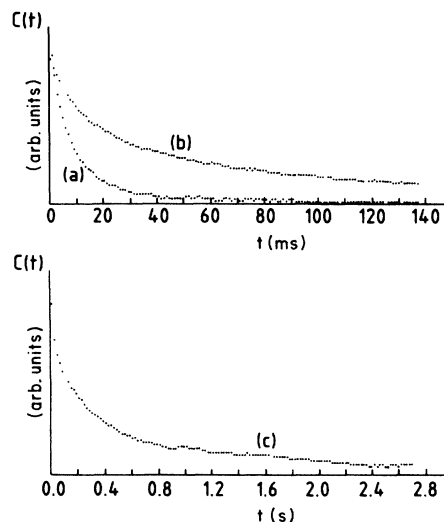


FIG. 3. Intensity correlation function: $\theta=40^\circ$, $V_g=0.50$ $\mu\text{m/s}$, (a) before pumping out the dissolved gas, $D=0.22 \times 10^{-9}$ cm^2/s , $R=0.85$ μm ; (b) after five pumping cycles, $D=0.46 \times 10^{-9}$ cm^2/s , $R=4$ μm , (c) after ten pumping cycles, $D=0.40 \times 10^{-10}$ cm^2/s , $R=46$ μm .

the range 0.29×10^{-10} – 0.69×10^{-10} cm^2/s , two orders of magnitude less than in the initial situation. All these measurements were confirmed at different growth rates, with the gradient kept fixed, and with $T_{\min}=40^\circ\text{C}$, $T_{\max}=100^\circ\text{C}$.

The latter results strongly suggest that a connection exists between the detected scattering and the gas dissolved in the liquid, in agreement with the bubble model. They are not necessarily incompatible with the mesophase model since we can not exclude that the concentration of dissolved gases might have an influence on the correlation length in the interface layer. But, as we show now, they are in a perfect qualitative agreement with the microbubbles model. A quantitative agreement could not be tested because of the lack of precise information on the actual gas concentration in the liquid.

In the microbubbles model⁵ one assumes a concentration C_g of dissolved gases in the liquid phase. After the steady state of growth is reached, the concentration C in

the liquid obeys the classical diffusion equation and we have

$$C(z) = C_g \left[1 + \left(\frac{1-k}{k} \right) \exp \left(\frac{-V_g z}{D} \right) \right],$$

where $k < 1$ is the partition coefficient, D the diffusion constant of the gas in the liquid, and z the distance to the interface. As a consequence, the concentration of gas at the interface is $C_i = C_g/k$. If k is small, C_i can surpass the saturation concentration C_s even if C_g is small. As solidification proceeds, the gas concentration increases from the initial value C_g towards C_g/k . Once it surpasses C_s , bubbles appear spontaneously, the threshold of their nucleation being lowered by the presence of the interface. Because of the existence of a surface tension σ , bubbles of radius $R < R_0$ will collapse. One has $R_0 = 2\sigma/[p(f-1)]$, with p the fluid pressure and $f = C_i/C_s$. Bubbles of radius $R > R_0$ will float upwards in the liquid and then reach unsaturated regions where they dissolve. This explains the small-diameter dispersion found in the experiments and the single-exponential character of the autocorrelation function of the scattered light.

As we can see, this model predicts two additional important aspects of our observations. First, no scattered light is expected during the melting, unless gas bubbles are captured by the solid during the solidification. This is not the case in succinonitrile at the imposed growth rates, the scattering intensity in the solid being at least two orders of magnitude smaller than that detected at the interface. More strikingly, the above expression of R_0 shows that this quantity is expected to increase markedly when C_g decreases. In agreement with this expectation, we found that before pumping, the bubbles radius is in the range 0.6 to 1.2 μm , while after five pumping cycles it is in the range 1.7 to 5.6 μm and after ten pumping cycles it is in the range 26 to 61 μm . The decrease of the scattered intensity after the pumping is also in good agreement with this model.

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¹H. Guttinger, J. H. Bilgram, and W. Kanzig, *J. Phys. Chem. Solids* **40**, 55 (1979).

²P. Boni, J. H. Bilgram, and W. Kanzig, *Phys. Rev. A* **28**, 2953 (1983).

³U. Durig, J. H. Bilgram, and W. Kanzig, *Phys. Rev. A* **30**, 946 (1984).

⁴O. N. Mesquita and H. Z. Cummins, *Physico-Chemical Hydrodynamics* **5**, 389 (1984).

⁵H. Z. Cummins, G. Livescu, Henry Chou, and M. R. Srinivasan, *Solid State Commun.* **60**, 857 (1986).

⁶G. Livescu, M. R. Srinivasan, Henry Chou, O. N. Mesquita,

and H. Z. Cummins, *Phys. Rev. A* **36**, 2293 (1987).

⁷O. N. Mesquita, L. O. Ladeira, I. Contijo, A. G. Oliveira, and G. A. Barbosa, *Phys. Rev. B* **38**, 1550 (1988).

⁸R. Steininger and J. Bilgram, *Helvetica Physica Acta* (to be published).

⁹*Atlas of Spectral Data and Physical Constants for Organic Compounds*, edited by J. G. Grasseffi and W. M. Ritchey (CRC Press, Cleveland, 1975).

¹⁰R. J. Schaeffer and F. R. Coriell, *Mat Processing in the Reduced Gravity Environment of Space*, edited by Guy E. Rindone (North-Holland, Amsterdam, 1982), p. 479.