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Dynamic light scattering at the nonequilibrium crystal-melt interface in biphenyl and naphthalene

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A strong-quasielastic laser light scattering at the growing crystal-melt interface of both biphenyl and naphthalene was observed in an experiment similar to the one first performed by Bilgram, Guttinger, and Kanzig [Phys. Rev. Lett. **40**, 1394 (1978)]. Since its first observation, the origin of this light scattering remained unexplained. Cummins *et al.* [Solid State Commun. **60**, 857 (1986)] suggested that this light scattering was caused by precipitated microbubbles of gases segregated at the growing interface. We report here the first quantitative confirmation of the microbubble hypothesis.

The first experiment using laser-light-scattering techniques to study the fluctuations at the crystal-melt interface of growing crystals was performed by Bilgram, Guttinger, and Kanzig.[1] The system studied was the growing ice-water interface. A very strong light scattering was observed with an exponentially decaying time autocorrelation function of the light intensity (relaxational scattering). The time autocorrelation function was fitted to $\langle I(t)I(t+\tau)\rangle = B + A\exp(-2\Gamma\tau)$, where A and B are constants and $\Gamma = D(q)^2$. D is a proportionality constant and q is the magnitude of the scattering wave vector.[1] Subsequently several other experiments were performed in ice, salol, and cyclohexanol.[2-9] We report here the observation of the relaxational scattering at the growing crystal-melt interface of both biphenyl and naphthalene. The corrugated interface model, originally proposed by Bilgram *et al.*[1] to explain the relaxational scattering, seemed correct at first, but it was later ruled out by a series of experiments in ice[2,5] and in salol.[6,7] Since 1978 several models to explain the relaxational scattering were proposed: Some were based on *ad hoc* assumptions[5] difficult to prove and the others were in direct conflict with the available experimental data.[6,8,10] Recently Cummins *et al.*[11] proposed that the relaxational scattering was caused by the Brownian motion of precipitated microbubbles of gases segregated at the growing interface. This model has the advantages that it can be checked in several different ways and, at least qualitatively, was not in conflict with the experimental data. Additionally, precipitation of gaseous microbubbles during crystal growth from the melt is a common and undesirable fact.[12,13] The microbubbles of gas can be included into crystals during the growth, deteriorating their optical and mechanical qualities. The nucleation of gaseous microbubbles during crystal growth is in general heterogeneous; impurities and imperfections on the crystal surface play an important role.[12-16]

We report here our observations on the slow transient scattering at the crystal-melt interface of growing biphenyl and naphthalene and the first quantitative confirmation of the microbubble hypothesis. We also demonstrated that the results of the transient scattering at the growing ice-water interface reported by Boni *et al.*[5] are quantitatively consistent with the microbubble hypothesis.

Our experiment was performed in an apparatus similar to the one in Ref. 6. We made, however, several improvements, mainly in the crystal-growth furnace. It was used as an optical window and as the central part of the furnace, a solid cylinder of optical glass BK-7 with height 5 cm and diameter 12 cm. A hole was bored through to allow a Pyrex growth tube (16 mm outside diameter and 14 mm inside diameter) to slide down through the furnace. The measured long-term stability of the furnace's temperature was ±0.02 °C. We used a Brookhaven Instruments Co. digital correlator model BI-2030, a Spectra Physics 165 Ar^+-ion laser operating at 5145 Å and the other parts of the apparatus were standard for photon correlation spectroscopy.[17]

Biphenyl ($C_{12}H_{10}$) is an organic crystal with monoclinic structure and melting point of 70.2 °C. At the melting temperature, the index of refraction is 1.58 and the viscosity is 0.014 P. Naphthalene ($C_{10}H_8$) is an organic crystal with monoclinic structure and melting point of 80.5 °C. At the melting temperature, the index of refraction is 1.59 and the viscosity is 0.0094 P. We grew our crystals by the vertical Bridgman technique and we always had an atomically rough face (faces with faster growth kinetics) growing along the direction of the growth tube. Typically we used a temperature gradient of 4 °C/cm and started with a growth velocity of 0.145 μm/s until a good piece of crystal was obtained. After that we could set another growth velocity, and we worked from 0.145 μm/s up to 0.725 μm/s. As we turned the growth on there was a time interval until the appearance of the light scattering, which was initially very weak. A slow transient period was observed where the scattered intensity increased to an approximately constant value. After this slow transient period we performed intensity measurements as a function of the scattering angle and recorded autocorrelation functions, to test the microbubble hypothesis as suggested in Ref. 11. The reproducibility of the data was not sufficient for clear conclusions. Then we decided to focus our attention on the properties of the slow transient scattering. Biphenyl and naphthalene are convenient for transient measurements due to their fast growth kinetics. The set growth velocity was reached in a few minutes. We started our experiment with the crystal at rest and no scattering observed. We then set the desired growth velocity and we measured the time interval necessary for the appearance of the light scattering. As soon as the scattering appeared we started recording intensity autocorrelation functions of the scattered light. If the microbubbles hypothesis is correct the diffusion coefficients measured are related to the radii of the microbubbles by the Einstein-Stokes equation,

$$R = k_B T / 6\pi\eta D_m , \tag{1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the melt, and D_m is the measured diffusion coefficient of the microbubbles. We summarize part of our data in Table I, where we indicate the average time interval ($\bar{t}$) for the onset of the scattering, the average radius ($\bar{R}$) of the first microbubbles precipitated, and the corresponding crystal growth velocity (V_G). For each growth velocity the averages were taken over the first four experimental points measured in the same run. The polydispersity of the measured radii varied from 15% for the smallest radius to 50% for the largest radius. This fact was reproducible: Smaller polydispersities corresponded to smaller radii.

We interpret our data assuming that there was a background concentration C_0 (the saturation concentration) of gas in the melt at temperature T in equilibrium with a pressure P_0 inside the growth tube. As the crystal growth is initiated, gas segregation takes place at the interface because the solubility of the gas in the solid is smaller than the solubility of the gas in the melt. The ratio of these solubilities is the distribution coefficient K, which is within the range 0.01 to 0.1 for gas segregation by solids in melt growth.[13-16] Thus, as the growth proceeds, the gas concentration near the interface increases above C_0 and it is then possible for precipitation of microbubbles to occur, preventing attainment of the steady-state interface gas concentration value C_0/K. The equation which describes the time dependence of the gas concentration C_i at the interface, considering only diffusion and no convective effects, is[16]

$$\frac{C_i}{C_0} = 1 + \frac{1-K}{K} \left[1 - \exp\left[-\frac{V_G^2 (1-K) K}{D} t \right] \right] , \tag{2}$$

where K is the distribution coefficient, V_G is the crystal growth velocity, and D is the gas diffusivity in the melt. Using $0.01 < K < 0.1$ and $D \sim 10^{-5}$ cm^2/s (Refs. 12 and 14) (estimated), for each growth velocity in Table I, the time interval for the onset of the scattering was much smaller than the corresponding time constant associated with Eq. (2). Therefore we can make a linear approximation in Eq. (2),

$$\frac{C_i}{C_0} \approx 1 + \frac{V_G^2 (1-K)^2}{D} t \approx 1 + \frac{V_G^2 t}{D} . \tag{3}$$

When the first microbubbles of radius R precipitate, the relative gas concentration at the interface is[12,15]

$$\frac{C_e}{C_0} = 1 + \frac{2\sigma}{P_0 R} \quad (C_e \approx C_i \text{ for low gas supersaturation}) , \tag{4}$$

where σ is the liquid-gas surface tension. Using Eqs. (3) and (4) we obtain

$$Rt \simeq \frac{2\sigma D}{P_0} \frac{1}{V_G^2} . \tag{5}$$

In Fig. 1 we show the plot of the measured values for the product Rt versus V_G^{-2} for (a) naphthalene and for (b) biphenyl. The points indicated in Fig. 1 are extreme data points and can be viewed as estimated error bars. Despite the difficulty of the experiment the reproducibility was good. The obtained slopes for the straight lines

TABLE I. Measurements of the transient parameters of biphenyl and naphthalene. $\bar{t}$ is the average time interval for the onset of the scattering; $\bar{R}$ is the average radius of the first microbubbles precipitated; V_G is the crystal-growth velocity. For each growth velocity the averages were taken over the first four experimental points in the same run. The radii polydispersity varied from 15% to 50%, being smaller for smaller radii.

Material	$\bar{t}$ (s)	$\bar{R}$ (μm)	V_G (μm/s)
Biphenyl	16 020	3.6	0.145
	6540	1.9	0.290
	3300	1.0	0.725
Naphthalene	19 890	8.2	0.145
	7740	4.6	0.290
	4380	1.7	0.725

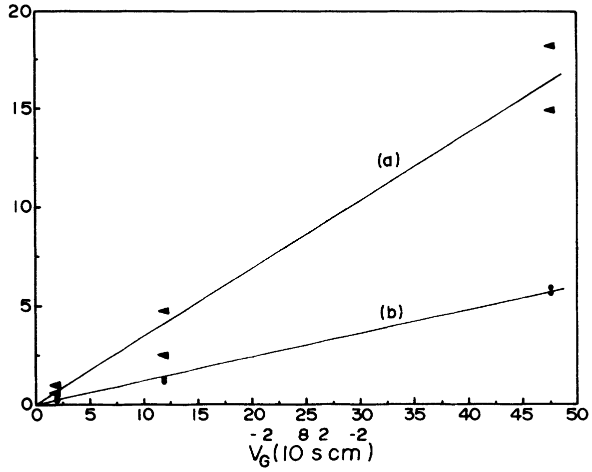

FIG. 1. Measured product of the time interval for the onset of the scattering by the radius of the first microbubbles precipitated versus the inverse of the square of the crystal-growth velocity. The points indicated are extreme data points and can be viewed as estimated error bars. The straight lines were obtained by linear regression, for (a) naphthalene and (b) biphenyl.

were 0.34×10^{-8} cm^3/s for naphthalene and 0.12×10^{-8} cm^3/s for biphenyl. Using the tabulated value for the liquid-gas surface tension for naphthalene[18] $\sigma=28.8$ erg/cm^2, $D\sim10^{-5}$ cm^2/s (Refs. 12 and 14) (estimated), and the slope of the straight line for naphthalene, we obtain $P_0\sim0.17\times10^6$ dyn/cm^2 which is a reasonable pressure inside of our growth tube. Cummins[19] observed that after pumping on the growth tube of growing salol for 24 h the light scattering disappeared. We are now performing new experiments where P_0 is a well-controlled parameter.

Another check to the microbubbles hypothesis was made by us by using the transient data in ice measured by Boni *et al.*[5] They observed that just after the appearance of the relaxational scattering, the light intensity I increased in time while the linewidth Γ decreased. They found a relation between Γ and I given by $\Gamma\propto(I)^{-0.23\pm1\%}$. In our proposed model, Γ is related to the radius of the microbubbles. Since the experiment was performed at fixed scattering angle of 90°, using $\Gamma=D_m q^2$ and the Einstein-Stokes equation we obtain $\Gamma=(6.61\times10^{-3})/R$, with Γ in s^{-1} and R in cm. The scattered intensity is related to the number of microbubbles and to their radius. It is reasonable to suppose that after the initial precipitation, due to depletion of the gas concentration near the interface, the new gases segregated were only consumed to inflate the microbubbles and not to produce new ones. This fact was observed in other experiments in ice growth.[14,15] Also, Γ varied from 2000 to 800 s^{-1}, which means that R varied from 330 to 826 Å in about 2.5 h, indicating a very low gas supersaturation after the precipitation. Therefore, we assume that the change in intensity during the transient period was only due to the change of the microbubble radius. If we can write $I=B(R)^n$ within the range studied where B and n are constants,

$$I=B(6.61\times10^{-3}/\Gamma)^n\ . \tag{6}$$

If $kR\ll1$ where k is the magnitude of the wave vector of the light in the water and R is the radius of the microbubbles, and the scattering is in the Rayleigh limit, then $I=BR^6$, $I=B(6.61\times10^{-3}/\Gamma)^6$, and $\Gamma\alpha(I)^{-0.17}$, which is far from the observed dependence. But in the range considered from 330 to 826 Å, $kR\sim1$, then Mie scattering theory must be used.[20] We used a Mie scattering computer program for spheres to calculate the intensity as a function of R (consequently as a function of Γ), for a fixed scattering angle of 90°. The relative index of refraction used was $m=1/1.34$, where 1 is the index of refraction of the microbubbles of gas and 1.34 is the index of refraction of the water. The curve obtained for I as a function of Γ calculated by the Mie scattering computer program is shown in Fig. 2 (dotted curve). Equation (6) was fit to the Mie curve with B and n as adjustable parameters. The fitting is shown in Fig. 2 (continuous curve). The exponent obtained from the best fit was $n=4.587$, resulting in $\Gamma\alpha(I)^{-0.22}$, which is quite close to the dependence obtained by Boni *et al.*

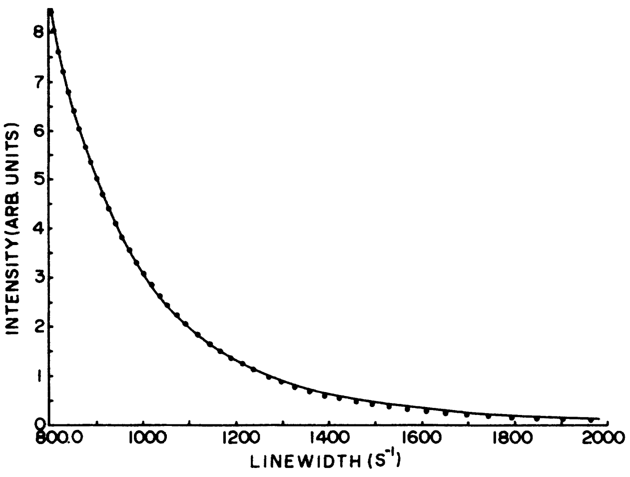

FIG. 2. The dotted curve is the scattered intensity calculated by the Mie scattering computer program for spheres, as a function of the linewidth of the transient relaxational scattering in the ice-water interface at a fixed scattering angle of 90°. The continuous curve is the best fit of $I=B(6.61\times10^{-3}/\Gamma)^n$ to the Mie curve. The exponent obtained was $n=4.587$ resulting in $\Gamma\propto(I)^{-0.22}$.

In conclusion, we presented the first quantitative confirmation of the microbubble hypothesis suggested by Cummins *et al.* to explain the relaxational scattering at the crystal-melt interface of growing crystals. A more detailed account of our experiment will appear elsewhere.[21]

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