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Anomalous Light Scattering at the Surface of Growing Ice Crystals and Thermodynamics of Irreversible Processes

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The framework of nonequilibrium thermodynamics is used to study the phenomenon of enhanced Rayleigh scattering from the liquid–solid interface of a growing crystal. The scattering is treated as resulting from small "objects" of finite lifetime produced at the interface by the growth process and confined thereafter to one phase or the other. The thermodyanmic analysis leads to the formation, adjacent to the interface, of a boundary layer, various properties of which are studied. The analysis is then used to discuss the data obtained in two different experiments on the anomalous light scattering from the ice–water interface. It is found that the various data presented in these two experiments cannot be reconciled with each other in all respects.

KEY WORDS: Crystal growth; irreversible thermodynamics; surface light scattering; ice.

1. INTRODUCTION

During the past 10 years Bilgram and co-workers(1–4) observed, in a series of very thorough experiments, the unexpected phenomenon of anomalous light scattering from the solid–liquid interface layer of growing ice crystals: a large central peak is observed in the light scattering spectrum when a critical growth velocity v^c is exceeded. The phenomenon is accompanied by hysteresis: the anomalous central peak persists if the growth velocity is subsequently reduced to values far below v^c. The anomalous scattering vanishes, however, in these experiments when growth is terminated. We

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have previously tried to explain these experiments on the basis of the existence of multiple steady states in the surface density of scattering "objects" at the ice–water interface, assuming these "objects" to be crystal defects.

A similar type of anomalous scattering phenomenon, but mostly without evidence for the existence of a critical growth rate, was subsequently found in the organic substances salol,(5,6) cyclohexanol,(7,8) biphenyl, and naphthalene.(9) Cummins and co-workers attributed the scattering to the formation of microbubbles from dissolved gases in the liquid. This hypothesis gained support from the experiments of Vesenka and Yeh,(10) in which ice crystals were grown from water saturated with inert gases. Vesenka and Yeh's experiments indicate that two types of dynamic light scattering occur at the surface of a growing ice crystal, one fast and one slow. The slow component closely resembles the scattering arising when inert gases are dissolved in water. The fast component, the only one which persists after rigorous purification, is similar to that observed by Bilgram's group,(1–4) and does not seem to find its origin in microbubble formation.

To help in the understanding of light scattering associated with crystal growth, we have recently applied the scheme of irreversible thermodynamics to the stable growth of a crystal separated by a flat interface from the melt.(11) This approach had the advantage that it is independent of mechanism and could be formulated in parallel fashion for the two cases that the "objects" responsible for the scattering reside in the solid or in the melt. This seemed significant to us since, in our opinion, the "fast" scattering component in ice has not yet been unambiguously assigned to either phase.

In this paper we give once more, in Sections 2–4, the analysis based on the thermodynamics of irreversible processes, and at the same time state some further consequences of this analysis. Thus, we show that one is also able, in addition to a number of results concerning the behavior of the scattering layer, to determine, from quantities which are in principle experimentally observable, a lower bound for the lifetime of the scattering objects when these reside in the liquid, or an upper bound when they only occur in the solid.

In Section 5, we discuss two experiments of anomalous light scattering observed at the water–ice interface. The first belongs to the group of experiments referred to above; the second is a new experiment, also performed by Bilgram and co-workers.(12) We show that our analysis is helpful in the understanding and the ordering of many of the data presented.

2. NONEQUILIBRIUM THERMODYNAMICS AND CRYSTAL GROWTH

In this section we briefly restate the nonequilibrium thermodynamic analysis presented previously.⁽¹¹⁾

We consider a two-component system, predominantly solvent, consisting of a liquid phase and a solid phase, separated by a macroscopically flat interface. The interface is located in the x–y plane of a Cartesian coordinate system at $z=0$, while the liquid and solid phases occupy the half-spaces characterized respectively by $z>0$ and $z<0$. The system contains as solute a component, to which we refer as the "objects," and which resides either only in the liquid or only in the solid. The growth rate v, the normal velocity of the solid at the interface, is positive for solidification and negative for melting. The subsequent analysis is based on the condition of stationary growth.

Thermodynamically the system is described by the following variables: its mass density ρ, momentum density $\rho\mathbf{v}$, energy density u, and in addition the number density of the objects n. The conservation laws for these variables in the bulk are the usual ones. In particular, if the objects exist only in the liquid phase, one has for their number density, denoted by n^+ in the liquid and n^- in the solid, the equations

$$\frac{\partial n^+}{\partial t} = -\nabla \cdot (n^+\mathbf{v}^+ + j^+) + J_R^+, \qquad (1)$$

$$n^- \equiv 0$$

where $\mathbf{v}^+$ is the mass velocity in the liquid, j^+ is the diffusion flux, and J_R^+ is the rate of creation or annihilation of the objects. In Eq. (1), $+$ and $-$ must be interchanged if the objects exist only in the solid.

We now turn to the conservation laws at the surface and denote surface densities and quantities pertaining to the surface by the superscripts s. We note that the normal component of $\mathbf{v}^s$ vanishes identically in the coordinate frame chosen above. We also put the tangential component, and therefore $\mathbf{v}^s$ itself, equal to zero, since there is no evidence that surface flows play any role in the problem under consideration. For stationary growth, the conservation law for mass density at the interface then is

$$\rho v_n^+ = \rho v_n^- = -\rho v \qquad (2)$$

where the subscript n denotes the component normal to the interface. For simplicity's sake we have neglected here the difference in mass density in the liquid and solid phase and put $\rho^+ = \rho^- = \rho$. In Eq. (2) and other equations relative to the surface we use the notation

$$f^{\pm} = \lim_{\varepsilon \to 0} f(x, y, \pm\varepsilon) \tag{3}$$

For the number density of objects one has at the surface the following balance equation:

$$\frac{\partial n^s}{\partial t} = -\nabla \cdot \mathbf{j}^s - v_n^+ n^+ - j_n^+ - J_R^s \tag{4}$$

when objects reside in the liquid or

$$\frac{\partial n^s}{\partial t} = -\nabla \cdot \mathbf{j}^s + v_n^- n^- + j_n^- + J_R^s \tag{5}$$

when they exist only in the solid.

We shall not write down here the conservation laws or balance equations for the other relevant quantities at the interface, but refer for these equations to our previous paper,$^{(11)}$ where we derive, following the scheme of nonequilibrium thermodynamics, the expression for the surface entropy production density σ^s. In this derivation we take the temperature to be continuous across the interface, so that $T^+ = T^- = T^s$, and for simplicity assume T^s to be independent of position. We neglect in this way thermal effusion across the interface as well as thermal diffusion in the surface. One then finds the following expression for σ^s:

$$T^s \sigma^s = -\mathbf{j}^s \cdot \nabla A^s - v\, \Delta\mu - J_R^s A^s \geqslant 0 \tag{6}$$

with $\Delta\mu = \mu^+ - \mu^-$.

Here A is the number-based affinity of the objects (which vanishes at equilibrium and thus determines their equilibrium concentration); the quantities $\mu^{\pm}$ are the chemical potentials of the liquid and the solid phases.

According to Eq. (6), three irreversible phenomena occur in the interface. The first is due to a vectorial phenomenon, the lateral diffusion of the objects, while the second and third account for the scalar processes of relaxation of the objects and growth of the solid. One can deduce$^{(14)}$ from the form of the entropy production the form of the linear phenomenological laws that couple the thermodynamic fluxes and forces in the interface.

Since, due to the Curie principle, no coupling of vectorial and scalar processes is allowed for a surface with isotropic properties, the most general constitutive relations are

$$\begin{aligned} \Delta\mu &= -l_{11} v - l_{12} A^s \\ J_R^s &= l_{12} v - l_{22} A^s \\ j^s &= -l \nabla A^s \equiv -D^s \nabla n^s \end{aligned} \tag{7}$$

where we have used in the second line the Onsager–Casimir reciprocity relation $l_{21} = -l_{12}$ and introduced the diffusion constant $D^s = l\,\partial A^s/\partial n^s$.

What one has found here is essentially different from the situation in the bulk phases, where only a single scalar phenomenon occurs, to wit, relaxation of the density of the objects, and where Curie's principle prohibits direct coupling of this process to any other process in the bulk phases. But a new phenomenon may occur at the surface, namely that growth of the solid may be coupled to the relaxation rate of the objects, or in other words, that growth can be a driving force for the production of objects.(11)

Since the solution of the interfacial differential equation for n^s determines a boundary condition for the differential equation for n^+, or n^-, the new coupling phenomenon will influence the bulk behavior by giving rise to a three-dimensional boundary layer.

We shall calculate the width of this layer, and the magnitude of its density, in the next section by solving the differential equations for n^s and n^+ (or n^-). To write down these equations we need in addition to the phenomenological equations (7) the phenomenological laws for the bulk quantities j^+ and J_R^+ (or j^- and J_R^-). These laws are

$$j^+ = -D\,\nabla n^+ - D'\,\nabla T^+ \tag{8}$$

and

$$J_R^+ = -(n^+ - n^e)/\tau \tag{9}$$

In Eq. (8), D is the diffusion coefficient and D' a thermal diffusion coefficient which characterizes the thermophoresis of the objects. The quantity τ in the fully linearized rate law (9) represents the lifetime of the objects and n^e their equilibrium density in bulk.

3. STEADY-STATE DISTRIBUTION OF OBJECTS IN BULK DURING GROWTH

The distribution of objects in the bulk of the phase in which they reside, which for definiteness we have chosen to be the liquid, obeys the conservation equation (1). If we substitute into this equation the phenomenological laws (8) and (9) we get in the steady state

$$D\,\nabla^2 n^+ = \nabla \cdot n^+ \mathbf{v}^+ + (n^+ - n^e)/\tau \tag{10}$$

It would seem that in writing this equation, the thermal diffusion term in Eq. (8) has not been taken into account. However, one is easily convinced, using the energy conservation law for an incompressible liquid in the absence of dissipative flow phenomena, or for a solid, that here the only effect of thermal diffusion in the steady state is to replace D by an effective diffusion coefficient which differs from D by a negligible amount.

The differential equation (10) must now be solved for the half-space which contains the objects, with boundary conditions at the interface and at infinity. The natural boundary condition at infinity is $n^+ = n^e$, while the boundary condition at the interface is obtained by solving the steady-state differential equation for the surface density n^s. This equation is obtained by substituting (7) and (8) into the surface conservation law (4) and reads

$$\nabla \cdot (D^s \nabla n^s) - n^+ v_n^+ + D\, \partial n^+/\partial z + D' G^+ + l_{12} v - l_{22} A^s = 0 \qquad (11)$$

Here $G^+ = \partial T^+/\partial z$ represents the positive thermal gradient in the liquid, which cannot be eliminated from this equation as the corresponding term involving $\nabla^2 T^+$ could be when obtaining Eq. (10). The above equation contains several sources of nonlinearity. Indeed, within the domain of validity of linear irreversible thermodynamics, D^s, l_{11}, l_{12}, and l_{22} may still depend on n^s, while A^s is in general a nonlinear function of n^s. Here we shall retain only the nonlinearity in l_{12}, which can lead to critical behavior under appropriate conditions.(13) Equation (11) then becomes

$$D^s \nabla^2 n^s - n^+ v_n^+ + D\, \partial n^+/\partial z + D' G^+ + l_{12}(n^s) v - (n^s - n^{se})/\tau = 0 \quad (12)$$

with n^{se} denoting the equilibrium density of objects at the interface and the lifetime τ equal to $(l_{22}\, dA^s/dn)^{-1}$. This last linearization had already been performed in bulk, c.f. Eq. (9) (strictly speaking, the lifetime τ need not be equal in bulk and at the surface, as we assumed here).

If the objects are confined to the solid phase, one has instead of Eq. (12)

$$D^s \nabla^2 n^s + n^- v_n^- - D\, \partial n^-/\partial z - D' G^- + l_{12}(n^s) v - (n^s - n^{se})/\tau = 0 \quad (13)$$

as follows from Eq. (5) and the phenomenological equation for j_n^-. This equation is essentially identical in form to the equation we introduced previously to study the behavior of defects at the ice–water interface, but also includes, as it should, terms for the effect of convection and of the thermal gradient.

Using the self-consistent ansatz $\partial n^+/\partial z = -(n^+ - n^e)/z_0^+$, Eq. (12) reduces to

$$D^s \nabla^2 n^s + l_{12}(n^s) v - (n^s - n^{se})/\tau_{\text{eff}}^+ + D' G^+ + v n^e = 0 \qquad (14)$$

where the effective lifetime is given by

$$\frac{1}{\tau_{\text{eff}}^+} = \frac{1}{\tau} - \frac{v}{d} + \frac{D}{d z_0^+} \qquad (15)$$

In this equation $d \equiv n^s/n^+$ represents the interfacial width.

In an earlier paper[(13)] we investigated the stability of the solutions of Eq. (13) for a step-function nonlinear dependence of l_{12} on n^s, which is of the type that leads to critical behavior. It was then found that for a sufficiently large interface the only stable solutions are uniform in the $x-y$ plane and are determined by

$$(n^s - n^{se} - D'G^+\tau^+_{\mathrm{eff}})/\tau^+_{\mathrm{eff}} v = l_{12}(n^s) + n^e \tag{16}$$

The solution of this equation provides the boundary value $n^+(0) \equiv n(v)$ at the interface, if one makes the substitution $n^s = n^+(0)d$.

One is now able to solve Eq. (10) for uniform convection, $\mathbf{v}^+ = v\hat{z}$, with $\hat{z}$ the unit vector in the z direction, which is the only case of interest here and which is automatically realized in the solid.

The solution of (10) then is

$$n^+(z) - n^e = [n^+(v) - n^e] \exp(-z/z_0^+) \tag{17}$$

where z_0^+, the width of the boundary layer, is

$$z_0^+ = -\tfrac{1}{2}v\tau + \tfrac{1}{2}(v^2\tau^2 + 4D\tau)^{1/2} \tag{18}$$

One easily shows τ^+_{eff} to be positive for all values of v if one substitutes Eq. (18) into the expression (15).

In case the objects reside in the solid, Eq. (16) [cf. also Eq. (13)] must be replaced by

$$(n^s - n^{se} + D'G^-\tau^-_{\mathrm{eff}})/\tau^-_{\mathrm{eff}} v = l_{12}(n^s) - n^e \tag{19}$$

with

$$\frac{1}{\tau^-_{\mathrm{eff}}} = \frac{1}{\tau} + \frac{v}{d} + \frac{D}{dz_0^-} \tag{20}$$

where now $d \equiv n^s/n^-$.

The distribution of objects in the solid is analogous to the one given by Eq. (17) and is

$$n^-(z) - n^e = [n(v) - n^e] \exp(z/z_0^-) \tag{21}$$

with the characteristic width

$$z_0^- = \tfrac{1}{2}v\tau + \tfrac{1}{2}(v^2\tau^2 + 4D\tau)^{1/2} \tag{22}$$

Equations (17) and (21) are valid for solidification, $v > 0$, as well as for melting, $v < 0$. The magnitude of the nonequilibrium density in the boundary layer, $n(v) - n^e$, results from the coupling of the growth process to the relaxation of the objects as described by Eqs. (16) and (19), respectively. The limiting behavior of the width of the boundary layer for large and small values of $v > 0$ is seen to be

$$z_0^{\pm} = (D\tau)^{1/2}, \qquad |v| \ll (4D\tau)^{1/2} \tag{23}$$

and

$$z_0^{+} = D/v, \qquad z_0^{-} = v\tau, \qquad |v| \gg (4D/\tau) \tag{24}$$

It can also be shown from Eqs. (18) and (22) that for $v > 0$ the derivative of $z_0^{+}(v)$ with respect to v is a negative function for all values of v, and that of $z^{-}(v)$ a positive function. Therefore the width of the boundary layer monotonically decreases as v increases if the objects reside in the liquid, and in the same way increases if they are in the solid. This implies in particular that

$$0 \leqslant z_0^{+}(v) \leqslant (D\tau)^{1/2} \tag{25}$$

and that

$$\tau \geqslant (z_{0,\max}^{+})^2/D \tag{26}$$

where $z_{0,\max}^{+}$ is the maximum width observed.

We have thus determined a lower bound for the lifetime τ in the case that the objects are in the liquid phase, a lower bound which can be calculated from the quantities $z_0^{+}(v)$ and D, when these are experimentally accessible. Similarly, one could determine an upper bound for τ, for the other case in which the solid contains the objects.

4. INTENSITY OF LIGHT SCATTERED FROM OBJECTS PRODUCED BY GROWTH

The spectral intensity $I(k, \omega)$ of light scattered by objects produced at an interface between a growing solid and its melt has been calculated previously$^{(13)}$ and is given by the expression

$$I(k, \omega) = \frac{\text{const} \cdot A z_0^{\pm}(v)\, n(v)(Dk^2 + 1/2\tau)}{(\omega - vk_z)^2 + Dk^2 + 1/\tau} \tag{27}$$

Here A is the cross section in the x–y plane of the observed scattering volume, k is the scattered wave vector, and ω is the frequency shift of scattered light. The other symbols in this expression have been defined in the previous sections. It is also understood that the quantity designated as "const" is only truly constant with respect to k, when the objects are small compared to the wavelength of the incident light.[(11)]

The above expression shows that one has a Lorentzian spectrum centered at $\omega = vk_z$, with a half-width $\Gamma = Dk^2 + 1/\tau$, and that the intensity depends on the growth velocity through the product of two factors. The first of these factors, the width of the boundary layer $z_0^{\pm}(v)$, has been calculated in Section 3 [cf. Eqs. (18) and (22)] and is a slowly varying function of v. The other factor, $n(v)$, is determined by the steady-state density of objects at the interface n^s, which is obtained by solving Eqs. (16) or (19). When the Onsager coefficient l_{12} is independent of n^s, these equations have only one single solution, which is a smooth function of v. Consequently there will be no critical behavior and hysteresis in this case, and no threshold to anomalous scattering.

However, if l_{12} is a sigmoidal function of the surface density of objects, then Eqs. (16) or (19) may have multiple steady-state solutions. These may be obtained graphically as the intersections of the curves representing the two sides of the equations. An illustration of this situation and procedure is given in Fig. 1. One sees[(13)] that for $v < v_1^c$ and $v_2^c < v$ there exists only one solution, while for $v_1^c < v < v_2^c$ there will be three, of which two are locally stable and the one with the intermediate value unstable. By plotting, as in Fig. 2, the locally stable solutions for increasing and decreasing values of v, one finds two critical growth velocities: the larger determines a true threshold to an increased density of objects in the surface layer, and

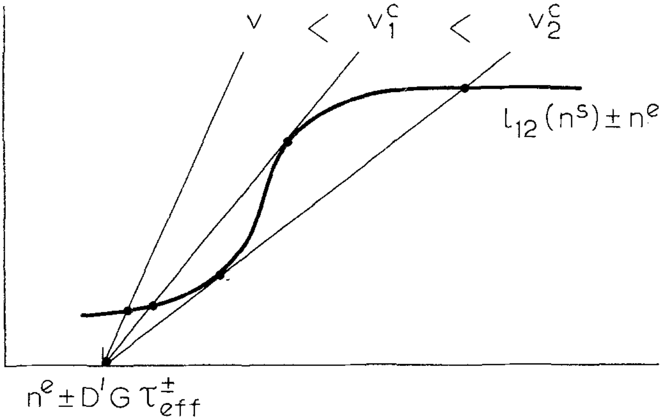

Fig. 1. The left- and right-hand sides of Eq. (16) or Eq. (19) plotted as a function of the surface density of defects n^s for the case that the right-hand side, $l_{12}(n^s)$, is a sigmoidal function. The intersections of the left- and right-hand sides for three values of v are shown as points. For $v < v_1^c$ and $v_2^c < v$ only one intersection, and therefore a unique steady state, occurs.

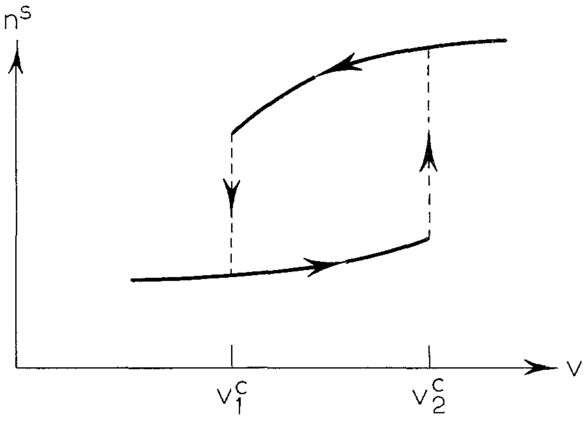

Fig. 2. A schematic representation of the stable steady states for n^s as a function of v for the sigmoidal function $l_{12}(n^s)$ illustrated in Fig. 1. Two stable states exist for $v_1^c < v < v_2^c$. The dashed lines represent jumps in n^s as v is increased above v_2^c on the lower branch and decreased below v_1^c on the upper branch.

thereby to anomalous light scattering, when v is increased. A decrease of v, following increase above v_2^c, leads to the hysteresis indicated by the downward arrows. Quantitative details of the behavior sketched here depend on the values of the kinetic parameters involved.

The graphic construction in Fig. 1 exhibits an important feature of the threshold velocities, namely their dependence on the temperature gradient G, which follows from the solutions of Eqs. (16) and (19): if the objects reside in the liquid, an increase of G results in a parallel displacement to the right of the straight line representing the left-hand side of Eq. (16) and therefore in a *decrease* of the critical growth velocities. On the other hand, if the objects are in the solid, one finds in a similar way that an increase of G causes an *increase* in the critical growth velocities.

The preceding analysis leads to the following conclusions.

1. Criticality and hysteresis may result from a surface instability in the distribution of objects due to a nonlinear coupling between the growth of the solid and the relaxation of the density of the objects.

2. Equation (16), or (19), shows that the same molecular mechanism cannot lead to behavior that is symmetric for freezing ($v > 0$) and for melting ($v < 0$).

3. If there are no objects and both bulk phases are uniform and homogeneous (and remain so during growth), there is no room within the thermodynamic description for anomalous scattering coupled to growth.

In addition to these conclusions of a general nature, the analysis implies more specific statements concerning the possible location of the objects.

4. Due to thermophoresis, the threshold to anomalous scattering depends on the temperature gradient G at the interface in such a way that $dv_1^c/dG > 0$ if the objects reside in the solid, and that $dv_1^c/dG < 0$ if they exist only in the liquid.

5. For sufficiently large v the width of the scattering layer is proportional to v if the objects are in the solid, and inversely proportional to v if they reside in the liquid [cf. Eq. (24)].

6. From the width of the scattering layer and the width of the spectral line associated with it, a lower bound can be found for the lifetime of the objects if these are confined to the liquid phase [cf. Eq. (26)], and an upper bound for the same quantity if they occur only in the solid.

One last remark is in order: in the preceding discussion it has been assumed that the term n^e is constant. It might, however, be that only a quasiequilibrium is realized and that n^e is a function of a slowly varying parameter. This then could lead to apparent instead of true hysteretic behavior, as we have argued elsewhere.(11)

5. THE SOLID–LIQUID INTERFACE LAYER OF GROWING ICE CRYSTALS: THE NATURE OF THE SCATTERING OBJECTS

We shall use here the analysis of the previous sections to discuss the results found in two different experiments in which anomalous light scattering was observed at the surface of a growing ice crystal. The first experiment was performed by Böni *et al.* (BBK),(3) the second by Halter *et al.* (HBK).(12) HBK state that they "observed the same phenomenon as Böni *et al.*" Indeed in both experiments:

1. Anomalous scattering is observed if a critical growth volocity $v_c \simeq 1.5\ \mu\text{m/sec}$ is exceeded.

2. Hysteresis occurs if the growth volocity is subsequently lowered.

3. The thickness z_0 of the scattering layer at growth velocities of $1.5\ \mu\text{m/sec}$ is about 3–4 μm (for BBK, $z_0 \simeq 4\ \mu\text{m/sec}$; for HBK, $z_0 \simeq 3\ \mu\text{m/sec}$).

4. A diffusion coefficient D is deduced from the linewidth of Rayleigh scattered light of 2–3 $\mu\text{m}^2/\text{sec}$ (for BBK, $D \simeq 3\ \mu\text{m}^2/\text{sec}$; for HBK, $D \simeq 2\ \mu\text{m}^2/\text{sec}$).

There are, however, differences in the results reported. Thus, for example:

5. It was observed in the BBK experiment that the critical growth velocity is an increasing function of the temperature gradient in the ice near the interface. The influence of the temperature gradient on the critical growth velocity at the interface has not been studied in the HBK experiment.

6. In the HBK experiment the growth velocity dependence of the scattering layer thickness z_0 was measured for decreasing velocities v. It was found that z_0 is inversely proportional to v and behaves as $z_0 \simeq D/v$. A maximum thickness of $\simeq 200\ \mu\text{m}$ was observed. No comparable data exist for the BBK experiment.

7. In the HBK experiment increased Rayleigh scattering is tentatively attributed to structures (or objects) of several H-bonded molecules, whose formation was inferred from Raman spectra measurements and which have a lifetime $\tau \simeq 4 \times 10^{-13}$ sec.

If we now apply to these data the analysis of the previous sections, we are led to conclude from the above items 5–7, taking also items 3 and 4 into account, the following.

For the BBK experiment, the scattering layer and the object exist on the solid side of the interface (cf. item 4 of Section 4). An upper bound can then be inferred, from the estimated thickness of the layer $z_0 \simeq 4\ \mu\text{m}$ and the measured diffusion coefficient $D \simeq 3\ \mu\text{m}^2/\text{sec}$, for the lifetime τ of the objects (cf. end of Section 3). This upper bound is about 5 sec.

Since it is well known that a solid growing from a pure liquid invariably incorporates structural defects, the BBK experiment therefore does not seem to be in disagreement with an explanation in which the objects which cause the anomalous light scattering in growing ice crystals are small, mobile defects that coalesce from interstitial defects during growth.(11,13) [3]

For the HBK experiment, we conclude that the scattering layer and the objects exist on the liquid side [see item 5 of section 4 and Eq. (23)] and that a *lower* bound for the lifetime τ of the objects is 2×10^4 sec. Clearly, then, the results of the two experiments do not seem to be compatible with each other in all respects. Moreover, in the HBK experiment the value 4×10^{-13} sec of the lifetime of the structures seen in the Raman experiments, which were conjectured by HBK to be responsible for the

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[3] Evidence that bubbles are not responsible for light scattering in cyclohexane has recently been provided in ref. 15.

enhanced Rayleigh scattering, is not compatible with the observed values of $z_0(v)$ and D.

As far as the differences in the results of the two experiments are concerned, one must keep in mind that they were not performed in the same way. In the BBK experiment a zone melting apparatus was used. The HBK experiment, on the other hand, was performed with the Czochralski growth technique and with ice crystals grown in a helium atmosphere kept at overpressure. The authors say: "Helium [was] chosen because its solubility in ice is a little higher than in water. Thus we prevent the segregation of gases at the solid liquid interface."(12) But could it be that unforseen "objects" are created in this procedure, especially in light of the evidence of Vesenka and Yeh(10) for helium bubbles at the ice surface when helium is present in the liquid phase?

It seems to us that more experimental data are required to determine, with the help of the analysis presented above, the origin of anomalous light scattering in a growing ice crystal in an unambiguous way.

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