

Reply to “Comment on ‘Fluctuations during freezing and melting at the solid-liquid interface of xenon’ ”

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Based on light-scattering experiments and model calculations a detailed discussion of the microbubble model has been given by R. Steininger and J. H. Bilgram [J. Cryst. Growth **112**, 203 (1991)], where the microbubble model has been ruled out. Complementary to this discussion a comparison of properties of the microbubble model with experimental observations is given in this response. It is found that the microbubble model is not compatible with experimental results obtained in pure systems. [S0163-1829(96)04326-3]

The microbubble model referred to in the preceding comment has been discussed on the basis of the properties of the scattered light in Ref. 1, which is mentioned in Ref. 2. In this response we discuss complementary properties predicted by the microbubble model.³ Two equations are given in Ref. 3 which can be confronted with experiments.

(a) It is assumed that gas bubbles with the critical radius of nucleation R_i are nucleated at the interface by some heterogeneous nucleation mechanism. The following equation is given:³

$$R_i t_i = \frac{2\sigma D_{\text{solute}}}{p} \frac{1}{v_G^2}, \quad (1)$$

where t_i is the time from the beginning of crystal growth until the appearance of bubbles of size R_i , σ the liquid-gas surface free energy, D_{solute} the impurity diffusion constant in the melt, p the vapor pressure of gas in equilibrium with liquid, and v_G the growth velocity of the crystal.

(b) A selection mechanism is proposed in Ref. 3 to explain the occurrence of monodisperse microbubbles. It is proposed that three forces are acting on the bubbles. (i) The viscous Stokes force $\mathbf{F}_v = 4\pi\eta R v_G$, where η is the dynamic shear viscosity and R the bubble radius. (ii) The thermocapillary force $\mathbf{F}_t = -2\pi R^2(d\sigma/dT)\mathbf{G}$, where σ is the liquid-gas interfacial tension and \mathbf{G} the temperature gradient in the liquid in the interface region. (iii) The buoyancy force $\mathbf{F}_b = (4/3)\pi R_i^3 \rho \mathbf{g}$, where ρ is the density difference between the liquid and the gas and \mathbf{g} is the acceleration of gravity. Only if these three forces are in equilibrium will the bubble be carried along ahead of the interface and detected in a light-scattering experiment.³

$$\mathbf{F}_v + \mathbf{F}_t + \mathbf{F}_b = \mathbf{0}. \quad (2)$$

If the size of the bubble does not satisfy this criterion, the bubble will be pushed out of the boundary layer.

In the following Eqs. (1) and (2) will be compared with the experimental results. A list of experimental results which have been obtained in earlier experiments is given in the Introduction of Ref. 2. In the following we refer to this list by means of the numbers I–XI. These results have been con-

firmed in experiments performed at the solid-liquid interface of xenon.²

(a) Relations deduced from Eq. (1) are as follows.

(1) $R_i \propto 1/t_i$. No difference in the results has been found for experiments performed with the zone-refining technique and the spherical-inward-growth technique (VII). The onset time in our zone-refining experiments can be explained by the change of thermal gradients when the zone closes. This has been confirmed by the spherical-inward-growth experiments, where thermal gradients can be neglected and no onset time after crystal growth has been observed.²

(2) $R_i \propto 1/v_G^2$. v_G has been varied in the range $0.05 < v_G < 1 \mu\text{m/s}$ in the experiments with xenon and in the range $0.15 < v_G < 30 \mu\text{m/s}$ in the experiments with cyclohexane. No dependence of Γ on v_G has been found (IX). No dependence of Γ on v_G has been found in experiments where zone-refined H₂O or zone-refined salol has been used. A change from growth to melting does not eliminate light scattering in experiments performed in a liquid sphere (VIII). This indicates that segregation of impurities is not essential for the phenomena under discussion.

(b) The selection mechanism Eq. (2) provides more relations that might be verified by experiments. The three forces acting on the bubbles depend on various experimental parameters.

(1) $\mathbf{F}_b \propto \mathbf{g}$. In the spherical-inward-growth experiment, solid-liquid interfaces with any orientation relative to gravity can be studied in the same experiment. No dependence of Γ on the direction of gravity has been observed (XI). In the case of spherical-inward-growth the thermal gradients can be neglected. Thus \mathbf{F}_b cannot be neglected in Eq. (2) as assumed in Ref. 3 for another technique of crystal growth.

(2) $\mathbf{F}_t \propto \mathbf{G}$. During zone-melting experiments thermal gradients exist at the ice-water interface and have been studied in some detail.⁴ In the spherical-inward-growth experiments no thermal gradients exist in the liquid. No dependence of Γ on thermal gradients has been found (VII) and (VIII).

(3) $\mathbf{F}_v \propto v_G$. A dependence of Γ on growth velocity has not been found (IX).

(4) $\mathbf{F}_v \propto \eta$. Experiments with various substances allow the study of the influence of the viscosity on R_i . Calculating R_i from the experimental data is the same procedure as calculating the correlation length ξ . In experiments with various

substances the viscosity at the melting point has been varied by a factor of about 15. No dependence of ξ on viscosity has been observed.²

From comparison of the properties of the microbubble model³ with the experimental results given in Refs. 1 and 2, one has to conclude that neither the optical¹ nor the mechanical nor the thermodynamical properties of the microbubble

model are compatible with the results of light-scattering experiments performed at the solid-liquid interfaces of pure systems. Mazur and Keizer⁵ have discussed the results of various light-scattering experiments performed at the solid-liquid interface. Mazur and Keizer⁵ conclude that liquids saturated with gas may behave differently from pure systems.

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¹R. Steininger and J. H. Bilgram, *J. Cryst. Growth* **112**, 203 (1991).

²S. Di Nardo and J. H. Bilgram, *Phys. Rev. B* **51**, 8012 (1995).

³H. Z. Cummins and L. M. Williams, in *Light Scattering by Liquid*

Surfaces and Complementary Techniques, edited by D. Langevin, Surfactant Science Series Vol. 41 (Dekker, New York, 1992), p. 287.

⁴P. Böni, J. H. Bilgram, and W. Känzig, *Phys. Rev. A* **28**, 2953 (1983).

⁵P. Mazur and J. Keizer, *Phys. Rev. A* **38**, 5267 (1988).