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Fluctuations during freezing and melting at the solid-liquid interface of xenon

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Dynamic light-scattering experiments have been performed to study the dynamical processes at the solid-liquid interface during freeezing and melting on a mesoscopic length scale. Xenon has been used as a model substance because it forms a simple liquid, and van der Waals forces are the only interactions between the atoms. A solid-liquid interface is formed by melting a sphere with a diameter of about 4 mm inside of a single crystal with a volume of about 80 cm^3, thus preventing any contamination of the melt. Anomalous light scattering has been observed in a layer at the solid-liquid interface. This phenomenon is initiated during freezing. Once initiated it can also be observed during melting. Then the scattering layer sticks to the melting crystal surface. No anomalous light scattering is observed in the bulk melt or in the bulk crystal. The linewidth of the scattered light is proportional to the scattering vector squared. Thus the dynamics in the interface layer can be described by a diffusion law. The diffusion constant has been determined to be $D_i \approx 8\times 10^{-9}$ cm^2/s. This is five orders of magnitude smaller than the thermal diffusivity of bulk liquid. D_i does not depend on growth rate or orientation of the solid-liquid interface relative to the direction of gravity. The measurements support the idea that a layer of preordered material is formed at the solid-liquid interface. The correlation length of the fluctuations in this layer has been determined to be $\xi \approx 260$ nm. This correlation length is the same for xenon, salol, and cyclohexane and is independent of the different bulk properties, like viscosity or triple-point temperature. Crystallization is a two-step process: the crystal grows into a metastable layer similar to the metastable layers found in Landau-Ginzburg models [J. Bechhoefer, H. Löwen, and L. S. Tuckerman, Phys. Rev. Lett. **67**, 1266 (1991)].

I. INTRODUCTION

A. The freezing transition

Freezing of a liquid and melting of a solid are omnipresent physical phenomena in everyday life. Thus, it might be astonishing that still no theory exists which describes the dynamical processes taking place during freezing and melting. A closer look at the physics exhibits severe problems, in experiment as well as in theory: (i) freezing and melting take place at the solid-liquid interface and are no bulk processes; (ii) freezing and melting are first-order phase transitions accompanied by a latent heat; (iii) the latent heat has to be transported away from or towards the interface in order not to stop the transition process; freezing and melting can be studied under nonequilibrium conditions only.

Löwen *et al.*[1,2] studied three-phase Ginzburg-Landau models where one of the phases is a metastable phase created dynamically. It has been shown that at conditions far from thermodynamic equilibrium the boundaries separating the stable high- and low-temperature phases split apart into two independently moving boundaries: thus a macroscopically large region of the metastable phase is created.

Burke, Broughton, and Gilmer[3] performed a molecular-dynamics simulation of a Lennard-Jones system. They conclude that the picture of atoms near the interface moving as in a liquid until a lattice site is found is not appropriate. Rather, a cooperative motion of atoms ("clusters") is observed. The [111] surface of the Lennard-Jones fcc crystal grows by addition of such clusters.

B. Anomalous light scattering

Anomalous diffusive light scattering at the solid-liquid interface during crystal growth has been observed on ice,[4-6] salol,[7] and cyclohexane.[8] The experimental observations can be summarized as follows.[9,10]

(1) The intensity autocorrelation function can be fitted by a single exponential, which is characterized by one decay time τ. The decay rate $1/\tau=\Gamma$ is the linewidth of the quasielastically scattered light.

(2) The linewidth Γ of the scattered light is proportional to the square of the scattering vector $\mathbf{q}$.

(3) The proportionality $D_i=\Gamma/q^2$ does not depend on the orientation of the scattering vector relative to the interface.

(4) D_i has found to be independent of the wavelength of light λ and the scattering vector $\mathbf{q}$.

(5) The intensity of the scattered light as a function of the scattering vector, $I(q)$, can be fitted by the Fourier transform of the Ornstein-Zernike pair correlation function or by the Fourier transform of the Debye-Bueche pair correlation function.

(6) Diffusive light scattering occurs on both atomically smooth and atomically rough interfaces.

(7) Using a zone-refining, Czochralski, or Bridgman growth technique, there is a critical growth velocity of the crystal, v_{crit}, for the onset of diffusive light scattering. v_{crit} depends on the thermal gradient ∇T in the liquid in

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front of the interface. No critical velocity has been observed in spherical inward growth experiments.

(8) Once diffusive light scattering is initiated, it persists to low growth rates. Reversing from growth to melting does not destroy immediately the scattering layer.

(9) No dependence of the linewidth of the scattered light on growth velocity has been found.

(10) The anomalous light scattering takes place at the liquid side of the solid-liquid interface.

(11) D_i does not depend on the direction of gravity relative to the solid-liquid interface.

In this paper we report on dynamic light-scattering experiments at the solid-liquid interface of xenon crystals: Dynamical processes at the interface have been examined by analyzing the temporal behavior of the intensity of the scattered light.

II. EXPERIMENTAL SETUP

A. Crystal growth

1. *Gas handling*

Special attention is paid to the purity of the xenon: we use a high-purity gas-handling system. The xenon gas with a purity of 99.998% was supplied by Linde; C_mH_n, CO_2, O_2, N_2, H_2, and H_2O are extracted by a rare gas purifier to 1 ppmV (part per million of volume) prior to every run. Just before flowing into the growth vessel, the xenon gas passes a Wafergard F Mini Inline Gas Filter, which asserts retention of all particles with a diameter of 3 nm and larger.

2. *Temperature control*

For light-scattering experiments as well as for crystal growth it is essential to have a thermally well controlled surrounding of the xenon. We use a cryostat similar to the one used in earlier work.[11] 13 liters of liquid isopentane are the thermostating medium, we achieve a stability of $\pm 10^{-3}$ K near the triple-point temperature of xenon (161.390 K). This temperature stability must be maintained for at least 8 weeks, the time needed to grow the crystal and to perform light-scattering experiments.

We use isopentane as the thermostating liquid because of its large liquid range ($-159.9\,^\circ$C to $+27.9\,^\circ$C, at atmospheric pressure). A laminar flow of the isopentane is induced by a stirrer and provides a homogeneous temperature distribution. The growth vessel with a volume of 150 cm^3 is immersed in this bath. A double-wall glass vessel contains the isopentane. The helium pressure between the walls is used to control the thermal contact of the isopentane with the liquid nitrogen outside of the Dewar. The helium pressure is chosen in such a way that the isopentane is cooled slightly below the temperature where we want to run the cryostat. By means of a PID-controlled heater element of about 10 W we control the temperature.

3. *Characterization of the crystal quality*

The crystals have been grown by a modified Bridgman growth technique. We use three means to characterize crystal quality: during crystal growth the whole crystal is kept very close to the melting temperature, grain boundaries become visible at the solid-liquid interface; the crystal can be scanned by the laser, grain boundaries scatter the light and thus can be detected; raising the temperature of the isopentane slightly above the melting point of the crystal, melting is preferentially initiated at the grain boundaries which can easily be observed by eye.

Neutron scattering would be a method to characterize crystal perfection, whereas the bulk of xenon crystals cannot be investigated with x rays, because xenon is a good x-ray absorber.

B. Light scattering

We use an argon-ion laser (Coherent Innova 90) at $\lambda=457.9$, 488.0, and 514.5 nm and a dye laser (Coherent CR 599; Rhodamine 6G) at $\lambda=620$ nm as light sources. The polarization of the incident light is chosen to be perpendicular to the scattering plane. An illuminating tube for a scattering angle $\theta=90^\circ$ is fixed close to the growth vessel. With our setup we can perform dynamic light-scattering experiments at four different scattering vectors.

The scattering volume is imaged to the photodetection system by a periscope which enables us to work with an illumination of very low irradiance. The optical resolution has been determined by test measurements to 3.5 μm which is close to the value of aperture-limited resolution.

The photodetection system is essentially the same as that used in earlier light-scattering experiments.[5] We tested our *in situ* optical setup with a suspension of latex spheres with a diameter $\varnothing=(91.0\pm5.8)$ nm according to the supplier. This is in good agreement with our measurements $\varnothing_{\mathrm{expt}}=(94.0\pm1.3)$ nm.

III. EXPERIMENTAL RESULTS

A. Bridgman growth

Performing light-scattering experiments at the solid-liquid interface during Bridgman growth at growth velocities up to 0.3 μm/s, we never observed anomalous light scattering even after very long growth times (several weeks). To prepare the solid-liquid interface during Bridgman growth for investigation in our optical setup, a liquid layer of about 10 mm has to be on top of the crystal. There was always thermal convection in the liquid xenon present.

B. Spherical inward growth

At the beginning of an experiment a liquid sphere is molten in the xenon crystal by means of a frozen-in thermistor. The thermistor has a diameter of 0.8 mm. Choosing an appropriate heater current, the sphere grows, until a steady-state diameter of 3–5 mm is reached (Fig. 1). No anomalous light scattering can be observed at the solid-liquid interface at that time. As the heater current is reduced, spherical inward growth begins and after the crystal has grown about 0.1 mm, light scattering sets in at the solid-liquid interface. No onset

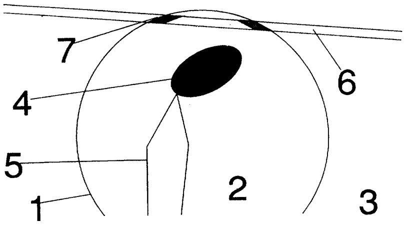

FIG. 1. Spherical inward growth (not to scale). A liquid sphere can be molten in the crystal by means of a thermistor. (1) Solid-liquid interface, (2) liquid xenon, (3) solid xenon, (4) thermistor (diameter ∅=0.8 mm), (5) thin leads to thermistor, (6) laser beam, (7) enhanced light scattering.

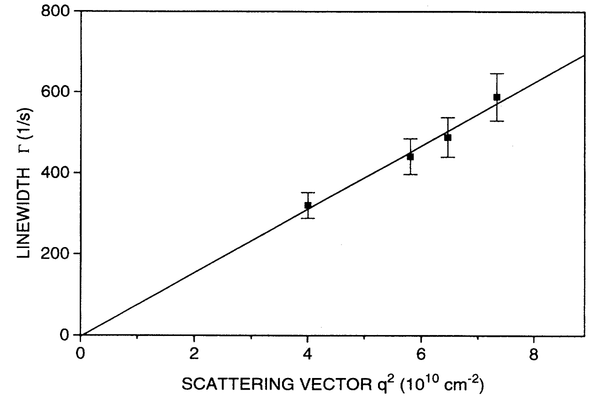

FIG. 3. Linewidth Γ of the scattered light vs the square of the scattering vector q. The linear dependence of Γ on q^2 shows that the dynamical processes at the solid-liquid interface layer can be described by a diffusion law with a single diffusion constant D_i. The data (■) are from one experiment. The solid line is a linear fit leading to a diffusion constant $D_i = 7.85 \times 10^{-9}$ cm²/s. The origin has not been used to fit the data.

time of the scattering has been observed. In bulk solid and liquid xenon no anomalous scattering can be detected. As crystal growth continues, the scattered intensity increases. Scattering does not disappear if the thermistor is again heated and growth is reversed to slow melting. Scattering then remains located at the solid-liquid interface. If the diameter of the liquid sphere is larger than ≈6 mm, then in most experiments no anomalous light scattering can be observed. This is due to thermal convection: The convective flow destroys the thick layer with the scattering inhomogeneities. A temperature gradient perpendicular to the solid-liquid interface is built up which inhibits the formation of the scattering layer. This can be avoided by melting small spheres only. Then convection does not set in and the temperature in the liquid is homogeneous. The diameter of the sphere, however, may not be chosen below 1.5 mm because laser light reflected at the thermistor disturbs the measurements in two ways: (i) the reflected light mixes with the scattered light and thus leads to a heterodyne component, (ii) the thermistor is heated by the laser beam. This leads to an increased temperature gradient in the melt. Thermal convection sets in.

The linewidth of the scattering light is measured by photon correlation spectroscopy. The autocorrelation function $G(\tau)$ can be fitted by a single exponential: $G(\tau) = A + Be^{-2\Gamma\tau}$ (Fig. 2). The linewidth is extracted by a cumulant analysis. The diffusion constant is then calculated by $D_i = \Gamma / q^2$. In various experiments diffusion constants D_i were measured: $5 \times 10^{-9} < D_i < 2 \times 10^{-8}$ cm²/s. During a single experiment, the value of D_i is constant within ±8% (Figs. 3 and 4). A typical value in our experiments is $D_i = 8 \times 10^{-9}$ cm²/s. The scatter of D_i in various experiments is due to a change in the scattering geometry: The laser beam has to be adjusted for every experiment. This changes the scattering geometry and thus the value of the scattering vector q. Furthermore, the amount of light reflected by the thermistor changes. It mixes with the scattered light from the solid-liquid interface and thus leads to heterodyne light scattering. In this case, the au-

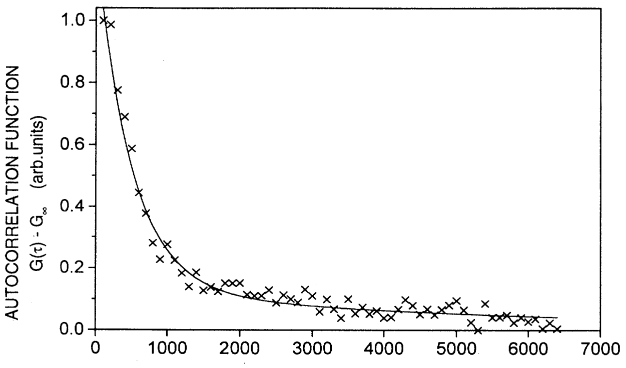

FIG. 2. Autocorrelation function. The crosses (×) are measured data; the solid line is an exponential fit, which leads to a linewidth $\Gamma = 970$ s^{-1}. The scattering angle was $\theta = 90°$, the wavelength $\lambda = 488$ nm.

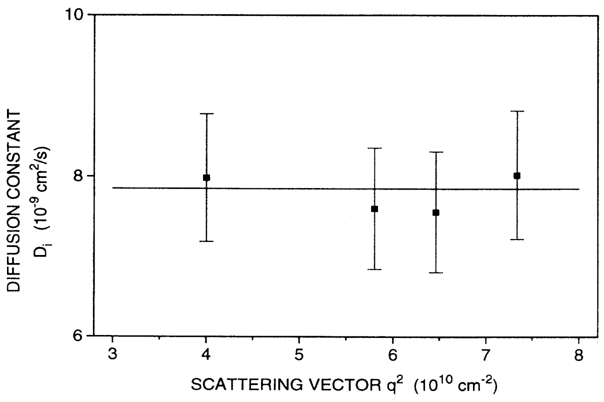

FIG. 4. Diffusion constant D_i vs the square of the scattering vector q. The data (■) are from the same experiment as in Fig. 3. The solid line corresponds to the slope of the linear fit in Fig. 3. D_i does not depend on the scattering vector q.

tocorrelation function decays according to $G(\tau)=A+Be^{-\Gamma\tau}$. This leads to an increase in the calculated diffusion constant D_i by a factor of 2.

In spherical inward growth experiments the growth velocity v_G has been varied from $0.05<v_G<1$ μm/s. Within the experimental uncertainty of D_i, the diffusion constant does not depend on growth velocity. No systematic trend has been found. It even does not change when crystal growth is reversed to melting.

Varying the wavelength of the incoming light, we change the scattering vector q. This can be done within a single experiment without changing the geometric arrangement of the experiment and the thermal conditions in the liquid sphere. We find $\Gamma \propto q^2$ (Fig. 3). The origin has not been used to fit the data. This confirms $\Gamma \propto q^2$. The proportionality D_i changes from experiment to experiment as mentioned above. A more stringent test for $\Gamma \propto q^2$ is the plot of Γ/q^2 for one experiment versus q^2 shown in Fig. 4.

Best signal-to-noise ratios are obtained at the interfaces of slowly growing spheres ($v_G \approx 0.1$ μm/s). After melting the initial liquid phase, the thermistor is heated with a lower heating power. The crystal grows until a new smaller steady-state radius is reached. Using this procedure, anomalous light scattering can be observed for hours. As the solid-liquid interface is stationary, long experimental times can be used to measure the correlation function. During inward growth, the experimental time is reduced to about 30 s, depending on the growth velocity.

The sphere can be illuminated at the upper part, at the lower part, or in between (Fig. 1). No change in the diffusion constant has been measured.

The measured diffusion constant is independent of the intensity of the incident light. Most experiments have been performed using an intensity of 200 mW.

IV. DISCUSSION

The Bridgman growth experiments show that there are no or not enough impurities accumulated at the solid-liquid interface to exhibit Rayleigh scattering, even after long growth times. During freezing a nucleation process seems to take place: a layer, which gives rise to the anomalous light scattering, is formed at the solid-liquid interface. The scattering layer can be destroyed either because of thermal gradients normal to the interface or because of thermal convective flow. This happens during Bridgman growth and during spherical inward growth of large liquid spheres. Once nucleated, the layer persists even if the crystal is slowly melted.

Choosing a scattering vector **q**, we investigate the cor-

TABLE I. Properties of solid xenon.

Solid				
Molar weight	M_m	131.30	g/mol	
Triple-point temperature	T_t	161.3897	K	a
Triple-point pressure	p_t	0.816901	bar	b
Triple-point molar volume	$V_m(s)$	38.59	cm^3/mol	c
Heat of fusion	L	2299	J/mol	d
Melting entropy	ΔS_m	14.24	J/mol K	
Jackson α factor $\alpha_{\text{Jackson}}=\Delta S_m/N_A k_B$	α_{Jackson}	1.71		i
Specific heat	$c_p(s)$	36.0	J/mol K	d
Thermal conductivity	λ_s	4.76×10^{-3}	W/cm K	e
Thermal diffusivity	α_s	4.96×10^{-3}	cm^2/s	
Solid-liquid interfacial free energy	γ_{SL}	1.073×10^{-6}	J/cm^2	Estimation according to f
Self-diffusion coefficient	D_s	6.62×10^{-10}	cm^2/s	At $T=160$ K[g]
Refractive index	n_s	1.4560		At T_t and 480.6 nm[h]

[a] R. E. Bedford, G. Bonnier, H. Maas, and F. Pavese, Metrologia **20**, 145 (1984).

[b] J. Ancsin, Metrologia **14**, 45 (1978).

[c] *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, New York, 1977).

[d] *Selected Values of the Thermodynamic Properties of the Elements* (American Society of Metals, Metals Park, OH, 1973).

[e] *Thermophysical Properties of Matter,* TPRC Data Series Vol. 3 (IFI/Plenum, New York, 1970).

[f] J. H. Hollomon and D. Turnbull, in *Progress in Metal Physics,* edited by B. Chalmers (Pergamon, London, 1953), Vol. IV, p. 357.

[g] W. M. Yen and R. E. Norberg, Phys. Rev. **131**, 269 (1963).

[h] A. C. Sinnock and B. L. Smith, Phys. Rev. **181**, 1297 (1969).

[i] Materials with $\alpha<2$ are usually not faceting in contact with the melt.

TABLE II. Properties of liquid xenon.

Liquid				
Triple-point molar volume	$V_m(l)$	44.31	$\mathrm{cm}^3/\mathrm{mol}$	a
Specific heat	$c_p(l)$	44.6	J/mol K	b
Thermal conductivity	λ_l	0.734×10^{-3}	W/cm K	c
Thermal diffusivity	α_l	7.29×10^{-4}	cm^2/s	
Self-diffusion coefficient	D_s	3.9×10^{-5}	cm^2/s	At T_t [d]
Dynamic shear viscosity	η	5.72×10^{-4}	$\mathrm{N\,s\,m}^{-2}$	At T_t [e]
Refractive index	n_l	1.3957		At T_t and 480.6 nm[f]

[a] *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, New York, 1977).

[b] *Selected Values of the Thermodynamic Properties of the Elements* (American Society of Metals, Metals Park, OH, 1973).

[c] *Thermophysical Properties of Matter,* TPRC Data Series Vol. 3 (IFI/Plenum, New York, 1970).

[d] W. M. Yen and R. E. Norberg, Phys. Rev. **131**, 269 (1963).

[e] P. Malbrunot, A. Boyer, E. Charles, and H. Abachi, Phys. Rev. A **27**, 1523 (1983).

[f] A. C. Sinnock and B. L. Smith, Phys. Rev. **181**, 1297 (1969).

responding Fourier component $F(\mathbf{q})$ of the scattering density. The single exponential decay of the autocorrelation function implies that the decay of the amplitude of this Fourier component can be described by a relaxation process with a single decay rate. $\Gamma\propto q^2$ is compatible with the description of the dynamics in the scattering layer by a diffusion process with a diffusion constant $D_i=\Gamma/q^2$. D_i is of the order of 8×10^{-9} cm^2/s in our experiment. This value is 5 orders of magnitude smaller than the thermal diffusivity and four orders of magnitude smaller than the self-diffusion coefficient in liquid xenon (see Tables I and II).

A similar behavior has been observed in the experiments at the solid-liquid interfaces of water, salol, and cyclohexane.[5,7,8] Assuming that static and dynamic light-scattering experiments probe the same structures, both types of experiments have been performed with cyclohexane.[8] Using the correlation length ξ deduced from static light scattering and the diffusion constant D_i measured in dynamic light-scattering experiments, we calculated the viscosity η in the interface layer from the Stokes-Einstein-Kawasaki relation $D_i=k_BT/6\pi\eta\xi$.[12] Surprisingly this viscosity turned out to be the same as the bulk-liquid value.

As a working hypothesis we use this result and calculate the correlation length in the interface layer of xenon from the measured diffusion constant and the viscosity of the bulk liquid of xenon using the Stokes-Einstein-Kawasaki relation. We obtain a correlation length $\xi=260$ nm. It is very astonishing that this correlation length is similar to the correlation lengths measured in the solid-liquid interfaces of water, salol, and cyclohexane (Table III). Although the diffusion constant $D_i(\mathrm{Xe})$ of xenon is larger than the diffusion constant $D_i(\mathrm{salol})$ of salol

TABLE III. Properties of the mesophase layer for various materials.

Scattering layer		Ice[a,b,c]	Salol[d]	Cyclohexane[e]	Xenon
Diffusion constant D_i	$\times10^{-9}$ cm^2/s	$14<D<57$	1.0 ± 0.25	6	8
Triple-point temperature T_t	K	273.15	314.75	279.70	161.39
Molar weight M_m	g/mol	18.01	214.22	84.16	131.30
Dynamic shear viscosity η at T_t	$\mathrm{N\,s\,m}^{-2}$	1.798×10^{-3}	8.4×10^{-3}	1.26×10^{-3}	5.72×10^{-4}
Critical velocity v_{crit}	$\mu\mathrm{m/s}$	1.5	$0.2<v<0.8$[f]	0.4[g]	[g]
Correlation length ξ[h]	nm	20–80	275	270	260

[a] H. Güttinger, J. H. Bilgram, and W. Känzig, J. Phys. Chem. Solids **40**, 55 (1979).

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

[c] P. U. Halter, J. H. Bilgram, and W. Känzig, J. Chem. Phys. **89**, 2622 (1988).

[d] U. Dürig, J.H. Bilgram, and W. Känzig, Phys. Rev. A **30**, 946 (1984).

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

[f] Along the [010] axis.

[g] No v_{crit} observed for spherical inward growth.

[h] From dynamic light-scattering experiments, using the Stokes-Einstein-Kawasaki relation.

by a factor of 8, the difference of the correlation lengths is only about 6%. Thus for substances with different lattice structures, lattice constants, different velocities at triple-point temperature, for faceting or nonfaceting materials, the correlation length in the interface is of the same order of magnitude, namely $\xi \approx 250$ nm. The anomalously scattering layer has a thickness of a few μm.[5,7,8]

There is only one correlation length and only one relaxation process active in our experiment. If there would be a distribution of ξ, then inhomogeneities with a long correlation length would dominate forward scattering and thus lead to an apparent dependence of D_i on q and to a deviation of $\Gamma \propto q^2$. This has not been found in our experiments (Figs. 3 and 4). Extensive measurements with polydisperse samples to test the deviation of $\Gamma \propto q^2$ have been performed by Steininger.[8]

All these observations are compatible with the mesophase layer model: A macroscopic layer of preordered material is formed at the solid-liquid interface during freezing. (A detailed discussion of various models can be found in Ref. 8.) This layer is characterized by fluctuations in the index of refraction. These fluctuations have a typical spatial extension of ξ. We interpret these regions of high and low index of refraction as regions which are more crystal-like or more liquidlike. The dynamical formation of a metastable phase has been studied by Löwen *et al.*[1,2] The correlation length within this metastable layer is between the correlation length of the solid $\xi_{\text{solid}} = \infty$ and the one of the liquid $\xi_{\text{liquid}} \approx$ few atomic spacings. The dynamical processes in the layer are typically 5 orders of magnitude slower than thermal fluctuations in the liquid.

A second means to determine the correlation length is static light scattering, which has been performed in the cyclohexane experiments.[8] The intensity of the scattered light as a function of the scattering angle can be fitted by an Ornstein-Zernike or by a Debye-Bueche correlation function $\gamma(r)$. The correlation lengths deduced from these measurements are in agreement with the correlation length measured in dynamic light scattering. It is therefore reasonable to use the viscosity of bulk liquid for the evaluation of ξ from the Stokes-Einstein-Kawasaki formula.

V. CONCLUSIONS

Anomalous light scattering at the solid-liquid interface of xenon can be attributed to light scattered at continuous fluctuations in a mesophase layer of preordered material which is formed at the solid-liquid interface during crystallization. The dynamical processes within the mesophase layer can be described as a random walk process characterized by a diffusion constant $D_i = 8 \times 10^{-9}$ cm^2/s. Thermal fluctuations in bulk liquid cannot be accounted for being the origin of the observed light scattering.

The fluctuations in the layer are characterized by a correlation length of $\xi = 260$ nm. Comparing this result with measurements on salol and cyclohexane, we find that anomalous light scattering seems to be a general phenomenon during freezing and melting and that a correlation length $\xi \approx 260$ nm is typical for the scattering layer, independent of viscosity of the bulk melt and of the triple-point temperature.

It is mandatory to prevent thermal convection in the liquid to observe high intensities of anomalously scattered light. This can be achieved by performing the experiment at the surface of a little sphere melted inside of a single crystal. This technique also prevents the melt from becoming contaminated.

Onset times found in earlier experiments with other interfacial geometries have to be attributed to convective instabilities. We showed that the data measured at various substances are in agreement with the mesosphere layer model: scatterers, which are small compared to the wavelength of light, are weakly bound to aggregates of molecules or atoms. The formation and decay of such aggregates give rise to fluctuations in the index of refraction. These fluctuations can be detected by dynamic light scattering.

We conclude that crystallization is a two-step process: a mesophase is formed at the liquid side of the solid-liquid interface. The crystal grows into this mesophase. The mesophase is an intermediate stage of the crystallization process, where the molecules are preordered.

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[3] E. Burke, J. Q. Broughton, and G. H. Gilmer, J. Chem. Phys. **89**, 1030 (1988).

[4] J. H. Bilgram, H. Güttinger, and W. Känzig, Phys. Rev. Lett. **40**, 1394 (1978).

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[7] U. Dürig, J. H. Bilgram, and W. Känzig, Phys. Rev. A **30**, 946 (1984).

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

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[12] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970).