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FREEZING TRANSITION PHENOMENA FAR FROM EQUILIBRIUM

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Abstract

The freezing transition of H_2O and salol has been studied in experiments where the solid-liquid interface is continuously driven into the melt. The dynamics of entropy fluctuations in a layer between the crystal and the melt are for H_2O about 5 orders of magnitude slower than in the bulk melt (for salol 6 orders of magnitude). Solidification rates are calculated, based on the Wilson-Frenkel model. They are determined by the same processes as the dynamics of entropy fluctuations in the interface layer. Decay rates of these fluctuations have been calculated using experimentally determined solidification rates. The calculated values agree with those determined in light-scattering experiments within the accuracy of the experiments.

1. Introduction

At conditions far from equilibrium, there exist states of matter, which do not exist at equilibrium conditions. In a light-scattering experiment we study the dynamics of density fluctuations at the solid-liquid interface of a growing crystal. We have found evidence for a layer of a mesophase in front of a growing ice crystal [1]. This interface layer has a thickness of a few micrometers and does not exist at equilibrium conditions. Experiments performed at the solid-liquid interface of salol lead to similar results. Therefore we assume, that the occurrence of a layer at the solid-liquid interface is not an anomaly of water, but a property of the freezing transition. During freezing it is necessary to extract latent heat from the interface region, where the phase transition takes place. Therefore the kinetics of freezing can be studied at non-equilibrium conditions only. This is different from critical phenomena.

In the first part of this paper the results of a light-scattering experiment at the solid-liquid interface are summarized. In a second part these results are used to calculate macroscopic growth rates of crystals on the basis of the Wilson-Frenkel model for crystal growth. These growth rates are in agreement with experimental values of directional solidification and lead to a scaling law for free solidification.

2. The Light Scattering Experiments

2.1. The Samples

In light-scattering experiments it is very important to reduce background light scattering from impurities. We produce our pure substances and our single crystals by zone refining. To prevent contamination of the melt we do our light-scattering experiments *in situ* during zone refining. For details see [2].

The solid-liquid interface is illuminated by a laser beam. The light scattered from bulk water is Brillouin or Raman scattered light. Rayleigh-scattered light can be neglected in H_2O due to the $4^{\circ}C$ density maximum. From bulk ice the intensity of Raman scattered light is dominant.

All our experiments have been done with single crystals. The melt far away from the interface has a temperature above the melting point and the latent heat is transported away from the solid-liquid interface through the crystal (positive temperature gradient in front of the interface).

2.2. Intensity Measurements

A crystal surface, which is in equilibrium with the melt, does not scatter light. The crystal grows at low growth rates by a lateral mechanism at faceted surfaces, or it grows normal to its surface if the surface is rough. During lateral growth there move steps across the interface. Their velocity has been measured at the solid-liquid interface of salol. The typical step velocity is $60 \mu m/s$. This is much higher than the average growth rate of the crystal which is typically $0.5 \mu m/s$ [3].

If the growth rate exceeds a critical value v_{crit} we

observe an onset of strong light scattering at the solid-liquid interface. After about half an hour a steady state is reached with a stationary scattering intensity. This intensity does not vanish if the growth rate is reduced below v_{crit} . It vanishes if the surface of the crystal is melted. After melting the surface it is necessary that the growth rate exceeds v_{crit} , for a re-initiation of light scattering (Hysteresis). A typical value of v_{crit} is 1.5 $\mu\text{m/s}$ for ice. It is increasing with increasing thermal gradients at the interface. The onset of the nonequilibrium steady state at the interface is also dependent on the way in which the state is reached [3]. This dependence on the history is typical for non-equilibrium experiments. In the light scattering experiments discussed below only the non-equilibrium steady state will be discussed. The data presented are mainly based on the measurements on the ice-water system. A discussion of the transient state which leads to this steady-state is beyond the scope of this paper.

Measurements of the intensity of the scattered light as a function of the scattering angle show, that the light is scattered isotropically in the space. The inhomogeneities which scatter the light act like Hertzian dipoles. This means, that the diameter of the inhomogeneities is smaller than the wavelength of the light. Three models have been discussed, which might lead to this scattering:

- a) a corrugated interface
- b) inhomogeneities in the melt in front of the interface
- c) the nucleation of a homogeneous phase at the surface of the growing crystal with properties different from those of the melt or of the crystal.

It is possible to calculate for these three models the intensities I of the light scattered under an angle of e.g. 90° , as a function of the angle of incidence Ψ_0 of the illuminating laser beam on the crystal surface [4]. For the case of ice, the solid has a lower index of refraction than the liquid. Therefore the light is reflected totally at the solid-liquid interface for $\Psi_0 > \Psi_{crit}$

Model a) leads to a maximum of the intensity at $\Psi_0 = \Psi_{\text{crit}}$

$$I(\Psi_0 = \Psi_{\text{crit}}) = 4 \cdot I(\Psi_0 \ll \Psi_{\text{crit}}); I(\Psi_0 = 90^\circ) = 0. \quad (1)$$

In model b) the light crosses the scattering volume twice if it is totally reflected

$$I(\Psi_0 > \Psi_{\text{crit}}) = 2 I(\Psi_0 < \Psi_{\text{crit}}) \quad (2)$$

Model c) is a layered structure and higher intensities than for model b) are expected.

In the measurements we detect high scattered intensities for $\Psi_0 > \Psi_{\text{crit}}$

$$I(\Psi_0 > \Psi_{\text{crit}}) \approx 4 I(\Psi_0 \ll \Psi_{\text{crit}}) \quad (3)$$

this rules out model b).

2.3. The Line Width Measurements

The line width of the quasi-elaistically scattered light is proportional to the square of the scattering vector k . That means: the decay of the density fluctuations can be described by a diffusion law. The diffusion constant in the interface layer is for ice $D_i(\text{ice}) \approx 3 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and for salol $D_i(\text{salol}) \approx 10^{-9} \text{ cm}^2/\text{s}$. By choosing the scattering geometry we can define scattering vectors parallel to the interface or perpendicular to the interface. We measure the same decay rates for both orientations. That means: the diffusion constant D_i is isotropic in space.

For a corrugated interface a scattering vector perpendicular to the interface does not exist. Only the projection on the interface is effective. Therefore the line-width measurements rule out model a). As the intensity measurements rule out model b) we conclude that there is a layer of homogeneous material in-between the crystal and the melt. The diffusion constant D_i is much smaller than the thermal diffusivity $\alpha \approx 10^{-3} \text{ cm}^2/\text{s}$ or the constant of self diffusion $D_s(\text{water}) \approx 10^{-5} \text{ cm}^2/\text{s}$.

It is difficult to decide what is diffusing in the interface layer. Probabely the expression "structure diffusion", which has been coined by J. Frenkel [5], describes best the quantity we are measuring.

3. Crystallization Rates

Figure 1 shows schematically the density in the region of a solid-liquid interface at conditions far from equilibrium and close to equilibrium. For H_2O the interface layer is a few micrometers thick [6]. The crystal grows into the interface layer and not into the bulk melt. For the calculation of the crystallization rates we use an equation, which has been proposed first by Wilson and later by Frenkel [7]. It is based on a simple rate theory where the number of the molecules, which are adsorbed at the crystal surface, is compared with the number of the molecules, which dissociate away from the crystal surface. The net flow of molecules to the interface is proportional to the growth

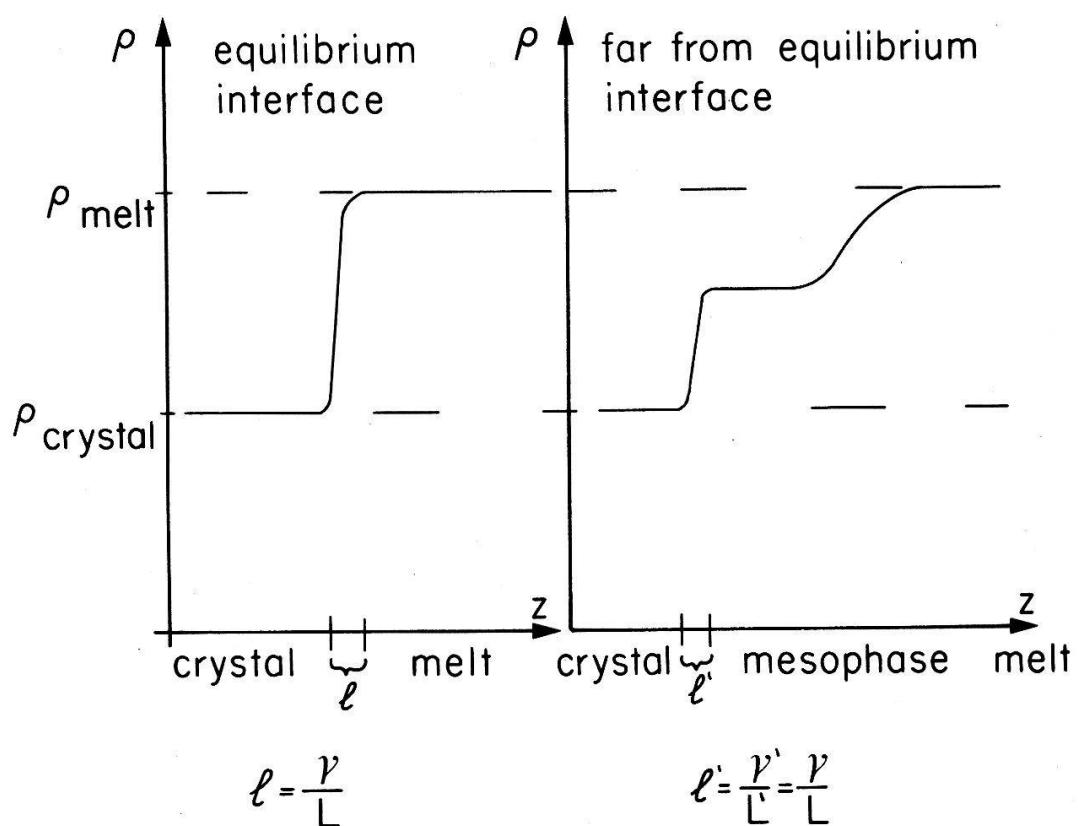


Figure 1. The density ρ in the region between the crystal and the bulk melt is plotted schematically for the case $\rho_L > \rho_s$.

rate v . For small supercooling one obtains:

$$v = D S \Delta T (\lambda T_E)^{-1} \quad (4)$$

S is the entropy of melting and ΔT is the supercooling at the interface. T_E is the equilibrium melting temperature. D is the diffusion coefficient of the quantity, which has to be transported through the interface with the thickness λ .

This diffusing quantity is "structure" as structure changes during freezing. Therefore we use in eq. 4 the constant of structure diffusion D_i . For freezing of water $S/k_B = 2.65$ where k_B is the Boltzmann constant. The molecules in the interface layer are to a higher degree polymerized than in the bulk melt. Therefore the entropy S_i of the transition of the material in the interface layer to the crystal is smaller than S . We set $S_i/k_B \approx 1$. For the thickness λ of the region, where the material properties change from crystal to mesophase properties, we use the quotient of the interfacial energy γ_i and the latent heat L_i . The solid-liquid interfacial energy γ is roughly proportional to the latent heat of melting L [8], γ/L does not depend on substance. We assume that γ_i/L_i of the interface crystal-interface layer is the same as γ/L of the interface crystal-bulk melt at equilibrium conditions. We use γ/L as the thickness of the phase boundary λ . The order of magnitude for λ is a few Angstroms. Inserting this into eq. 4 we obtain for the growth rate of the crystal which grows with a planar surface

$$v = D_i \frac{L}{\gamma} \frac{\Delta T}{T_E} . \quad (5)$$

This is exactly the same formula, which we have deduced from free-energy considerations and from dimensional analysis [2,9]. There exist two ways to determine D_i : from light-scattering experiments and from measurements of solidification rates (eq. 5). For a comparison of the results see Table 1.

During free growth, the crystal has a curved surface. Transport of latent heat away from the tip of a dendrite is easier than the transport away from a plane surface. The tip of a

		ICE	SALOL
S	$J/cm^3 K$	1.1	0.324
L/c_p	K	80	60
α (liquid)	cm^2/s	$1.3 \cdot 10^{-3}$	$0.9 \cdot 10^{-3}$
γ	J/cm^2	$2.9 \cdot 10^{-6}$	$2 \cdot 10^{-6}$
$\mu = v/\Delta T$	$cm/s \cdot K$	10^{-2}	$2.3 \cdot 10^{-4}$ 10^{-4}
D_i from eq. 5	cm^2/s	$2.6 \cdot 10^{-8}$	$1.5 \cdot 10^{-9}$ $6.5 \cdot 10^{-10}$
light scattering experiment D_i	cm^2/s	$3 \cdot 10^{-8}$	$\sim 10^{-9}$

Table 1. Values of material properties employed in the discussion of the growth rates.

References to these data are given in [12].

crystal is always in a cooler medium during the growth into supercooled melt, than the crystal regions behind it. The faster a tip grows the further it reaches into the supercooled melt and the more it is accelerated relative to other crystal regions or relative to a plane surface.

Based on the assumption that heat transport only is rate limiting for freezing, growth rates of dendrites growing freely into supercooled melt have been calculated numerically [10]. It has been shown by Glicksman that the hypothesis of maximum growth velocity is incorrect [11]. Therefore calculations of free growth rates are still an unsolved problem.

In this paper we do not try to calculate the growth rates of dendrites on the basis of heat-flow considerations. We

assume that the mechanism which determines the tip velocity is the same as the one which determines the growth of planar crystals [12]. Therefore we start with eq. 5 which we transform to dimensionless variables:

$$\tilde{v} \equiv \frac{v}{2\alpha/d_o} = \frac{D_i}{2\alpha} \frac{\Delta T}{L/c_p} \quad (6)$$

where α is the thermal diffusivity of the melt, d_o is the capillarity $d_o = (\gamma/L)(c_p/S)$ and c_p is the heat capacity of the melt. We do not know ΔT at the surface of the crystal tip. Therefore we replace in eq. 6 ΔT by $F \cdot (T_m - T_\infty)$ where T_m is the melting temperature of the crystal and T_∞ is the temperature of the melt far away from the crystal. F is an unknown func-

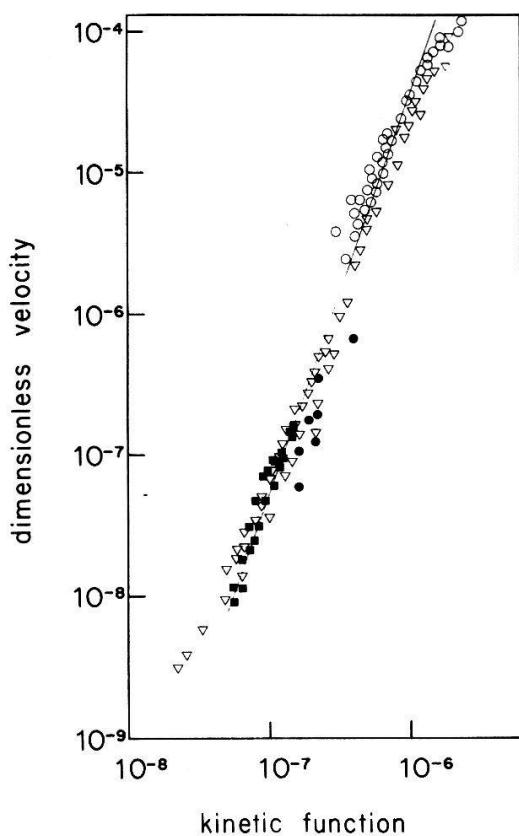


Figure 2. Dimensionless growth rates $\tilde{v} = v(\alpha/d_o)^{-1}$ are plotted versus the kinetic function $(D_i/\alpha)(T_m - T_\infty)(L/c_p)^{-1}$ for ice dendrites (open symbols) and salol crystals (full symbols). The slope of the drawn line is $a=2.8$. The proportionality constant is $F \approx 3 \cdot 10^4$.

tion. It may depend on the material, the growth rate, the supercooling of the melt etc. Based on experiments we assume that the acceleration of a crystal tip relative to growth rates of planar crystals can be described by a power law. We make the ansatz:

$$\tilde{v}_{\text{tip}} = \left(F \frac{D_i}{2\alpha} \frac{(T_m - T_\infty)}{L/c_p} \right)^a \quad (7)$$

where F is an unknown function.

In Figure 2 the dimensionless growth rates \tilde{v} of ice and salol (12) are plotted as a function of $(D_i/2\alpha)(T_m - T_\infty) \cdot (L/c_p)^{-1}$, a quantity which we know from eq. 6. This quantity determines the kinetics of freezing and we call it the kinetic function of crystal growth. From Figure 2 we can determine $a = 2.8$. This power law is well known from crystal-growth experiments. We can also determine F , and we find that $F \approx 3 \cdot 10^4$ is a constant and does not depend on growth rate or material. F has been determined for ice and salol only. Whether F is indeed a quantity which is independent of substance has to be confirmed by experiments with other materials.

4. Conclusions

A layer is formed in between a growing crystal and the melt. The molecules in this layer are ordered to a higher degree than in the bulk of the melt. This phase does not exist under equilibrium conditions. There are continuous flows into and out of this interface layer. Melt is flowing in, crystalline material and latent heat are flowing out. Such an open system can be influenced much more by noise than an equilibrium system. Therefore we observe fluctuations which are not visible at a solid-liquid interface at equilibrium conditions.

Fluctuations in the degree of order are entropy fluctuations. Light, which is scattered at these fluctuations, provides information about the dynamics of aggregation and thus about the processes which take place during freezing. This is the reason why light-scattering experiments can provide the diffusion con-

stant which is necessary for the calculation of growth rates of crystals on the basis of the Wilson-Frenkel model. There have been other attempts to calculate solidification rates on the basis of the Wilson-Frenkel model. In the approach presented in the present paper, the constant of "structure diffusion" D_i is used. D_i and the melting temperature T_E are the only material-specific quantities, which are necessary to calculate solidification rates with eq. 5, and both quantities can be measured.

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