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Non-isothermal nucleation in strongly supercooled liquids*

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In a strongly supercooled liquid at a temperature below the unit supercooling, a solid nucleus may grow such that the latent heat of freezing stays essentially within the nucleus. The temperature in the nucleus is then higher than in the surrounding liquid. We investigate the possibility that nucleation there may occur nonisothermally. We conclude that this is generally not the case.

KEYWORDS: nucleation, crystal growth, numerical simulation, nonisothermal nucleation

1. Introduction

The formation of a solid nucleus in a supercooled liquid is associated with the production of latent heat and its diffusion into the surrounding liquid. It has been suggested that the nucleation process[1] for supercoolings below the unit supercooling L/C_p (this situation is sometimes called "hypercooling") is adiabatic rather than isothermal[2], where L is the latent heat and C_p the specific heat of the liquid. Although the nucleus growth at the late stage is well understood[3], a possible nonisothermal behavior at earlier stages where the nucleus has a small size has not been studied so far from the dynamical point of view. There remains the question whether the critical nucleus remains isothermal during the nucleation process. Obviously, it would depend upon the relation between the rate at which the latent heat produced during nucleation diffuses away, and the rate at which the nucleus is formed.

In order to simulate the temporal evolution of nucleus size and temperature we introduce a simple model[4] that accounts for a random driving force, in addition to the deterministic driving force, for crystalline growth, and that describes the nucleation phenomena with heat production and diffusion. Using the standard technique of computer simulations, as well as an analytical solution, we investigate with this model the competition between nucleus growth and heat diffusion, and the relation to the critical size of the nucleus.

2. Model

In our model, we assume the nucleus to be a sphere of time-dependent radius $R(t)$. In this case, the temperature distribution has a spherical symmetry and can be written as $T(t, r)$. Nucleation means then that, by virtue of the random driving force, $R(t)$ exceeds a critical value

$$R_c = 2\gamma_I T_M / L(T_M - T_I), \quad (1)$$

where T_M is the melting temperature, $T_I = T(t, R(t))$ the temperature at the solid-liquid interface and γ_I the interface energy. We consider the following coupled sys-

tem for $R(t)$ and $T(t, r)$:

$$\frac{dR}{dt} = \alpha \left(\frac{1}{R_c} - \frac{1}{R} \right) + \frac{\epsilon}{R} \eta(t), \quad (2)$$

$$\frac{L}{C_p} \frac{dR}{dt} = D \left(\frac{\partial T}{\partial r} \Big|_{r=R-0} - \left(\frac{\partial T}{\partial r} \Big|_{r=R+0} \right) \right), \quad (3)$$

$$\frac{\partial T}{\partial t} = D \nabla^2 T. \quad (4)$$

The first term on the right-hand-side of (2) treats the Bibbs-Thomson effect of the surface free energy. If the radius R is smaller than R_c , then the evaporation process dominates the growth process and vice versa. The parameter α characterizes the growth kinetics. The second term on the right-hand-side of (2) simulates the effect of thermal fluctuations; $\eta(t)$ is the random size fluctuation obeying $\langle \eta(t)\eta(t') \rangle = 2\delta(t-t')$ and ϵ denotes the strength of the random force. Eqs.(3) and (4) represent the heat production and diffusion, which are similar to those encountered in the theory of dendritic growth[5, 6]. Here L is the latent heat and D the thermal diffusivity. The boundary condition at the interface here is, however, not given by $T_I = T_M$ but by (2) and (3). Equations (2)-(4) together with the boundary condition $T(t, \infty) = T_0$ at infinite radius (and $R(t) > 1$ atomic distance forced by the numerical code) offer the complete set of equations determining $R(t)$ and $T(t, r)$.

In our detailed calculations we have approximated the solid nucleus temperature by its spatial average. Hence the temperature inside the solid is equal to T_I everywhere: The temperature gradient at the interface evaluated from the solid side, $\partial T / \partial r|_{r=R-0}$, in (3) is related to the heat flux into the solid at the boundary and, in this case, should be replaced by $(R/3D)dT_I/dt$. The meaning of this term is clear if one multiplies $4\pi R^2$ in both sides of (3). That is, this equation indicates the relation between the heat production due to the volume change and the shift of the temperature throughout the solid.

The present model is essentially one-dimensional in space because all the quantities depend only on radius r and time t . We use the coordinate frames illustrated in Fig.1; one is the rest frame whose origin is fixed at the center of the nucleus and the other is the moving

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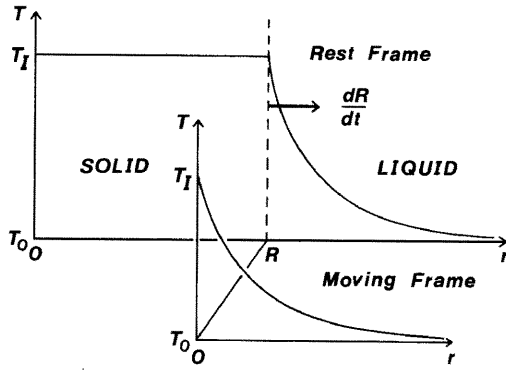


Figure 1. The rest coordinate and the moving coordinate frames. It is tractable to use the latter coordinate in order to solve the diffusion equation. The temperature profile is schematically shown in both coordinate frames.

frame whose origin is located at the moving front of the nucleus. It is more convenient to introduce the latter frame in order to solve the diffusion equation with the mobile boundary. Using this frame, we rewrite the diffusion equation (4) as

$$\frac{\partial T}{\partial t} = D \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{[R(t) + r]} \frac{\partial T}{\partial r} \right) + \frac{\partial R}{\partial t} \frac{\partial T}{\partial r}. \quad (5)$$

We solve this equation analytically in the stationary regime. Numerically we discretize both r and t using an explicit method[7]. The time-derivative dR/dt reads $[R(t) - R(t - \Delta t)]/\Delta t$. At each time step, the solution of the diffusion equation is compared with the two boundary conditions (2) and (3) in order to determine $R(t)$ and T_I .

3. Results

We first derive an analytical result for the stationary regime at the late stage of nucleation. The nucleus size in this regime is so large that we may drop the terms proportional to $1/R$ in (2). Then the growth velocity dR/dt becomes α/R_c and, from (3), the temperature gradient at the interface is identified as $(\partial T/\partial r)_{r=R+0} = -L\beta/C_p$, where we put $\beta = \alpha/DR_c$. We fix the supercooling temperature at $T_0 = T(\infty, t)$. We subtract then T_0 from all temperatures. The stationary solution of the diffusion equation (5) which satisfies the desired boundary conditions is obtained as

$$T(R+r) - T_0 = \frac{L}{C_p} \beta R^2 \left\{ \frac{e^{-\beta r}}{R+r} + \beta e^{\beta r} \text{Ei}[-\beta(R+r)] \right\}, \quad (6)$$

where $\text{Ei}[-x]$ is the exponential integral. Thus the interface temperature T_I should approach its stationary value given by

$$T_I - T_0 = \frac{L}{C_p} \beta R \left\{ 1 + \beta R e^{\beta R} \text{Ei}[-\beta R] \right\}$$

$$\sim \frac{L}{C_p} \sum_{n=0}^{\infty} (-1)^n \frac{n!}{(\beta R)^n}. \quad (7)$$

If the value of β is not too small, then $T_I - T_0$ approaches the unit supercooling L/C_p . On the other hand, if β is equal to zero or very close to zero, then $T_I - T_0$ continues to take quite small values until R reaches the order of $1/\beta$. The important fact is that the parameter $\beta = \alpha/DR_c$ characterizes the speed of the solid phase formation relative to the speed of heat diffusion.

In the present model, there are three physical dimensions, i.e. temperature, space and time, and we choose these units so as to $L/C_p = 10\Delta r = 500D\Delta t = 1$, in the following. ($\Delta r =$ atomic scale $\sim 5 \times 10^{-8}$ cm.) Note that, under this choice, Eqs.(3) and (5) become nondimensional. Then four parameters are left: the dimensionless growth factor $A = \alpha/D$, the degree of supercoolings $T_M - T_0$, the capillarity length $\Gamma = 2T_M\gamma_I/(T_M - T_0)L$ and the dimensionless strength of the fluctuation $E = \epsilon/D$. Since our main interest lies in the situation of strong supercoolings, we fix the melting temperature at $T_M = 100 + T_0$.

At the initial state of nucleation where the nucleus repeats appearing and disappearing, the size fluctuation considerably affects the solid temperature T_I and the thermal fluctuation becomes large.

For large values of Γ and E , which correspond to slow nucleation in the fluctuation regime for large R_c , the evolution of the nucleus is sufficiently slow to keep the temperature close to the supercooling temperature T_0 . We show in Fig.2a the corresponding result of our simulation with the parameter set of $\Gamma = 5$, $E = 60$ and $A = 2$. In the figure, one may identify an initial stage at which the nucleus repeats to appear and disappear under large temperature fluctuations, and an intermediate stage at which the nucleus starts growing and T_I fluctuates around T_0 . The similar result can be obtained also for small dimensionless growth rate A . Fig.2b shows the case of $\Gamma = 1$, $E = 6$ and $A = 0.1$. This situation occurs in the case of very rapid diffusion. A qualitatively different behavior is observed in the case of small Γ and large A . Figure 2c represents the case of $\Gamma = 1$, $E = 6$ and $A = 2$. In this case, T_I starts growing simultaneously with R when R exceeds its critical value. This indicates a slight deviation from isothermal nucleation, but a real effect would require an order of magnitude bigger ratio $\beta \sim A/\Gamma$. Note, however, that the parameters of our model are not really independent.

4. Discussion

Nonisothermal or even adiabatic nucleation requires, that the time for the spreading of latent heat over a distance of nucleus-size is large compared to the time for nucleus-formation. The problem consists of a static part characterized by energy scales and a dynamic part characterized by time scales. In simple liquids on atomic length scales, all relevant energy ratios, i.e. T_M/γ_I , T_M/T_0 , γ_I/L and similar combinations, are typically of order unity[8]. Ignoring mass transport and density differences, the liquid-solid transformation requires lo-

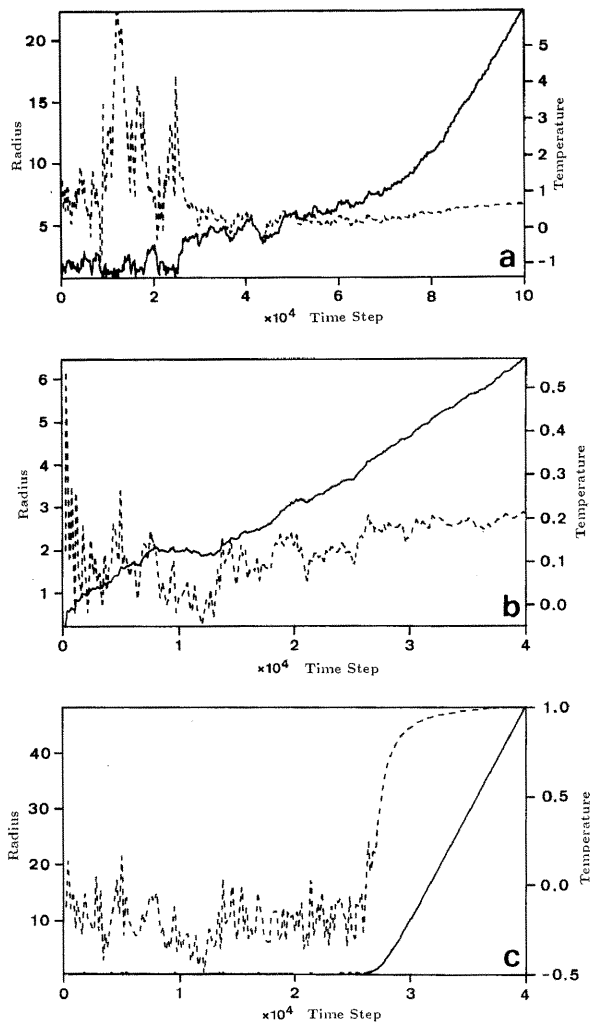


Figure 2. The time evolutions of the nucleus size R (solid line) and the interface temperature $T_I - T_0$ (dotted line). The parameters of the system are set, respectively, as (a) $\Gamma = 5$, $E = 60$ and $A = 2$, (b) $\Gamma = 1$, $E = 6$ and $A = 0.1$ and (c) $\Gamma = 1$, $E = 6$ and $A = 2$. The nucleation region does not show a trend for temperature increase. For the other details, see the text.

cal rearrangements of atoms as the fastest time scale, or “phonon excitation” in a different formulation. The competing heat transport also is mediated by the same “phonons”. Any other process like mass transport in

multicomponent systems or reordering of macromolecules slows down the time scale for the material order, while electronic contributions to thermal conductivity in metals speed up the heat transport. On atomic length scales, therefore, heat transport is not slower than material reordering. As mentioned in Section 3, therefore, our model parameters are not independent.

Combining the static and the dynamic argument, we conclude that, for a critical radius of atomic length, heat transport is not slower than material reordering; the nucleus is isothermal. (Note also, that on atomic scales the fluctuations of material order and temperature becomes independent.) For larger critical nuclei (less pronounced supercooling), the nucleation time increases exponentially[9] while the dissipation time of heat increases only quadratically with the nucleus size. This makes isothermal nucleation even more favorable. We conclude therefore, that isothermal nucleation theory should be applicable as long as the critical nucleus is not smaller than an atomic unit or as long as one is not inside the spinodal region.

- 1) In the discussion of nucleation growth, we assume here that the supercooling should not exceed the stability limit where spinodal decomposition takes place.
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- 7) W. F. Ames, *Nonlinear Partial Differential Equations in Engineering*, Vol.1, *Mathematics in Science and Engineering*, Vol.18-1 (Academic Press, New York, 1965) p.320.
- 8) In principle one may shift T_0 to the absolute zero, but then R_c becomes smaller than atomic scale. If L becomes very small, it becomes irrelevant as there is no superheating.
- 9) An explicit check for water and copper gives an exponential factor $e^{\Delta\epsilon/T}$ of order ~ 10 for a critical nucleus twice as big as a lattice constant in diameter, at supercooling temperature T_0 about $T_M/3$.