DYNAMICS OF FREEZING

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ABSTRACT

Different aspects of dynamics of freezing in a supercooled liquid are discussed with emphasis on recent theoretical developments. A unified description of the dynamics which pays proper attention to the local structure of the liquid is presented. The theory is a natural generalization of the recently developed order parameter theory of freezing and is based on a hydrodynamic description appropriate for the dynamics of liquid-solid transitions.

1. INTRODUCTION

FREEZING of a simple, one-component system is a first-order phase transition which is usually accompanied by a sizable change in volume and entropy. There are several features that are distinctive of this transition. First, it does not end in a critical point. Secondly, a pure liquid may be supercooled to a large degree without the appearance of the solid phase. This implies the existence of a large metastable region in the configuration space. Crystalline solid, on the other hand, can hardly be superheated. The asymmetry between freezing and melting is also manifested in the dynamics of these two transitions[1,2].

Dynamics of a first-order phase transition is usually divided into two parts. The first stage is the formation of a nucleus of critical size of the new phase. This is an activated process and can be quite slow for liquid → solid transitions. The activation energy of the critical nucleus can be expressed[3,4] in terms of the bulk properties of the two phases and in terms of the surface energy of the nucleus. The prefactor of the exponential term is not presently well understood.

The second stage of freezing is the growth of the critical nucleus to macroscopic dimensions. Excepting a transient period in the initial stage of growth, the second stage can be modelled as the growth of a large (on microscopic scale) crystallite into the supercooled melt. This process can be quite rapid and is usually controlled by the thermodynamic driving force (proportional to the degree of supercooling) and by the ability of the system to transport the latent heat of freezing away from the interface[5,6].

In this article we report some of the recent developments in the theory of the dynamics of freezing. We shall not review older work for which excellent reviews exist in the literature[6,7]. The main emphasis of this article is on understanding the dynamics of freezing from a microscopic basis and we shall mainly consider those theories that are molecular in nature.

Recent upsurge of interest in the theory of dynamics of freezing is partly motivated by the success of the order-parameter theory of freezing[8-10] to describe the equilibrium phase transition at least semi-quantitatively. In freezing/melting transitions the appropriate order parameters are the Fourier components of the density distribution evaluated at the reciprocal lattice vectors (RLV) of the solid. These order parameters are zero in the liquid and have non-zero constant values in the solid phase. These order-parameters can be related to the Debye-Waller factors[8] of the solid. The order parameter theory has been applied successfully to study freezing transition in various model systems[8-10] and in liquid sodium[8]. Recently this order-parameter theory (also known as the density functional theory (DFT)), has been applied to understand the stability of icosahedral crystals[11].

In order to generalize the equilibrium theory

of freezing to treat dynamics, we need to consider time-and/or space-dependent order parameters. There have been several attempts[12, 13] in the past in this direction, but these studies were not based on correct description of the statics. In this article we shall present a description of dynamics that is consistent with the static description of freezing.

The organization of the rest of this article is as follows. In §2, we discuss recent developments in the theory of nucleation. Section 3 contains a theoretical analysis of liquid instability and dynamics of freezing. In §4 we consider dynamics at the solid-liquid interface. Section 5 contains a brief discussion on crystal growth. Section 6 concludes with a discussion on the experimental aspect of dynamics of freezing.

2. NUCLEATION

Homogeneous nucleation can be defined[14] as the instability of the pure supercooled liquid against a finite amplitude, localized fluctuation that leads to the decay of the metastable liquid phase. Thus nucleation is an activated process. For low super-coolings the amplitude of the fluctuation necessary for decay of the metastable liquid may be quite large and the nucleating process involves passage over a large activation barrier. The nucleation process can, therefore, be slow and rate determining in the dynamics of freezing.

The conventional approach[14] towards nucleation employs the "capillarity approximation" which gives the excess free energy of a crystallite of radius R as sum of separate contributions from bulk and surface energies

$$\Delta G(R) = \frac{4}{3}\pi R^3 \Delta G_v + 4\pi R^2 \sigma_{SL},$$

where ΔG_v is the bulk free energy difference per unit volume between the solid and the liquid and σ_{SL} is the surface free energy of a planar solid-liquid interface. One obtains an expression for the critical Gibbs free energy by maximizing $\Delta G(R)$ with respect to R to obtain

$$\Delta G^* = 16\pi\sigma_{SL}^3/3(\Delta G_v)^2.$$

Next, one uses Eyring's[15] expression for the rate

of barrier crossing to obtain an expression for the nucleation rate.

The above phenomenological approach suffers from several drawbacks. First, the separation of ΔG into $(\Delta G)_{bulk}$ and $(\Delta G)_{surf}$ may not be justified for a small nucleus. Secondly, a good estimate of σ_{SL} is seldom available.

Recently Harrowell and Oxtoby[16] presented an interesting first principles theory of crystal nucleation from a supercooled melt. This theory was formulated by combining the order-parameter theory of freezing of Ramakrishnan and Yussouff[8] (R-Y) with a square gradient approximation[17] for the nonlocal dependence of free energy on density. Here we shall sketch the important steps. Firstly, the free energy associated with a coarse-grained local number density $\rho(\mathbf{r})$ is given by

$$\frac{F\{\rho\}}{k_B T} = \int d\mathbf{r}\, \rho(\mathbf{r})\left[ln\, \frac{\rho(\mathbf{r})}{\rho_l} - 1 \right]$$

$$-\frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2\, c(\mathbf{r}_1 - \mathbf{r}_2)$$

$$[\rho(\mathbf{r}_1) - \rho_l]\,[\rho(\mathbf{r}_2 - \rho_l)], \qquad (1)$$

where k_B is Boltzmann constant, T is the temperature, ρ_l is the density of the uniform liquid and $c(\mathbf{r})$ is the two-particle direct pair correlation function. The Fourier transform of the direct correlation function is related to the structure factor $S(q)$ through the relation

$$S(q) = \frac{1}{1 - c(q)}, \quad c(q) = \rho_l \int d\mathbf{r} c(r)\exp(-i\mathbf{q}\cdot\mathbf{r}).$$
$$(2)$$

By minimizing (1) with respect to $\rho(\mathbf{r})$, we get

$$\rho(\mathbf{r})/\rho_l = c'\exp[\int d\mathbf{r}'\, c(r - r')\,[\rho(r') - \rho_l], \quad (3)$$

where c' is a normalization constant. Equation (3) plays a central role in the theory. The second step involves the expansion of the inhomogeneous density in terms of position dependent order parameters[16]

$$\rho(\mathbf{r}) = \rho_l[1 + \phi_0(\mathbf{r}) + \sum_{\{G\}} \phi_G(\mathbf{r})\exp(i\mathbf{G}\cdot\mathbf{r}), \quad (4)$$

where the sum is over all the reciprocal lattice

vectors (RLV) of the solid. ϕ_0 and ϕ_G are the order parameters that are zero in the pure liquid and have nonzero constant values in the pure solid. For a nucleus of spherical shape, ϕ_0 and ϕ_G depend on the radial distance only. The last assumption ignores microscopic faceting, as discussed by Harrowell and Oxtoby[16]. The last step involves extremization of the grand canonical free energy ΔW with respect to the order parameters. The expression for ΔW is given by[18]

$$\Delta W = -\int dr [\rho(r) - \rho_l] + \tfrac{1}{2} \int dr_1 \int dr_2 \, c(r_1 - r_2)$$

$$[\rho(r_1) - \rho_l][\rho(r_2) + \rho_l]. \qquad (5)$$

Harrowell and Oxtoby[16] obtained the order parameter profiles $\phi_0(r)$ and $\phi_G(r)$ and the free energy surfaces for several supercoolings by considering only a *single* set of RLV for the bcc-sodium system. They used the experimentally known values of $S(k)$ and $S(o)$ above the freezing temperatures to extrapolate them below the freezing temperature. The main conclusions of this work are summarized below. First, the interface between crystal nucleus and liquid is broad, of the order of 6–7 atomic diameters thick. This is consistent with the square gradient approximation. The interfacial width appears to be independent of supercooling. Secondly, the fractional density change, ϕ_0, falls off faster with distance from the centre than ϕ_1. Thirdly, as the supercooling ΔT increases, the value of ϕ_1 remains essentially constant at ϕ_1 (solid) at the centre $(r = 0)$ of the nucleus while $\phi_0 (r = 0)$ decreases. The last result is surprising because for most substances ϕ_0 increases as temperature is decreased which can be understood from the strong temperature dependence of the pressure along the coexistence line in the P–T plane. It is difficult to understand the reason for the anomalous behaviour of ϕ_0 because of the many approximations that are involved in this theory.

By taking an observable rate of 1 nucleus/sec and using Turbull Fisher's formula[3], an estimate of the maximum supercooling can be obtained. Harrowell and Oxtoby found it to be lying between 127 and 150°C for the bcc-sodium system, which is reasonable. Subsequently, Grant and Guuton[19] used the order parameter theory

to obtain an expression of the Zeldovich factor[14] for the nucleation rate of a crystalline solid from its melt. Their expression[18] for rate of nucleation is yet to be tested against experiments.

The order-parameter theory of solid-liquid nucleation constitutes an important advancement over the previous phenomenological theories. In the next section, we shall consider the dynamical aspects of nucleation.

3. DYNAMICS OF FREEZING AND LIQUID INSTABILITY

There have been several studies, both experimental[19,20] and theoretical[12,13] to locate the limit of stability of a supercooled liquid. The criteria of the stability limit is that at this limit the liquid becomes unstable with respect to infinitesimal fluctuations. Thus, the search for a stability limit has been essentially a search for the classical spinodal point. It has been suggested[12] that the stability limit is achieved when the value of the liquid structure factor, $S(k_0)$, at the first peak (k_0), becomes infinitely large. Given that the liquid is a homogeneous spatially random system, it is doubtful if the structure factor at all diverges at any finite temperature. In this section we shall present a theoretical study of the stability limit which suggests that a spinodal point (in the classical sense) does not exist for solid-liquid transitions. However, a stability limit with some of the characteristics of a spinodal point can be identified.

Our analysis starts with the following Ginzburg–Landau expression[14] for the time dependence of the density field $n(r, t)$

$$\frac{\partial n}{\partial t}(r, t) = -\nabla . J, \qquad (6)$$

where the flux J is given by

$$J = -Dn(r,t) \nabla \frac{\delta F\{[n(r,t)]\}}{\delta n(r,t)}. \qquad (7)$$

The coarse-grained free energy functional F is assumed to be given by (1) with $\rho(r)$ replaced by $n(r, t)$ and D is the self-diffusion coefficient of the liquid. Equation (1), (6) and (7) can be combined to obtain the following non-linear diffusion

equation

$$\frac{\partial n}{\partial t}(\mathbf{r}, t) = D\nabla.[\nabla n(\mathbf{r}, t) - n\beta \mathbf{F}], \qquad (8)$$

where the force-field $\mathbf{F}$ is given by

$$\beta \mathbf{F}(\mathbf{r}, t) = \nabla \int d\mathbf{r}' c(r - r') [n(r', t) - \rho_l]. \qquad (9)$$

Our stability analysis takes the following form. We study the stability of the system with respect to a density wave of the following form

$$n(\mathbf{r}, t) = \rho_l(1 + \phi_0(t)) + \rho_l \sum_{\{G\}} \phi_G(t) \exp(i\mathbf{G}, \mathbf{r}). \qquad (10)$$

As in (4), the sum is over all the reciprocal lattice vectors. Use of (10) in (8) gives the following expressions for time dependence of $\phi_0(t)$ and $\phi_G(t)$

$$d\phi_0/dt = 0 \qquad (11)$$

$$d\phi_G(t)/dt = -G^2 D\phi_G(t)[1 - (1 + \phi_0) c(G)]$$

$$+ D \sum_{\{G'\}} \phi_{G'} \phi_{G - G'} c(G - G') [G.(G - G')], \qquad (12)$$

where

$$c(G) = \rho_l \int d\mathbf{r}\, c(r) \exp(-iG.r) \qquad (13)$$

Thus, ϕ_0 has no time dependence and we shall denote the initial value by ϕ_0. At this juncture we must point out that it would be a mistake to set ϕ_0 equal to zero as done in all the previous studies[12,13] on the dynamics of freezing. The time dependence of $\phi_G(t)$ is, however, nontrivial and involves couplings between different RLV's. As a result, liquid fluctuations at different wave vectors are also coupled. As we show below, this coupling plays an important role in the dynamics of freezing. Also note the ϕ_0 dependence in (12).

Next we perform a Laplace transform on (12) and write the resulting expression in the following form

$$\phi_G(s) = \frac{\phi_G}{s + G^2 \hat{D}(G) - I(G)} \qquad (14)$$

where $\phi_G = \phi_G$ (t = 0) and the effective self-

diffusion is given by

$$\hat{D}(G) = \frac{D}{\hat{S}(G)}, \qquad (15)$$

with

$$\hat{S}(G) = [1 - \rho_l(1 + \phi_0)c(G)]^{-1}. \qquad (16)$$

$I(G)$ is an operator which acts on any function $f(G, s)$ to give

$$I(G)f(G, s) = D \sum_{G'} [G \cdot (G - G')] c(G - G')$$

$$\times \frac{1}{2\pi i} \int_{BI} ds' f(G', s') f(G - G', s - s'), \qquad (17)$$

where the Bromwich path has to be so chosen that Re $s >$ Re s'. Equation (14) can be used to evaluate $\phi_G(s)$ perturbatively with $G^0 = [s + \hat{D} G^2]^{-1}$ as the Green's function. A stability limit shall be reached when the relaxation time of $\phi_G(s)$ becomes infinitely large.

We have carried out the perturbative analysis and the details will be published elsewhere[20]. Here we summarize the main conclusions of this analysis.

(i) There is no spinodal point in the classical sense. There is, however, an instability point with ϕ_G's infinitesimally small but ϕ_0 finite. This can happen because $\hat{S}(k_0)$ can diverge even though $S(k_0)$ remains finite. This can happen when the following relation is satisfied:

$$1 - \rho_l(1 + \phi_0) C(|G| = k_0) = 0$$

and

$$\phi_G = 0, \qquad \text{for all } \phi_G\text{'s.} \qquad (18)$$

In an analysis of the order-parameter diagram of the equilibrium freezing transition, Bagchi et al[9] earlier suggested that this point is the spinodal point in the freezing transition. They found that (18) is satisfied at $\rho_l = 1.20$ and $\phi_0 = 0.15$ for hard spheres. Note that ρ_l is very close to the random close packing density of hard spheres. Here we find a justification of the conjectures of Bagchi et al[9] from dynamical consideration.

(ii) For bcc-sodium system, an one order

parameter

$$\left(G_1 = (\pm 1, 0, \pm 1)\frac{2\pi}{a}, (0, \pm 1, \pm 1)\frac{2\pi}{a}, (\pm 1, \right.$$

$$\left. \pm 1, 0)\frac{2\pi}{a} \right)$$

theory with perturbation up to first order in $I(G)$, (second order in $\phi(G)$) gives the following condition for the stability limit[20]

$$\phi(G_1) = [c(G_1) S(G_1)]^{-1}, \tag{19}$$

which gives a value of $\phi(G_1) = 0.5$ at the freezing point. This is in fair agreement with the value[8] $\phi(G_1) = 0.63$ from the equilibrium theory of freezing. However, this agreement is deceptive. If we include the next order parameter $(G_2 = (\pm 2, 0, 0), (0, \pm 2, 0), (0, 0, \pm 2))$ then a substantially different picture emerges. We then find a large supercooling and finite density change ($\phi_0 > 0$) is necessary for freezing to occur. This is because $c(G_2)$ is large and *negative* (a typical value is $c(G_2) = -0.4$ at $100°C$) and resists freezing. Higher order parameters are less important for bcc systems but are important for fcc systems.

(iii). This study suggests that the reason for large supercooling necessary for freezing to occur is the existence of the deep negative region in the structure factor which is probed by an important RLV of the solid

$$\left((\pm 2, \pm 2, 0)\frac{2\pi}{a}, (0, \pm 2, \pm 2)\frac{2\pi}{a}, (\pm 2, 0, \right.$$

$$\left. \pm 2)\frac{2\pi}{a} \right)$$

for fcc lattice. As supercooling is increased, both $c(G_1)$ and $|c(G_2)|$ increases (that is $S(G_2)$ decreases) and finally a point is reached where fluctuations at $G_1 = k_0$ cease to decay leading to the formation of the solid.

4. DYNAMICS AT THE SOLID-LIQUID INTERFACE

A quantitative understanding of the dynamical processes at the solid-liquid interface is crucial for many branches of condensed matter physics[6].

However, our understanding of this field is still largely incomplete. The reason is that it is difficult to carry out experimental study of this interface which is very narrow, on a macroscopic scale, and is bounded by two condensed phase which have similar short range order. Also, it is difficult to treat this interface theoretically because it is a strongly inhomogeneous system. Here we shall briefly summarize the theoretical developments in this field.

Recently Klupsch[21] presented a theoretical analysis of the elementary kinetic processes at the interface. He used a Smoluchowski equation description to investigate the time necessary for a particle to undergo transition from the liquid to the coexisting solid phase. An order-parameter description was used for the interface with a mean-field expression for the localizing potential which arises from the inhomogeneity at the interface. For the fcc Lennard-Jones system, Klupsch obtained a value of 10^{-10} sec for the solid-liquid transition time. No experimental confirmation of this result is yet available.

An important transport property at the interface is the self-diffusion coefficient, D. D is of the order of 10^{-5} cm^2/sec in liquid and it is almost zero in the solid phase. Since the solid-liquid interface is quite narrow, the self-diffusion coefficient must change sharply across the interface. Recently Bagchi[22] presented a theoretical study of the variation of the self-diffusion coefficient across a solid-liquid interface by using an order parameter description of the interface and a nonlinear integral equation similar to (8) but with the force term time-independent. The self-diffusion coefficient is obtained perturbatively and the final expressions are[22,23]:

$$D(Z_0) = D_0\left[1 - \frac{8}{3}(c_G \phi_G)^2 - \frac{2}{3}(c_G \phi_G)^4 \cdots \right],$$

for fcc lattice, (20)

and

$$D(Z_0) = D_0[1 - 4(c_G \phi_G)^2 - 5(c_G \phi_G)^4 \cdots],$$

for bcc lattice, (21)

where D_0 is the liquid-phase self-diffusion coefficient and Z_0 is a coarse-grained distance which specifies a position in the interface. $\phi_G(Z_0)$ gives

the interface profile of the topological order. This is zero in the pure liquid phase and has nonzero constant value in the solid phase. As we traverse from liquid to solid, $\phi_G(Z_0)$ increases and $D(Z_0)$ decreases and eventually goes to zero. It is interesting to find the values of the order parameters for the two lattices at which $D(Z_0)$ equals zero. We find[23] $\phi_G(\text{bcc}) = 0.67$ and $\phi_G(\text{fcc}) = 0.9$ which is in good agreement with the values obtained from the theory of freezing[8-10].

A quantity of experimental interest is the dynamic structure factor, $S(k, \omega)$, at the solid-liquid interface. This quantity can be studied by inelastic neutron scattering, although extracting information about the interface may prove difficult. The dynamic structure factor is defined by the following expression[24]

$$S(\mathbf{k}, \omega) = \int d\mathbf{r} \exp(-i\mathbf{k}.\mathbf{r}) \int_{-\infty}^{\infty} dt \exp(i\omega t)$$

$$\langle \delta n(\mathbf{0}, 0)\, \delta n(\mathbf{r}, t) \rangle, \tag{22}$$

where $\delta n(\mathbf{r}, t)$ is the fluctuation in number density and $\langle \ \rangle$ denotes an average over an equilibrium distribution. Recently Bagchi[25] presented a calculation of $S(k, \omega)$ at the interface for large values of the wave vector $\mathbf{k}$. An analytic expression was derived which show the evolution of the elastic peak ($\omega = 0$) as the solid surface is approached from the liquid side.

There also exist several model-dependent studies of the interface dynamics[6]. We shall not review these studies except to mention that these studies are mainly applicable to the solid-vapour interface and may not be applicable to solid-liquid interface where short-range order of liquid plays an important role.

5. KINETICS OF CRYSTAL GROWTH

The dynamics of crystal growth is a vast subject and we shall not attempt to review any of the standard theories which can be obtained elsewhere[7,26]. Here we shall briefly discuss a theoretical approach recently initiated by Kirkpatrick and the author[27]. This theory is based on an order-parameter description of the interface and pays proper attention to the local structure present in the liquid and in the solid-liquid interface. The dynamics is based on a nonlinear diffusion equation that contains a mean-field force term due to the local structure and a temperature gradient term to account for the temperature difference between the solid and the melt. The temperature gradient provides the driving force for the growth of the crystal. The nonlinear diffusion equation is of the following form[27]

$$\frac{\partial n}{\partial t}(\mathbf{r}, t) = \nabla.\vec{D}(\mathbf{r}).[\nabla n - n\beta F]$$

$$- \nabla \vec{D}\, n \nabla \ln\beta(\mathbf{r}, t), \tag{23}$$

where $\beta(r, t) = [k_B T(r, t)]^{-1}$, $T(r, t)$ is the space and time dependent temperature. The justification of using a nonlinear diffusion equation to describe dynamics of crystal growth has been discussed elsewhere[27]. Here we briefly mention the salient points. Firstly, (23) has correct limiting properties. At equilibrium, solution of (23) is the standard mean-field expression for the inhomogeneous density distribution that has been used successfully in the equilibrium theory of freezing[8]. In a homogeneous system, in the absence of a temperature gradient, (23) leads to an expression of the dynamic structure factor $S(k, \omega)$ which can describe neutron scattering by dense classical liquids fairly well for large values of the wave vector $\mathbf{k}$. Secondly, the recent work of de Schepper and Cohen[28], and also of Kirkpatrick[29], on short wavelength collective modes show that the dynamics at large wave numbers are dominated by a self-diffusion like mode alone. This is because at large wave numbers momentum relaxation is very rapid and only the density conservation is relevant. Thirdly, the mean free path in a liquid at freezing density is extremely small, only 3–5% of molecular diameter.

The next step is the expansion of the number density $n(r, t)$ in suitable order parameters

$$n(\mathbf{r}, t) = \rho_l(1 + \phi_0(\mathbf{r}, t)) + \rho_l \sum \phi_G(\mathbf{r}, t)$$
$$\exp(i\mathbf{G}.\mathbf{r}). \tag{24}$$

Note that the order parameters are now both time- and space-dependent. Substitution of (24) in (23) leads to a system of equations for $\phi_0(t)$ and $\phi_G(t)$. These equations involve time-dependent temperature field which is described by a thermal diffusion equation. The resulting expressions are rather complicated and we refrain from presenting them here; they are available elsewhere[27]. By assuming a steady-state temperature distribution in the interface and by making some simplifying assumptions, one can obtain the following simple expression for the velocity, V, of crystal growth

$$V = -\frac{1}{Z_W} \int_{Z_s}^{Z_l} dZ\, D(Z)\frac{1}{T}\frac{\partial}{\partial Z} T(Z), \qquad (25)$$

where Z_W is the width of the interface, and Z_l and Z_s denote positions where the order parameters reach their liquid-like and solid-like values, respectively. If we further assume a linear dependence of $T(Z)$ on Z, we recover the usual[5] linear dependence of V on ΔT—the temperature difference between the crystal and the melt.

The preceding analysis of crystal growth is valid only for steady, slow growth of the crystalline front. A different approach is needed to describe the dynamics during a rapid growth of the crystal. Recent dynamic light scattering experiments[1,2,30] at the interface of a growing crystal have uncovered an interesting nonequilibrium phenomenon—a dramatic narrowing of the linewidth of the Rayleigh peak when the velocity of growth exceeds certain critical value. The physical reason for this dramatic slow down of the relaxation rate is not well understood at present.

Lastly we comment that a molecular theory for the kinetics of crystal growth is far from complete at present. This field provides an interesting challenge to the experimentalists and the theoreticians alike.

6. DISCUSSION

A major obstacle to our understanding of the dynamical processes involved in freezing is the unavailability of precise experimental data against which theoretical predictions can be tested. This is reflected in many apparently contradictory results reported in literature[12,31]. Recent computer simulation experiments on nucleation[32,33], on interfacial structure[34,35] and on crystal growth[36] have provided significant new insight into the different aspects of the dynamics of freezing. There is, however, a difficulty in obtaining precise results even in computer simulations because molecular dynamics simulations in supercooled liquids involve very long runs. With the rapid development in computer science, these difficulties may soon be eliminated. We expect interesting new results from computer experiments in near future.

There are several important theoretical problems that need to be explored. First, we need a many order parameter theory of nucleation. It is evident from the results of §2 that even for bcc lattice systems, we need at least two order parameters to obtain a reliable description of dynamics. Secondly, no theoretical study is yet available for fcc systems, although many computer simulation results are available for these systems. Thirdly, we need a more precise understanding of the stability of supercooled liquids to density waves of the form given by (10). An interesting problem here would be to study density waves of icosahedral symmetry[11]. Dynamics at the solid-liquid interface is another problem that is little understood at present, especially at an advancing crystalline front. We have already mentioned the problems that are unsolved in the dynamics of crystal growth. Thus, dynamics of freezing remains an exciting field of research where interesting developments can be expected in near future.

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