Generalized structural theory of freezing

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The first-principles order-parameter theory of freezing, proposed in an earlier work, has been successful in yielding quantitative agreement with known freezing parameters for monatomic liquids forming solids with one atom per unit cell. A generalization of this theory is presented to include the effects of a basis set of many atoms per unit cell. The basic equations are modified by the "density structure factors" f_i which arise from the density variations within the unit cell. Calculations are presented for the important case of monatomic liquids freezing into hexagonal close packed solids. It is concluded that all freezing transitions can be described by using structural correlations in the liquid instead of the pair potential and that the three-body correlations are important in deciding the type of solid formed after freezing.

I. INTRODUCTION

In an earlier work[1] (hereafter called RY), an order-parameter theory of freezing was described which uses the structural correlations in the liquid instead of the interatomic potential. This approach has several advantages. First, it has been able to explain the similarities of freezing transitions in different real and computer-simulated systems. This is basically due to the fact that structural correlations in different systems show many similarities[2,3] although their pair potentials may be widely different. For example, the highest peaks of the static structure factor S_q near freezing are similar for liquids with attractive Lennard-Jones, purely repulsive Coulomb (one-component plasma), and hard-sphere-type pair potentials. The second advantage of using structural correlations is that the dominant pair correlations can be measured directly by actual and computer experiments. In fact, this provides an important check for the theoretical predictions. Another advantage is the ease with which three-body correlations can be introduced in the theory as compared to the introduction of three-body forces. The physical reason for the importance of three-body effects is quite simple. When an atom is surrounded by other atoms, the two-body forces would determine the interatomic separation and the three-body forces depending upon the angles would influence the nearest-neighbor arrangements. Finally, the systematic approximation scheme described in RY enables one to handle a many-order-parameter theory incorporating many-body correlations with easy, step by step approximations which converge rapidly.

The input information consists of the compressibility (and its variation with density) of the liquid near freezing and an assumption about the type of lattice for the solid to be formed after freezing (the actual lattice constant is scaled out). Then the order parameters are chosen to be proportional to the lattice Fourier transforms of the density. It is often possible to assign the same order parameter corresponding to all the reciprocal-lattice vectors (RLV) of the same magnitude. The output information depends on the approximation step. The first step is to take one order parameter and examine whether a transition is at all possible. If a transition is predicted, then the output also consists of the predicted values of the fractional change of density and the structure factor $c_q (=1 - S_q^{-1})$ corresponding to the first peak. The second step is to choose judiciously[1] a second-order parameter and get predicted values for the freezing parameters. The next step is to improve these predictions by including three-body effects. Usually it is not necessary to go any further because all other effects add to less than 5%. Applications[1,4] of these procedures to the freezing of *monatomic* liquids into solids with *one atom per unit cell* leads to quantitative agreement with experimentally known freezing characteristics.

The purpose of the present paper is to generalize this structural theory of freezing to include the effects of a *basis set of many atoms* per unit cell. It is necessary to rewrite the basic equations of the earlier work, RY, in suitably simplified form before generalizing them. This is done in the next section. Section III shows that the effects of the reciprocal lattice should be suitably weighted in the presence of a basis set of many atoms per unit cell. The generalized equations are given in Sec. IV. An important test of these equations is provided by the example of a monatomic liquid freezing into a hexagonal close packed (hcp) solid. This is described in Sec. V where the important conclusions are also summarized.

II. BASIC EQUATIONS OF RY THEORY

When a liquid approaches freezing transition, the external conditions like temperature and pressure, *etc.*, affect the structural correlations and also set up density fluctuations. Energy of the system increases by setting up the density fluctuations but the consequent change in pressure lowers energy. The relative effects of the two processes are determined by the structural correlations and the freezing transition takes place when the two energy contributions balance each other. The theory described in RY treats this process of spontaneous finite-amplitude density-fluctuation instability in the mean-field approximation. The basic equations are as follows.

Consider a N-particle system with Hamiltonian H_N confined in a volume V, whose thermodynamic potential Ω is sought in a grand canonical ensemble. Assuming that this system would freeze into a given type of lattice (actual lattice constant is scaled out) described by reciprocal-lattice vectors $\{\vec{K}_i\}$, the order parameters λ_i are defined to be directly proportional to the lattice Fourier transforms $\rho_i \equiv \rho_{\vec{K}_i}$
$= \sum_{j=1}^{N} 2\cos(\vec{K}_i \cdot \vec{r}_j)$ of the density $\rho(\vec{r}) = \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_j)$. The adequacy of such order parameters has been discussed in detail in RY. Note that here ρ_i has been chosen to be real in contrast to the complex ρ_i in RY. It has been shown that Ω as a function of λ_i can be calculated from

$$\exp[-\beta\Omega(\{\lambda_i\})]$$
$$= \mathrm{Tr}\left[\exp\left(-\sum_i (\lambda_i - \epsilon_i \rho_i)^2 - \beta(H_N - \mu N)\right)\right] \quad . \quad (1)$$

Here μ is the chemical potential, $\beta = 1/k_B T$ and ϵ_i are real constants so that λ_i are also real. Writing the mean-field expansion $\rho_i^2 = 2\langle \rho_i \rangle \rho_i - \langle \rho_i \rangle^2$ where $\langle \cdots \rangle$ denotes the ensemble average, one obtains

$$\frac{\partial}{\partial \lambda_k}\left[\beta\Omega(\{\lambda_i\}) - \sum_i \lambda_i^2\right] = -2\epsilon_k \langle \rho_k \rangle \quad . \quad (2)$$

In addition, evaluation of $\langle \rho_i \rangle$ is *mathematically* equivalent [using Eq. (1)] to the problem of computing $\langle \rho_i \rangle$ for a liquid placed under a *fictitious* periodic potential (the *actual* liquid experiences *no* such potential!):

$$\beta v(\vec{r}) = \sum_i (2\epsilon_i^2 \langle \rho_i \rangle - 2\epsilon_i \lambda_i) 2\cos(\vec{K}_i \cdot \vec{r}) \quad . \quad (3)$$

The hypernetted chain (HNC) method[5] can be used to develop a systematic approximation scheme involving liquid-state correlation functions. The self-consistent equations involving only two-particle correlations are

$$\langle \rho(\vec{r}) \rangle = \rho_0 \exp[-\beta v_{\mathrm{eff}}(\vec{r})] \quad (4a)$$

and

$$\beta v_{\mathrm{eff}}(\vec{r}) = \beta v(\vec{r}) - \int c(\vec{r} - \vec{r}')[\langle \rho(\vec{r}') \rangle - \rho_0]d\vec{r}' \quad . \quad (4b)$$

Here $c(\vec{r})$ is the direct correlation function with $c_q = 1 - S_q^{-1}$ and S_q is the static structure factor, which can be directly measured by experiments. ρ_0 is the uniform part of the density. The expansions

$$c(\vec{r}) = \frac{1}{N_0} \sum_{\vec{q}} c_q 2\cos(\vec{q} \cdot \vec{r}) \quad (5)$$

and

$$\langle \rho(\vec{r}) \rangle = \rho_0(1 + \eta) + \rho_0 \sum_i \mu_i 2\cos(\vec{K}_i \cdot \vec{r}) \quad , \quad (6)$$

with the fractional volume change η and $2\mu_i = \langle \rho_i \rangle / N_0$, can be used in Eqs. (4). Note that μ_i defined here is half of μ_i used in RY. The μ_i-dependent terms will cancel out if one sets

$$\epsilon_i = (c_i / 2N_0)^{1/2} \quad . \quad (7)$$

Finally, one defines the reduced order parameters $\xi_i = 2\epsilon_i \lambda_i$ and the functions

$$\phi(\{\xi_i\}) = \int \frac{d\vec{r}}{V} \exp\left[\sum_i 2\xi_i \cos(\vec{K}_i \cdot \vec{r})\right] \quad (8a)$$

and

$$\phi_k(\{\xi_i\}) = \int \frac{d\vec{r}}{V} 2\cos(\vec{K}_k \cdot \vec{r}) \exp\left[\sum_i 2\xi_i \cos(\vec{K}_i \cdot \vec{r})\right] \quad (8b)$$

to get

$$\eta = \ln\phi(\{\xi_i\})/(1 - c_0) \quad . \quad (9)$$

Then, integration of Eq. (2) yields

$$\beta\Delta\Omega(\{\xi_i\}) = \frac{\beta}{N_0}[\Omega(\{\xi_i\}) - \Omega(\{0\})]$$
$$= \sum_i \frac{\xi_i^2}{2c_i} - (1 - c_0)\left[\eta + \frac{\eta^2}{2}\right] \quad . \quad (10)$$

This analytic expression for thermodynamic potential gives freezing transition. For $\xi_i = 0$, one has the liquid state. For $\xi_i \neq 0$, $\beta\Delta\Omega(\{\xi_i\})$ should be, as in the Landau theory of phase transitions,[6] a minimum as a function of order parameters ξ_i and also vanish to give the freezing transition. In practice, ϕ, ϕ_k and η are evaluated using Eqs. (8) and (9), and one gets

$$\frac{\xi_i}{c_i} = (1 + \eta)\frac{\phi_i}{\phi} \quad . \quad (11)$$

Equation (11) represents the minimal condition, and one looks for the following equation to be satis-

fied for the phase transition to take place:

$$\sum_i \frac{\xi_i^2}{2c_i} = (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right) . \tag{12}$$

If three-body correlations with Fourier transforms $c_{i,i'}^{(3)}$ are included (see RY), then Eq. (12) would be modified to give

$$\sum_i \mu_i \xi_i = (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right) + c_{00}^{(3)}\left(\frac{\eta^2}{2} + \frac{\eta^3}{3}\right)$$

$$+ \sum_i c_{i0}\mu_i^2(2\eta + 1) + \sum_i \frac{8}{3}c_{i'i''}^{(3)} n_i^{(3)}\mu_i^3 . \tag{13}$$

Here $c_{00}^{(3)}$ is related to the variation of c_0 with density and c_0 is related to the isothermal compressibility B_T by the relation $(1 - c_0) = \beta/\rho_0 B_T$. $n_i^{(3)}$ is the number of vectors in the set $\{\vec{K}_i\}$ whose linear combination with a given vector of this set gives another vector of the same set. It is a geometrical effect which is explained in RY.

The above equations are applicable to freezing of *monatomic* liquids into solids with *one atom per unit cell*. The existence of a basis of many atoms per unit cell affects the choice and effectiveness of the various order parameters as described in the next section.

III. "DENSITY STRUCTURE FACTOR"

Consider the freezing of a polyatomic liquid which has the following special properties. (1) There are in general n_b different kinds of atoms. (2) There are N_1 atoms of each kind. (3) The interactions are such that segregation of different types of atoms is prevented. (4) The solid formed has N_1 lattice sites with a basis of n_b different atoms at positions $\vec{\tau}_j$, $j = 1, \ldots, n_b$. The total number of atoms is $N = N_1 n_b$.

The density for each constituent of such a polyatomic liquid becomes periodic after freezing. Close to the freezing transition, the density function may be generalized as

$$\rho^b(\vec{r}) = \sum_{k=1}^{N_1} \sum_{j=1}^{n_b} w_j \delta(\vec{r} - \vec{r}_k - \vec{\tau}_j) ,$$

where the "weight factors" w_j represent, in some approximation, the relative differences (if any) of the constituent atoms in the unit cell. For monatomic liquids, $w_j = 1$ for all j. For two or more types of atoms, the properties of the constituent atoms would determine w_j in a complicated way and here it suffices to treat w_j as adjustable parameters (one of which should always be chosen as unity).

It was shown in RY that the imaginary part of the complex order parameter can be integrated out and

only the real part enters the final equations of the theory. Therefore we consider only the real part of the Fourier transform of $\rho^b(\vec{r})$ which may be written as

$$\rho_i^b = f_i^R \sum_{k=1}^{N} 2\cos(\vec{K}_i \cdot \vec{r}_k) - f_i^I \sum_{k=1}^{N} 2\sin(\vec{K}_i \cdot \vec{r}_k) , \tag{14}$$

where f_i^R and f_i^I are the real and imaginary parts of the *density structure factor*

$$f_i = \frac{1}{n_b} \sum_{j=1}^{n_b} w_j \exp(i\vec{K}_i \cdot \vec{\tau}_j) . \tag{15}$$

In Eq. (14), $n_b \sum_{k=1}^{N_1}$ has been replaced by $\sum_{k=1}^{N}$ to take care of the number of atoms undergoing freezing. The effect of the basis appears through f_i in Eq. (14) and leads to substantial modifications of the different order-parameter modes. Indeed, some of the order-parameter modes will be completely suppressed due to $f_i = 0$. Three simple examples below illustrate such cases.

A. bcc as sc with a basis of two atoms

Consider a monatomic liquid that freezes into a body centered cubic (bcc) structure. One procedure is to view this structure as a one atom per unit cell case, construct the reciprocal lattice (which is fcc) and start with the smallest reciprocal-lattice vector set to discuss freezing in one order-parameter approximation. This is exactly the procedure that was followed in RY. But one can also look upon the bcc structure as a simple cubic (sc) structure with a basis set of two identical atoms placed at $\vec{\tau}_1 = 0$ and $\vec{\tau}_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the units of the lattice constant of the sc lattice. Then, one has the reciprocal-lattice vectors of sc lattice[7] as $\vec{K}_i = h\vec{A} + k\vec{B} + l\vec{C}$ where $\vec{A}$, $\vec{B}$, and $\vec{C}$ are the primitive translation vectors of the sc reciprocal lattice and h, k, and l are integers. Now $w_j = 1$ and $f_i = \frac{1}{2}[1 + (-1)^{h+k+l}]$. For odd values of $(h + k + l)$ one gets $f_i = 0$ and for even values $f_i = 1$. It follows from Eq. (14) that $\rho_i^b = 0$ when $(h + k + l)$ is odd. Thus, the shortest reciprocal-lattice vector with $h = 1$, $k = 0$, and $l = 0$ does not enter bcc freezing. The next vector with $h = 1$, $k = 1$, and $l = 0$ has $f_i^R = 1$ and $f_i^I = 0$ so that $\rho_i^b = \sum_{k=1}^{N} 2\cos(\vec{K}_i \cdot \vec{r}_k)$. This is exactly the smallest reciprocal-lattice vector in the former description. Thus, the two procedures, with the help of f_i and ρ_i^b, lead to the same freezing equations. In fact, f_i effectively throws away all those order parameters of sc that are "inadmissible" for the bcc case.

B. fcc as sc with a basis of four atoms

In analogy with the bcc case, one can consider the face centered cubic (fcc) as a one atom per unit cell

structure and then the smallest reciprocal-lattice vector set yields the one parameter approximation as in RY. Also in the units of the lattice constant, a basis set of four atoms situated at $\vec{\tau}_1 = 0$, $\vec{\tau}_2 = (\frac{1}{2}, \frac{1}{2}, 0)$, $\vec{\tau}_3 = (0, \frac{1}{2}, \frac{1}{2})$, and $\vec{\tau}_4 = (\frac{1}{2}, 0, \frac{1}{2})$ attached to a simple cubic lattice represents a fcc lattice. Then the density structure factor corresponding to $\vec{K}_i = h\vec{A} + k\vec{B} + l\vec{C}$ becomes

$$f_i = \tfrac{1}{4}[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{l+h}] \ .$$

This is unity when h, k, and l are all odd or all even integers, and zero otherwise. The first nonvanishing f_i corresponds to $h = 1$, $k = 1$, and $l = 1$, which is the smallest vector of the reciprocal lattice of fcc. Again, like bcc, the two procedures are equivalent, and f_i and ρ_i^b help in sorting out the RLV set appropriate for fcc structure from the RLV of simple cubic lattice.

C. hcp structure

The lattice is hexagonal with lattice constants a and c, with the ideal value of $\beta = c/a$ for close packing being $(\frac{8}{3})^{1/2}$. The primitive translation vectors are[7] $\vec{a} = a(\sqrt{3}\hat{x} + \hat{y})/2$, $\vec{b} = a(-\sqrt{3}\hat{x} + \hat{y})/2$, and $\vec{c} = a\beta\hat{z}$, where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors along the Cartesian axes. The reciprocal-lattice vectors are expressed in terms of the primitive translation vectors $\vec{A} = 2\pi(\hat{x}/\sqrt{3} + \hat{y})/a$, $\vec{B} = 2\pi(-\hat{x}/\sqrt{3} + \hat{y})/a$, and $\vec{C} = 2\pi(\hat{z}/\beta)/a$. Thus, $\vec{K}_i = h\vec{A} + k\vec{B} + l\vec{C}$. There are identical atoms per unit cell at $\vec{\tau}_1 = (0, 0, 0)$ and

$\vec{\tau}_2 = \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c}$. Then the density structure factor is

$$f_i = \tfrac{1}{2}\{1 + \exp[i\pi(4h + 2k + 3l)/3]\} \ . \tag{16}$$

This vanishes when $(4h + 2k + 3l)$ is an odd multiple of three. The corresponding order-parameter modes will be absent for hcp freezing. Equation (16) will be further used in Sec. V.

IV. GENERALIZED EQUATIONS OF FREEZING

The generalized equations of freezing may be obtained by choosing the order parameters λ_i to be proportional to ρ_i^b of Eq. (14) for freezing into a solid with a basis of many atoms per unit cell. This generalization is nontrivial because now one has two different terms in ρ_i^b whose mean field linearization must be done properly. Also, the term with f_i^I may assume different signs for RLV of same lengths. Now, one can define two averages

$$\mu c_i = \left\langle \sum_{j=1}^{N} 2\cos(\vec{K}_i \cdot \vec{r}_j) \right\rangle \ , \tag{17a}$$

and

$$\mu s_i = \left\langle \sum_{j=1}^{N} 2\sin(\vec{K}_i \cdot \vec{r}_j) \right\rangle \ , \tag{17b}$$

so that the proper mean-field linearization of $(\rho_i^b)^2$ may be written as

$$(\rho_i^b)^2 = (f_i^R)^2 \left[2\mu c_i \sum_{j=1}^{N} 2\cos(\vec{K}_i \cdot \vec{r}_j) - \mu c_i^2 \right] + (f_i^I)^2 \left[2\mu s_i \sum_{j=1}^{N} 2\sin(\vec{K}_i \cdot \vec{r}_j) - \mu s_i^2 \right]$$

$$+ 2f_i^R f_i^I \left[\mu c_i \mu s_i - \mu c_i \sum_{j=1}^{N} 2\cos(\vec{K}_i \cdot \vec{r}_j) - \mu s_i \sum_{j=1}^{N} 2\sin(\vec{K}_i \cdot \vec{r}_j) \right] \ .$$

This expression must be used in Eq. (1) where ρ_i is now replaced by ρ_i^b. Then the differential equation in order parameters [the counterpart of Eq. (2)] becomes

$$\frac{\partial}{\partial \lambda_k} \left[\beta\Omega(\{\lambda_i\}) - \sum_i \lambda_i^2 \right] = -2\epsilon_k(f_i^R \mu c_i - f_i^I \mu s_i) \ . \tag{18}$$

This reduces to Eq. (2) for $f_i^R = 1$ and $f_i^I = 0$. The equivalent fictitious potential for calculating the fluid response is now given by

$$\beta v(\vec{r}) = \sum_i [2\epsilon_i^2(f_i^R \mu c_i - f_i^I \mu s_i) - 2\epsilon_i \lambda_i][2f_i^R \cos(\vec{K}_i \cdot \vec{r}) - 2f_i^I \sin(\vec{K}_i \cdot \vec{r})] \ . \tag{19}$$

It may be noted that this long-range oscillatory potential has both sine and cosine oscillations superposed with weighting factors of f_i^I and f_i^R. The fluid density will show similar oscillations in response to this $v(\vec{r})$. The HNC Eqs. (4) will now contain ρ_i^b in place of ρ_i and the Fourier expansion of Eq. (5) for $c(\vec{r})$ remains unchanged. However, the expansion of $\langle \rho^b(\vec{r}) \rangle$ has to follow that of $v(\vec{r})$ in Eq. (19). It must also contain additional f_i^R and f_i^I as factors for μc_i and μs_i to govern the effects of various RLV sets. Thus, one gets

$$\langle \rho^b(\vec{r}) \rangle = \rho_0^b(1 + \eta) + \rho_0^b \sum_i (f_i^R \mu c_i - f_i^I \mu s_i)[2f_i^R \cos(\vec{K}_i \cdot \vec{r}) - 2f_i^I \sin(\vec{K}_i \cdot \vec{r})] \ . \tag{20}$$

The first factor of the last term in Eq. (20) is simply the average of ρ_i^p of Eq. (14). Again the f_i factors suppress the "inadmissible" RLV sets and as an example of this, one obtains the correct expansion for bcc from that of sc by using the f_i of Sec. III A.

Using the expansion of Eq. (20), one gets rid of μc_i and μs_i terms in the self-consistent HNC equations by the same choice of ϵ_i as in Eq. (7). Then the final form of βv_{eff} becomes

$$\beta v_{\text{eff}}(\vec{r}) = -c_0 \eta - \sum_i \xi_i [2f_i^R \cos(\vec{K}_i \cdot \vec{r}) - 2f_i^I \sin(\vec{K}_i \cdot \vec{r})] \ ,$$

with $\xi_i = 2\epsilon_i \lambda_i$ as defined before. The ϕ and ϕ_k functions are now defined as follows:

$$\phi(\{\xi_i\}) = \int \frac{d\vec{r}}{V} \exp \sum_i \xi_i [2f_i^R \cos(\vec{K}_i \cdot \vec{r}) - 2f_i^I \sin(\vec{K}_i \cdot \vec{r})] \ , \tag{21a}$$

$$\phi_k(\{\xi_i\}) = \int \frac{d\vec{r}}{V} [2f_k^R \cos(\vec{K}_k \cdot \vec{r}) - 2f_k^I \sin(\vec{K}_k \cdot \vec{r})] \exp \sum_i \xi_i [2f_i^R \cos(\vec{K}_i \cdot \vec{r}) - 2f_i^I \sin(\vec{K}_i \cdot \vec{r})] \ . \tag{21b}$$

Note that these forms of ϕ and ϕ_k are more complicated than those of Eqs. (8), specially in view of the fact that the new $\sin(\vec{K}_i \cdot \vec{r})$ terms have a factor f_i^I whose sign may change for RLV of same magnitudes. As expected, Eqs. (21) reduce to Eqs. (8) for $f_i^R = 1$ and $f_i^I = 0$. Integration of Eq. (18) leads to the final conditions for freezing:

$$\sum_i \frac{f_i^* f_i \xi_i^2}{2c_i} = (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right) \tag{22}$$

and

$$\mu_i \equiv \frac{f_i^* f_i \xi_i}{c_i} = (1 + \eta)\frac{\phi_i}{\phi} \ , \tag{23}$$

where η, as before, equals $\ln\phi/(1 - c_0)$. These equations explicitly exhibit the effects of the basis set. They vanish identically for $f_i = 0$ and reduce to Eqs. (11) and (12) for $f_i = 1$. Finally, one can include the three-body effects. Then Eq. (23) gets modified to the condition

$$\sum_i \frac{f_i^* f_i \xi_i^2}{2c_i} = (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right) + c_{00}^{(3)}\left(\frac{\eta^2}{2} + \frac{\eta^3}{3}\right) + \sum_i c_{i0}^{(3)} \mu_i^2 (2\eta + 1) + \frac{8}{3}\sum_i c_{i'i''}^{(3)} n_i^{(3)} \mu_i^3, \ldots, \tag{24}$$

with the usual definitions of the three-body correlations (see RY) $c_{00}^{(3)}$, $c_{i0}^{(3)}$, and $c_{i'i''}^{(3)}$. The order parameters ξ_i must be replaced by

$$x_i = \xi_i + 2c_{i0}^{(3)} \mu_i \eta + 2n_i^{(3)} c_{i'i''}^{(3)} \mu_i^2$$

in evaluating the functions ϕ and ϕ_k for Eq. (24) as discussed in detail in RY. The generalized Eqs. (21) to (24) of freezing also provide good quantitative results for the important case of hcp solids.

V. FREEZING INTO hcp SOLIDS

An important test of the generalized equations of freezing is provided by the example of monatomic liquids freezing into hcp solids. The complication of the hcp structure has often come on the way of theoretical studies of hcp solids. For example, the electronic structure of hcp metals has not yet been studied as extensively[8] as those of fcc metals although the number of elements forming hcp solids

is more than[7] the number of elements forming the equally close packed fcc solids. One of the stated goals of RY was to study the freezing into hcp solids and the generalized theory here is the appropriate approach for this study. On the other hand, this also provides a very clean test for the generalized equations because the large number of sets of RLV whose magnitudes are in the region of the second peak of S_q can easily lead to quantitative disagreement for any inaccurate theory. The density structure factors f_i effectively sort out the appropriate RLV sets and lead to the expected results.

The direct and reciprocal-lattice vectors of the hexagonal lattice are described in Sec. III C and the density structure factor for *monatomic hcp* structure is given by Eq. (16). The reciprocal-lattice vector sets, together with their (h,k,l) values, f_i^R, f_i^I, and $|K_i|^2$ are tabulated for $\beta = \sqrt{8/3}$, in the increasing order of length in Table I. The system under study is chosen to be the hard sphere fluid with $c_0 = -49.0$ and $c_{00}^{(3)} = -183.0$ for ease of comparison with known numbers. As described in RY, one should look for

TABLE I. Some sets of reciprocal-lattice vectors (RLV) of hcp lattice with the corresponding density structure factors f_i^R and f_i^I. Following Kittel (Ref. 7), we write $\vec{K} = h\vec{A} + k\vec{B} + l\vec{C}$ where $\vec{A} = (2\pi/a)(\hat{x}/\sqrt{3} + \hat{y})$, $\vec{B} = (2\pi/a)(-\hat{x}/\sqrt{3} + \hat{y})$, and $\vec{C} = (2\pi/a)(\hat{z}/\beta)$. A scaling procedure described in the text determines the form of $w_{i,\cos}$ and $w_{i,\sin}$ that are used in functions ϕ.

Set	No. of RLV	(h,k,l)	$\left[\dfrac{a}{2\pi}\right]^2 \lvert\vec{K}_i\rvert^2$	$w_{i,\cos} = \dfrac{\sum_\alpha \cos(\vec{K}_{i_\alpha}\cdot\vec{r})}{} = \sum 2\cos[h(x+y)+k(-x+y)+lz]$
1	2	(0,0,1)(0,0−1)	0.375	$2\cos z$
2	6	(1,0,0)(0,1,0)(1,−1,0)(−1,0,0) (0,−1,0)(−1,1,0)	1.333	$2(\cos 2x + 2\cos x\cos y)$
3	2	(0,0,2)(0,0,−2)	1.500	$2\cos 2z$
4	12	(1,0,1)(−1,0,1)(0,1,1)(0,−1,1) (1,−1,1)(−1,1,1)(−1,0,−1) (1,0,−1)(0,−1,−1)(0,1,−1) (−1,1,−1)(1,−1,−1)	1.708	$4\cos z\,(\cos 2x + 2\cos x\cos y)$
5	12	(1,0,2)(−1,0,2)(0,1,2)(0,−1,2) (1,−1,2)(−1,1,2)(−1,0,−2)(1,0,−2) (0,−1,−2)(0,1,−2)(−1,1,−2)(1,−1,−2)	2.833	$4\cos 2z\,(\cos 2x + 2\cos x\cos y)$
6	2	(0,0,3)(0,0,−3)	3.375	$2\cos 3z$
7	6	(1,1,0)(2,−2,0)(−1,2,0)(−1,−1,0) (−2,2,0)(1,−2,0)	4.000	$2(\cos 2y + 2\cos y\cos 3x)$
8	12	(1,1,1)(2,−2,1)(−1,2,1)(−1,−1,1) (−2,2,1)(1,−2,1)(−1,−1,−1) (−2,2,−1)(1,−2,−1)(1,1,−1) (2,−2,−1)(−1,2,−1)	4.375	$4\cos z\,(\cos 2y + 2\cos y\cos 3x)$
9	12	(1,0,3)(−1,0,3)(0,1,3)(0,−1,3) (1,−1,3)(−1,1,3)(−1,0,−3) (1,0,−3)(0,−1,3)(0,−1,−3) (0,1,−3)(−1,1,−3)(1,−1,−3)	4.708	$4\cos 3z\,(\cos 2x + 2\cos x\cos y)$
10	6	(2,0,0)(0,2,0)(2,−2,0)(−2,0,0) (0,−2,0)(−2,2,0)	5.333	$2(\cos 4x + 2\cos 2x\cos 2y)$
11	12	(1,1,2)(−1,−1,2)(2,−1,2)(−2,1,2) (1,−2,2)(−1,2,2)(−1,−1,2)(1,1,−2) (−2,1,−2)(2,−1,−2)(−1,2,−2) (1,−2,−2)	5.500	$4\cos 2z\,(\cos 2y + 2\cos y\cos 3x)$
12	12	(2,0,1)(−2,0,1)(0,2,1)(0,−2,1) (2,−2,1)(−2,2,1)(−2,0,−1)(2,0,−1) (0,−2,−1)(0,2,−1)(−2,2,−1)(2,−2,−1)	5.708	$4\cos z\,(\cos 4x + 2\cos 2x\cos 2y)$

TABLE I (*Continued*).

f_i^R	$\sum_\alpha \sin(\vec{K}_{i_\alpha} \cdot \vec{r}) P_{i\alpha}$ $w_{i,\sin} = \sum_i \pm \sin[h(x+y)+k(-x+y)+lz]$	f_i^I	Comments
0	$2\sin z$	0	Ineffective due to $f_i = 0$
1/4	$2(\sin 2x - 2\sin x \cos y)$	$\sqrt{3}/4$	(a) Two dimensional (b) Length too small (c) No solution
1	$2\sin 2z$	0	(a) One dimensional (b) Length too small (c) No solution
3/4	$4\cos z(-\sin 2x + 2\sin x \cos y)$	$\sqrt{3}/4$	(a) Correct length (b) First o.p. (c) Reasonable solution
1/4	$4\cos 2z(\sin 2x - 2\sin x \cos y)$	$\sqrt{3}/4$	(a) Too long to be first set (b) Too small to be second set (c) "Reasonable solution"
0	$2\sin 3z$	0	Ineffective due to $f_i = 0$
1	$2(\sin 2y + 2\sin y \cos 3x)$	0	(a) Two dimensional (b) Too small to be second set
0	$4\cos z(\sin 2y + 2\sin y \cos 3x)$	0	Ineffective due to $f_i = 0$
3/4	$4\cos 3z(-\sin 2x + 2\sin x \cos y)$	$\sqrt{3}/4$	(a) Too small to be second set (b) No good solution
1/4	$2(-\sin 2x + 2\sin 2x \cos 2y)$	$\sqrt{3}/4$	(a) Two dimensional (b) No good solution
1	$4\cos 2z(\sin 2y + 2\sin y \cos 3x)$	0	Good to be second set
3/4	$4\cos z(\sin 4x - 2\sin 2x \cos y)$	$\sqrt{3}/4$	(a) Good second set (b) Gives good solution together with set 11.

the set of shortest RLV to choose the first order parameter. However, $f_i = 0$ for set 1 in Table I. Then, one would naturally examine set 2 which is only two dimensional. In fact, this set was used for freezing of hard disks in RY yielding a solution of $c_j = 0.86$ and $\eta = 0.013$ in the one order-parameter approximation. The same solution would have appeared here without the generalized equations.

The generalized equations lead to no solution for

set 2 for hcp. Some details of the computational procedure are as follows. The functions ϕ and ϕ_k of Eqs. (21) are evaluated for given values of ξ_j. The integrations are over the primitive cell which now contains two atoms and whose volume would appear in the denominators. Some odd factors can be scaled out (for example, the $\sqrt{3}$ associated with the x component and the β associated with the z component do not appear in the final formulas). Then one gets

$$\phi = \pi^{-3} \int_0^\pi dx \int_0^\pi dy \int_0^\pi dz \exp \sum_i \xi_i (f_i^R w_{i,\cos} - f_i^I w_{i,\sin}) \tag{25a}$$

and

$$\phi_j = \pi^{-3} \int_0^\pi dx \int_0^\pi dy \int_0^\pi dz \frac{(f_j^R w_{j,\cos} - f_j^I w_{j,\sin})}{n_j} \exp \sum_i \xi_i (f_i^R w_{i,\cos} - f_i^I w_{i,\sin}) \ . \tag{25b}$$

Here, it is assumed that there are n_j vectors of the same magnitude in the RLV set $\{\vec{K}_j\}$. Let these vectors be designated as $\vec{K}_{j\alpha}$, $\alpha = 1, 2, \ldots, n_j$. Then the quantity $w_{j,\cos} = \sum_{\alpha=1}^{n_j} \cos(\vec{K}_{j\alpha} \cdot \vec{r})$ where $\vec{r}$ has been properly scaled. In fact, for hcp, one has $(\vec{K}_{j\alpha} \cdot \vec{r}) = h(x+y) + k(-x+y) + lz$. So far, the procedure is analogous to that described in RY. But the sine summation here needs special care because $f_{j\alpha}^I$ may change sign with α (although $f_{j\alpha}^R$ remains the same for all α). Let $P_{j\alpha}$ be the sign of $f_{j\alpha}^I$. Then $w_{j,\sin} = \sum_{\alpha=1}^{n_j} P_{j\alpha} \sin(\vec{K}_{j\alpha} \cdot \vec{r})$. Table I contains the expressions for $w_{j,\cos}$ and $w_{j,\sin}$ for the different sets of RLV. In the one order-parameter approximation, one chooses a value for ξ_j, evaluates ϕ, ϕ_j, and η. Assuming that the minimum condition of Eq. (23) is satisfied, one tests the equality of thermodynamic potentials in the two phases by using Eq. (22) [or Eq. (24) when the three-body effects are included]. This search continues by changing ξ_j values and a solution may or may not exist corresponding to a given RLV set $\{\vec{K}_j\}$. It does not exist fo the RLV set 2.

The fact that no solution is found for the RLV set 2 in the one parameter approximation is an expected result which also shows the validity of the generalized equations. The essential argument is that the hard sphere fluid could also freeze into a fcc structure with a lattice constant of $\sqrt{2} a$ (a is the lattice constant for hcp lattice). Then the smallest RLV set would correspond to about $(a/2\pi)^2 |K_j|^2 \rangle 1.5$ in Table I. Therefore, the magnitudes of RLV sets 1, 2, or 3 do not correspond to the position of the first peak position of the structure factor and these RLV sets cannot provide the first order parameter. This conjecture is borne out by the generalized equations. The RLV set 1 is ineffective due to $f_i = 0$ and the sets 2 and 3 give no solution. The one order-parameter approximation corresponding to RLV set 4 yields a solution that is tabulated as theory I in Table II. This is comparable to the one order-parameter solution for fcc case

where $c_j \simeq 0.96$ and $\eta = 0.029$ (see RY, Table II). The present values of both these quantities are better than those for fcc implying a possible preference for hcp freezing.

The RLV set 5 was also tried as corresponding to first order parameter and yields a reasonable solution as shown in theory III of the Table II. However it is unacceptable because (a) its magnitude is too large, (b) it does not combine with a proper second order-parameter set, and (c) the previous set has the proper magnitude and combines perfectly well with a second set to give the two order parameter approximation (see below). This establishes set 4 as the set for the first order parameter and now one can search for the set of RLV that would correspond to the second order parameter. The systematic procedure can be followed to test all the subsequent sets as the set for the second order parameter and the results are shown as theorys IV, V, VI, and VII of Table II, for which solutions exist. But Table I shows the interesting fact that the RLV sets 11 and 12 have magnitudes very close to each other so that both of these together should correspond to the second order parameter. Also, their magnitudes lie very close to the position of the second peak of the structure factor. The result of assigning the same order parameter for the 24 vectors of sets 11 and 12, is shown as theory VIII in Table II and inclusion of $c_{00}^{(3)}$ term gives theory IX of Table II. In fact, one could have tabulated theory I, VIII, and IX only as logical conclusions drawn from the magnitudes of RLV and the structure factor curve. The satisfactory solution found with the proper two order-parameter theory represents the solution to the problem of hcp freezing. It must be remarked that the small value of η can be improved to agree with experiment if a small positive $c_{i0}^{(3)}$ is introduced.

In conclusion, it may be stated that all freezing transitions can be described by using the structural

TABLE II. Freezing parameters for hard sphere hcp freezing. Here η denotes the fractional density change, c_j and c_n are structure factors c_q ($=1-S_q^{-1}$) corresponding to $q=|\vec{K}_j|$ and $q=|\vec{K}_n|$, respectively. The reciprocal-lattice vector (RLV) sets $\{\vec{K}_j\}$ and $\{K_n\}$ are designated according to the labels described in Table I.

Description	c_j	c_n	η	ξ_j	$\{\vec{K}_j\}$ set label	ξ_n	$\{\vec{K}_n\}$ set label
Theory I: One order parameter	0.93	...	0.032	0.57	4	...	...
Theory II: One order parameter with $c_{00}^{(3)} = -183.0$	0.91	...	0.018	0.43	4	...	...
Theory III: One order parameter	0.91	...	0.040	1.11	5	...	...
Theory IV: Two order parameters	0.91	0.19	0.033	0.58	4	0.08	10
Theory V: Two order parameters	0.82	0.28	0.055	0.66	4	0.14	11
Theory VI: Two order parameters with $c_{00}^{(3)} = -183.0$	0.80	0.30	0.053	0.64	4	0.15	11
Theory VII: Two order parameters	0.84	0.30	0.052	0.66	4	0.15	12
Theory VIII: Two order parameters	0.67	0.31	0.070	0.59	4	0.19	11 and 12 together
Theory IX: Two order parameters with $c_{00}^{(3)} = -183.0$	0.64	0.28	0.05	0.51	4	0.15	11 and 12 together
Experiment	0.65	0.29	0.10	...	...	...	...

correlations in the liquid instead of the pair potential. The generalized equations of freezing presented here describe in general the phenomena of freezing into solids with a basis set of many atoms per unit cell. The density structure factor accounts for the effect of the basis set and yields good quantitative agreement with known results. The approach of using structural correlations avoids the usual difficulties with manipulations involving two-body potentials with large repulsive cores. It also avoids the difficulties associated with formulation of many-body forces in fluids. This is important because at least three-body forces must be introduced in understanding the various nearest-neighbor coordination numbers. Indeed, there are evidences for the important role played by three-body interactions in systems with long-range and short-range orders.[9,10]

The present theory enables one to easily study the role of three-body correlations in the phenomena of freezing. The conclusion is that every liquid should freeze into a bcc structure if three-body correlation is attractive ($c_{\parallel}^{(3)}$ is negative). The other extreme of very strongly repulsive three-body correlation would yield a simple cubic structure which is not found in nature. Weakly repulsive three-body correlations would produce hcp structures and very weak three-body correlations imply fcc structure. In fact, these two close packed structures appear to have a small dividing line in terms of three-body correlations so that slight changes in three-body forces can possibly bring about changes from hcp structure to the fcc structure and vice versa. These conclusions appear to be close to the observed facts. Therefore, it is fair to state that the present theory of freezing helps in understanding the effects of three-body forces in the formation of solids besides yielding quantitative results for the freezing parameters.

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[1]T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B 19, 2775 (1979). Other important references are cited there.
[2]J. P. Hansen and L. Verlet, Phys. Rev. 184, 150 (1969).
[3]L. Verlet, in Statistical Mechanics, edited by K. Freed and J. C. Light (University of Chicago, Chicago, 1974).
[4]M. Yussouff, in Recent Developments in Condensed Matter Physics (Plenum, New York, 1981).

[5]K. C. Ng, J. Chem. Phys. 61, 2680 (1974).
[6]See, for example, M. Luben, in Phase transitions and Critical Phenomena, edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 5A.
[7]C. Kittel, Introduction to Solid State Physics (Wiley, New York, 1971).
[8]M. Yussouff and R. Zeller, J. Phys. F (in press).
[9]See, for example, F. A. Khwaja (unpublished).
[10]W. A. Harrison, Phys. Rev. B 7, 2408 (1973).