First-principles order-parameter theory of freezing

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A first-principles order-parameter theory of the fluid-solid transition is presented in this paper. The thermodynamic potential Ω of the system is computed as a function of order parameters $\lambda_i (= \lambda_{\vec{K}_i})$ proportional to the lattice periodic components of the one-particle density $\rho(\vec{r})$, $\vec{K}_i$'s being the reciprocal-lattice vectors (RLV) of the crystal. Computation of $\Omega(\{\lambda_i\})$ is shown to require knowing Ω for a fluid placed in lattice periodic potentials with amplitudes depending on λ_i. Using systematic nonperturbative functional methods for calculating the response of the fluid to such potentials, we find $\Omega(\{\lambda_i\})$. The fluid properties (response functions) determining it are the Fourier coefficients c_i ($= c_{\vec{K}_i}$)and c_o ($= c_{\vec{q} = 0}$) of the direct correlation function $c(\vec{r})$. The system freezes when at constant chemical potential μ and pressure P, locally stable fluid and solid phases [i.e., minima of $\Omega(\{\lambda_i\})$ with $\{\lambda_i\} = 0$ and $\{\lambda_i\} \neq 0$, respectively] have the same Ω. The order-parameter mode most effective in reducing $\Omega(\{\lambda_i\})$ corresponds to $\vec{K}_j$ being of the smallest-length RLV set ($c_{\vec{q}}$ is largest for $|\vec{q}| \simeq |\vec{K}_j|$). In some cases one has to consider a second order parameter λ_n with a RLV $\vec{K}_n$ lying near the second peak in $c_{\vec{q}}$. The effect of further order-parameter modes on Ω is shown to be small. The theory can be viewed as one of a strongly first-order density-wave phase transition in a dense classical system. The transition is a purely structural one, occurring when the fluid-phase structural correlations (measured by c_j, etc.) are strong enough. This fact has been brought out clearly by computer experiments but had not been theoretically understood so far. Calculations are presented for freezing into some simple crystal structures, i.e., fcc, bcc, and two-dimensional hcp. The input information is only the crystal structure and the fluid compressibility (related to c_o). We obtain as output the freezing criterion stated as a condition on c_j or as a relation between c_j and c_n, the volume change V, the entropy change Δs, and the Debye-Waller factor at freezing for various RLV values. The numbers are all in very good agreement with those available experimentally.

I. INTRODUCTION

Freezing is a basic physical phenomenon, the most inevitable of all phase changes. All substances freeze into either a crystalline or a glassy phase under suitable conditions of pressure and temperature. We describe in this paper a microscopic structural theory of the classical-fluid–crystalline-solid transition.[1] To begin with, we summarize some salient common features of this transition brought out by experiments[2] and by computer experiments.[3-5] These have not been theoretically understood so far. We then mention briefly other earlier attempts at a theory of melting or freezing.[6-14] Our approach is then introduced and is developed in succeeding sections of this paper; numerical calculations for freezing into simple structures are also presented.

The fact that a system, if sufficiently dense, probably[15] freezes into a crystalline solid has been brought out by computer experiments.[3,16,17] Starting from the unexpected phenomenon of hard-sphere solidification (Alder and Wainwright[17]) the fluid-solid transition has been found to take place for all classical monatomic systems with purely repulsive two-body potentials $V(r) = A(r/a)^{-n}$, where n ranges from infinity (hard sphere) to unity (one-component plasma).[18] The transition continues to exist of course if there is an attractive term

additionally present.[3,4]

Evidence for the geometrical nature of the transition is provided by the structural similarity of dense classical fluids.[19,20] The structure factor $S(q)$ curves (see Fig. 1, for example) are very similar, and can be simulated by the hard-sphere structure factor[21] (calculated, for example, in the Percus-Yevick approximation[22]). The main differences between $S(q)$ for various liquids are seen for small and large values of q. For intermediate values of q, the only scale seems to be q_m, the value of q at the highest (first) peak in $S(q)$, which depends on density. $S(q/q_m)$ curves for dense fluids near freezing are nearly identical in this range. Verlet[4,20] observed that near freezing, $S(q_m)$ is nearly 2.85 for all classical fluids. Computer results for the Lennard-Jones[6-12] liquid along the melting curve,[4] for the hard-sphere fluid,[23] the one-component plasma,[24] and experimental results for Ar,[25] Na,[26] Rb,[27] Pb,[28] all show $S(q_m)$ to be between 2.8 and 3.1 near freezing. The $S(q_m)$ values for fluids freezing into fcc and bcc structures cluster around 2.8 and 3.0, respectively. In the solid phase, the analogue of Verlet's rule is perhaps the Lindemann criterion of melting,[6] i.e., the criterion that the mean-square displacement $\langle u^2 \rangle$ scaled by the square of the interatomic separation r_{int}^2 has nearly a constant value (0.01).[29]

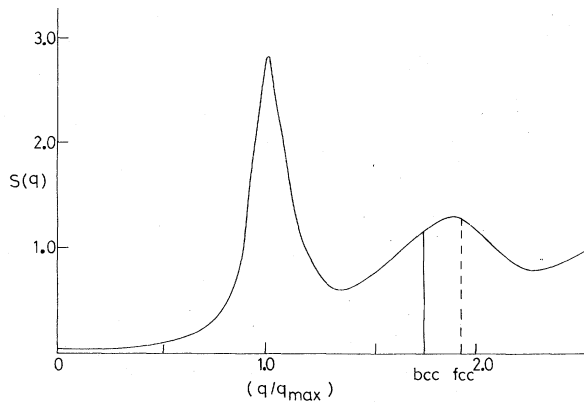The freezing parameters of simple fluids are

FIG. 1. $S(q)$ of a monoatomic liquid near freezing, with q in units of q_{max} which is the position of the first peak. q_{max} is identified with $|\vec{K}_j|$, the smallest reciprocal-lattice vector of the solid formed after freezing. The dominant order parameter corresponds to the density fluctuation mode with wave vector $\vec{K}_j$. The second order parameter corresponds to a mode with wave vector $\vec{K}_n$. $|\vec{K}_n|_{bcc}/q_{max}$ and $|\vec{K}_n|_{fcc}/q_{max}$ are shown in the figure as full and broken lines, respectively.

closely related.[2,3,5] For example, Stishov has shown from the pressure dependence of the freezing parameters of argon that they tend to those of an r^{-12} fluid (studied on a computer). Longuet-Higgins and Widom[30] showed (see also Rowlinson[31] and Rosenfeld[32]) that the freezing parameters of argon at various pressures can be obtained from those of a hard-sphere fluid by adding a Van der Waals like term to the computer experimental free energy.

There are of course freezing parameters which vary widely from system to system. Examples are the melting temperature T_m and the volume change at freezing. However, the variation of the former is largely due to that of the interatomic potential strength, and disappears if the freezing condition is expressed as a structural condition of the fluid [$S(q_m) \simeq 2.85$, Verlet's rule]. The variation in volume change is primarily due to that in compressibility and its density dependence, which is affected for example by the attractive tail in the two-body potential. The entropy change Δs at freezing also shows considerable variation, although for many monatomic systems it has nearly the value $k_B \ln 2$ per atom after the part $(\Delta s)_v$ due solely to volume change, is separated out.

We now describe briefly the theoretical situation. Many of the theoretical approaches are not quantitative, and at best derive conditions for the transition to take place. Very few can be pushed so far as to calculate freezing parameters. None can explain the underlying unity of the freezing phenomenon mentioned above, nor of course the variety in

some freezing parameters. It is fair to say that much of the information and insight gained in this field comes from computer experiments.

The first important contribution to the melting problem is due to Lindemann[6] whose melting criterion has been mentioned above. It is a criterion for the absolute instability of the solid phase, obtainable also as a shear instability criterion in a self-consistent phonon theory.[33] It can be used for calculating T_m if $\langle u^2 \rangle$ is known. Obviously, this temperature need not (and for a first-order transition such as melting, will not) correspond to that for the relative stability of the solid vis a vis the fluid. A straightforward approach for locating T_m is to calculate the fluid and solid free energies and to equate them. There are very few systems for which this can be done accurately enough [Ref. 34 describes a calculation for Na where a $T_m(P)$ curve is obtained]. Clearly this approach yields no insight into the freezing phenomenon, and many parameters cannot be calculated. Lennard-Jones and Devonshire[8] proposed a cell-like model for fluids which for certain model parameters, and with additional short-range correlation between cells,[35] is capable of reproducing reasonably well the first-order liquid solid transition in, for example, argon. The precise relation between this model (and its parameters) and a real fluid is not clear. In the dislocation model,[11,14] the solid is assumed to melt when it becomes unstable with respect to spontaneous generation of dislocations. This local instability criterion has been discussed recently by Thouless and Kosterlitz[14] for the two-dimensional case, and by Edwards.[36] A detailed computer analysis of this approach is due to Jensen et al.[37]

In the pioneering work of Kirkwood and Monroe,[9] an equation for the density $\rho(\vec{r})$ is obtained by considering one particle of the system whose coupling to the $N-1$ other particles is turned on to full strength as the coupling parameter $\xi \to 1$. The equation for $\rho(\vec{r})$ involves the interatomic potential $u(\vec{r} - \vec{r}')$, the density $\rho(\vec{r}')$ and the two-particle correlation function $g(\vec{r}, \vec{r}', \xi)$ for all ξ. Kirkwood and Monroe found solidlike solutions for $\rho(\vec{r})$ below a certain temperature, [i.e., $\langle \rho_i \rangle = \langle \rho_{\vec{K}_i} \rangle$ $= \langle \int \rho(\vec{r}) e^{i\vec{K}_i \cdot \vec{r}} d\vec{r} \rangle$ is of order N]. They discussed objections to the use of one-particle density to characterize the solid state.[38] Their theory has however four major difficulties, namely, the following: (i) The interatomic potential $u(\vec{r})$ is used explicitly and thus the theory cannot explain the underlying unity of the freezing phenomenon. (ii) Neither the nature of their approximation [e.g., $g(\vec{r}, \vec{r}', \xi) = g(\vec{r} - \vec{r}')_{liquid}$] nor the effect of these approximations on the results obtained is clear. (iii) The phase transition obtained by them for Ar (fcc) is close to second order. (iv) The numerical re-

sults obtained by them are poor. No significant progress in formulating a fundamental theory of freezing along this line has been made since then, though there have been some attempts.[12,13]

In this paper we first formulate the liquid solid transition problem as an order-parameter theory, i.e., we show how the thermodynamic potential Ω can be projected on to the order-parameter space $\{\lambda_i\}$ (related to $\{\rho_i\}$) and define the function $\Omega(\{\lambda_i\})$ (Sec. II). We show there that $\Omega(\{\lambda_i\})$ can be found through the calculation of the density $\langle \rho(\vec{r}) \rangle$ of a fluid in presence of lattice periodic potentials with partial amplitudes dependent on $\{\lambda_i\}$. In Sec. III systematic functional approximation methods are applied to find $\langle \rho(\vec{r}) \rangle$. For the oscillatory, moderately strong potential at hand, the scheme appropriate is formally similar to the hypernetted chain (HNC) approximation used in the theory of fluid two-particle correlation function. The first term in the functional Taylor series is the dominant term and for completeness (also because it is significant in some cases) the second term is discussed in the Appendix. In Sec. IV the analytical expressions for Ω and for freezing parameters are derived. The physical meaning of our result for $\Omega(\{\lambda_i\})$ and the freezing mechanism implied are discussed in this section. Calculations for freezing parameters are presented in Sec. V. We first analyze the question of the dominant order-parameter modes, and then describe computations for fcc, bcc, and two-dimensional hcp structures. The results are shown to be stable with respect to the inclusion of other order-parameter modes, and are in excellent agreement with experiment and computer experiment where these results are available. In addition, we are able to explain the structural unity of the phenomenon, and obtain freezing criteria similar to that of Verlet. We also present results for the Debye-Waller factor of the crystal structures studied. In Sec. VI we discuss two objections commonly raised against a theory of this type, namely that order-parameter fluctuation effects are not included and that the lattice periodic component of the density is not a good order parameter. We then mention some open problems and applications of our approach.

II. PARTITION FUNCTION AND THE ORDER-PARAMETER APPROACH

We describe here a method of obtaining an order-parameter expression for the thermodynamic potential Ω. Consider a classical system with volume V, and N particle Hamiltonian H_N. The grand partition function Z_G is given by

$$Z_G = e^{-\beta\Omega} = \text{Tr}\{\exp[-\beta(H_N - \mu N)]\}, \qquad (1a)$$

where the trace is over the momenta and coordinates of the N particles, and over N. Also, $\beta = 1/k_B T$ and μ is the chemical potential. The system is in the crystalline solid phase if the equilibrium density $\langle \rho(\vec{r}) \rangle$ has lattice periodic components, and in the fluid phase if $\langle \rho(\vec{r}) \rangle$ is independent of $\vec{r}$. Here the density operator for an N-particle system is $\rho(r) = \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_j)$ with Fourier transform $\rho_{\vec{q}}^* = \sum_{j=1}^{N} \exp(i\vec{q} \cdot \vec{r}_j)$ representing the density fluctuation operator with wave vector $\vec{q}$. If the reciprocal lattice vectors of the crystalline solid are $\vec{K}_i$, $\langle \rho_{\vec{K}_i} \rangle \equiv \langle \rho_i \rangle = O(\overline{N})$ for the solid. Here $\overline{N}$ is the average of N over the grand canonical ensemble. In the fluid $\langle \rho_i \rangle$ as well as $\langle \rho_{\vec{q}}^* \rangle$ for any $\vec{q}$, vanish. Because of this difference, we express and examine Ω as a function of order-parameter quantities $\{\lambda_i\}$ related to $\langle \rho_i \rangle$. Ideally, one would like to predict transitions from the fluid without prior specification of the other phase. However, we examine here the transition from the fluid to specific crystalline phases (e.g., fcc, bcc). This makes the theoretical development precise, and enables us to reliably compute other freezing parameters which can be compared with experimental results for these structures.

The order parameters λ_i are defined and introduced as follows. Consider the normalized Gaussian

$$\int \exp(-|\lambda_i - \epsilon_i \rho_i|^2)\left(\frac{d\lambda_i}{\pi}\right) = 1,$$

where since λ_i and ρ_i are complex (ϵ_i is a real constant, with a value chosen later) we integrate from $-\infty$ to $+\infty$ over the real and imaginary parts λ_i^R and λ_i^I of λ_i. It is identically true that

$$\exp(-\beta\Omega) = \text{Tr}\left\{\int \cdots \int \prod_i \left(\frac{d\lambda_i}{\pi}\right)\right.$$
$$\times \exp(-|\lambda_i - \epsilon_i \rho_i|^2) \qquad (1b)$$
$$\left. \times \exp[-\beta(H_N - \mu N)]\right\}.$$

If in Eq. (1b) the order of taking the trace and of integration over λ_i's is interchanged, we have

$$\exp(-\beta\Omega) = \int \cdots \int \prod_i \left(\frac{d\lambda_i}{\pi}\right)$$
$$\times \exp[-\beta\Omega(\{\lambda_i\})], \qquad (2a)$$

where

$$\exp[-\beta\Omega(\{\lambda_i\})] = \text{Tr}\left[\exp\left(-\sum_i |\lambda_i - \epsilon_i \rho_i|^2 \right.\right.$$
$$\left.\left. - \beta(H_N - \mu N)\right)\right]. \qquad (2b)$$

We now argue that $\Omega(\{\lambda_i\})$ is the desired order-parameter expression. To see this, consider the

quantity

$$\epsilon_k \langle \rho_k \rangle = \exp(\beta\Omega) \mathrm{Tr}\left\{\epsilon_k \rho_k \exp[-\beta(H_N - \mu N)]\right\}.$$

(3a)

Again we introduce the Gaussians as in Eq. (1b), and interchange the order of integration over $\{\lambda_i\}$ with that of taking the trace. We then write $\epsilon_k \rho_k \exp(\lambda_k^* \epsilon_k \rho_k)$ as $(\partial/\partial\lambda_k^*)\exp(\lambda_k^* \epsilon_k \rho_k)$ and integrate over λ_k^* by parts. We then find that

$$\epsilon_k \langle \rho_k \rangle = \exp(\beta\Omega) \int \cdots \int \prod_i \left(\frac{d\lambda_i}{\pi}\right)\lambda_k$$

$$\times \exp[-\beta\Omega(\{\lambda_i\})]$$

$$= \langle \lambda_k \rangle.$$

(3b)

Thus, $\langle \rho_k \rangle$ is, apart from a scale factor ϵ_k, the expectation value $\langle \lambda_k \rangle$ of λ_k in the $\{\lambda_i\}$ ensemble, where the statistical mechanical probability of the system having a given set of values $\{\lambda_i\}$ is given by $\rho(\{\lambda_i\}) = \exp(\beta\Omega)\exp[-\beta\Omega(\{\lambda_i\})]$. This justifies our identification $\Omega(\{\lambda_i\})$ as the order-parameter expression needed. Defining a tempered density matrix

$$\rho_{\{\lambda_i\}} = \exp\left(-\sum_i |\lambda_i - \epsilon_i \rho_i|^2 - \beta(H_N - \mu N)\right)$$

(4a)

the expectation value of a general operator O is given by

$$\langle O \rangle = \left[\int \cdots \int \mathrm{Tr}(\rho_{\{\lambda_i\}}O) \prod_i \left(\frac{d\lambda_i}{\pi}\right)\right]$$

$$\times \left\{\left[\int \cdots \int \left(\prod_i \frac{d\lambda_i'}{\pi}\right)\mathrm{Tr}\rho_{\{\lambda_i'\}}\right]\right\}^{-1}.$$

(4b)

The general order-parameter strategy is to calculate $\Omega(\{\lambda_i\})$ using Eq. (2b), whence $\langle \rho_k \rangle$ can be obtained from Eq. (3b). For other physical quantities, Eq. (4) is needed. There is great simplification if $\Omega(\{\lambda_i\})$ has minima (as it must have for a stable system). First, we note that the natural scale of λ_i is $O(\overline{N}^{1/2})$ since $\langle \rho_i \rangle$ is $O(\overline{N})$ and we will choose ϵ_i of order $(\overline{N})^{-1/2}$. Suppose the minima of $\Omega(\{\lambda_i\})$ are at $\{\lambda_i\} = \{\lambda_i^m\}$. $\{\lambda_i^m\} \equiv 0$ obviously corresponds to a fluidlike phase (this is always present for $c_i < 1$) whereas $\{\lambda_i^m\} \neq 0 = O(\sqrt{N})$ describes a crystalline solidlike minimum. Now because the scale of $\{\lambda_i\}$ is $O(\sqrt{N})$, the probability distribution $\Omega(\{\lambda_i\})$ is very sharply peaked around the minima, with a relative width of order $(\overline{N})^{-1/2}$. Further, since the $\Omega(\{\lambda_i^m\})$ for different minima will in general differ by a quantity of order $\overline{N}$, $\Omega(\{\lambda_i^m\})$ for the lowest minimum $\{\lambda_i^{lm}\}$ will exceed that of other minima by an overwhelming factor of order $\exp(\overline{N})$. Therefore, in Eq. (3), expanding $\rho(\{\lambda_i\})$ around the minima, and retaining only the contribution from the lowest minimum, we find to relative accuracy $\overline{N}^{-1}$, that

$$\epsilon_k \langle \rho_k \rangle = \lambda_k^{lm}.$$

(5a)

Using the same argument in Eq. (4b), we have

$$\langle O \rangle = \langle O \rangle_{\{\lambda_i^{lm}\}}.$$

(5b)

Thus, one calculates $\Omega(\{\lambda_i\})$ and locates its lowest minimum. If this occurs with $\{\lambda_i^{lm}\} \equiv 0$, it is clear from Eq. (5a) that the stable phase is a fluid. On the other hand, if it is for $\{\lambda_i^{lm}\} \neq 0$, the system is a crystalline solid. As the appropriate system variables are changed, the lowest minimum of $\Omega(\{\lambda_i\})$ can be expected to shift from that corresponding to a fluid to that for a solid. The freezing transition occurs when there is both a fluidlike and a solidlike minimum and the two have the same thermodynamic potential, i.e., $\Omega(\{\lambda_i^m\} \equiv 0) = \Omega(\{\lambda_i^{lm}\} \neq 0)$. Physical properties of the two phases, and hence the freezing parameters can be obtained through Eq. (5).

We now discuss the actual method for calculating $\Omega(\{\lambda_i\})$, defined in Eq. (2b). Clearly, if the expectation values $\langle \rho_i \rangle_{\{\lambda_i\}}$ of interest are $O(\overline{N})$, we can write the exponent of the Gaussian, to a relative accuracy $O(\overline{N}^{-1})$ as

$$-\sum |\lambda_i - \epsilon_i \rho_i|^2 = \sum_i \left[-\lambda_i^{I^2} - \lambda_i^{R^2} + \epsilon_i^2 |\langle \rho_i \rangle_{\{\lambda_i\}}|^2\right.$$

$$\left. + (2\epsilon_i \lambda_i^R - 2\epsilon_i^2 \langle \rho_i \rangle_{\{\lambda_i\}})\rho_i\right],$$

(6)

where $\langle \rho_i \rangle_{\{\lambda_i\}}$ is $\langle \rho_i \rangle$ evaluated for a given set of $\{\lambda_i\}$. In the right-hand side of Eq. (6), we have assumed $\langle \rho_i \rangle_{\{\lambda_i\}} = \langle \rho_i^* \rangle_{\{\lambda_i\}} \equiv \langle \rho_{-i} \rangle_{\{\lambda_i\}}$ (true for any centrosymmetric crystal) and therefore take $\lambda_i = \lambda_{-i}$ as well as $\epsilon_i = \epsilon_{-i}$. It is clear from Eq. (6) that $\rho(\{\lambda_i\})$ depends independently on λ_i^I and on λ_i^R and is a Gaussian of width $O(\overline{N}^{-1/2})$ centered around zero for the former. We can take $\lambda_i^I = 0$, and λ_i is purely real. For brevity, we write $\lambda_i^R = \lambda_i$. Substituting in Eq. (3), we see that

$$\exp[-\beta\Omega(\{\lambda_i\})]$$

$$= \exp\left[\sum_i (-\lambda_i^2 + \epsilon_i^2 |\rho_i \rangle_{\{\lambda_i\}}|^2)\right]$$

$$\times \mathrm{Tr}\left(\exp[-\beta(H_N - \mu N)\right.$$

$$\left. + \sum_i 2(\epsilon_i \lambda_i - \epsilon_i^2 \langle \rho_i \rangle_{\{\lambda_i\}})\rho_i]\right).$$

(7)

Thus

$$\Omega(\{\lambda_i\}) = k_B T \sum_i (\lambda_i^2 - \epsilon_i^2 |\langle \rho_i \rangle_{\{\lambda_i\}}|^2)$$

plus the thermodynamic potential of a fluid in a periodic potential

$$v(\vec{r}) = k_B T \sum_i 2(\epsilon_i^2 \langle \rho_i \rangle_{\{\lambda_i\}} - \epsilon_i \lambda_i) e^{i\vec{K}_i \cdot \vec{r}} . \qquad (8)$$

The system has not actually been placed in an external periodic potential, but the above interpretation of $\Omega(\{\lambda_i\})$ enables us to calculate it. To compute $\Omega(\{\lambda_i\})$, we use the general result

$$-\frac{\partial}{\partial \lambda_k} \left(\beta \Omega(\{\lambda_i\}) - \sum_i \lambda_i^2 \right) = 2 \epsilon_k \langle \rho_k \rangle_{\{\lambda_i\}} , \qquad (9)$$

which can be obtained by differentiation from Eq. (7). Thus, if we calculate $\langle \rho_k \rangle_{\{\lambda_i\}}$ or the average density $\langle \rho(\vec{r}) \rangle$ for a given $\{\lambda_i\}$ [that is, from Eq. (8), for a given $v(\vec{r})$] and integrate with respect to $\{\lambda_i\}$, we can obtain $\Omega(\{\lambda_i\})$. Thus, the technical problem is one of calculating $\langle \rho(\vec{r}) \rangle$ for a given one-body potential $v(\vec{r})$ acting on the fluid (Sec. III).

We point out an important general feature here. In the classical system at hand, one can always write $\langle \rho(\vec{r}) \rangle \propto \exp[-\beta v_{\text{eff}}(\vec{r})]$, where $v_{\text{eff}}(\vec{r}) = v(\vec{r}) + v_{\text{resp}}(\vec{r})$, $v_{\text{resp}}(\vec{r})$ being the response potential of the system. We shall calculate $v_{\text{resp}}(\vec{r})$ as a functional of the density change $[\langle \rho(\vec{r}) \rangle - \rho_0]$ of the system (Sec. III). Now at the minimum of $\Omega(\{\lambda_i\})$, we have $\epsilon_k \langle \rho_k \rangle_{\{\lambda_i\}} = \lambda_k^m$ [Eq. (5a)], and thus the "external" potential $v(r)$ [see Eq. (8)] is zero. If $v_{\text{resp}}(\vec{r}) \neq 0$, one has a self-consistently stable system with lattice periodic density components, i.e., a crystalline solid. We emphasize that at the minima, there is *no* "external" periodic potential, so that $P(\{\lambda_i^{lm}\})$, $\langle \rho_k \rangle_{\{\lambda_i^{lm}\}}$, etc., describe the actual system and not an artificial or metastable construct. Our approach enables us to locate the $\{\lambda_i^{lm}\}$'s for which this occurs, and to calculate physical properties of the system so specified.

It is also clear that since $v_{\text{eff}}(\vec{r}) = 0$ at the transition point, the criterion obtained would involve properties of the actual fluid. In Sec. VI we show that to fix the phases of $\langle \rho_k \rangle$, an additional "box confining" potential is needed. But its effect on the physical properties is in the ratio of surface to volume and hence vanishes in the thermodynamic limit.

III. FLUID IN A PERIODIC POTENTIAL AND $\langle \rho(\vec{r}) \rangle$

The calculation of density $[\langle \rho(\vec{r}) \rangle]$ when a potential field is present is a standard problem in the theory of liquids. It occurs for example in the calculation of the two particle correlation function.[16] If one of the particles is fixed at $r = 0$, and the two body potential $\sum_{i=1}^{N-1} u(\vec{r}_i, 0)$ is regarded as an external potential, $\int v(\vec{r}) \rho(\vec{r}) d\vec{r}$, the resulting $\langle \rho(\vec{r}) \rangle$ is just the two-body (density) correlation function $g(\vec{r})$ for the separation $\vec{r}$. The approximation methods used in this case can be systematized in a functional scheme.[40] The Percus-Yevick approximation results when $[\langle \rho(\vec{r}) \rangle e^{\beta v(\vec{r})} - \rho_0]$ is expanded

as a functional of density change $\langle \rho(\vec{r}') \rangle - \rho_0$ and the first term in the functional Taylor series is retained. The HNC approximation corresponds to expanding $\ln[\langle \rho(\vec{r}) \rangle e^{\beta v(\vec{r})} / \rho_0]$ as a functional power series of $\langle \rho(\vec{r}) \rangle - \rho_0$. The functional approach has the advantage of being systematic, in that (at least in principle, and to some extent in practice) the higher-order terms in the functional Taylor series expansion can be retained and their effect can be evaluated. However, obviously, it is highly desirable to have the first term as the leading one. This brings one to the question of the choice of a suitable (functional) approximation scheme.

Experience shows that the Percus-Yevick scheme gives good results for $g(\vec{r})$ if the interatomic potential is of short range and varies rapidly with distance, as in the case of hard spheres or argon.[16,24] On the other hand, the HNC represents $g(\vec{r})$ very well for the classical one-component plasma,[41] i.e., for a system with long-range interatomic potential. The reason for this is roughly as follows. If $v(\vec{r})$ varies very rapidly with $\vec{r}$, e.g., by more than $k_B T$ in a particle correlation length (average interatomic separation), then the fluid is unable to respond to the rapidly changing $v(\vec{r})$ and $\langle \rho(\vec{r}) \rangle \sim e^{-\beta v(\vec{r})}$. The residual effect, i.e., response of the fluid, is obtained by expanding $[\langle \rho(\vec{r}) \rangle e^{\beta v(\vec{r})} - \rho_0]$ as a power series in $[\langle \rho(\vec{r}') \rangle - \rho_0]$. On the other hand, if $v(\vec{r})$ varies slowly with $\vec{r}$, as in a one-component plasma $[v(r) \sim r^{-1}]$ then one can imagine local equilibrium and at each point a $v_{\text{eff}}(\vec{r})$ which determines $\langle \rho(\vec{r}) \rangle$ via $\langle \rho(\vec{r}) \rangle / \rho_0 = e^{-\beta v_{\text{eff}}(\vec{r})}$. In the HNC one attempts to calculate $[v_{\text{eff}}(\vec{r}) - v(\vec{r})]$ as a functional Taylor series in the density change $[\langle \rho(\vec{r}') \rangle - \rho_0]$.

In the problem at hand, $v(\vec{r})$ of Eq. (8) is a lattice periodic potential. It is smoothly varying, of long range and not too large ($\lesssim k_B T$). The HNC is thus expected to be a better approximation for calculating $\langle \rho(\vec{r}) \rangle$ in this case. We therefore consider

$$\ln[\langle \rho(\vec{r}) \rangle e^{\beta v(\vec{r})} / \rho_0] = -\beta[v_{\text{eff}}(\vec{r}) - v(\vec{r})] ,$$

as a function of the density change $[\langle \rho(\vec{r}') \rangle - \rho_0]$. Here ρ_0 is the density of the unperturbed fluid. This scheme is self consistent, because $\langle \rho(\vec{r}) \rangle$ depends on $v_{\text{eff}}(\vec{r})$ which depends on $\langle \rho(\vec{r}') \rangle$. It is easily seen that

$$\beta v_{\text{eff}}(\vec{r}) = \beta v(\vec{r}) - \int c(\vec{r} - \vec{r}') [\langle \rho(\vec{r}') \rangle - \rho_0] d\vec{r}' , \qquad (10)$$

where

$$c(\vec{r} - \vec{r}') = \left\{ \partial \left[\ln\left(\frac{\langle \rho(\vec{r}) \rangle}{\rho_0} e^{\beta v(\vec{r})} \right) \right] \Big/ \partial \langle \rho(\vec{r}') \rangle \right\}_{\langle \rho(\vec{r}) \rangle = \rho_0}$$

$$(11)$$

is the fluid phase direct correlation function, $[S_{\vec{q}} = (1 - c_{\vec{q}})^{-1}]$. The effect of fluid phase short-range

correlations on $v_{eff}(\vec{r})$ has thus been included through $c(\vec{r} - \vec{r}')$. In Eq. (10) we have omitted higher-order terms (see Appendix for a discussion of these). We express $\langle \rho(\vec{r}) \rangle$ and $c(\vec{r})$ in terms of their Fourier components and substitute in Eq. (10), i.e., we write

$$\langle \rho(\vec{r}) \rangle = \bar{\rho} + V^{-1} \sum_i \langle \rho_i \rangle_{\lambda_i} e^{i\vec{K}_i \cdot \vec{r}} \qquad (12a)$$

$$= \rho_0(1 + \eta) + \rho_0 \sum_i \mu_i e^{i\vec{K}_i \cdot \vec{r}}, \qquad (12b)$$

where η is the fractional density change $(\bar{\rho} - \rho_0)/\rho_0$, and $\langle \rho_i \rangle_{\lambda_i} = N_0 \mu_i$. Further,

$$c(\vec{r}) = N_0^{-1} \sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q} \cdot \vec{r}}. \qquad (12c)$$

Substituting Eqs. (12b) and (12c) in Eq. (10), we have

$$\beta v_{eff}(\vec{r}) = -\ln[\langle \rho(\vec{r}) \rangle / \rho_0]$$

$$= -c_0 \eta + \sum_i (2\epsilon_i^2 N_0 \mu_i - 2\epsilon_i \lambda_i - c_i \mu_i) e^{i\vec{K}_i \cdot \vec{r}} \qquad (13)$$

where the value of $v(\vec{r})$ [Eq. (8)] has been substituted. Our aim is to integrate $\langle \rho(\vec{r}) \rangle$ over λ_i to get $\Omega(\{\lambda_i\})$ [Eq. (9)]. We see from Eq. (13) that $\langle \rho(\vec{r}) \rangle$ depends on λ_i explicitly as well as through the $\{\lambda_i\}$ dependence of μ_i and η. To obtain the latter, one has to solve self-consistently the coupled equation (12b) and (13). This complicated problem can be circumvented by a judicious choice of ϵ_i. A look at Eq. (13) shows that the choice

$$\epsilon_i^2 = c_i / 2N_0, \qquad (14)$$

eliminates μ_i completely from its right-hand side, leading to an effective potential

$$\beta v_{eff}(\vec{r}) = -c_0 \eta - \sum_i \left(\frac{2c_i}{N_0}\right)^{1/2} \lambda_i e^{i\vec{K}_i \cdot \vec{r}}. \qquad (15)$$

Using the definition $\beta v_{eff}(\vec{r}) = -\ln[\langle \rho(\vec{r}) \rangle / \rho_0]$ we have the following equations for the Fourier components of $\langle \rho(r) \rangle$ [Eq. (12)]:

$$\mu_k = e^{c_0 \eta} V^{-1} \int d\vec{r} e^{-i\vec{K}_k \cdot \vec{r}} \exp\left[\sum_i \left(\frac{2c_i}{N_0}\right)^{1/2} \lambda_i e^{i\vec{K}_i \cdot \vec{r}}\right] \qquad (16a)$$

$$1 + \eta = e^{c_0 \eta} V^{-1} \int d\vec{r} \exp\left[\sum_i \left(\frac{2c_i}{N_0}\right)^{1/2} \lambda_i e^{i\vec{K}_i \cdot \vec{r}}\right]. \qquad (16b)$$

We show in the next section how these equations can be used to find $\Omega(\{\lambda_i\})$.

It is also possible to include the effect of the quadratic term in the functional Taylor series (see Appendix) and then one gets

$$-\beta v_{eff}(\vec{r}) = c_0 \eta + \tfrac{1}{2} c_{00}^{(3)} \eta^2 + \frac{1}{2} \sum_i c_{i,-i}^{(3)} \mu_i^2$$

$$+ \sum_i \left[\left(\frac{2c_i}{N_0}\right)^{1/2} \lambda_i + c_{i0}^{(3)} \mu_i \eta \right.$$

$$\left. + \tfrac{1}{2} n_i^{(3)} c_{i'i''}^{(3)} \mu_i^2 \right] e^{i\vec{K}_i \cdot \vec{r}}. \qquad (17)$$

In Eq. (17),

$$c_{00}^{(3)} = -c_0 + \rho_0 \left(\frac{\partial c_0}{\partial \rho}\right)_{\rho = \rho_0}, \qquad (18a)$$

$$c_{i0}^{(3)} = c_{i,-i}^{(3)} = -c_i + \rho_0 \left(\frac{\partial c_i}{\partial \rho}\right)_{\rho = \rho_0}, \qquad (18b)$$

and

$$c_{i'i''}^{(3)} = -1 - \rho_0^{-3} S_{i'',i'',-i'-i''}^{(3)}(c_{i'} - 1)$$

$$\times (c_{i''} - 1)(c_{i'+i''} - 1). \qquad (18c)$$

Here $c_{00}^{(3)}$ and $c_{i0}^{(3)}$ [or $c_{i,-i}^{(3)}$] are Fourier transforms of direct three-particle correlation functions expressible in terms of the density derivatives of c_0 and c_i, respectively. The quantity $c_{i'i''}^{(3)}$ involves three density fluctuations, with wave vectors $\vec{K}_{i'}$, $\vec{K}_{i''}$, $-\vec{K}_{i'} - \vec{K}_{i''}$, which are members of the reciprocal-lattice vector set $\{\vec{K}_i\}$, i.e., the set of reciprocal-lattice vectors related to each other by the crystal point group symmetry transformations, $n_i^{(3)}$ is the number of pairs in the set $\{\vec{K}_i\}$ that can add to give a particular member of that set. $c_{i'i''}^{(3)}$ is related to the Fourier transform of the three-particle correlation functions $S^{(3)}$ as shown in Eq. (18c).

IV. THERMODYNAMIC POTENTIAL AND FREEZING PARAMETERS

We show in this section how the thermodynamic potential $\Omega(\{\lambda_i\})$ can be calculated from Eq. (9) relating $\langle \rho_k \rangle$ with $\partial \Omega(\{\lambda_i\}) / \partial \lambda_k$, and Eq. (16) defining $\langle \rho_k \rangle (= N_0 \mu_k)$ as functions of λ_i. We then discuss the physical meaning of the expression obtained for Ω, and show how various freezing parameters can be calculated.

It is convenient to work with a reduced order parameter

$$\xi_i = (2c_i / N_0)^{1/2} \lambda_i. \qquad (19)$$

This is a quantity of order unity [since $\lambda_i \sim O(N^{1/2})$]. Defining the function

$$\phi(\{\xi_i\}) = V^{-1} \int d\vec{r} \exp\left(\sum_i \xi_i e^{i\vec{K}_i \cdot \vec{r}}\right), \qquad (20)$$

it is clear from Eq. (16a) that

$$\eta = \ln \phi(\{\xi_i\}) / (1 - c_0), \qquad (21)$$

where we have used $1 + \eta \simeq e^{\eta}$ since $\eta \ll 1$. Further,

$$\langle \rho_k \rangle_{\lambda_i} = N_0 \mu_k = N_0 (1 + \eta) \frac{\partial}{\partial \xi_{-k}} [\ln \phi(\{\xi_i\})] \qquad (22a)$$

$$= N_0 \frac{\partial}{\partial \xi_{-k}} \{ \ln \phi(\{\xi_i\}) + \tfrac{1}{2}(1 - c_0)^{-1}$$

$$\times [\ln \phi(\{\xi_i\})]^2 \} . \qquad (22b)$$

Thus, from Eq. (9), we have

$$\beta \Delta\Omega(\{\xi_i\}) \equiv \beta\Omega(\{\xi_i\}) - \beta\Omega(\{0\})$$

$$= N_0 \left[\sum_i \frac{\xi_i^2}{2 c_i} - (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right) \right] . \qquad (23)$$

This equation, representing the thermodynamic potential as a function of the order parameters ξ_i $[= (2 c_i/N_0)^{1/2} \lambda_i]$ is a basic result of our paper. The physical mechanism of freezing implied by Eq. (23) is the following. Setting up lattice periodic density fluctuations of partial amplitudes λ_i requires an energy $k_B T \sum_i \lambda_i^2$. This is the first term of Eq. (23). The system condenses (density increases) as a consequence, and this leads to a pressure $\Delta P \simeq (\partial P/\partial \rho)\Delta \rho$. The consequent lowering in Ω is $\Delta\Omega = -V\Delta P = k_B T(1 - c_0)\eta$ from the definition of compressibility. This is basically the second term in the above equation. Now for the energy lowering to be sufficiently large, a given periodic potential proportional to λ_i must cause a sizeable density change. This requires [Eq. (16b)] that the correlation function c_i be large. Thus as the system becomes strongly correlated, the attractive term in Eq. (23) increases, and it is possible to satisfy the freezing condition

$$\beta \Delta\Omega(\{\xi_i\}) = 0 , \qquad (24)$$

for $\{\xi_i\} \neq 0$. The relevant $\{\xi_i\}$ values are determined by the stability criterion

$$\frac{\partial \beta \Delta\Omega(\{\xi_i\})}{\partial \xi_k} = 0 , \qquad (25)$$

i.e., one picks $\{\xi_{is}\} \neq 0$, such that $\Omega(\{\xi_{is}\})$ is a minimum ($\{\xi_i\} = 0$ is always a local minimum provided $c_i \leq 1$). Equation (25) translates [using Eqs. (20)–(23)] into

$$\frac{\xi_k}{c_k} = (1 + \eta)\left(\frac{\phi_k}{\phi}\right) \qquad (26a)$$

$$= (1 + \eta) \frac{\partial}{\partial \xi_k} \ln \phi , \qquad (26b)$$

where explicitly

$$\phi_k = V^{-1} \int e^{i \vec{K}_k \cdot \vec{r}} \exp\left(\sum_i \xi_i e^{i \vec{K}_i \cdot \vec{r}}\right) d\vec{r} . \qquad (27)$$

If η is neglected in comparison to unity in Eqs.

(23) and (26), one has

$$\beta \Delta\Omega(\{\xi_i\}) = \beta\Omega(\{\xi_i\}) - \beta\Omega(\{0\})$$

$$= N_0 \left[\sum_i \left(\frac{\xi_i^2}{2 c_i}\right) - \ln \phi(\{\xi_i\}) \right] , \qquad (28)$$

and

$$\frac{\xi_k}{c_k} = \frac{\partial \ln \phi(\{\xi_i\})}{\partial \xi_{-k}} . \qquad (29)$$

We note that the compressibility c_0 does not enter these equations and only the crystal structure and the structural correlation functions c_i do.

Including the quadratic response terms [in the expression for $\beta \Delta\Omega(\{\xi_i\})$] we find that the integration over ξ_i can again be carried out and that the expression for $\beta \Delta\Omega(\{\xi_i\})$ is now given by

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

$$+ c_{00}^{(3)}\left(\frac{\eta^2}{2} + \frac{\eta^3}{3}\right) + \sum_i c_{i0}^{(3)} \mu_i^2 \left(\eta + \frac{1}{2}\right)$$

$$+ \frac{1}{3} \sum_i c_{i'i''}^{(3)} n_i^{(3)} \mu_i^3 . \qquad (30)$$

The third and fourth terms are due to the density dependence of the compressibility (or c_0) and of c_i, respectively. The last term is a geometrical reinforcement effect due to the possibility of three reciprocal-lattice vectors adding to zero. This can lower Ω if $c_{i'i''}^{(3)}$ is negative, and thus the lowering need not come entirely from the condensation effect [second term of Eq. (30)]. The fractional density change η is given explicitly as

$$\eta = (1 - c_0)^{-1} \ln \psi(\{\xi_i\}) , \qquad (31a)$$

where

$$\psi(\{\xi_i\}) = \phi(\{x_i\}) , \qquad (31b)$$

with

$$x_i = \xi_i + c_{i0}^{(3)} \mu_i \eta + \tfrac{1}{2} n_i^{(3)} c_{i'i''}^{(3)} \mu_i^2 . \qquad (31c)$$

The free energy minimum condition (25) can be written

$$\mu_k = \frac{\xi_k}{c_k} = (1 + \eta)\left(\frac{\partial \ln \phi(\{x_i\})}{\partial x_{-k}}\right) . \qquad (32)$$

Equation (25) determines the values of the quantities $\{\xi_k\}$ for a locally stable solid phase. In case more than one set $\{\xi_k\}$ satisfies the minimum condition, we choose the one with lower Ω. The freezing condition (24) gives one relation between the material parameters c_i and c_0 of the fluid. We use the known compressibility so that c_0 is fixed. If only one order-parameter mode ξ_j of the reciprocal-lattice vector set $\{\vec{K}_j\}$ is effective in lowering Ω, the freezing condition gives the corresponding

value of c_j. If two modes are significant, we obtain a relation between the corresponding c_i's for freezing to take place. Thus we obtain the structural criterion for freezing, and not the freezing temperature [without the intervention of a theory of the fluid which gives $c_i(T)$]. Given $\{\xi_{is}\}$, the fractional density change $\eta = (\rho_s - \rho_1)/\rho_1$ can be directly obtained from Eq. (21). The entropy change Δs can be obtained by calculating the free energy per particle in the fluid and solid phases, using our expression for Ω and standard thermodynamic relations. We find that the entropy loss Δs on freezing has two parts, one due to just the volume change and the other due to the structure that develops, i.e.,

$$\Delta s = (\Delta s)_v + (\Delta s)_c \tag{33a}$$

$$= \eta \rho_1^{-1} \left(\frac{\partial P}{\partial T} \right)_v - \frac{k_B T}{2} (1+\eta)^{-2} \sum_i \mu_i^2 \left(\frac{\partial c_i}{\partial T} \right)_v. \tag{33b}$$

We can calculate from our theory the lattice periodic components of the solid phase density near freezing. For the order-parameter modes,

$$\frac{\langle \rho_i \rangle}{N_s} = \frac{\mu_i}{1+\eta} = \tilde{\mu}_j = \frac{1}{1+\eta} \frac{\xi_i}{c_j}. \tag{34}$$

To find $\langle \rho_i \rangle$ for reciprocal-lattice vectors such that the corresponding order parameter is zero, we use Eq. (16a), and obtain,

$$\tilde{\mu}_k = \mu_k (1+\eta)^{-1}$$

$$= V^{-1}(1+\eta)^{-1} \int d\vec{r} \, e^{-i\vec{K}_k \cdot \vec{r}} \left[\exp \left(\sum_i \xi_i e^{i\vec{K}_i \cdot \vec{r}} \right) \right]. \tag{35}$$

The quantity $\tilde{\mu}_k^2$ is obviously the Debye-Waller factor, and can be measured in an experiment or a computer experiment.

V. NUMERICAL RESULTS FOR SIMPLE STRUCTURES

We begin this rather long section with general remarks on the choice of order parameters and the calculational procedure. Then the details of calculations for fcc, bcc, and two-dimensional hcp structures are described and the results are compared with experiment wherever possible. We also obtain and discuss results for the Debye-Waller factor for these structures near freezing.

A. Choice of order-parameter modes

The theory developed above is in principle a many order-parameter theory with one order pa-

rameter for each reciprocal-lattice vector. However, λ_i or ξ_i should be taken to be the same for all reciprocal-lattice vectors (same magnitude) of the set $\{\vec{K}_i\}$ whose n_i vectors $\vec{K}_{i\alpha}$ $(\alpha = 1, \ldots, n_i)$ transform into each other under point group transformations from crystal symmetry. Then the function $\phi(\{\xi_i\})$ of Eq. (20) can be written

$$\phi(\{\xi_i\}) = V^{-1} \int d\vec{r} \exp \left(\sum_i \xi_i \omega_i(\vec{r}) \right), \tag{36a}$$

where

$$\omega_i(\vec{r}) = \sum_\alpha \exp(i\vec{K}_{i\alpha} \cdot \vec{r}). \tag{36b}$$

Now, the increase in Ω due to a particular order-parameter mode ξ_i is clearly [see Eq. (23)] small if the corresponding c_i is large. But $c_{\vec{q}}$ is sharply peaked (near freezing) around $|\vec{q}| \simeq |K_j|$, corresponding to the smallest reciprocal-lattice vector set. Thus, it is possible that taking only *one* order-parameter mode ξ_j to be nonzero (and all other $\xi_i = 0$), we might get a good description of freezing. Very often however, a second order-parameter mode with its wave vector in the second broad peak region of $c_{\vec{q}}$ is effective in lowering Ω. The requirements for an effective second order-parameter mode are that (i) the corresponding c_i is large, (ii) there are many members in the reciprocal-lattice vector set $\{\vec{K}_i\}$, and (iii) the density fluctuations ρ_i couple effectively to the ρ_j and among themselves to produce spatially homogeneous terms (for Ω). The first requirement reduces the positive $\xi_i^2/2c_i$ term in $\Delta\Omega$. The second increases the density condensation, as does the third. As an example, in the fcc case, $|\vec{K}_j|$ [the set $(2\pi/a)(\pm 1, \pm 1, \pm 1)$] is close to the first large sharp peak in $c_{\vec{q}}$. In the second peak region, there are two reciprocal-lattice vector sets $(2\pi/a)$ $(\pm 3, \pm 1, \pm 1)$ and $(2\pi/a)(\pm 2, \pm 2, \pm 2)$. The former set has 24 members while the latter has eight. We therefore choose the former.

The above arguments are general and serve as broad guidelines. The safest procedure, and the one that we follow, is to compute Ω separately with each of the alternative choices for ξ_i, and to retain that which leads to the smallest Ω. We have also found that provided a good first-order transition is obtained with one or two properly chosen order-parameter modes, inclusion of other modes ξ_r does not change Ω and the freezing parameter very much. This can be understood analytically by expanding the change $\delta\Omega$ as a power series in λ_r. If Ω is at a well-defined solidlike minimum, and if c_r and n_r are small (as they are by choice), then $\delta\Omega$ is seen to be very small. We now discuss some actual calculations.

B. Computation for the fcc structure

The fcc structure (of which two well-studied examples are argon and the hard-sphere solid) has eight smallest reciprocal-lattice vectors $(2\pi/a)$ $(\pm 1, \pm 1, \pm 1)$. Assuming that only the single (real) order-parameter ξ_j associated with density fluctuations of this reciprocal-lattice vector set is non-zero, the procedure for computing freezing parameters is as follows. For a given c_j value, we vary ξ_j until the stability criterion Eq. (25) or (26a) is satisfied. We then check if the freezing or Ω equality condition is satisfied, with Eq. (23) for $\beta\Delta\Omega(\{\xi_i\})$, and with η given by Eq. (21). The calculation is repeated until the value of c_j satisfying the freezing criterion is found. If a value is used for the compressibility or c_0, one finds η. Otherwise the approximate equations (28) and (29) can be used to obtain ξ_j and c_j with crystal structure (or the set $\{\vec{K}_j\}$) as the only input.

The quantities to be numerically calculated are the integrals $\phi(\{\xi_j\})$ and $\phi_j(\{\xi_j\})$. For the reciprocal-lattice vector set $(2\pi/a)(\pm 1, \pm 1, \pm 1)$, Eq. (36b) gives $\omega_j = 8\cos x \cos y \cos z$, and from (36a) one gets

$$\phi(\xi_j) = \pi^{-3} \int_0^\pi dx \int_0^\pi dy \int_0^\pi dz$$

$$\times \exp(8\xi_j \cos x \cos y \cos z).$$

$$(37)$$

This integral is evaluated by the n-point Gaussian quadrature formula. The value of n, generally in the range of 6–12, is varied till convergence up to five significant figures is obtained.[42]

On computing $\phi(\xi_j)$ and $\phi_j(\xi_j)$ for various values of ξ_j, we find that the approximate equations (28) and (29) are satisfied for $\xi_j = 0.62$ and $c_j = 0.98$. Using the known compressibility value for argon[43,44] $(c_0 = -18.9)$ and the more accurate equations (23) and (26), the one order-parameter theory gives $\xi_{js} = 0.60$ and $c_j = 0.95$ (these and other freezing

parameters are listed in Table I under theory I). The c_j value for the hard-sphere system[45] $(c_0 = -49.0)$ is very nearly the same (Table II, theory I). The values obtained are to be compared with the experimental result $c_j \simeq 0.65$.[25] The discrepancy is quite glaring when phrased in terms of the structure factor $S_j = (1 - c_j)^{-1}$ for which the value obtained is 20.0, the experimental value being 2.85. The transition obtained is very close to being second order ($c_j = 1$ or $S_j = \infty$, see Sec. VI). The geometrical reason for expecting this is the following.

The fcc structure is a closed structure in position space and somewhat open in reciprocal space. There are only eight members in the smallest reciprocal-lattice vector set (while for bcc this number is twelve). They do not combine to produce an η that can lower the $\beta\Delta\Omega(\xi_j)$ sufficiently to cause a strong first-order transition.

We note here the strong mathematical resemblance between the result of our one order-parameter approximation and the results of Kirkwood and Monroe[9] for the case of argon. Kirkwood and Monroe considered an equation for the one-particle density $\rho(\vec{r}, \xi)$ when the coupling between a particle at $\vec{r} = 0$ and other particles is turned on (ξ, the fractional coupling strength grows from 0 to 1). They find equations somewhat similar to Eqs. (28) and (29) with a quantity β_i instead of our c_j. The quantity β_i is a (complicated) function of the interatomic potential, the two-particle correlation function and the temperature. The fact that β_i is a model approximation for c_j (at least for small periodic density changes) has been made plausible by the work of Saitoh and Nagai.[46] These authors made an assumption independent analysis of the Kirkwood instability criterion,[47] $\beta_i = 1$ (for which the fluid phase becomes unstable with respect to infinitesmal density fluctuations) and found that this criterion becomes the somewhat tautological

TABLE I. Freezing parameters for argon (fcc). Here $|\vec{K}_n| = \frac{11}{3}^{1/2}|\vec{K}_j|$.

	Structure factors $c_q = 1 - S_q^{-1}$		Fractional density	Lattice periodic density		Order parameters	
	c_j	c_n	change η	$\tilde{\mu}_j$	$\tilde{\mu}_n$	ξ_j	ξ_n
Theory I (one order parameter)	0.95	0.00	0.074	0.59	0.20	0.60	0.00
Theory II (two order parameters)	0.65	0.23	0.270	0.90	0.75	0.77	0.23
Theory III (two order parameters with $c_{00}^{(3)} = -110.0$)	0.65	0.23	0.166	0.91	0.74	0.71	0.21
Experiment	0.65	0.23	0.148	$\cdots$	$\cdots$	$\cdots$	$\cdots$

TABLE II. Freezing parameters for the hard-sphere system (fcc). Here $|\vec{K}_n| = \frac{11}{3}^{1/2} |\vec{K}_j|$.

| | Structure factors $c_q = 1 - S_q^{-1}$ | | Fractional density | Lattice periodic density | | Order parameters | |
	c_j	c_n	change η	$\tilde{\mu}_j$	$\tilde{\mu}_n$	ξ_j	ξ_n
Theory I (one order parameter)	0.96	0.00	0.029	0.57	0.18	0.52	0.00
Theory II (two order parameters)	0.65	0.26	0.113	0.90	0.75	0.67	0.22
Theory III (two order parameters with $c_{00}^{(3)} = -183.0$).	0.65	0.26	0.093	0.90	0.75	0.67	0.22
Experiment	0.65	0.24	0.103	$\cdots$	$\cdots$	$\cdots$	$\cdots$

statement that $c_j = 1$ or $S_j = \infty$. The Kirkwood-Monroe result of $\beta_i = 0.95$ which appears to be good for argon when expressed in terms of temperature (with a potential and two-particle correlation put in) is actually rather poor in the light of the above identification with c_j. The other freezing parameters like η, are too low and the transition is close to being second order.

The two order-parameter approximation is necessary as well as justifiable because experimentally the second peak of c_q^- is more than one-third of the magnitude of first peak, both in argon and hard-sphere systems. As already discussed, the effect of this second peak is included by taking a nonzero order parameter corresponding to the set $\{\vec{K}_n\}$ for which the number of vectors is large and for which $|\vec{K}_n|$ lies in the region of the second peak. In case of fcc structure, there are two sets with magnitudes lying in the second peak region, namely, $\{\vec{K}_n\} = (2\pi/a)(\pm 3, \pm 1, \pm 1)$ with 24 vectors and $\{\vec{K}_{n'}\} = (2\pi/a)(\pm 2, \pm 2, \pm 2)$ with eight vectors. Obviously, the better choice of the second order parameter ξ_n corresponds to the set $\{\vec{K}_n\}$ with $n_n = 24$. The effect of the other set $\{\vec{K}_{n'}\}$ was also computed and found to be negligible. The location of $|\vec{K}_n|$ on the $S(q)$ versus q curve is shown in Fig. 1, where $|\vec{K}_j|$ exactly corresponds to the first peak position.

The computation for the two order-parameter case proceeds as before; with

$$\phi(\xi_j, \xi_n) = \pi^{-3} \int \int \int dx\, dy\, dz \exp(\xi_j \omega_j + \xi_n \omega_n),$$

(38a)

where

$$\omega_n = 8(\cos 3x \cos y \cos z + \cos x \cos 3y \cos z$$

$$+ \cos x \cos y \cos 3z).$$

(38b)

The calculation procedure consists in choosing c_j and c_n and for the given c_0, locating the minimum of Ω [using Eq. (25)] in the ξ_j, ξ_n plane. We then cal-

culate $\beta \Delta \Omega$ and the calculation is repeated by varying c_j, c_n until the condition $\beta \Delta \Omega = 0$ is satisfied. We use the 12-point Gaussian quadrature formula to evaluate the integrals of Eq. (38) and obtain several pairs of numbers for c_j and c_n which satisfy the freezing condition. We have plotted them as a c_j vs c_n graph as shown in Fig. 2 for argon. A similar graph can be drawn for the case of hard spheres. An interesting feature of this graph is that it is a straight line with a negative slope, showing that if c_j increases, then freezing occurs for a smaller c_n and vice versa. A remarkable property of this graph is that other freezing parameters like η, μ_j, and μ_n remain approximately the same for all values of c_j and c_n on the straight line. This line can be considered as a freezing line described in terms of structural correlations. Above the line, the solid phase is more stable due to strong structural correlations while below the line, the fluid phase is more stable. Effects due
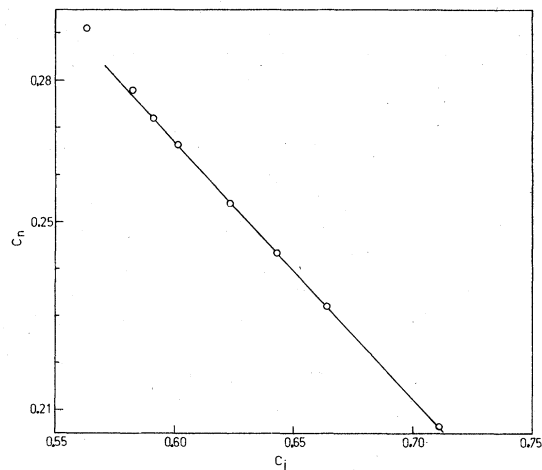

FIG. 2. Curve of calculated values of c_j and c_n for which freezing is possible into the fcc structure.

to other (omitted) order-parameter modes and three-body correlations broaden this line into a relatively narrow strip. The actual values of c_j and c_n for various conditions of temperature and pressure will lie on a different curve whose intersection with the above straight line determines $T(P)$ if $c_j(T, P)$ and $c_n(T, P)$ are known. Since we do not have here a theory of the fluid which would predict or relate c_j and c_n under the given thermodynamic conditions, we display from the c_j and c_n values obtained by us, numbers lying closest to the experimental values near the triple point for argon, and the freezing density for hard spheres. These are shown as theory II in Tables I and II for argon and hard spheres, respectively. For example the predicted c_n values are found to agree almost perfectly with the experimental results in both the cases if c_j is chosen to be the experimentally observed value 0.65. To check the influence of other order parameters, we include additionally in $\beta \Delta \Omega$ the effects of ξ_k corresponding to the set $\{\vec{K}_k\} = (2\pi/a)$ $(\pm 2, \pm 2, 0)$ with $n_k = 12$,

$$\omega_k = 4(\cos 2x \cos 2y + \cos 2y \cos 2z + \cos 2z \cos 2x)$$

and ω_l corresponding to the set $\{\vec{K}_l\} = (2\pi/a)(\pm 2, \pm 2, \pm 2)$ with $n_l = 8$ and

$$\omega_l = 8(\cos 2x \cos 2y \cos 2z).$$

Detailed computation yields $\xi_k \sim 0.005$ and $\xi_l \sim 0.03$ for transition and none of the numerical values shown against theory II of Tables I and II vary by more than five per cent (this is not shown in the Tables I and II). Thus, we conclude that the two order-parameter theory is often good enough (and other order parameters are set equal to zero thoughout this paper).[48] The vectors of the set $\{\vec{K}_n\}$ corresponding to ξ_n combine among themselves and with those of the set $\{\vec{K}_j\}$ corresponding to the dominant order parameter ξ_j in a highly effective way so that η increases and the solid phase is stabilized.

While the two order-parameter theory is very good as far as c_j and c_n values are concerned, Tables I and II clearly show that the value of the fractional density change η is too large (theory II) in comparison with experiment. As discussed above, inclusion of more order parameters does not make any difference to this large values of η (change <4%).

For such a large fractional density change in dense system, the compressibility changes a great deal. Experimentally it is known that as one goes from liquid to solid argon at the freezing point, the compressibility nearly halves.[43,44] Thus, the assumption of linear response with respect to density

change, with c_0 as the response coefficient, is physically unrealistic. The decrease in compressibility with increasing density will reduce η with respect to the above value. Formally, this effect can be included by considering quadratic response terms, i.e., Eq. (17) for $v_{\text{eff}}(\vec{r})$, Eq. (30) for $\beta \Delta \Omega$ and Eq. (32) for the stability condition. The new response coefficients involved are the density derivatives $c_{00}^{(3)}$ and $c_{j0}^{(3)}$ and the three reciprocal-lattice vector fluctuation term $c_{j''j''}^{(3)}$. Since neither within the set $\{\vec{K}_j\}$ nor in the set $\{\vec{K}_n\}$ can three reciprocal-lattice vectors add to zero, the term $c_{j''j''}^{(3)}$ is not present in the fcc structure. The term $c_{j0}^{(3)} = -c_i + \rho_0 (\partial c_i/\partial \rho)_{\rho = \rho_0}$ can be estimated, e.g., from the Verlet-Weis fit[49] (of a Percus-Yevick-like equation) to the hard-sphere structure factor. It turns out for example that $c_{j0}^{(3)} = 0.08$. With this $c_{j0}^{(3)}$, calculation shows that the change in freezing parameters is small. However, since c_0 decreases rapidly with increasing density, $c_{00}^{(3)}$ is quite large and negative. Keeping only $c_{00}^{(3)}$, we get

$$\beta \Delta \Omega(\{\xi_i\}) = \sum_i \left(\frac{\xi_i^2}{2c_i}\right) - (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right)$$
$$+ c_{00}^{(3)}\left(\frac{\eta^2}{2} + \frac{\eta^3}{3}\right) \tag{39}$$

the last being the additional term. The minimum or stability condition [Eq. (32)] is unchanged. It is clear from Eq. (39) that the inclusion of the $c_{00}^{(3)}$ term does not affect anything except η. The experimental values for $c_{00}^{(3)}$ are nearly -110.0 for argon and -183.0 for hard spheres. These values extrapolate fairly close to the observed c_0 of the corresponding solid phases. Using these values, one gets numbers for η which are shown against theory III in Tables I and II. Now there is excellent agreement between theory and experiment for the density change η also.

The calculation of entropy change using Eq. (33) requires the knowledge of $(\partial P/\partial T)_{V,\mu}$ and $(\partial c_i/\partial T)_{V,\mu}$. The former is easily found from the equation of state. No experimental information is available on $(\partial c_i/\partial T)_{V,\mu}$. To obtain an estimate, we use the Percus-Yevick hard sphere expression[22] for $c_i(\rho)$ where ρ is the density, and compute $(\partial c_i/\partial T)_{V,\mu}$ by employing the equation of state. An additional difficulty is due to the fact that some c_i's increase with temperature while others decrease. We therefore keep only the dominant term due to the $(\partial c_j/\partial T)_{\mu,V}$ where $\{\vec{K}_j\}$ is the smallest reciprocal-lattice vector set. For the hard-sphere fluid at the freezing density, we find

$$(\Delta s)_v = 0.75 k_B,$$

$$(\Delta s)_c = 0.54 k_B.$$

Together they add to $1.29k_B$, fortuitously close to the experimental value of $1.2k_B$.

An interesting feature of the phase transition in the fcc structure is the large value of the periodic density component. $\bar{\mu}_j$, for example, is 0.9. The liquid solid transition is thus strongly first order. Our numbers for the $\bar{\mu}_i$'s may be a slight overestimate because we have ignored entirely the nonlinear response coefficients $c_{10}^{(3)}$ and $c_i^{(3)}{}_i$. However, since the best available estimates indicate that these are small, we do not expect $\bar{\mu}_j$, etc. to be too high by more than about 15%. The Debye-Waller factor $D_j = \bar{\mu}_j^2$ is also large.

C. Body-centered-cubic structure

Here we study freezing into bcc structure with particular reference to sodium. The reciprocal lattice is fcc and the smallest reciprocal-lattice vector set has 12 members $(n_j = 12)$ given by $\{\vec{K}_j\}$ $= (2\pi/a)(\pm 1, \pm 1, 0)$ so that here

$$\omega_j = 4(\cos x \cos y + \cos y \cos z + \cos z \cos x).$$

This ω_j is used to calculate $\phi(\xi_j)$ [Eq. (36)]. Proceeding as above in the one order-parameter case, we find the solution $c_j = 0.71$ for $\xi_j \simeq 0.51$. Unlike the case of the fcc structure, this is a perfectly acceptable first-order transition. The difference arises from the fact that the bcc structure is rather closed in momentum space. There are twelve members in the smallest reciprocal-lattice vector set (in contrast to eight for fcc), and these couple strongly amongst themselves to promote freezing. We take the value of $c_0 \simeq -40$ from compressibility data[26,50] to obtain the results of our theory for the one order parameter approximation. The result is shown as theory I in Table III. The value of c_j is quite tolerable but the value of η is almost double the experimental value. This is to be contrasted with theory I in Table I for argon where η is half of its experimental value and for hard spheres, where η is about one third of the experi-

mental value. Therefore one suspects that some fundamental process is responsible for this basically different behavior of η in fcc and bcc structures. As will be seen below, this process is the effect of the three-body correlation $c_{i'i''}^{(3)}$ whose coefficient vanishes for fcc structure but which is quite significant in bcc structure.

The second order parameter ξ_n which is most effective in the case of bcc lattice corresponds to 24 reciprocal-lattice vector $(n_n = 24)$ $\{\vec{K}_n\} = (2\pi/a)(\pm 2, \pm 1, \pm 1)$ whose magnitude is in the region of the second peak of c_q^{-} and for which

$$\omega_n = 8(\cos 2x \cos y \cos z + \cos 2y \cos z \cos x$$

$$+ \cos 2z \cos x \cos y).$$

$|\vec{K}_n|$ in this case is also shown in Fig. 1.

Then the two order-parameter approximation yields "best" numbers shown as theory II in Table III. There is reasonably good agreement with experimental values of c_j and c_n but the value for η becomes worse (even higher than theory I). This is obviously expected and did happen in the case of fcc structures. However, if η is large, the effect of the density dependence of c_0, i.e., of the nonlinear term $c_{00}^{(3)}$, can be significant. In case of bcc, one finds[50] that $c_{00}^{(3)} \simeq -75$. Using this in Eq. (39), we find that neither the initial density change nor the density dependence of the compressibility is large and the reduction in η is marginal. This leads to an examination of all the other effects that have not been included. More order parameters were included in the calculation and it was found that their effect is again less than a few percent (as anticipated). Again there is reason to believe that $c_{10}^{(3)}$ would be small and therefore the only significant quantity is $c_{i'i''}^{(3)}$ representing a special aspect of the three-body correlation.

It is clear from Eq. (30) that $c_{i'i''}^{(3)}$ is effective through $n_i^{(3)}$ which gives the number of pairs in the reciprocal-lattice vector set $\{\vec{K}_i\}$ such that their sum is a particular member of this very set. Such

TABLE III. Freezing parameters for sodium (bcc). Here $|\vec{K}_n| = \sqrt{3}\,|\vec{K}_j|$.

	Structure factors $c_q = 1 - S_q^{-1}$		Fractional density	Lattice periodic density		Order parameters	
	c_j	c_n	change η	$\bar{\mu}_j$	$\bar{\mu}_n$	ξ_j	ξ_n
Theory I (one order parameter)	0.69	0.00	0.048	0.70	0.31	0.48	0.00
Theory II (two order parameters)	0.63	0.07	0.052	0.71	0.42	0.47	0.03
Theory III (two order parameters, $c_{00}^{(3)} = -75.0$, $c_{i'i''}^{(3)} = -0.103$)	0.67	0.13	0.029	0.63	0.34	0.42	0.05
Experiment	0.66	0.12	0.026	$\cdots$	$\cdots$	$\cdots$	$\cdots$

combinations do not exist for the fcc structure. However, for the bcc structure such pairs exist. For example, in the set of the smallest reciprocal-lattice vectors, we have

$$(2\pi/a)(1, 1, 0) + (2\pi/a)(-1, 0, 1) = (2\pi/a)(0, 1, 1).$$

There are four such pairs in the set $\{\vec{K}_j\}$ for each vector $\vec{K}_j$. Thus $n_j^{(3)} = 4$ and from Eq. (30) one gets for the bcc structure

$$N_0^{-1}\beta\Delta\Omega(\xi_j, \xi_n)$$

$$= \frac{6\xi_j^2}{c_j} + \frac{12\xi_n^2}{c_n} - (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right)$$

$$+ c_{00}^{(3)}\left(\frac{\eta^2}{2} + \frac{\eta^3}{3}\right) + 16c_{j'j''}^{(3)}\mu_j^3, \quad (40)$$

where the term for $c_{n'n''}^{(3)}$ is omitted.[51] Equation (31c) becomes

$$x_j = \xi_j + 2c_{j'j''}^{(3)}\mu_j^2 \quad (41a)$$

and

$$x_n = \xi_n. \quad (41b)$$

It is clear from Eq. (40) that an attractive $(-ve)c_{j'j''}^{(3)}$ additionally lowers $\Delta\Omega$, and one can have a solid phase for a relatively small η without significantly altering other freezing parameters. Unfortunately, however, nothing is known about $c_{j'j''}^{(3)}$, experimentally or theoretically. We therefore tried various numerical values between +0.2 to -0.2 for $c_{j'j''}^{(3)}$ and computed freezing parameters. In the case of only one order parameter ξ_j, we find for $c_{j'j''}^{(3)} = -0.02$, the values $c_j = 0.706$ and $\eta = 0.042$. η is somewhat lowered, but c_j is in worse accord with experiment. Making $c_{j'j''}^{(3)}$ more negative lowers η but the corresponding c_j is even further off from experiment. We also notice that a rather small $c_{j'j''}^{(3)}$ ($= -0.02$) has a significant effect on freezing parameters. This is because $n_j^{(3)} = 4$ (i.e., *four* pairs can add to produce a member of the set $\{\vec{K}_j\}$), and because μ_j^3 is sizeable ($\mu_j \sim 0.6$ to 0.7) [see Eq. (40)]. Performing a similar calculation for the two order-parameter case, we obtain, for $c_{j'j''}^{(3)}$ in the neighborhood of -0.10, sets of acceptable freezing parameters. One such (for $c_{j'j''}^{(3)} = -0.103$) is shown in Table III (theory III). The agreement with experimental values of η, c_j, and c_n is very good indeed. We assume that $c_{j'j''}^{(3)}$ has this value in sodium.

We point out an important implication of the $c_{j'j''}^{(3)}$ term in the framework of the present theory. When this term is set at zero, we find that for a common acceptable set of c_j and c_n values (corresponding to fluid being in a particular thermodynamic state) the bcc phase is more stable than the fcc phase. The three-body contribution disfavors the bcc if

$c_{j'j''}^{(3)}$ is positive, and disfavors the fcc still further if it is negative. Thus, depending on the size and sign of the three-body term, the bcc or the fcc phase will be more stable. It is interesting that in the pseudopotential theory of metals, the strongly crystal structure sensitive term has been found to be an effective three ion interaction.[52,53]

D. Two-dimensional hcp structure

A phase transition for hard disks in two dimensions was found by Alder and Wainwright[16,17] through computer experiments. Here, we apply our theory to the freezing of this two-dimensional system into a close packed hexagonal lattice. The smallest reciprocal-lattice vector set has six members ($n_j = 6$) and

$$\omega_j = 2\cos2y + 4\cos x\cos y,$$

is to be substituted in the expression (36a) for $\phi(\xi_j)$. The numerical value of c_0 has been computed by using the Padé approximant fit to equation of state[16,54] and the result is $c_0 = -51.5$. Using this the one order-parameter approximation yields results shown as theory I in Table IV. Comparing with the only experimentally known quantity, $\eta = 0.028$, we find that the one order parameter theory requires improvement, since η_{theory} is too low.

In this case, the choice of the second order parameter is not quite obvious because the c_q^- vs q curve is not known. Therefore several choices of the second order parameter ξ_n were tried out and the one that is found most effective for the transition corresponds to

$$\{\vec{K}_n\} = (0, \pm2)4\pi/(3a)^{1/2}, \ (\pm\sqrt{3}, \pm1)4\pi/(3a)^{1/2},$$

with $n_n = 6$ and

$$\omega_n = 2(\cos4y + 2\cos2x\cos2y).$$

The freezing parameters computed by using this ξ_n are shown as theory II in Table IV. We see that η agrees very well with experiment. But the phase transition is rather close to second order with $c_j = 0.86$. (We get $c_j = 0.86$ always and choose c_n such that the corresponding η is close to experiment.) We also note that the fractional density change η is very small and the periodic density component $\bar{\mu}_j = 0.68$ is rather small for a close-packed structure (compare, for example, with Tables I and II for fcc structure). The fact that the transition is not strongly first order leads one to expect that there will be some softening of lattice modes near melting. Evidence for this appears in the work of Alder (Ref. 16, p. 98). The experimental information available so far is in agreement with our finding that in two dimensions,[55] the transition takes place to a closed-packed hexagonal structure

TABLE IV. Freezing parameters for hard disks (closed-packed hexagonal in two dimensions). Here $|\vec{K}_n| = 2|\vec{K}_j|$.

| | Structure factors $c_q = 1 - S_q^{-1}$ | | Fractional density | Lattice periodic density | | Order parameters | |
	c_j	c_n	change η	$\bar{\mu}_j$	$\bar{\mu}_n$	ξ_j	ξ_n
Theory I (one order parameter)	0.86	0.00	0.013	0.51	0.10	0.44	0.00
Theory II (two order parameters)	0.86	0.16	0.025	0.69	0.31	0.60	0.05
Experiment	...	...	0.028	...	...	...	...

with $\eta = 0.025$.

E. Debye-Waller factor

One of the basic quantities appearing in our finite amplitude density wave instability theory is the amplitude of the density wave. In terms of the order parameters ξ_i, the density is

$$\langle \rho(\vec{r}) \rangle / \bar{\rho} = \exp\left(\sum_i \xi_i e^{i\vec{K}_i \cdot \vec{r}}\right) \Big/ \phi(\{\xi_i\}). \tag{42}$$

We have described above how the set of values ξ_{is} at the solidification point is determined. This being given, $\langle \rho(\vec{r}) \rangle$ is known completely. It is clear from earlier discussion that we expect $\langle \rho(\vec{r}) \rangle$ to be dependent mainly on the crystal structure of the solid and on the (very similar) structural correlations c_i in the fluid, and to be relatively independent of the details of the interatomic potential. We thus have here another quasiuniversal quantity associated with freezing. The best way of exhibiting it is through the Fourier coefficients of $\langle \rho(\vec{r}) \rangle$. We define

$$\bar{\mu}_k = \int \frac{\langle \rho(\vec{r}) \rangle}{\bar{\rho}} e^{-i\vec{K}_k \cdot \vec{r}} \frac{d\vec{r}}{V} = \frac{1}{N_s} \int \langle \rho(\vec{r}) \rangle e^{-i\vec{K}_k \cdot \vec{r}} d\vec{r}$$

$$= \frac{\mu_k}{1 + \eta}. \tag{43}$$

The Debye-Waller factor for Bragg diffraction with wave-vector change $\vec{K}_k$ is $D_k = \bar{\mu}_k^2$. We present below our calculations for fcc and bcc structures. The quantity $\langle \rho(\vec{r}) \rangle$ itself can be "measured" directly in a computer experiment. For example, Alder[16] has presented results which may be related to $\langle \rho(\vec{r}) \rangle$ in a two-dimensional hcp hard disk solid at the freezing point.

The periodic component $\bar{\mu}_k$ has already been computed for the reciprocal-lattice vectors $\vec{K}_j, \vec{K}_n$ for which the order parameters ξ_j, ξ_n do not vanish (e.g., theory III, Tables I–III). We calculate $\bar{\mu}_k$ for other reciprocal-lattice vectors $\{\vec{K}_k\}$ using Eq. (35) with values of $\{\xi_{is}\}$ appropriate to theory III of Tables I and III. We find that $\bar{\mu}_k$ is well approx-

imated by a Gaussian, $\bar{\mu}_k = e^{-\lambda^2 K_k^2}$ (Fig. 3). The inverse width of the Gaussian has the value $\lambda_{bcc} = 0.34/|\vec{K}_j|$ and $\lambda_{fcc} = 0.19/|\vec{K}_j|$. Here $|\vec{K}_j|$ is the length of the smallest reciprocal-lattice vector.

The fact that $\langle \rho_k \rangle$ is well fitted by a Gaussian implies a quasiharmonic model for lattice vibrations as follows. In a monatomic solid, one has

$$\langle \rho_k \rangle = \bar{N} \langle e^{i\vec{K}_k \cdot \vec{r}} \rangle = \left\langle \sum_{j=1}^{\bar{N}} e^{i\vec{K}_k \cdot \vec{R}_j} \right\rangle = \left\langle \sum_{j=1}^{\bar{N}} e^{i\vec{K}_k \cdot \vec{u}_j} \right\rangle,$$

where $\vec{R}_j$ $(=\vec{R}_j^0 + \vec{u}_j)$ are the coordinates of the jth atom, $\vec{R}_j^0$ being its mean position and $\vec{u}_j$ being the displacement therefrom. For an assembly of har-
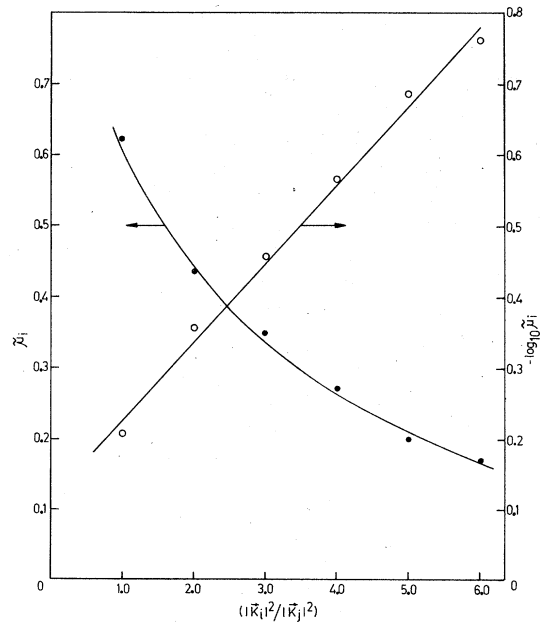

FIG. 3. Lattice periodic component $\bar{\mu}_i$ of the density corresponding to the reciprocal-lattice vector $\vec{K}_i$ shown as a function of $|\vec{K}_i|^2/|\vec{K}_j|^2$ (dots). Here $\vec{K}_j$ is the smallest reciprocal lattice vector. We have also plotted $-\log_{10} \bar{\mu}_i$ (circles). The results are for bcc structure.

monic oscillators,

$$\left\langle \sum_{j=1}^{\bar{N}} e^{i\vec{K}\cdot\vec{u}_j} \right\rangle = \bar{N}\exp[-\tfrac{1}{2}\langle(\vec{K}\cdot\vec{u}_j)^2\rangle] \ .$$

For a crystal with cubic symmetry, this is $\bar{N}\exp[-\tfrac{1}{6}K^2\langle(u_j)^2\rangle]$. Thus the coefficient of the Gaussian found by us can be related to the mean-square displacement. The values quoted above lead to $\langle u_j^2\rangle^{1/2}/r_{\text{interatomic}} = 0.06$ for the fcc structure, and 0.112 for the bcc structure.

The best way of comparing the above theoretical predictions with experiment would be to measure $\langle \rho_k \rangle$ or the Debye-Waller factor, either in an actual experiment or in a computer experiment. At present, there do not seem to be any reliable absolute measurements on the Debye-Waller factor at the melting point. No computer experimental results are available either. However, $\langle u_j^2 \rangle$ has been determined from computer experiments for argon, two values quoted[56,57] being $(\langle u_j^2\rangle/r_{\text{int}}^2)^{1/2}$ $= 0.14$ and 0.10. Another way of estimating $\langle u_j^2\rangle$ is by using the Debye model for phonons. With standard values[58] for Θ_D, one finds the values 0.080 and 0.140 for argon and sodium, respectively. The theoretical numbers are lower, the difference being large for the fcc structure. This could be due to the following reasons. We have neglected the effect of the density increase on c_i. As density increases, so does c_i. This will effectively reduce the μ_i's. Secondly, the theory developed here is based on response functions in the fluid state. In the solid state, these response functions are diagonal in wave vector only up to a reciprocal-lattice vector, i.e., there are umklapp terms. These terms stabilize the solid and thus smaller ξ_i's and μ_i's are sufficient. We note that in the fcc structure, the density change is large so that the first effect can be sizeable, whereas for the bcc structure the density change is small. Also, in the bcc structure, the presence and inclusion of the third-order term μ_i^3 in some sense takes partial account of the nondiagonality of the response function. Within the constraints of these limitations, our predicted numbers are in fair agreement with the Debye model predictions. An interesting result is that we obtain a Gaussian fit for the Debye-Waller factor without any assumption of a quasiharmonic model for lattice vibrations.

F. High-temperature solid

It is clear from Sec. II that one can discuss not only the fluid-solid transition, but also the high-temperature crystalline solid. For c_i less than the value c_i^f at which freezing occurs (i.e., for $T > T_f$), we calculate $\Omega(\{\lambda_i\})$, see if it has minima for $\{\lambda_i\}$ $\neq 0$, and locate the lowest-lying minimum. For

$c_i^f - c_i \lesssim 0.03$ there is indeed such a minimum, and the corresponding $\Omega(\{\lambda_i^m\})$ lies higher than that of the fluid. Thus, in this range of c_i or temperatures above melting point, a metastable solid exists, and we can locate the absolute thermodynamic instability limit of the solid. For $c_i > c_i^f$ (or $T < T_f$) the crystalline solid has lower Ω, and hence is the thermodynamically stable phase. However, so long as $c_i < 1$ the fluid is metastable. This implies a large metastability region for the fluid, since c_i^f is only 0.65. Experimentally, the supercooling temperature range is much larger than the superheating temperature range, thus supporting our result. Since the properties of the solid phase, e.g., density, Debye-Waller factor, etc. can be calculated as described in Sec. IV, we have here a theory of the "hot" solid $(T \lesssim T_f)$ based not on lattice dynamics, but on an approach from the fluid phase.

G. Remarks on computational results

We note that while a first-order liquid solid transition is easily found in a simple approximation, obtaining accurate, stable freezing parameters requires systematic refinement of the approximation. This is not surprising since the freezing transition is strongly first order, involving large changes in order parameters, density, etc. Furthermore, it occurs in a dense system whose structural and thermodynamic properties depend strongly on density. Because of the systematic nature of our theory, we are able to converge quickly to the correct set of order parameters and nonlinear response terms. The freezing parameters obtained there from are in very good agreement with experiment. Our results are not much altered on inclusion of other order-parameter modes.

In our calculations for simple structures, we have predicted many physical quantities near freezing. There is very good agreement for all those freezing parameters which have been measured. For quantities like the lattice periodic density component and the correlation function in a two-dimensional (hard disk) fluid, there are no measurements available near the freezing point to compare with. We also find that a small attractive three-body correlation term $c_{j'j''}^{(3)}$ is needed to reduce η in bcc sodium to a value close to that observed. The relative stability of fcc and bcc structures (approached from the fluid side) seems to depend on the size and sign of $c_{j'j''}^{(3)}$ about which no information exists. In addition to these experimentally testable predictions, we find a few more results for the actual values of $S(q)$ near freezing. For example, in the fcc case, c_j and c_n at freezing

are not fixed, but can be on the curve shown in
Fig. 2. There are no accurate experiments for
$S(q)$ (say as a function of pressure, on the freezing
line) to check whether this is true. Hansen and
Verlet[4,56] in their computer study of the freezing
of a Lennard-Jones fluid find that $[S(q)]_{max} = 2.85$
along the freezing line. More extensive experi-
ments are needed. We also find that $(c_j)_{bcc} > (c_j)_{fcc}$
while $(c_n)_{bcc} < (c_n)_{fcc}$, the difference being small
(see Tables I–III). This is indeed observed, being
strikingly evident in a plot of $S(q)$ (with q properly
scaled) for argon[25] (fcc and rubidium[27] (bcc) in the
same figure.[59] (The peak value for Na obtained by
Greenfield et al.[26] is $[S(q)]_{max} \simeq 2.9$, whereas for
Rb,[27] $[S(q)]_{max} \simeq 3.1$.)

Whether this difference is systematic can be con-
firmed only by accurate and detailed experiment.
The present absolute accuracy of measurement[60]
of $S(q)$ (~5%) is barely sufficient for this purpose.
(For q in the second peak region, this accuracy
translates into an uncertainty ~20% in $c_q^{\rightarrow}$.)

Of the simple three-dimensional structures, the
simple cubic and the hexagonal close packed have
not yet been investigated computationally. The
former is very strongly disfavored on account of
its poor connectivity, and the latter is interesting
as the unit cell has a basis. Work on these as also
on the relative stability of bcc and fcc phases is in
progress. On its completion one might hope to un-
derstand the domains of stability of various simple
crystal structures for monoatomic solids in terms
of fluid phase structural correlations.

VI. DISCUSSION AND CONCLUSION

We first discuss here two objections which are
commonly raised against the type of theory of
freezing presented here, namely that order-pa-
rameter fluctuation effect have been ignored,[10] and
that the lattice periodic component of the density
is not a good order parameter.[38,61] We then con-
clude by pointing out open problems and applica-
tions of the theory of freezing described above.

A. Fluctuation effects

In the mean-field theory presented here, we have
expressed the thermodynamic potential Ω as a
function of variables λ_i related to ρ_i. The effect
of all other density fluctuations, e.g., $\rho_{\vec{K}_i+\vec{\delta}}^{\rightarrow}$ ($|\vec{\delta}|$
small) on Ω has been included exactly, as it occurs
in the fluid phase, through the direct correlation
function c_i and other higher-order correlation
functions. The observed c_i is influenced by vari-
ous short-range correlations, i.e., coupling among
density fluctuations of various wavevectors. It is
simply that we exhibit Ω explicitly only as a func-
tion of a few variables λ_i.

However, this approach starting from the fluid
is insufficient in one way. Mermin[62] has shown
that the excitation energy of the density fluctuation
$\rho_{\vec{K}_i+\vec{\delta}}^{\rightarrow}$ has a part going as $k_B T(\delta^2/K_i^2)(|\langle \rho_{\vec{K}_i}^{\rightarrow}\rangle|^2/\overline{N}^2)$.
Clearly, this is a purely solid-state effect. The
presence of such a term will affect the correlation
functions, but we cannot see this effect in a theory
which uses only fluid phase correlation functions.
This low-lying excitation spectrum is of crucial
qualitative importance, since this together with the
density of states factors for one and two dimen-
sions, leads to the conclusion that a crystalline
phase (i.e., a phase with $\langle \rho_{\vec{K}_i}^{\rightarrow}\rangle \sim O(\overline{N})$) is self-con-
sistently unstable in one and two dimensions.
Since we do not, by the nature of our scheme, con-
sider (implicitly or explicitly) such a term in the
excitation spectrum of $\rho_{\vec{K}_i+\vec{\delta}}^{\rightarrow}$ and its effect on the
response function c_i, we may find a fluid solid
transition in one or in two dimensions. Actually,
we find that there is freezing to an hcp phase in
two dimensions, and there is no freezing in one
dimension.

Computer experiments on hard disks show a
phase transition. This is easily reconciled with
the rigorous result due to Mermin.[62] The instabil-
ity of the crystalline phase is due to an infrared
divergence effect caused by density fluctuations
$\rho_{\vec{K}_i+\vec{\delta}}^{\rightarrow}$ with $\vec{\delta} \rightarrow 0$. Now the computer experiments
are done with finite size systems. Considering a
two-dimensional system with density ρ and number
of particles N, its size (area) is $N\rho^{-1}$. The small-
est value of δ probed by the computer experiment
is then $\delta_{min} \sim 2\pi/(N\rho^{-1})^{1/2}$ or $(\delta_{min}/2\pi)(\rho^{-1})^{1/2} \sim 1/\sqrt{N}$.
This is nonzero, and typically (for $N = 256$) $\sim \frac{1}{16}$.
Because of this effective lower cutoff, there is no
infrared divergence, and a crystalline solid phase
is found. Our theory gives (for η) a value in
close agreement with the computer experimental
result for hard disks. This implies that the solid
state finite $\delta_{min}[\simeq 2\pi/(N\rho^{-1})^{1/2}]$ fluctuation effects
are quantitatively small. This is expected since
freezing is a strongly first-order phase transi-
tion and the infrared divergence is only log-
arithmic for two dimensions.

B. Choice of order parameter

We have chosen λ_i ($= \epsilon_i \rho_i$) as the order pa-
rameter, since in the solid, $\langle \rho(\vec{r})\rangle$ has lattice
periodic components. However, if the center-
of-mass coordinate of the system is not fixed, but
can be random (e.g., due to Brownian motion),
$\langle \rho(\vec{r})\rangle$ would be of the form $\sum_i \langle \rho_i\rangle e^{i\vec{K}_i \cdot (\vec{r}+\vec{\alpha})}$, where
$\vec{\alpha}$ is a random vector, and on the average, the
periodic components of $\langle \rho(\vec{r})\rangle$ will be blurred out.
It has therefore been suggested that $\langle \rho(\vec{r})\rangle$ is not a
good index of crystalline ordering, but that one

needs to calculate a five-point function.[61] Here, four points serve to determine the frame in which the crystalline ordering is probed by the fifth point. This suggestion while strictly correct, is obviously impractical and perhaps unnecessary. The physical reason for the appropriateness of $\langle \rho(\vec{r}) \rangle$ has been known for a long time. In any condensed system with fixed volume V, the position of its center of mass and its orientation are fixed, say by imposing suitable external forces. Such restraining forces are implicit in all statistical mechanical calculations in which the configuration space available to each atom or molecule is restricted to a particular volume V. Thus, if we assume that these external forces or potentials are present and give the system a fixed center-of-mass coordinate as well as fixed orientation, the calculation of $\langle \rho(\vec{r}) \rangle$ is "relieved of all ambiguity."[38] These potentials can be included in H_N [see Eq. (1)]. We can safely assume them to have no effect on the fluid phase bulk correlation functions c_i, etc. Thus, the theory developed above can be carried through exactly as before. If the system is confined to a cubical box of side $(V)^{1/3}$, and the density $\rho(\vec{r})$ vanishes on the sides of the box, then $\rho(\vec{r})$ is expressible as a combination of sine functions rather than exponentials, $\rho(\vec{r}) = \sum c_i \sin(\vec{q}_i \cdot \vec{r})$, where $q_{i\alpha} = 2\pi n_{i\alpha}/V^{1/3}$, $n_{i\alpha}$ being a positive integer.[62] Calculations for this representation of $\rho(\vec{r})$ give results identical with the Fourier exponential representation results of Sec. III.

C. Applications

It is clear that the problem of melting can be discussed in a similar way starting from the solid phase, and calculating $\Omega(\{\lambda_i + \lambda_i^0\})$ (λ_i^0 corresponds to the equilibrium value in the solid phase). It can be shown that there is always a local minimum at $\lambda_i + \lambda_i^0 = 0$, i.e., a fluid phase. Due to the absence of homogeneity of space in the solid phase, the correlation function $c(\vec{r}, \vec{r}') \neq c(\vec{r} - \vec{r}')$ and hence it is not diagonal in momentum space. This creates complications. The advantage in working from the solid side is that we can calculate the correlation functions from a good dynamical model, e.g., self-consistent phonon theory. Calculations are under way in this direction.

Beyond the liquid-solid transition problem, one can expect that this approach will be useful in all first order transitions where structural correlations play an important role. Examples are transitions between various phases of liquid crystals. Using our method, the thermodynamic potential difference can be expressed in terms of a small number of structural correlation functions directly

accessible to theory and experiment. The resulting theory can be expected to be simpler and more accurate than the Kirkwood-Monroe approach which is the only fundamental approach tried so far.[63]

For a quantum system, the Hamiltonian does not commute with, for example, the operator ρ_i, and so the theory cannot be carried through as it stands. Extension to cover this case can be done using time labeled operators. Such functional methods for quantum systems are well known.[39] Such an extension will be useful not only in discussing solidification of quantum fluids, e.g., ^{4}He, but also the very important case of electrons in solids. The latter can be viewed as an electron fluid which develops lattice periodic components in the density in the presence of the "external" ion potentials disposed on a lattice. Knowing the electron density and the dependence of system energy on this, could well constitute a fundamental theory of bonding and cohesion in solids in which the periodic potential is not regarded as a weak perturbation, and short-range correlations in the electron fluid are properly included.

APPENDIX

Here we discuss the effect of nonlinear terms in the potential response (HNC) scheme described in Sec. III. Retaining up to quadratic terms in the functional Taylor series expansion, Eq. (10) becomes

$$\beta v_{\text{eff}}(\vec{r}) = \beta v(\vec{r}) - \int c(\vec{r} - \vec{r}')[\langle \rho(\vec{r}') \rangle - \rho_0] \, d\vec{r}'$$

$$- \frac{1}{2} \int c^{(3)}(\vec{r}, \vec{r}', \vec{r}'')[\langle \rho(\vec{r}') \rangle - \rho_0]$$

$$\times [\langle \rho(\vec{r}'') \rangle - \rho_0] \, d\vec{r}' \, d\vec{r}'', \quad \text{(A1a)}$$

where

$$c^{(3)}(\vec{r}, \vec{r}', \vec{r}'') = \frac{\partial^2 \ln[\langle \rho(\vec{r}) \rangle e^{\beta v(\vec{r})}/\rho_0]}{\partial \langle \rho(\vec{r}') \rangle \partial \langle \rho(\vec{r}'') \rangle} \Bigg|_{v(\vec{r}) = 0},$$

$$\text{(A1b)}$$

is the direct three-particle correlation function. Since $c^{(3)}(\vec{r}, \vec{r}', \vec{r}'')$ is a quantity evaluated in the homogeneous fluid phase, it is a function of the form $c^{(3)}(\vec{r} - \vec{r}', \vec{r} - \vec{r}'')$. Further, since

$$\langle \rho(\vec{r}) \rangle - \rho_0 = \rho_0 \left(\eta + \sum_i \mu_i e^{i\vec{K}_i \cdot \vec{r}} \right),$$

it is clear from Eq. (A1a) that we need only the

Fourier components $c_{00}^{(3)}$, $c_{0i}^{(3)}$, $c_{i'i''}^{(3)}$, where

$$c_{\vec{q}'\vec{q}''}^{(3)} = \rho_0^2 \int c^{(3)}(\vec{r}-\vec{r}', \vec{r}-\vec{r}'')$$

$$\times e^{-i\vec{q}'\cdot(\vec{r}-\vec{r}') - i\vec{q}''\cdot(\vec{r}-\vec{r}'')} d\vec{r}' d\vec{r}''$$

$$= \rho_0^2 \int c^{(3)}(\vec{\rho}', \vec{\rho}'')$$

$$\times e^{-i(\vec{q}'\cdot\vec{\rho}' + \vec{q}''\cdot\vec{\rho}'')} d\vec{\rho}' d\vec{\rho}''.$$

$c_{00}^{(3)}$ and $c_{0i}^{(3)}$ involve density derivatives of c_0 and c_i (known experimentally in some cases) whereas $c_{i'i''}^{(3)}$ (except for $i'' = -i'$) is not thus known. To see this, we use the definition (A1b) to write

$$c^{(3)}(\vec{r}-\vec{r}', \vec{r}-\vec{r}'') = -\frac{1}{\rho_0^2} \delta(\vec{r}-\vec{r}')\delta(\vec{r}-\vec{r}'')$$

$$+ \frac{\partial^2[\beta v(\vec{r})]}{\partial\langle\rho(\vec{r}')\rangle\partial\langle\rho(\vec{r}'')\rangle}\bigg|_{v=0}. \quad (A2)$$

The second term on the right side of Eq. (A2) can be written using a well-known result in functional differentiation,

$$\frac{\partial^2\beta v(\vec{r})}{\partial\langle\rho(\vec{r}')\rangle\partial\langle\rho(\vec{r}'')\rangle}\bigg|_{v=0} = -\int \frac{\partial^2\langle\rho(\vec{r}_1)\rangle}{\partial\beta v(\vec{r}_1')\partial\beta v(\vec{r}_1'')}\bigg|_{v=0}$$

$$\times\left(\frac{\partial\beta v(\vec{r}_1)}{\partial\langle\rho(\vec{r})\rangle}\frac{\partial\beta v(\vec{r}_1')}{\partial\langle\rho(\vec{r}')\rangle}\right.$$

$$\times\left.\frac{\partial\beta v(\vec{r}_1'')}{\partial\langle\rho(\vec{r}'')\rangle}\right)$$

$$\times(d\vec{r}_1 d\vec{r}_1' d\vec{r}_1''). \quad (A3)$$

Using the fact that $[\partial^2\langle\rho(\vec{r}_1)\rangle/\partial\beta v(\vec{r}_1')\partial\beta v(\vec{r}_1'')]_{v=0}$ is just the fluid three-particle correlation function

$$S^{(3)}(\vec{r}_1, \vec{r}_1', \vec{r}_1'') = S^{(3)}(\vec{r}_1-\vec{r}_1', \vec{r}_1-\vec{r}_1'') = \langle\rho(\vec{r}_1)\rho(\vec{r}_1')\rho(\vec{r}_1'')\rangle$$

and Fourier transforming equations (A2) and (A3), we find

$$c_{\vec{q}',\vec{q}''}^{(3)} = -1 + c_{\vec{q}',\vec{q}''}^{3a}, \quad (A4a)$$

where

$$c_{\vec{q}',\vec{q}''}^{3a} = -\frac{1}{\rho_0^3} S_{\vec{q}',\vec{q}''}^{(3)} \tilde{c}_{-\vec{q}'-\vec{q}''} \tilde{c}_{\vec{q}'} \tilde{c}_{\vec{q}''}, \quad (A4b)$$

and

$$\tilde{c}_{\vec{q}} = c_{\vec{q}} - 1. \quad (A4c)$$

From Eqs. (A4a–A4c), it is easy to obtain expressions for the desired Fourier components $c_{\vec{q}',\vec{q}''}^{(3)}$. If one of the vectors $\vec{q}'$, $\vec{q}''$, or $\vec{q}'+\vec{q}''$ is zero, the corresponding $c^{(3)}$ can be expressed in terms of density derivative of a two-particle correlation function. In particular,

(i) $$c_{00}^{(3)} = -c_0 + \rho_0\left(\frac{\partial c_0}{\partial\rho}\right)_{\rho=\rho_0}, \quad (A5a)$$

(ii) $$c_{0i}^{(3)} = -c_{i0}^{(3)} = c_{i,-i}^{(3)} = -c_i + \rho_0\left(\frac{\partial c_i}{\partial\rho}\right)_{\rho=\rho_0}. \quad (A5b)$$

In the general case, we need to know the appropriate Fourier components of the three-particle correlation function, i.e.,

(iii) $$c_{i,i}^{(3)} = -1 - \frac{1}{\rho_0^3} S_{i,i}^{(3)} \tilde{c}_i\tilde{c}_i\tilde{c}_{i+i'}. \quad (A5c)$$

We thus see that if the density dependence of the compressibility and of the structure factor S_i are known, we can calculate the nonlinear response functions $c_{00}^{(3)}, c_{0i}^{(3)}, c_{i0}^{(3)}, c_{i,-i}^{(3)}$. However, the general response function $c_{i',i}^{(3)}$ is not known, since the three particle correlation function $S^{(3)}$ is not known experimentally. There are theoretical approximations available for $S^{(3)}$, but their accuracy is not well established.

We now turn to the question of evaluating Ω, given a certain set of nonvanishing $c_{i',i}^{(3)}$. The equation (A1a) for $\beta v_{\text{eff}}(\vec{r})$ can be written

$$-\beta v_{\text{eff}}(\vec{r}) = -\beta v(\vec{r}) + \left(c_0\eta + \tfrac{1}{2}c_{00}^{(3)}\eta^2 + \frac{1}{2}\sum_i c_{i,-i}^{(3)}\mu_i^2\right)$$

$$+ \sum_i (c_i\mu_i + c_{i0}^{(3)}\mu_i\eta)e^{i\vec{K}_i\cdot\vec{r}}$$

$$+ \frac{1}{2}\sum_{i',i''} \mu_{i'}\mu_{i''}c_{i',i''}^{(3)}e^{i(\vec{K}_{i'}+\vec{K}_{i''})\cdot\vec{r}}. \quad (A6)$$

In order to calculate Ω, we use the definition $\langle\rho(\vec{r})\rangle = \rho_0\exp[-\beta v_{\text{eff}}(\vec{r})]$, and then the relation between $\partial\Omega/\partial\lambda_k$ and $\langle\rho_k\rangle$ [Eq. (9)]. Since $\langle\rho(\vec{r})\rangle$ depends on $v_{\text{eff}}(\vec{r})$ which depends on $\langle\rho(\vec{r})\rangle$, there is a self-consistency problem to be tackled. In the linear response case, it was possible to choose a scale factor ϵ_i such that $v_{\text{eff}}(\vec{r})$ is a function only of the density fluctuation amplitude or order parameter λ_i, and the self-consistency problem is solved easily. Clearly this cannot be done now, since after canceling the term $c_i\mu_i$ from Eq. (A6), we are left with terms in $v_{\text{eff}}(\vec{r})$ depending explicitly on μ_i, η, etc. It turns out to be still possible to integrate over λ_i and obtain $\Omega(\{\lambda_i\})$. We consider, to be specific, a case where in the last term of Eq. (A6), the vectors $\vec{K}_{i'}$ and $\vec{K}_{i''}$ are members of the same reciprocal-lattice vector set, and add to another member of the same set. Suppose $n_i^{(3)}$ pairs add to a single member of the set $\{\vec{K}_i\}$. Then, Eq. (A6) can be written

$$-\beta v_{\text{eff}}(\vec{r}) = \left(c_0\eta + \tfrac{1}{2}c_{00}^{(3)}\eta^2 + \frac{1}{2}\sum_i c_{i,-i}^{(3)}\mu_i^2\right)$$

$$+ \sum_i (2\epsilon_i\lambda_i - 2\epsilon_i^2\langle\rho_i\rangle\lambda_i + c_i\mu_i + c_{i0}^{(3)}\mu_i\eta$$

$$+ \tfrac{1}{2}n_i^{(3)}c_{i'i''}^{(3)}\mu_i^2)e^{i\vec{K}_i\cdot\vec{r}}. \quad (A7)$$

Using the choice $\epsilon_i = (c_i/2N_0)^{1/2}$, we can integrate

over ξ_i to find that

$$\beta\Delta\Omega(\{\xi_i\}) = \sum_i \left(\frac{\xi_i^2}{2c_i}\right) - (1 - c_0)\left(\eta + \frac{\eta^2}{2}\right)$$
$$+ c_{00}^{(3)}\left(\frac{\eta^2}{2} + \frac{\eta^3}{3}\right) + \sum_i c_{i0}^{(3)}\mu_i^2(\eta + \tfrac{1}{2})$$
$$+ \sum_i \left(\frac{1}{3}\right) c_{i'i''}^{(3)}n_i^{(3)}\mu_i^3 , \tag{A8}$$

where the equations

$$\left[(1 - c_0)\eta - \tfrac{1}{2}c_{00}^{(3)}\eta^2 - \frac{1}{2}\sum_i c_{i,-i}^{(3)}\mu_i^2\right] = \ln\phi(\{x_i\}), \tag{A9a}$$

$$\frac{\partial \ln\phi(\{x_i\})}{\partial x_k} = \frac{\mu_k}{1 + \eta} , \tag{A9b}$$

and

$$x_i = \xi_i + c_{i0}^{(3)}\mu_i\,\eta + \tfrac{1}{2}n_i^{(3)}c_{i'i''}^{(3)}\mu_i^2 \tag{A9c}$$

determine η and μ_i for given $\{\xi_i\}$. At the extrema

$$\mu_i = \xi_i/c_i . \tag{A10}$$

These equations can be used to calculate freezing parameters.

We wish to emphasize that there is *no* reason to conclude from the inadequacy of the first-order HNC and Percus-Yevick approximations for the two particle correlation function in dense hard-sphere-like fluids that they would be insufficient here, and consequently that higher-order response terms are necessarily important. Even in dense fluids, for a one-component plasma where $V(r_{ij})$ varies very slowly (though, overall, by much more than k_BT) the first order or simple HNC works very well for $g(r)$ and for the equation of state.[41] Our case is much less demanding, with a smoothly oscillatory $v(r)$, and with $|v(r)| \lesssim k_BT$. Thus the adequacy of the simple HNC (or "linear response") theory here is to be examined on its own, using the higher-order expressions derived in this Appendix. This is done in Sec. V.

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