PHYSICAL REVIEW A VOLUME 31, NUMBER 3 MARCH 1985

Theory of freezing in simple systems

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(Received 22 June 1983; revised manuscript received 12 September 1984)

The transition parameters for the freezing of two one-component liquids into crystalline solids are evaluated by two theoretical approaches. The first system considered is liquid sodium which crystallizes into a body-centered-cubic (bcc) lattice; the second system is the freezing of adhesive hard spheres into a face-centered-cubic (fcc) lattice. Two related theoretical techniques are used in this evaluation: One is based upon a recently developed bifurcation analysis; the other is based upon the theory of freezing developed by Ramakrishnan and Yussouff. For liquid sodium, where experimental information is available, the predictions of the two theories agree well with experiment and each other. The adhesive-hard-sphere system, which displays a triple point and can be used to fit some liquids accurately, shows a temperature dependence of the freezing parameters which is similar to Lennard-Jones systems. At very low temperature, the fractional density change on freezing shows a dramatic increase as a function of temperature indicating the importance of all the contributions due to the triplet direction correlation function. Also, we consider the freezing of a one-component liquid into a simple-cubic (sc) lattice by bifurcation analysis and show that this transition is highly unfavorable, independent of interatomic potential choice. The bifurcation diagrams for the three lattices considered are compared and found to be strikingly different. Finally, a new stability analysis of the bifurcation diagrams is presented.

I. INTRODUCTION

The proper characterization of the liquid-to-solid freezing transition remains an outstanding theoretical challenge. The various statistical-mechanical approaches to the study of this transition rely on the pioneering work of Kirkwood and Monroe,[1] who investigated it by studying the solutions of the nonlinear equations for the single-particle distribution function, and who identified the transition with a spontaneous bifurcation of periodic solutions (which are characteristic of the fluid phase). Broadly speaking, the subsequent development of this method of analysis has proceeded in two directions. The first of these concentrates on bifurcations in the solutions of nonlinear integral equations for the singlet density expressed in terms of either the pair correlation function[2–4] or the direct correlation function.[5,6] These equations arise from some form of the truncated Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. The second approach emphasizes the use of thermodynamic criteria for the solution of a nonlinear integral equation for the direct correlation function.[7,8]

In the work reported here, a promising method originally suggested by Ryzhov and Tareeva[6] and extended recently by Bagchi, Cerjan, and Rice[9] is applied to several physical systems. Specifically, the bifurcation analysis developed earlier to describe the hard-sphere system is applied to investigate the freezing transition in liquid sodium and in the system of adhesive hard spheres; the former crystallizes in the body-centered-cubic (bcc) geometry, and the latter in the face-centered-cubic (fcc) geometry.

Previous studies of the freezing transition which use a bifurcation condition have met with limited success. For example, those approaches using the pair correlation function fail in the sense that a phase transition is predicted for one-dimensional hard rods, but succeed in finding a transition for three-dimensional hard spheres. Correspondingly, the direct correlation function approach does not predict a transition for the hard rods, but then fails to predict a transition for the three-dimensional hard-sphere system. There are clearly two major difficulties here: First, the theories disagree with each other despite their similar physical basis; second, they are both incorrect in their physical predictions.

As emphasized by Kayser and Raveché, both approaches have identical physical content and produce identical bifurcation diagrams.[10] The difference in the two theories arises from an inconsistency in the treatment of the expansion about the solid-state singlet density function. The pair correlation function formulation mixes orders in the expansion, and hence is inconsistent when truncated.[6,8] Stated another way, the replacement of the solid-state pair correlation function by the liquid-state correlation function is inconsistent within this approach. In contrast, this inconsistency is avoided in the direct correlation function formulation since it arises from a systematic functional Taylor-series expansion[5,6] about the liquid state.

The second difficulty above still remains. Removal of the nonphysical behavior of the direct correlation function approach is provided in the work of Ryzhov and Tareeva.[6] This method explicitly includes the discontinuity in the density upon freezing, and thus incorporates bifurcation points which are not continuously connected to the fluid phase solution. That is, the bifurcation point which is produced by a nonzero discontinuity in the density change is chosen to be the physically relevant bifurcation point. In this way the physically important features of a first-order phase transition underlie the structure and analysis of the equations.

The Ryzhov-Tareeva (RT) bifurcation technique is similar in several respects to the thermodynamic theory. Both start with the direct correlation function formulation; both use an order-parameter expansion for the singlet density which may then be decomposed into a system of coupled nonlinear integral equations; both assume that the expansion in terms of the liquid-state functions will converge to the solid-state partition function and that this expansion is valid away from the transition point (the series expansion may be analytically continued). The approaches differ in several important respects also. Although the set of equations derived is the same, their subsequent manipulation differs since equality of the liquid and solid fugacities is not implemented in the bifurcation technique. In the bifurcation theory, the compressibility and fugacities are removed from the integral equations and thus become derived quantities which can be used as a test of the theory. Finally, the condition used in the bifurcation theory for the evaluation of the transition parameters is that the lowest density should be chosen which is consistent with the previously evaluated bifurcation information. This choice obviously differs from the equality of the grand thermodynamic potential and external condition imposed in the thermodynamic approach.

It should be emphasized that the order-parameter theory of freezing is a mean-field theory since the fluctuations in the order parameters are not included. As a result, the equality of the liquid- and solid-phase grand thermodynamic potentials must be imposed or demonstrated to satisfy the requirements of an equilibrium thermodynamic phase transition. Thus, the bifurcation theory presented in this paper cannot predict a thermodynamic freezing transition.

On the other hand, there are compelling reasons to base a study of the freezing transition upon a bifurcation analysis. First, the theory may predict a transition from the liquid to a metastable solid phase. Although care is needed when interpreting the significance of the metastable solid, its appearance in a self-consistent theory is of considerable theoretical interest. Second, it is well known that a crystalline solid cannot be superheated much above its melting temperature. The transition parameters predicted by the bifurcation theory and those predicted by a thermodynamic calculation within the same theoretical framework may provide insight into this important, poorly understood phenomenon. Thus, a bifurcation calculation may complement the Lindemann criterion in the sense that the bifurcation theory uses only liquid-state information whereas the Lindemann criterion is based solely on solid-phase information.

In fact, our theoretical calculations seem to justify these expectations. We find that the transition parameters predicted by the present bifurcation theory are indeed very close to the predictions of the thermodynamic theory of Ramakrishnan and Yussouff.

In the work of Bagchi, Cerjan, and Rice[9] the formalism of Ryzhov and Tareeva was extended to include higher-order parameters in the Fourier expansion of the singlet density in terms of the reciprocal lattice vectors of the fcc lattice. The improved version of the theory produces liquid- and solid-phase densities at the transition point which are in satisfactory agreement with computer simulations for the hard-sphere system.[9] This improvement in the theory for the hard-sphere system leads naturally to an examination of the theory for other systems and lattice geometries.

Our motivation for studying the bcc structure arises from the observation that many fluids, e.g., sodium, form a bcc lattice. By using the experimentally determined structure factor of the liquid phase, a freezing temperature can be predicted, in addition to a value for the solid density. The predictions made below for sodium constitute the first physical application of the bifurcation theory in the form suggested by Ryzhov and Tareeva. Furthermore, the results for sodium are representative of the alkali metals in general, since it is known that the interparticle potentials, and hence their derived properties, satisfy a scaling relationship.[11] This work then, is a preliminary step in a rigorous investigation of the applicability of the general bifurcation analysis to real systems.

The second application presented below, freezing of a fluid of adhesive hard spheres, serves as a useful model study. Indeed, the model was first proposed to interpret certain discontinuities observed in computer-simulation studies of Lennard-Jones fluids.[12] This system is also of interest in the study of the critical points associated with the gas-to-liquid transition and it may display a triple point.[13] The model is useful for empirical fits. It has been shown to give an accurate description of the structure factors for liquid lead and aluminum at high density.[14] Since an analytic expression for the temperature-dependent direct correlation function is available,[12] the statistical-mechanical analysis of freezing may be developed without the constraints imposed by limited experimental data or by approximations needed to obtain the direct correlation function for the Lennard-Jones fluid.

In addition to a calculation of the transition parameters for several systems, a general analysis of the relative stabilities of different crystal lattices near the bifurcation points is given. A consequence of this analysis is the prediction that no transition from a one-component simple liquid to a simple cubic (sc) lattice structure is possible within a two-order-parameter theory. The stability analysis also justifies some conjectures proposed earlier by Bagchi, Cerjan, and Rice.[9]

The structure of the present work is as follows. Section I contains a description of the general theoretical background necessary for the specific applications presented later. Section II gives the results of the analysis for both the body-centered-cubic lattice for sodium and the face-centered-cubic lattice for the adhesive-hard-sphere model and the stability analysis mentioned above. Section III presents a short discussion of these results and their physical significance.

II. THEORETICAL BACKGROUND

The notation adopted below is that of Bagchi, Cerjan, and Rice[9] (hereafter referred to as BCR). The equations and their derivations are given in greater detail in BCR and will be quoted without explicit justification below. The elements required for the bifurcation analysis and subsequent transition density determination for either bcc sodium or the fcc adhesive hard spheres are the reciprocal-lattice vectors of the solid and a density and temperature-dependent expression for the Fourier transform of the direct correlation function of the homogeneous liquid phase.

The analysis then proceeds in two distinct steps. First, the bifurcation diagram is constructed solely from the structure of the nonlinear equations and the geometric information contained in the reciprocal-lattice vectors. Second, liquid and solid densities are determined from some specific direct correlation function using consistency conditions on the bifurcation points found in the first step. The reciprocal-lattice vectors which are included in the analysis are selected on physical grounds. Namely, successive lattice vectors are chosen in terms of increasing magnitude; if two vectors have identical magnitude, the set with the largest number of terms which produces the maximum value of the Fourier-transformed direct correlation function is the favored choice. Retention of one set of vectors is denoted a one-order-parameter theory, two vector sets a two-order-parameter theory, and so forth. The corresponding nonlinear equations for these reciprocal-lattice vectors are solved for the one- and two-order-parameter theories in the same fashion as that presented in BCR.

Briefly, this system of equations arises from an expansion of the density in terms of the liquid density ρ_l and reciprocal-lattice vectors

$$\rho(\mathbf{r})=\rho_l+\Delta\rho(\mathbf{r})$$

$$=\rho_l+\rho_l\sum_{\mathbf{q}_\alpha}\phi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r}) \tag{1}$$

with

$$\lim_{V\to\infty}\left[\frac{1}{V}\int_V d\mathbf{r}\,\rho(\mathbf{r})\right]=\rho_s \tag{2}$$

and

$$\phi_{\mathbf{q}_\alpha}=\frac{1}{\Delta}\int_\Delta \frac{\Delta\rho(\mathbf{r})}{\rho_l}e^{-i\mathbf{q}_\alpha\cdot\mathbf{r}}d\mathbf{r}\ , \tag{3}$$

where Δ is the volume of a unit cell. $\xi_{\mathbf{q}_\alpha}(\mathbf{r})$ represents the $\mathbf{q}_\alpha$th reciprocal-lattice vector. Then, using the generating functional expansion for the inhomogeneous singlet density in terms of the n-particle direct correlation functions c_n,[15,16] and truncating after one term, the basic relation

$$\frac{\rho_l+\Delta\rho(\mathbf{r})}{z_s}=\frac{\rho_l}{z_l}\exp\left[\int c_2(\mathbf{r}_{12},\rho_l)\Delta\rho(\mathbf{r}_2)d\mathbf{r}_2\right] \tag{4}$$

is obtained. In Eq. (4), z_l and z_s are the liquid- and solid-phase fugacities. Introducing Eq. (1) into Eq. (4), after a few manipulations the following system of nonlinear equations for any reciprocal-lattice vector is found:

$$\frac{\rho_l}{\rho_s}\Delta_{\mathbf{q}_\alpha}\phi_{\mathbf{q}_\alpha}=\frac{\int_\Delta d\mathbf{r}\,\xi_{\mathbf{q}_\alpha}(\mathbf{r})\exp[B(\mathbf{r})]}{\int_\Delta d\mathbf{r}\exp[B(\mathbf{r})]} \tag{5}$$

with

$$\Delta_{\mathbf{q}_\alpha}\equiv\frac{1}{\Delta}\int_\Delta d\mathbf{r}\,\xi^2_{\mathbf{q}_\alpha}(\mathbf{r})\ , \tag{6}$$

and

$$B(\mathbf{r})=\rho_l\sum_{\mathbf{q}_\alpha(\neq 0)}c_{\mathbf{q}_\alpha}\phi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r})\ , \tag{7a}$$

$$c_{\mathbf{q}_\alpha}=\left[\int c_2(\mathbf{r}_{12})e^{-i\mathbf{q}_\alpha\cdot\mathbf{r}_{12}}d\mathbf{r}_2\right]_{\mathbf{q}_\alpha=|\mathbf{q}_\alpha|}\ , \tag{7b}$$

$$\lambda_{q_\alpha}\equiv\rho_s c_{\mathbf{q}_\alpha}\ . \tag{7c}$$

That is, $c_{\mathbf{q}_\alpha}$ is the Fourier transform of the direct correlation function evaluated at the magnitude of the $\mathbf{q}_\alpha$th reciprocal-lattice vector. Equation (5) is the set of nonlinear equations yielding the bifurcation diagrams. By truncating at the nth reciprocal-lattice vector, n simultaneous equations are obtained in terms of n order parameters. As emphasized in BCR, the solution to these equations is universal in the sense that only structural information from the solid phase is needed and no interparticle potential-dependent information is used at this stage.

In a first approximation, Eq. (5) is given by

$$\frac{\rho_l}{\rho_s}\Delta_{\mathbf{q}_\alpha}\phi_{\mathbf{q}_\alpha}=\frac{\int_\Delta\xi_{\mathbf{q}_\alpha}(\mathbf{r})\exp[B(\mathbf{r})+D(\mathbf{r})]d\mathbf{r}}{\int_\Delta\exp[B(\mathbf{r})+D(\mathbf{r})]d\mathbf{r}}\ , \tag{8a}$$

where

$$D(\mathbf{r})=\rho_l^2\phi_0\sum_{\mathbf{q}_\alpha(\neq 0)}c_3(\mathbf{q}_\alpha,0)\phi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r})\ ,$$

$$c_3(\mathbf{q}_\alpha,0)=\left[\int e_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)e^{-i\mathbf{q}_\alpha\cdot\mathbf{r}_{12}}d\mathbf{r}_2\right]_{\mathbf{q}_\alpha=|\mathbf{q}_\alpha|}\ , \tag{8b}$$

and where the terms $c_3(q,q')$ and higher-order correlation functions have been neglected, which constitutes the approximation. It is interesting to note that for Eq. (8a) the bifurcation analysis will remain unchanged, but the calculated transition densities will change. The quantity $c_3(q,0)$ can be obtained from the relation

$$c_3(\mathbf{q}_\alpha,0)=\frac{\partial c_2}{\partial\rho_l}(\mathbf{q}_\alpha)$$

if a reliable estimate of the derivative is known.

A. Bifurcation analysis

After locating the appropriate bifurcation points $\lambda^*_{q_\alpha}$ of the diagram, application of the subsidiary conditions

$$\lambda^*_{q_\alpha}=\rho_s c_{q_\alpha}(\rho^*_s,\rho^*_l)\ , \tag{9a}$$

$$\left[\frac{\partial\lambda_{q_\alpha}}{\partial\rho_s}\right]\Bigg|_{(\rho^*_s,\rho^*_l)}=0\ , \tag{9b}$$

$$\lambda_{q_\beta}(\rho^*_s,\rho^*_l)=\lambda^*_{q_\beta} \tag{9c}$$

produces the liquid and solid transition densities ρ^*_l, ρ^*_s. Only the first two conditions are necessary for the one-order-parameter theory, while the third condition is needed for the two-order-parameter theory. The first and third conditions are consistency conditions on the densities and bifurcation points. The second condition, Eq. (9b), ensures that the smallest densities are chosen to satisfy the consistency equations. Equation (9c) is equivalent to the graphical condition that the pair $(\lambda^*_{q_\alpha},\lambda^*_{q_\beta})$ lie on the freezing curve.

It is worth emphasizing that the condition (9b) is quite general and is likely to be satisfied for all liquid-to-solid phase transitions. This condition arises solely from the convexity of the function $\lambda_{q_\alpha}(\rho_s,\rho_l)$, which underlies the short-range ordered structure of the liquid phase at high density. The existence of this condition is essential to determine unique transition densities from the bifurcation analysis.

So far, two approximations have been introduced. First, neglect of the triplet and higher-order correlation functions incurred by writing Eq. (4) and, second, truncation of the order parameter expansion (1) at second order. Because of these approximations, bifurcation analysis does not produce solutions with equal thermodynamic potential for the two phases. This point will be discussed at greater length below.

Ramakrishnan and Yussouff,[7] in their calculation of freezing parameters for the liquid-sodium bcc transition, observed that the triplet correlation function for the liquid makes an important contribution. In fact, for this particular system, the neglect of the triplet correlation function introduces a more serious error than the truncation of the order parameter expansion for the density after the second term. Therefore, it is worthwhile to investigate the effect of the triplet correlation function on the results of the bifurcation analysis. More details will be given in a future publication. Here, only the modifications that arise in the above equations are quoted.

In the BCR analysis of the bifurcation diagrams for three-, two-, and one-dimensional hard-sphere systems, the existence of a "universal" bifurcation point at $\lambda_{q_\alpha}=1$ was noted. As investigation of the physical relevance of this bifurcation point for fcc lattices led BCR to conjecture that the fcc bifurcation point at $\lambda_{q_\alpha}=1$ is to be identified with the limit of packing of the hard-sphere system. For example, in the three-dimensional case, this bifurcation point predicts densities which are very close to the liquid random close-packed value and to the crystal close-packed value. In one dimension, it corresponds to the maximum achievable densities $\rho_s=\rho_l=1.0$. In fact, an even more definite statement about the change in the relative fugacities of the liquid and solid phases about a bifurcation point may be made. Starting with the one-order-parameter theory expression for the ratio of fugacities

$$\frac{z_l}{z_s}=\left\{\left[\frac{\rho_l}{\rho_s}\right]\frac{1}{\Delta_{q_\alpha}}\exp\left[\left[\frac{\rho_s-\rho_l}{\rho_l}\right]c_0\right]\right\}\int_\Delta e^{\lambda_{q_\alpha}\psi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r})}d\mathbf{r} \tag{10}$$

and using the relationship obtained in BCR[9]

$$\int_\Delta e^{\lambda_{q_\alpha}\psi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r})}d\mathbf{r}=e^{\beta\lambda_{q_\alpha}\psi^2_{\mathbf{q}_\alpha}}\ , \tag{11}$$

where $\beta=\Delta_{q_\alpha}/2$, a simple expression for the derivative of (z_1/z_s) with respect to λ_{q_α} is found, namely

$$\begin{aligned}\frac{\partial}{\partial\lambda_{q_\alpha}}\left[\frac{z_l}{z_s}\right]=&\left[\frac{\partial}{\partial\lambda_{q_\alpha}}\left[\frac{\rho_2}{\rho_s\Delta_{q_\alpha}}e^{(\rho_s-\rho_l)c_0/\rho_l}\right]\right]e^{\beta\psi^2_{\mathbf{q}_\alpha}\lambda_{q_\alpha}}\\&+\left[\frac{\rho_l}{\rho_s\Delta_{q_\alpha}}e^{(\rho_s-\rho_l)c_0/\rho_l}\right]\beta\psi^2_{\mathbf{q}_\alpha}e^{\beta\psi^2_{\mathbf{q}_\alpha}\lambda_{q_\alpha}}\\&+\left[\frac{\rho_l}{\rho_s\Delta_{q_\alpha}}e^{(\rho_s-\rho_l)c_0/\rho_l}\right]\\&\times2\beta\psi_{\mathbf{q}_\alpha}\lambda_{q_\alpha}\left[\frac{\partial\psi_{\mathbf{q}_\alpha}}{\partial\lambda_{q_\alpha}}\right]\ .\end{aligned} \tag{12}$$

Near a bifurcation point the third term in Eq. (12) dominates all others, leaving

$$\frac{\partial}{\partial\lambda_{q_\alpha}}\left[\frac{z_l}{z_s}\right]\Bigg|_{\lambda_{q_\alpha}=\lambda^*_{q_\alpha}}\simeq\text{const}\times\left[\frac{\partial\psi_{\mathbf{q}_\alpha}}{\partial\lambda_{q_\alpha}}\right]\Bigg|_{\lambda_{q_\alpha}=\lambda^*_{q_\alpha}}\ . \tag{13}$$

Since the constant term is intrinsically positive, this relation demonstrates that it is strictly the sign of the derivative near the bifurcation point which indicates the direction of the stability change in the system. Figures 1 and 2 illustrate this result for the three-dimensional and one-dimensional fcc one-order-parameter theories, respectively. Near $\lambda_{q_\alpha}=1$, the change in $\psi_{\mathbf{q}_\alpha}$ with respect to λ_{q_α} is of opposite sign for the different dimensions. As demonstrated by BCR, the one-dimensional system has no

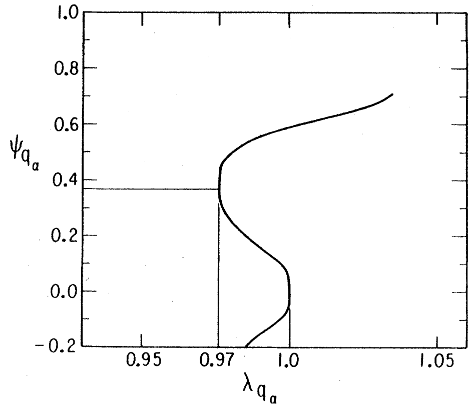

FIG. 1. Three-dimensional fcc bifurcation diagram displaying symmetry about the λ_{q_α} axis and two bifurcation points within the one-order-parameter theory.

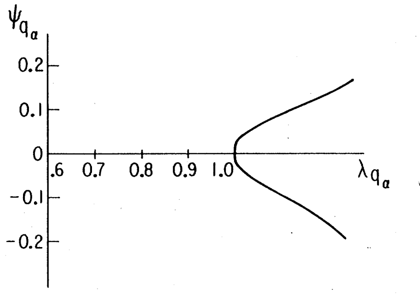

FIG. 2. One-dimensional bifurcation diagram displaying symmetry about the λ_{q_α} axis and one bifurcation point within the one-order-parameter theory.

liquid-to-solid transition, whereas the three- and two-dimensional systems do. This comparison then suggests that the changes in the sign of the derivative do indicate a change in the stability of the system about the bifurcation points. For the three-dimensional fcc system the stability properties will reverse at the next bifurcation point, $\lambda_{q_\alpha}=0.973$. In fact, the above analysis predicts that the upper branch of the ordered phase becomes more stable, and the lower branch becomes less stable, than the homogeneous liquid phase as one moves away from the bifurcation point $\lambda_{q_\alpha}=0.973$.

It should be noted that the bifurcation diagram for one particular three-dimensional system, the simple cubic lattice, is similar to that for the one-dimensional system (see Fig. 3) in that it does not display a transition in the first-order-parameter theory and has the same positive derivative sign about the $\lambda_{q_\alpha}=1$ bifurcation point. The highly unfavorable nature of this transition has also been noted by Ramakrishnan and Yussouff[7] on the basis of topological connectivity arguments.

For the simple-cubic lattice, the first set of reciprocal-lattice vectors is given by

$$\xi_{q_\alpha}(\mathbf{r})=6\left[\cos\left[\frac{2\pi}{a}x\right]+\cos\left[\frac{2\pi}{a}y\right]+\cos\left[\frac{2\pi}{a}z\right]\right] \tag{14a}$$

with

$$\Delta_{q_\alpha}=54\ . \tag{14b}$$

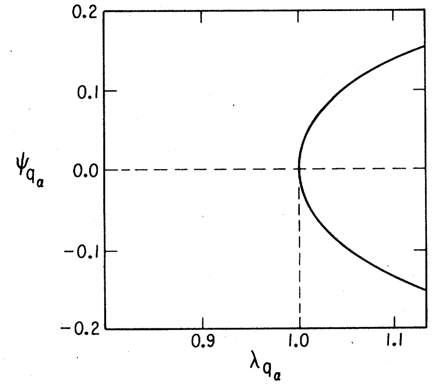

FIG. 3. Three-dimensional sc bifurcation diagram displaying symmetry about the λ_{q_α} axis and only one bifurcation point within the one-order-parameter theory. This diagram is qualitatively similar to the one-dimensional bifurcation diagram.

For the one-order-parameter theory, the system of equations (5) becomes

$$54\psi_{q_\alpha}=\frac{\int_\Delta \xi_{q_\alpha}(\mathbf{r})e^{\lambda_{q_\alpha}\psi_{q_\alpha}\xi_{q_\alpha}(\mathbf{r})}d\mathbf{r}}{\int_\Delta e^{\lambda_{q_\alpha}\psi_{q_\alpha}\xi_{q_\alpha}(\mathbf{r})}d\mathbf{r}}\ . \tag{15}$$

But this expression, in three dimensions, reduces to a one-dimensional equation

$$3\psi_{q_\alpha}=\frac{\int_0^a \cos\left[\frac{2\pi}{a}x\right]\exp\left[6\lambda_{q_\alpha}\psi_{q_\alpha}\cos\left[\frac{2\pi}{a}x\right]\right]dx}{\int_0^a \exp\left[6\lambda_{q_\alpha}\psi_{q_\alpha}\cos\left[\frac{2\pi}{a}x\right]\right]dx} \tag{16}$$

which has a bifurcation curve similar to Fig. 2. No freezing transition is predicted for the one-order-parameter theory. Likewise, a calculation with the introduction of a second order parameter was performed and does not induce a transition. Hence any transition predicted by this theory is weak in the sense that it must occur, if at all, with the inclusion of triplet correlation functions. This result holds for one-component systems because of the form of Eq. (5). In multicomponent systems, such as molten NaCl, the basic structure of these equations is altered and the analysis here must be modified accordingly. From the bifurcation diagrams presented here and in BCR it is clear that the bifurcation analysis alone provides useful information concerning the physical differences expected upon freezing to different lattice structures and as a function of dimensionality. The number of bifurcation points, the symmetry of the diagram, and the relative change of sign of the derivatives around the bifurcation points all yield qualitative information about the nature of the transition.

B. Thermodynamic calculation

Instead of applying Eq. (9b), a condition which forces the equality of the thermodynamic potential for the two phases may be employed. For this calculation, the nonlinear integral equations given in the form above were used to find the order parameters. The compressibility c_0 must be known from an analytic expression for the direct correlation function, or from experimental data. As mentioned above, this information is necessary for the Ramakrishnan-Yussouff (RY) theory but not for the bifurcation analysis. The thermodynamic potential in terms of the order parameters and densities[6,7,15]

$$\Delta W=(\rho_l c_0-1)\phi_0+\tfrac{1}{2}c_0\rho_l\phi_0^2+\tfrac{1}{2}\rho_l\sum_{q_\alpha}\phi_{q_\alpha}^2 \tag{17}$$

was used and the lowest values of the densities that produce $\Delta W=0$ were sought. These values provide another prediction for the transition densities. The thermodynamic calculations were carried out by solving Eqs. (8a) and

(17) simultaneously. Equation (8a) provides the entire order-parameter plane (ψ_G, λ_G) while Eq. (17) is the Maxwell construction in this plane. Thus the liquid density at transition predicted by this method must be higher than or equal to the transition density predicted by the bifurcation analysis.

This thermodynamic theory is similar to the RY analysis, though not equivalent to it. It differs from that theory in the choice of the density constraint and the self-consistent determination of the reciprocal-lattice vector used to calculate the order parameters. In the strict RY analysis, the values of these reciprocal vectors are fixed at their maximum values. The procedure above is an extension of previous thermodynamic calculations because it relaxes this constraint.

III. RESULTS

Before proceeding to the specific systems it is perhaps worthwhile to mention the general calculational scheme employed. Once the number of order parameters to be used is fixed and the associated reciprocal-lattice vectors formed, the nonlinear system of equations is solved using a modified finite-difference Levenberg-Marquardt[17] algorithm for the root search. The required integrals over the unit cell were evaluated by a 20-point Gauss-Chebyshev quadrature in each of the three spatial dimensions. This procedure produced a stable root search; the solutions obtained were as accurate as the integration scheme.

A. Body-centered-cubic systems

As outlined above, the application of the bifurcation analysis requires the reciprocal lattice vectors and the density-dependent direct correlation function of the liquid. The first reciprocal-lattice vector (smallest magnitude) of the bcc lattice is characterized by the set of vectors

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

or

$$\xi_{\mathbf{q}_\alpha}(\mathbf{r}) = 4 \left[\cos\left[\frac{2\pi}{a}x\right] \cos\left[\frac{2\pi}{a}y\right] + \cos\left[\frac{2\pi}{a}x\right] \cos\left[\frac{2\pi}{a}z\right] + \cos\left[\frac{2\pi}{a}y\right] \cos\left[\frac{2\pi}{a}z\right] \right] , \tag{18}$$

which has 12 members. Here, a is the lattice spacing so that the volume of a unit cell is a^3. Since there are two lattice points in each cell, the solid density ρ_s is $2/a^3$ so that $a = (2/\rho_s)^{1/3}$. The magnitude of the first reciprocal-lattice vector may then be expressed as

$$|\mathbf{q}_\alpha| = \frac{2\pi}{a}\sqrt{2} = 2\pi\sqrt{2}(\rho_s/2)^{1/3} .$$

Likewise, the second reciprocal-lattice vector is described by the set

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

or

$$\xi_{\mathbf{q}_\alpha}(\mathbf{r}) = 8 \left[ws \left[\frac{4\pi x}{a}\right] \cos\left[\frac{2\pi}{a}y\right] \cos\left[\frac{2\pi}{a}z\right] + \cos\left[\frac{2\pi}{a}x\right] \cos\left[\frac{4\pi}{a}y\right] \cos\left[\frac{2\pi}{a}z\right] + \cos\left[\frac{2\pi}{a}x\right] \cos\left[\frac{2\pi}{a}y\right] \cos\left[\frac{4\pi}{a}z\right] \right] \tag{19}$$

with magnitude

$$|\mathbf{q}_\beta| = \frac{2\pi}{a}\sqrt{6} = \sqrt{3}\,|\mathbf{q}_\alpha| .$$

The corresponding values for Δ_{q_α} and Δ_{q_β} are 12 and 24, respectively.

The two-order-parameter theory yields two equations from the system in Eq. (5)

$$12\psi_{\mathbf{q}_\alpha} = \frac{\int_\Delta \xi_{\mathbf{q}_\alpha}(\mathbf{r}) \exp[\lambda_{q_\alpha}\psi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r}) + \lambda_{q_\beta}\psi_{\mathbf{q}_\beta}\xi_{\mathbf{q}_\beta}(\mathbf{r})]d\mathbf{r}}{\int_\Delta \exp[\lambda_{q_\alpha}\psi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r}) + \lambda_{q_\beta}\psi_{\mathbf{q}_\beta}\xi_{\mathbf{q}_\beta}(\mathbf{r})]d\mathbf{r}} \tag{20}$$

and

$$24\psi_{\mathbf{q}_\beta} = \frac{\int_\Delta \xi_{\mathbf{q}_\beta}(\mathbf{r}) \exp[\lambda_{q_\alpha}\psi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r}) + \lambda_{q_\beta}\psi_{\mathbf{q}_\beta}\xi_{\mathbf{q}_\beta}(\mathbf{r})]d\mathbf{r}}{\int_\Delta \exp[\lambda_{q_\alpha}\psi_{\mathbf{q}_\alpha}\xi_{\mathbf{q}_\alpha}(\mathbf{r}) + \lambda_{q_\beta}\psi_{\mathbf{q}_\beta}\xi_{\mathbf{q}_\beta}(\mathbf{r})]d\mathbf{r}} \tag{21}$$

with

$$\begin{aligned} \lambda_{q_\alpha} &= \rho_s c_{q_\alpha} , \\ \lambda_{q_\beta} &= \rho_s c_{q_\beta} , \\ \psi_{\mathbf{q}_\alpha} &= \rho_l/\rho_s \phi_{\mathbf{q}_\alpha} , \\ \psi_{\mathbf{q}_\beta} &= \rho_l/\rho_s \phi_{\mathbf{q}_\beta} . \end{aligned} \tag{22}$$

The simpler one-order-parameter theory is obtained from Eq. (19) by setting $\psi_{\mathbf{q}_\beta} = 0$.

At this point, the bifurcation diagram for the bcc system may be calculated. Figure 4 displays the two-order-parameter-theory results, and Fig. 5 depicts the freezing curve obtained. It is immediately apparent that the bcc bifurcation curves differ from the corresponding fcc curves since the symmetric displacement of the curves about the λ_{q_α} axis is lost in the bcc system. As Kirkwood and Monroe pointed out,[1] the symmetry in the fcc case is due to a translational invariance in the lattice. By displacing the origin from (0,0,0) to $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $\xi_{\mathbf{q}_\alpha}(\mathbf{r})$ changes sign

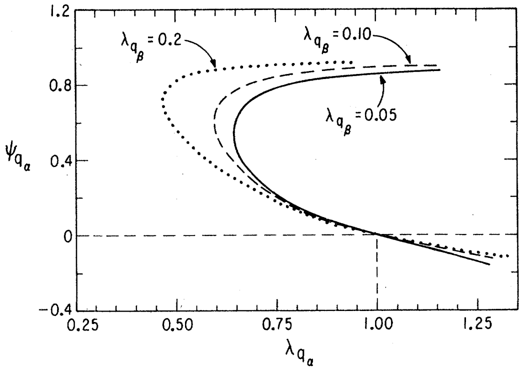

FIG. 4. Three-dimensional bcc bifurcation diagram in the two-order-parameter theory. The diagram is asymmetric and only possesses one bifurcation point.

so that a compensating change in sign for ψ_{q_α} leaves the system (5) invariant. This feature is also obviously shared by the simple-cubic structure, but not by the bcc lattice. No translation of the origin preserves the system of equations. Figure 4 shows this asymmetry graphically. Note that there is no bifurcation point at $\lambda_{q_\alpha}=1$.

The one-order-parameter theory possesses a bifurcation point at $\lambda_{q_\alpha}=0.673$ which signals the onset of the freezing transition. The two-order-parameter theory again yields a family of similar bifurcation curves, all of which are coincident at $\lambda_{q_\alpha}=1$, $\psi_{q_\alpha}=0$. The freezing curve constructed for the two-order-parameter theory gives the functional relationship between λ_{q_α} and λ_{q_β}. This information and Eq. (9b) are sufficient to evaluate the densities at the transition.

Two different three-dimensional bcc systems were examined in this fashion: hard spheres and liquid sodium. In the first case, the Wertheim-Thiele[18] solution of the Percus-Yevick equation for the direct correlation function is used, while x-ray diffraction data reported for the sodium structure factor is used for the second.[19] In both instances it is possible to apply the subsidiary conditions of Eq. (9) to determine the densities, since both direct correlation functions are monotonically increasing functions of ρ_l. The Wertheim-Thiele solution is an analytic function, so there is no difficulty in its application. However, the construction of the density-dependent direct correlation function from the experimental data presents a new problem.

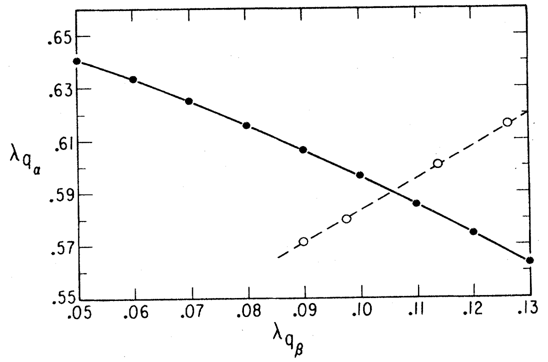

FIG. 5. The freezing curve generated by the bcc lattice in the two-order-parameter theory. The intersection of the curve with the dashed line determines the liquid-sodium freezing parameters.

The experimentally observable quantity is the structure factor, $S(q,T)$, as a function of momentum q and temperature T. It is straightforward to relate the temperature-dependent direct correlation function $c(q,T)$ to $S(q,T)$ by[20]

$$c(q,T)=\frac{S(q,T)-1}{\rho_l S(q,T)} . \tag{23}$$

The required values of $S(q,T)$ as a function of q were obtained by using a cubic spline to interpolate the data points. Only two temperatures were reported for each q, so the temperature dependence was assumed to be linear. In addition, the liquid density is given empirically as a function of temperature as[21]

$$\rho_l(T)=0.02429-6.236\times10^{-6}(T-100.0) \tag{24}$$

which is almost constant over the temperature ranges studied. Using these values, the subsidiary conditions (9) were satisfied by varying the temperature and solid density rather than the liquid and solid densities. The freezing curve generated is given in Fig. 5. The thermodynamic conditions require the compressibility as a function of temperature; this relationship is also known experimentally:[21]

$$\chi(T)=0.0177149T+17.3324 . \tag{25}$$

The temperature units in these equations are degrees centigrade.

The numerical values for the freezing transition of liquid sodium into a bcc lattice are collected in Table I for both the bifurcation analysis and the RY theory. It should be noted that the thermodynamic calculations reported here are slightly more accurate than those given by

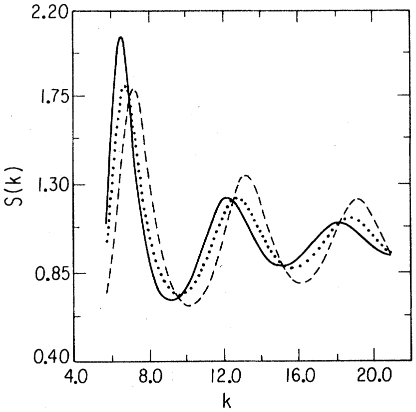

FIG. 6. The adhesive-hard-sphere structure factor as a function of dimensionless temperature plotted against wave vector magnitude. Solid line corresponds to $\tau=5.0$, the dashed corresponds to $\tau=1.0$, and the dotted line corresponds to $\tau=0.2$. All graphs are at the reduced density $\rho_0<\rho_{\text{freezing}}$.

TABLE I. Freezing transition parameters for liquid sodium.

	$\lambda^*_{q_\alpha}$	$\lambda^*_{q_\beta}$	$\psi^*_{q_\alpha}$	$\psi^*_{q_\beta}$	ρ^*_l	ρ^*_s	ϕ_0	T (°C)
One-order-parameter theory	0.672		0.490		0.0245	0.0262	0.072	71.2
Two-order-parameter theory	0.595	0.106	0.690	0.414	0.0236	0.0256	0.084	210.5
Two-order-parameter theory with thermodynamic constraint ($\Delta W=0$)	0.606	0.117	0.754	0.485	0.0237	0.0256	0.08	190.0
Thermodynamic consistency check	0.65	0.17	0.88	0.68	0.0242	0.0267	0.103	100.0
RY (one order)	0.69		0.700	0.310			0.048	
RY (two order)	0.67	0.07	0.630	0.340			0.029	
Experimental	0.677	0.123			0.0254	0.0261	0.026	99.26

the original RY technique.[7,8] The increased accuracy arises from our retention of the solid density dependence of the reciprocal-lattice vector magnitude and to our full treatment of the liquid-state information.

As is obvious from Table I, the predicted transition densities for both theories are in very good agreement with the experimental results. There are, though, two unsatisfactory features. First, the predicted transition temperature worsens upon inclusion of the second-order parameter. The wide variation in temperature is due to the very weak dependence of the liquid-sodium structure factor upon the temperature. Large variations in temperature have little effect upon the density, as is readily seen in Eq. (24). One interesting feature of the results is that the predicted transition densities and temperature are almost identical for the bifurcation analysis and thermodynamic analysis within a two-order-parameter theory. We believe that this agreement is due to the small metastability of the solid phase.

As a consistency check on these results, the temperature was fixed at the experimental value, 100 °C, and the transition densities then evaluated. The predicted densities are shown in Table I.

The second unsatisfactory feature of our results is the overly large fractional density change. In fact, the fractional density change increases from 7.2% to 8.5% upon inclusion of the second order parameter. This trend indicates that the level of theory employed here is insufficient; the triplet correlation function and a few more order parameters should be added. We found that inclusion of the triplet correlation function reduces the fractional density change from 8.5% to 4.5%. Though the improvement is substantial, it is still not accurate enough.

B. Adhesive hard spheres

The second set of results arises from a study of the adhesive-hard-sphere system. This model incorporates some features of the more realistic Lennard-Jones system and shows a gas-liquid transition. The potential has the form

$$\phi(r)\equiv u(r)=\begin{cases}+\infty, & r<\sigma\\ -\ln[(a/12\tau)(a-\sigma)], & \sigma<r<a\\ 0, & r>a\end{cases} \tag{26}$$

where τ is a dimensionless measure of temperature. A thorough discussion of the properties of this system, including the solution of the Percus-Yevick equation, is given by Baxter.[12] The necessary details of the Fourier-transformed direct correlation function appear in the Appendix. It is important to note that this system has a triple point, though we are unaware of either theoretical analysis or computer simulation that has addressed this feature.

The study of the adhesive-hard-sphere system was restricted to the fcc lattice structure. Previous bifurcation results[9] for this lattice were used. The solution of Eq. (9) was performed to several fixed temperatures. The temperature dependence of the structure factor is given in Fig. 6. The predicted transition densities as a function of temperature τ are noted in Table II. The results using the

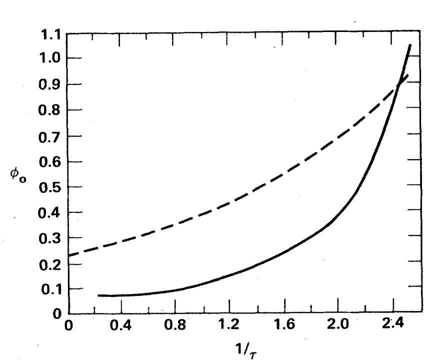

FIG. 7. Scaled temperature variation of the fractional density change. Solid line indicates the thermodynamic result; dashed line is the bifurcation result.

TABLE II. Three-dimensional (fcc) adhesive-hard-sphere freezing transition parameters as a function of scaled temperature τ.

τ	$\lambda^*_{q_\alpha}$	$\lambda^*_{q_\beta}$	ρ^*_l	ρ^*_s	ϕ_0
0.3	0.643	0.246	0.513	1.388	1.706
0.4	0.626	0.253	0.706	1.335	0.940
0.5	0.625	0.253	0.767	1.297	0.710
1.0	0.654	0.242	0.865	1.209	0.400
5.0	0.710	0.220	0.885	1.110	0.260
(Hard-sphere limit)	0.720	0.217	0.884	1.085	0.227

RY theory are collected in Table III.

The single most interesting feature of the results displayed in Tables II and III is the pronounced temperature dependence of the fractional density change ϕ_0. This change is a decreasing function of τ. It is noteworthy that the computer experiments on the Lennard-Jones system show a similar trend in the fractional density change on freezing. The decrease is less dramatic for the Lennard-Jones system, though, from a value of about 13% at $T^*=0.75$ to about 5% at $T^*=2.75$. In a separate calculation, BCR found that the use of Weeks-Chandler-Andersen (WCA) perturbation theory in the present theoretical framework fails to reproduce the "experimental" fractional density change of the Lennard-Jones system. These workers attributed the failure to the inadequacy of WCA theory. Thus it is interesting to find that the adhesive-hard-sphere calculation reproduces the expected temperature dependence of ϕ_0. This temperature dependence is chiefly attributable to the attractive part of the potential.

The temperature variation of ϕ_0 with τ is plotted in Fig. 7. It should be noted that ϕ_0 reduces to the hard-sphere values[9] at large values of τ. The rapid increase in ϕ_0 as τ is decreased below a value of 0.75 is rather puzzling. Since the lowest value of τ examined is much higher than the triple-point value (which must be less than the critical temperature $\tau_c \simeq 0.1$), the only consistent explanation is that the neglect of the triplet correlation in Eq. (4) is too drastic an approximation.

In order to rectify this deficiency, we tried including two triplet contributions, $\tilde{c}_3(0,0)$ and $\tilde{c}_3(\mathbf{G},0)$, but neglecting $\tilde{c}_3(\mathbf{G},\mathbf{G}')$ since it could not be evaluated. It should be emphasized that we do not know the relative importance of the $\tilde{c}_3(\mathbf{G},\mathbf{G}')$ term, so the approximation generated by retaining these two terms and ignoring the third is uncontrolled. Indeed, including just two of the triplet contributions produced an even larger value of ϕ_0 at small values of τ. It appears then that all the triplet terms must be included. The magnitude of this contribution, though not totally unexpected, implies a serious inadequacy of the present theories of freezing.

IV. DISCUSSION

Let us first summarize the basic results of this work. We have considered crystallization of liquid sodium into a bcc lattice and of an adhesive-hard-sphere fluid into a fcc lattice. In each case two separate calculations were performed. The first of these attempted to calculate the lowest liquid density at which a periodic solidlike solution can first appear. At this density, the liquid is thermodynamically more stable than the solid phase so that the predicted solid density is a metastable extension of the solid phase. Despite this phenomenon, this approach has the advantage of predicting the freezing transition solely from structural information independent of any subsidiary thermodynamic constraint. The second, thermodynamic, calculation presented is a careful implementation of the freezing theory of Ramakrishnan and Yussouff. The predicted transition densities for the liquid-sodium bcc transition are in excellent agreement with the observed results, but the predicted transition temperature is not correctly reproduced. Another failure is the prediction of the fractional density change which is too large. One interesting result that arises is the *agreement* of the bifurcation and thermodynamic theories with a two-order-parameter calculation. This close agreement between the two theories may be due to the fact that the

TABLE III. Three-dimensional (fcc) adhesive-hard-sphere freezing transition parameters from the thermodynamic constraint condition as a function of scaled temperature.

τ	λ_{G_α}	λ_{G_β}	ψ_{G_α}	ψ_{G_β}	ρ_l	ρ_s	ϕ_0
0.4	0.567	0.278	0.815	0.600	0.58	1.19	1.050
0.5	0.587	0.284	0.865	0.666	0.81	1.12	0.383
0.75	0.591	0.275	0.842	0.631	0.92	1.06	0.152
1.0	0.629	0.282	0.883	0.689	0.94	1.07	0.143
2.0	0.633	0.265	0.856	0.643	0.93	1.02	0.090
5.0	0.636	0.257	0.837	0.614	0.90	0.97	0.080

metastable branch of the solid phase is quite small because a solid cannot be superheated much above its melting point without destroying its long-range order. Thus, the "van der Waals" loop in the coexistence region is quite narrow for the freezing transition. Caution is warranted, though, in the identification of this agreement with experiment because of the approximations made in both of the calculations.

Interesting results for the adhesive-hard-sphere liquid-fcc transition are also obtained. The main result is the temperature dependence of the fractional density change ϕ_0 upon freezing. This dependence is similar to that in a Lennard-Jones system. At small values of τ, ϕ_0 becomes abnormally large. We attribute this result to the importance of the triplet direct correlation function.

A consideration of a one-component liquid freezing into a simple-cubic lattice is found to predict no transition simply on the basis of the bifurcation diagram. This diagram is similar to that found for a one-dimensional system in that there is no jump discontinuity in the order parameters. We conclude that a first-order phase transition from any one-component liquid to a sc lattice is highly unfavorable. Physically, this may be attributed to the poor connectivity of the sc lattice, as noted previously by Ramakrishnan and Yussouff.[7] In the bifurcation analysis, no explicit use is made of liquid-state information other than translational invariance.

Finally, we suggest the possibility of applying the order-parameter theory above to describe the coexistence of all three phases: gas, liquid, and crystalline solid. Recently, Imry and Schwartz[22] have considered this problem in the context of a modified lattice-gas model and have found that by coupling the crystalline order parameters (the ϕ_G's above) to the usual liquid-gas transition, it is possible to produce phase diagrams with the correct qualitative features. The adhesive-hard-sphere system would be a natural system to study in this fashion for coexistence of the three phases for two reasons. First, this is a simple system which displays a gas-liquid transition. Second, an accurate analytic expression for the direct correlation function is available. The work above indicates, though, that information about the triplet direct correlation functions is necessary to achieve this goal. We feel that further study of this aspect of the problem will be worthwhile.

ACKNOWLEDGMENTS

The authors are grateful to Professor S. A. Rice for a careful reading of the manuscript and for his numerous improvements in the text. It is a pleasure to thank Peter Harrowell and Patricia Radloff for illuminating conversations. The authors would like to thank Professor Y. Oono for directing their attention to the adhesive-hard-sphere systems, and for his stimulating discussions and encouragement. This work has been supported in part by grants from the National Science Foundation, and under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. B. B. acknowledges the support of the National Science Foundation Grant No. CHE-77-16308.

APPENDIX

The development and notation in this appendix are due to Baxter.[12] More details may be found in his review article. By use of a factorization theorem, the Fourier transform of the direct correlation function

$$\hat{c}(k)=4\pi\int_0^a dr\,\cos(kr)c(r) \tag{A1}$$

for the adhesive-hard-sphere potential in Eq. (26) may be decomposed into the product

$$\hat{c}(k)=\frac{1-\hat{Q}(k)\hat{Q}(-k)}{\rho}\ , \tag{A2}$$

where

$$\hat{Q}(k)=1-2\pi\rho\int_0^a dr\,e^{ikr}Q(r)\ . \tag{A3}$$

This form is more convenient to manipulate since $Q(r)$ relates $c(r)$ and $h(r)$ over finite ranges despite the long-range nature of $h(r)$. The function $\hat{Q}(k)$ must satisfy certain regularity conditions: it may only possess roots in the lower half of the complex plane. This condition on the roots is used to distinguish the physical and nonphysical domain of the solution.

The function $Q(r)$ may be shown to have the form[12]

$$Q(r)=\frac{\alpha}{2}(r^2-a^2)+a\beta(r-a)+\frac{\lambda a^2}{12}\ , \tag{A4}$$

where

$$\begin{aligned}\alpha&=(1+2\eta-\mu)/(1-\eta)^2\ ,\\ \beta&=\tfrac{1}{2}(\mu-3\eta)/(1-\eta)^2\ ,\end{aligned} \tag{A5}$$

and η is the usual package fraction $\eta=\pi\rho a^3/6$ and where $\mu=\lambda\eta(1-\eta)$. Once the parameter λ has been evaluated the Fourier transform for $Q(r)$ and hence $c(r)$, follow immediately. At this point the Percus-Yevick approximation is used to establish a condition between the dimensionless temperature τ and the parameter λ

$$\lambda\tau=\frac{1+\eta/2}{(1-\eta)^2}-\frac{\eta\lambda}{(1-\eta)}+\frac{\eta\lambda^2}{12}\ . \tag{A6}$$

Since this equation is simply a quadratic it is trivial to solve for λ in terms of η and τ, the only remaining difficulty is the choice of physical roots. As Baxter argues by using the regularity conditions, the physical root is the value which satisfies

$$\mu\geq 1+2\eta\ . \tag{A7}$$

If both roots fulfill this condition, then the smaller one is the correct choice, by thermodynamic arguments.

Using the physical value of μ above, all the required variables may be evaluated. The final form of the Fourier transformed direct correlation function becomes

$$\hat{c}(k)=2\pi[\hat{Q}(k)+\hat{Q}(-k)]-(2\pi)^2\rho\hat{Q}(k)\hat{Q}(-k)\ , \tag{A8}$$

where

$$\hat{Q}(k)+\hat{Q}(-k)=2\left[\frac{a^2\alpha}{2}+a^2\beta+D\right]\frac{\sin(ka)}{k}+[2a(\alpha+\beta)\cos(ka)-2a\beta]/k^2-2\alpha\sin(ka)/k^3\,, \tag{A9}$$

$$\hat{Q}(k)\hat{Q}(-k)=\left[\left[\frac{a^2\alpha}{2}+a^2\beta+D\right]^2-D(2D+a^2\alpha+2\beta a^2)\cos(ka)\right]\Big/k^2+(2\alpha aD-a^3\alpha\beta-2a^3\beta^2)\sin(ka)/k^3$$

$$+[(2\beta^2a^2-4\alpha D)+(4\alpha D-2a^2\beta^2+a^2\alpha^2)\cos(ka)]/k^4-2a\alpha^2\sin(ka)/k^5+2\alpha^2[1-\cos(ka)]/k^6\,, \tag{A10}$$

where $D=(\lambda/12-\alpha/2-\beta)a^2$. These expressions provide the necessary density- and temperature-dependent function for transition density evaluation.

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