Theoretical analysis of the achievement of random close packing of hard spheres and a conjecture on spinodal decomposition

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We report the results of an analysis of bifurcation points of the nonlinear equation for the density distribution in an inhomogeneous system. The theory used predicts the freezing transition. In addition, if the unstable fluid branch of the solution beyond the freezing point is followed to higher density, another bifurcation point is found. This latter bifurcation point is identical with the limit of compression of the system, i.e., achievement of random close packing in the fluid. The density of random close packing of hard spheres is predicted to be 1.202, in very good agreement with computer simulation data. We show that the second bifurcation point is a limit of the first bifurcation point and that no freezing transition is possible beyond this point. Comparison of the behavior of the hard-sphere and Lennard-Jones fluids leads to the conjecture that spinodal decomposition of the Lennard-Jones fluid occurs when the density, computed with a temperature- and density-dependent effective hard-sphere diameter, reaches the value corresponding to random close packing of hard spheres.

I. INTRODUCTION

In 1959 Bernal predicted the existence of a random-close-packed (RCP) state for an assembly of hard spheres.[1] In this state, in which the spheres are jammed together in a fashion that prevents movement, there is short-range order but not long-range order. Bernal estimated the density at which random close packing was achieved from a study of mechanical models; he found $\rho^*_{\rm RCP}\equiv(N\sigma^3/V)_{\rm RCP}\cong 1.2$. Subsequent more sophisticated investigations,[2–5] including computer simulations, have confirmed Bernal's prediction and refined the estimate of the density of the RCP state to $\rho^*_{\rm RCP}=1.18-1.215$. However, to date there has not been any theoretical analysis which predicts the existence of the RCP state of a hard-sphere fluid, nor any statistical mechanical calculation of its density. In this paper we present a first-principles analysis which both demonstrates the existence of a RCP state of the hard-sphere fluid and leads to an accurate calculation of its density. Our analysis also leads to some interesting insights into the nature of the freezing transition, the metastability of the hard-sphere fluid, and spinodal decomposition.

It is well known that the hard-sphere fluid crystallizes in a face-centered-cubic (fcc) lattice when the fluid density reaches $\rho^*\cong 0.93$, well below the value characteristic of random close packing.[6] A theory of the achievement of random close packing must, therefore, be capable of both accounting for and bypassing the freezing transition. We have recently advanced a theory of freezing based on the analysis of solutions of the nonlinear integral equation describing the inhomogeneous density distribution at phase equilibrium.[7–9] The analysis takes the form of a search for a bifurcation point at which the uniform density characteristic of the fluid phase becomes unstable relative to the periodic density distribution characteristic of the crystalline phase. The fundamental nonlinear equation studied is derived under the following approximations: (a) truncation of the exact expansion for the density of an inhomogeneous system at the level of the direct correlation function for pairs of molecules, (b) use of a convenient but inexact pair direct correlation function for the liquid, (c) use of an order-parameter expansion which neglects vibrational motion in the solid, and (d) truncation of the order-parameter expansion for the density difference between liquid and crystal phases after a few terms. It was shown that, despite these approximations, the theory successfully predicts the existence of the freezing transition and accounts moderately well for the values of the transition parameters. It was also found that if the fluid solution was followed past the freezing transition into the region where it is unstable with respect to the crystal a new, universal, bifurcation point is found.[7] For the hard-sphere fluid we identified this latter bifurcation point with the end of possible compression of the system, i.e., with the attainment of random close packing of the fluid and face-centered close packing of the crystal. This identification is consistent with the results of a bifurcation analysis of the corresponding nonlinear equation for a one-dimensional system, which can be carried out exactly.[7] To reduce the chance that for the three-dimensional system the second bifurcation point and our interpretation of its physical implications are artifacts of the approximations used to derive the fundamental nonlinear equation of the theory, we have extended our analysis to include higher-order terms in the reciprocal-lattice vector expansion of the density difference between phases. This is a cogent extension of the earlier calculations in that it tests the sensitivity of the existence and location of the bifurcation point to the series expansion for the inhomogeneous density. Note that the calculations for the one-dimensional hard-rod system can be thought of as testing

the adequacy of the approximation for the pair direct correlation function. In addition, we have discovered that there are conditions such that the first bifurcation point coalesces with the second, and as a result the freezing line terminates at the second bifurcation point.

II. THEORETICAL ANALYSIS

Briefly stated, our analysis starts with the following exact expression for the singlet density distribution as a function of position $\rho(\vec{R}_1)$ of an inhomogeneous fluid,[9,10]

$$\frac{\rho(\vec{R}_1)}{z}=\exp\left[\sum_{k=1}^{\infty}\frac{1}{k!}\int S_{k+1}(\vec{R}_1,\ldots,\vec{R}_{k+1})\times\rho(\vec{R}_2)\cdots\rho(\vec{R}_{k+1})d\vec{R}_2\cdots d\vec{R}_{k+1}\right]$$
$$=\exp[F(\vec{R}_1,\{\rho(\vec{R}_i)\})]\ , \tag{1}$$

where $S_{k+1}(\vec{R}_1,\ldots,\vec{R}_{k+1})$ is the sum of all irreducible Mayer cluster diagrams of order $k+1$ and the fugacity z is determined by the usual normalization condition on $\rho(\vec{R}_1)$. Since $F(\vec{R}_1,\{\rho(\vec{R}_i)\})$ is the generating function of the n-particle direct correlation function $c_n(\vec{R}_1,\ldots,\vec{R}_n)$, a functional Taylor-series expansion about its liquid-state value $F(\vec{R}_1,\{\rho_l\})$, truncated after the first two terms,[7,8] gives

$$\frac{\rho(\vec{R}_1)}{z_s}=\frac{\rho_l}{z_l}\exp\left[\int d\vec{R}_2 C_2(\vec{R}_{12},\rho_l)\Delta\rho(\vec{R}_2)\right]\ , \tag{2}$$

where $\Delta\rho(\vec{R})$ is the density difference $\rho(\vec{R})-\rho_l$, ρ_l, and z_l are the density and fugacity of the liquid phase, and ρ_s and z_s the analogous quantities for the solid phase.

The singlet density distribution is now expanded in a Fourier series[9]

$$\rho(\vec{R})=\rho_l+\Delta\rho(\vec{R})$$
$$=\rho_l(1+\phi_0)+\rho_l\sum_{\vec{G}}\phi_{\vec{G}}e^{i\vec{G}\cdot\vec{R}}\ , \tag{3}$$

where the $\{\vec{G}\}$ are the reciprocal-lattice vectors of some chosen lattice, $\phi_{\vec{G}}$ are the expansion coefficients,

$$\phi_{\vec{G}}=\frac{1}{\Delta}\int\frac{\Delta\rho(\vec{R})}{\rho_l}e^{-i\vec{G}\cdot\vec{R}}d\vec{R}\ , \tag{4}$$

and ϕ_0 is the fractional density change in the transition, equal to $(\rho_s-\rho_l)/\rho_l$. Combining Eqs. (2)—(4) we obtain the system of equations[7,8]

$$\psi_{\vec{G}_n}=\frac{\int_\Delta d\vec{R}_1\xi_{\vec{G}_n}(\vec{R}_1)\exp\left[\sum_{\vec{G}}\psi_{\vec{G}}\lambda_{\vec{G}}\xi_{\vec{G}}(\vec{R}_1)\right]}{\int_\Delta d\vec{R}_1\exp\left[\sum_{\vec{G}}\psi_{\vec{G}}\lambda_{\vec{G}}\xi_{\vec{G}}(\vec{R}_1)\right]}\ , \tag{5}$$

where $\vec{G}_n$ is nth reciprocal-lattice vector, $\xi_{\vec{G}}$ is the function describing the vector position of $\vec{G}$, and $\psi_{\vec{G}}$ and $\lambda_{\vec{G}}$ are defined by

$$\frac{\rho_l}{\rho_s}\phi_{\vec{G}}\equiv\psi_{\vec{G}}\ ,$$
$$\rho_s\tilde{C}_2(\vec{G})\equiv\lambda_{\vec{G}}\ , \tag{6}$$

where $\tilde{c}_2(\vec{G})$ is the Fourier transform of the pair direct correlation function, $c_2(\vec{R}_{12})$, evaluated at $\vec{G}$.

Since a hard-sphere fluid preferentially freezes into a fcc lattice, we consider the reciprocal-lattice vectors of this lattice only. In order to make calculations feasible, we truncate Eq. (5) after three order parameters, denoted by α, β, and γ. The order parameters are chosen according to their importance, as described in Ref. 7. The three order parameters used in this work are $(\pm1,\pm1,\pm1)$ (α), $(\pm3,\pm1,\pm1)$ (β), and $(\pm2,\pm2,\pm2)$ (γ). Then Eq. (5) gives rise to a system of three nonlinear equations which can be solved for bifurcation points. It is worth emphasizing that Eq. (5) can be solved without using any information about the liquid state other then its translational invariance. Thus the bifurcation diagram generated by Eq. (5) can be regarded as "universal" for a chosen lattice.[7]

Figure 1 displays a typical bifurcation diagram. In Fig. 1 we have plotted the order parameter of the first reciprocal-lattice vector, $\psi_{\vec{G}_\alpha}$, against $\lambda_{\vec{G}_\alpha}$, for fixed values of $\lambda_{\vec{G}_\beta}$ and $\lambda_{\vec{G}_\gamma}$. As $\lambda_{\vec{G}_\beta}$ and $\lambda_{\vec{G}_\gamma}$ are varied the bifurcation points $(\lambda^*_{\vec{G}_\alpha},\lambda^*_{\vec{G}_\beta},\lambda^*_{\vec{G}_\gamma})$ define a surface in three-dimensional space. Figure 1 shows that for each pair $(\lambda_{\vec{G}_\beta},\lambda_{\vec{G}_\gamma})$ there are *two* bifurcation points. The bifurcation points for lower values of $\lambda_{\vec{G}_\alpha}$ denote the first instability of the liquid with respect to the periodic density distribution of the solid, characterized by nonzero values of $\psi_{\vec{G}_\alpha}$. When projected on the $(\lambda_{\vec{G}_\alpha},\lambda_{\vec{G}_\beta})$ plane, $(\lambda^*_{\vec{G}_\alpha},\lambda^*_{\vec{G}_\beta})$ define a curve which is approximately linear. The second bifurcation point is at $\lambda_{\vec{G}_\alpha}=1$ and is *invariant* to changes in the values of $\lambda_{\vec{G}_\beta}$ and $\lambda_{\vec{G}_\gamma}$.

The most interesting feature of Fig. 1 is that as the

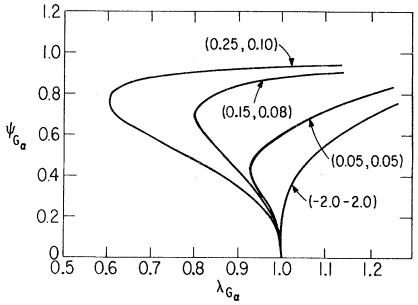

FIG. 1. Three—order-parameter bifurcation curves for the fcc solid at several values of the pair $(\lambda_{\vec{G}_\beta},\lambda_{\vec{G}_\gamma})$. Note that the first bifurcation point approaches the second "universal" bifurcation point at $\lambda_{\vec{G}_\alpha}=1$ as the values of $\lambda_{\vec{G}_\beta},\lambda_{\vec{G}_\alpha}$ are decreased.

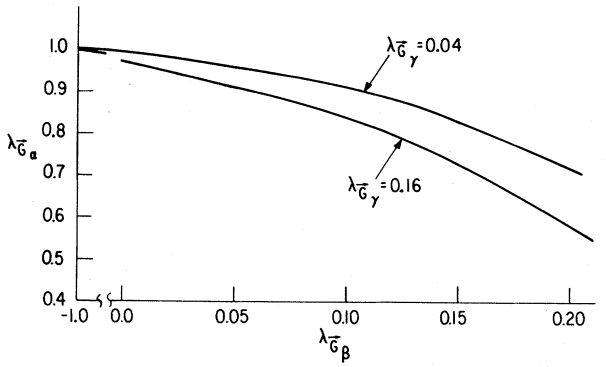

FIG. 2. The bifurcation curves generated for the fcc system when the bifurcation triplet $(\lambda^*_{\vec{G}_\alpha},\lambda^*_{\vec{G}_\beta},\lambda^*_{\vec{G}_\gamma})$ is projected on the $(\lambda_{\vec{G}_\alpha},\lambda_{\vec{G}_\beta})$ plane.

values of $\lambda_{\vec{G}_\beta}$ and $\lambda_{\vec{G}_\gamma}$ are lowered, the first bifurcation point approaches the second, and for sufficiently small values of $\lambda_{\vec{G}_\beta}$ and/or $\lambda_{\vec{G}_\gamma}$ it is identically 1. That is, the bifurcation line ends at the value $\lambda_{\vec{G}_\alpha}=1$ in the $(\lambda_{\vec{G}_\alpha},\lambda_{\vec{G}_\beta})$ or in the $(\lambda_{\vec{G}_\alpha},\lambda_{\vec{G}_\gamma})$ plane, as illustrated in Fig. 2, which implies that there can be no freezing transition beyond the value $\lambda_{\vec{G}_\alpha}=1$. A stability analysis shows that the liquid is unstable beyond this point. We shall now show, by explicit numerical calculation of densities, that the point $\lambda_{\vec{G}_\alpha}=1$ corresponds to the dense RCP state of the hard-sphere fluid.

The liquid- and solid-phase transition densities are calculated by solving the following system of equations:

$$\lambda_{\vec{G}_\alpha}(\rho_l,\rho_s)\big|_{\rho_l=\rho_l^*,\rho_s=\rho_s^*}=1\ , \tag{7}$$

$$\frac{\partial}{\partial\rho_s}\lambda_{\vec{G}_\alpha}(\rho_l,\rho_s)\Big|_{\rho_l=\rho_l^*,\rho_s=\rho_s^*}=0\ , \tag{8}$$

$$\begin{aligned}&\lambda_{\vec{G}_\beta}(\rho_l,\rho_s)\big|_{\rho_l=\rho_l^*,\rho_s=\rho_s^*}=\lambda^*_{\vec{G}_\beta}\ ,\\ &\lambda_{\vec{G}_\delta}(\rho_l,\rho_s)\big|_{\rho_l=\rho_l^*,\rho_s=\rho_s^*}=\lambda^*_{\vec{G}_\gamma}\ ,\end{aligned} \tag{9}$$

where ρ_l^*,ρ_s^* are transition densities and $(1,\lambda^*_{\vec{G}_\beta},\lambda^*_{\vec{G}_\gamma})$ is a triplet of values on the bifurcation surface.

The significance of these conditions has been discussed in Refs. 7 and 8. Here we just mention that Eq. (8) is a structural condition which arises from the existence of a sharp maximum in the direct correlation function for the liquid near $|\vec{G}_\alpha|$, the magnitude of the first reciprocal-lattice vector of the crystal. This condition, along with conditions (7) and (9), guarantees that the liquid and solid densities predicted by the solutions to the nonlinear integral equations correspond to the lowest density for which the liquid becomes unstable.

We have solved Eqs. (7)—(9) using the Wertheim-Thiele solution[11] of the Percus-Yevick equation, which gives quite an accurate description of $\tilde{c}_2(\vec{k})$ for large values of the wave vector $\vec{k}$. The result of our calculations for the densities is

$$\rho_l^*=1.202,\ \ \rho_s^*=1.381\ \ \text{for}\ \lambda_{\vec{G}_\alpha}=1\ . \tag{10}$$

The predicted density of the liquid for $\lambda_{\vec{G}_\alpha}=1$ corresponds exactly to the known value of the density of the RCP state, while the predicted density of the solid is very close to the fcc close-packed limit. The above result was conjectured in Ref. 7 on the basis of a two—order-parameter theory. However, the termination of the bifurcation line at $\lambda_{\vec{G}_\alpha}=1$ was not recognized then.

For the one-dimensional fluid there is only the bifurcation point at $\lambda_{\vec{G}_\alpha}=1$.[7] Since the direct correlation function for the hard rod fluid is exactly known, we can calculate the densities that correspond to $\lambda_{\vec{G}_\alpha}=1$. We find $\rho_l=\rho_s=1.0$, the maximum achievable density in this case. There is no phase transition in this system.

III. DISCUSSION

We have shown, for a hard-sphere fluid, that there exists a density beyond which further compression is impossible. The numerical value of this density is in excellent agreement with estimates of the density of the RCP state. To find this limiting behavior of the hard-sphere fluid we followed the fluid branch of the equation for the density distribution of an inhomogeneous system past the density corresponding to freezing, in which region the fluid is unstable relative to the fcc crystal. Given the similar behavior of the fluid solutions when $\lambda_{\vec{G}_\alpha}=1$ in one and three dimensions, and the insensitivity of our results to extension of the set of retained reciprocal-lattice vector terms in the expansion of the inhomogeneous density distribution, we believe our numerical calculations and the interpretation proposed to be robust.

Landau proved that the coexistence line between two phases with inherently different symmetries cannot terminate in a critical point.[12] Our statement that the freezing line ends at the value $\lambda_{\vec{G}_\alpha}=1$ is in agreement with Landau's theorem. To see this we note, first, that the properties of a hard-sphere assembly depend only on the density, and not on the temperature. Thus the fluid-to-crystal transition occurs at a particular density, and the freezing line in the temperature-density plane is degenerate in the sense that it is perpendicular to the density axis and parallel to the temperature axis. Stated another way, there is no temperature above which freezing of the hard-sphere fluid is impossible since, for any temperature, all that need be achieved is a density greater than 0.93. (Of course, the pressure required to achieve this density increases with the temperature.) Second, the freezing point of the hard-sphere system is determined by the intersection of the line of bifurcations of the nonlinear Eq. (5) and the line generated by solution of Eqs. (7)—(9). The

line of bifurcations, taken alone, follows the fluid-to-crystal transition as the values of the Fourier components of the pair direct correlation function evaluated at the first and second reciprocal-lattice vectors vary. The intersection of the line of bifurcations with the solution of Eqs. (7)—(9) pick out those values which self-consistently define the densities of the two phases at the transition point. We can think of a general point on the line of bifurcations in the $(\lambda_{\vec{G}_\alpha},\lambda_{\vec{G}_\beta})$ plane as one defining, for densities other than the density of freezing, the fluid-to-crystal transition with particular values of the amplitudes of $\tilde{c}_2(\vec{G}_\alpha)$ and $\tilde{c}_2(\vec{G}_\beta)$. Our interpretation implies that such constrained transitions cannot occur after the density of the fluid reaches the RCP value. Given the definition of the hard-sphere interaction, the volume of the RCP state is irreducible, hence fluctuations in density are suppressed, and it is reasonable to find that transitions involving configurational change cannot occur.

It is interesting to invert the line of argument used above. The RCP state of the hard-sphere fluid must be at an extremum with respect to sensitivity to fluctuations in configuration. That this is so follows from the observation that an infinitesimal decrease in density permits the fluid-to-crystal transition to occur. This inordinate sensitivity to fluctuations leads us to ask if there exists some relationship between the seemingly diparate phenomena of random close packing and spinodal decomposition.

We have described elsewhere a study of freezing in the Lennard-Jones system using the same method of analysis as described for the hard-sphere system, with necessary modifications.[8] Since the Lennard-Jones interaction is soft, there is no limit to the density of the system, and the fluid-to-crystal transition occurs along a nontrivial line in the temperature-density plane. In our analysis of the Lennard-Jones fluid we also found a second bifurcation point, universal in the same sense as described for hard spheres at $\lambda_{\vec{G}_\alpha}=1$. We interpreted that second bifurcation point as signaling spinodal decomposition of the fluid, i.e., at that density and temperatures the fluid becomes unstable to infinitesimal fluctuations. Of course, the temperature and density at which such instability occurs can vary because the intermolecular potential is soft, so the analysis traces a spinodal line. We now conjecture that the spinodal line for the Lennard-Jones fluid corresponds to the state of random close packing of spheres with a temperature- and density-dependent diameter. To support this conjecture we show in Table I a comparison of the temperature- and density-dependent equivalent hard-sphere diameters, computed from the Weeks-Chandler-Andersen[13] analysis of the Lennard-Jones fluid, and the values obtained by taking the spinodal point as corresponding to the state of random close packing of (equivalent) hard spheres. The agreement between these values is striking. We also show in Table I the predicted values for the RCP density of the fluid and the close-packed density of the fcc lattice, computed from the actual densities at the bifurcation point $\lambda_{\vec{G}_\alpha}=1$ and the Weeks-Chandler-Andersen temperature- and density-dependent equivalent hard-sphere diameters; the corresponding values for the hard-sphere fluid are 1.202 and 1.381, respectively. We attribute the small drift with temperature to the increasing inadequacy of the Weeks-Chandler-Andersen approximation as temperature increases. Generally, the constancy of these densities, and their agreement with the hard-sphere values, is very good.

The conjecture that the spinodal decomposition of a fluid state occurs when the density reaches that equivalent to random close packing of hard spheres focuses attention on the different roles of static and dynamic fluctuations in a system. In the RCP state of a hard-sphere fluid there are frozen-in local density inhomogeneities but, because no motion can occur, all dynamical fluctuations are

TABLE I. Test of conjecture relating the spinodal in the Lennard-Jones fluid to random close packing of effective hard spheres. WCA denotes the Weeks-Chandler-Andersen analysis (Ref. 13).

			Hard-sphere fluid		$\rho^*_{l,\mathrm{RCP}}$	$\rho^*_{s,\mathrm{fcc}}$
					1.202	1.381
			Lennard-Jones fluid			
T^*	ρ_l^*	ρ_s^*	$[\sigma(T^*,\rho_l^*)]_{\mathrm{WCA}}$[a]	$[\sigma(T^*,\rho_l^*)]_{\mathrm{RCP}}$[b]	$[\rho^*_{l,\mathrm{RCP}}(LJ)]_{\mathrm{WCA}}$[c]	$[\rho^*_{s,\mathrm{fcc}}(LJ)]_{\mathrm{WCA}}$[d]
0.5	1.111	1.272	1.029	1.030	1.211	1.386
0.75	1.155	1.323	1.014	1.018	1.204	1.380
1.15	1.213	1.392	0.996	1.000	1.199	1.375
1.35	1.237	1.422	0.989	0.994	1.197	1.375
2.75	1.358	1.574	0.956	0.964	1.187	1.376

[a]Values computed in Ref. 13.
[b]Values obtained by assuming the value of ρ^*_{RCP} for the Lennard-Jones system is 1.215 for all T^* and ρ_l^*.
[c]Values for the liquid random close packing computed from $[\sigma(T^*,\rho_l^*)]_{\mathrm{WCA}}$.
[d]Values for the fcc solid close packing computed from $[\sigma(T^*,\rho_l^*)]_{\mathrm{WCA}}$.

suppressed. On the other hand, in the equivalent of random close packing of the Lennard-Jones fluid fluctuations can occur continuously, since the energy required for such is always bounded. While the existence of configurational disorder implies the existence of local density fluctuations in any fluid, it is the dynamic exploration of the accessible phase space that drives a liquid-to-solid transition.

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