AIP | The Journal of Chemical Physics

On the stability of the infinite dimensional fluid of hard hyperspheres: A statistical mechanical estimate of the density of closest packing of simple hypercubic lattices in spaces of large dimensionality

Biman Bagchi and Stuart A. Rice

Citation: The Journal of Chemical Physics **88**, 1177 (1988); doi: 10.1063/1.454237
View online: http://dx.doi.org/10.1063/1.454237
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/88/2?ver=pdfcov
Published by the AIP Publishing

On the stability of the infinite dimensional fluid of hard hyperspheres: A statistical mechanical estimate of the density of closest packing of simple hypercubic lattices in spaces of large dimensionality

Biman Bagchi[a] and Stuart A. Rice
The Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 18 September 1987; accepted 2 October 1987)

We report an analysis of the bifurcation of the solution to the nonlinear equation for the inhomogeneous singlet density in a system of hard hyperspheres; the instability examined corresponds to the liquid-to-simple hypercubic lattice transition. We propose that in the limit $d \to \infty$ the continuous bifurcation which occurs is at the maximum achievable density in a simple hypercubic lattice. Extension of this result to $1 < d < \infty$ leads to estimates of the closest packing densities of simple hypercubic lattices in d dimensions. An examination of the liquid-to-simple hypercubic lattice transition for particles with a Gaussian pair repulsion leads to the identification of that transition with the onset of absolute instability, i.e., the spinodal of the liquid.

I. INTRODUCTION

This paper is concerned with the question: Is a liquid-to-hypercubic lattice transition in a hard hypersphere system ever thermodynamically preferred over other possible transitions? In two and three dimensions (d) the answer is known to be no; we examine the case for other values of d, in particular the limit as $d \to \infty$. The stimulus to this work was a recent paper by Frisch and Percus, who pointed out that the statistical mechanics of a fluid of particles interacting via a finite range repulsive potential is considerably simplified as the dimensionality of the system increases. Indeed, in the limit $d \to \infty$ the equation of state can be calculated exactly for a system of hard hyperspheres.[1] Moreover, Kirkpatrick[2] has shown that in this limit all the loop diagrams in the Mayer cluster expansion disappear, so that the three- and higher-order direct correlation functions vanish and the representation of the spatial variation of singlet density in an inhomogeneous system as a functional of the two-particle direct correlation function becomes exact. In fact, simple analytic expressions for the two-particle direct correlation function for both hard hyperspheres[3] and hard hypercubes[2] can be obtained in the limit $d \to \infty$, and both of these systems can be shown to possess an instability with respect to infinitesimal fluctuations of simple hypercubic symmetry with nonzero wave number.[2-4] Frisch and Percus[3] have found that this Kirkwood-type instability occurs at a density which falls between the estimated lower and upper bounds[5] for the closest packing density of a simple hypercubic lattice of hard hyperspheres.

In this paper we explore several aspects of the putative liquid-to-simple hypercubic crystal transition as a function of dimensionality in a system of hard hyperspheres. We present a bifurcation analysis of the equation for the singlet density in an inhomogeneous system for the case that the density waves have simple hypercubic symmetry. Our analysis shows that for this symmetry the bifurcation diagram (which is of supercritical type[7]) is invariant with respect to the dimensionality of the system. We find that for a system of one-dimensional hard rods the bifurcation condition is satisfied exactly at the close-packed density,[8] and we advance the proposition that the bifurcation in d dimensions occurs at the density of closest packing, thereby removing an apparent contradiction with the Landau theorem which precludes a continuous transition between phases with different symmetries. To deepen our understanding of the system behavior at the bifurcation point we have also carried out an analysis of Fixman's model[9,10] of motion in anharmonic crystals of simple hypercubic symmetry in d dimensions. We show that the effective spring constant of this system goes to zero as $d \to \infty$, which leads to the suggestion that the simple hypercubic solid is unstable to small fluctuations for all $d > 1$, i.e., that the simple hypercubic solid does not correspond to a minimum on the free energy surface, hence Landau's theorem concerning transitions between phases with different symmetries does not apply.

We have also examined the effect of temperature on the liquid-to-simple hypercubic solid transition, in various dimensions, for a system of hyperspherical particles interacting with a repulsive Gaussian potential. We find that for a fixed but large dimension the transition is bounded by two temperatures—no transition is found to occur outside these bounds. The physical reason for this rather surprising result is discussed.

II. COMMENT ON DENSITY FUNCTIONAL THEORY

In density functional theory, the free energy and other thermodynamic properties of an inhomogeneous system are calculated using perturbation theory and a reference homogeneous system. The smallness parameter is usually the position dependent density difference between the reference system and the inhomogeneous system, and the expansion coefficients are the n-particle direct correlation functions of the reference system. In the application of density functional

[a] Present address: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India.

theory to the description of the freezing transition,[11-16] the density difference between liquid and crystal is a periodic function with the characteristics of the chosen lattice. In a recent extension of density functional theory, Singh *et al.*[17] and Kirkpatrik and Wolynes[6] have suggested using aperiodic density fluctuations to describe the transition to a glassy state. At present we have reliable experimental and theoretical estimates of the two-particle direct correlation function, but not of any higher-order direct correlation functions. For this reason, the various applications of density functional theory use a truncated description in which terms involving higher than two-particle direct correlation functions are neglected. Our understanding of the reliability of the predictions so generated is severely limited by the unavailability of reliable three-particle and higher many-particle direct correlation functions for the systems studied.

As mentioned earlier, our study was partly motivated by the observation that in the limit $d \to \infty$ the three-particle and higher-order direct correlation functions do not contribute to the properties of fluids with purely replusive finite range interactions, hence the equilibrium statistical mechanics of these systems becomes exceptionally simple. We also note that one can construct an exact density functional theory to describe the ordering transition in both the $d = 1$ and the $d \to \infty$ limits. Thus, both for $d = 1$ and for $d \to \infty$ we have the following exact relation between the singlet density of an inhomogeneous system and the two-particle direct correlation function:

$$\frac{\rho(\mathbf{r})}{z} = \frac{\rho_l}{z_l} \exp\left\{\int d\mathbf{r}' \, c(r - r', \rho_l)\left[\rho(\mathbf{r}') - \rho_l\right]\right\}. \tag{2.1}$$

In Eq. (2.1), ρ is the density and z the fugacity, and the subscript l refers to the homogeneous liquid. The free energy of the inhomogeneous system can be computed exactly. It is

$$F = \int d\mathbf{r}' \, \rho(\mathbf{r}')\left[\ln \rho(\mathbf{r}') - 1\right] - \frac{1}{2}\int d\mathbf{r}' \int d\mathbf{r} \, \rho(\mathbf{r})\rho(\mathbf{r}')c(r - r'). \tag{2.2}$$

The two-particle direct correlation function is given, in the $d \to \infty$ limit, by[2,3]

$$\rho_l c(r) = \rho_l f(r), \tag{2.3}$$

where $f(r)$ is the Mayer f function. Equation (2.3) is valid for purely repulsive pair interaction potentials. Kirkpatrick[2] showed that for a system of parallel hard cubes there is a continuous transition to an ordered state within the range of validity of Eq. (2.3) and Frisch and Percus[3] have shown that in the $d \to \infty$ limit a system of hard hyperspheres undergoes a Kirkwood-type instability at a density which lies between the estimated upper and the lower bounds for the closest packing density in a simple hypercubic lattice.[5] Moulder[18] has observed a similar instability in a system of perfectly aligned hard cylinders, using an analysis that employs Eqs. (2.2) and (2.3). This author also studied the influence of the higher-order terms on the density dependence of the transition. And Kirkpatrick and Wolynes,[6] in their study of the glass transition in the limit $d \to \infty$, also found a transition, again at a density between the upper and lower bounds for the closest packing density.

The instabilities analyzed by Kirkpatrick,[2] Frisch and Percus,[3] and by Moulder,[18] are all with respect to a simple hypercubic density wave. We show below that Eq. (2.1) gives rise to a bifurcation of the supercritical type[7] if the density wave has a simple hypercubic symmetry. In this case the calculation of the location of the transition becomes very simple.

We shall first analyze the stability of a d-dimensional fluid to a density fluctuation of the simple hypercubic lattice symmetry type. We write

$$\delta\rho(\mathbf{r}) = \rho_l\left[\phi_0 + \sum_{l=1}^{\infty}\phi(l)\xi_l(\mathbf{r})\right], \tag{2.4}$$

with

$$\xi_l(\mathbf{r}) = 2\sum_{i=l}^{d'}\cos(k_l x_i), \tag{2.5}$$

where d' is the dimension of the simple hypercubic lattice, $d' \leqslant d$. The case $d' < d$ corresponds to a lattice of dimensionality d' embedded in a space of dimensionality d. ϕ_0 and $\phi(l)$ are the usual order parameters,[16] $k_l = (2\pi/a)l$, a is the cell length.

Equation (2.4) is now substituted in Eq. (2.1). We then obtain the following expression for the order parameters:

$$\Delta_l \psi(l) = \frac{\int_\Delta d\mathbf{r}\, \xi_l(\mathbf{r})\exp[B(\mathbf{r})]}{\int_\Delta d\mathbf{r}\, \exp[B(\mathbf{r})]}, \tag{2.6}$$

where

$$\psi(l) = \frac{\rho_l}{\rho_s}\phi(l), \tag{2.7}$$

$$\Delta_l = \frac{1}{\Delta}\int_\Delta d\mathbf{r}\, \xi_l^2(\mathbf{r}), \tag{2.8}$$

$$B(\mathbf{r}) = \sum_{l=1}^{\infty}\lambda_l \psi(l)\xi_l(\mathbf{r}), \tag{2.9}$$

$$\lambda_l = (\rho_s/\rho_l)c(k_l), \tag{2.10}$$

with

$$c(k_l) = \rho_l\left[\int d\mathbf{r}\, c(r)e^{-i\mathbf{k}\cdot\mathbf{r}}\right]_{|\mathbf{k}| = k_l}. \tag{2.11}$$

Note that Eq. (2.6) is exact for $d = 1$ and in the limit $d \to \infty$.

In the present problem, Eq. (2.6) simplifies further to

$$\psi_l = \frac{\int_0^a dx\, \cos(k_l x)\exp[2\Sigma\lambda_l\psi(l)\cos(k_l x)]}{\int_0^a dx\, \exp[2\Sigma\lambda_l\psi(l)\cos(k_l x)]}. \tag{2.12}$$

The structural properties of the fluid enter in Eq. (2.12) through λ_l as defined in Eq. (2.10). Equation (2.12) can be solved for the order parameters $\{\psi(l)\}$ as functions of λ_l.

We show in Fig. 1 the behavior of $\psi(1)$ as a function of λ_1 for a two order parameter calculation. Each curve in the figure corresponds to a different value of $\psi(2)$. The essential features of Fig. 1 are invariant to the dimensionality of the lattice. Furthermore, inclusion of higher order parameters does not change the nature of this diagram. We note that the several curves in Fig. 1 imply a series of bifurcations at different values of λ_1 and that all the bifurcations are continuous.

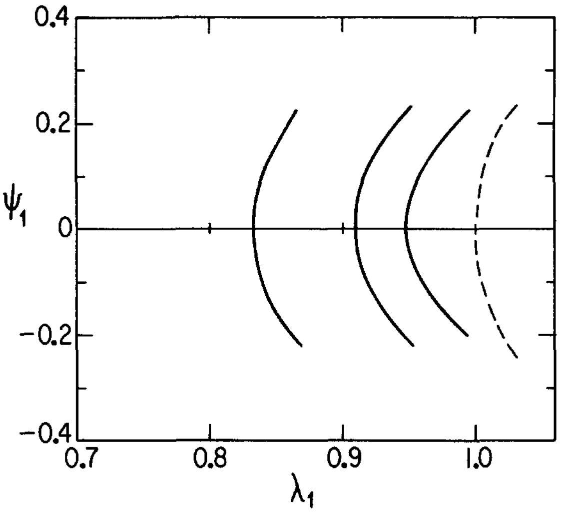

FIG. 1. The two order parameter bifurcation diagram for simple hypercubic lattice geometry. The bifurcation at $\lambda_1 = 1$ is identified as the limit of stability of the system. The dashed region of $\psi_1(\lambda_1)$ is not realizable because the density cannot exceed the closest packing density. Each curve that intersects $\psi_1 = 0$ with $\lambda_1 < 1$ corresponds to a different nonzero value of $\psi(2)$.

In the mathematical literature a bifurcation of this type is denoted supercritical.[7] It is important to realize that density functional theory will give rise to a bifurcation diagram of the type shown in Fig. 1 whenever the density fluctuation has the symmetry of the simple hypercubic lattice [as in Eqs. (2.4) and (2.5)]. If a fluctuation of different symmetry is chosen, a completely different bifurcation diagram is obtained.[8] Thus, the continuous nature of the bifurcation obtained here is a direct consequence of the symmetry of the density wave.

The bifurcation diagram shown in Fig. 1 has several interesting features. First, at each of the bifurcation points with $\lambda_1 < 1$ the value of $\lambda_2 = \rho c(k_2)$ is equal to unity. But, both for $d = 1$ and for $d \to \infty$, λ_2 cannot be unity with λ_1 less than one. Thus, those bifurcation points with $\lambda_1 < 1$ do not represent physical instabilities of the system since they occur for unrealizable system densities. The only bifurcation that has any physical relevance is at $\lambda_1 = 1$, $\psi(l) = 0$. For hard rods, this bifurcation defines the limit of packing in the system in the sense that λ_1 is bounded from above by unity, which in turn implies that the dashed portion of the bifurcation diagram where $\lambda_1 > 1$ is not realizable. The density at which $\lambda_1 = 1$ is the maximum achievable density in a system of hard rods (see Sec. III).

Returning to a system with arbitrary repulsive pair potential, we now carry out a parametric expansion of ϕ around the bifurcation point ($\lambda_c = 1, \phi_c = 0$). This can be done most simply by expanding Eq. (2.12) in a smallness parameter leading to the following expression for the dependence of ϕ on λ near $\lambda = 1$:

$$\phi = (\lambda - 1)^{1/2}. \tag{2.13}$$

Equation (2.13) clearly shows the mean-field nature of the transition, which is expected in the limit $d \to \infty$. Note that Eq. (2.13) is independent of the dimensionality of the simple hypercubic lattice. Equation (2.13) can be used to obtain an interesting prediction concerning the equation of state of the simple hypercubic solid for density greater than the transition density. Within the one-order parameter approximation we obtain for the pressure of the solid phase

$$\left(\frac{pV}{Nk_BT}\right)_{\text{solid}} = \left(\frac{pV}{Nk_BT}\right)_{\text{liquid}} + \alpha + d(\lambda - 1), \tag{2.14}$$

where α is a function of the compressibility. Equation (2.14) shows that the pressure of the simple hypercubic solid diverges as $d \to \infty$ when the density exceeds the transition density.

Equations (2.13) and (2.14) do not apply to a system of hard rods, because $\lambda_1 = 1$ occurs at the limit of maximum density achievable in this system. We will later argue that they also do not apply to a system of hard hyperspheres. Nevertheless, Eq. (2.14) is meaningful for a system of hyperspheres with soft repulsive pair potential.

It is worthwhile to demonstrate the exchange of stability between liquid and simple hypercubic solid at the bifurcation point. For the case of one order parameter, Eq. (2.1) can be written in the form

$$\frac{z_l}{z_s} = \frac{\rho_l}{\rho_s}\left[\frac{1}{a}\int_0^a dx \exp(2\lambda_1\psi_1 \cos k_1 x)^3\right]. \tag{2.15}$$

Near the bifurcation point we can expand the exponential, with ψ_1 as the smallness parameter, to obtain

$$\frac{z_l}{z_s} \simeq \frac{\rho_l}{\rho_s}(1 + 3\lambda_1^2\psi_1^2), \tag{2.16}$$

which is differentiated with respect to λ_1 to obtain

$$\frac{\partial}{\partial\lambda_1}\left(\frac{z_l}{z_s}\right) \simeq \frac{\partial}{\partial\lambda_1}\left(\frac{\rho_l}{\rho_s}\right)(1 + 3\lambda_1^2\psi_1^2) + 6\left(\frac{\rho_l}{\rho_s}\right)\lambda_1\psi_1^2 + 6\lambda_1^2\psi_1\left(\frac{\rho_l}{\rho_s}\right)\left(\frac{\partial\psi_1}{\partial\lambda_1}\right). \tag{2.17}$$

Near the bifurcation point the third term in Eq. (2.17) dominates, and the sign of the derivative indicates the direction of stability change in the system. Note that this analysis is meaningful for systems with soft repulsive potentials, but not for a system of hard hyperspheres for which $\lambda_1 = 1$ corresponds to the maximum achievable density in the simple hypercubic lattice configuration.

III. THE $d=1$ AND $d \to \infty$ HARD HYPERSPHERE SYSTEMS

An analysis of ordering in the one-dimensional hard rod system was carried out in Ref. 8, but we recount some aspects of that study because of its relevance to the work reported in this paper. First, note that the density functional theory representation of the one-particle distribution function as a functional of the two-particle direct correlation function is exact for this case. The Fourier transform of the direct correlation function of a one-dimensional hard rod liquid is given by

$$c(k) = \frac{2}{(1-\rho_l L)^2}\left\{\frac{\rho_l^2}{k^2}[\cos(kL) - 1] + \frac{\rho_l \sin kL}{k}(\rho_l L - 1)\right\}, \tag{3.1}$$

where L is the length of a hard rod. For a continuous transition of the type depicted in the bifurcation diagram, the critical wave vector is given by $k = 2\pi\rho_l$. The bifurcation condition $c(k_l L) = 1$ is satisfied when $\rho_l L = 1$, as can be seen by taking the limits $\rho_l L \to 1$ and $kL \to 2\pi$ simultaneously in Eq. (3.1). This bifurcation corresponds to close packing of the rods. There is no two-phase transition to an ordered state in the conventional sense, and there is no two-phase coexistence. We find the same to be true in the $d\to\infty$ limit for a system of hard hyperspheres when the density waves have the form of Eq. (2.4), again corresponding to the fact that the bifurcation point $\lambda_1 = 1$ occurs at the maximum achievable density of the simple hypercubic lattice.

We shall now confirm the above stated interpretation of the simple bifurcation to a hypercubic lattice in an infinite-dimensional system of hard hyperspheres. To do so we calculate the density at the instability by following Frisch and Percus.[3] The transition density is given by

$$\rho_c = [\tilde{f}(k)]^{-1}, \tag{3.2}$$

where $\tilde{f}(k)$ is given by[3]

$$\tilde{f}(k) = \left(\frac{2\pi}{k^2}\right)^{d/2} \int_0^\infty d(kr)\, f(r)\, (kr)^{d/2} J_{d/2-1}(kr) \tag{3.3}$$

with $f(r)$ the Mayer function and $J_\nu(z)$ the Bessel function of order ν. For hard hyperspheres of diameter σ we have

$$\tilde{f}(k) = \left(\frac{2\pi}{k^2}\right)^{d/2} (\sigma)^d J_{d/2}(k\sigma)/(k\sigma)^{d/2}. \tag{3.4}$$

In standard notation,[19] the reduced transition density is now given by

$$\rho_c^* = \frac{(k_c\sigma)^{d/2}}{2^{3d/2} J_{d/2}(k_c\sigma)(d/2)!}, \tag{3.5}$$

where $k_c\sigma$ is determined by the first minimum of the Bessel function.

The values of ρ_c^* predicted by Eq. (3.5) are compared in Table I with available estimates of, and upper and lower bounds[5] for, the densities of closest packing in simple hypercubic lattices of various dimensionalities. We see that the values predicted by Eq. (3.5) remain rather close to the best estimates available for the densities of closest packing. In general, our value of ρ_c^* for given d is much closer to the upper bound than the lower bound. For $d = 8$ our estimate is slightly larger than the best available estimate, but this may be so because $d = 8$ is too small for Eq. (3.5) to be reliable.

In the $d\to\infty$ limit an asymptotic analysis of the first mimimum of $J_{d/2}(k\sigma)$ can be made.[3] This analysis yields

$$k_c\sigma = d/2 + 1 + z_0(d/2+1)^{1/3}, \tag{3.6}$$

with $z_0 = 1.8558$. The value of the Bessel function at this value of $k_c\sigma$ is obtained in the following way:

$$J_{d/2}(k_c\sigma) = J_{d/2}\left[\frac{d}{2} + 1 + z_0\left(\frac{d}{2}+1\right)^{1/3}\right], \tag{3.7}$$

$$\simeq J^{d/2}\left[\frac{d}{2} + \left(\frac{d}{2}\right)^{1/3} z_0\right] + \frac{1}{3}(z_0+1) J'_{d/2}\left[\frac{d}{2} + \left(\frac{d}{2}\right)^{1/3} z_0\right]. \tag{3.8}$$

Next we use the representation of J_ν in terms in Airy functions,[20]

$$J_{d/2}\left[\frac{d}{2} + \left(\frac{d}{2}\right)^{1/3} z_0\right] \sim \frac{2^{1/3}}{(d/2)^{1/3}} \mathrm{Ai}(-2^{1/3} z_0) + \frac{2^{1/3}}{d/2} \mathrm{Ai}'(-2^{1/3} z_0), \tag{3.9}$$

and

$$J'_{d/2}\left[\frac{d}{2} + \left(\frac{d}{2}\right)^{1/3} z_0\right] \sim -\frac{2^{2/3}}{(d/2)^{2/3}} \mathrm{Ai}'(-2^{1/3} z_0). \tag{3.10}$$

The first term in Eq. (3.9) is zero because $-2^{1/3} z_0$ is the first zero of the Airy function. The second term is of the order of $2/d$ and is neglected. Then we have

$$J_{1/2}(k_c\sigma) \simeq -1.135(4/d)^{2/3}, \tag{3.11}$$

so that ρ_c^* is given in the $d\to\infty$ limit by

$$\rho_c^* = 0.239(e/8)^{d/2} \exp[z_0(d/2)^{1/3}] d^{1/6}. \tag{3.12}$$

This expression differs slightly from that obtained by Frisch and Percus.[3]

It is interesting to compare Eq. (3.12) with the upper and lower bounds for the density of close packing in a simple hypercubic lattice. The main terms behave as follows:

$$\rho_U \sim (d+2) 2^{(-d/2)-1}, \tag{3.13}$$

$$\rho_L \sim (2d/e) 2^{-d}, \tag{3.14}$$

$$\rho_c^* \sim \exp - (1.473 d^{1/3})(2.94)^{-d/2}. \tag{3.15}$$

Thus, our value of ρ_c^* falls in between the two estimates and closer to the upper bound.

The preceding analysis supports the interpretation of ρ_c^* already stated. This interpretation is further strengthened by the universal nature of the bifurcation diagram and the instability of the simple hypercubic lattice (see Sec. IV). Therefore, we propose that Eq. (3.13) gives precisely the density of closest packing of a simple hypercubic lattice in the limit $d\to\infty$.

TABLE I. Values of the density of closest packing of simple hypercubic lattices from Eq. (3.5) compared with available bounds, for several values of d.

d	ρ_c^*	ρ_c (Rogers)[a]	ρ_c (upper)[a]	ρ_c (lower)[a]
8	0.265	0.254	0.3125	0.023
10	0.13	>0.092	0.188	0.007
12	0.057	>0.049	0.1094	0.002
20	0.0017	···	0.011	1.4×10^{-5}

[a] From Ref. 5, Table I, p. 3.

IV. STABILITY OF A SIMPLE HYPERCUBIC LATTICE AS $d\to\infty$

In this section we present an analysis of the stability of a simple hypercubic lattice in the limit $d\to\infty$. Our analysis is based on Fixman's model of a strongly anharmonic crystal.[9,10] We extend this model to the case $d > 3$. We find, as in the case of the Mayer cluster expansion for a fluid, that considerable simplification occurs as the $d\to\infty$ limit is taken.

Fixman's study of the hard-sphere crystal is based on a single occupancy model with the constraint that each particle can move only in its own Wigner–Seitz cell, which has volume v. The basic idea is that, at high densities, a hard sphere will interact predominantly with the nearest-neighboring hard spheres and only very infrequently will feel the presence of the Wigner–Seitz cell wall. Thus, at high densities the thermodynamic properties of the crystal are influenced primarily by short-range correlations involving only a few surrounding particles. The free energy of the constrained hard-sphere crystal is then evaluated using a Hermite polynomial expansion of the Boltzmann factor of the canonical partition function. We note that Fixman's method also offers a practical tool to calculate the entropy of the anharmonic hard-sphere crystal.

Fixman considered two approximations to evaluate the partition function. First, he examined an independent oscillator approximation which retains only the first term in the Hermite polynomial expansion of $\exp(-1/2\Sigma_j\phi_{ij})$, where ϕ_{ij} is the interaction potential between particles i and j. This amounts to computing a Gaussian average over the position of the central particle in the Wigner–Seitz cell. Second, a better approximation is obtained by retaining the succeeding two terms in the expansion. The first approximation has been improved by Ree[10] who also compared the theoretical predictions for spheres, disks, and rods with results from computer simulations.

In the independent oscillator approximation[9,10] the canonical partition function is given by

$$Q_N=\left\{\int_v d\mathbf{r}\exp[-v_e(\mathbf{r})]\right\}^N, \tag{4.1}$$

where Q_N is the canonical partition function for N particles in volume V, the integration is over the Wigner–Seitz cell ($v=V/N$), and the effective potential $v_e(\mathbf{r})$ is given by

$$v_e(\mathbf{r})=\sum_j \ln[1+h(\mathbf{R}_j-\mathbf{r})], \tag{4.2}$$

where $\mathbf{R}_j$ is the position vector from the center of cell i to the center of cell j and the sum is over the nearest-neighbor cells. The function $h(\mathbf{R}_j-\mathbf{r})$ is obtained by a Gaussian average over the jth particle in the jth Wigner–Seitz cell,

$$\begin{aligned}1&+h(\mathbf{R}_j-\mathbf{r})\\&=\left(\frac{t}{\pi}\right)^{d/2}\int d\mathbf{r}_j\exp\left[-\frac{1}{2}\phi_{ij}(|\mathbf{R}_j-\mathbf{r}+\mathbf{r}_j|)-tr_j^2\right],\end{aligned} \tag{4.3}$$

where t is the spring constant of the reference potential.[9] The reference potential spring constant is next calculated by imposing the following self-consistency condition:

$$\frac{d}{2t}=\int_v d\mathbf{r}\, r^2\exp[-v_e(\mathbf{r})]\Big/\int_v d\mathbf{r}\exp[-v_e(\mathbf{r})]. \tag{4.4}$$

The calculations can be greatly simplified if $v_e(\mathbf{r})$ is replaced by the truncated Taylor expansion

$$v_e(\mathbf{r})=\epsilon+\gamma r^2, \tag{4.5}$$

where

$$\epsilon=-\sum_j\ln[1+h(R_j)], \tag{4.6}$$

$$\begin{aligned}\gamma=&-(2d)^{-1}\sum_j\{[1+h(R_j)]\nabla^2_{R_j}h(R_j)\\&-[\nabla_{R_j}h(R_j)]^2\}[1+h(R_j)]^{-2}.\end{aligned} \tag{4.7}$$

We now proceed to calculate $h(\mathbf{R}_j-\mathbf{r})$ for a simple hypercubic hard-sphere solid when $d\to\infty$.

As a first step we rewrite Eq. (4.3) in the form

$$h(\mathbf{W})=-\left(\frac{t}{\pi}\right)^{d/2}\int_{|\mathbf{W}+\mathbf{r}_j|<\sigma}d\mathbf{r}_j\,e^{-tr_j^2}, \tag{4.8}$$

where the integral is over the domain $|\mathbf{W}+\mathbf{r}_j|<\sigma$, σ being the hard-sphere diameter, and $\mathbf{W}=\mathbf{R}_j-\mathbf{r}$. With the change of variable $\mathbf{x}=\mathbf{W}+\mathbf{r}_j$, Eq. (4.8) reduces to

$$\begin{aligned}h(\mathbf{W})=&-\left(\frac{t}{\pi}\right)^{d/2}S_{d-1}(1)\int_0^1 dx\,x^{d-1}\\&\times\int_0^\pi d\theta\sin^{d-2}\theta(e^{-t(\mathbf{x}-\mathbf{W})^2}),\end{aligned} \tag{4.9}$$

where we have set $\sigma=1$. $S_{d-1}(1)$ is the surface area of a $(d-1)$ dimensional hypersphere of unit diameter. Equation (4.9) gives

$$\begin{aligned}h(W)=&-2tW^{1-d/2}e^{-tW^2}\\&\times\int_0^1 dx\,x^{d/2}e^{-tx^2}I_{d/2-1}(2txW),\end{aligned} \tag{4.10}$$

where $I_\nu(z)$ is the modified Bessel function of order ν. In the limit of large d we can use the asymptotic expansion of $I_\nu(z)$ (Ref. 20) to obtain the following simple expression for $h(W)$:

$$\begin{aligned}h(W)\sim&-2t\,e^{-tW^2}(\pi d)^{-1/2}\left(\frac{2t}{d}\right)^{d/2-1}\\&\times\int_0^1 dx\,x^{d-1}e^{-tx^2}.\end{aligned} \tag{4.11}$$

Next, note that $h(W)$ must be between -1 and 0, because of Eq. (4.3). If t grows as d^α, $h(W)$ goes to zero at least as fast as $(2d^\alpha)e^{-d^\alpha W^2}(2d^{\alpha-1})^{d/2-1}$. The effective spring constant is then given, for simple hypercubic lattice geometry, by

$$\begin{aligned}\gamma=&\left\{\left(\frac{dh(R)}{dR}\right)^2-[1+h(R)]\frac{d^2h(R)}{dR^2}\right\}\\&\times[1+h(R)]^{-2},\end{aligned} \tag{4.12}$$

where we have considered only the nearest neighbors. Ree[10] has found that this approximation gives reasonable results for rods, disks, and spheres. Then in the limit $d\to\infty$,

$$\begin{aligned}\gamma\sim&\,2t(R_1^2-1)e^{-tR_1^2}(\pi d)^{-1/2}\left(\frac{2t}{d}\right)^{d/2-1}\\&\times\int_0^1 dx\,x^{d-1}e^{-tx^2},\end{aligned} \tag{4.13}$$

where R_1 is the radius of the Wigner–Seitz cell. Equation (4.12) shows that $\gamma\to 0$ as $d\to\infty$ even when t grows with d as d^α with $\alpha>0$.

The asymptotic disappearance of the effective spring constant γ suggests that a simple hypercubic lattice is not a stable phase in the limit $d \to \infty$. Thus, Landau's theorem, which states there cannot be a continuous phase transition between phases of differing symmetry, does not apply to the type of ordering transition considered in this paper.

V. GAUSSIAN CORE MODEL

We consider now the system with pair interaction

$$\phi(r) = \phi_0 e^{-\alpha r^2}. \tag{5.1}$$

Phase transitions in this system have been studied by Stillinger[21] and by Stillinger and Weber[22]; in three dimensions (and for $T = 0$) it undergoes a spontaneous ordering transition from a face-centered cubic to a body-centered cubic lattice as the density is increased. The properties of this model display some surprising anomalies, e.g., for any fixed $T > 0$ sufficient compression always produces a fluid phase.

In the $d \to \infty$ limit, Fourier transform of the direct correlation function of a system with purely repulsive pair interactions can be written in the form[3]

$$c(k) = \rho_l \left(\frac{2\pi}{k^2}\right)^{d/2} \int_0^\infty d(kr) f(r) (kr)^{d/2} J_{d/2-1}(kr). \tag{5.2}$$

For the Gaussian core model Eq. (5.1) can be integrated to obtain

$$c(k) = \rho_l \left(\frac{\pi}{\alpha}\right)^{d/2} \sum_{n=1}^{\infty} (-1)^n \frac{\beta^n}{n!} n^{-d/2} e^{-k^2/4n\alpha}, \tag{5.3}$$

with $\beta = (k_B T)^{-1}$. Equation (5.2) is a convergent sum which we evaluate numerically. An instability towards a density fluctuation of the form of Eq. (2.4) occurs when $c(k)$ is equal to unity. We show, in Fig. 2, the calculated direct correlation function for several values of $d > 3$ and for several values of β. Clearly, there is no structure in the direct correlation function when β is small (high temperature). As β is increased, a well-defined peak in the direct correlation function develops for intermediate values of the wave vector, implying the appearance of short-range correlations in the liquid. By using the relation $\rho_l^* c(k_1) = 1$, one finds the value of the liquid density at the instability point. This transition density is a strong function of the temperature. In Fig. 3 we show ρ_l^* as a function of β for several values of d. Note that there is no transition for $\beta > \beta_c$ for any given d. We find this to be true for any value of d, although the value β_c increases (almost linearly) with d. Thus, the Gaussian core model has

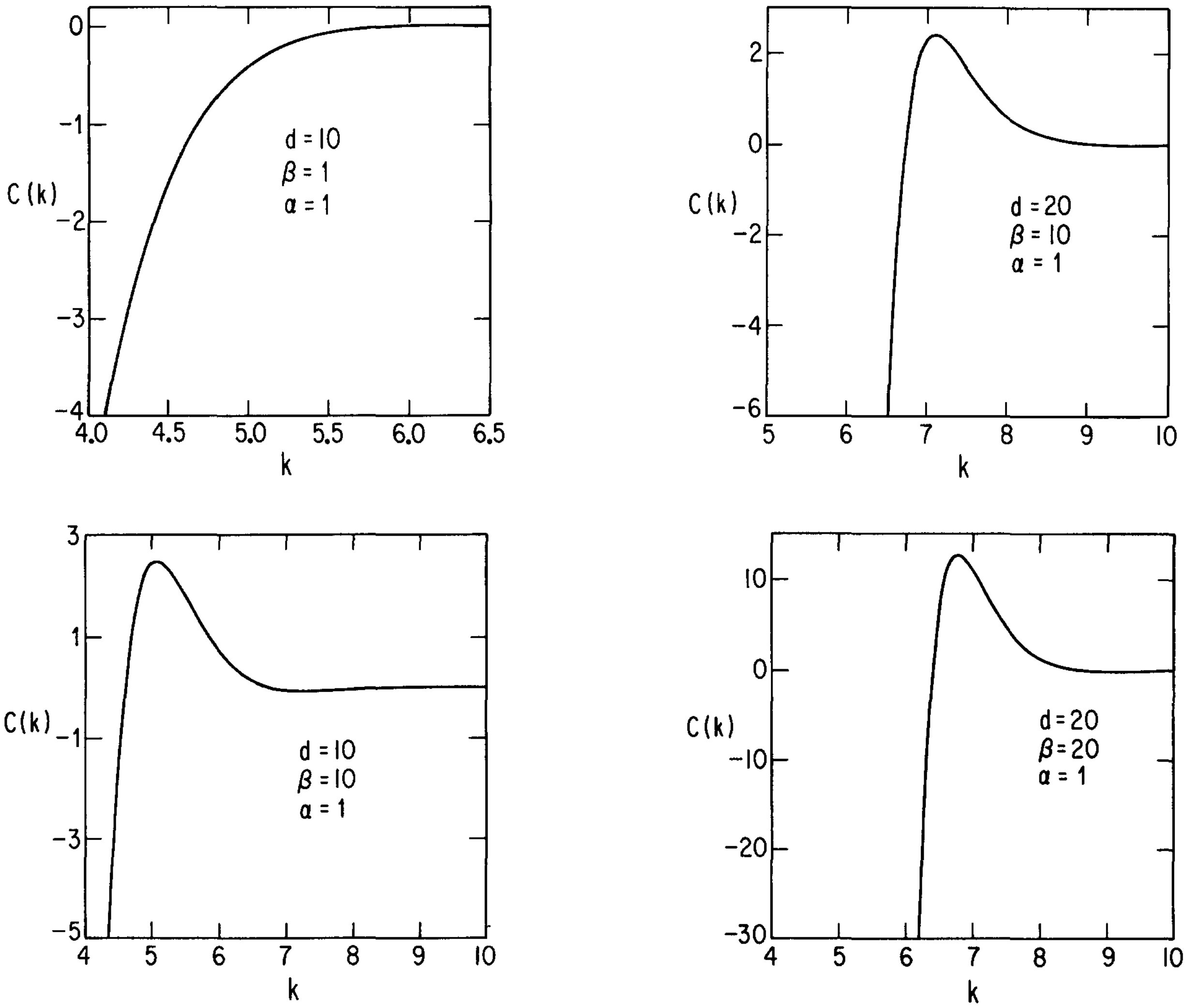

FIG. 2. Direct correlation function $c(k)$ as a function of wave vector k. (a) $d = 10, \beta = 1, \alpha = 1$; (b) $d = 10, \beta = 10, \alpha = 1$; (c) $d = 20, \beta = 10, \alpha = 1$; and (d) $d = 20, \beta = 20, \alpha = 1$.

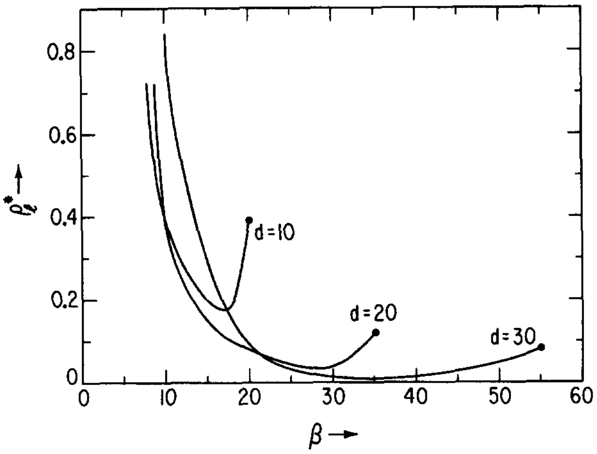

FIG. 3. Transition density ρ_f^* of the Gaussian core model as a function of β for several values of d, shown on each curve. The black dot on each line indicates the limit beyond which no transition is observed.

a liquid-to-simple hypercubic lattice transition only in a limited region of the $\beta - d$ plane, as shown in Fig. 4.

The disappearance of the liquid-to-simple hypercubic lattice transition as β is increased beyond β_c (with d fixed) can be understood in the following way. For the Gaussian core model we can define a temperature dependent distance R by

$$R(\beta) = (\ln \beta)^{1/2}. \tag{5.4}$$

Then, in the $\beta \to \infty$ limit, the Mayer f function behaves more and more like the corresponding hard-sphere f function with a diameter that scales with $R(\beta)$. So, as β increases at constant d, the number density of the system decreases, as shown by the values of the transition density ρ_f^* which initially shift to lower value as β is increased. But beyond a certain value of β the decrease in the fluid number density becomes so great that the buildup of short-range order necessary for freezing is no longer possible, and so the liquid-to-simple hypercubic lattice transition disappears. We should point out that this disappearance of the liquid-to-simple hypercubic lattice transition need not occur in three dimensions where higher-order correlation functions are important in the representation of the inhomogeneous singlet density.

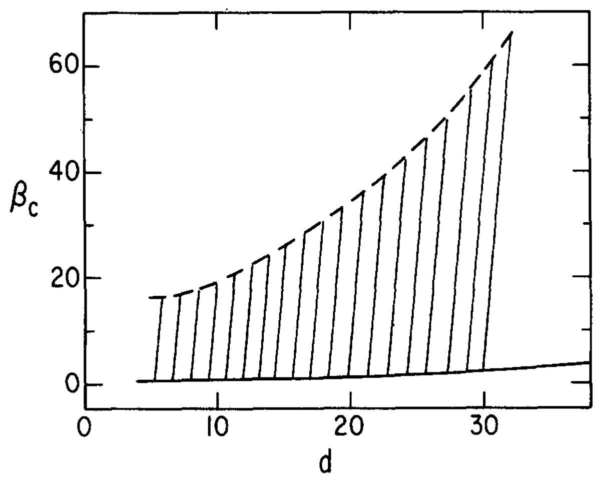

FIG. 4. Critical temperature beyond which no transition is observed as a function of d (dashed curve). The lower solid line gives the value of β below which the value of the transition density becomes very large. The hatched area gives an approximate representation of the region where a bifurcation point can be used to locate the spinodal of the liquid.

VI. CONCLUSIONS

The study reported in this paper focuses on the interpretation of the instability of a hard hypersphere liquid with respect to the simple hypercubic crystal. In an earlier paper[8] we examined the implication of this instability, signaled by a bifurcation in the solution of the nonlinear equation for the density, for one-dimensional hard rods, and have shown that it occurs only at the maximum achievable density of the system. Since the density functional theory used is *exact* for both $d = 1$ and in the limit $d \to \infty$, it is natural to ask whether a similar conclusion can be reached for a system of particles interacting via a hard-sphere potential when $d \to \infty$. Our analysis gives an affirmative answer. Although it is not possible to conclusively prove that our answer is correct, there is sufficient evidence to believe that in the limit $d \to \infty$ the continuous bifurcation at $\lambda_1 = 1$ does signal the limiting density for simple hypercubic packing. We then hypothesize that the same analysis for $1 < d < \infty$ provides an estimate of the density of hypercubic close packing of hard hyperspheres for any d.

We have also examined the liquid-to-simple hypercubic lattice transition for a system with Gaussian repulsion between pairs of molecules, and found that temperature has a strong effect on the ordering transition. Our numerical results imply that there is a critical value of the inverse temperature, beyond which no transition occurs. The value of β_c increases with the dimension of the system. An interpretation is provided for this rather unusual result.

We have shown that for hard hyperspheres a simple hypercubic lattice is not a stable state of the system. For a system of soft hyperspheres, however, the situation is different. Although $\lambda_1 = 1$ corresponds to the state of close packing for hard hyperspheres, so no larger densities are allowed, for soft repulsive hyperspheres simple hypercubic lattice densities greater than that at the transition $\lambda_1 = 1$ are not mechanically prohibited. But a continuous transition which occurs at $\lambda_1 = 1$ means $c(k) = 1$, so this bifurcation point defines the onset of instability of the liquid due to infinitesimal density fluctuations with nonzero wave numbers, which we interpret as the spinodal of the liquid. That is, we use Landau's theorem, which precludes a continuous phase transition between two phases of different symmetries, to infer that the bifurcation in the Gaussian core hypersphere system represents an absolute instability of the liquid.

ACKNOWLEDGMENT

This research was supported by the NSF under Grant No. CHE 84-14012.

[1]H. L. Frisch, N. Rivier, and D. Wyler, Phys. Rev. Lett. **54**, 2061 (1985).
[2]T. R. Kirkpatrick, J. Chem. Phys. **85**, 3515 (1986).
[3]H. L. Frisch and J. K. Percus, Phys. Rev. A **35**, 4696 (1987).
[4]W. Klein and H. L. Frisch, J. Chem. Phys. **84**, 2 (1986).
[5]C. A. Rogers, *Packing and Covering* (Cambridge University, Cambridge, 1964), Chaps. 1, 4, and 7.

[6]T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).
[7]J. T. Stuart, in *Applications of Bifurcation Theory*, edited by P. H. Rabinowitz (Academic, New York, 1977), p. 127.
[8]B. Bagchi, C.Cerjan, and S. A. Rice, J. Chem. Phys. **79**, 5595 (1983).
[9]M. Fixman, J. Chem. Phys. **51**, 3270 (1969).
[10]F. H. Ree, J. Chem. Phys. **53**, 920 (1970).
[11]T. V. Ramakrishnan and V. M. Yussouff, Phys. Rev. B **19**, 2775 (1979); T. V. Ramakrishnan, Phys. Rev. Lett. **48**, 541 (1982).
[12]A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981).
[13]A. D. J. Haymet, J. Chem. Phys. **78**, 4641 (1983); Rev. Lett. **52**, 1013 (1984).
[14]P. Tarazona, Mol. Phys. **52**, 81 (1984); G. L. Jones and U. Mohanty, *ibid.* **54**, 1241 (1985).
[15]M. Baus and J. L. Colot, Mol. Phys. **55**, 653 (1985).
[16]B. Bagchi, C. Cerjan, and S. A. Rice, J. Chem. Phys. **79**, 5595, 6222 (1983); Phys. Rev. B **28**, 6411 (1983); B. Bagchi, C. Cerjan, U. Mohanty, and S. A. Rice, Phys. Rev. B **29**, 2857 (1984); P. Radloff, B. Bagchi, C. Cerjan, and S. A. Rice, J. Chem. Phys. **81**, 1406 (1984); C. Cerjan, B. Bagchi, and S. A. Rice, *ibid.* **83**, 2376 (1985).
[17]Y. Singh, J. P. Stoessel, and P. G. Wolynes, Phys. Rev. Lett. **54**, 1059 (1985).
[18]B. Moulder, Phys. Rev. A **35**, 3095 (1987).
[19]J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).
[20]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D.C., 1964).
[21]F. H. Stillinger, J. Chem. Phys. **65**, 3968 (1976).
[22]F. H. Stillinger, and T. A. Weber, J. Chem. Phys. **68**, 3837 (1978).