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Ornstein–Zernike-like Equations in Statistical Geometry: Stable and Metastable Systems

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Statistical geometric methods based on nearest-neighbor distributions are used, in connection with hard-particle systems, to develop Ornstein–Zernike-like equations that have already been of considerable value in the statistical thermodynamic analysis of such systems and that promise to have even greater value. In this paper, we use these equations to (1) develop a relation that is valid for a hard particle system in unconstrained equilibrium and that shows that the insertion probability cannot vanish (short of closepacking) in such a system, (2) study the still incompletely settled issue concerning the equality of the hard-particle densities on the peripheries of cavities which are and are not occupied by hard particles and, in so doing, arrive at a relation that holds in a system in stable equilibrium but fails in a metastable system, (3) provide insight into the geometric mechanism of hard-particle phase transitions and allow simple estimates of the freezing densities, and (4) suggest a new physical interpretation for the direct correlation function.

1. Introduction

There has been an increased interest in *nearest-neighbor distributions* (and neighbor distributions in general) in the statistical mechanics of fluids and related systems.^{1–7} Interest has also been focused on the functions that comprise the neighbor distributions. In this paper, dealing with hard particle systems, we make use of these functions to develop Ornstein–Zernike-like equations and to derive relations that are valid on the *stable* branches of hard particle pressure–density isotherms and that are not necessarily valid on metastable branches. We also investigate some unresolved issues concerning the conditional particle density at the surface of a cavity and find a rather unique relation involving these densities that undergoes an abrupt change as the system passes from stable to metastable equilibrium. Byproducts of this study are some simple ideas concerning the “mechanism” of hard particle phase transitions and an alternative physical interpretation of the direct correlation function. (See Appendix C.)

The term “statistical geometric characterization” is adopted to imply that the analysis is conducted with the aid of neighbor distributions and their component functions.

2. Nearest Neighbor Distribution

Consider an arbitrary point in a uniform system of N particles (not necessarily hard particles) contained in a volume V . Selecting this point as the origin, we ask for the probability $\beta_0(\mathbf{r}) \, d\mathbf{r}$ that the center of the particle nearest to the origin is located at the point \mathbf{r} in the volume element $d\mathbf{r}$. This probability can be expressed as

$$\beta_0(\mathbf{r}) \, d\mathbf{r} = [1 - \int^r \beta_0(\mathbf{r}') \, d\mathbf{r}'] \rho G_0(\mathbf{r}) \, d\mathbf{r} \quad (2.1)$$

where the notation \int^r indicates that the integration is performed throughout the volume $4\pi r^3/3$ where $r = |\mathbf{r}|$. ρ is the uniform bulk number density N/V , and $G_0(\mathbf{r})$ is defined so that $\rho G_0(\mathbf{r})$ is the conditional density in $d\mathbf{r}$ (conditional on the interior volume $4\pi r^3/3$ being devoid of particle centers). The structure of eq 2.1 is obvious; the factor in square brackets is the

probability that the interior volume is empty, while $\rho G_0(\mathbf{r}) \, d\mathbf{r}$ is the chance that at least one particle center will be found in $d\mathbf{r}$, given that the interior volume is empty.

In general, we shall be interested in nearest neighbor distributions that are spherically symmetric so that we can ask for the probability that the center of the particle nearest to the arbitrary point at the origin lies in the spherical shell of volume $4\pi r^2 \, dr$. By denoting this probability by $\alpha_0(r) \, dr$, we have

$$\alpha_0(r) \, dr = [1 - \int_0^r \alpha_0(r') \, dr'] 4\pi r^2 \rho G_0(r) \, dr \quad (2.2)$$

where

$$\alpha_0(r) = 4\pi r^2 \beta_0(r) \quad (2.3)$$

From these equations, it is clear that $\alpha_0(r)$ and $\beta_0(r)$ are fully determined by $G_0(r)$ and vice versa.

We can also place the center of a molecule at the origin and ask for the probability that the center of the nearest *other* molecule lies in $d\mathbf{r}$ at \mathbf{r} . In this case, denote probability distributions by $\beta(r)$ and $\alpha(r)$, dropping the zero subscript, and eqs 2.1 and 2.3 are once again applicable to the unsubscripted quantities.

If we consider a two-dimensional system, eqs 2.2 and 2.3 become

$$\alpha_0(r) \, dr = [1 - \int_0^r \alpha_0(r') \, dr'] 2\pi r \rho G_0(r) \, dr \quad (2.4)$$

$$\alpha_0(r) = 2\pi r \beta_0(r) \quad (2.5)$$

while, for a one-dimensional system, we define the nearest-neighbor distribution to the *right or left* of the origin by $\alpha_0(x)$, where x may be positive or negative, and the equations become

$$\alpha_0(x) \, dx = [1 - \int_0^x \alpha_0(x') \, dx'] \rho G_0(x) \, dx \quad (2.6)$$

$$\alpha_0(x) = \beta_0(x) \quad (2.7)$$

For both the one- and two-dimensional systems, we denote (similar to the three-dimensional case) the distributions about

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a particle at the origin by the same symbols *without* zero subscripts. Again the same set of equations applies to these quantities.

In this paper, we specialize consideration to hard particles of diameter (spheres, disks) or length (rods) σ . Then it is sometimes convenient to think of the “empty” interior volume of radius r (spheres, disks) or half-length x (rods) as having been created by a hard particle of radius $r - (\sigma/2)$ or half-length $x - (\sigma/2)$. This is so even when there is a particle at the origin, provided that $r, x > \sigma$.

3. Insertion Probability

The quantity in square brackets in eq 2.2, since it represents the chance of finding an empty spherical region large enough to accommodate a hard sphere of radius $r - (\sigma/2)$ is the “insertion probability”⁸ for a sphere of this radius. For a system of hard spheres, in thermodynamic equilibrium, it is well-known^{9,10} that this insertion probability, which we now denote by $P_0(r)$, is related to the chemical potential $\mu(r - (\sigma/2))$ of the added hard sphere, regarded as a “solute” sphere, through the relation

$$\mu\left(r - \frac{\sigma}{2}\right) = kT \ln \left\{ \frac{\left[\Lambda\left(r - \frac{\sigma}{2}\right)\right]^3}{VP_0(r)} \right\} \quad (3.1)$$

where k is the Boltzmann constant, T the temperature, and $\Lambda(r - (\sigma/2))$ the de Broglie wavelength of the solute sphere. If $r = \sigma$, the solute sphere is identical to the “solvent” sphere of radius $\sigma/2$, and eq 3.1 is replaced by

$$\mu\left(\frac{\sigma}{2}\right) = kT \ln \left[\frac{\left[\Lambda\left(\frac{\sigma}{2}\right)\right]^3 N}{VP_0(\sigma)} \right] \quad (3.2)$$

where the addition of the factor N to the argument of the logarithm is related to the reduction of entropy that accompanies the indistinguishability of the solute from the solvent spheres. These ideas can of course be extended to disks and rods.

If we consider “empty” interior volumes which we may now refer to as “solute cavities”^{11–13} that *contain* a particle centered at the origin, then the probability of observing such a cavity cannot be regarded as an insertion probability, since the presence of the particle at the origin blocks the addition of another particle, but for convenience, we will continue to refer to it as an insertion probability and denote it by $P(r)$, again dropping the zero subscript.

Next we derive a useful relation between $P_0(r)$ and $G_0(r)$ by noting that $P_0(r + dr)$ may be expressed as

$$P_0(r + dr) = P_0(r)[1 - 4\pi r^2 \rho G_0(r) dr] \quad (3.3)$$

where the right-hand side is the product of the simultaneous probabilities that there is an empty volume of radius r and an empty spherical shell of volume $4\pi r^2 dr$ so as to assure an empty volume of radius $r + dr$. Expanding the left side of eq 3.3 to terms linear in dr leads to an equation for dP_0/dr that can be integrated immediately, subject to the condition $P_0(0) = 1$, to yield

$$P_0(r) = \exp\left\{-\rho \int_0^r 4\pi(r')^2 G_0(r') dr'\right\} = 1 - \int_0^r \alpha_0(r') dr' \quad (3.4)$$

so that $P_0(r)$ is fully determined by either $G_0(r)$ or $\alpha_0(r)$ and

vice versa. Comparison of eq 3.4 with eqs 2.2 and 2.3 shows that

$$\beta_0(r) = \frac{\alpha_0(r)}{4\pi r^2} = \rho G_0(r) P_0(r) \quad (3.5)$$

Substitution of the first equation of eq 3.4 into eq 3.5 shows that

$$\int_0^\infty 4\pi r^2 \beta_0(r) dr = \int_0^\infty \alpha_0(r) dr = 1 \quad (3.6)$$

so that the nearest-neighbor distributions are indeed normalized. Equations 3.4 through 3.6 hold for disks and rods except that for disks, $4\pi r^2$ is replaced by $2\pi r$ and for rods, r is replaced by x and $4\pi r^2$ by unity.

The equation for $P(r)$, similar to eq 3.4, is

$$P(r) = \exp\left\{-\rho \int_\sigma^r 4\pi(r')^2 G(r') dr'\right\} = 1 - \int_\sigma^r \alpha(r') dr', \quad r \geq \sigma \quad (3.7)$$

In this case, the counterpart of eq 3.5 is

$$\beta(r) = \frac{\alpha(r)}{4\pi r^2} = \rho G(r) P(r) \quad (3.8)$$

Substitution of eq 3.7 into eq 3.8 now shows that

$$\int_\sigma^\infty 4\pi r^2 \beta(r) dr = \int_\sigma^\infty \alpha(r) dr = 1 \quad (3.9)$$

so that the nearest-neighbor distribution for this case is also normalized. It should be noted that the lower limits on the integrals in eq 3.9 could be set to zero, since $\beta(r)$, $\alpha(r) = 0$ for $r < \sigma$, due to the presence of the hard sphere centered at the origin. Similar results apply to hard disks where $4\pi r^2$ is replaced by $2\pi r$ and for hard rods where r is replaced by x and $4\pi r^2$ by unity.

The above relations can be applied to crystalline solids where G_0 , β_0 , α_0 and G , β , α can be considered as rotationally averaged quantities.

Now, Speedy¹⁴ has given proof that, as long as averages are taken over *all* possible (nonoverlapping) configurations of hard spheres within the volume in which they are contained, the following relation is valid:

$$G(r) = 0, \quad r < \sigma$$

$$G(r) = G_0(r), \quad r > \sigma \quad (3.10)$$

In simple language, this implies that if a hard sphere is centered within a spherical region whose radius is larger than its own diameter, then another hard sphere, not being able to contact the central sphere, cannot be aware of its presence in all configurations in which the empty spherical region is maintained. However, Speedy presents a more rigorous argument. Later, we argue that eq 3.10 fails for a hard-particle system that is not at *complete* (unconstrained) equilibrium. “Complete” equilibrium implies that averages are taken over “all” configurations limited only by the principle of no overlap, i.e., that the averages correspond to the *full* thermodynamic state of the hard-sphere system. For example, if one included only those configurations in, say a low density system, in which the centers of all spheres were fixed to the sites of a rigid lattice, eq 3.10 could certainly not hold. This would be a case in which almost all of the most abundant configurations would be disallowed, amounting to a very severe internal configurational constraint.

Notice, however, that at the density where the hard-sphere solid is stable, the crystalline configurations are the *most* abundant ones, disordered structures (because of inefficient packing) being in natural short supply. In the crystalline phase, the spheres are not rigidly fixed to lattice sites.

This brings us to our first consideration of a metastable or even unstable *fluid* branch of the pressure–density isotherm of the hard-sphere system. As in the first example presented above, the system on this branch must be limited to configurations that represent only a minor fraction of the total. For example, configurations displaying the long-range order of the *stable* crystal must be disallowed; otherwise, they would overwhelm (because of their relatively large number) the averages so that the system would no longer be metastable or unstable. This severe configurational restriction could invalidate the proof leading to eq 3.10. We return to this point later.

Substitution of eq 3.10 into eq 3.4 yields

$$P_0(r) = \exp\{-\rho \int_0^r 4\pi r'^2 G_0(r') dr'\} \exp\{-\rho \int_r^\infty 4\pi r'^2 G(r') dr'\}$$

$$P_0(r) = P_0(\sigma)P(r), \quad r > \sigma \quad (3.11)$$

where we have used eq 3.7. Substitution of this equation and eq 3.10 into eq. 3.8 gives

$$\beta(r) = \rho G_0(r) \frac{P_0(r)}{P_0(\sigma)}$$

$$\beta(r) = \frac{\beta_0(r)}{P_0(\sigma)}, \quad r > \sigma \quad (3.12)$$

where, in the final step, we have used eq 3.5.

It is clear from the foregoing that the fundamental problem in the statistical mechanics of the hard-sphere system is the evaluation of $G_0(r)$ since that function can be used in eq 3.4 to determine $P_0(\sigma)$ which, in turn, can be used in eq 3.2 to evaluate $\mu = \mu(\sigma/2)$. For example, the central effort of scaled particle theory (SPT)^{10,15,16} is directed toward the evaluation of $G_0(r)$.

4. Ornstein–Zernike-like Equations

Consider now the pair correlation function $g(\mathbf{r}_2)^{17}$ between a hard sphere whose center is chosen as the origin and one whose center is at \mathbf{r}_2 . We may express this function by the following equation:

$$\rho g(r_2) = \beta(r_2) + \rho \int \beta(r_3) \bar{g}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \quad (4.1)$$

where $\rho \bar{g}(\mathbf{r}_2, \mathbf{r}_3)$ is the conditional density of hard-sphere centers in $d\mathbf{r}_2$, given that there is a sphere at the origin whose nearest neighbor is in $d\mathbf{r}_3$ at \mathbf{r}_3 . Figure 1 diagrams this situation. An important feature of $\bar{g}(\mathbf{r}_2, \mathbf{r}_3)$ is that it must vanish if $|\mathbf{r}_3|$ exceeds $|\mathbf{r}_2|$; otherwise, the particle at \mathbf{r}_3 would cease to be the nearest neighbor to the one at the origin. Thus, insofar as the particle at \mathbf{r}_2 is considered, within the integral on the right side of eq 4.1, there is a hard sphere of radius $r_3 - (\sigma/2)$ centered at the origin, which it cannot penetrate. This sphere is the dotted one in Figure 1. Since it is clear from the figure that $r_3 - (\sigma/2)$ can never be less than $\sigma/2$, the sphere with center at \mathbf{r}_2 cannot sense the one at the origin (in the absence of some special configurational constraint that might be equivalent to an intermolecular potential). Thus, $\bar{g}(\mathbf{r}_2, \mathbf{r}_3)$ may be regarded as an unsymmetrical triplet distribution function involving the three

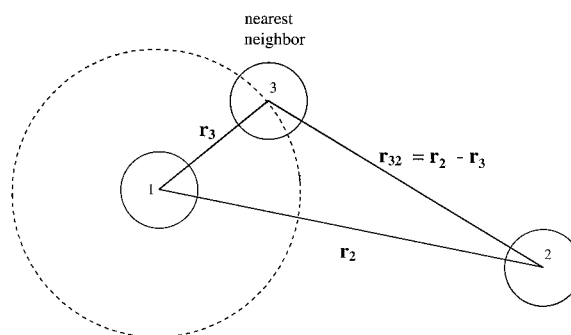


Figure 1. Illustrates the basis for eq 4.1. Particle 3, the shaded particle, is the nearest neighbor to particle 1. The pair correlation function refers to particles 1 and 2. The large circle is the “effective” hard sphere that particle 2 sees.

particles—nearest neighbor at \mathbf{r}_3 , sphere at \mathbf{r}_2 , and effective sphere of radius $r_3 - (\sigma/2)$ centered at the origin.

The structure of eq 4.1 is elementary. The density $\rho g(\mathbf{r}_2)$ in $d\mathbf{r}_2$ may be due to the *nearest neighbor* if the center of the nearest neighbor is in $d\mathbf{r}_2$. This accounts for the first term on the right of eq 4.1. If the nearest neighbor is not in $d\mathbf{r}_2$, but rather in $d\mathbf{r}_3$, then the density in $d\mathbf{r}_2$ is given by $\rho \bar{g}(\mathbf{r}_2, \mathbf{r}_3)$, i.e., by the density, *conditional* on the nearest neighbor being in $d\mathbf{r}_3$, the probability of which is $\beta(\mathbf{r}_3) d\mathbf{r}_3$. The product of this probability and the density conditional on its contributes to the overall density in $d\mathbf{r}_2$ and leads to the integrand in eq 2.1 which is then summed over all allowable positions \mathbf{r}_3 to yield the total density when added to $\beta(\mathbf{r}_2)$. The result is eq 4.1.

We refer to eq 4.1 (and equations that resemble it, some of which we discuss below) as an “Ornstein–Zernike-like (OZ-like) equation”, because of its strong resemblance to the Ornstein–Zernike equation.¹⁸ In many instances, this resemblance is more than incidental, and we elaborate on this issue in Appendix D. OZ-like equations are especially useful because of the penetrating insights that they afford into the physical features of what might appear to be a predominantly mathematical problem. For example, eq 4.2, below, has been used in conjunction with SPT to evaluate the hard-sphere pair correlation function with an accuracy that slightly exceeds that derived from the Percus–Yevick theory.¹ By writing OZ-like equations for a hard sphere of arbitrary radius at the origin, a continuum of OZ-like equations can be produced whose value in the theory of fluids may be considerable but has yet to be tested.

We can write the analogue of eq 4.1 for the pair correlation function between an “arbitrary point” at the origin and a hard sphere at \mathbf{r}_2 . Since the point at the origin is arbitrary, it follows that, in this case, $g(r_2) = 1$ and $\beta \rightarrow \beta_0$. Then, eq 4.1 is replaced by

$$\rho = \beta_0(r_2) + \rho \int \beta_0(r_3) \bar{g}_0(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \quad (4.2)$$

where the argument for the structure of eq 4.2 is the same as that for eq 4.1. We have appended the subscript zero to \bar{g} to indicate that the function might possibly differ in eq 4.2 from its value in eq 4.1.

However, it should be evident from Figure 1 that, if the sphere at the origin is removed, it makes no difference to the sphere at \mathbf{r}_2 as long as \mathbf{r}_3 exceeds σ ; i.e., in the absence of a configurational constraint, the sphere at \mathbf{r}_2 cannot sense what is at the origin, in either case, as long as $r_3 > \sigma$. Thus,

$$\bar{g}_0(\mathbf{r}_2, \mathbf{r}_3) = \bar{g}(\mathbf{r}_2, \mathbf{r}_3), \quad r_3 > \sigma \quad (4.3)$$

Now, we substitute eq 3.12 into eq 4.1 and eq 4.3 into eq 4.2,

bearing in mind that the integral in eq 4.1 cannot have $\mathbf{r}_3 < \sigma$ since then $\beta(r_3)$ would vanish. Equation 4.1 becomes

$$P_0(\sigma)\rho g(r_2) = \beta_0(r_2) + \rho \int_{\sigma}^{\infty} \beta_0(r_3) \bar{g}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \quad (4.4)$$

while eq 4.2 may be expressed as

$$\rho = \beta_0(r_2) + \rho \int_{\sigma}^{\infty} \beta_0(r_3) \bar{g}_0(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 + \rho \int_{\sigma}^{\infty} \beta_0(r_3) \bar{g}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \quad (4.5)$$

where the notation \int^{σ} and \int_{σ} indicates, respectively, that the ranges of r_3 are $r_3 < \sigma$ and $r_3 > \sigma$. Subtracting eq 4.5 from eq 4.4 yields

$$P_0(\sigma)g(r_2) = 1 - \int_{\sigma}^{\infty} \beta_0(r_3) \bar{g}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \quad (4.6)$$

This is in many respects a remarkable relation. Because its validity depends upon the validity of eq 3.10 which we have used in its derivation, we will refer to it as the “constraint-free condition”; i.e., it applies to a system of spheres in which averages are freely taken, restricted only by the requirement that spheres do not overlap. We analyze some of its properties in the next section.

5. Constraint-Free Condition

Referring to eq 4.6, the first thing to note is that, although it specifies a function $g(r_2)$ where r_2 may be much larger than σ (\mathbf{r}_2 may even $\rightarrow \infty$), the integral that determines this function is limited to values of r_2 that are *smaller* than σ . Suppose we let $\mathbf{r}_2 \rightarrow \infty$. Then, both $g(r_2)$ and $\bar{g}(\mathbf{r}_2, \mathbf{r}_3)$ will become unity (no correlation at infinite separation) and eq 4.6 will read

$$P_0(\sigma) = 1 - \int_{\sigma}^{\infty} \beta_0(r_3) d\mathbf{r}_3 = 1 - \int_0^{\sigma} 4\pi r_3^2 \beta_0(r_3) dr_3$$

$$P_0(\sigma) = 1 - \int_0^{\sigma} \alpha_0(r_3) dr_3 \quad (5.1)$$

which, according to eq 3.4, is a correct result.

Now, let us try something else. Assume that $P_0(\sigma) = 0$. This implies that the insertion probability is zero and that the chemical potential (see eq 3.2) is infinite. But if $P_0(\sigma) = 0$, eq 3.5 requires $\beta_0(\sigma) = 0$ so that the upper limit in the integral of eq 4.6 may be set to infinity without incurring any error. Then, in this case, eq 4.6 becomes

$$\int_{\sigma}^{\infty} \beta_0(r_3) \bar{g}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 = 1 \quad (5.2)$$

At this same time, eq 3.6 may be expressed as

$$\int_{\sigma}^{\infty} \beta_0(r_3) d\mathbf{r}_3 = 1 \quad (5.3)$$

In eq 5.2, \mathbf{r}_2 can be varied arbitrarily, and it would require a mathematical miracle for $\bar{g}(\mathbf{r}_2, \mathbf{r}_3)$ to compensate in just the right way, at any value of \mathbf{r}_2 , so that the relation would continue to hold and accomplish the same end as eq 5.3 in spite of the appearance of the additional factor $\bar{g}(\mathbf{r}_2, \mathbf{r}_3)$ in the integrand.

If eq 5.2 is invalid, we must look for the invalid step that led to it. The only assumption was that $P_0(\sigma)$ could vanish. That was responsible for the disappearance of the left side of eq 4.6 and the appearance of eq 5.2. Thus, at first, it is implied that for unconstrained equilibrium, i.e., under full thermodynamic equilibrium, the insertion probability for the hard sphere system cannot vanish at any density, and therefore, the chemical potential cannot be infinite.

On the other hand, at closepacking, even though $P_0(\sigma)$ may vanish, $g(r_2)$ will exhibit infinities corresponding to spheres in contact. Thus, the left side of eq 4.6 may remain finite and the unlikely result, eq 5.2, would not be generated.

At first sight, this result may seem to belabor the obvious since one's intuition, alone, might suggest that $P_0(\sigma)$ and the chemical potential should not vanish or be infinite, respectively, for densities smaller than that of closepacking. Furthermore, there is an abundance of evidence, both theoretical and experimental (simulation), that this is the case.^{20,10}

On the other hand, it is possible to generate innumerable configurations, at densities far below that of closepacking, for which $P_0(\sigma)$ vanishes. In view of the above result, we have shown that none of these can correspond to a state of unconstrained equilibrium!

As an important corollary, eq 4.6 is valid for the constraint-free, fully equilibrated, hard sphere system!

Returning to the consideration of states that do not correspond to constraint-free equilibrium, we emphasize that such states need not be confined to any particular metastable fluid condition of the system or, for that matter, to a metastable crystalline condition. For example, the microscopic constraint might correspond to the analytic continuation of the stable fluid branch of the pressure–density isotherm. Perhaps a better (although less convenient) choice can be based on the following.

Denote the density at which the hard-sphere fluid begins to freeze by ρ_f . In the constraint-free system, as ρ begins to exceed ρ_f , those configurations that correspond to a solid with long-range order begin to become relatively abundant because of the limited packing options available to disordered fluid configurations. As ρ increases, the ordered configurations become overwhelmingly abundant in comparison to the fluid configurations. Therefore, to maintain the fluid branch of the phase diagram, it is necessary to apply an extremely severe configurational constraint in order to disallow the majority of configurations that the hard-sphere system would like to adopt. The most benign constraint that achieves this situation would be the one that allows all configurations except those corresponding to long-range order, i.e., crystalline configurations, and therefore, it might be possible to define the metastable state as that in which the system achieves equilibrium subject *only to this constraint* in addition to the proscription against the overlap of spheres.

Generally, a metastable state corresponds to a local minimum of free energy in a coarse grained region of the system's phase space. Then, allowing the system infinite time to achieve equilibrium, the free-energy barrier between the local minimum and the global one (stable equilibrium) must be augmented so as to completely exclude the possibility of transition to the global minimum. The constraint may therefore be viewed as an additional intermolecular potential or an additional potential of mean force. The additional potential need not be pairwise additive.

The choice of the analytic continuation of the stable fluid isotherm as representative of the metastable fluid can only be given a molecular interpretation in terms of a given molecular theory for the stable fluid. Usually, however, the metastable fluid is defined in terms of some “experimental” continuation of the stable branch of the isotherm. In the case of hard spheres, such a continuation generally means the extension of a computer simulation into the metastable regime. It has been suggested that the terminus of such an extension is the state of “random closepacking”.²¹

We have discussed several prescriptions for the metastable fluid, and it should be clear that there are many others. We

will argue that eq 4.6 need not apply to a metastable fluid so that there may be prescriptions under which $P_0(\sigma) = 0$ even though the system is not closepacked. That $P_0(\sigma)$ can vanish in the absence of closepacking is easily proved by simply demonstrating a nonclosepacked configuration for which this occurs. Many such configurations can be demonstrated so that it is not even necessary to present detailed proof that eq 4.6 need not apply to a metastable system. However, there is another issue, dealing with the applicability of eq 3.10 to a metastable system, that is somewhat controversial and needs to be resolved. We address this issue in section 7. The nonapplicability of eq 3.10 is equivalent to the nonnecessity of eq 4.6, since the former is used in the proof of the latter.

In closing this section, it is worth reiterating that although simulative extensions of the stable fluid isotherm for a hard-sphere system suggest that $P_0(\sigma)$ does not vanish until the random closepacking density is achieved, this represents only one (poorly defined) of many possible metastable configurations. Indeed, such an "experimental" isotherm may be dominated by kinetics and unavoidable long computational relaxation times, so the constraints to which it corresponds may never be discovered. For this reason, among others, in this paper we make no special appeal to this prescription of the metastable fluid.

6. Test of the OZ Equations Using the Hard-Rod System

Since relations such as eqs 4.1, 4.2, and 4.6 will be used in studying the applicability of eq 3.10 to a metastable fluid, it is useful to gain further assurance concerning their validities by referring them to a system in which all of the involved functions are known exactly. Such a system is the one-dimensional system of hard rods. However, before proceeding to a test of the relations in this way, it should be emphasized that the test is really unnecessary since the original derivations of those relations are presumed to be free of error. Nevertheless, there is no harm in acquiring additional confidence by means of the proposed test.

We consider a one-dimensional system of N hard rods, each of length σ , in a container of length L . As indicated in section 2, we denote the coordinate of position by x and the pair correlation function between rods by $g(x)$. It is convenient to define the "pair correlation function to the right" by $g_+(x)$ such that

$$\begin{aligned} g_+(x) &= g(x), & x > 0 \\ g_+(x) &= 0, & x < 0 \end{aligned} \quad (6.1)$$

Similarly, the correlation function to the left is denoted by

$$\begin{aligned} g_-(x) &= g(x), & x < 0 \\ g_-(x) &= 0, & x > 0 \end{aligned} \quad (6.2)$$

Clearly, we can write

$$g(x) = g_+(x) + g_-(x) \quad (6.3)$$

Furthermore, because of the symmetry of $g(x)$, we have

$$g_-(x) = g_+(-x) \quad (6.4)$$

As indicated in section 3, in the hard-rod system, $\beta_0(x)$ and $\beta(x)$ are identical with $\alpha_0(x)$ and $\alpha(x)$, respectively, and we also define $\alpha_{0+}(x) = \beta_{0+}(x)$ and $\alpha_+(x) = \beta_+(x)$ by $\alpha_+(x) = \alpha(x)$, $x > 0$, and $\alpha_+(x) = 0$, $x < 0$, similar to $g_+(x)$. The same is true

of $\alpha_{0+}(x)$ and for both $\alpha_-(x)$ and $\alpha_{0-}(x)$, where the definitions are reversed. The equivalent of eq 4.1 becomes

$$\rho g_+(x_2) = \alpha_+(x_2) + \rho \int_0^{x_2} \alpha_+(x_3) g_+(x_2 - x_3) dx_3 \quad (6.5)$$

for which the rationale is the same as for eq 4.1 and where $\rho = N/L$, where L is the length of the system. $\rho g_+(x_2)$ is the density of hard-rod centers at x_2 . The first term on the right is the density contributed by the nearest neighbor if the rod center in dx_2 happens to be that of the nearest neighbor. The integrand, $\rho \alpha_+(x_3) g_+(x_2 - x_3)$ is the density of rod centers at x_3 if the center at x_2 is not that of the nearest neighbor. Thus, $\alpha_+(x_3) dx_3$ represents the probability that the nearest neighbor is in dx_3 , while $\rho g_+(x_2 - x_3)$ is the conditional density at x_2 , given that there is a center at x_3 . We do, however, note the following important difference. Although three centers are involved, i.e., the one at the origin and those at x_3 and x_2 , respectively, we need not involve triplet correlation functions since, in the hard-rod system, the chance that there is a center at x_2 is not influenced by the center at the origin when it is known to be present.

The upper limit on the integral in eq 6.5 is x_2 because if x_3 exceeds x_2 , the center at x_3 will no longer be the nearest neighbor to the one at the origin. However, because of eq 6.1, we might just as well set the limit at ∞ , since $g_+(x_2 - x_3) = 0$ when $x_3 > x_2$ so that $x_2 - x_3 < 0$. Thus, we can write

$$\rho g_+(x_2) = \alpha_+(x_2) + \rho \int_0^\infty \alpha_+(x_3) g_+(x_2 - x_3) dx_3 \quad (6.6)$$

The equivalent of eq 4.2 becomes

$$\rho = \alpha_{0+}(x_2) + \rho \int_0^\infty \alpha_{0+}(x_3) g_+(x_2 - x_3) dx_3 \quad (6.7)$$

where, for the same reason as in eq 6.6, we have been able to replace x_2 , in the upper limit, by ∞ and where we have used the analogue of eq 4.3.

Now, in Appendix A, we show that, for the constraint-free system,

$$\begin{aligned} \alpha_{0+}(x) &= \beta_{0+}(x) = \rho, & 0 < x \leq \sigma \\ \alpha_{0+}(x) &= \rho \exp\left[-\frac{\rho(x - \sigma)}{1 - \rho\sigma}\right], & x > \sigma \end{aligned} \quad (6.8)$$

and that

$$\begin{aligned} \alpha_+(x) &= 0, & x \leq \sigma \\ \alpha_{0+}(x) &= \frac{\rho}{1 - \rho\sigma} e^{-[\rho(x - \sigma)/(1 - \rho\sigma)]}, & x > \sigma \end{aligned} \quad (6.9)$$

Some other important results are known. These are, again for the constraint-free system,²²

$$\begin{aligned} G_0(x) &= \frac{1}{1 - \rho\sigma}, & x \leq \sigma \\ G_0(x) &= \frac{1}{1 - \rho\sigma}, & x > \sigma \end{aligned} \quad (6.10)$$

and

$$\begin{aligned} G(x) &= 0, & x \leq \sigma \\ G(x) &= \frac{1}{1 - \rho\sigma}, & x > \sigma \end{aligned} \quad (6.11)$$

and finally, still for the unconstrained system,²³

$$g_+(x) = -\sum_{n=1}^{\infty} H(x - n\sigma) \frac{[\omega(x - n\sigma)]^{n-1}}{(n-1)!} e^{-\omega(x-n\sigma)} \quad (6.12)$$

where $H(x - n\sigma)$ is the unit step function ($H = 0, x < n\sigma$; $H = 1, x > n\sigma$) and where

$$\omega = \frac{\rho}{1 - \rho\sigma} \quad (6.13)$$

The one-dimensional version of eq 4.6, based on the same reasoning that led to that equation, is

$$P_{0+}(\sigma)g_+(x_2) = 1 - \int_0^\sigma \alpha_{0+}(x_3)g_+(x_2 - x_3) dx_3 \quad (6.14)$$

where, for the constraint-free case,

$$P_{0+}(x) = \exp\{-\rho \int_0^x G_{0+}(x) dx\} = 1 - \rho x, \quad x \leq \sigma$$

$$P_{0+}(x) = (1 - \rho\sigma) \exp\left\{-\frac{\rho(x - \sigma)}{1 - \rho\sigma}\right\}, \quad x > \sigma \quad (6.15)$$

and where we have used eq 6.10.

Now, for the hard rod system, the validity of eq 5.2 would consist of the vanishing of the right side of eq 6.14 at a density short of closepacking, i.e., for $\rho\sigma < 1$, and with the upper limit in the integral replaced by ∞ . This, in turn, would require $P_{0+}(\sigma)$ to vanish short of closepacking. But it is clear from eq 6.15 that $P_{0+}(\sigma) = 1 - \rho\sigma$ and therefore cannot vanish for $\rho\sigma < 1$. Thus, at least for the hard rod system, we have proved that eq 5.2 cannot be valid when the system is in unconstrained equilibrium.

Next we demonstrate the simultaneous validities of eqs 6.6 and 6.7 by the direct substitution of eqs 6.9 and 6.13 into eq 6.6 and the direct substitution of eqs 6.8 and 6.13 into eq 6.7. Working through the algebra demonstrates that the equations are simultaneously satisfied by these substitutions. Although we expected this result on the basis of the arguments on which their derivations are based, it is reassuring to see them confirmed starting from another point of departure.

7. Nonequality of G and G_0 in a Structurally Constrained System

The structure of a hard sphere system is in part defined by its pair correlation function $g(r)$. The introduction of a severe structural constraint is therefore likely to generate an altered function $g'(r)$. A constraint severe enough to exclude the dominant configurations of a system is surely expected to perturb $g(r)$, and this would include a constraint necessary to maintain the hard-sphere system in a metastable fluid state by the exclusion of crystalline configurations. Certainly, fluid and crystalline correlation functions will differ.

As indicated earlier, a configurational constraint is equivalent to the introduction of an additional intermolecular potential that may or may not be pairwise additive. Indeed, an alteration of $g(r)$ corresponds, by definition, to the appearance of an additional potential of mean force. This additional inter-

molecular potential (additional to the hard sphere potential) provides a means of communication between spheres, beyond that implicit in the hard-sphere potential itself so that the applicability of eq 3.10, in a structurally constrained system, must be reexamined. For example, we explained eq 3.10 as a consequence of the fact that a hard sphere “buried” in a cavity could not influence other hard spheres at the cavity’s periphery because the hard sphere potential had no long-range component. However, the additional potential corresponding to the constraint could supply a longer range component such that spheres outside of the cavity could sense the one in it and thereby vitiate eq 3.10.

The proof of eq 4.6, the constraint-free condition, rested on the assumption that spheres could not sense another sphere buried in a cavity and concomitantly on the validity of eq 3.10. The fact that it is easy to construct nonclosepacked constrained configurations for which $P_0(\sigma)$ vanishes indicates that eq 4.6 is invalid for these structures and therefore that eq 3.10 does not apply. Thus, we know that there are at least *some* constrained configurations for which eq 3.10 does not hold. The bigger question is, does eq 3.10 fail for *all* states of the system subject to a configurational constraint? In posing this question, notice that we are not simply asking whether eq 3.10 fails for metastable phases. For example, since a one-dimensional hard-rod system has no phase transition, the state it achieves, when subject to a configurational constraint, does not correspond to a metastable phase in the conventional sense, but we can still ask whether eq 3.10 applies in the presence of the constraint.

The question is not trivial. On the basis of the analysis presented in ref 14, Speedy argues that eq 3.10 applies to metastable as well as stable phases. Although his analysis is in essence more detailed, it depends on the argument that the removal of a hard sphere from a configuration can produce a cavity without eliminating any of the configurations of the remaining spheres that were present before the removal of the sphere whose absence is responsible for the cavity. Although this argument is compelling, one could also argue that the configurational constraint was such that it did not allow a sphere to be removed (while it was maintained) without some reconfiguration of the remaining spheres. This is just what would be required if the constraint was equivalent to an additional intermolecular potential. Thus, there is some disagreement over whether eq 3.10 can be applied to a system subject to a configurational constraint.

Without claiming to fully resolve this disagreement, we offer, in the present section, evidence that eq 3.10 fails in the presence of a configurational constraint severe enough to alter $g(r)$. Our proof makes use of eqs 4.1 and 4.2. Actually, our analysis will involve the hard rod system, and so we look for alterations in $g_+(x)$. Because the proof is only given for a one-dimensional system, we will not be able to claim with certainty that eq 3.10 fails for higher dimensional systems. Furthermore, we cannot say anything about metastable *phases* since there is no phase transition in the hard rod system. On the other hand, we do not believe (although we cannot yet prove it) that the issue of the validity of eq 3.10 is connected to the existence or nonexistence of a phase transition but only to the effects of a configurational constraint.

What we shall be able to show is that for a *hard rod* system, subject to a constraint severe enough to alter $g_+(x)$, eq 3.10 must fail. This means that, in this particular situation, Speedy’s argument must fail. Whether it fails in general remains to be proved.

Our proof proceeds as follows: eq 2.6 written for G_{0+} and its analogue for G_+ show that G_{0+} and G_+ are entirely

determined by α_{0+} and α_+ . Furthermore, $\alpha_+(x_2)$ and $\alpha_{0+}(x_2)$ can be obtained by Laplace transforming eqs 6.6 and 6.7, respectively. The results are

$$\hat{\alpha}_+ = \frac{\rho \hat{g}_+}{1 + \rho \hat{g}_+} \quad (7.1)$$

and

$$\hat{\alpha}_{0+} = \frac{\rho}{s(1 + \rho \hat{g}_+)} \quad (7.2)$$

where s is the transform parameter and the accent signifies the Laplace transform. In arriving at these results, the convolution theorem has been used. Now we already know that the constraint-free α_{0+} , α_+ , and g_+ satisfy both eqs 6.6 and 6.7. Hence, the constraint-free transforms derived from these functions satisfy eqs 7.1 and 7.2. The proof of the above was obtained by direct substitution.

The application of the structural constraint will, by definition, manifest itself in the appearance of an altered correlation function $g'_+(x)$ as well as altered nearest-neighbor distributions $\alpha'_{0+}(x)$ and $\alpha'_+(x)$. These functions will satisfy the analogues of eqs 7.1 and 7.2; namely,

$$\hat{\alpha}'_+ = \frac{\rho \hat{g}'_+}{1 + \rho \hat{g}'_+} \quad (7.3)$$

$$\hat{\alpha}'_{0+} = \frac{\rho}{s(1 + \rho \hat{g}'_+)} \quad (7.4)$$

We can show the following. If eq 3.10 is still applicable in the presence of a structural constraint, then the \hat{g}'_+ that solves eqs 7.3 and 7.4 is identical with the constraint-free \hat{g}_+ that solves eqs 7.1 and 7.2, even when $\alpha'_{0+}(x)$ and $\alpha'_+(x)$, the structurally altered nearest-neighbor distributions, remain in the equations; i.e., the result $g'_+(x) = g_+(x)$ is generated, contradicting the fact that we began the analysis with the assumption that the correlation function was altered by the constraint. The origin of this contradiction must be the assumption that the "buried" rod at $x = 0$ in eq 6.6 cannot be sensed by the rod at x_2 and that, concomitantly, eq 3.10 remains valid even in the presence of the constraint, since this was the *only* assumption made. We are thus forced to conclude that eq 3.10 fails in the presence of the structural constraint.

The details of the mathematical analysis leading to this conclusion can be found in Appendix B, where it is also shown why the same proof cannot be given for higher dimensional systems.

Nevertheless, by using the idea that a configurational constraint is equivalent to an intermolecular potential of considerable range, we think that it is highly plausible that eq 3.10 will fail in a constrained hard-particle system of any dimensionality. Equation 3.10 then becomes a rather unique relation, especially in multidimensional systems where phase transitions are possible. In those cases, it represents a condition that holds on a stable isotherm but fails to hold on a metastable one.

In closing this section, it is worth noting that Rintoul et al.²⁴ have shown that eq 3.10 is invalid in a wholly nonequilibrium system such as that produced by random sequential adsorption (RSA). They speculate that it is not valid in general for nonequilibrium systems.

8. Speculation on the Mechanistic Features on the Hard-Sphere and Hard-Disk Phase Transitions

The Helmholtz free energies F of hard-sphere and hard-disk systems may be expressed as²⁵

$$F = NkT \left\{ \ln \frac{\Lambda^D}{n_c v} - 1 - \frac{\sigma s}{2Dv} \right\} \quad (8.1)$$

where D is the dimensionality of the system, n_c is the ratio of the number of "cavities" to the number of particles, v is the average "volume" of a cavity, and s is its average "surface area". The precise definition of a cavity may be found in refs 26 and 27. In terms of the above variables, the insertion probability is given by

$$P_0(\sigma) = \frac{N n_c v}{V} \quad (8.2)$$

Now, in the case of hard spheres, for example, s/v varies, approximately, as $v^{-1/3}$ at densities near closepacking,²⁸ while $-(\ln v)$, arising from the first term in curly brackets in eq 8.1, cannot by itself overcome the $v^{-1/3}$ in the last term so as to ensure that $F \rightarrow +\infty$ at closepacking. This task must then be left to n_c , which must then decrease exponentially in order for F to avoid becoming $-\infty$ at closepacking. Indeed, it can be shown almost exactly (see section 7 of ref 28) that the asymptotic behavior of F near the closepacking density is dominated by the $\ln n_c v$ term in eq 8.1. From various approximate theories as well as from simulation,²⁹ it appears as though the same is true near the freezing density ρ_f . We assume that the same is true at densities in the range extending from just below ρ_f to closepacking. In this range, we therefore concentrate on the logarithmic term in eq 8.1 and write

$$F \cong NkT \ln \left(\frac{\Lambda^D}{VP_0(\sigma)} \right) \quad (8.3)$$

This equation shows that, to maintain the Helmholtz free energy as small as possible, $P_0(\sigma)$ should be as large as possible and that, in the absence of a structural constraint, the equilibrium configuration of the system will be that for which this is achieved, subject only to the requirement that spheres do not overlap. However, attention should be drawn to one qualification. This concerns the fact that $P_0(\sigma)$ is a quantity obtained by averaging the available space over *all* configurations of the hard particles. There are configurations having very large values of available space—which are, at the same time, very rare so that there is more to the problem than a simple maximization of available space. We discuss this point, further, below.

In order to speculate on the mechanistic features of the hard-sphere phase transition, we start by assuming that a fluid–solid phase transition *does* exist. Before proceeding, we note that statistical geometric methods^{25,30} have allowed some exact statements concerning the structure of the hard-sphere phase transition. For example, it can be shown that $n_c v$ has the same value in the coexisting liquid and solid phases, while $n_c s$ is less in the coexisting solid phase than in the fluid.³⁰ This implies that s/v decreases on going from the coexisting fluid to the solid and suggests that the cavities in the solid are more spherical. Furthermore, it has been shown *exactly*³⁰ that the density at which $n_c s$ has a maximum cannot lie in the coexistence region. In contrast to these *exact* results, our present discussion, although motivated by statistical geometric considerations, is presented as an exercise in physical intuition, aimed at illuminating the geometric features of the transition mechanism. Nevertheless,

based on these features, we shall be able to make an interesting estimate of the freezing densities for both spheres and disks.

We introduce the following fluid model. We assume that near the freezing density, the fraction of the total volume not covered by spheres or disks, i.e., $1 - y$ where y is the packing fraction, will be partitioned into small recognizable “interstices” bounded by sphere surfaces or disk edges. An interstice may be defined as a “cage” produced by particles, such that if a sphere or disk were placed in it, that particle could not escape unless one or several of the caging particles were moved. It is clear that “cavities”, as they are defined^{26,27} in statistical geometric developments, are contained within interstices. A cavity is a portion of the “available space”¹⁰ in the system. A point in the available space cannot be closer than σ to the center of a hard sphere or disk. The cavity is therefore *smaller* than the interstice.

It is appropriate to present our approach in a more organized and detailed manner. We begin by indicating that our analysis will be based on several principles, some of which are exact:

1. We **assume** at the outset that a fluid–solid transition (freezing transition) **does** occur.

2. In accordance with the discussion surrounding eq 8.3, we require the system to configure itself so that, at any density, $P_0(\sigma)$ is as large as possible.

3. The system should be as uniform as possible. It is true that certain nonuniform configurations can be found such that $P_0(\sigma)$ is very large. For example, all the spheres or disks could be closepacked into one “corner” of the total volume V . This would leave an enormous unoccupied volume and correspond to an exceedingly large insertion probability. However, it must be remembered that $P_0(\sigma)$ is an average quantity; i.e., it is averaged over all configurations of the spheres or disks except those that involve overlap. The nonuniform configurations are so few in number that they carry very little weight in the average and can be disregarded. The exception occurs at densities corresponding to the coexistence regime of the phase transition. There the system is clearly nonuniform (because any uniform distribution at those densities could require $P_0(\sigma)$ to vanish), but the **individual coexisting phases** will be uniform. The requirement for uniformity should operate, to a degree, on the microscopic as well as the macroscopic level, i.e., very “structured”, even if still fluid phases would be of low probability and bring little weight to the average. However, on the microscopic level, the importance of such locally nonuniform phases depends on the balance between the insertion probability that they correspond to and the number of configurations that they represent.

4. We assume that, in the fluid, at a density near the freezing transition, $P_0(\sigma)$ is always very small. This assumption is supported by computations based on various approximate analytical theories and by simulation studies. For example, in the case of hard disks, simulation²² indicates that $P_0(\sigma) \approx 10^{-6}$ at the freezing transition. Furthermore, almost any reasonable model of the fluid shows (on the basis of continuity within the model) that, when $P_0(\sigma)$ is very small, it quickly becomes zero with only a very slight increase of density.

5. The analysis of section 5 has shown that $P_0(\sigma)$ cannot vanish on the stable isotherm. We assume, therefore, that in the absence of some additional constraint that prevents $P_0(\sigma)$ from vanishing (i.e., in the absence of a constraint that maintains a metastable state), the fluid, when $P_0(\sigma)$ becomes very small, avoids this catastrophe by undergoing a phase transition and escaping to the crystalline state. As indicated above, this allows the insertion probability to remain nonzero through the introduction of the nonuniformity implicit in the coexistence of the two

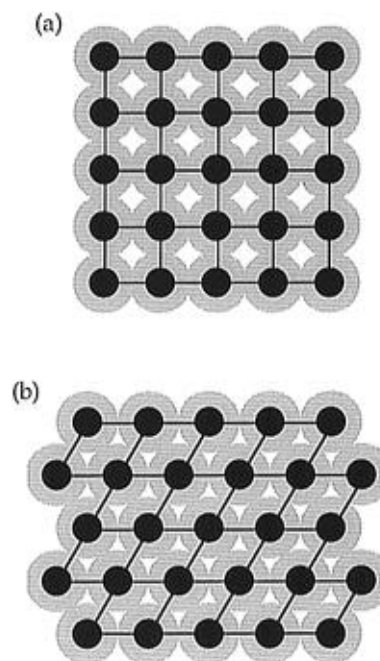


Figure 2. Loose square (upper) lattice, loose hexagonal (lower) lattice, showing interstices (shaded) and cavities (clear).

phases. In accordance with the discussion in item 4, we can use the density at which $P_0(\sigma)$ vanishes (within the model) as a marker, i.e., as a close upper limit for the density at which the insertion probability becomes small. The assumption that the insertion probability is small in the coexisting solid at the phase transition can account for the observation that $P_0(\sigma)$ is small, in the coexisting fluid, since it has been proved, **exactly**,^{25,30} that the fluid phase must have a nonzero insertion probability equal to that in the coexisting solid multiplied by the ratio of the density of the liquid to that of the solid.

In the interest of expositional simplicity, we begin our analysis (based on the above five principles) with hard disks. We build on an idea that the fluid, very near the freezing density, may be regarded as a locally distorted, simple crystalline lattice, such that the local distortions destroy any long-range order. The interstices mentioned earlier are then, in fact, the interstices in this quasilattice. For hard disks, the simplest structures that we can consider are those in which the disks are located at the sites of simple square and hexagonal lattices. The packing fraction y , i.e., the fraction of the total area of the system covered by the disks, is given by

$$y = \pi\sigma^2\rho/4 \quad (8.4)$$

For the simple square and hexagonal lattices y_{cp} , the values of y at closepacking are $\pi/4$ and $\pi/2\sqrt{3}$, respectively. However, we are not interested in the densest arrangements but are interested in those that contain cavities and possess the maximum $P_0(\sigma)$. In order to create these cavities, we can either expand the lattices considerably so that cavities appear or expand them only slightly, while removing disks so that cavities appear at the positions of the vacancies that are consequently formed. In the first case, we get loose simple square and hexagonal lattices with w , the number of cavities per disk, equal to 2 and 1, respectively (see Figure 2). In the second case, we get “hollowed” square and hexagonal lattice (Figure 3) with w equal to $1/3$ and $1/2$, respectively. The hollowed hexagonal structure is a “honeycomb” lattice. In order to determine which of these four structures has the largest $P_0(\sigma)$, we can regard the cell volume as composed of three domains, namely, filled space

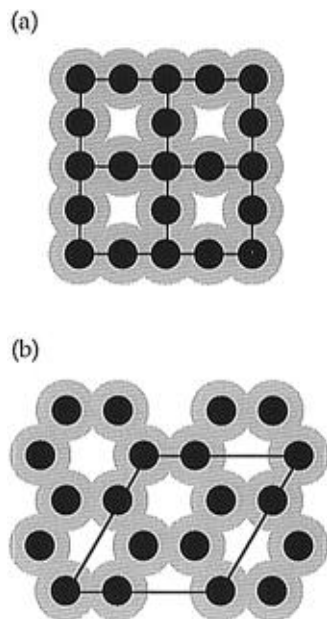


Figure 3. Hollowed square (upper) lattice, hollowed hexagonal (lower) lattice, showing interstices (shaded) and cavities (clear).

TABLE 1: Dependence of the Insertion Probability $P_0(\sigma)$ on Packing Fraction y for the Simple and Hollowed Square Lattices

$32y/\pi$	$P_0(\sigma)$	
	simple sq. lattice	hollowed sq. lattice
3	0.038 02	0.107 30
3.5	0.008 55	0.063 82
4	0	0.036 79

(covered by a portion of a disk), interstitial space (outside of both the filled space and cavity space), and cavity space. These domains are indicated by solid, shaded, and unshaded regions in Figures 2 and 3. Denoting the cavity space by v_c , the filled space by v_f , and the interstitial space by v_i , we can write

$$P_0(\sigma) = \frac{v_c}{v} = \frac{v - v_f - v_i}{v} = 1 - y - \frac{v_i}{v} \quad (8.5)$$

where v is the cell volume.

Now, for a given packing fraction y , it is clear, from eq 8.5, that the structures with maximum $P_0(\sigma)$ are those with minimum v_i , i.e., with minimum shaded area or, in other words, those in which there is overlapping of the shaded areas of neighboring disks. It can be shown that this situation corresponds to the hollowed structures. For example, in the simple square lattice with lattice parameter a such that $\sqrt{2}\sigma \leq a \leq 2\sigma$, we have

$$P_0(\sigma) = 1 - \sqrt{\frac{16y}{\pi} - 1} - \frac{8y}{\pi} \left(\arcsin \sqrt{\frac{\pi}{16y}} - \arcsin \sqrt{1 - \frac{\pi}{16y}} \right) \quad (8.6)$$

while the hollowed square structure, with $\sigma \leq a \leq \sqrt{2}\sigma$,

$$P_0(\sigma) = \frac{1}{2} - \frac{4y}{3} + \frac{16y}{3\pi} \arcsin \sqrt{\frac{\pi}{16y}} - \arcsin \sqrt{1 - \frac{\pi}{16y}} - \frac{1}{2} \sqrt{\frac{32y}{3\pi} - 1} \quad (8.7)$$

and Table 1 clearly shows that, for any given value of y , $P_0(\sigma)$ is larger for the hollowed structure than for the simple one. The same conclusion applies to the hexagonal case, and in ac-

cordance with the principle enunciated in item 2 above, this requires the system to select the hollowed structures.

In the hollowed square structure, $P_0(\sigma)$ vanishes when $y = y_f = 6\pi/32 = 0.589$, while in the honeycomb structure it vanishes when $y = \pi/3\sqrt{3} = 0.605$. These two values are essentially the same from the point of view of an estimate of the freezing density, but again, the principle in item 2 requires us to select the hexagonal structure. At this point, it is necessary to reemphasize that we are not really dealing with a crystal but rather with a fluid represented by a locally distorted crystal. Thus, slight distortions of some quasihexagonal "vacancies" will allow some other distorted vacancies to contain cavities even at $y = y_f = 0.605$. Thus, $P_0(\sigma)$ cannot be expected to vanish at a value of y precisely equal 0.605 but instead at some higher density. Computer simulation^{29,31,32} indicates the freezing transition to occur at

$$y \cong 0.69 \quad (8.8)$$

Thus, the prediction of a freezing density

$$y_f \geq 0.605 \quad (8.9)$$

is in reasonable agreement with that predicted by simulation.

The above degree of correspondence between the estimated and simulated results was obtained through the application of the principles embodied in items 1–5 above. For example, a larger value of $P_0(\sigma)$, at a given y , could be obtained by considering a compact, simple square lattice (i.e., with $a = \sigma$) and removing alternating lattice lines parallel to one of the two crystal axes. But this arrangement would be very nonuniform, since it alternates closepacked and void lines and in accordance with item 3 would be poorly weighted in the average configuration. Even more important, such an arrangement would not allow $P_0(\sigma)$ to vanish (even when it was closepacked) so that no phase transition could be anticipated, contrary to our assumption in item 1. Similar arguments rule out distributions with both closepacked and void domains as well as structures where bases do not allow the insertion probability to vanish. Furthermore, although we can think of other structures obtained from simple square and hexagonal lattices, obtained by introducing vacancies having more complicated patterns it seems unreasonable that the cavities in a fluid would exhibit that degree of cooperation necessary to match such complicated pictures. Thus, we are left with the simplest, uniform, hollowed structures considered above.

Next, we turn to the consideration of the hard sphere system, using, as much as possible, the same approach as in the case of disks. The simplest hollowed structure, having a high degree of overlap of shaded interstitial volumes, can be obtained by stacking honeycomb lattice planes in place of hexagonal lattice planes that would produce a cubic closepacked (ccp) three-dimensional lattice. In other words, we produce the simple hollowed three-dimensional lattice by creating vacancies in a three-dimensional ccp lattice in a manner similar to the production of the two-dimensional hollowed lattice by creating vacancies in the planar hexagonal lattice (see Figure 4). For this three-dimensional lattice, $P_0(\sigma)$ will vanish when the honeycomb structures become closepacked. For hard spheres, the packing fraction is given by

$$y = \pi\sigma^3\rho/6 \quad (8.10)$$

and the three-dimensional closepacking density in question can be shown to correspond to

$$y = \sqrt{2}\pi/9 = 0.494 \quad (8.11)$$

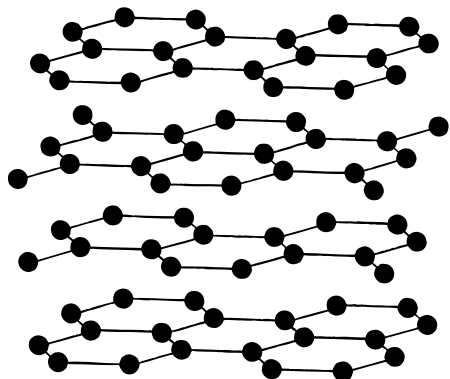


Figure 4. Hollwed three-dimensional lattice created by introducing vacancies into the cubic closepacked lattice.

The freezing density obtained by means of computer simulation^{31,32} corresponds to

$$y_f = 0.492 \quad (8.12)$$

These estimates of the freezing densities were obtained using an extremely simple method and lend support to the mechanistic picture expressed by that method. The mechanistic picture of the phase transition, rather than the successful numerical prediction, should be regarded as the most important result of the above analysis.

We note that our estimate of ρ_f differs in a somewhat fundamental way from previous estimates, based on the comparisons of the pressures and chemical potentials for model fluid and solid phases, i.e., determining the density at which the p 's and μ 's are, respectively, equal. This method is also involved implicitly in density functional approaches^{33,34} where static density modes for the solid have to be selected and where direct correlation functions need to be computed from some model theory (e.g., the Percus–Yevick theory) of the fluid. In the present method, the particular properties of the solid are never specified.

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Appendix A

In this appendix, we derive the hard-rod nearest-neighbor distributions $\alpha_{0+}(x)$ and $\alpha_+(x)$ for the *constraint-free* fully equilibrated system.

We begin with $\alpha_{0+}(x)$ which, according to the one-dimensional version of eq 3.5, is given by

$$\alpha_{0+}(x) = \rho G_{0+}(x) P_{0+}(x) \quad (A1)$$

while $P_{0+}(x)$ is given by the one-dimensional version of eq 3.4, namely,

$$P_{0+}(x) = \exp\{-\rho \int_0^x G_{0+}(x') dx'\} \quad (A2)$$

Substitution of eq A2 into eq (A1) gives

$$\alpha_{0+}(x) = \rho G_{0+}(x) \exp\{-\rho \int_0^x G_{0+}(x') dx'\} \quad (A3)$$

Now it is well-known that, for the fully equilibrated constraint-free system, $G_{0+}(x)$ is given by eq 6.10 which, for convenience,

we repeat here as

$$G_{0+}(x) = \frac{1}{1 - \rho x}, \quad x \leq \sigma$$

$$G_{0+}(x) = \frac{1}{1 - \rho \sigma}, \quad x > \sigma \quad (A4)$$

Substitution of eq A4 into eq A3 then yields

$$\alpha_{0+}(x) = \rho, \quad x \leq \sigma$$

$$\alpha_{0+}(x) = \rho \exp\left\{-\frac{\rho(x - \sigma)}{1 - \rho \sigma}\right\}, \quad x > \sigma \quad (A5)$$

For the derivation of $\alpha_+(x)$, we replace eq A1 by

$$\alpha_+(x) = \rho G_+(x) P_+(x) \quad (A6)$$

with $P_+(x)$ given by

$$P_+(x) = \exp\{-\rho \int_0^x G_+(x') dx'\} \quad (A7)$$

Now, obviously,

$$G_+(x), \alpha_+(x) = 0, \quad x \leq \sigma \quad (A8)$$

and since eq 3.10 holds in the constraint-free system,

$$G_+(x) = G_{0+}(x) = \frac{1}{1 - \rho \sigma}, \quad x > \sigma \quad (A9)$$

Substitution of eqs A8 and A9 into eq A6 into which eq A7 has been substituted gives

$$\alpha_+(x) = 0, \quad x \leq \sigma$$

$$\alpha_+(x) = \frac{\rho}{1 - \rho \sigma} \exp\left\{-\frac{\rho(x - \sigma)}{1 - \rho \sigma}\right\}, \quad x > \sigma \quad (A10)$$

Appendix B

In this appendix, we prove that, in a hard rod system, a constraint severe enough to alter $g(x)$ invalidates eq 3.10.

The proof proceeds as follows. First, we show that $\alpha'_{0+}(x)$ is independent of the constraint in the interval $0 < x \leq \sigma$ as long as that constraint does not violate the hard rod nature of the particles, i.e., as long as hard rod overlap remains forbidden. The basis for this result is the fact that the center of only one hard rod can lie in the interval $0 < x \leq \sigma$. In that case, the chance that the center of at least one rod will be found between 0 and x is ρx , and the chance that there will not be at least one rod center between 0 and x , i.e., the chance that the interval is empty, must then be $1 - \rho x$. But the chance that the interval is empty is $P'_{0+}(x)$ so that

$$P'_{0+}(x) = 1 - \rho x, \quad 0 < x \leq \sigma \quad (B1)$$

independent of the presence of the constraint, i.e., $P'_{0+}(x) = P_{0+}(x)$ in the relevant interval.

The one-dimensional analogue of eq 3.4 is

$$P'_{0+}(x) = \exp\{-\rho \int_0^x G'_{0+}(x') dx'\} \quad (B2)$$

so that we obtain, by differentiation,

$$G'_{0+}(x) = -\frac{1}{\rho} \frac{\partial \ln P'_{0+}(x)}{\partial x} \quad (B3)$$

which shows that $G'_{0+}(x)$ is fully determined by $P'_{0+}(x)$. Then, since in the interval $0 < x \leq \sigma$, $P'_{0+}(x)$ is independent of the constraint, the same must be true of $G'_{0+}(x)$; i.e., $G'_{0+}(x) = G_{0+}(x)$ in the relevant interval. But $\alpha'_{0+}(x)$ is given by the one-dimensional analogue of eq 3.5; namely,

$$\alpha'_{0+}(x) = \rho P'_{0+}(x) G'_{0+}(x) = \rho P_{0+}(x) G_{0+}(x) = \alpha_{0+}(x), \quad 0 < x \leq \sigma \quad (\text{B4})$$

Next, if eq 3.10 applies in the presence of the constraint (note that at this point we make the assumption), then the one-dimensional analogue of eq 3.12, whose derivation depended on the assumption of the validity of eq 3.10, must also hold. This analogue is

$$\alpha'_{0+}(x) = P'_{0+}(\sigma) \alpha'_{+}(x) = P_{0+}(\sigma) \alpha'_{+}(x), \quad x > \sigma \quad (\text{B5})$$

where we have used the fact that $P_{0+}(\sigma)$, since it lies in the interval $0 < x \leq \sigma$, is independent of the constraint.

Now we can write

$$\begin{aligned} \hat{\alpha}'_{0+} &= \int_0^\sigma e^{-sx} \alpha'_{0+}(x) dx + \int_\sigma^\infty e^{-sx} \alpha'_{0+}(x) dx = \\ &= \int_0^\sigma e^{-sx} \alpha_{0+}(x) dx + P_{0+}(\sigma) \int_0^\infty e^{-sx} \alpha'_{+}(x) dx = \\ &= \alpha_{0+}^* + P_{0+}(\sigma) \hat{\alpha}'_{+} \quad (\text{B6}) \end{aligned}$$

where s again is the transform parameter and where the integral involving $\alpha'_{+}(x) = 0$, $x < \sigma$, and where

$$\alpha_{0+}^* = \int_0^\sigma e^{-sx} \alpha_{0+}(x) dx \quad (\text{B7})$$

In eq B6, we have used eqs B4 and B5.

Substitution of eq B6 into eqs 7.3 and 7.4, followed by the elimination of α'_{+} between the equations, yields the relation

$$\hat{g}'_{+} = \frac{1 - \frac{s}{\rho} \alpha_{0+}^*}{s[\alpha_{0+}^* + P_{0+}(\sigma)]} \quad (\text{B8})$$

Because of eq B4, α_{0+}^* is the same function when eq B6 is written for $\hat{\alpha}_{0+}$. Therefore, $\hat{\alpha}_{0+} = \alpha_{0+}^* + P_{0+}(\sigma) \hat{\alpha}_{+}$. Then, beginning with eqs 7.1 and 7.2 and eliminating $\hat{\alpha}_{+}$ between these equations, we find following a route similar to that which led to eq B8

$$\hat{g}_{+} = \frac{1 - \frac{s}{\rho} \alpha_{0+}^*}{s[\alpha_{0+}^* + P_{0+}(\sigma)]} \quad (\text{B9})$$

Comparison of the right-hand sides of eqs B8 and B9 then shows that

$$\hat{g}'_{+} = \hat{g}_{+} \quad (\text{B10})$$

Thus, we arrive at a contradiction which proves that, at least for the hard rod system, eq 3.10 must fail in the presence of a structural constraint capable of altering $g_{+}(x)$.

The same proof cannot be carried out for the hard-sphere (disk) system since \bar{g} in eqs 4.1 and 4.2 is not the same as g , and therefore, the analogues of eqs 7.1 and 7.2 are not available. However, a somewhat different but related proof might be possible. In any event, eq 3.10 is invalid for the structurally constrained hard-rod system, and we believe that it is also likely invalid for higher dimensional systems. Since a metastable phase must, as we have argued, be defined by a severe structural

constraint, this implies that eq 3.10, and therefore eq 4.6 that follows from it, need not hold in such a phase.

Appendix C

In this appendix, we discuss a physical interpretation of the direct correlation function (DCF). We have referred to eqs 4.1 and 4.2 as Ornstein–Zernike (OZ)-like equations. Indeed, the analogue of eq 4.1 for the one-dimensional hard rod system can actually be converted to the standard OZ form, and in that guise, it suggests a physical interpretation of the direct correlation function which may be more satisfactory than the conventional one. To motivate the analysis leading to these results, we define the total correlation functions $h_{+}(x)$ and $h_{-}(x)$ to the right and left, respectively. Thus, we write

$$h_{+}(x) = g_{+}(x) - 1$$

$$h_{-}(x) = g_{-}(x) - 1 \quad (\text{C1})$$

and from eqs 6.1 and 6.2, it follows that

$$h_{+}(x) = h(x), \quad x < 0$$

$$h_{+}(x) = -1, \quad x < 0 \quad (\text{C2})$$

$$h_{-}(x) = h(x), \quad x < 0$$

$$h_{-}(x) = -1, \quad x > 0 \quad (\text{C3})$$

and

$$h_{-}(x) = h_{+}(-x) \quad (\text{C4})$$

where

$$h(x) = g(x) - 1 \quad (\text{C5})$$

Note, however, that $h(x) \neq h_{+}(x) + h_{-}(x)$.

For the hard-rod system, eq 2.7 and the similar equation for $\alpha(x)$ indicate that $\beta_0(x)$ and $\beta(x)$ are identical with $\alpha_0(x)$ and $\alpha(x)$, respectively, and we also define $\alpha_{0+}(x) = \beta_{0+}(x)$ and $\alpha_{+}(x) = \alpha(x)$, $x > 0$, $\alpha_{+}(x) = 0$, $x < 0$, in a manner similar to that for $g_{+}(x)$. The same is true for both $\alpha_{-}(x)$ and $\alpha_0(x)$, where the definitions are reversed. Then, the density $\rho g_{+}(x_2)$ of hard rod centers at some point x_2 may be expressed as

$$\rho g_{+}(x_2) = \alpha_{+}(x_2) + \rho \int_0^{x_2} \alpha_{+}(x_3) g_{+}(x_2 - x_3) dx_3 \quad (\text{C6})$$

for which the rationale is the same as for eq 4.1 and where $\rho = N/L$, where L is the length of the system and $\rho g_{+}(x_2)$ is the density of hard-rod centers at x_2 . The first term on the right is the density contributed by the nearest neighbor if the rod center in dx_2 happens to be that of the nearest neighbor. The integrand, $\rho \alpha_{+}(x_3) g_{+}(x_2 - x_3)$ is the density of rod centers at x_3 if the center at x_2 is not that of the nearest neighbor. Thus, $\alpha_{+}(x_3) dx_3$ represents the probability that the nearest neighbor is in dx_3 , while $\rho g_{+}(x_2 - x_3)$ is the conditional density at x_2 given that there is a center at x_3 .

Although three centers are involved, i.e., the one at the origin and those at x_3 and x_2 , respectively, we need not involve triplet correlation functions since, in the constraint-free hard rod system, the chance that there is a center at x_2 is not influenced by the center at the origin when it is known to be present.

The upper limit on the integral in eq C6 is x_2 because if x_3 exceeds x_2 , the center at x_3 will no longer be the nearest neighbor to the one at the origin. However, because of eq 6.1, we might

just as well set the limit at ∞ , since $g_+(x_2 - x_3) = 0$ when $x_3 > x_2$ so that $x_2 - x_3 < 0$. Thus, we can write

$$\rho g_+(x_2) = \alpha_+(x_2) + \rho \int_0^\infty \alpha_+(x_3) g_+(x_2 - x_3) dx_3 \quad (C7)$$

Substitution of eq C1 into eq C7 yields

$$\rho h_+(x_2) = \alpha_+(x_2) + \rho \int_0^\infty \alpha_+(x_3) h_+(x_3 - x_3) dx_3 \quad (C8)$$

where we use the normalization condition

$$\int_0^\infty \alpha_+(x_3) dx_3 = 1 \quad (C9)$$

Then, by using the definition

$$c_+(x) = \frac{\alpha_+(x)}{\rho} \quad (C10)$$

and substituting eq C10 into eq C8, we may write

$$h_+(x_2) = c_+(x_2) + \rho \int_0^\infty c_+(x_3) h_+(x_3 - x_3) dx_3 \quad (C11)$$

since $c_+(x_3)$ vanishes when x_3 is negative since $c_+(x_3)$ is defined to the right and may be set to zero on the left. Therefore, eq C11 may be rewritten as

$$h_+(x_2) = c_+(x_2) + \rho \int_{-\infty}^\infty c_+(x_3) h_+(x_3 - x_3) dx_3 \quad (C12)$$

Note that this equation is valid even when x_2 is negative since it then gives $h_+(x_2) = -1$. Equation C12 is exactly of the form of the Ornstein–Zernike equation with the nearest-neighbor distribution (essentially $c_+(x)$) playing the role of the “direct correlation function”. Although this result (as an exact relation) is limited to hard rods, it suggests that, in general, the DCF might be considered as a distortion (even though at times severe) of the nearest-neighbor function. For example, the nearest-neighbor function remains short ranged even at the critical temperature, a property that derives from the DCF as a mathematical construct (i.e., as the solution of the Ornstein–Zernike equation) notwithstanding its use as a convenient intermediate function, in density functional theory,³⁴ and its description in terms of diagrammatic expansions.³⁵ In contrast, the above interpretation assures its short-range nature on purely

physical grounds since the nearest-neighbor distribution is always short ranged. If one is pressed to offer a physical interpretation, the distortion of the nearest-neighbor distribution seems, therefore, to be particularly appropriate. The DCF is of course not “direct”.

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