Iso-$g^{(2)}$ Processes in Equilibrium Statistical Mechanics[†]

Frank H. Stillinger,*[,‡,§] Salvatore Torquato,[§,||] Juan M. Eroles,[§,||] and Thomas M. Truskett[⊥]

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974, Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544, Department of Chemistry, Princeton University, Princeton, New Jersey 08544, and Department of Pharmaceutical Chemistry, University of California−San Francisco, San Francisco, California 94118

The pair correlation function $g^{(2)}(r)$ in a classical many-body system depends in a nontrivial way both on the number density ρ and on the pair interactions $v(r)$, and a long-standing goal of statistical mechanics has been to predict these effects quantitatively. The present investigation focuses on a restricted circumstance whereby simultaneous isothermal changes in ρ and $v(r)$ have exactly canceling effects on $g^{(2)}$. By appealing to the isothermal compressibility relation, we establish that an upper limit for density increase exists for this "iso-$g^{(2)}$" process, and at this limit in three dimensions the correspondingly modified pair interaction develops a long-ranged Coulombic character. Using both the standard hypernetted chain and Percus−Yevick approximations, we have examined the iso-$g^{(2)}$ process for rigid rods in one dimension that starts at zero density, and maintains the simple step-function pair correlation during density increase, a process that necessarily terminates at a covering fraction of one-half. These results have been checked with detailed Monte Carlo simulations. We have also estimated the effective pair potentials that are required for the corresponding rigid-sphere model in three dimensions, for which the simple step-function pair correlation can be maintained up to a covering fraction of one-eighth.

I. Introduction

At any given temperature, the thermodynamic and transport properties of a material system are controlled by the interactions operating between the constituent particles of that system. These interactions are specific to each substance, and give rise to wide variations in crystal structures,[1] and in the short-range order that X-ray and neutron diffraction experiments reveal to be present in liquids and amorphous solids.[2] One of the most basic challenges perennially facing statistical mechanics is to provide logical and quantitative connections between interactions on the one hand, to long-range and short-range order in material systems on the other hand. Computer simulation has been used aggressively and productively for this purpose, while suffering obvious system-size and time scale limitations. More analytic approaches in statistical mechanics that are designed to attain the same goals have a long history, marked by substantial but still incomplete success.

The present paper intends to illuminate a small aspect of the general problem of interaction-order connections. In particular, attention focuses on the existence and nature of a family of continuous isothermal processes that simultaneously change the system density, as well as the interactions, in such a way that pair correlations remain invariant. The resulting theoretical analysis leads inevitably to conclusions about particle arrangements in space, and the way in which they can be produced, that in our opinion seem less than obvious. In particular, this line of investigation offers novel insights into the subject of hard-particle packings, e.g. for hard rods, disks, and spheres in one, two, and three dimensions, respectively.

The following section II includes a precise definition of the processes at issue, the "iso-$g^{(2)}$" processes. Section II also illustrates these processes by exact low-density results, connects them to the well-known isothermal compressibility and Ornstein−Zernike relations, and stresses the relevance of the venerable HNC and PY approximate closures. For the purpose of providing a tangible example, Section III reports results for the one-dimensional rigid rod system, including calculation of an approximate effective pair potential that supplements the hard-core interaction during the iso-$g^{(2)}$ process, and presents a Monte Carlo test of the accuracy of that effective potential. Section IV exhibits the corresponding effective pair potential for hard spheres in three dimensions. A final section V presents discussion of several issues that extend beyond the scope of this initial investigation, but which represent natural research directions for further development of the concepts introduced and explored here.

II. Iso-$g^{(2)}$ Processes

In the interests of completeness we begin with the definition of equilibrium correlation functions $g^{(n)}$ of arbitrary order n for a single-component system, assuming that the classical canonical ensemble at inverse temperature parameter $\beta = (k_B T)^{-1}$ provides a proper representation.[3]

$$g^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n) = [V^n N!/N^n(N-n)!Z] \int_V d\mathbf{r}_{n+1}, ...,$$

$$\int_V d\mathbf{r}_N \exp[-\beta \Phi(\mathbf{r}_1, ..., \mathbf{r}_N)] \quad (2.1)$$

where Z is the configurational partition function for the N particles inside volume V:

[†] Part of the special issue "Bruce Berne Festschrift".
[‡] Bell Laboratories.
[§] Princeton Materials Institute.
[||] Department of Chemistry.
[⊥] Department of Pharmaceutical Chemistry.

Iso-$g^{(2)}$ Processes

J. Phys. Chem. B, Vol. 105, No. 28, 2001 **6593**

$$Z(N,\beta) = \int_V d\mathbf{r}_1, ..., \int_V d\mathbf{r}_N \exp[-\beta\Phi(\mathbf{r}_1, ..., \mathbf{r}_N)] \quad (2.2)$$

In these equations Φ stands for the interaction potential for the N particles, and periodic boundary conditions apply at the boundary of container volume V, so that free translation of the entire system is possible.

The functions $g^{(n)}$ are respectively proportional to the probabilities that infinitesimal volume elements $d\mathbf{r}_1, ..., d\mathbf{r}_n$ are simultaneously occupied by particle centers. The large-system limit will be of primary interest in the following, whereby both N and V pass to infinity at constant number density $\rho = N/V$.

The isothermal compressibility $\kappa_T = -(\partial\ln V/\partial p)_{N,T}$ has a representation as a spatial integral of the pair correlation function, which in fluid phases depends spatially only on scalar distance r:[4]

$$\rho\beta^{-1}\kappa_T = 1 + \rho\int[g^{(2)}(r) - 1]d\mathbf{r} \quad (2.3)$$

This relation between short-range order at the molecular level and a macroscopic thermodynamic property is very general. It is true regardless of the presence of nonadditive interactions in Φ, and is valid in the quantum-statistical, as well as classical-statistical, regime. It can even be used for the isothermal isotropic compressibility of an equilibrium crystal phase if the angle-averaged pair correlation function for that phase is inserted in (2.3). Note that for a pure phase in equilibrium $\rho\beta^{-1}\kappa_T$ is never negative, but can range from a very small positive value (cold dense liquids and solids) to arbitrarily large positive values (neighborhood of a critical point). The corresponding values of the spatial integral in (2.3) range from negative through zero to positive.

For the remainder of this paper Φ will be restricted to a pairwise additive form, involving only spherically symmetric pair potentials:

$$\Phi(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{i=2}^{N}\sum_{j=1}^{i-1} \nu(r_{ij}) \quad (2.4)$$

This is not an essential restriction, but suffices for present purposes to demonstrate the basic principles involved in iso-$g^{(2)}$ processes.

We now inquire about the possibility of changing the density isothermally from some initial value ρ_0 to a displaced value ρ_1, while requiring that the short-range order measured by $g^{(2)}$ remain unchanged. This requirement can only be satisfied if at the same time the interactions change in such a way that the normal density variation of $g^{(2)}$ is exactly canceled. To establish that this may indeed be possible, consider first the special case where ρ_0 vanishes, and ρ_1 is small enough that a density expansion through first-order suffices. The invariant pair correlation function at issue then is just the Boltzmann factor for pair potential ν:

$$g^{(2)}(r,\rho_0=0) = \exp[-\beta\nu(r)] \quad (2.5)$$

while the same function must emerge from the joint influence of a small density increase to $\rho_1 > 0$ and a change in pair interaction to $\nu(r) + \delta\nu(r)$. By drawing upon the known density series for $g^{(2)}$,[5] one finds that in this leading density order the change in the pair interaction must satisfy the following relation:

$$\beta\delta\nu(r_{ij}) = \rho_1\int\{\exp[-\beta\nu(r_{ik})] - 1\}\{\exp[-\beta\nu(r_{kj})] - 1\}d\mathbf{r}_k + O(\rho_1^2) \quad (2.6)$$

This invariance criterion can in principle be carried explicitly to higher orders in the final density ρ_1, although the subsequent terms rapidly become complicated.

One might note in passing that the reverse process with $\rho_0 > 0$ and $\rho_1 = 0$ is trivial. The combination $\nu + \delta\nu$ must simply be the pair potential of mean force at the starting density:[3,6]

$$\nu(r) + \delta\nu(r) = -\beta^{-1}\ln g^{(2)}(r,\rho_0), \quad (\rho_0 > 0, \rho_1 = 0) \quad (2.7)$$

However, this alone does not guarantee the existence of a $\delta\nu(r)$ over the entire intermediate density interval $0 < \rho_1 < \rho_0$.

Although (2.6) is suggestive, it does not establish how far ρ_1 could be increased above zero, or even if (2.6) involves a convergent series in ρ_1. Further insight requires that we return for the moment to the more general case where both ρ_0 and ρ_1 might be arbitrary nonnegative number densities. Consider how the isothermal compressibility (at fixed $\nu + \delta\nu$) behaves as a continuous function of the final density ρ_1 along an iso-$g^{(2)}$ path:

$$\rho_1\beta^{-1}\kappa_T(\rho_1) = 1 + \rho_1\int[g^{(2)}(r,\rho_0) - 1]d\mathbf{r} \quad (2.8)$$

If the $g^{(2)}(r,\rho_0) - 1$ integral is negative (crystal or cold liquid), then an increase in ρ_1 above ρ_0 would cause the right member of (2.7) to decline, reaching zero at

$$\rho_1^*(\rho_0) = \{-\int[g^{(2)}(r,\rho_0) - 1]d\mathbf{r}\}^{-1} \quad (2.9)$$

As a result

$$\kappa_T(\rho_1^*) = 0 \quad (2.10)$$

indicating that ρ_1^* is a singular end point of the iso-$g^{(2)}$ process, at which the system becomes completely incompressible, i.e., infinitely rigid with respect to volume change. No singular density limit would arise if the $g^{(2)}(r,\rho_0) - 1$ integral were to vanish, or were positive as would certainly be the case in the neighborhood of the critical point.

Further understanding of the singular density limit requires consideration of the supplemental pair interaction $\delta\nu$ generated by the iso-$g^{(2)}$ process. Aside from the (possibly convergent) density series (2.6), and the special case (2.7), no exact results for $\delta\nu$ are currently available. However we can use well-known statistical-mechanical approximations for guidance. For this purpose we need first to recall the definition of the direct correlation function $c(r,\rho)$, provided by the Ornstein−Zernike integral equation:[7]

$$c(r_{12},\rho) = g^{(2)}(r_{12},\rho) - 1 - \rho\int c(r_{13},\rho)[g^{(2)}(r_{32},\rho) - 1]d\mathbf{r}_3 \quad (2.11)$$

The hypernetted chain (HNC)[8] and Percus−Yevick (PY)[9] approximations then connect $g^{(2)}$ and its relative c to the pair potential that produces them in the thermal equilibrium setting:

$$\beta\nu(r) = g^{(2)}(r) - 1 - \ln g^{(2)}(r) - c(r) \quad \text{(HNC)} \quad (2.12)$$

$$\beta\nu(r) = \ln\left[1 - \frac{c(r)}{g^{(2)}(r)}\right] \quad \text{(PY)} \quad (2.13)$$

The following sections III and IV will examine effective interactions $\nu + \delta\nu$ that are applicable to the rigid-rod and rigid-sphere systems.

Let $G(k)$ and $C(k)$ respectively stand for the D-dimensional Fourier transforms of $g^{(2)}(r) - 1$ and $c(r)$, the generic forms of which are

6594 *J. Phys. Chem. B, Vol. 105, No. 28, 2001*

Stillinger et al.

$$F(k) = \int \exp(i\mathbf{k}\cdot\mathbf{r})f(k)d\mathbf{k},$$

$$f(r) = (2\pi)^{-D} \int \exp(-i\mathbf{r}\cdot\mathbf{k})F(k)d\mathbf{k} \quad (2.14)$$

Then application of the Ornstein−Zernike relation (2.11) to the iso-$g^{(2)}$ process leads to the following:

$$C(k,\rho_1) = \frac{G(k,\rho_0)}{1 + \rho_1 G(k,\rho_0)} \quad (2.15)$$

For small values of k we will have the expansion

$$G(k) = G_0 + G_2 k^2 + G_4 k^4 +, ... \quad (2.16)$$

where normally G_2 will have a sign opposite to that of G_0 [e.g., (4.2) below]. The denominator of eq 2.15 at $k = 0$ is just the right member of the compressibility expression (2.8), which vanishes at the singular density ρ_1^*. Consequently the small-k behavior of C at the singular density must be

$$C(k,\rho_1^*) = (G_0/\rho_1^* G_2 k^2) + O(k^0) \quad (2.17)$$

In three dimensions this form corresponds to an **r**-space function that possesses a Coulombic tail asymptotically at large r:

$$c(r,\rho_1^*) \sim G_0/(4\pi\rho_1^* G_2 r) \quad (2.18)$$

Thus, the direct correlation function at the singular density is very long-ranged, far exceeding the range of the deviation from unity of the pair correlation function itself (assuming that the starting state was not a critical point). Appealing next to the HNC and PY approximations (2.12) and (2.13), one concludes for ρ_1^* that the effective pair interaction must itself display a positive Coulombic form at large separations. This must arise from the supplementary contribution $\delta\nu$ itself ($G_0/G_2 < 0$)),

$$\delta\nu(r) \sim -G_0/(4\pi\beta\rho_1^* G_2 r) \quad (2.19)$$

Evidently it is this long-ranged repulsive Coulomb interaction that confers upon the system infinite resistance to volume change in the limit of the singular density ρ_1^*.

A more detailed analysis of the continuous approach to singular density ρ_1^* shows that the Coulombic effective interaction appears first in an exponentially damped ("Yukawa") form, and that this damping or shielding diminishes to zero at the singularity with a decay length proportional to the inverse square root of the density deficit.

The pressure p can be obtained from the isothermal compressibility by performing an isothermal density integration:

$$\beta p = \int_0^\rho \frac{d\rho'}{\rho'\beta^{-1}\kappa_T(\rho')} \quad (2.20)$$

and with the proper choices for κ_T this applies both to the conventional situation as well as to an iso-$g^{(2)}$ path.

Alternatively, the pressure can be obtained from the virial relation.[10] As a result of carrying out an iso-$g^{(2)}$ process from ρ_0 to ρ_1 with an attendant supplementary pair interaction $\delta\nu$, the pressure at ρ_1 will possess the following integral representation:

$$\beta p(\rho_1) = \rho_1 - (2\pi r_1^2\beta/3) \int_0^\infty r^3[\nu_r(r) + \delta\nu_r(r,\rho_1)]g^{(2)}(r,\rho_0)dr + 2\pi\beta\rho_1^3 \int_0^\infty r^2\nu_\rho(r,\rho_1)g^{(2)}(r,\rho_0)dr \quad (2.21)$$

where subscripts r and ρ denote partial derivatives with respect to those variables. Under proper circumstances, comparison of these two pressure expressions can yield a useful integral constraint on the supplementary interaction $\delta\nu$.

III. Rigid Rod System

One of the simplest models for interacting particles is the one-dimensional system of rigid rods of length a. The Tonks equation of state provides an exact description of its equilibrium pressure,[11]

$$\beta p = \rho/(1 - \rho a) \quad (3.1)$$

diverging at the close-packed density $1/a$. Note that, in this one-dimensional system, the dimensionless quantity ρa is just the "covering fraction" ϕ, i.e., the fraction of the available space covered by the rigid rods. The corresponding expression for the isothermal compressibility is

$$\rho\beta^{-1}\kappa_T = (1 - \rho a)^2 \equiv 1 + \rho G(0,\rho) \quad (3.2)$$

This permits evaluation of the isothermal compressibility along an iso-$g^{(2)}$ path, starting at density ρ_0, and proceeding to the displaced density ρ_1.

$$\rho_1\beta^{-1}\kappa_T(\rho_1|\rho_0) = 1 + \rho_1 G(0,\rho_0) = 1 + (\rho_1/\rho_0)[(1 - \rho_0 a)^2 - 1] \quad (3.3)$$

This last expression vanishes at the upper singular density

$$\rho_1^*(\rho_0)a = (2 - \rho_0 a)^{-1} \quad (3.4)$$

Consequently, if the starting density ρ_0 is very low, the iso-$g^{(2)}$ process can only extend up to $\phi_1 \equiv \rho_1 a = 1/2$, half of the close-packed density, but higher starting density permits closer approach to the close-packed limit.

We now analyze more fully the $\rho_0 \rightarrow 0$ situation, for which the pair correlation function is just a simple unit step function U;

$$g^{(2)}(x,\rho_0 = 0) = U(x - a) \quad (3.5)$$

We thus have

$$G(k,\rho_0 = 0) = -(2/k) \sin(ka) \quad (3.6)$$

and consequently

$$c(x,\rho_1) = -\frac{2}{\pi} \int_0^\infty \frac{\sin(ka) \cos(kx)}{k - 2\rho_1 \sin(ka)}d\mathbf{k} \quad (3.7)$$

Although this integral is not a standard form, apparently, with due attention to convergence issues it can be evaluated numerically provided $\rho_1 a < 1/2$. However it appears to diverge to $+\infty$ for all x upon approach to the singular upper limit.

The HNC and PY approximations, (2.12) and (2.13), applied to the present $\rho_0 = 0$ case give particularly simple connections between the direct correlation function and the effective pair potential ($x > a$):

$$\beta\delta\nu(x,\rho_1) = -c(x,\rho_1) \quad \text{(HNC)}$$

$$\beta\delta\nu(x,\rho_1) = \ln[1 - c(x,\rho_1)] \quad \text{(PY)} \quad (3.8)$$

Figures 1−3 present numerical results for these approximate $\delta\nu$ at the final densities $\rho_1 a = 0.1, 0.3,$ and 0.45.

Iso-$g^{(2)}$ Processes

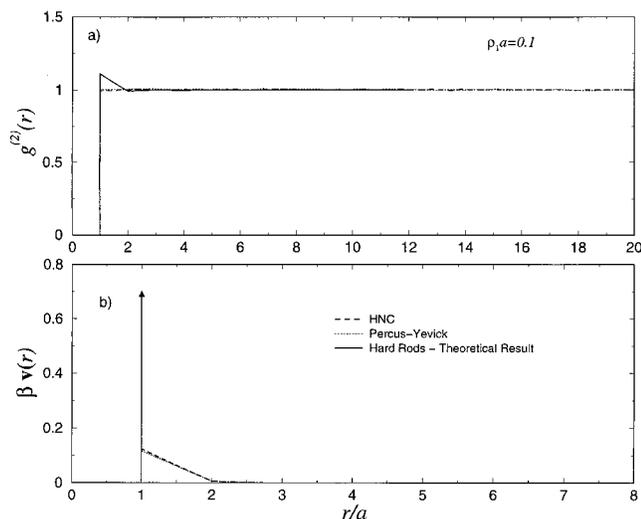*J. Phys. Chem. B, Vol. 105, No. 28, 2001* **6595**

Figure 1. Characteristics of the rigid-rod iso-$g^{(2)}$ process at $\rho_1 a = 0.1$, which begins at zero density. (a) The exact conventional pair correlation function[11(a)] (solid curve) and the Monte Carlo results for the HNC (dashed curve) and PY (dotted curves). (b) The approximate interactions used for the Monte Carlo simulation.
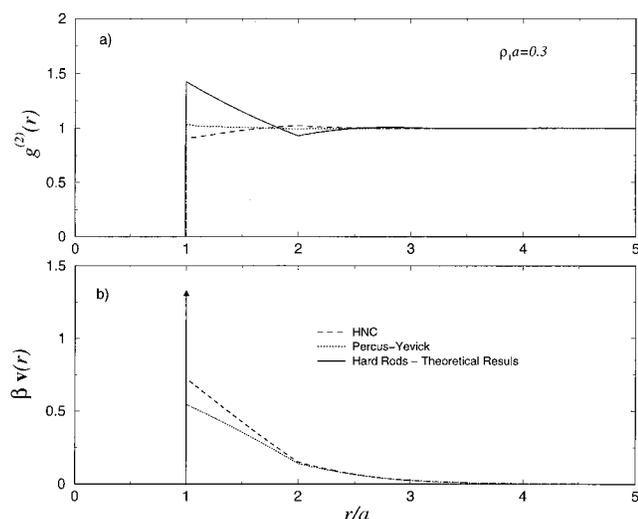

Figure 3. Characteristics of the rigid-rod iso-$g^{(2)}$ process at $\rho_1 a = 0.45$, which begins at zero density. The legends are the same as in Figures 1 and 2, augmented with curves (dotted–dashed) referring to an empirical interpolation interaction, a modification of the HNC approximation as described in the text.

Figure 2. Characteristics of the rigid-rod iso-$g^{(2)}$ process at $\rho_1 a = 0.3$, which begins at zero density. The legends are the same as in Figure 1.

Figure 4. Representative samples of rigid-rod configurations, extracted from 500-particle simulations at $\rho_1 a = 0.45$, indicating the influence of the supplementary interaction required to enforce the iso-$g^{(2)}$ constraint. The upper portion shows the conventional "bare" rigid rods; the lower portion shows the iso-$g^{(2)}$ case. The rods have been stretched vertically to enhance ease of pattern visualization.

It is important to carry out a consistency test of the HNC and PY approximations in the present context. For this reason we have performed 500-particle Monte Carlo simulations for the rigid rod system, with and without the supplemental pair interactions eq 3.8 in place. If no approximation errors were present, the computed pair correlation functions for the former should replicate the unit step function, while deviation from that ideal result would indicate the level of inaccuracy of the HNC and PY approximations. Figures 1−3 also present pair correlation functions for $\rho_1 a = 0.10, 0.30,$ and 0.45, to indicate the extent to which the additional interaction succeeds in suppressing local order beyond the rigid rod diameter. To stress that the process involved actually removes short-range order beyond the rigid rod collision distance, exact pair correlation functions for the conventional system at the given density have also been included in these figures.[11] As one can easily see, the PY approximation performs better than the HNC approximation at the densities considered, though both lead to increasing deviations from the ideal step-function $g^{(2)}$ as $\rho_1 a$ increases toward the upper limit 0.50. In particular, for the highest density that we have studied ($\rho_1 a = 0.45$), the calculated pair correlation
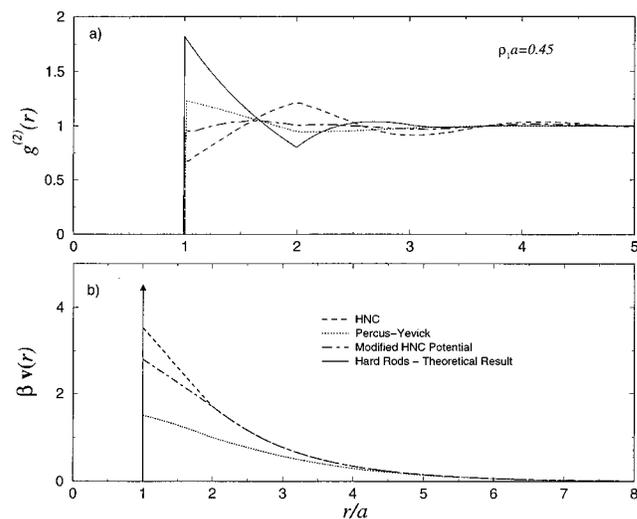
functions deviate appreciably from the step function, especially close to contact. To check that there indeed exists a potential with the desired features at this density, we have modified the HNC potential by decreasing the slope in the nearly linear portion from $r/a = 1$ to $r/a = 2$ while keeping the value at $r/a = 2$ fixed. This modified potential is plotted in Figure 3 and results in a pair correlation function that produces the best agreement with the step function. No doubt further small changes in the interaction could reduce the discrepancy even further.

Figure 4 presents a pair of configurations for $\rho_1 a = 0.45$, both for the conventional "bare" rigid rods, and for the iso-$g^{(2)}$ variant. Our experience suggests that these are roughly typical. The visual impact suggests a pattern difference, with a more uniform distribution of nearest-neighbor separations in the iso-$g^{(2)}$ case. This observation is consistent with the expectation that the mean nearest-neighbor distance between the particles
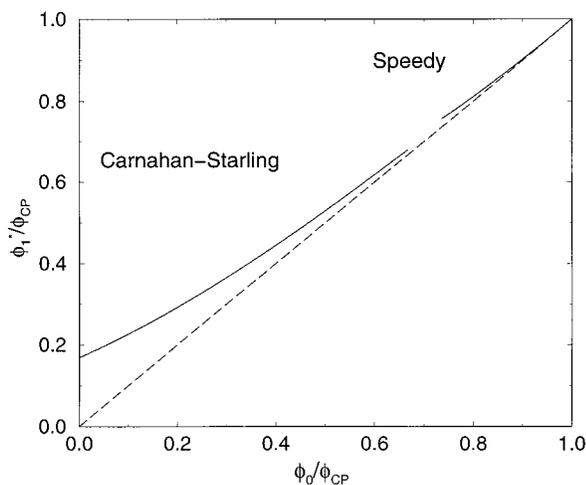
Figure 5. Dependence of the upper singular density ϕ_1^* upon the initial density ϕ_0, for the rigid sphere model. The calculations were based on the Carnahan−Starling pressure equation for the fluid,[14] and the Speedy pressure equation for the face-centered cubic crystal.[15]

Figure 6. Effective pair interactions $\delta\nu(r,\rho_1)$ for the rigid sphere model in the HNC and PY approximations. The iso-$g^{(2)}$ process involved starts at vanishing number density, and maintains the corresponding step-function pair correlation as density increases to final values of ρ_1 for which the covering fractions ϕ are 1/16 and 1/10.

λ for the step-function $g^{(2)}$ system should generally be larger than the corresponding quantity for the standard equilibrium hard-rod system, with the difference increasing with increasing density. Indeed, our simulations show that this is the case. For example, at $\rho_1 a \equiv \phi = 0.45$, $\lambda/a \cong 1.75$ for the step-function $g^{(2)}$ system, compared to $\lambda/a \cong 1.61$ for the equilibrium system as obtained from the analytical expression[12]

$$\lambda/a = 1 + (1 - \phi)/2\phi \qquad (3.9)$$

IV. Rigid Spheres

An obvious shortcoming of the rigid rod model examined in the preceding section III is that it has no freezing transition. The corresponding three-dimensional rigid sphere case however has been known for many years to have just that property, preferring to form a face-centered cubic crystal when the density is sufficiently high.[13]

The coexistence interval for this first-order phase change is approximately the following:[14]

$$0.943 < \rho a^3 < 1.041 \qquad (4.1)$$

Pressure isotherms for both the fluid phase (Carnahan−Starling[15]) and the crystal phase (Speedy[16]) are available, and can be used to calculate the isothermal compressibilities. The general relation (2.3) then supplies $G(0,\rho_0)$ for each phase, and subsequently (2.9) becomes applicable for evaluation of $\rho_1^*(\rho_0)$.

Numerical results for these singular upper density limits of the iso-$g^{(2)}$ process have been plotted in Figure 5.

One sees from Figure that, as ρ_0 increases, a shrinking density interval for compression is available before the singular upper limit is encountered, although passing through the freezing transition relieves this situation somewhat.

The $\rho_0 = 0$ pair correlation function, again a unit step function, leads to the expression:

$$G(k,\rho_0 = 0) = (4\pi/k^3)[(ka)\cos(ka) - \sin(ka)] =$$
$$-(4\pi a^3/3)\{1 - (ka)^2/10 + (ka)^4/280 - O[(ka)^6]\} \quad (4.2)$$

Following the now familiar procedure, this can be used as the starting point to evaluate the direct correlation function at $0 <$
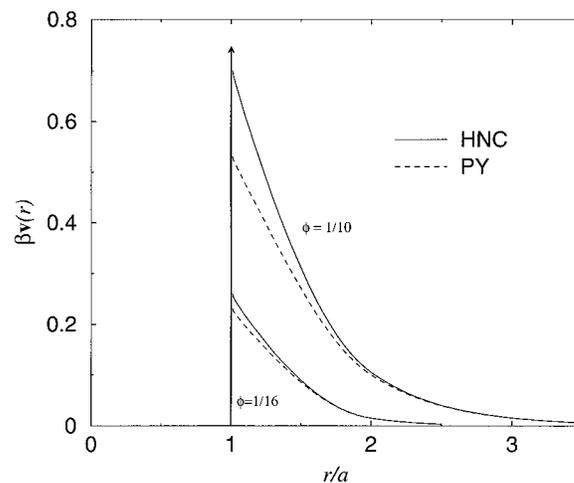
$\rho_1 < \rho_1^*(0)$:

$$c(r,\rho_1) = \frac{2}{\pi r} \int_0^\infty \frac{k\sin(kr)[(ka)\cos(ka) - \sin(ka)]}{k^3 + 4\pi\rho_1[(ka)\cos(ka) - \sin(ka)]}\, \mathrm{d}k \qquad (4.3)$$

Once again a nonstandard integral arises, but numerical evaluation is feasible. The HNC and PY approximations, (2.12) and (2.13), indicate that $-\beta\delta\nu(r,\rho_1)$ is equal respectively to $c(r,\rho_1)$ and to $-\ln[1 - c(r,\rho_1)]$, just as in the rigid rod case of section III. Figure 6 graphically presents results for this supplemental pair interaction at several densities. While both the HNC and PY approximations may be qualitatively correct for this rigid sphere application, we suspect that an improvement in performance may again require an interpolation of some sort analogous to that used above for rigid rods.

It is easy to see from (4.2) that the singular upper-limit density $\rho_1^*(\rho_0=0)$ for the rigid sphere iso-$g^{(2)}$ process that starts at zero density must be

$$\rho_1^*(\rho_0 = 0)a^3 = 3/(4\pi) \qquad (4.4)$$

which corresponds exactly to a covering density ϕ of one-eighth. We note in passing, that Markov and Willis, using a different approach, have also observed that $\phi = 1/8$ is a singular limit for locally uncorrelated arrangements of rigid spheres.[17] The result in (4.4), and the corresponding upper limit for rigid rods are two examples of a simple but more general result for rigid D-dimensional "spheres", for which the covering fraction has the form

$$\phi = \rho V_D(a) \qquad (4.5)$$

here $V_D(a)$ is the volume of a radius-a hypersphere in D-dimensional space. Owing to the obvious fact that the "volume" of exclusion measured by $G(k=0,\rho_0=0)$ has a radius equal to twice the "sphere" radius, the covered volume fraction ϕ_1^* at $\rho_1^*(\rho_0=0)$ must be exactly 2^{-D}.

V. Discussion

Moving a many-body system along an iso-$g^{(2)}$ path does not constrain correlation functions $g^{(n)}$ for $n > 2$ to remain invariant. However in the reversed situation, where an n-body supple-

Iso-$g^{(2)}$ Processes

J. Phys. Chem. B, Vol. 105, No. 28, 2001 **6597**

mentary potential were used to carry out the iso-$g^{(n)}$ generalization, all lower-order correlation functions would necessarily exhibit invariance during that process. This follows from the definitions in (2.1). One might note in passing that the venerable Kirkwood superposition approximation[18] which expresses $g^{(3)}$ as a product of $g^{(2)}$'s suggests that at least an approximate invariance automatically carries upward in order from the pair to the triplet level. Nevertheless, some level of error in this Kirkwood approximation must be expected, and it will eventually be illuminating to determine how this error behaves upon approach to the upper density limit $\rho_1{}^*$.

If one were to implement an iso-$g^{(3)}$ process, starting at low density in a rigid sphere system, it should be expected that an upper singular density would again be encountered as in the iso-$g^{(2)}$ case considered above. But because this generalization involves a more powerful constraint, its singular density presumably could not be higher than for the pair case that starts at the same low density. But whether the iso-$g^{(3)}$ singular density is actually less than that of the pair case is not obvious, and at the moment must be regarded as a legitimate object for future research.

An unambiguous theoretical procedure has recently been advocated for separating the isothermal compressibility κ_T into two parts, structural and vibrational.[19] This separation is based upon a mapping of all system configurations onto "inherent structures" (potential energy minima), using a steepest-descent connection on the multidimensional potential energy hypersurface. In particular, the pair correlation functions before and after this mapping differ, and the difference reflects the anharmonic vibrational effects. A significant extension of the analysis presented herein would be to monitor, perhaps best by computer simulation, the way that inherent structures and their pair correlations evolve during the course of an iso-$g^{(2)}$ process, and how the balance shifts between inherent structural and vibrational contributions to κ_T. One should not expect the post-mapping $g^{(2)}$'s to display invariance.

The spherically averaged pair correlation function for a crystal phase will exhibit relatively long-ranged fluctuations about the limiting value unity, owing to the presence of periodic order.[20] If ρ_0 were selected to correspond to a stable crystal state at the prevailing temperature, and ρ_1 were then taken to zero, (2.7) above would indicate that the supplementary interaction required to effect an iso-$g^{(2)}$ process would itself be relatively long-ranged. Specifically this supplementary interaction would have to maintain an image of the coordination shells of the crystal (with vibrational smearing), which is certainly an unnatural situation for a dilute gas. We speculate that no phase transition would exist along this iso-$g^{(2)}$ path, in contrast to the conventional situation for isothermal reduction in density to zero. If this speculation is correct, such an iso-$g^{(2)}$ process might qualify as a convenient thermodynamic path for calculating the absolute entropy of the crystal.

Although it has been mentioned above, for three-dimensional systems, that the upper density limit $\rho_1{}^*$ entails Coulombic supplementary pair potentials, it would be inappropriate to view

that state as corresponding to a conventional electrolyte. First, all particles bear the same electrostatic charge (though one could imagine that a uniform neutralizing background charge density were present). Second, and more significantly, the fixed short-range pair correlation order is not obviously subject to the exact zeroth and second moment conditions that apply to conducting media.[21] In fact this upper-density-limit state appears to be incapable of electrolytic conduction, though it evidently can support local stirring motions. The one qualitative attribute that the $\rho_1{}^*$ state shares with conventional electrolytes is that the interaction range far exceeds that of the correlation length, owing apparently to an intrinsic shielding phenomenon.

It was noted above [following (2.10)] that if the spatial integral of $g^{(2)} - 1$ vanished or were positive, no singular density associated with a vanishing isothermal compressibility would occur. This situation would arise in the presence of attractive interparticle interactions, and in particular would develop in the critical region of such systems. This alternative scenario, an obvious candidate for future investigation, may well involve divergence of the direct correlation function Fourier transform $C(k,\rho_1{}^*)$ at some $|k| > 0$, which in turn suggests that long-range oscillatory interactions would have to be present at $\rho_1{}^*$.

References and Notes

(1) Kittel, C. *Introduction to Solid State Physics*, 2nd ed.; John Wiley and Sons: New York, 1956.

(2) Gaskell, P. H., Ed. *The Structure of Non-Crystalline Materials*; Taylor and Francis, Ltd.: London, 1977.

(3) Hill, T. L. *Statistical Mechanics*; McGraw-Hill: New York, 1956; Chapter 6.

(4) Reference 3, p 236.

(5) Rice, S. A.; Gray, P. *The Statistical Mechanics of Simple Liquids*; Interscience Publishers: New York, 1965; Section 2.5.

(6) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: New York, 1976; Chapter 2.

(7) Ornstein, L. S.; Zernike, F. *Proc. Akad. Sci. (Amsterdam)* **1914**, *17*, 793.

(8) Van Leeuwen, J. M. J.; Groeneveld, J.; De Boer, J. *Physica* **1959**, *25*, 792.

(9) Percus, J. K.; Yevick, G. J. *Phys. Rev.* **1958**, *110*, 1.

(10) Reference 3, p 190.

(11) (a) Zernike, F.; Prins, J. A. *Z. Phys.* **1927**, *41*, 184. (b) Tonks, L. *Phys. Rev.* **1936**, *50*, 955.

(12) Torquato, S. *Phys. Rev. Lett.* **1995**, *74*, 2156.

(13) Woodcock, L. V. *Nature* **1997**, *385*, 141.

(14) Hoover, W. G.; Ree, F. H. *J. Chem. Phys.* **1968**, *49*, 3609.

(15) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.

(16) Speedy, R. J. *J. Phys.: Condens. Matter* **1998**, *10*, 4387.

(17) Markov, K. Z.; Willis, J. R. In *Mathematical Models and Methods in Applied Sciences*; World Scientific Publishers: Singapore, 1998; Vol. 8, pp 359−377.

(18) Kirkwood, J. G.; Boggs, E. M. *J. Chem. Phys.* **1942**, *10*, 394.

(19) Stillinger, F. H.; Debenedetti, P. G.; Sastry, S. *J. Chem. Phys.* **1998**, *109*, 3983.

(20) Stillinger, F. H. *Phys. Rev.* **1966**, *142*, 237.

(21) Stillinger, F. H.; Lovett, R. *J. Chem. Phys.* **1968**, *49*, 1991.