One-Dimensional Rigorous Hole Theory of Fluids: Internally Constrained Ensembles

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A "hole" in a fluid is specified in a well-defined manner. The concentration of "holes" is a thermodynamic property of the fluid and we derive this concentration in three different ensembles for a one-dimensional fluid of hard rods. The thermodynamics of these rigorously defined holes is developed, and the properties of holes are explored. The ensemble in which the concentration of holes is maintained fixed exhibits dramatic properties. Finally, pair correlation functions for hard rods in the various ensembles are computed. Contrary to a frequently made assumption, the equilibrium number of holes is found to never be proportional to the probability of finding a single hole in the fluid. Constraining the concentration of holes as well as the density leads to dramatic structural effects prominently displayed by the pair correlation function. The ensemble in which the concentration of holes is fixed is an example of an "internally constrained" metastable system.

1. INTRODUCTION

Free volume and hole theories[1-4] achieved considerable popularity in the development of heuristic, modelistic approaches to fluids. These theories have either been of the lattice variety[5] (which are in fact theories of crystalline rather than fluid systems), or of the fluctuation type,[6] in which estimates of the probability of appearance of at least one "hole" in the fluid are used to calculate the average number of simultaneous holes occurring at equilibrium. Among other things, this average number is presumed to have relevance with respect to transport processes characterized by viscosity and self-diffusion coefficients.

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685

As long as the focus has been on the achievement of approximate, heuristic descriptions of fluid properties, the hole and free volume theories have proved convenient and serviceable. One wonders, therefore, whether it is possible to develop a *rigorous* theory of holes, in the sense that, in principle, it can be made as exact as possible simply by the expenditure of more work (even though that work may be prohibitive in human terms). The "equilibrium number of holes," properly defined, is a thermodynamic property of the fluid, and should, in principle, be calculable. The ultimate usefulness of such an exact theory remains to be demonstrated, but a number of interesting questions are easily posed. For example, in dense fluids, are the holes mutually isolated, leading to an *ideal* solution of holes, or does the potential of mean force between holes become so long range that this is not possible? Since holes are a thermodynamic property, can a low concentration of holes make it easier to design theories of dense fluids? Another question concerns the behavior of holes in a hard-sphere fluid in the neighborhood of the hard-sphere phase transition.[7] Since the number of holes constitutes a thermodynamic property, does this number, calculated along the analytic continuation of the fluid branch of the hard-sphere system, give rise to configurations which exceed the close packing of spheres? If so, light may be thrown on the mechanistic reasons for the occurrence of the hard-sphere transition.

In the present paper we develop a rigorous fluid theory of holes for a one-dimensional system of hard rods, e.g., we actually calculate the equilibrium number of a well-defined species of hole. At this late date, one needs to ask why additional work on such an unreal system (and one which does not even possess a phase transition) should be performed. One answer is usual; it provides an opportunity to develop insight into real systems, in view of the possibility of developing the theory *exactly*. Beyond this, however, we have in mind the development of a theory, prefatory to the investigation of certain nonequilibrium properties of hard rods. Nonequilibrium theories of hard rods have recently been the subject of attention by a number of authors.[8-11]

One feature, of particular interest, deals with the properties of ensembles which are "internally constrained."[12,13] For example, we shall be able to constrain the fluid internally, by *fixing* the number of holes, i.e., by treating the number of holes as a controllable thermodynamic variable. The resulting system has many interesting properties.

2. DERIVATION OF THE BASIC THEORY

We consider a system of N hard rods, each of length a, confined to a one-dimensional volume (length L). At the outset, it is necessary to define

what we mean by a "hole." Consider a particular configuration of the rods. Into this configuration we now insert as many additional hard rods as can be fitted into the system without disturbing the original configuration. This maximum number of additional rods is *defined* as the number of "holes" corresponding to the particular configuration under consideration. If we denote a particular configuration by the symbol C, then the number of holes going with the Cth configuration will be denoted by h_C. Suppose that P_C is the probability of occurrence of the Cth configuration when the system is in thermodynamic equilibrium. Then the equilibrium number of holes will be given by $\langle h \rangle$, where

$$\langle h \rangle = \sum_C h_C P_C \qquad (1)$$

We note that the addition of rods, in order to "measure" the number of holes, must in no way perturb the various configurations to which they are added. Thus it is improper to think of the holes as "solute" rods which can themselves come to equilibrium with the original solvent rods. If this were the case it would be relatively easy to provide a general formula for the equilibrium number of holes, even in a three-dimensional system. As it stands, we have not yet been able to advance such a formula (even in terms of quantities, such as partition functions, which themselves cannot be evaluated exactly) for anything beyond a one-dimensional system. If such a formula were available it would be possible to arrive at well-defined approximations for the equilibrium number of holes which might be continually improved, using a well-defined process. The provision of such a formula remains an important task for the future. In this paper we restrict attention to the one-dimensional case.

In order to evaluate $\langle h \rangle$ for our system of hard rods, it is convenient, for the purpose of mathematical analysis, to quantize all distances in terms of a quantum u which we will allow to become zero (so that we pass to the continuum) after the most difficult formulas have been derived. We choose u so that the number of quanta in the length a of a rod is an integer ω. Thus

$$a = \omega u \qquad (2)$$

The number of quanta in the length L will be denoted by

$$\mathscr{L} = L/u \qquad (3)$$

Now, in the hard-rod system, additional rods can only be fitted into the unoccupied spaces between pairs of the N original rods. However, such an unoccupied space must have a length greater than $2a$ (measured in

terms of the distance between the centers of hard rods) or contain a number of quanta greater than 2ω. In fact, if the unoccupied interval has a length lying between $2a$ and $3a$ it will accommodate only one hard rod, at the most, and will contribute *one* hole to the system. If its length lies between $3a$ and $4a$ it will accommodate two hard rods and contribute two holes to the system. In general, if the length lies between $(n+1)a$ and $(n+2)a$ it will contribute n holes. We denote the number of intervals in a configuration, capable of contributing n holes, and of length λ, measured in units of the quantum u, by $g_{n\lambda}u$. The quantum u plays the role of a differential of length, and $g_{n\lambda}$ is therefore a linear density. Clearly λ is constrained by n to lie in the range

$$(n+1)\omega < \lambda \leqslant (n+2)\omega \tag{4}$$

We shall characterize a configuration by the set of numbers $g_{n\lambda}u$ corresponding to it. The number of distinct arrangements corresponding to a distribution characterized in this manner is given by

$$\Omega = \frac{N!}{\prod_n \prod_\lambda (g_{n\lambda}u)!} \tag{5}$$

where N appears in the numerator because the total number of spaces between the rods is N. We are of course considering a system in the thermodynamic limit, in which end effects can be neglected. Conservation of spaces requires

$$\sum_{n=0}^{\infty} \sum_{\lambda=(n+1)\omega+1}^{(n+2)\omega} g_{n\lambda}u = N \tag{6}$$

Similarly the conservation of length requires

$$\sum_{n=0}^{\infty} \sum_{\lambda=(n+1)\omega+1}^{(n+2)\omega} \lambda(g_{n\lambda}u) = \mathscr{L} \tag{7}$$

According to our definition the number of "holes" in the system is given by

$$h = \sum_{n=0}^{\infty} \sum_{\lambda=(n+1)\omega+1}^{(n+2)\omega} n(g_{n\lambda}u) \tag{8}$$

In order to obtain the equilibrium distribution of $g_{n\lambda}u$, we maximize Ω in Eq. (5) subject to the constraints, Eqs. (6) and (7). Employing the method of undetermined multipliers, in the usual manner, we obtain

$$g_{n\lambda}u = K\alpha^\lambda \tag{9}$$

In which K and α are parameters to be determined by substitution of Eq. (9) into Eqs. (6) and (7). All the sums prove to be geometric series and, except for a certain amount of tedium, are easily evaluated. They lead to the results

$$\frac{\mathscr{L}}{N\omega} = \frac{L}{Na} = 1 + \frac{\alpha}{\omega(1-\alpha)} + \frac{1}{\omega} \tag{10}$$

$$K = \frac{N(1-\alpha)}{\alpha^{\omega+1}} \tag{11}$$

At this point we pass to the continuum, allowing u to approach zero, and ω to approach infinity. Examination of Eq. (10) shows that if α is not infinitesimally different from unity, the ratio L/Na will be unity. Since we know this not to be the case, it is clear that, in the continuum limit, α must have the form

$$\alpha = 1 - \varepsilon \to 1 \tag{12}$$

where ε is an infinitesimal. Then

$$\alpha^{\omega} = (1-\varepsilon)^{\omega} = e^{-\xi} \tag{13}$$

where

$$\xi = \varepsilon\omega \tag{14}$$

in which the right-hand member of Eq. (13) is the limiting expression when ω goes to infinity while ε is infinitesimal.

Continuing to regard ω as infinite and substituting Eqs. (12), (13), and (14) into Eq. (10) yields the result

$$\xi = \frac{N}{L/a - N} \tag{15}$$

Substituting Eqs. (12) and (13) into Eq. (11) yields

$$K = Ne^{\xi}\varepsilon \tag{16}$$

The result of substituting Eq. (9) into Eq. (8) is

$$\langle h \rangle = \frac{N\alpha^{\omega}}{1 - \alpha^{\omega}} \tag{17}$$

in which we have used Eq. (11) for K. Making use of Eqs. (12) and (13) in Eq. (17) finally gives, for the equilibrium number of holes,

$$\langle h \rangle = \frac{Ne^{-\xi}}{1 - e^{-\xi}} \tag{18}$$

As indicated earlier, it is of some interest to consider an ensemble in which the number of holes h is constrained while the length L is allowed to fluctuate freely. The average value L of the length, at equilibrium, may then be calculated as follows. Ω in Eq. (5) is maximized subject to the constraints specified by Eqs. (6) and (8) in which, now, h is held constant. The form of $g_{n\lambda}u$ is then given by

$$g_{n\lambda}u = K'\beta^n \tag{19}$$

in which the parameters K' and β are to be determined by substituting Eq. (19) back into Eqs. (6) and (8). One finds

$$K' = \frac{N(1 - \beta)}{\omega} \tag{20}$$

$$\beta = \frac{h}{N + h} \tag{21}$$

$$\langle L \rangle = a[h + \tfrac{3}{2}N] \tag{22}$$

where we have substituted Eqs. (20) and (21) into Eq. (19) and the latter into Eq. (7) in order to obtain $\langle L \rangle$. Once again, all the sums are simple geometric series.

The ensemble in which the number of holes is maintained fixed may be regarded as (and in fact is) internally constrained. Sometimes, a statistical mechanical analysis of an internally constrained system is easier than one dealing with a closely related non-internally-constrained system. For example, lattice free volume theories of fluids involve systems in which molecules are constrained to move within the free volume of a lattice cell. Often if the two systems are close enough, in some average sense, thermodynamic properties calculated using the mathematically simpler internally constrained system may be reasonable approximations to the corresponding quantities of the unconstrained system. For this reason it is of interest to compare the equilibrium relation between the fixed value of h and the average value, $\langle L \rangle$, in the internally constrained system with the corresponding relation between the average value, $\langle h \rangle$, and the fixed value of L in the non-internally-constrained one. We can use Eqs. (18) and (22) for this purpose. Thus, substituting Eq. (15) into Eq. (18) yields

$$\langle h \rangle = \frac{N \exp[-N/(L/a - N)]}{1 - \exp[-N/(L/a - N)]} \tag{23}$$

Solving Eq. (22) for h yields

$$h = \frac{\langle L \rangle}{a} - \frac{3}{2} N \tag{24}$$

Equations (23) and (24) are quite different, except in systems of low density, where

$$L \gg Na \tag{25}$$

Then the exponentials in Eq. (23) may be expanded to linear terms to give

$$\langle h \rangle = \frac{L}{a} - 2N \tag{26}$$

Except for having $2N$ in place of $3N/2$, Eq. (26) is identical with Eq. (24), if the average value h is interpreted as a fixed value. Thus the thermodynamic properties derived from the internally constrained ensemble are not well matched to those of the corresponding non-internally-constrained one.

For many reasons it is appropriate to define a "hole," as we have, by using "additional rods" having the same length a as the original rods in the fluid. If the "hole" is defined in terms of additional rods of increasingly smaller length, it is easy to show (although we do not do so here) that the thermodynamic properties of the internally constrained system correspond more and more closely to those of the non-internally-constrained one. Ultimately, when the holes are of zero length, the properties of both systems become identical. This is not surprising; fixing the number of holes of zero length represents no constraint at all.

Equation (23) indicates that in the non-internally-constrained system the equilibrium number of holes goes to zero only when the system is close packed, i.e., when $L = Na$. In contrast Eq. (22) shows that, in the internally constrained system, setting $h = 0$ does not lead to an average value of L equal to Na. Instead with $h = 0$, $L = 3Na/2$. Expressed in another way, Eq. (22) states that when the number of holes in the internally constrained system vanishes, the system has a density smaller than the close-packing density.

It is natural to inquire into the thermodynamic properties of an ensemble in which *both* the number of holes and the length are constrained. To accomplish this Ω in Eq. (5) must be maximized subject to N, $\mathscr{L}$, and h being held constant in Eqs. (6), (7), and (8). When this is done, the form of $g_{n\lambda} u$ is given by

$$g_{n\lambda} u = K'' \alpha_1^\lambda \beta_1^n \tag{27}$$

in which K'', α_1, and β_1 are to be determined by substituting Eq. (27) into Eqs. (6), (7), and (8). Once again the various sums are geometric series, and we find

$$N = K'' \frac{\alpha_1^{\omega+1}}{1 - \beta_1 \alpha_1^\omega} \frac{1 - \alpha_1^\omega}{1 - \alpha_1} \tag{28}$$

$$\mathcal{L} = \frac{K'' \alpha_1^{\omega+1}(1 - \alpha_1^\omega)}{(1 - \alpha_1)(1 - \beta_1 \alpha_1^\omega)} \left[\frac{1}{1 - \alpha_1} + \frac{\omega(1 - 2\alpha_1^\omega)}{1 - \alpha_1^\omega} + \frac{\omega\beta_1\alpha_1^\omega}{1 - \beta_1\alpha_1^\omega} \right] \tag{29}$$

$$h = K''\beta_1 \left(\frac{\alpha_1^\omega}{1 - \beta_1\alpha_1^\omega} \right)^2 \frac{1 - \alpha_1^\omega}{1 - \alpha_1} \alpha_1 \tag{30}$$

Dividing Eq. (30) by Eq. (28) yields

$$\frac{h}{N} = \frac{\beta_1\alpha_1^\omega}{1 - \beta_1\alpha_1^\omega} \tag{31}$$

Now we wish to pass to the continuum so that ω becomes infinite. From Eq. (31), we see that, in this limit, α_1 must be only infinitesimally different from unity unless h is zero. Thus once again we are forced to write an equation like Eq. (12), namely,

$$\alpha_1 = 1 - \varepsilon_1 \to 1 \tag{32}$$

in which ε_1 is infinitesimal. Furthermore, we obtain, similar to Eq. (13),

$$\alpha_1^\omega = (1 - \varepsilon_1)^\omega = e^{-\phi} \tag{33}$$

where

$$\phi = \varepsilon_1 \omega \tag{34}$$

Using Eqs. (33) and (34) in Eqs. (28), (29), and (30) we can solve simultaneously for α_1, β_1, and K''. These parameters may be substituted into Eq. (27) to yield for $g_{n\lambda}$ the result

$$g_{n\lambda} = \frac{N^2}{ha} \frac{\phi}{1 - e^{-\phi}} \left(\frac{he^\phi}{N + h} \right)^{n+1} e^{-\lambda\phi/\omega} \tag{35}$$

in which it is understood that λ satisfies Eq. (4). It is convenient to write Eq. (35) in terms of $l = \lambda u$ where l has the dimensions of length. We obtain

$$g_{nl} = \frac{N^2}{ha} \frac{\phi}{1 - e^{-\phi}} \left(\frac{he^\phi}{N + h} \right)^{n+1} e^{-l\phi/a} \tag{36}$$

As a result of the simultaneous solutions of Eqs. (28), (29), and (30) we find that ϕ is determined by the following relation:

$$\frac{1}{\phi} - \frac{1}{e^{\phi} - 1} = \frac{L}{Na} - \frac{N+h}{N} = \bar{Q} \tag{37}$$

where we have defined a quantity $\bar{Q}$ in an obvious manner. From Eq. (37), it is clear that ϕ has the following bounds,

$$-\infty \leqslant \phi \leqslant \infty \tag{38}$$

The upper bound being realized when $\bar{Q} = 0$, and the lower bound when $\bar{Q} = 1$. When $\bar{Q} = 0.5$, ϕ is equal to zero. The limit $\bar{Q} = 1$ is characterized by the relation

$$L = a(2N + h) \tag{39}$$

While the limit $\bar{Q} = 0$ corresponds to

$$L = a(N + h) \tag{40}$$

Equation (40) implies that "holes" and rods are "close packed." One way of achieving Eq. (39) is to consider a configuration in which "holes" are "close packed" while each rod is allowed to wander through a free volume of length $2a$. We shall have more to say about these relations later.

3. VARIOUS ASPECTS OF THERMODYNAMIC BEHAVIOR

We first investigate (for the one-dimensional hard-rod system) the relation between the equilibrium number of holes and the probability of finding at least one hole at a particular location in the system. The latter probability is simply the probability of finding a space of length greater than $2a$ between two rods, and has been calculated by Helfand, Frisch, and Lebowitz.[14] These authors show that the probability P_0 of having such a space is

$$P_0 = (1 - \rho a)\, e^{-\rho a/(1-\rho a)} \tag{41}$$

in which ρ is N/L. Expressing $\langle h \rangle$ in Eq. (23) in terms of ρ, and comparing the result with Eq. (41) we find

$$\langle h \rangle = \frac{L\rho}{(1 - \rho a)(1 - e^{-\rho a/(1-\rho a)})}\, P_0 \tag{42}$$

From this equation it is evident that (not unexpectedly) h is not directly proportional to P_0. Occasionally, the assumption of such proportionality has been made in the development of hole theories of fluids.

In the limit of vanishing density, ρ, Eq. (42) reduces to

$$\langle h \rangle = \frac{L}{a} P_0 \qquad (43)$$

so that, in this limit, proportional behavior occurs. The quantity L/a can be given the following interpretation. If "holes" and rods are considered to be close packed, then L/a becomes the sum of the number of rods and holes, or the number of lattice cells in a lattice model in which the total number of sites is equal to the sum of the numbers of rods and holes. In this interpretation, the hole reduces to a lattice vacancy and P_0 is simply the mole fraction of vacancies.

Unfortunately, one cannot generalize Eq. (42) to the three-dimensional case. It it were possible to do so, we would have a well-defined (in the sense mentioned earlier) method for approximating the equilibrium number of holes, since well-defined methods exist for approximating P_0.

Although the "hole" may not be regarded as an ordinary solute species engaging in *short-range* interaction with the hard rods (because "holes" are not allowed to perturb the configuration of the hard rods), it is nevertheless a component of the "solution." It is therefore possible to express the Helmholtz free energy of the system as a function of the number of holes, and to calculate the chemical potential of a hole. The canonical ensemble partition function for the system may be expressed as

$$Q(N, h, L, T) = \frac{1}{\Lambda^N N!} \frac{N! \, u^N}{\prod_n \prod_\lambda (g_{n\lambda} u)!} \qquad (44)$$

where the quantity, in parentheses on the right, is the configuration integral, and the products over n and λ are subject to the constraints embodied in Eqs. (6), (7), and (8). Λ is the usual de Broglie wavelength and depends only upon the temperature, T. The Helmholtz free energy is obtained in the conventional manner as

$$A = -k_B T \ln Q \qquad (45)$$

where k_B is the Boltzmann constant. The chemical potential of a hole is then

$$\mu_h = \left(\frac{\partial A}{\partial h} \right)_{N,T,L} \qquad (46)$$

Substitution of Eq. (44) into Eq. (45), and the result into Eq. (46) gives

$$\mu_h = k_b T\phi + k_b T \ln \frac{h}{N+h} \qquad (47)$$

In arriving at Eq. (47), by this method, it is necessary to use Eqs. (35) and (37). If we denote the mole fraction of the holes by

$$X_h = \frac{h}{N+h} \qquad (48)$$

Eq. (47) may be written in the form

$$\mu_h = k_B \ln(e^\phi) X_h \qquad (49)$$

from which it is apparent e^ϕ plays the role of an activity coefficient for holes, and that the chemical potential in the standard state to which we refer is zero.

If we do not constrain the number of holes in the system, the equilibrium number can be obtained from the relation

$$\left(\frac{\partial A}{\partial h}\right)_{N,T,L} = 0 \qquad (50)$$

Comparison with Eq. (46) then indicates that the state achieved when the number of holes is unconstrained has

$$\mu_h \ (h \text{ not constrained}) = 0 \qquad (51)$$

Thus, according to the discussion following Eq. (49), the standard state to which reference is made in that equation is the state in which the number of holes is not constrained. Setting $\mu_h = 0$ in Eq. (49) leads to the result

$$\phi = \ln \frac{N + \langle h \rangle}{\langle h \rangle} = \frac{N}{L/a - N} = \xi \qquad (52)$$

where Eq. (37) has again been used in arriving at the third member of this equation. Solving Eq. (52) for $\langle h \rangle$ gives Eq. (18) so that we do indeed recover the correct result for the equilibrium number of holes when that number is not constrained.

Equation (52) shows that as the system becomes close packed ϕ does not become constant. Thus, in spite of the dilution of the holes they do not behave as ideal solutes.

We can also write the expression for the pressure of the system when the number of holes is fixed at h. Again, we first evaluate the Helmholtz free energy by employing Eqs. (35), (44), and (45). Then the pressure is given by

$$p = -\left(\frac{\partial A}{\partial L}\right)_{h,N,T} \tag{53}$$

Evaluating the derivative in Eq. (53), again making use of Eq. (37), we find

$$p = \frac{k_B T \phi}{a} \tag{54}$$

from which it is evident that ϕ is proportional to the compressibility factor Z. In fact we have

$$\phi = \frac{Na}{L} Z = \rho a Z \tag{55}$$

Since, according to Eq. (38), ϕ can be either positive or negative, Eq. (54) indicates that the pressure can be either positive or negative, i.e., when ϕ is negative the pressure actually represents a tension causing the system to contract.

From this point of view, the hard-rod system with a fixed number of holes behaves somewhat like a one-dimensional polymer molecule. However, the forces holding the system together are not due to nearest-neighbor "backbone" connections, but rather to a more subtle long-range interaction embodied in the requirement that only configurations consistent with the fixed number of holes are permissible.

These considerations dealing with the chemical potential and the pressure, lead us naturally toward investigation of the *allowable* "space" of the thermodynamic variables of the system. This study is facilitated by Eq. (37). It is also convenient to introduce a parameter $\theta = h/N$ which is a reduced number of holes. Equation (37) allows us to construct Fig. 1 in which ρa is plotted versus θ for values of $\bar{Q} = 0$, 0.5, and 1.0, respectively (solid curves). The region lying between the curves for $\bar{Q}$ corresponding to 0 and 1.0, respectively, represents the permissible thermodynamic space for the system. Points lying above the curve for $\bar{Q} = 0$ correspond to states in which the rods and the required fixed number of holes would have to be more than close packed; an impossibility if the number of holes is to remain fixed. Points lying below the curve for which $\bar{Q} = 1.0$ represent states in which the fixed number of holes would have to be exceeded. The curve for $\bar{Q} = 0.5$ corresponds to the situation in which $\phi = 0$. According to
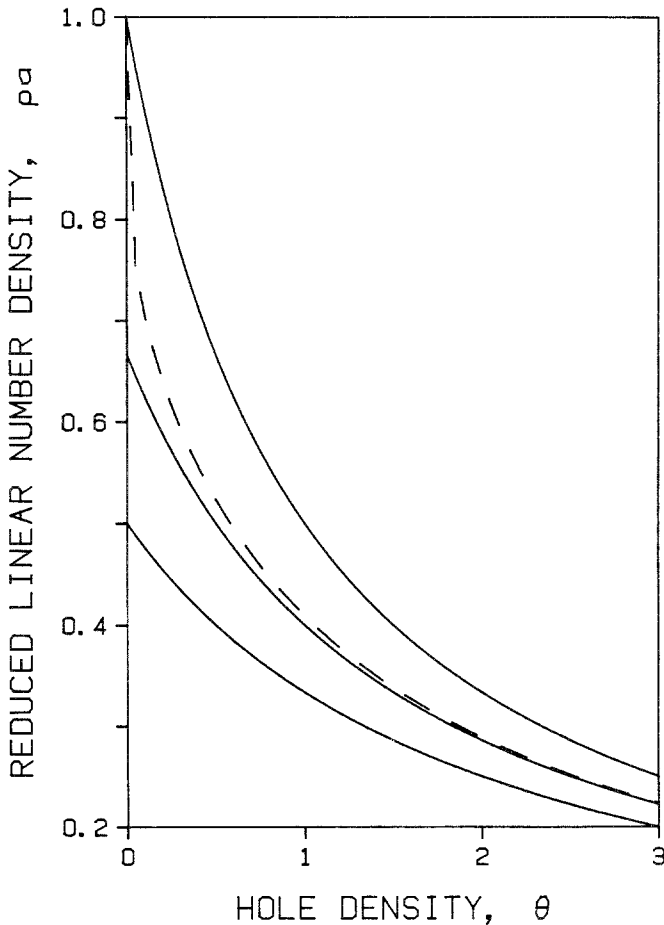
Fig. 1. Allowable space of the thermodynamic variables for a hard-rod system with holes and density constrained. The solid curves represent values of $\bar{Q} = 0$, 0.5, and 1.0, respectively, from top to bottom. For comparison, the dashed curve represents a system where the number of holes is not fixed, though the density is.

Eq. (49), the activity coefficient of holes is unity along this curve, and the system behaves as an ideal solution of holes. Furthermore according to Eq. (54) the pressure is zero along this curve; the system exerts neither contractive nor expansive forces.

The dashed curve is a plot of ρa versus θ for a system in which the number of holes is not constrained, i.e., it is a plot of Eq. (23). We see that the plot for the unconstrained system lies above the curve for $\bar{Q} = 0.5$ but very close to it, except when $\theta = 0$, in which case it joins the "close packed" curve corresponding to $\bar{Q} = 0$.

The region lying below the curve for $\bar{Q} = 0.5$ corresponds to negative pressure and the system exhibits a tendency to contract. When the number of holes is unconstrained (dashed curve), the hole content can only vanish when $\rho a = 1.0$, i.e., when the rods are close packed. However, this is clearly not true when $\bar{Q}$ is constrained to be greater than zero. For example, when $\bar{Q}$ is constrained to be 0.5, Figure 1 shows that the hole content vanishes when ρa is in the neighborhood of 0.67.

Figure 2 is a plot of the free energy surface derived from Eq. (45) (the appropriate substitutions having been made) as a function of θ and $1/\rho a$. In this plot the free energy corresponding to kinetic energy is ignored, since for hard rods it depends only on temperature, and not on configuration. To
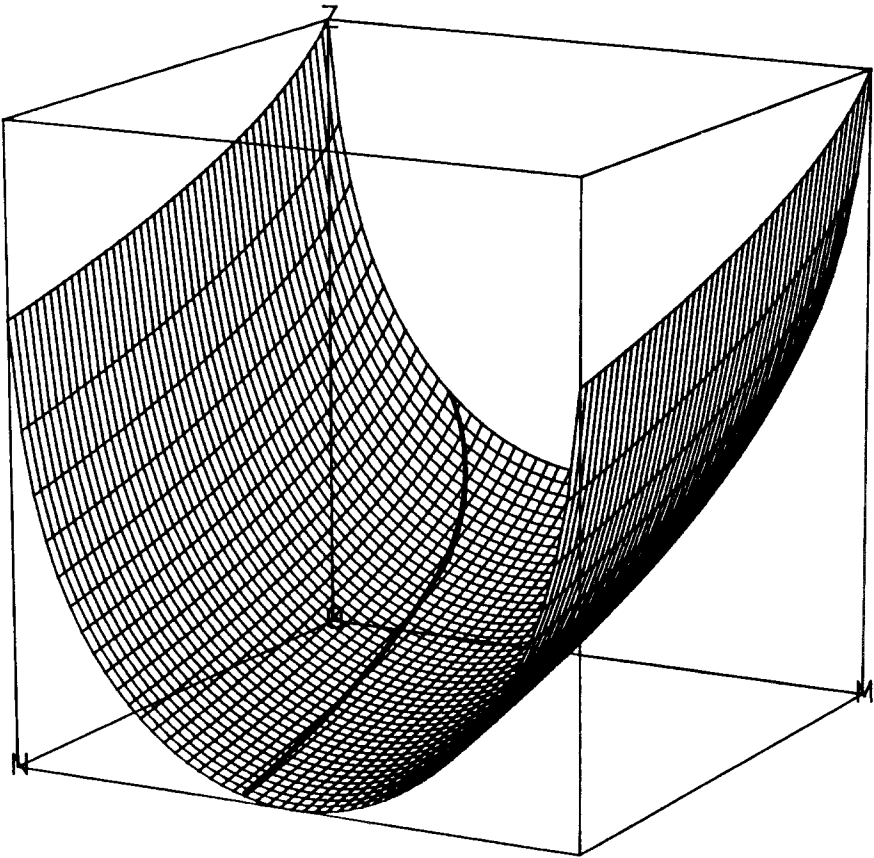

Fig. 2.   Free energy surface for the constrained system rotated clockwise through 45° in the θ, $1/\rho a$ plane; $(N, M) = (1/\rho a + \theta, 1/\rho a - \theta)$. The solid line denotes the free energy of the unconstrained system.

facilitate a three-dimensional drawing, the surface was rotated clockwise through $45°$ in the θ, $1/\rho a$ plane. Hence the N dimension of the figure corresponds to $1/\rho a + \theta$ and the M dimension to $1/\rho a - \theta$. From the figure it can be seen that when θ is maintained constant (equivalent to constant N), the minimum free energy occurs at values of density corresponding to the curve for $\bar{Q} = 0.5$, i.e., at the points where the pressure is zero. On the rotated surface these points are defined by $M = 1/\rho a - \theta = 1.5$. On the other hand when ρa is held constant the minimum occurs at a value of θ corresponding to the dashed curve of Fig. 1, i.e., the hole content is that which is normal for the unconstrained system. The loci of points corresponding to the unconstrained system is denoted by the smooth curve on the rotated free energy surface. This surface is best viewed in conjunction with the following figure.

Figure 3 is the pressure surface given by Eq. (54), plotted as a function of θ and $1/\rho a$. The same rotation matrix was employed as for Fig. 2 and the perspective view is also identical. Hence the depicted surface corresponds to the transformation $(\theta, \rho a) \rightarrow (1/\rho a + \theta, 1/\rho a - \theta) = (N, M)$. The figure clearly shows the pressure range of $+\infty$ on the left where $\bar{Q} = 0$ and $M = 1$ to $-\infty$ on the right where $\bar{Q} = 1$ and $M = 2$. A straight line through the middle of the surface parallel to the N axis at $M = 1.5$ defines those states where the pressure is zero ($\bar{Q} = 0.5$). The smooth curve on the surface indicates the allowed values of pressure for the unconstrained system.

Figure 4 is a schematic expanded version of a portion of the region in Fig. 1 lying between the curves for $\bar{Q} = 0$ and $\bar{Q} = 0.5$. We show portions of these two curves as well as the dashed curve corresponding to the unconstrained system. If the system is constrained initially, we have a fixed number of holes such that its state lies at point 1 on the curve for $\bar{Q} = 0.5$, then its average density will be fixed at the value of ρa prescribed by point 1. The fluctuation in this average density can be ignored in the thermodynamic limit, so that if we now fix the length L of the system to correspond to this average density, such fixing will not represent the imposition of an additional constraint. If we then release the constraint on the number of holes, the system will decrease its free energy and move to point 2 on the dashed curve where the hole content will adopt an average value corresponding to that of an unconstrained system of length L. Now the hole content can fluctuate. However, again, in the thermodynamic limit, such fluctuations will be negligible. We can then reimpose a constraint on the number of holes maintaining that number exactly at the value corresponding to point 2. Again this represents no additional constraint. At this point, we are able to lift the constraint on the density (of the length) of the system, and it will decrease its free energy and move to point 3. By a similar sequence of steps it can be carried to points 4 and 5 in succession.
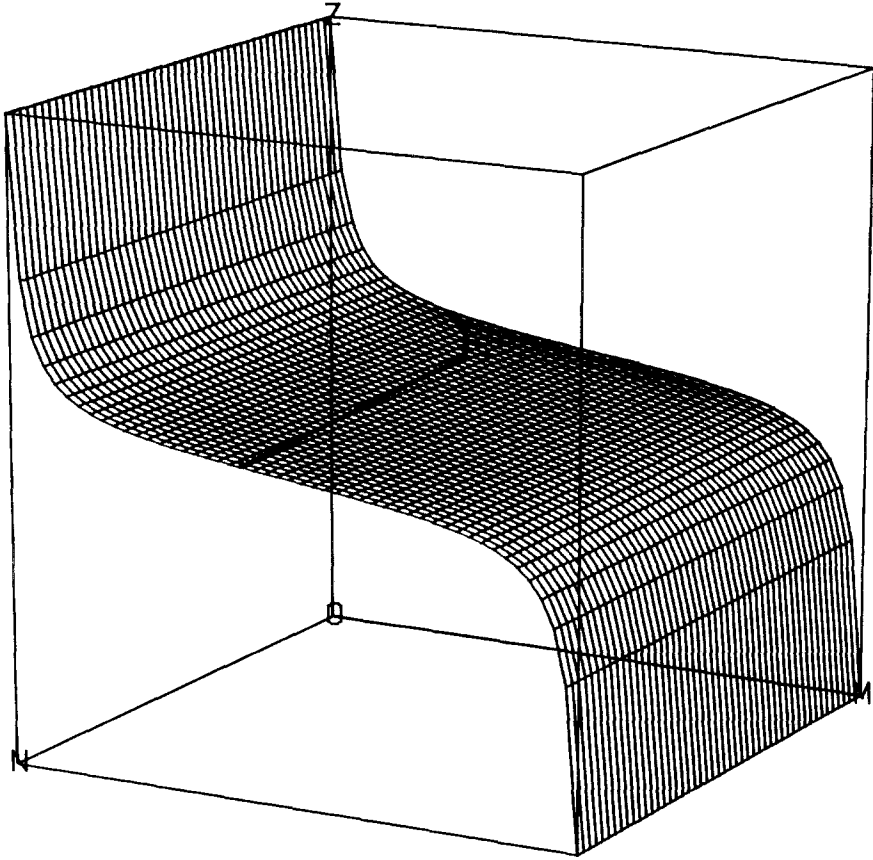
Fig. 3. Pressure surface for the constrained system with perspective view parameters identical with those of Fig. 2. The pressure variation of the unconstrained system is shown as the solid line.

We thus see that, ultimately lifting the constraints on the number of holes and the length of the system, leads to a continued expansion, and with it, an increase in the number of holes. Ultimately the system follows the curve $\bar{Q} = 0.5$ to infinite length. Lifting the constraint on the number of holes leads to an increase in hole content, while imposing a constraint on the number of holes and lifting the constraint on the length leads to the expansion. However, the expansion is always bounded by the curve for which $\bar{Q} = 0.5$. Below this curve a tensile force would be required in order to cause further expansion. Lifting a constraint, always increases the entropy, as it should.
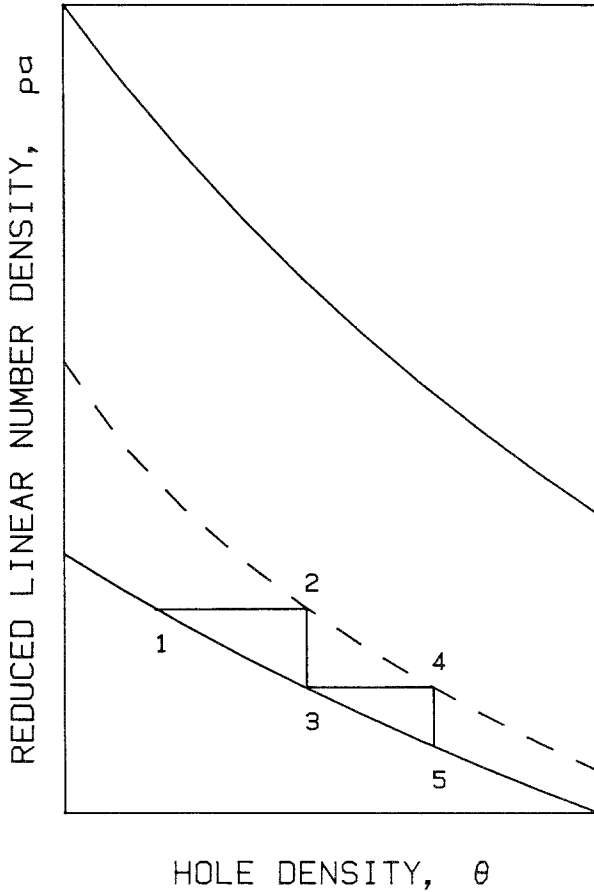
Fig. 4.   Response of the constrained system to a sequential removal of constraints placed
upon the number of holes then upon the density.

4. INTERNAL STRUCTURE

It is useful to employ our development to investigate aspects of the structure of the hard-rod fluid, and especially to note the effect of "holes on the structure." Ultimately this analysis will be useful in connection with the nonequilibrium behavior of the pair correlation function for hard rods. To this end, we will concentrate on characterizing the structure using both the nearest-neighbor   distribution   functions,   and   the   conventional   pair correlation function.

In fact, we have already derived the nearest-neighbor distribution function in Eq. (36). If that equation is divided by N it becomes the

probability density $P_1(l)$ for the nearest neighbor to a given rod. This follows from the fact that l represents a space between the centers of two adjoining rods, and that g_{nl} when divided by N gives the probability density for the distribution of l which is the same as the distribution of nearest neighbors. In discussing the distribution function we find it convenient to use x in place of l. Then, according to what has been said, the nearest-neighbor distribution function is given by

$$P_1(x)\, dx = \frac{N}{ha}\frac{\phi}{1 - e^{-\phi}}\left(\frac{he^{\phi}}{N + h}\right)^{n+1} e^{-x\phi/a}\, dx, \qquad (n+1)a < x \leqslant (n+2)a$$

$$(56)$$

where the limitation on the range of x originates in the condition, Eq. (4). Thus, $P_1(x)\, dx$ which represents the probability that the nearest neighbor will be found at x, in the interval dx, is a piecewise function in the sense that when x lies between a and $2a$ the exponent $n+1$ in the equation is unity. When x lies between $2a$ and $3a$ the exponent is 2, etc. However, in the special case that h is unconstrained, i.e., when h is given by Eq. (18), and ϕ, according to Eq. (52), is identical with ξ given by Eq. (15), then it is easy to show that the factor being raised to the power in question in Eq. (56) is unity. In fact, for this case in which the number of holes is not constrained, it can be shown that

$$P_1(x) = \frac{\rho}{1 - \rho a}\, e^{-(x-a)\rho/(1-\rho a)} \qquad (57)$$

This result follows immediately from Eq. (56) upon setting the above-mentioned factor equal to unity and writing for $\phi = \xi$ the quantity prescribed in Eq. (15). Actually, we can also write Eq. (56) in terms of θ, the reduced number of holes. Thus we find, in place of Eq. (56),

$$P_1(x)\, dx = \frac{1}{a\theta}\frac{\phi}{1 - e^{-\phi}}\left(\frac{\theta e^{\phi}}{1 + \theta}\right)^{n+1} e^{-x\phi/a}\, dx, \qquad (n+1)a < x \leqslant (n+2)a$$

$$(58)$$

The fact that the *unconstrained* system has a continuous nearest-neighbor distribution function, i.e., Eq. (57), while, when the number of holes is *constrained*, the nearest-neighbor function becomes *immediately* discontinuous, indicates the severe and detailed nature of the constraint. Such a constraint would be very difficult to apply or remove, in a *reversible* manner, by any reasonable process. To accomplish a reversible removal, for example, it would be necessary to have a "handle" on almost every molecule (rod) so that the maximum work could be extracted from the system, during removal.

The situation is analogous to that of a mixture of hydrogen and oxygen gases, constrained against reaction by the absence of a catalyst. If, for example, the constraint is removed by introducing a platinum catalyst, the reaction will proceed explosively, irreversibly. The only way to remove the constraint reversibly would be to again have a "handle" on each atom so that they can be "moved around" to allow the extraction of the maximum work.

Thus the system in which the number of holes is constrained resembles a "metastable" one. From the purely thermodynamic point of view there is no difference between metastable and stable equilibrium. The only difference resides in the ability to apply and remove constraints *reversibly*. However, thermodynamics is not concerned with the history of a system, and, hence, not with the manner in which it became constrained. Reiss has defined those constraints which can be applied reversibly as belonging to "class 1" while those which cannot be so applied belong to "class 2."[15]

Using Eq. (58) it is possible to prescribe the distribution function for the *second nearest* neighbor. The almost obvious result, which we denote by $P_2(x)$, is

$$P_2(x) = \int_a^{x-a} P_1(x-x')\,P_1(x')\,dx', \qquad x > 2a$$

$$= 0, \qquad\qquad\qquad\qquad\qquad x \leqslant 2a \tag{59}$$

In general for the jth nearest neighbor, whose distribution we denote by $P_j(x)$, we have

$$P_j(x) = \int_{(j-1)a}^{x-a} P_1(x-x')\,P_{j-1}(x')\,dx', \qquad x > ja$$

$$= 0, \qquad\qquad\qquad\qquad\qquad\qquad x \leqslant ja \tag{60}$$

By repeated application of the convolution theorem for the Laplace transform to the relation, Eq. (60), we find that

$$P_j(t + ja) = \mathscr{L}^{-1}\{\mathscr{L}[P_1(t+a)]^j\} \tag{61}$$

in which $\mathscr{L}$ signifies the Laplace transform while $\mathscr{L}^{-1}$ represents the inverse transform [$\mathscr{L}$ should not be confused with the quantity introduced in Eq. (3)], and where

$$\mathscr{L}\{P_1(t+a)\} = \int_0^{\infty} e^{-st} P_1(t+a)\,dt \tag{62}$$

in which s is the transform variable. It is frequently more convenient to derive the formula for the distribution of the jth nearest neighbor by

repeated numerical application of Eq. (60) rather than by invoking the method of the Laplace transform.

The conventional pair correlation function $g(x)$ is given by

$$\rho g(x) = \sum_{j=1}^{\infty} P_j(x) \tag{63}$$

We have evaluated $g(x)$ for a variety of system states. Use has been made of Eq. (63) in which the various $P_j(x)$ are determined by the repeated numerical application of Eq. (60), as indicated above. Figures 5–8 exhibit selected examples of these evaluations. In all of these figures $\theta = 1$ (but, in Fig. 5, h is not constrained so that only $\langle \theta \rangle$, the average θ, is set at unity), and the fluid is reasonably dense. In the figures we plot $g(x)$ versus x/a.

Figure 5 corresponds to the case in which h is unconstrained and in which $\rho a = 0.409384$. In generating the figure, P_1 from Eq. (57) was employed. The result is identical with the hard-rod pair correlation function, derived previously by several other means.[16]

Figures 6–8 are examples of the pair correlation function for situations in which h is constrained, i.e., θ, and not $\langle \theta \rangle$, is set to unity. The dramatic effects of this constraint are graphically apparent. In Fig. 6 we illustrate a case for which $\phi = 0.371220$, so that the system exhibits normal *positive*
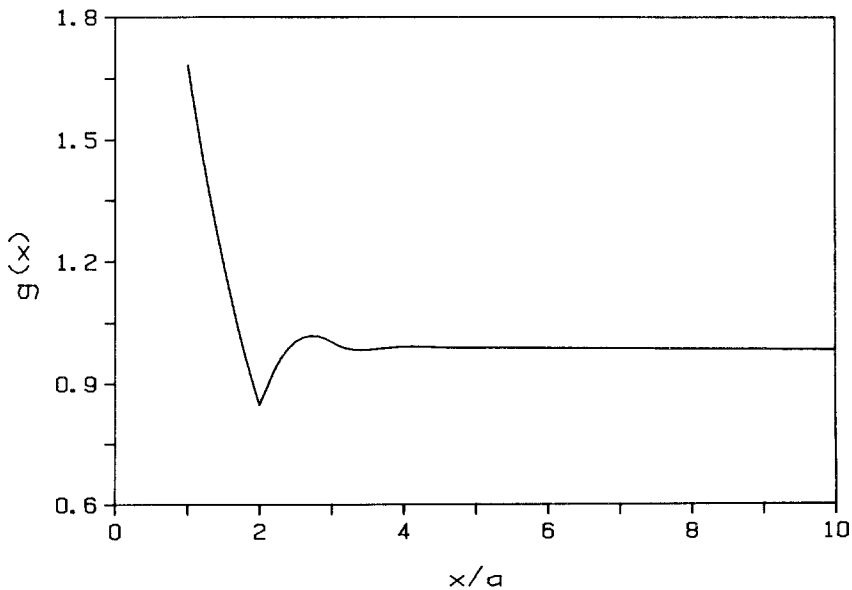

Fig. 5. Pair correlation function for the unconstrained system of hard rods where $\rho a = 0.409384$ and $\langle \theta \rangle = 1$.
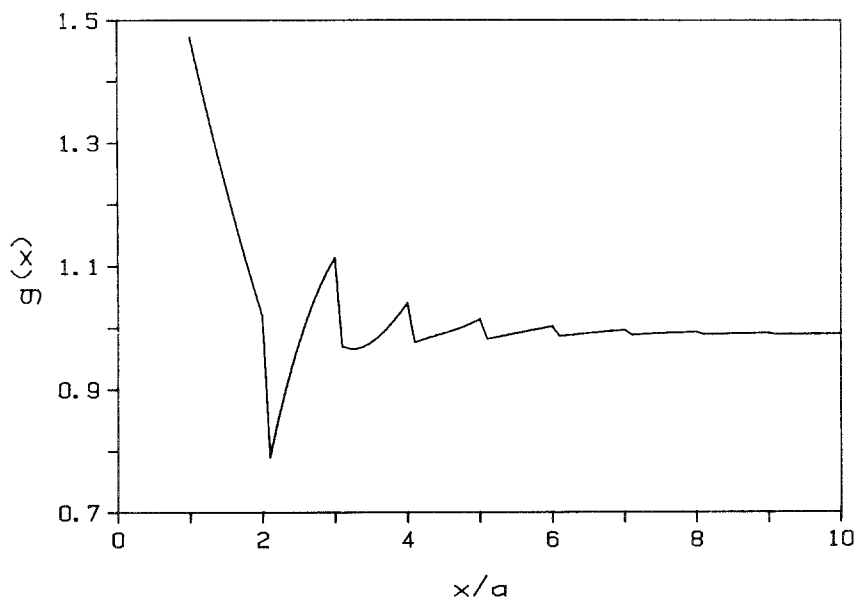
Fig. 6.   Pair correlation function for the constrained system, where $\rho a = 0.405$ and $\theta = 1$, indicative of positive pressure; $\phi = 0.371220$.
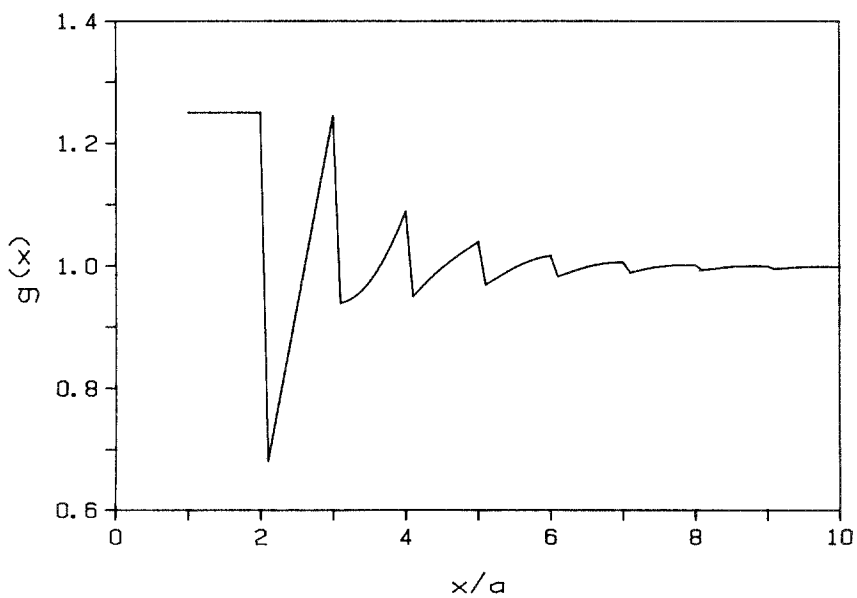

Fig. 7.   Pair correlation function for the constrained system, where $\rho a = 0.4$ and $\theta = 1$, when the pressure is zero; $\phi = 0$.
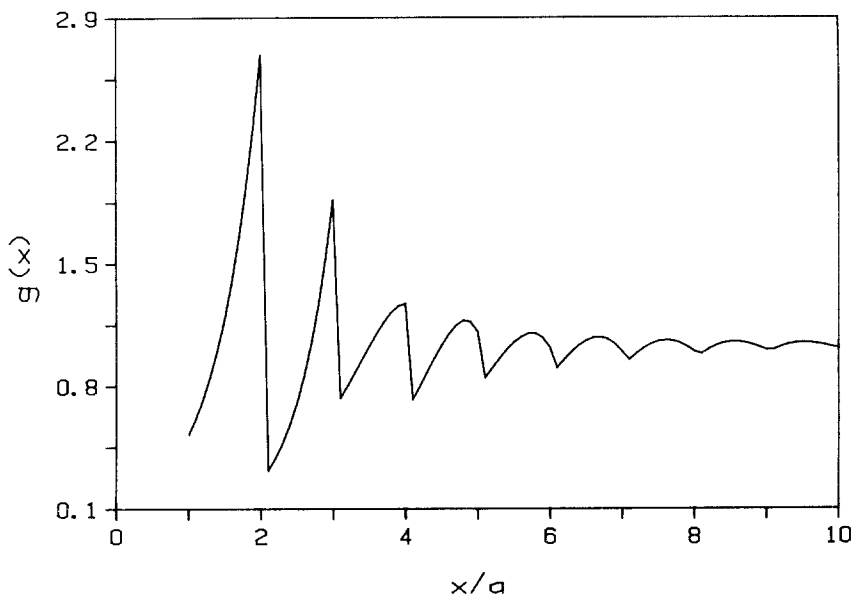
Fig. 8.   Pair correlation function for the constrained system, where $\rho a = 0.38$ and $\theta = 1$, for a case of negative pressure; $\phi = -1.64917$.

pressure. The correlation function begins in the same fashion as the unconstrained one in Fig. 5, but beyond $x/a = 2$, it exhibits pronounced saw toothlike oscillations with a period of $\Delta x = a$. The discontinuities in the first derivative of $g(x)$ are connected to the range discontinuities, specified in Eq. (56).

Figure 7 exhibits an example with $\phi = 0$, i.e., with zero pressure. Here again we see the saw tooth oscillations and discontinuities, but we note that $g(x)$ for $x < 2a$ has zero slope. Thus there is *no* mean force between rods spaced within this interval. This is not surprising for a system which exhibits neither expansive or compressive tendencies.

Figure 8, finally, shows a case with $\phi = -1.64917$. This, of course, corresponds to a negative pressure, and the system tends to contract. Again we note the discontinuities in slope. However now $g(x)$ commences with a *positive* slope, indicating an *attractive* mean force. In Fig. 6, corresponding to positive pressure ($\phi > 0$) the initial slope is negative, corresponding to a repulsive *mean* force.

One might ask whether any derivative of pressure with respect to ϕ, at fixed h, shows a discontinuity at $\phi = 0$, indicating a higher-order phase transition. Investigation of this point, however, shows that there are no such discontinuities.

5. SUMMARY

We have introduced a well-defined structural entity which we refer to as a "hole" in a one-dimensional fluid of hard rods. These "holes" may be treated as thermodynamic species, and we derive the equilibrium concentration of holes as a function of fluid density.

The concentration of holes is a thermodynamic variable and it is possible to investigate an ensemble in which this concentration is maintained fixed while the density of the fluid is allowed to fluctuate. It turns out that there is poor correspondence between the properties of systems in which, on the one hand, holes are allowed to fluctuate and density is held fixed and, on the other hand, density is allowed to fluctuate but holes are held fixed. Thus the possible use of the "internally constrained" ensemble in which the concentration of holes is fixed, in place of the usual ensemble in which density is fixed, is compromised.

The ensemble in which *both* holes and density are constrained is also developed. This ensemble exhibits *both* expansive and contractive behavior, i.e., positive and negative pressures.

The "thermodynamics" of the rigorously defined holes is investigated. In particular, when the concentration of holes is unconstrained, the chemical potential of the hole is zero. Furthermore, at high densities, when the concentration of holes is small, the system assumes an increasingly latticelike character. However, the holes never form an ideal dilute solution; the potentials of mean force become apparently of infinite range!

The equilibrium concentration of holes is *never* proportional to the probability of finding a *single* hole in the fluid, an assumption which has been made frequently in the past.

The internal structure of the fluid in which the concentration of holes is constrained is investigated. Fixing the number of holes has a dramatic effect on the pair correlation function, giving rise to discontinuities in slope.

It would be interesting, and probably very useful, to develop a *rigorous* three-dimensional theory of holes. However, we have not yet been able to accomplish this.

ACKNOWLEDGMENT

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