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Explicit Relations for the Radial Distribution Functions for One-Dimensional Lattice (Arbitrary Spacing) Fluids and Solutions

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It is pointed out that the size of the matrix required to formulate the grand partition function for a one-dimensional lattice fluid for a fixed and finite range of the interatomic potential varies linearly with the density of lattice points used and hence is much smaller and more manageable than the expected size (which varies exponentially with the same quantity) and thus allows very fine grids to be examined. Using the matrix treatment of the grand partition function, it is shown that the radial distribution function for a one-dimensional fluid or solution can be formulated as an explicit matrix product which is simply performed by computer. The resulting distribution functions (which can be extrapolated to the continuum by varying the lattice spacing) are useful as starting solutions for the iterative solution of integral equations for three-dimensional fluids.

KEY WORDS: Radial distribution function; lattice solution; one-dimensional; matrix formulation.

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1. GRAND PARTITION FUNCTION FOR A ONE-DIMENSIONAL LATTICE FLUID

Several years ago, working on the matrix formulation of the conformational partition function for nucleic acids,(1,2) the author noticed that if a simple translation of symbols was made (like the translation magnet to lattice gas), a simple version of the nucleic acid partition function became the grand partition function (g.p.f.) for a one-dimensional lattice fluid. One of the main results of that work was that the size of the matrix required to treat the nucleic acid model was very much smaller than at first sight seemed necessary, and hence the same was true for the lattice fluid. The upshot was that it became practical to treat very fine grids of lattice points (i.e., the lattice spacing much smaller than the size of a particle and, by examining the properties as a function of lattice spacing, extrapolate to the continuum. Since the matrix products are much easier to handle than the integral equations that result from a continuum treatment, and, for fine enough grids, the two yield the same result, we present here the matrix treatment. The formulation of the g.p.f. for a one-dimensional lattice fluid has been discussed briefly in connection with helix-coil transitions in biopolymers (Ref. 2, Chapter 10). In this work, we review the construction of the g.p.f. and then turn in more detail to the derivation of explicit formulas for the radial distribution functions of one-dimensional fluids and solutions and display some numerical results.

For explicitness, we consider a short-range (e.g., Lennard-Jones or Buckingham) interatomic potential $\phi(r)$ which has a minimum at r_0, where we truncate the potential at a distance $2r_0$

$$\phi(r) = 0, \qquad r \geqslant 2r_0 \tag{1}$$

Equation (1) implies that the total energy of the one-dimensional system can be calculated as a sum of pair interactions between nearest neighbors (since a more distant neighbor cannot come significantly closer to an atom than $2r_0$); the short range of the potential and specifically Eq. (1), while introduced to simplify the discussion and the resulting formulas, are not necessary to proceed and can be considerably relaxed without losing workability (truncation of short-range potentials has been shown to influence critical parameters in three dimensions,(3) a worry we do not have in one dimension). We introduce a lattice spacing parameter δ, which is the inverse of the number of fragments into which the distance r_0 is divided; δ can vary from one to zero, the latter being the continuum limit. The number of pieces into which the distance $2r_0$ is divided is designated n_0,

$$n_0 = 2/\delta \tag{2}$$

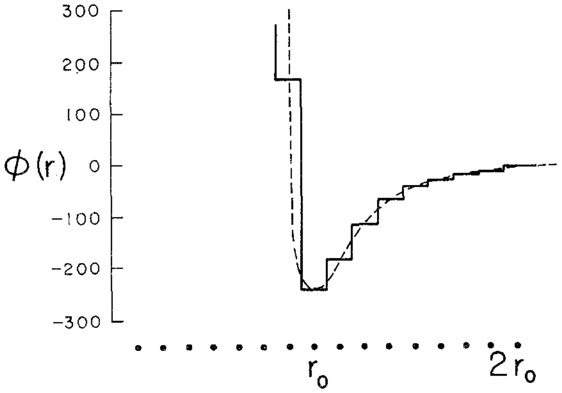

Fig. 1. Argon potential. The dotted curve shows the continuous potential, while the solid curve shows the lattice potential for $\delta = 1/8$; energy in cal/mole, distance in angstroms.

The smooth potential $\phi(r)$ thus is divided into a series of n_0 steps $\phi(n)$; this is illustrated in Fig. 1 for $\delta = 1/8$ for a potential characteristic of argon [see Eq. (46)]. We next introduce Boltzmann factors q_n,

$$\begin{aligned} q_n &= e^{-\phi_n/kT}, \qquad 0 < n < n_0 \\ &= 1 \qquad\qquad\quad n \geqslant n_0 = 2/\delta \end{aligned} \tag{3}$$

Now, each lattice site can either be occupied by a particle or not, a dichotomy we represent by assigning a "1" or "0," respectively, to sites with particles and with holes. The state of the lattice thus is given by a vector whose components are occupation numbers (1 or 0); the factors q_n are assigned depending on the number of zeros between successive 1's, as illustrated below:

$$\ldots 0\ 1\ \overbrace{0\ 0\ 0\ 0\ 0}^{q_6}\ 1\ \overbrace{0\ 0}^{q_3}\ 1\ 0 \ldots$$

We note from the above example that the state of the lattice is characterized by N sequences of zeros, where N is the total number of particles on the lattice. If we number the sequences, letting σ be an index, then the canonical partition function is given by a sum over all possible values of the sizes n_σ of the N sequences,

$$Z(M, N, T, \delta) = \sum_{n_\sigma} \prod_{\sigma=1}^{N} \delta q_{n_\sigma}/\Lambda = e^{-\beta F} \tag{4}$$

where M is the number of lattice sites ($M = L/\delta$ if L, the length of the lattice, is neasured in units of r_0), $\beta = 1/kT$, and Λ has the usual meaning (the one-dimensional integral over the momentum; the factor δ arises from integration of the coordinate over the interval δ). The following constraints accompany Eq. (4):

$$\sum_{\sigma=1}^{N} n_\sigma = M = \text{const} \qquad N = \text{const} \tag{5}$$

Since the constraints of (5) make life difficult, we pass to the g.p.f.:

$$\begin{aligned}\Xi(M, T, \mu, \delta) &= \sum_{N=0}^{M} Z(M, N, T, \delta)\, e^{\beta N \mu} \\ &= \sum_{N=0}^{M} \sum_{n_\sigma} \prod_{\sigma=1}^{N} y q_{n_\sigma} \qquad (y = \delta e^{\beta\mu}/\Lambda) \\ &= e^{\beta p L} = e^{\beta p M \delta}\end{aligned} \tag{6}$$

where y is the (slightly doctored) fugacity, p is the pressure (for one dimension), μ is the chemical potential, and L is the length of the lattice [see remarks preceding Eqs. (5)]. Equation (6) has a single constraint,

$$\sum_{\sigma=1}^{N} n_\sigma = M = \text{const} \tag{7}$$

which we can eliminate by passing to the generalized partition function:

$$\begin{aligned}Y(T, p, \mu, \delta) &= \sum_{M=0}^{\infty} \Xi(M, T, \mu, \delta)\, e^{-\beta p L} \\ &= \sum_{M=0}^{\infty} \sum_{N=0}^{M} \sum_{n_\sigma} \prod_{\sigma=1}^{N} y q_{n_\sigma}/x^{n}\end{aligned} \tag{8}$$

where

$$x = e^{\beta p \delta} \tag{9}$$

Changing Eq. (8) to a sum over N from zero to infinity and rearranging the order of operations leads to

$$\begin{aligned}Y(T, p, \mu, \delta) &= \sum_{N=0}^{\infty} \left(\sum_{n=1}^{\infty} y q_n / x^n \right)^{N} \\ &= \left(1 - \sum_{n=1}^{\infty} y q_n / x^n \right)^{-1}\end{aligned} \tag{10}$$

For the proper value of x, $\Xi = e^{\beta pL}$ and Y blows up (as it should); this value of x is simply given from the condition that the denominator in Eq. (10) equal zero, i.e.,

$$\sum_{n=1}^{\infty} yq_n/x^n = 1 \tag{11}$$

Since from Eq. (9) x is related to the pressure, Ξ can be expressed in terms of the largest root x_1 of Eq. (11):

$$\Xi = x_1{}^M = e^{\beta pM\delta} \tag{12}$$

where the most probable number of particles, N^*, on the lattice is given by

$$\partial(\ln \Xi)/\partial(\ln y) = N^* \tag{13}$$

giving for the density

$$\rho = (1/\delta)\ \partial(\ln x_1)/\partial(\ln y) \tag{14}$$

where unit density implies a particle every distance r_0 on the lattice. From Eqs. (12) and (14), the equation of state is

$$p/\rho kT = (1/\delta)(\ln x_1)/[\partial(\ln x_1)/\partial(\ln y)] \tag{15}$$

The Helmholtz and Gibbs free energies per particle are

$$\begin{aligned} f &= (1/\beta)[\ln \Lambda + \ln y - (1/\rho\delta) \ln x_1] \\ g &= \mu = f + p/\rho \end{aligned} \tag{16}$$

Thus the study of the thermodynamic properties of a one-dimensional lattice fluid reduces to the use of the simple generating function of Eq. (11). Using Eq. (3), Eq. (11) can further be simplified to

$$y\left\{\sum_{n=1}^{n_0-1} (q_n/x^n) + [1/x^{n_0-1}(x-1)]\right\} = 1 \tag{17}$$

which is seen to be an n_0th-order polynomial in x.

Our model of a one-dimensional fluid may alternatively be formulated as a Markof chain represented as a matrix product. Since we have two states per lattice site (occupied or unoccupied) in our problem, the size of the matrix required to correlate n_0 lattice sites is $2^{n_0-1} \times 2^{n_0-1}$, which, if we divide r_0 into ten parts (i.e., $\delta = 1/10$), gives $n_0 = 20$, or a $2^{19} \times 2^{19}$ matrix, which is very large indeed. However, since both the generating function or matrix product route must lead to the same result, and since

$$\begin{aligned} \Xi &= \mathbf{e}\mathbf{W}^{M}\mathbf{e}^{+} \\ (1/M)\ln \Xi &= \ln \lambda_1 \qquad \text{(for large } M\text{)} \end{aligned} \tag{18}$$

where $\mathbf{W}$ is the matrix of transition probabilities and $\mathbf{e}$ and $\mathbf{e}^{+}$ are end vectors reflecting the desired boundary conditions, and λ_1 is the largest eigenvalue of $\mathbf{W}$, we have [compare Eqs. (18) and (12)] that $\lambda_1 = x_1$ and hence Eq. (17) is the secular equation of the matrix $\mathbf{W}$. We have already noted that Eq. (17) is an n_0th-order polynomial and hence $\mathbf{W}$ can be drastically reduced from $2^{n_0-1} \times 2^{n_0-1}$ to $n_0 \times n_0$ (the reason for this is that the larger matrix contains much more information than is required, e.g., detailed correlation of zeros). The method of reducing $\mathbf{W}$ and its structure have been discussed elsewhere (2, 4); we note here that from linear algebra the matrix of the characteristic polynomial is readily constructed. The structure of $\mathbf{W}$ is as follows:

$$\begin{aligned} w_{1j} &= yq_j\,, & j &= 1, n_0 \\ w_{j+1,j} &= 1 & j &= 1, n_0 - 1 \\ w_{n_0,n_0} &= 1 & & \\ w_{i,j} &= 0 & &\text{all other} \quad i, j \end{aligned} \tag{19}$$

We proceed now to a formulation of the radial distribution function in terms of $\mathbf{W}$.

2. RADIAL DISTRIBUTION FUNCTIONS

In one dimension, it is convenient to introduce the conditional probability $P(1 \mid n \mid 1)$ that an occupied site will be followed by an occupied site n sites away. The radial distribution function then is the ratio of the local density $P(1 \mid n \mid 1)$ to the average site density $\delta\rho$,

$$g(n) = P(1 \mid n \mid 1)/\delta\rho \tag{20}$$

The quantity $P(1 \mid n \mid 1)$ is calculated as the ratio of the g.p.f.'s for the following lattice configurations:

$$\begin{array}{ll} \text{I} & (1) \cdots (1/0)^{n-1} \cdots (1) \cdots (1/0)^{J} \\ \text{II} & (1) \cdots (1/0)^{n+J} \end{array}$$

where configuration I indicates that there is an occupied site, (1), followed by $n - 1$ sites that may be occupied or unoccupied, (1/0), followed by an occupied site, which then is followed by $J\,(1/0)$ sites; configuration II starts with an occupied site followed by $n + J\,(1/0)$ sites. We then have

$$P(1 \mid n \mid 1) = \lim_{J\to\infty} \Xi_{\mathrm{I}}/\Xi_{\mathrm{II}} \tag{21}$$

where lim $J \to \infty$ eliminates end effects. The g.p.f.'s in Eq. (21) are

$$\begin{aligned} \Xi_{\mathrm{I}} &= (\mathbf{e}_1\mathbf{W}^n\mathbf{e}_1{}^+)(\mathbf{e}_1\mathbf{W}^J\mathbf{e}_x{}^+) \\ \Xi_{\mathrm{II}} &= \mathbf{e}_1\mathbf{W}^{n+J}\mathbf{e}_x{}^+ \end{aligned} \tag{22}$$

where **W** is given by Eq. (19) and where the end vectors reflect, and this is of some importance, the specific boundary conditions of the configurations I and II, where in particular, $\mathbf{e}_x{}^+$ means that the last unit can be followed by 1 or 0, and $\mathbf{e}_1$ and $\mathbf{e}_1{}^+$ mean, respectively, that the preceding and following units are 1's. For $J \to \infty$, we have

$$\begin{aligned} \lim_{J\to\infty} \mathbf{e}_1\mathbf{W}^J\mathbf{e}_x{}^+ &= c_1\lambda_1{}^J \\ \lim_{J\to\infty} \mathbf{e}_1\mathbf{W}^{n+J}\mathbf{e}_x{}^+ &= c_1\lambda_1^{J+n} \end{aligned} \tag{23}$$

where λ_1 is the largest eigenvalue and c_1 is a factor arising from the similarity transformation and specific end vectors. Use of Eqs. (22) and (23) in Eq. (21) yields

$$P(1 \mid n \mid 1) = \mathbf{e}_1\mathbf{W}^n\mathbf{e}_1{}^+/\lambda_1{}^n \tag{24}$$

and $g(n)$ from Eq. (20). Expressing Ξ in terms of the eigenvalues of **W**, with the specific boundary conditions

$$\mathbf{e}_1\mathbf{W}^n\mathbf{e}_1{}^+ = \sum_{i=1}^{n_U} c_i\lambda_i{}^n \tag{25}$$

gives

$$P(1 \mid n \mid 1) = \sum_{i=1}^{n_U} c_i(\lambda_i/\lambda_1)^n \tag{26}$$

However, since use of Eq. (26) requires the computation of all the eigenvalues and eigenvectors of **W**, it is much simpler to use Eq. (24) explicitly, i.e., explicitly perform the matrix multiplication (the calculation of the largest eigenvalue is very simple). We note

$$\lim_{J\to\infty} P(1 \mid n \mid 1) = c_1(\lambda_1/\lambda_1)^n = c_1 = \delta\rho \tag{27}$$

The above formulation can easily be extended to treat one-dimensional solutions, i.e., mixtures of several species of arbitrary density. First, we note that the g.p.f. for a solution of two species a and b (generalization to an arbitrary number of species being clear) can be written in terms of the hypermatrix

$$\mathbf{M} = \begin{pmatrix} \mathbf{W}_{aa} & \mathbf{W}_{ab} \\ \mathbf{W}_{ba} & \mathbf{W}_{bb} \end{pmatrix} \tag{28}$$

where $\mathbf{W}_{aa}$ and $\mathbf{W}_{bb}$ have the same structure as given in Eq. (19) (with fugacities y_a and y_b and Boltzmann factors q_{aa} and q_{bb}), while $\mathbf{W}_{ab}$ is given by

$$\begin{aligned} w_{1j} &= y_a q_{ab}(j), & j &= 1, n \\ w_{ij} &= 0, & &\text{all other} \quad i, j \end{aligned} \tag{29}$$

and $\mathbf{W}_{ba}$ by

$$\begin{aligned} w_{1j} &= y_b q_{ba}(j), & j &= 1, n_0 \\ w_{ij} &= 0, & &\text{all other} \quad i, j \end{aligned} \tag{30}$$

The reason the $\mathbf{W}_{ab}$ and $\mathbf{W}_{ba}$ do not contain the off-diagonal run of 1's found in $\mathbf{W}_{aa}$ and $\mathbf{W}_{bb}$ is that this would overcount the possibilities for holes.

To construct, for example, the conditional probability $P(a \mid n \mid b)$ that, given a site occupied by an a particle, it is followed n sites away by a particle b, we consider the two configurations

$$\begin{array}{ll} \text{I} & (a) \cdots (a/b/0)^{n-1} \cdots (b) \cdots (a/b/0)^{J}(a) \\ \text{II} & (a) \cdots (a/b/0)^{n+J}(a) \end{array}$$

where $(a/b/0)$ means that a site can be occupied by a or b, or be unoccupied. Then, proceeding as in the case for a homogeneous fluid, we have

$$\begin{aligned} P(a \mid n \mid b) &= \lim_{J\to\infty} (\Xi_{\text{I}}/\Xi_{\text{II}}) \\ &= \lim_{J\to\infty} (\mathbf{e}_a \mathbf{M}^n \mathbf{e}_b^{+})(\mathbf{e}_b \mathbf{M}^J \mathbf{e}_a^{+})/(\mathbf{e}_a \mathbf{M}^{n+J} \mathbf{e}_a^{+}) \\ &= (c_{ba}/c_{aa})(\mathbf{e}_a \mathbf{M}^n \mathbf{e}_b^{+})/\lambda_1^{\,n} \end{aligned} \tag{31}$$

where again the end vectors reflect the specific boundary conditions of configurations I and II.

To use Eq. (31), we must evaluate the factor c_{ba}. In analogy with Eq. (27), we have

$$\begin{aligned} c_{aa} &= \delta\rho_a = (\ln \lambda_1)[\partial(\ln \lambda_1)/\partial(\ln y_a)] \\ c_{bb} &= \delta\rho_b = (\ln \lambda_1)[\partial(\ln \lambda_1)/\partial(\ln y_b)] \end{aligned} \tag{32}$$

To proceed, we note that the construction and properties of the matrices and end vectors lead to the following relations:

$$y_b \mathbf{e}_a \mathbf{M}^n \mathbf{e}_b{}^+ = y_a \mathbf{e}_b \mathbf{M}^n \mathbf{e}_a{}^+ \tag{33}$$

$$\lim_{n\to\infty} (\mathbf{e}_a \mathbf{M}^n \mathbf{e}_b{}^+)(\mathbf{e}_b \mathbf{M}^n \mathbf{e}_a{}^+)/(\mathbf{e}_a \mathbf{M}^{2n} \mathbf{e}_a{}^+) = \delta \rho_b \tag{34}$$

Combining Eqs. (33) and (34), we have

$$\lim_{n\to\infty} (y_a/y_b)(\mathbf{e}_b \mathbf{M}^n \mathbf{e}_a{}^+)^2/(\mathbf{e}_a \mathbf{M}^{2n} \mathbf{e}_a{}^+) = (y_a c_{ba}^2/y_b c_{aa}) = \delta \rho_b \tag{35}$$

giving

$$c_{ba} = \delta(\rho_a \rho_b y_b/y_a)^{1/2} \tag{36}$$

Thus,

$$\begin{aligned} P(a \mid n \mid b) &= (\rho_b\, y_b/\rho_a\, y_a)^{1/2}(\mathbf{e}_a \mathbf{M}^n \mathbf{e}_b{}^+)/\lambda_1{}^n \\ P(b \mid n \mid a) &= (\rho_a\, y_a/\rho_b\, y_b)^{1/2}(\mathbf{e}_b \mathbf{M}^n \mathbf{e}_a{}^+)/\lambda_1{}^n \end{aligned} \tag{37}$$

where

$$\begin{aligned} \lim_{n\to\infty} P(a \mid n \mid b) &= \delta \rho_b \\ \lim_{n\to\infty} P(b \mid n \mid a) &= \delta \rho_a \end{aligned} \tag{38}$$

The radial distribution functions become

$$\begin{aligned} g_{ab}(n) &= P(a \mid n \mid b)/\delta \rho_b = P(b \mid n \mid a)/\delta \rho_a = g_{ba}(n) \\ g_{aa}(n) &= \mathbf{e}_a \mathbf{M}^n \mathbf{e}_a{}^+/\delta \rho_a \lambda_1{}^n \\ g_{bb}(n) &= \mathbf{e}_b \mathbf{M}^n \mathbf{e}_b{}^+/\delta \rho_b \lambda_1{}^n \end{aligned} \tag{39}$$

3. ILLUSTRATIONS

Hard Rods. The simplest fluid is the case where the potential $\phi(r)$ is a hard core:

$$\begin{aligned} \phi(r) &= \infty, \qquad r < r_0 \\ &= 0, \qquad r > r_0 \end{aligned} \tag{40}$$

In one dimension, exact relations$^{(5-8)}$ are known both for the equation of state and the radial distribution function, the former being simply

$$p/\rho kT = 1/(1-\rho) \tag{41}$$

where ρ is defined as in Eq. (14), i.e., $\rho = 1$ is close packing; we will not diplay the fairly complicated series expression for $g(r)$. Lee and Yang$^{(9)}$ have

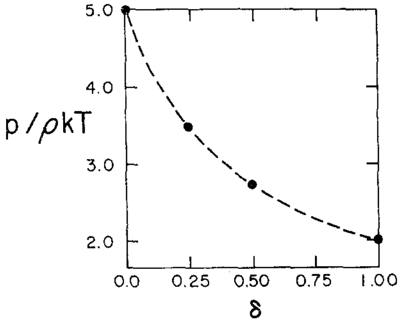

Fig. 2. Equation of state, $p/\rho kT$, as a function of the lattice parameter δ for a one-dimensional fluid of hard rods; the density relative to close packing is 0.8.

given the analog of Eq. (41) for the case of a lattice fluid of hard rods; their result is (in our notation)

$$p/\rho kT = (1/\rho\delta)\ln[1 + \rho\delta/(1-\rho)] \tag{42}$$

It is easily shown that in the limit $\delta \to 0$, Eq. (42) becomes identical with Eq. (41). Hoover *et al.*(10) and later Poland and Scheraga(2) have compared the results of Eq. (42) as a function of δ with the continuum result, Eq. (41), i.e., $\delta \to 0$. Hoover *et al.* found that to calculate the pressure to 1 %, one needs a grid parameter of $\delta = 1/50$; such a grid would imply a 50×50 matrix in our treatment (see below), which is quite manageable on present-day computers. Figure 2 shows $p/\rho kT$ as a function of δ at $\rho = 0.8$; one sees that convergence to the continuum limit ($\delta = 0$) is rapid and smooth, thus bestowing a measure of confidence on the extrapolation of the properties of lattice fluids to the continuum.

With the potential of Eq. (40), Eq. (17) reduces to

$$y = x^{n_0/2} - x^{(n_0/2)-1} \tag{43}$$

which is seen to be an $(n_0/2)$th-order polynomial ($n_0/2 = 1/\delta$) in this particular case [the potential in this case extends only to r_0, not $2r_0$ as in Eq. (2)]. The matrix for this model is so simple as to be worth illustrating (for $\delta = 1/8$):

$$\mathbf{W} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & y \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \end{bmatrix} \tag{44}$$

Figure 3 (the dots) shows $g(n)$ for the model of hard rods for $\rho = 0.71$ and $\delta = 1/8$ calculated from Eqs. (20), (24), and (44). Fig. 4 shows all the eigenvalues of the matrix of Eq. (44) for $y = 2.0$ (which gives $\rho = 0.71$). One notes that since the matrices are not symmetric, one expects and finds complex eigenvalues (the largest being real); the eigenvalues are seen to be arranged regularly in the complex plane, being slightly skewed from the unit circle in the direction of positive x [recall that we use Eq. (24) directly to compute $g(n)$ by performing the matrix multiplication explicitly and do not use the eigenvalues (except the largest), which are shown here simply for illustration].

Very accurate Monte Carlo radial distribution functions for hard disks [the two-dimensional use of Eq. (40)] have recently been published.⁽¹¹⁾ These

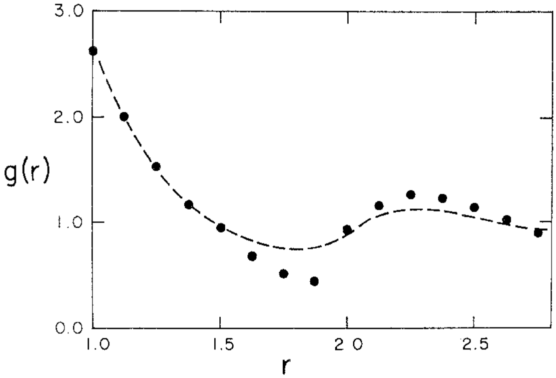

Fig. 3. Radial distribution function for hard particles. The smooth curve is the Monte Carlo calculation⁽¹¹⁾ for a two-dimensional fluid of hard disks, $\rho = 0.5$. The points are for a one-dimensional fluid of hard rods, $\rho = 0.71$, $\delta = 1/8$ as calculated by this work.

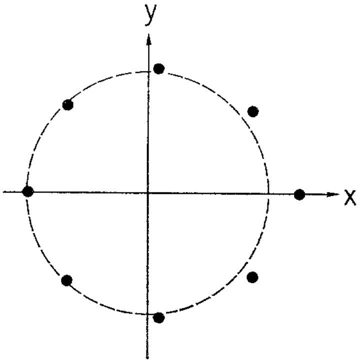

Fig. 4. The location of the eigenvalues in the complex plane of the matrix [Eq. (44)] for one-dimensional hard rods; $\rho = 0.71$, $y = 2.0$, $\rho = 1/8$.

results raise the question of how the one-dimensional and two-dimensional radial distribution functions compare. The problem in making such a comparison is that there is no proper way to compare one- and higher-dimensional densities. However, if we assume that the average coordination (e.g., rough square, rough hexagonal) remains constant as a function of density, then the density relative to close-packing density is related to the one-dimensional density ρ_1 for m dimensions as

$$\rho_m = \rho_1{}^m \tag{45}$$

In particular, $\rho_2 = \rho_1{}^2$. Using this admittedly crude relation, we have that for $\rho_2 = 0.5$, $\rho_1 = 0.71$. The smooth curve in Fig. 3 shows $g(r)$ for $\rho_2 = 0.5$ as computed by Monte Carlo techniques for a two-dimensional fluid of hard disks,(11) while the dots give $g(n)$ for $\rho_1 = 0.71$ as computed in this work. The similarity is fairly striking, the main difference being that the one-dimensional function has more pronounced hills and valleys due to the higher lining-up requirement of one dimension. For two-dimensional densities (relative to close packing) of 0.4, 0.5, and 0.6, the Monte Carlo calculations give [using $g(r_0)$ and the virial theorem] $p/\rho kT = 2.058$, 2.683, and 3.637, respectively, while the scaled one-dimensional approximation for the appropriate one-dimensional densities gives $p/\rho kT = 2.216$, 2.644, and 3.167, respectively; the error is seen to be about 10 %. The author does not propose that scaling of one-dimensional radial distribution functions and equations of state be taken as a serious approach to two- and three-demensional fluids; the author does feel that it is worth pointing out that for half an inch of IBM cards and pennies of computer time, fairly good starting solutions can be obtained, e.g., for the iterative solution of integral equations for two- and three-demensional fluids.

Neon–Xenon Mixtures. For a mixture of neon and xenon, we use a simple "6–12" potential:

$$\phi(r) = \epsilon[(r_0/r)^{12} - 2(r_0/r)^6] \tag{46}$$

for Ne–Ne, Xe–Xe, and Ne–Xe (=Xe–Ne) interactions with the parameters(12)

$$\begin{array}{lll} \text{Ne–Ne} & r_0 = 3.12\ \text{Å} & \epsilon = 70\ \text{cal/mole} \\ \text{Xe–Xe} & r_0 = 4.60\ \text{Å} & \epsilon = 442\ \text{cal/mole} \\ \text{Ne–Xe} & r_0 = 3.86\ \text{Å} & \epsilon = 176\ \text{cal/mole} \end{array} \tag{47}$$

Figure 5 gives $g_{\text{Ne–Ne}}$, $g_{\text{Xe–Xe}}$, and $g_{\text{Ne–Xe}} = g_{\text{Xe–Ne}}$ for $\rho_{\text{Ne}} = 0.11$, $\rho_{\text{Xe}} = 0.62$, $T = 100$ °K, and $\delta = 1/9$ computed from the potentials given

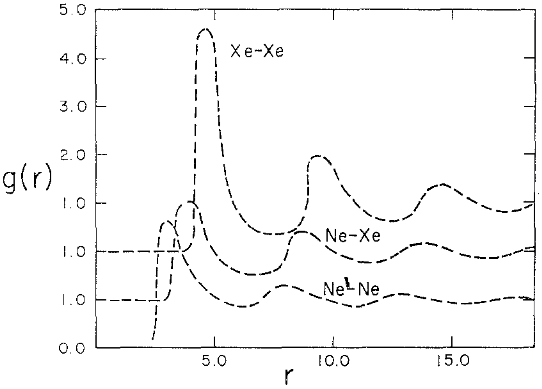

Fig. 5. The radial distribution functions for a one-dimensional mixture of neon and xenon; $T = 100\,^\circ\mathrm{K}$, $\delta = 1/9$, $\rho_{\mathrm{Ne}} = 0.11$, and $\rho_{\mathrm{Xe}} = 0.62$ (densities relative to close-packed Xe).

in Eq. (47) used in Eqs. (39) (densities are relative to close-packed Xe). We speculate that radial distribution functions for one-dimensional solutions may be useful estimates, e.g., of g_{aa} for three-dimensional solutions in the limit $\rho_A \to 0$, but not for solutions of arbitrary density of particles of very different size, since one dimension does not introduce the packing problems inherent in three dimensions.

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