Pair Correlation Function Realizability: Lattice Model Implications†

Frank H. Stillinger* and Salvatore Torquato

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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Despite their long history in experiment, simulation, and analytical theory, pair correlation functions that describe local order in many-body systems still retain a legacy of mathematical mysteries. One such open question concerns "realizability" of a given candidate pair correlation function, namely whether it actually represents the pair correlation for some spatial distribution of particles at number density $\rho > 0$. Several necessary conditions that must be satisfied by the candidate are known, including nonnegativity of the function and its associated structure factor, as well as constraints on implied local density fluctuations. However, general conditions sufficient to ensure realizability are not known. To clarify this situation, we have examined realizability for a simple one-dimensional lattice model, with single-site occupancy, and nearest-neighbor exclusion. By virtue of exhaustive enumeration for systems of 15 or fewer sites subject to periodic boundary conditions, several conclusions have been formulated for the case of a constant pair correlation beyond the exclusion range. These include (a) pair correlation realizability over a nonzero density range, (b) violation of the Kirkwood superposition approximation for many such realizations, and (c) inappropriateness of the so-called "reverse Monte Carlo" method that uses a candidate pair correlation function as a means to suggest typical many-body configurations.

I. Introduction

The subject of atomic and molecular distribution functions has enjoyed a long and rich history. This stems both from the experimental use of radiation scattering to determine such functions at least at the pair level,[1,2] as well as a wide range of theoretical developments motivated by the presence of exact relations for thermodynamic properties in terms of those distribution functions.[3,4] This combination of experimental measurements and theoretical insights has been an indispensable component of condensed-matter physical chemistry and physics. However, not surprisingly for a scientific area so characterized by intrinsic complexity, some deep problems of incomplete understanding still persist.

One of the basic problems concerns pair correlation function realizability. In its simplest version, this concerns $g(\mathbf{r})$, the pair correlation function for a statistically homogeneous single-component many-body system comprising structureless (spherically symmetric) particles. In the large system limit, this function is conventionally defined to approach unity as $r \rightarrow \infty$. By definition, it cannot be negative:

$$g(\mathbf{r}) \geq 0 \tag{I.1}$$

Furthermore, its corresponding structure factor cannot be negative for any value of the wavevector $\mathbf{k}$ ($\rho = N/V$ is number density):[5]

$$S(\mathbf{k}) = 1 + \rho \int [g(\mathbf{r}) - 1] \exp(i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} \geq 0 \tag{I.2}$$

If the many-body system of interest is isotropic, in addition to being statistically homogeneous, then $g(\mathbf{r})$ and $S(\mathbf{k})$ reduce to functions of scalar variables, $g(r)$ and $S(k)$.

The relations I.1 and I.2 are necessary conditions that any spatial distribution of particles at number density $\rho > 0$ must satisfy.[6] Beyond these, other necessary conditions have been derived that become applicable in various circumstances.[7−10] At present no sufficient condition with finite implementation for a given function $g(r)$ has been identified that would guarantee its realizability as the correlation function for a point process.

One context in which the pair correlation realizability problem arises is in the so-called iso-$g(r)$ process.[11,12] It is explained in the following section, section II, with some supplemental detail appearing in the Appendix. To attain at least a modest contribution to the overall realizability problem, we have elected to reexamine the iso-$g(r)$ problem while confining our analysis to the elementary case of a one-dimensional lattice model. This choice allows an essentially complete enumeration of system configurations for small systems, and a full mathematical solution for configuration weights required under an iso-$g(r)$ constraint. Section III briefly outlines basic properties of the lattice model considered. Section IV describes the required enumeration process. Section V presents results deduced for the lattice model. In short, the lattice model calculations provide support for the proposition that, in the infinite system limit, the necessary conditions I.1 and I.2 for any $g(r)$ are also sufficient to ensure realizability, at least over a nonvanishing density range that includes $\rho = 0$ (an illustrative example appears in ref 10). This presentation ends with a few concluding remarks in section VI about our results and about the general realizability problem.

II. Iso-*g* Problem

Consider a classical many-body system in which structureless particles interact only with pair potentials $v(r)$. If this system is in a state of thermal equilibrium at absolute temperature T, then in the low-density limit, the pair correlation function for this system is equal to the pair Boltzmann factor:

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$$g(r,\rho = 0) = \exp[-\beta v(r)] \quad \text{(II.1)}$$

where as usual $\beta = 1/k_BT$. The "iso-*g(r)* problem" consists of asking if the pair potential $v(r)$ can be continuously perturbed isothermally, as number density ρ increases from zero, in such a way that the pair correlation function remains unchanged:[11,12]

$$g(r,\rho > 0) = g(r,0) \quad \text{(II.2)}$$

In other words, the density increase and the changing interaction are to have precisely canceling effects at the pair correlation level. If in fact it exists, the corresponding perturbed pair potential might be denoted by $v^*(r,\rho)$. An Appendix outlines a formal argument, based on the density series for the pair correlation function, suggesting that such a perturbed pair potential indeed exists for some density interval, in the form of a density series:

$$v^*(r,\rho) = v(r) + \sum_{n=1}^{\infty} \rho^n v_n^*(r) \quad \text{(II.3)}$$

However, that formal argument falls short of a rigorous existence proof, and furthermore, it fails to establish what, if any, upper terminal density exists for the iso-*g(r)* process.

An exceptionally simple case of the iso-*g(r)* process involves the unit step function, the pair Boltzmann factor for the rigid sphere (or disk, or rod) potential in dimension $D = 3$ (or 2, or 1):

$$g(r,0) = U(r - a) \quad \text{(II.4)}$$

where a is the collision diameter. Obviously this choice obeys the first necessary condition, eq I.1. The corresponding structure–function is the following

$$\begin{aligned} S(k) &= 1 - (2\rho/k)\sin(ka) \quad (D = 1) \\ &= 1 - (2\pi\rho a/k)J_1(ka) \quad (D = 2) \\ &= 1 + (4\pi\rho/k^3)[ka\cos(ka) - \sin(ka)] \quad (D = 3) \end{aligned} \quad \text{(II.5)}$$

where J_1 is the Bessel function of order 1.[13,14]

When the number density ρ is sufficiently small (but still positive), the structure factor forms in (II.5) obey the second nonnegativity condition I.2. However, as ρ increases, a terminal density ρ_t is reached at which that necessary condition no longer is satisfied. The violation first occurs at $k = 0$ for $D = 1$, 2, and 3. Expanding the expressions displayed in eq II.5 around the origin shows that

$$\begin{aligned} \rho_t a &= 1/2 \quad (D = 1) \\ \rho_t a^2 &= 1/\pi \quad (D = 2) \\ \rho_t a^3 &= 3/4\pi \quad (D = 3) \end{aligned} \quad \text{(II.6)}$$

Each of these results falls well below the close-packed limit for rigid rods, disks, and spheres, respectively.

Although this establishes an upper terminal density above which the step-function $g(r)$ cannot exist, it does not guarantee that this simple pair correlation function is actually achievable up to that density. In other words, sufficiency of constraints I.1 and I.2 for this case (eq II.4) mathematically remains an open question (although some limited numerical evidence supporting the proposition is available[15]). The step-function $g(r)$ is not special in this regard; any $g(r)$ for which the integral term in its $S(k)$ has a negative region leads to a qualitatively similar situation. The objective of the following section III is to develop a simple testing ground to aid in deciding whether the two conditions I.1 and I.2 are indeed sufficient.

III. Lattice Model

To permit an exact and complete analysis, we now restrict attention to the case of a linear array of M equally spaced sites. This array will be subject to periodic boundary conditions, so the first and the Mth sites topologically are nearest neighbors. The sites in principle can act as single occupancy locations for $0 \le N \le M$ point particles. The configurations of particles in this array can conveniently be specified by a binary string of occupancy variables $\xi_j = 0,1$ $(1 \le j \le M)$, for empty and filled sites, respectively, so that

$$\sum_{j=1}^{M} \xi_j = N \quad \text{(III.1)}$$

Furthermore, we shall suppose that the point particles exclude one another from occupying nearest neighbor sites, i.e., $\xi_j\xi_{j+1} = 0$. As a result, N will be restricted to $0 \le N \le \mathrm{int}(M/2)$, where int($x$) stands for the greatest integer in x. When M is even and N is at its upper limit, the system displays a perfect alternating pattern of particles and vacant sites. With odd M, two contiguous vacant sites must be present somewhere in the system when N is at its maximum. This lattice system will be treated as closed, that is, N will be fixed for each case considered.

The number of distinct particle configurations in the array, with first-neighbor exclusion, is

$$\Omega(M, N) = \frac{M[M - N - 1]!}{N![M - 2N]!} \quad \text{(III.2)}$$

Each of these configurations will be assigned a weight $W(\{\xi_i\}) \ge 0$, subject to normalization:

$$\sum_{\{\xi_i\}} W(\{\xi_i\}) = 1 \quad \text{(III.3)}$$

Because the underlying array has periodic boundary conditions, and has nothing to distinguish forward and backward directions, it is appropriate henceforth to assume that the weights are symmetric under translation and inversion (mirror reflection) of the configurations. As a result, the site-occupancy distribution functions

$$\langle \xi_j \cdots \xi_s \rangle = \sum_{\{\xi_i\}} \xi_j \cdots \xi_s W(\{\xi_i\}) \quad \text{(III.4)}$$

will themselves possess translational and inversion symmetries. Note that

$$\begin{aligned} \langle \xi_j \rangle &= N/M \\ \sum_{j,l=1}^{M} \langle \xi_j \xi_l \rangle &= N(N - 1) \end{aligned} \quad \text{(III.5)}$$

The primary objective will be to determine, for given M and N, what sets of weights (if any) will produce a flat site-pair distribution function for distances beyond the excluded first-neighbor:

$$\langle \xi_i \xi_{i+n} \rangle = 0 \quad (n = 1)$$
$$= K > 0 \quad (2 \le n \le \mathrm{int}(M/2)) \tag{III.6}$$

Notice that for int(M/2) < n, the periodic boundary conditions simply cause the pair distribution function to fold back on itself:

$$\langle \xi_i \xi_{i+n} \rangle \equiv \langle \xi_i \xi_{i+M-n} \rangle \tag{III.7}$$

Inserting form III.6 into the second part of eq III.5 serves to identify K:

$$K = \frac{N(N-1)}{M(M-3)} \tag{III.8}$$

The lattice model version of the pair correlation function $g(r)$ will be denoted by $\hat{g}(n)$. The lattice spacing will serve as the distance unit. In the case of the flat pair distribution III.6, this leads to the following:

$$\hat{g}(n) = 0 \quad (n = 0, \pm 1)$$
$$= \langle \xi_i \xi_{i+n} \rangle / K = 1 \quad (n = \pm 2, \pm 3, ..., \pm \mathrm{int}(M/2)) \tag{III.9}$$

Collective density variables $\rho(k)$ can be defined for any pattern of particles on the lattice

$$\rho(k) = \sum_{j=1}^{M} \xi_j \exp(ikj) \tag{III.10}$$

where the wavevectors obey

$$k = 0, \pm 2\pi/M, \pm 4\pi/M, ... \tag{III.11}$$

Consequently, one has

$$N^{-1} \langle [\rho(0)]^2 \rangle = N \tag{III.12}$$

and for $k \neq 0$

$$N^{-1} \langle \rho^*(k) \rho(k) \rangle = 1 + (M/N) \sum_{l=2}^{M} \langle \xi_1 \xi_l \rangle \exp[ik(l-1)]$$
$$\ge 0 \tag{III.13}$$

When the pair distribution has the "flat" form (eq III.6) beyond the nearest-neighbor distance, one can rewrite the above equation as follows:

$$N^{-1} \langle \rho^*(k) \rho(k) \rangle = 1 + (M/N) \{ \sum_{l=2}^{M} [\langle \xi_1 \xi_l \rangle - K] \times \exp[ik(l-1)] - K \}$$
$$= 1 - \left(\frac{N-1}{M-3} \right) [1 + 2 \cos k]$$
$$\equiv \hat{S}(k) \tag{III.14}$$

This expression serves as the structure factor for the lattice model with flat pair correlation.

For nonzero k, the last expression attains its minimum value at $|k| = 2\pi/M$, the points closest to the origin. Because $\hat{S}(k)$ cannot be negative, it is necessary that N not exceed a terminal upper limit $N_t(M)$ derivable from eq III.14, specifically the following:

$$N_t(M) = 1 + \frac{M-3}{1 + 2\cos(2\pi/M)}$$
$$= \frac{M}{3} + \frac{4\pi^2}{9M} - \frac{4\pi^2}{3M^2} + O(M^{-3}) \tag{III.15}$$

Whether N can actually rise to the value int[$N_t(M)$] while maintaining a flat pair distribution function in the lattice is one of the main questions to be answered below.

IV. Enumeration Details

The $\Omega(M,N)$ configurations of N particles distributed on M sites, subject to nearest-neighbor exclusion, need to be separated into pattern classes. Each class collects all configurations that differ only by the symmetry operations of translation and/or inversion. The weights $W(\{\xi_i\})$ will be the same for all members of the same class, and can be denoted as w_j for the jth class. If m_j is the number of configurations belonging to class j, then the normalization eq III.3 can be restated as

$$\sum_{j=1}^{C} m_j w_j = 1 \tag{IV.1}$$

where $C(M,N)$ is the number of classes.

For the sake of illustration, consider the case $M = 11$, $N = 3$. Five distinct patterns for the three particles are possible. They correspond to the following binary strings $\{\xi_j\}$ with respective weights $w_1 ... w_5$:

$$10101000000 \quad (m_1 = 11)$$
$$10100100000 \quad (m_2 = 22)$$
$$10100010000 \quad (m_3 = 22)$$
$$10010010000 \quad (m_4 = 11)$$
$$10010001000 \quad (m_5 = 11) \tag{IV.2}$$

Notice that the second and third patterns are not inversion invariant, so twice as many class members occur as for the first, fourth, and fifth patterns which possess that symmetry.

Table 1 presents the values of $C(M,N)$ for all cases with $M \le 17$. The central objective is to search for sets of class weights w_j which produce a flat pair distribution function. No such set can exist if N exceeds the terminal value $N_t(M)$.

To examine the possibility of attaining a flat pair distribution function, it is necessary to evaluate the contribution of individual classes to each $\langle \xi_i \xi_{i+n} \rangle \equiv \langle \xi_1 \xi_{n+1} \rangle$. This requires identifying how many members of each class exhibit simultaneous occupancy of sites 1 and n, and attributing a weight w_j to each. For the specific $M = 11$, $N = 3$ case considered above, this process yields the following expressions:

$$\langle \xi_1 \xi_3 \rangle = 2w_1 + 2w_2 + 2w_3 = K$$
$$\langle \xi_1 \xi_4 \rangle = 2w_2 + 2w_4 + w_5 = K$$
$$\langle \xi_1 \xi_5 \rangle = w_1 + 2w_3 + 2w_5 = K$$
$$\langle \xi_1 \xi_6 \rangle = 2w_2 + 2w_3 + w_4 = K \tag{IV.3}$$

These are the only independent pair distribution values beyond the nearest neighbor exclusion distance, and the requirement of a flat pair distribution function sets each of these equal to K, eq III.7, as shown. Analogous sets of linear expressions apply to all other M, N cases, each of which must equal $K(M,N)$ to

TABLE 1: Numbers $C(M,N)$ of Configuration Classes for the One-Dimensional Lattice System, with Nearest-Neighbor Exclusions, and Periodic Boundary Conditions

M	$N = 2$	$N = 3$	$N = 4$	$N = 5$	$N = 6$	$N = 7$	$N = 8$
4	1						
5	1						
6	2	1					
7	2	1					
8	3	2	1				
9	3	3	1				
10	4	4	3	1			
11	4	5	4	1			
12	5	7	8	3	1		
13	5	8	10	5	1		
14	6	10	16	10	4	1	
15	6	12	20	16	7	1	
16	7	14	29	26	16	4	1
17	7	16	35	38	26	8	1

TABLE 2: Classification of Outcomes for the Flat-Correlation Constraint in Finite-Size One-Dimensional Lattices[a]

M	$N = 2$	$N = 3$	$N = 4$	$N = 5$	$N = 6$	$N = 7$	$N_t(M)$
4	f						2.000 00
5	f						2.236 07
6	f	n					2.500 00
7	f	n					2.780 17
8	f	n	n				3.071 07
9	f	f	n				3.369 59
10	f	f	n	n			3.673 67
11	f	m(1)	n	n			3.982 28
12	f	m(2)	f	n	n		4.294 23
13	f	m(3)	m(5)	n	n		4.608 92
14	f	m(4)	m(10)	n	n	n	4.925 85
15	f	m(6)	m(14)	n	n	n	5.244 65

[a] Number of sites = M, number of particles = N. The symbols used are: "n" for no acceptable solution, "f" for a fixed set of configurational weights (unique solution) that produces a flat pair correlation, m(i) for multiple solution sets of configurational weights having i parametric degrees of freedom. The formal terminal filling number $N_t(M)$ is defined in eq III.14.

produce the required flat pair distribution. It is then necessary to verify which of these equation sets have solutions with all weights $w_i \geq 0$.

V. Results

The four linear equations in eq IV.3 for the illustrative example $M = 11$, $N = 3$ can formally be solved in terms of w_1:

$$\begin{aligned} w_2 &= K/3 - 3w_1/2 \\ w_3 &= K/6 + w_1/2 \\ w_4 &= 2w_1 \\ w_5 &= K/3 - w_1 \end{aligned} \tag{V.1}$$

To avoid having any of these four weights become negative, it is necessary to restrict w_1 to the interval

$$0 \leq w_1 \leq 2K/9 = 1/66 \tag{V.2}$$

but otherwise w_1 is unconstrained. Consequently, for this illustrative case, the set of acceptable solutions for the five weights constitutes a finite, simply connected, one-dimensional manifold.

Similar considerations apply to other M, N choices, although the outcomes can be quite different. Table 2 describes the results qualitatively for all cases with $M \leq 15$. Those cases M, N for which a fixed (i.e. unique) set of weights produces the desired flat pair correlation are designated by "f" in Table 2; in particular this is true whenever $N = 2$, the lowest density situation for which pair correlation is meaningfully defined. If no solution with nonnegative weights exists, the corresponding entry in Table 2 is "n", and this is necessarily true whenever $N > N_t(M)$. The remaining cases have multiple solution sets that constitute bounded convex manifolds with some positive dimension i; these cases have been identified in Table 2 by the symbol "m(i)". For some of the cases in this last category, numerical exploration was used to identify exact positive rational values for the w_j satisfying the flat pair distribution constraint, i of which could then be independently varied while still satisfying that constraint.

Examination of Table 2 reveals the presence of two cases for which no solution exists ("n"), although $N < N_t(M)$. These are M, $N = 8$, 3 and 15, 5, and for both the N value is just below the $N_t(M)$ boundary by less than unity. The reason for nonexistence of acceptable solutions is not the same for both of these anomalous cases. In the former, only two distinct configuration types exist [$C(8,3) = 2$], while three pair distribution constraints need to be imposed; thus the two weights are overconstrained. In the latter, more than enough distinct configurations are available [$C(15,5) = 16$] to satisfy the six pair distribution flat constraints; however no solution with nonnegative weights for those configurations exists.

Because eq III.15 indicates for large M that $N_t(M) \sim M/3$, the number of particle configurations available at this boundary can be estimated by applying Stirling's asymptotic approximation:

$$\Omega(M,M/3) = \frac{M[(2M/3) - 1]!}{[(M/3)!]^2} \sim (3^{3/2}/2\pi^{1/2})2^{2M/3} \tag{V.3}$$

This enumerates all configurations; they fall into classes as noted above, but with no more than $2M$ configurations per class. Consequently, the number of classes rises essentially exponentially with M at the boundary. In view of this fact it is not possible for any other "n" cases analogous to 8, 3 to occur, in which overdetermination of an insufficient number of class weights exists with N just less than N_t. However, at present one cannot exclude further isolated "n" cases analogous to 15,5, with $M > 15$ and with N in a narrow strip just less than N_t. Indeed these may proliferate as M increases, and in the large-M limit (for the flat pair correlation case) may place an upper limit on N that is a fraction of N_t less than unity.

Yamada[7] has derived a necessary condition for pair correlation functions that concerns number variance in subregions ("windows") of the full system.[14] For the present context, the fluctuating quantity of interest is N_a, the number of particles occurring in $1 \leq a \leq M$ contiguous sites:

$$N_a = \sum_{j=1}^{a} \xi_j \tag{V.4}$$

Let θ denote the noninteger part of $\langle N_a \rangle$:

$$\theta = \langle N_a \rangle - \mathrm{int}\langle N_a \rangle \tag{V.5}$$

Then the Yamada necessary condition is

$$\langle N_a^{\,2} \rangle - \langle N_a \rangle^2 \geq \theta(1 - \theta) \tag{V.6}$$

Of course this inequality must be satisfied for all of the cases listed in Table 2 that have solutions, and for all a. However, the two anomalous cases M, $N = 8$, 3 and 15, 5 need not formally satisfy it. The variance can always be expressed in terms of the pair correlation function, and is straightforward to evaluate under our specific assumption of a flat form. The required calculations show that the M, $N = 8$, 3 overdetermined case violates inequality V.6 when $a = 4$. By contrast, M, $N = 15$, 5 formally satisfies eq V.6 for all a, suggesting that some further necessary condition or conditions must be involved in preventing its realizability.

VI. Concluding Remarks

The principal focus of this paper has been the pair distribution function realizability problem, illustrated by study of finite-size lattice systems in one dimension. These lattice systems involve single-occupancy lattice sites, nearest-neighbor exclusion, and periodic boundary conditions. The objective was to determine what configurational probabilities, if any, would lead to a preassigned pair distribution function. The specific situation examined involved a "flat" pair distribution function, i.e., one which is independent of distance beyond the excluded nearest-neighbor separation. Table 2 summarizes the results obtained (without approximation) for various modest values of the number of sites M and of the number of particles N. These results include cases in which (a) no solution is possible, (b) an unique set of configurational probabilities produces the desired flat pair distribution, and (c) a multidimensional manifold of configurational-weight sets exists yielding the desired flat pair distribution.

Although the flat pair distribution is perhaps the simplest example that might be chosen to illustrate the realizability issue, alternatives could equally well have been analyzed using the same basic enumeration approach. One such alternative could have been a pair distribution function with a maximum value at the second-neighbor separation, then a smaller constant value beyond. One would expect that the corresponding entries analogous to those shown in Table 2 would be somewhat altered, but still would present a qualitatively similar pattern.

For any M, N case that admits of at least an unique set of configurational weights, those weights can always be expressed as normalized Boltzmann factors:

$$w_i = D(M,N,\beta)\exp[-\beta\Phi_i] \qquad \text{(VI.1)}$$

In this expression Φ_i is the potential energy for the N particles arranged in configuration i on the M-site lattice, $\beta = 1/k_BT$, and $D(M,N,\beta)$ is the normalization constant. In general, the potential energy function appearing here would consist of a sum of 2-particle, 3-particle, ..., N-particle contributions. Any weight w_i that vanishes corresponds to $\Phi_i \rightarrow +\infty$, i.e. to a multiparticle hard core.

The overall pattern of configuration-weight solution types presented by Table 2 has some significant implications. In particular, the reader will notice that for a given system size $M > 10$, the midrange values of the particle number N lead to solutions that are not unique, and that the maximum dimensionality of the solution sets appears to rise with increasing system size M. Although the pair distribution function remains invariant over these multidimensional solution sets, the higher-order distribution functions will not. This is clear from the fact that the potential energy function in eq VI.1 will vary across the solution sets involved. To paraphrase, fixing the pair distribution function generally does not fix the higher-order distribution functions, and specifically, it does not determine the triplet distribution function. This last observation points out an explicit violation of the Kirkwood superposition approximation.[16,17]

Another area of relevance for the present analysis is the so-called "reverse Monte Carlo" method.[18−21] This method attempts to infer typical full-system configurations using only measured pair correlation functions as input, and utilizes a stochastic procedure to move particles spatially so as to conform closely to that input. However, as just stressed in connection with the Kirkwood superposition approximation, fixing the pair distribution generally leaves higher-order distribution functions undetermined. The final pattern of particle positions produced by a reverse Monte Carlo computation implicitly depends on details of that computation in a way that will bias that result in an unanticipated, perhaps even unphysical, manner. Examples such as M, $N = 15$, 4 above directly illustrate the underlying difficulty, because the 7 pair constraints that would be applied by the reverse Monte Carlo method cannot resolve the 14-dimensional degeneracy [m(14) in Table 2] presented by this case. Consequently, one may legitimately question the logical basis of the reverse Monte Carlo approach to the extent that it presumes uniquely to produce valid many-particle spatial patterns.

Of course it would be desirable to extend the present calculations in a variety of directions, not the least of which would be increasing M substantially above the present upper limit 15. It seems unlikely to the authors that the presently revealed trends would be qualitatively overturned by that substantial increase. Specifically, in the large-system limit (whether lattice or continuum models are involved) it appears that pair distribution realizability is feasible over a nonvanishing density range that includes $\rho = 0$. The appearance of the two anomalous cases M, $N = 8$, 3 and 15, 5 with no solution, with $N < N_t$, illustrates the fact that the two necessary conditions I.1 and I.2 generally cannot be sufficient. In particular, it has been pointed out[7,10] that local number-fluctuation constraints exist that are not implied by (I.1) and (I.2). Furthermore, the specific failure of the M, $N = 15$, 5 case to possess any solution hints that at least one additional necessary condition beyond those already known has yet to be articulated. However, whether a finite set of necessary conditions will ultimately suffice to ensure pair correlation function realizability remains a challenging open question.

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Appendix

The conventional density expansion for the pair correlation function $g(r_{12},\rho)$, in an infinite system of spherically symmetric particles, can be expressed in the following way:[22]

$$\ln g(r_{12},\rho) = -\beta v(r_{12}) + \sum_{n=1}^{\infty}\rho^n \gamma_n(r_{12}) \qquad \text{(A.1)}$$

Here ρ is the number density, $\beta = 1/k_BT$, and $v(r_{12})$ is the pair potential that is normally construed to be independent of density. The functions $\gamma_n(r_{12})$ are sums of doubly rooted Mayer cluster integrals with n field points, subject to the proviso that those field points be connected among themselves and have no articulation points:

$$\gamma_n(r_{12}) = (1/n!)\sum \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_{n+2} \prod_{\text{conn.}} f(r_{ij})$$
$$f(r_{ij}) = \exp[-\beta v(r_{ij})] - 1 \qquad (A.2)$$

Although these expressions and those to follow refer to continuum systems, they can be formally modified so as to apply equally well to lattice systems such as that considered at length in the main body of this paper.

The objective of the iso-g problem is to find a ρ-dependent pair interaction $v^*(r_{12},\rho)$ to stand in place of $v(r)$, which causes $g(r_{12})$ to be independent of ρ, at least for some interval of this variable including the origin. Suppose that the required effective pair interaction has at least a formal density expansion:

$$v^*(r_{ij},\rho) = v(r_{ij}) + \sum_{k=1}^{\infty} \rho^k v_k^*(r_{ij}) \qquad (A.3)$$

The fixed pair correlation function then would be

$$g(r_{12}) = \exp[-\beta v(r_{12})] \qquad (A.4)$$

and successive terms in expansion A.3 have the task of maintaining this form as density increases from zero.

Let the series A.3 for v^* be inserted into each of the Mayer f functions in eq A.2 in place of v, followed by density expansion of each of those f functions. As a result, each of the γ_n likewise becomes a power series in ρ:

$$\gamma_n(r_{12},\rho) = \sum_{l=0}^{\infty} \rho^l \gamma_{n,l}(r_{12}) \qquad (A.5)$$

in which the $\gamma_{n,l}$ contain only pair interactions v, v_1^*, ..., v_l^*. When both density series in eqs A.3 and A.5 are inserted into eq A.1, the result is

$$\ln g(r_{12}) = -\beta v(r_{12}) + \sum_{n=1}^{\infty} \rho^n \{ -\beta v_n^*(r_{12}) + \sum_{l=0}^{n-1} \gamma_{n-l,l}(r_{12})\} \qquad (A.6)$$

In order to satisfy the iso-g constraint, each bracketed combination {....} for $n \geq 1$ must individually vanish:

$$\beta v_n^*(r_{12}) = \sum_{l=0}^{n-1} \gamma_{n-l,l}(r_{12}) \qquad (A.7)$$

The right-hand member of this last equation can only contain the lower-order functions v, v_1^*, ..., v_{n-1}^*. Consequently, these relations (eq A.7) amount to a sequence of explicit expressions for sequential determination of the entire set of v_n^*. Only the n = 1 result in this sequence has been previously displayed.[11]

References and Notes

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