

Realizability issues for iso- $g^{(2)}$ processes

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Iso- $g^{(2)}$ processes in the equilibrium regime concern density-dependent interactions that identically cancel the usual density variation of many-body pair correlation functions. This paper considers the formal density expansion for effective pair potentials with this iso- $g^{(2)}$ property, showing how successive terms in that expansion can be determined iteratively. Explicit results through second density order have been obtained for two types of ‘target’ pair correlation functions: (a) a unit step function (hard core), and (b) unity augmented by an origin-centred Gaussian profile with numerical multiplier A . For the unit step function and the $-1 \leq A < 0$ Gaussian cases, realizability appears to be attainable up to a finite terminal density. However, when the Gaussian $A > 0$, the terminal density diverges to infinity while the effective pair interaction series is non-convergent, though possibly valid as an asymptotic expansion.

1. Introduction

Particle distribution functions fulfil a basic role in the statistical description of all phases of matter [1, 2]. Among these distribution functions of all orders, the conceptually relatively simple pair distribution functions $\rho^{(2)}$ possess special significance. This is partly due to their experimental accessibility for real substances through X-ray and neutron diffraction measurements [3, 4], but it is also due to the relevance and popularity of theoretical many-body models with interactions that are pairwise additive [3, 5]. However, in spite of the long scientific history of their use, some deep theoretical problems regarding ‘realizability’ of all such particle distribution functions still remain. It is the persistence of those problems which supplies the underlying motivation for the present paper.

For convenience, we concentrate on the direction-averaged pair distribution, expressed in terms of the pair correlation function $g^{(2)}(r) = \rho^{(2)}(r)/\rho^2$ that is normalized at any particle number density ρ so as to approach unity at large pair separation. An implicit assumption in the analysis to follow is that the infinite-system limit applies. Two well-known necessary conditions must be satisfied by any realizable pair correlation function [6–8], specifically

$$g^{(2)}(r) \geq 0 \quad (\text{all } r), \quad (1.1)$$

and

$$S(k) \geq 0 \quad (\text{all } k). \quad (1.2)$$

Here $S(k)$ is the structure factor determined by $g^{(2)}(r)$:

$$S(k) = 1 + \rho \int \exp(i\mathbf{k} \cdot \mathbf{r}) [g^{(2)}(r) - 1] d\mathbf{r}. \quad (1.3)$$

No generally applicable sufficient condition or conditions are known to assure that a given $g^{(2)}(r)$ actually represents a many-body system. That is, given a ‘target’ function $g_0(r)$ that satisfies necessary conditions (1.1) and (1.2), the challenge is to determine the range of number density ρ (if any) over which $g_0(r)$ is the pair correlation function for a many-body system. The existence of this pair correlation function realizability problem constitutes a fundamental and vexing gap in the theory for continuum systems. Nevertheless, it should be noted that for single-occupancy lattice models Koralov has demonstrated that a non-vanishing realizability density interval always exists, and at each realizable density corresponds to an equilibrium ensemble with pairwise additive interactions [9].

Section 2 introduces and examines the apparent division of realizable pair correlation functions into two categories, those that are valid representatives for all $\rho \geq 0$, and those that are valid only up to a finite positive terminal density ρ_t . In the course of illustrating

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these two possibilities with specific examples, section 2 also alludes briefly to a third necessary condition due to Yamada [10], which supplements those in equations (1.1) and (1.2). Section 3 develops a density expansion method for effective pair potentials that define many-body ensembles for a given $g_0(r)$, at least for a small density interval. The possibility of such an expansion was briefly indicated in a prior publication, but without full details [11]. Section 4 contains an application of the formalism developed in section 3, specifically deriving the first three density orders of the effective pair potential, respectively for two elementary $g_0(r)$ choices. The final section 5 presents a discussion of our results, and highlights some remaining theoretical problems. An Appendix contains some relevant results from previously published literature required for evaluation of effective pair interactions.

2. Terminal densities

We shall now examine a specific, but contrasting, pair of ‘target’ pair correlation functions. The first is just a simple unit step function, with discontinuity located at a positive pair separation a :

$$\begin{aligned} g_0(r) &= 0 & (0 \leq r \leq a) \\ &= 1 & (a < r < \infty). \end{aligned} \quad (2.1)$$

The corresponding structure factors in dimensions $D = 1, 2, 3$ are

$$\begin{aligned} S(k) &= 1 - 2\rho a \left[\frac{\sin(ka)}{ka} \right] & (D = 1) \\ &= 1 - 2\pi\rho a^2 \left[\frac{J_1(ka)}{ka} \right] & (D = 2) \\ &= 1 - 4\pi\rho a^3 \left[\frac{\sin(ka) - (ka)\cos(ka)}{(ka)^3} \right] & (D = 3). \end{aligned} \quad (2.2)$$

In the second of these expressions, J_1 as usual is the first-order Bessel function.

The step-function $g_0(r)$ represents the zero-density limiting form of the pair correlation function for impenetrable rods, disks, or spheres with collision diameter a . The corresponding dimensionless pair interaction is very familiar ($\beta = 1/k_B T$):

$$\begin{aligned} \beta v_0(r) &= +\infty & (0 \leq r < a) \\ &= 0 & (a \leq r < \infty). \end{aligned} \quad (2.3)$$

On account of the impenetrability, it is obvious that with this step-function $g_0(r)$ the number density ρ

cannot exceed its value at close-packing in 1, 2, or 3 dimensions, respectively. But in each of these three cases the close-packed arrangements involve periodic (i.e. crystalline) configurations, which produce pair correlation functions with successive discrete coordination shells that present patterns far different from the targeted unit step function. The non-negativity requirement for $S(k)$ however requires that ρ not exceed a rather smaller density bound, which we can tentatively identify as the upper terminal density ρ_t . This upper bound is set by the criterion $S(0) = 0$, on account of the fact that in each dimension the minimum value of the structure factor for the unit-step $g_0(r)$ occurs at $k=0$, and that this minimum decreases in value with increasing ρ . The expressions (2.2) easily lead to the following results for terminal densities:

$$\begin{aligned} \rho_t a &= 1/2 & (D = 1), \\ \rho_t a^2 &= 1/\pi & (D = 2), \\ \rho_t a^3 &= 3/4\pi & (D = 3). \end{aligned} \quad (2.4)$$

The second ‘target’ pair correlation function has the following assigned form:

$$g_0(r) = A \exp(-\alpha r^2) + 1, \quad (2.5)$$

where $A \geq -1$, and $\alpha > 0$. This assumed form corresponds in the vanishing-density limit to a reduced pair interaction:

$$\beta v_0(r) = -\ln[A \exp(-\alpha r^2) + 1]. \quad (2.6)$$

However it must be noted that when $A > 0$ this pair interaction is everywhere negative, and if it were the only interaction present at positive density in a many-particle system, that system would collapse into a single compact cluster with a non-extensive energy. Nevertheless, it is conceivable that some neutralizing mechanism could be present to maintain this second $g_0(r)$ into the positive density regime when $A > 0$. For whatever A values it is possible to retain the target form (2.5), the structure factor would be the following ($D=3$):

$$S(k) = 1 + A(\pi/\alpha)^{3/2} \rho \exp(-k^2/4\alpha). \quad (2.7)$$

When $A > 0$, this $S(k)$ remains positive for all k and all positive densities. Consequently, in contrast to the preceding example, no violation of necessary condition (1.2) would arise to impose a finite terminal density. But when $-1 \leq A < 0$ the structure factor has

a minimum at $k = 0$, thereby imposing a finite terminal density:

$$\rho_t = (\alpha/\pi)^{3/2}(-A)^{-1}. \tag{2.8}$$

Focusing on the $A > 0$ situation, the Fourier transform $C(k)$ of the direct correlation function [3] corresponding to the target function in equation (2.5) has the following form:

$$C(k) = \frac{A(\pi/\alpha)^{3/2} \exp(-k^2/4\alpha)}{1 + \rho A(\pi/\alpha)^{3/2} \exp(-k^2/4\alpha)}. \tag{2.9}$$

In the large- ρ asymptotic limit, the second denominator term in this expression dominates the first for

$$|k| < k_1(\rho), \tag{2.10}$$

where

$$k_1(\rho) = \{4\alpha \ln[A(\pi/\alpha)^{3/2} \rho]\}^{1/2} \tag{2.11}$$

is the k value at which both denominator terms are equal. On account of the very rapid relative rate at which the Gaussian function declines when its argument is large, $C(k)$ switches rapidly from one value to another in the asymptotic large- ρ regime. In other words, it essentially displays a discontinuity at k_1 :

$$\begin{aligned} C(k) &\cong 1/\rho && (|k| < k_1(\rho)) \\ &\cong 0 && (k_1(\rho) < |k|). \end{aligned} \tag{2.12}$$

By carrying out the inverse transform, the corresponding real-space form of the direct correlation function in $D = 3$ is found to be

$$c(r) \cong \frac{\sin[k_1(\rho)r] - k_1(\rho)r \cos[k_1(\rho)r]}{2\pi^2 \rho r^3}. \tag{2.13}$$

The noteworthy characteristics of this result are that it is weak, that it decays algebraically with increasing distance, and that it oscillates with a wavelength approaching zero in the high-density limit. If indeed this second example has no finite terminal density, then the combination of effective interactions that must be present to maintain the target $g_0(r)$, equation (2.5), must also generate this unusual asymptotic $c(r)$.

It is worth remarking that the density range of realizability will never consist of two (or more) distinct intervals that are separated by a non-realizability gap (or gaps). In the thermodynamic (large-system) limit, random removal of particles from a distribution exhibiting a given pair correlation function will not alter that pair correlation function. However the

consequent density reduction can produce a distribution within the alleged gap (or gaps). Of course this also automatically leads to inclusion of arbitrarily small densities. The reader should realize that this kind of process is not reversible however. Random addition of particles will not maintain a target pair correlation function.

There still exists the possibility that other necessary conditions beyond those in equations (1.1) and (1.2) could require that the tentative finite terminal densities in equations (2.4) and (2.8), and the unrestricted density for the second Gaussian example with $A > 0$, be revised downward. One type of additional constraint has been advocated by Yamada [10]. This condition concerns the particle number variance

$$\sigma^2 = \{[N - \langle N \rangle]^2\}_w \tag{2.14}$$

in a ‘window’ w . The fact that the number N of particles inside w is an integer, and not a continuous variable, sets a lower limit on the variance that is logically independent of the basic necessary conditions (1.1) and (1.2). However, for the two specific target functions $g_0(r)$ considered here, the Yamada condition poses no additional restrictions on realizability.

3. Density expansion formalism

Suppose one has a pair correlation function that is known to be realizable over a non-vanishing density interval including $\rho = 0$. It is natural to inquire, within the context of thermal equilibrium, if a density-dependent interaction exists which reproduces that pair correlation function over at least a portion of the density interval. In particular, we now examine the implications of assuming that an effective pair potential suffices, where that potential has a power series expansion:

$$v(r, \rho) = v_0(r) + \sum_{n=1}^{\infty} \rho^n v_n(r). \tag{3.1}$$

The leading term in this series is fixed by the chosen form of the target pair correlation function:

$$g_0(r) = \exp[-\beta v_0(r)]. \tag{3.2}$$

The functions $v_n(r)$ appearing in the series (3.1) can be sequentially determined by a procedure which starts with the well-established formal density expansion of the logarithm of the pair correlation function for systems in which the potential involves only isotropic pair

interactions [11]:

$$\ln g^{(2)}(r, \rho) = -\beta v(r) + \sum_{n=1}^{\infty} \rho^n \gamma_n(r). \quad (3.3)$$

It should be stressed that under conventional circumstances the pair potential $v(r)$ appearing in this series is independent of density. Here the coefficient functions $\gamma_n(r)$ consist of sums of doubly-rooted cluster integrals whose integrands involve products of Mayer f functions,

$$f(r) = \exp[-\beta v(r)] - 1, \quad (3.4)$$

that are connected among themselves, and that contain no articulation points [3]. The overall strategy required is to insert the power series (3.1) representing the effective pair potential in place of $v(r)$ in the Mayer f functions, then to use those f functions in the cluster expansion (3.3), and finally to fully and consistently expand equation (3.3) in ascending powers of density. As a result, the $v_n(r)$ will be uniquely determined by the requirement that each successive density order beyond ρ^0 in $\ln g^{(2)}(r, \rho)$ should vanish identically.

For the first stage of this strategy one has [$f_0 = \exp(-\beta v_0) - 1$]:

$$\begin{aligned} f(r, \rho) &= \exp\left[-\beta \sum_{n=0}^{\infty} \rho^n v_n(r)\right] - 1 \\ &= f_0(r) - \beta v_1(r) \exp[-\beta v_0(r)]\rho + \left\{ -\beta v_2(r) \right. \\ &\quad + (1/2)[\beta v_1(r)]^2 \left. \right\} \exp[-\beta v_0(r)]\rho^2 + \left\{ -\beta v_3(r) \right. \\ &\quad + \beta^2 v_1(r)v_2(r) - (1/6)[\beta v_1(r)]^3 \left. \right\} \exp[-\beta v_0(r)]\rho^3 \\ &\quad + \left\{ -\beta v_4(r) + (1/2)[\beta v_2(r)]^2 + \beta^2 v_1(r)v_3(r) \right. \\ &\quad \left. - (1/2)[\beta v_1(r)]^2 \beta v_2(r) + (1/24)[\beta v_1(r)]^4 \right\} \\ &\quad \times \exp[-\beta v_0(r)]\rho^4 + O(\rho^5). \end{aligned} \quad (3.5)$$

When each of the f functions appearing in the cluster integral sums $\gamma_n(r)$ is replaced by this last series, and then all terms of the same density order gathered, one formally obtains expansions of the following sort:

$$\gamma_n(r, \rho) = \sum_{l=0}^{\infty} \rho^l \gamma_{n-l}(r). \quad (3.6)$$

As noted in an earlier publication [11], insertion of this expanded form as well as equation (3.1) into equation (3.3) produces the following relation:

$$\ln g_0(r) = -\beta v_0(r) + \sum_{n=1}^{\infty} \rho^n \left\{ -\beta v_n(r) + \sum_{l=0}^{n-1} \gamma_{n-l}(r) \right\}. \quad (3.7)$$

Imposition of the iso- $g^{(2)}(r)$ condition requires that each bracketed quantity within the n summation of the last expression must vanish identically:

$$\beta v_n(r) = \sum_{l=0}^{n-1} \gamma_{n-l}(r). \quad (3.8)$$

Owing to the fact that $\gamma_{n-l}(r)$ can only depend on $v_0(r) \cdots v_l(r)$, one sees that equations (3.8) uniquely specify each $v_n(r)$ in terms of those of lower order, i.e. all of the $v_n(r)$ in principle can be determined in sequence.

The two lowest-order γ_n have the following explicit integral forms:

$$\begin{aligned} \gamma_1(r_{12}) &= \int d\mathbf{r}_3 f(r_{13}) f(r_{23}); \quad (3.9) \\ \gamma_2(r_{12}) &= \int d\mathbf{r}_3 \int d\mathbf{r}_4 f(r_{13}) f(r_{34}) f(r_{24}) \\ &\quad + 2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 f(r_{13}) f(r_{14}) f(r_{34}) f(r_{24}) \\ &\quad + (1/2) \int d\mathbf{r}_3 \int d\mathbf{r}_4 f(r_{13}) f(r_{14}) f(r_{34}) f(r_{23}) f(r_{24}) \end{aligned} \quad (3.10)$$

The next order term $\gamma_3(r_{12})$ contains twelve distinct cluster integrals. Notice that the $\gamma_{n,0}(r_{12})$ have exactly the same forms as the $\gamma_n(r_{12})$, except for replacement of each integrand factor $f(r_{ij})$ with the corresponding $f_0(r_{ij})$.

The coefficient function of the first-order term of the effective pair potential, from equations (3.8) and (3.9), is

$$\beta v_1(r_{12}) = \gamma_{1,0}(r) = \int d\mathbf{r}_3 f_0(r_{13}) f_0(r_{23}). \quad (3.11)$$

That this first density correction to the pair interaction has the same spatial form as the conventional first density contribution to the pair correlation is not surprising, since they have opposing signs and thus have cancelling effects. In the second order in density, one has

$$\begin{aligned} \beta v_2(r_{12}) &= \gamma_{2,0}(r_{12}) + \gamma_{1,1}(r_{12}) \\ &= \gamma_{2,0}(r_{12}) - 2 \int d\mathbf{r}_3 \beta v_1(r_{13}) \exp[-\beta v_0(r_{13})] f_0(r_{23}). \end{aligned} \quad (3.12)$$

Needless to say, succeeding orders become increasingly complicated, but are fully determined by the procedure just described.

4. Illustrative calculations

The leading order terms $v_n(r)$ will now be evaluated for the two target pair correlation functions, equations (2.1)

and (2.5). For brevity, the calculations will be confined to $D = 3$. The corresponding zero-density Mayer f functions are very simple for these targets. The step-function $g_0(r)$ involves a step-function $f_0(r)$:

$$f_0(r) = -1 \quad (0 \leq r < a),$$

$$= 0 \quad (a \leq r). \tag{4.1}$$

By contrast, the target function (2.5) has:

$$f_0(r) = A \exp(-\alpha r^2). \tag{4.2}$$

This latter case possesses the feature that any cluster integral involving just such Gaussian integrand factors, however complicated the corresponding cluster topology, can always be carried out explicitly by diagonalizing a quadratic form in the integrand exponent.

Upon inserting $f_0(r)$ from equation (4.1) into equation (3.11), one obtains the $O(\rho^1)$ contribution to the unit-step- $g_0(r)$ effective pair potential (cf. [1], p. 211):

$$\beta v_1(r) = \pi a^3 \left[\frac{4}{3} - \frac{r}{a} + \frac{1}{12} \left(\frac{r}{a} \right)^3 \right] \quad (r \leq 2a),$$

$$= 0 \quad (2a \leq r). \tag{4.3}$$

By virtue of the fact that $\beta v_0(r)$, equation (2.3), is a hard-sphere singular interaction, the polynomial form shown in the first part of equation (4.3) actually has relevance only for $a \leq r$. This establishes the initial density trend for the effective pair potential that is charged with the responsibility to hold the pair correlation function at its simple step-function form.

Passing to the next density order $\beta v_2(r)$ for the step-function $g_0(r)$, one sees that equation (3.12) involves two contributions. The first, $\gamma_{2,0}(r)$, is the $O(\rho^2)$ component of the conventional hard-sphere $\ln g^{(2)}(r)$. The required cluster integrals have been evaluated by Nijboer and Van Hove [12]. Their results and the implied explicit form of $\gamma_{2,0}(r)$ have been collected in the Appendix. The other component requires the first-order result (4.3) as an integrand factor. After performing the somewhat tedious integration, one finds the following expression:

$$\beta v_2(r) = \gamma_{2,0}(r) + \pi^2 a^6 \left[-\frac{11}{30} \left(\frac{r}{a} \right) + \frac{17}{18} - \frac{9}{35} \left(\frac{a}{r} \right) \right]$$

$$(a \leq r \leq 2a),$$

$$= \gamma_{2,0}(r) + \pi^2 a^6 \left[\frac{1}{630} \left(\frac{r}{a} \right)^6 - \frac{1}{10} \left(\frac{r}{a} \right)^4 + \frac{1}{3} \left(\frac{r}{a} \right)^3 \right.$$

$$\left. + \frac{1}{2} \left(\frac{r}{a} \right)^2 - \frac{18}{5} \left(\frac{r}{a} \right) + \frac{9}{2} - \frac{27}{35} \left(\frac{a}{r} \right) \right]$$

$$(2a \leq r \leq 3a),$$

$$= 0 \quad (3a \leq r). \tag{4.4}$$

With each increase in density order, the range of the functions $\beta v_n(r)$ increases by one collision diameter a , as a result of the same property exhibited by the bare hard-sphere quantities $\gamma_{n,0}(r)$. Figures 1 and 2 show graphs for the first and second order density contributions to the effective pair interaction for the unit-step function $g_0(r)$.

The contrasting Gaussian target, equation (2.5), formally has the following first-order density dependence for its effective pair interaction:

$$\beta v_1(r) = (\pi/2\alpha)^{3/2} A^2 \exp[-(\alpha/2)r^2], \tag{4.5}$$

which interestingly is independent of the sign of A . Because this is a Gaussian form, one should note that

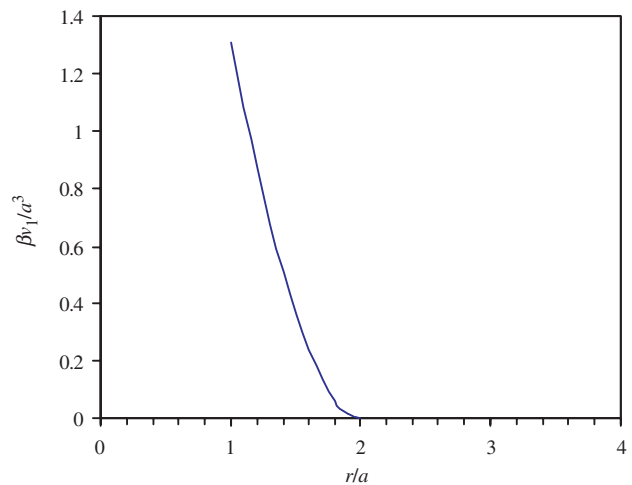


Figure 1. Plot of the first-order density contribution to the effective pair interaction for the unit-step-function pair correlation function.

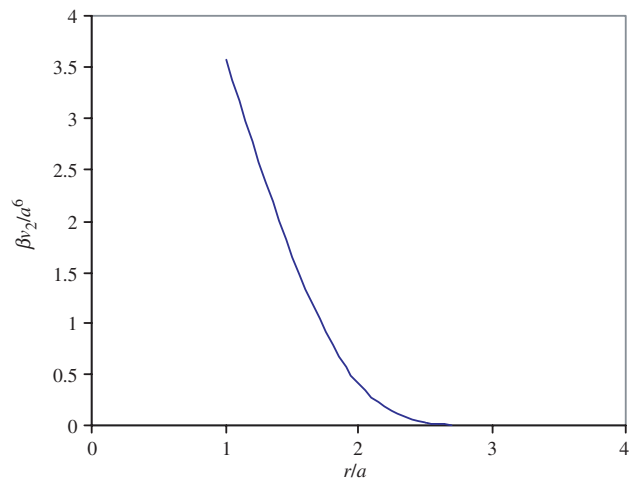


Figure 2. Plot of the second-order density contribution to the effective pair interaction for the unit-step-function pair correlation function.

in the next order, both contributions indicated in equation (3.12) above for $\beta v_2(r)$ involve only integrands that are products of Gaussian functions, and therefore both contributions are amenable to closed-form evaluations. And because the results themselves must always be finite sums of Gaussian functions of the pair distance r , this characteristic must formally persist in all density orders.

Upon carrying out the required integrals, one finally obtains an explicit form for $\beta v_2(r)$:

$$\beta v_2(r) = (\pi/\alpha)^3 \left\{ -3^{-3/2} A^3 \exp[-(\alpha/3)r^2] + 2^{-(11/2)} A^5 \exp[-\alpha r^2] \right\}. \quad (4.6)$$

In contrast to the first-order result, equation (4.5), this second-order contribution to the effective interaction is an odd function of the Gaussian amplitude A . However, there is currently no reason to believe that in higher orders the $\beta v_n(r)$ terms will display either pure even or pure odd parity in A . As was observed above for the step-function target pair correlation function, the range of the effective interaction increases with increasing order, a trend expected to continue in all higher orders.

5. Discussion

The family of ‘iso- $g^{(2)}(r)$ ’ processes within the regime of thermal equilibrium requires identification of a density-dependent effective interaction with the property that it cancels what would otherwise be a natural density variation of the pair correlation function $g^{(2)}(r)$. Consequently that correlation function remains invariant over some density range $0 \leq \rho \leq \rho_t$, where the upper terminal density limit ρ_t in some cases may be infinite. These iso- $g^{(2)}(r)$ processes have been introduced as a component of the theoretical study of correlation function realizability [7, 11, 13, 14].

The present analysis assumes that the effective interaction that is charged with the task of maintaining $g^{(2)}(r)$ invariance is pairwise additive. In fact it is presently unknown whether this is always possible, or if it is, whether such an assumption reduces the terminal density ρ_t below what it might be for a more general type of many-particle effective interaction. This question is certainly a candidate for future investigation. However, upon introducing the assumption of pairwise additivity for the effective potential, a formal procedure becomes available for developing that effective pair interaction in a density series, the terms of which can be successively and uniquely determined. This procedure has been explicitly carried out through second order in density for two distinct target pair correlation functions, the unit step function for hard-core particles, and the

pair correlation function possessing a simple Gaussian distance variation at small separations. Calculation of higher density order terms rapidly becomes increasingly difficult for the step function target. Similar terms for the Gaussian target are relatively much simpler to evaluate, though eventually become impractically difficult.

Naturally the radius of convergence of the density series for the effective pair interaction, equation (3.1), has fundamental significance. Evidently it cannot exceed the terminal density ρ_t , and in some cases might be substantially less as a result of singularities lying elsewhere in the complex ρ plane rather than on the positive axis at ρ_t . The example of the Gaussian target function, equation (2.5), is especially interesting in this regard when $A > 0$, a situation that has no useful analogue in the single-occupancy lattice scenario analysed by Korolov [9]. As remarked earlier, this is a case where absence of repulsive cores in the particles makes the extended many-particle system immediately susceptible to collapse into a single massive cluster with tiny linear dimension whenever density rises above zero. This can only be countered by immediate switching on of repulsive interactions, not with a magnitude proportional to density, but essentially discontinuously. The inference seems to be that the formal density expansion for $\beta v(r, \rho)$ in the infinite system limit has a vanishing radius of convergence. This must be true in spite of the fact that the structure factor positivity condition, equation (1.2), indicates that the terminal density for this $A > 0$ circumstance is unbounded. It is worth keeping in mind that although the convergence radius of the series might be zero, the series nevertheless may be Borel-summable [15, 16].

Even in circumstances for which the $\beta v(r, \rho)$ series has a small convergence radius, or indeed is only an asymptotic non-convergent series, the character of the first few terms in that series could provide important guidance for numerical simulation studies. Such studies in principle could search iteratively for effective interactions in finite, but reasonably large systems that yield a desired target pair correlation function.

It is obvious that the $g^{(2)}(r)$ realizability problem in general, and the iso- $g^{(2)}(r)$ problem in particular, currently retain many theoretical loose ends. It is our hope that the remarks and results contained in this paper will help to highlight those gaps in understanding, and so will encourage further investigations in this subject.

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Appendix

The hard-sphere quantity $\gamma_{2,0}(r)$ consists of three cluster-integral parts, shown generically in equation (3.10) of the main text. Following the notation of Nijboer and Van Hove [12], that equation (3.10) would be rewritten:

$$\gamma_{2,0}(r) = a^6[\varphi(r/a) + 2\psi(r/a) + (1/2)\chi(r/a)]. \quad (\text{A.1})$$

For the readers' convenience, we repeat the explicit results derived in [12] for φ , ψ , and χ :

$$\begin{aligned} \varphi(s) &= \pi^2 \left[-\frac{s^6}{1260} + \frac{s^4}{20} - \frac{s^3}{6} - \frac{s^2}{4} + \frac{9s}{5} - \frac{9}{4} + \frac{27}{70s} \right] \\ &\quad (1 \leq s \leq 3), \\ &= 0 \quad (3 \leq s); \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} \psi(s) &= \pi^2 \left[\frac{s^6}{1260} - \frac{s^4}{20} + \frac{s^3}{6} + \frac{s^2}{4} - \frac{97s}{60} + \frac{16}{9} - \frac{9}{35s} \right] \\ &\quad (1 \leq s \leq 2), \\ &= 0 \quad (2 \leq s); \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} \chi(s) &= -[g_1(s)]^2 + \pi \left[-\frac{3s^4}{280} + \frac{41s^2}{420} \right] (3 - s^2)^{1/2} \\ &\quad + \pi \left[-\frac{23s}{15} + \frac{36}{35s} \right] \arccos \left\{ \frac{s}{[3(4 - s^2)]^{1/2}} \right\} \\ &\quad + \pi \left[\frac{3s^6}{560} - \frac{s^4}{15} + \frac{s^2}{2} + \frac{2s}{15} - \frac{9}{35s} \right] \arccos \left\{ \frac{s^2 + s - 3}{[3(4 - s^2)]^{1/2}} \right\} \\ &\quad + \pi \left[\frac{3s^6}{560} - \frac{s^4}{15} + \frac{s^2}{2} - \frac{2s}{15} + \frac{9}{35s} \right] \arccos \left\{ \frac{-s^2 + s + 3}{[3(4 - s^2)]^{1/2}} \right\} \\ &\quad (1 \leq s \leq 3^{1/2}), \\ &= -[g_1(s)]^2 \quad (3^{1/2} \leq s \leq 2), \\ &= 0 \quad (2 \leq s). \end{aligned} \quad (\text{A.4})$$

This last function incorporates the definition:

$$\begin{aligned} g_1(s) &= \pi[(4/3) - s + (s^3/12)] \quad (1 \leq s \leq 2), \\ &= 0 \quad (2 \leq s), \end{aligned} \quad (\text{A.5})$$

which is recognizable as merely a scaled version of the hard-sphere $\beta v_1(r)$, equation (4.3).

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