

Equi- $g(r)$ sequence of systems derived from the square-well potential

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We introduce the idea of an “equi- $g(r)$ sequence.” This consists of a series of equilibrium many-body systems which have different number densities ρ but share, at a given temperature, the same form of pair correlation function, termed “target $g(r)$.” Each system is defined by a pair potential indexed by ρ as in $u_\rho(r)$. It is shown that for such a sequence a terminal density ρ^* exists, beyond which no physically realizable system can be found. As an illustration we derive explicit values of ρ^* for target $g(r)$ that is based on a square-well potential in the limit $\rho \rightarrow 0$. Possible application of this terminal phenomenon to the investigation into limiting amorphous packing structures of hard spheres is proposed. Virial expansions of $u_\rho(r)$ and pressure are carried out and compared with the corresponding expressions for imperfect gas. The behaviors of $u_\rho(r)$ and pressure close to $\rho = \rho^*$ are examined as well, and associated exponents extracted when they exist. The distinction between equi- $g(r)$ sequence and the related, recently introduced concept of “iso- $g^{(2)}$ process” is briefly discussed. © 2002 American Institute of Physics.
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I. INTRODUCTION

Given the interaction potential of a many-body system of atoms or molecules, statistical mechanics provides a means of determining the structure and therefore the macroscopic properties of the system.¹ We term this traditional and fruitful approach the “forward” problem of statistical mechanics. By contrast, in light of the important role that the structure plays in setting the macroscopic properties of the system, it may be more meaningful to specify the structure at some level of description and then find the corresponding interaction potential and bulk properties of the system. This is the “inverse” problem of statistical mechanics² and is considerably less well developed than the forward problem. We believe that this inverse approach will lead to new and valuable physical insights regarding the nature of many-body systems and opens up fascinating avenues of inquiry.

An interesting question that has recently been posed³ is, for what range of densities at a given temperature can one maintain a specified but fixed pair correlation function $g(r)$ and how does the potential change over this range of densities? This inverse question has been answered for the case of a simple step-function pair correlation in d dimensions.³ It was shown that there exists an upper limit on the packing fraction ($\eta = 1/2^d$) and the pair interaction develops a long-ranged Coulombic character as this “terminal” density is approached. It is natural to ask what additional features must the pair correlation function possess to increase the terminal density above that value. The answer to this question will shed light on the nature of the information contained in the pair correlation, and has fundamental implications for understanding geometric packing effects in many-body systems.

In the present paper, we take an initial step to address

this question by studying a pair correlation function that extends the one studied in Ref. 2 by adding attractive interactions. Specifically, we consider a pair correlation function corresponding to the dilute limit of the well-known square-well potential. In what follows, we describe the problem setup and then determine the terminal density for this class of amorphous packings. We then derive expressions for the pair potential and pressure under dilute conditions and near the terminal density. Finally, we remark on the distinction between so-called equi- $g(r)$ sequences and iso- $g^{(2)}$ processes (Ref. 20).

II. PROBLEM SETUP

We consider a family of equilibrium many-body systems defined by a series of pair potentials, $\{u(r)\}$. At a given temperature, T , these systems each have different number densities, $\{\rho\}$, but share the special characteristic of having a pair correlation function, $g(r)$, of an identical form. [In this paper we will use the shorthand notations of $u(r)$ and $g(r)$ for $u_2(r)$ and $g^{(2)}(r)$, respectively.] According to classical statistical mechanics, $g(r)$ is determined uniquely by the set $(T, u(r), \rho)$.⁴ Since $u(r)$ represents an internal attribute of a system while T and ρ serve as parameters that may be varied externally, it is natural, and common, to examine the behavior of $g(r)$ as a function of T and ρ with $u(r)$ fixed.¹ In this study we are interested in fixing $g(r)$ instead and letting $u(r)$ be determined by the requirement that this “target $g(r)$ ” be produced. We thus reinterpret the mapping principle of “ $(T, u(r), \rho) \mapsto g(r)$ ” and regard the alternative set $(T, g(r), \rho)$ as uniquely determining $u(r)$; in fact, T in this case simply sets the energy scale of $u(r)$ and the mapping is reduced to “ $(g(r), \rho) \mapsto \beta u(r)$ ” where $\beta = 1/k_B T$ and k_B de-

notes the Boltzmann constant. Since ρ will be the primary tuning parameter, we index the series of pair potentials by ρ as in $\{u_\rho(r)\}$ and refer to the systems as forming an “equi- $g(r)$ sequence,” which is closely related to the recently introduced concept of “iso- $g^{(2)}$ process,”³ the distinction between the two is one of the topics we discuss. How the r dependence of $u_\rho(r)$ changes with ρ will depend, of course, on the specific choice of target $g(r)$ one makes. We explore one such example.

Although its existence and uniqueness are well established,⁴ the mapping relation above is analytically tractable only at very low densities.^{1,5} Furthermore, it is only in the limit $\rho \rightarrow 0$ that an expression in a mathematically closed form is possible, given by

$$\beta u(r) = -\ln\{g(r)\} \quad (\rho \rightarrow 0). \quad (1)$$

In the familiar case of fixed $u(r)$, denoted by $u_0(r)$, the properties of a so-called imperfect gas are studied around $\rho = 0$.^{1,5} For example, the virial expansion of $g(r)$ describes how, as ρ is gradually increased, $g(r)$ departs from the limiting behavior determined by Eq. (1) and $u_0(r)$:

$$g(r) = \exp\{-\beta u_0(r)\}. \quad (2)$$

In an equi- $g(r)$ sequence, the connection between $u(r)$ and $g(r)$ is reversed. Once $g(r)$ is specified to maintain a target form $g_0(r)$, the objective is to examine how $u_\rho(r)$ departs from the limiting form determined by $g_0(r)$,

$$\beta u(r) = -\ln\{g_0(r)\}. \quad (3)$$

Change in the r dependence of $u_\rho(r)$ in turn affects how the properties of the systems such as pressure vary with ρ . Since $u(r)$ will appear most often in the form “ $\beta u(r)$,” we will occasionally use the term “pair potential” to refer to the product $\beta u(r)$ itself.

We may conduct a systematic comparison between the behaviors of an imperfect gas and an equi- $g(r)$ sequence by choosing $u_0(r)$ and $g_0(r)$ such that at some temperature $T = T_{\text{ref}}$, they satisfy

$$g_0(r) = \exp\{-\beta_{\text{ref}} u_0(r)\}, \quad (4)$$

where $\beta_{\text{ref}} = 1/k_B T_{\text{ref}}$. This establishes a common reference state between the two in the limit $\rho \rightarrow 0$ and allows us to study how, for example, the pressures along the two pathways digress from each other as ρ is slowly increased. For this purpose, we assign a square-well pair potential⁶ to $u_0(r)$:

$$u_0(r) = \begin{cases} +\infty, & 0 \leq r \leq \sigma, \\ -\varepsilon, & \sigma < r < \gamma\sigma, \\ 0, & r \geq \gamma\sigma. \end{cases} \quad (5)$$

Here σ is the hard-core diameter of the atoms or particles and the depth of the attractive well is specified by $\varepsilon > 0$. If $\varepsilon < 0$, $u_0(r)$ represents a hard-core potential with a repulsive shoulder of height $|\varepsilon|$ attached; our analyses will encompass both possibilities. The width of the well or shoulder is given by $(\gamma - 1)\sigma$ with the condition $\gamma \geq 1$ imposed. The target $g_0(r)$ follows from Eqs. (4) and (5):

$$g_0(r) = \begin{cases} 0, & 0 \leq r \leq \sigma, \\ \exp(\theta), & \sigma < r < \gamma\sigma, \\ 1, & r \geq \gamma\sigma, \end{cases} \quad (6)$$

where θ is defined as

$$\theta = \beta_{\text{ref}} \varepsilon. \quad (7)$$

By setting $\varepsilon = 0$ or $\gamma = 1$, one recovers the $u_0(r)$ of a hard-sphere system and $g_0(r)$ of a simple step-function form; this special case was studied in a previous paper.³

Since the square-well potential embodies the van der Waals idea of a short-range repulsive core embellished by a longer-range attractive tail for two-body interaction, systems derived therefrom exhibit physically reasonable behaviors, i.e., behaviors that are exhibited also by real systems. For example, for certain combinations of ε and γ , a liquid–gas phase transition appears in the phase diagram.⁶ The related $g_0(r)$, on the other hand, does not necessarily represent a physically reasonable form of $g(r)$, especially at high densities. Granted, this $g_0(r)$ by construction corresponds to a square-well system in the limit $\rho \rightarrow 0$, but experience tells us that as ρ increases, $g(r)$ in general develops oscillatory features that reflect the discrete, atomic nature of many-body systems, a feature absent in the $g_0(r)$ above. The flat profile of $g_0(r)$ for $r \geq \gamma\sigma$, and to a lesser extent in the finite range $\sigma < r < \gamma\sigma$, can be maintained in an equi- $g(r)$ sequence only if $u_\rho(r)$ develops an r dependence that successfully counteracts the tendency of any oscillatory behavior to appear in $g(r)$. The burden of maintaining such an unnatural form of $g(r)$, however, becomes increasingly stringent upon $u_\rho(r)$ with increasing ρ , and leads eventually to a physical impossibility at a finite density, $\rho = \rho^*$, at which point the equi- $g(r)$ sequence is terminated: this is shown in the next section.

Maintaining $g(r) = g_0(r)$ at a fixed ρ but under changing temperature T is trivial (in the context of classical statistical mechanics), regardless of the form of target $g_0(r)$. From Eqs. (3) and (4), we have

$$u(r) = \frac{T}{T_{\text{ref}}} u_0(r) \quad (8)$$

and T emerges simply as a proportionality factor. An equi- $g(r)$ sequence is thus never terminated along the temperature axis. From here on, we treat T as a fixed parameter and take ρ to be the only variable of interest.

III. TERMINAL DENSITY DEDUCED FROM STRUCTURE FACTOR

The existence of a terminal density ρ^* can be demonstrated on purely geometric grounds. Although we focus on three-dimensional systems in what follows, the argument is equally applicable in any other space dimension.

For isotropic systems in three dimensions, the structure factor, $S(k)$, is related to ρ and $g(r)$ by^{1,5}

$$S(k) = 1 + \rho \int_0^\infty 4\pi r^2 \{g(r) - 1\} \frac{\sin kr}{kr} dr \quad (9)$$

with k denoting the modulus of reciprocal vector. This equation is in effect the three-dimensional Fourier transform of $\{g(r) - 1\}$ reduced in form to a one-dimensional integral via angular integrations. The structure factor satisfies the non-negativity condition⁷

$$S(k) \geq 0 \quad \text{for all } k. \tag{10}$$

This inequality is a consequence of geometric constraints: $S(k)$ is defined such that no arrangement of points representing a collection of atoms or particles, nor any ensemble of such arrangements, can produce an $S(k)$ that violates this condition.^{7,8} Since geometric realizability by itself does not guarantee physical realizability, Eq. (10) is only a necessary condition that an $S(k)$ must satisfy in order for a corresponding $u(r)$ to exist. Nevertheless, by combining the mapping relation “ $(g(r), \rho) \mapsto S(k)$ ” provided by Eq. (9) with the condition $S(k) \geq 0$, one may not only ascertain the existence of ρ^* for a given target $g_0(r)$ but also obtain an upper bound on ρ^* .

For the purpose of presentation, we set

$$\hat{h}_0(k) = \int_0^\infty 4\pi r^2 \{g_0(r) - 1\} \frac{\sin kr}{kr} dr \tag{11}$$

and

$$S_\rho(k) = 1 + \rho \hat{h}_0(k). \tag{12}$$

The subscript 0 in $\hat{h}_0(k)$ denotes that we are now considering the target $g_0(r)$ derived from square-well $u_0(r)$, and the subscript ρ in $S_\rho(k)$ is intended to accentuate the importance of the ρ dependence of $S(k)$ in the following analysis. Carrying out the integration over r yields

$$\hat{h}_0(k) = 4\pi\sigma^3 \left\{ (e^\theta - 1) \frac{\gamma^2 j_1(\gamma x) - j_1(x)}{x} - \frac{j_1(x)}{x} \right\}, \tag{13}$$

where $x = k\sigma$ is the scaled reciprocal-vector modulus and $j_1(x)$ the spherical Bessel function of order one:⁹ $j_1(x) = \sin(x)/x - \cos(x)/x$. The function $\hat{h}_0(k)$ has the form of a decaying oscillation, approaching the asymptote $\hat{h}_0(k) = 0$ in the limit $k \rightarrow \infty$. If $\varepsilon = 0$ or $\gamma = 1$, the first term inside $\{\cdot\}$ vanishes and the $\hat{h}_0(k)$ based on hard-sphere $u_0(r)$ is recovered.³

The condition $S(k) \geq 0$ is automatically satisfied for $\rho \rightarrow 0$ since $S_\rho(k) \rightarrow 1$ in this limit: in fact, this is true regardless of the choice of $g_0(r)$. For any given combination of ε and γ , however, one can always find ranges of k in which $\hat{h}_0(k) < 0$ occurs and the non-negativity condition will be violated at a finite density ρ^* as ρ is increased from 0. The initial point of violation is determined by the value of $\hat{h}_0(k)$ at its minimum $k = k_{\min}$:

$$\rho^* = \frac{-1}{\hat{h}_0(k_{\min})}. \tag{14}$$

Since $\hat{h}_0(k_{\min}) < 0$, we have $\rho^* > 0$. This proves the existence of a terminal density for the square-well-based $g_0(r)$, and more generally for equi- $g(r)$ sequence of any target $g_0(r)$ whose transform $\hat{h}_0(k)$ assumes a negative value at its mini-

mum. Although, strictly speaking, the expression on the right-hand side provides only an upper bound on ρ^* as geometric realizability does not ensure physical realizability, we have assumed equality. The task of calculating ρ^* is reduced to computing k_{\min} .

We have found Eq. (13) to be analytically intractable for obtaining an expression of k_{\min} in terms of ε and γ . For example, the first derivative of $\hat{h}_0(k)$ is given by

$$\frac{d\hat{h}_0(k)}{dk} = 4\pi\sigma^4 \left\{ (e^\theta - 1) \frac{-\gamma^3 j_2(\gamma x) + j_2(x)}{x} + \frac{j_2(x)}{x} \right\}, \tag{15}$$

where $j_2(x)$ is the spherical Bessel function of order two.⁹ Since its roots are not easily derived, we have resorted to numerical calculations. Nonetheless, it is possible to make a few analytical statements. The Taylor expansion of Eq. (13) around $k = 0$ yields

$$\begin{aligned} \hat{h}_0(k) = 8\pi\sigma^3 \left[\frac{1}{3!} \{ (e^\theta - 1)(\gamma^3 - 1) - 1 \} \right. \\ \left. - \frac{2}{5!} \{ (e^\theta - 1)(\gamma^5 - 1) - 1 \} x^2 \right. \\ \left. + \frac{3}{7!} \{ (e^\theta - 1)(\gamma^7 - 1) - 1 \} x^4 \right. \\ \left. - \frac{4}{9!} \{ (e^\theta - 1)(\gamma^9 - 1) - 1 \} x^6 + \dots \right]. \tag{16} \end{aligned}$$

We focus on the sign of the coefficient of the x^2 term and set

$$\alpha = (e^\theta - 1)(\gamma^5 - 1) - 1. \tag{17}$$

If $\alpha < 0$, the function $\hat{h}_0(k)$ is convex downward at the origin and $x = 0$ represents a local minimum. For $\alpha = 0$, the point $x = 0$ is again a local minimum because the coefficient of the x^4 term is positive,

$$\begin{aligned} (e^\theta - 1)(\gamma^7 - 1) - 1 \\ = \{ (e^\theta - 1)(\gamma^5 - 1) - 1 \} + (e^\theta - 1)(\gamma^7 - \gamma^5) \\ = \frac{1}{\gamma^5 - 1} \gamma^5 (\gamma^2 - 1) > 0. \tag{18} \end{aligned}$$

The inequality follows from the original condition $\gamma \geq 1$ combined with the additional condition of $\gamma \neq 1$ when $\alpha = 0$. Numerical analyses turn out to show that $x = 0$ is in fact the global minimum of $\hat{h}_0(k)$ when $\alpha \leq 0$. Therefore

$$k_{\min} = 0 \quad \text{for } (e^\theta - 1)(\gamma^5 - 1) \leq 1. \tag{19}$$

For $\alpha > 0$, an analytical expression for k_{\min} is out of reach and full numerical evaluations have had to be carried out.

We proceed to compute ρ^* for $\alpha \leq 0$. The value of $\hat{h}_0(k)$ at $k_{\min} = 0$ is given by the first term of Eq. (16),

$$\begin{aligned} \hat{h}_0(k_{\min}) = \frac{4}{3} \pi \sigma^3 \{ (e^\theta - 1)(\gamma^3 - 1) - 1 \} \\ \text{for } (e^\theta - 1)(\gamma^5 - 1) \leq 1. \tag{20} \end{aligned}$$

Instead of ρ^* , it is more convenient to consider the terminal packing fraction, η^* , a dimensionless quantity defined as the product of ρ^* and the volume of a sphere of diameter σ ,¹

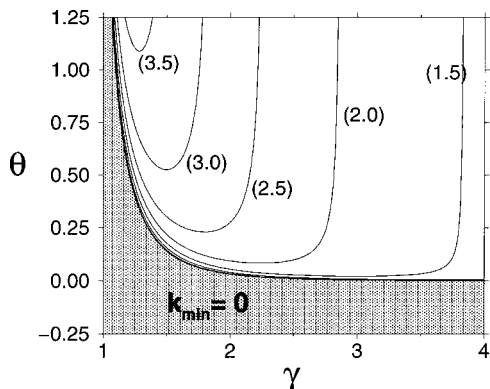


FIG. 1. Contour plot of constant k_{\min} in the plane θ versus γ . The gray background denotes that $k_{\min}=0$ everywhere below the boundary. The numbers in parentheses show the values of k_{\min} of each contour curve. The curves for $k_{\min}=1.0$ and 0.5 , though not annotated in the graph, run between the boundary and $k_{\min}=1.5$, and eventually turn upward at large γ .

$$\eta^* = \frac{\pi}{6} \sigma^3 \rho^* \quad (21)$$

It then follows from Eq. (14) that

$$\eta^* = \frac{1}{8\{1 - (e^\theta - 1)(\gamma^3 - 1)\}} \quad \text{for } (e^\theta - 1)(\gamma^3 - 1) \leq 1. \quad (22)$$

Here θ is related to ϵ by Eq. (7). A small check can be performed on this result: setting $\epsilon=0$ or $\gamma=1$ satisfies the condition $\alpha \leq 0$ and correctly yields $\eta^*=1/8$, the three-dimensional hard-sphere value derived previously.³

We combine Eqs. (19) and (22) with the results of numerical calculations performed for $\alpha > 0$. Figures 1 and 2 summarize the outcome in the form of contour plots of constant k_{\min} and η^* , respectively, in the plane θ versus γ . We recall from Eq. (5) that $\theta > 0$ and $\theta < 0$ correspond, respec-

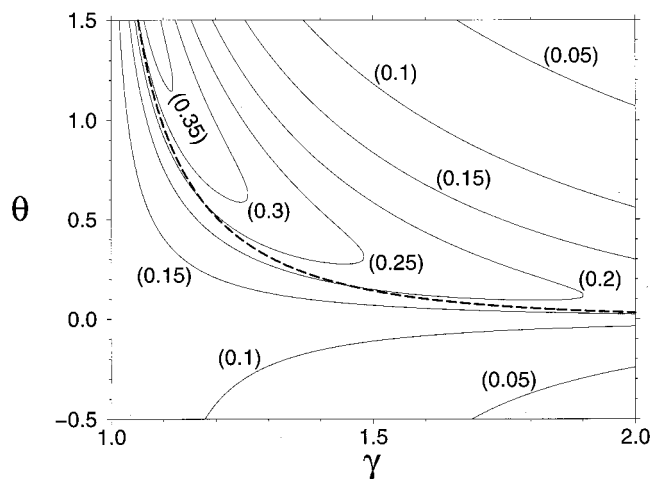


FIG. 2. Contour plot of constant η^* in the plane θ versus γ . The thick dashed line denotes the boundary defined by Eq. (23). The numbers in parentheses show the values of η^* of each contour curve. The curves for $\eta^*=0.15$ above and below the boundary meet each other at large γ ; those for $\eta^*=0.1$ and 0.05 do not. The curve for $\eta^*=0.35$ never crosses the boundary.

tively, to square-well and repulsive-shoulder $u_0(r)$'s. In both plots, a special boundary is defined by the curve $\alpha=0$,

$$\theta = \ln\left(\frac{1}{\gamma^3 - 1} + 1\right) \quad [\text{Boundary}]. \quad (23)$$

Below this boundary, $k_{\min}=0$ everywhere and the contour curves of constant η^* are obtained by rearranging Eq. (22),

$$\theta = \ln\left\{\left(1 - \frac{1}{8\eta^*}\right)\frac{1}{\gamma^3 - 1} + 1\right\}. \quad (24)$$

Since the region $\theta < 0$ lies entirely below the boundary, the terminal point of an equi- $g(r)$ sequence derived from repulsive-shoulder $u_0(r)$ is given full analytical characterization.

Above the boundary, contour curves of nonzero k_{\min} develop smoothly off the region of $k_{\min}=0$ as Fig. 1 shows. Higher values of k_{\min} are found for smaller γ and larger θ , that is, in the upper-left direction of the plot. As one moves away from the boundary, the curves become steeper and k_{\min} becomes increasingly independent of θ : for square-well $g_0(r)$ with large ϵ and γ , the value of k_{\min} is determined predominantly by γ . This is reasonable since γ sets the width of the attractive well, i.e., the spatial characteristic of $g_0(r)$.

The contour plot of η^* in Fig. 2 also exhibits continuous behavior across the boundary. Along its upper side, η^* shows an oblique turnover feature: by fixing θ and increasing γ , or conversely by fixing γ and increasing θ , one observes η^* to increase initially from the boundary, quickly reach a maximum, and then decrease monotonically to an apparent asymptotic value of 0. Far from the boundary, the curves show monotonic and hyperbolalike dependences on both θ and γ . The contour curves above and below meet each other at some point for $0.125 < \eta^* < 0.3125$. Curves with $\eta^* > 0.3125$ exist only above the boundary.

Bounds on η^* in the region $\theta < 0$ are derived without difficulty from Eq. (22):

$$0 < \eta^* < \frac{1}{8} \quad [\text{Repulsive-shoulder } g_0(r)]. \quad (25)$$

The lower bound 0 is obtained in the limit $\gamma \rightarrow \infty$ while the upper bound $1/8$ arises in the hard-sphere limit of either $\theta \rightarrow 0^-$ or $\gamma \rightarrow 1^+$. Bounds for $\theta > 0$, on the other hand, are given by

$$0 < \eta^* < \eta_{\max}^* \quad \text{with } \eta_{\max}^* > \frac{5}{16} \quad [\text{Square-well } g_0(r)]. \quad (26)$$

The lower bound 0 appears in the limits $\theta \rightarrow \infty$ and $\gamma \rightarrow \infty$ while the maximum packing fraction, η_{\max}^* , occurs in Fig. 2 along the upper side of the boundary in the limit $\theta \rightarrow \infty$. Although the precise value of η_{\max}^* is unknown, its lower bound $5/16$ can be derived by focusing on the contour curves that cross the boundary. At this intersection, both Eqs. (22) and (23) hold, so we have

TABLE I. Some important limiting densities in one, two, and the three dimensions. Terminal densities for the step function $g(r)$ and square well $g(r)$. Included are the maximum densities for hard spheres.

State	$d=1$	$d=2$	$d=3$
Terminal density [step-function $g(r)$], η^*	0.5	0.25	0.125
Terminal density [square-well $g(r)$], η^*	0.75	0.5	0.3125
Maximum density, η^{\max}	1.0	$\pi\sqrt{12}\approx 0.907$	$\pi/\sqrt{18}\approx 0.740$

$$\eta^* = \frac{1}{8 \left\{ 1 - \frac{1}{\gamma^5 - 1} (\gamma^3 - 1) \right\}} = \frac{1}{8} \left\{ 1 + \frac{\gamma^2 + \gamma + 1}{\gamma^3 (\gamma + 1)} \right\}. \quad (27)$$

It then follows that for boundary-crossing curves,

$$\frac{1}{8} < \eta^* < \frac{5}{16}, \quad (28)$$

where $1/8$ and $5/16$ result from taking the limits $\gamma \rightarrow \infty$ and $\gamma \rightarrow 1^+$, respectively, and $\eta_{\max}^* > 5/16$ is obtained. Curves with $\eta^* > 5/16$ thus remain above the boundary.

The value $\eta_{\max}^* > 5/16$ is an improvement over the hard-sphere value of $1/8$, improvement in the sense that the threshold has been pushed higher and the range of existence of equi- $g(r)$ sequence widened accordingly. This improvement arises because the square-well $g_0(r)$ has a physically more reasonable form than does the simple hard-sphere one: the hump in the $g_0(r)$ right outside the hard core more or less mimics the first peak of oscillation that develops in the $g(r)$ of real systems and accommodates for the formation of what may resemble a first shell of nearby neighbors. By the same reasoning, we expect η_{\max}^* to be improved even further if $u_0(r)$, currently of a square-well form, is dressed with an additional repulsive hill outside the attractive well, somewhat like a truncated Friedel oscillation.¹⁰ The new target $g'_0(r)$ would then be

$$g'_0(r) = \begin{cases} 0, & 0 \leq r \leq \sigma, \\ \exp(\theta), & \sigma < r < \gamma\sigma, \\ \exp(-\theta'), & \gamma\sigma \leq r < \gamma'\sigma, \\ 1, & r \geq \gamma'\sigma, \end{cases} \quad (29)$$

where $\theta > 0$, $\theta' > 0$, and $\gamma' > \gamma > 1$. The additional dent in the range $\gamma\sigma \leq r < \gamma'\sigma$ augments the incipient oscillatory behavior expressed by the square-well $g_0(r)$ and enhances the physical realizability of $g'_0(r)$. An immediate extension of this procedure is to continue modifying $g_0(r)$ so that η_{\max}^* keeps improving until one reaches a limit. What is the value of η_{\max}^* in this limit? What type of r dependence does the corresponding $g_0(r)$ attain? And what kind of hard-sphere packing structure does this limit represent?^{11,12} Addressing these questions, however, is beyond the scope of the present work.

Similarly, the bounds on η^* for repulsive-shoulder $g_0(r)$ show diminishment in the range of equi- $g(r)$ sequence: the depletion zone built into this $g_0(r)$ right outside the hard core frustrates the way a many-body system naturally packs with increasing ρ and it quickly becomes untenable to maintain such $g_0(r)$.

The bounds can be generalized to d dimensions. For an isotropic d -dimensional system, $S(k)$ is related to ρ and $g(r)$ by¹³

$$S(k) = 1 + \rho \int_0^\infty (2\pi)^{d/2} r^{d-1} \{g(r) - 1\} \frac{J_{(d/2)-1}(kr)}{(kr)^{(d/2)-1}} dr, \quad (30)$$

where $J_{(d/2)-1}(kr)$ is the Bessel function of order $\{(d/2) - 1\}$. Applying the same analysis as above leads to

$$0 < \eta^* < \frac{1}{2^d} [\text{Repulsive-shoulder } g_0(r)] \quad (31)$$

and

$$0 < \eta^* < \eta_{\max}^* \quad \text{with} \quad \eta_{\max}^* > \frac{d+2}{2^{d+1}} [\text{Square-well } g_0(r)]. \quad (32)$$

Table I compares the terminal density in one, two, and three dimensions to limiting densities in other systems. Specifically, we compare our results to the terminal density for the step-function $g(r)$ as well as the maximum density for hard spheres.

IV. FUNCTIONAL FORM OF $u_\rho(r)$ AROUND THE LIMITS $\rho \rightarrow 0$ AND $\rho \rightarrow \rho^*$

A target $g_0(r)$, once specified, uniquely determines $\beta u_\rho(r)$ for all $\rho \leq \rho^*$. This in turn determines all the properties of the systems within the sequence. Here we derive the expression for $\beta u_\rho(r)$ around two limiting values of ρ ; the results are used in the next section to calculate the pressure. We first present what amounts to a virial expansion of $\beta u_\rho(r)$ around $\rho = 0$ and compare it with that of $g(r)$ of imperfect gas. We then show that as ρ approaches ρ^* from below, $\beta u_\rho(r)$ develops a singular behavior that signals the end of equi- $g(r)$ sequence.

A general relationship between $\beta u(r)$ and $g(r)$ is given by¹

$$\beta u(r) = -\ln\{g(r)\} + h(r) - c(r) + B(r). \quad (33)$$

Here $h(r)$, the total correlation function, represents the fluctuational part of $g(r)$, namely,

$$h(r) = g(r) - 1, \quad (34)$$

$c(r)$ is the direct correlation function defined in terms of ρ and $h(r)$ via the Ornstein-Zernike relation

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(|\mathbf{r}'|) d\mathbf{r}', \quad (35)$$

and $B(r)$ is the so-called bridge function. Unless explicitly shown, the range of integration for all the integrals is $(-\infty, \infty)$ for each Cartesian coordinate. Although Eq. (33) is formally exact, its usefulness hinges on how tractable $B(r)$ is: In the limit $\rho \rightarrow 0$, one can carry out a density expansion of $B(r)$ in terms of $h(r)$, and in the other limit $\rho \rightarrow \rho^*$, a mild assumption on $B(r)$ allows us to extract the salient feature of $\beta u(r)$, but away from these two limits, the intractability of $B(r)$ renders Eq. (33) of little practical use. For notational

convenience, we rewrite Eq. (35) in a form that involves particle indices,

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})h(r_{32})d\mathbf{r}_3 \quad (36)$$

Here $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the scalar distance between two particles indexed by i and j , and \mathbf{r}_3 is a dummy variable of integration.

First we consider the density expansion of Eq. (33). For $c(r)$, the Ornstein–Zernike relation leads to⁵

$$c(r_{12}) = h(r_{12}) - \rho \int h(r_{13})h(r_{32})d\mathbf{r}_3 + \rho^2 \int \int h(r_{13})h(r_{34})h(r_{42})d\mathbf{r}_3 d\mathbf{r}_4 - \rho^3 \int \int \int h(r_{13})h(r_{34})h(r_{45})h(r_{52})d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + \dots \quad (37)$$

For $B(r)$, the corresponding density expansion is given by¹⁴

$$B(r_{12}) = \frac{\rho^2}{2} \int \int h(r_{13})h(r_{14})h(r_{34})h(r_{32})h(r_{42})d\mathbf{r}_3 d\mathbf{r}_4 + \rho^3 \int \int \int h(r_{13})h(r_{14})h(r_{34})h(r_{45})h(r_{32})h(r_{52}) \times \left[h(r_{15}) \left\{ 1 + h(r_{35}) + \frac{1}{2}h(r_{42}) + \frac{1}{6}h(r_{35})h(r_{42}) \right\} + h(r_{35}) \right] d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + \dots \quad (38)$$

Since the coefficient of the leading ρ^2 term here is a multiparticle integral, $B(r)$ in general is expected to be shorter ranged than $h(r)$.¹⁴ By inserting Eqs. (37) and (38) into (33), the density expansion of $\beta u_\rho(r)$ is obtained in terms of $h_0(r) = g_0(r) - 1$,

$$\beta u_\rho(r_{12}) = -\ln\{g_0(r_{12})\} + \rho \int h_0(r_{13})h_0(r_{32})d\mathbf{r}_3 + \rho^2 \int \int h_0(r_{13})h_0(r_{34})h_0(r_{42}) \left\{ \frac{1}{2}h_0(r_{14})h_0(r_{32}) - 1 \right\} d\mathbf{r}_3 d\mathbf{r}_4 + \rho^3 \int \int \int h_0(r_{13})h_0(r_{34})h_0(r_{45})h_0(r_{52}) \left\{ 1 + h_0(r_{14})h_0(r_{32}) \left[h_0(r_{15}) \left\{ 1 + h_0(r_{35}) + \frac{1}{2}h_0(r_{42}) + \frac{1}{6}h_0(r_{35})h_0(r_{42}) \right\} + h_0(r_{35}) \right] \right\} d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + \dots \quad (39)$$

This is the virial expansion of $\beta u_\rho(r)$. It expresses how $\beta u_\rho(r)$ departs from the initial form $-\ln\{g_0(r)\}$ as ρ is increased from 0 while the constancy of $g_0(r)$ is maintained.

It is instructive to compare this virial expansion with that of $g(r)$ for a conventional imperfect gas. For emphasis we denote the latter $g(r)$, governed by a fixed pair potential $u_0(r)$, by $g_\rho(r)$. Its virial expansion is given by⁵

$$g_\rho(r_{12}) = \exp\{-\beta u_0(r_{12})\} \left\{ 1 + \rho \int f_0(r_{13})f_0(r_{32})d\mathbf{r}_3 + \frac{\rho^2}{2} \int \int [2f_0(r_{13})f_0(r_{34})f_0(r_{42}) \times \{1 + 2f_0(r_{32})\} + f_0(r_{13})f_0(r_{14})f_0(r_{32})f_0(r_{42}) \times \{1 + f_0(r_{34})\}] d\mathbf{r}_3 d\mathbf{r}_4 + \dots \right\} \quad (40)$$

where $f_0(r)$ stands for the Mayer function,

$$f_0(r) = \exp\{-\beta u_0(r)\} - 1. \quad (41)$$

The virial expansion of $\ln\{g_\rho(r)\}$ is then derived to be

$$\ln\{g_\rho(r_{12})\} = -\beta u_0(r_{12}) + \rho \int f_0(r_{13})f_0(r_{32})d\mathbf{r}_3 + \rho^2 \int \int f_0(r_{13})f_0(r_{34})f_0(r_{42}) \times \left\{ 1 + 2f_0(r_{32}) + \frac{1}{2}f_0(r_{14})f_0(r_{32}) \right\} d\mathbf{r}_3 d\mathbf{r}_4 + \dots \quad (42)$$

which is the expression to be compared with Eq. (39).

The condition Eq. (4) is equivalent to setting

$$f_0(r) = h_0(r). \quad (43)$$

A term-by-term comparison between Eqs. (42) and (39) then shows that the effects of increasing ρ on $\ln\{g_\rho(r)\}$ and $\beta u_\rho(r)$ are identical to linear order in ρ ,

$$\rho \int f_0(r_{13})f_0(r_{32})d\mathbf{r}_3 = \rho \int h_0(r_{13})h_0(r_{32})d\mathbf{r}_3. \quad (44)$$

This result can be given a physically intuitive interpretation. For the ranges of r_{12} in which this first-order term is positive, $g_\rho(r_{12})$ exhibits an increase as ρ is increased from 0. In an equi- $g(r)$ sequence, such impending changes in $g(r)$, changes that would occur if the initial form of $u_0(r)$ were maintained, are suppressed, and the constancy of $g_0(r)$ attained, by a corresponding increase in $\beta u_\rho(r_{12})$, that is, by a development of repulsive interactions. Likewise, for r_{12} where the first-order term is negative, the depletion that takes place in $g_\rho(r_{12})$ and which would have taken place in $g_0(r)$ is offset by the emergence of attractive interactions in $\beta u_\rho(r_{12})$. Although the coefficients no longer match each other at order ρ^2 and presumably beyond, the notion of $\beta u_\rho(r)$ being tuned so as to balance out what would otherwise occur to $g(r)$ should still be valid. Given the square-well $g_0(r)$ and $f_0(r)=h_0(r)$, one can derive analytical expressions for the first few virial coefficients of $\beta u_\rho(r)$ in terms of ϵ and γ by adapting the known results for imperfect gas.^{15,16}

The virial expansion above shows that $\beta u_\rho(r)$ remains a short-ranged function of r around $\rho=0$ if $g_0(r)$ itself is short ranged. This is not necessarily the case away from $\rho=0$. By rewriting Eq. (33) in notations that stress the importance of ρ dependences, namely,

$$\beta u_\rho(r) = -\ln\{g_0(r)\} + g_0(r) - 1 - c_\rho(r) + B_\rho(r), \quad (45)$$

it is seen that $\beta u_\rho(r)$ may become long ranged if either $c_\rho(r)$ or $B_\rho(r)$ develops such a singular behavior.³ Indeed, it follows from the Ornstein-Zernike relation that the Fourier transform, $\hat{c}_\rho(k)$, of $c_\rho(r)$ is related to $S_\rho(k)$ by¹

$$\hat{c}_\rho(k) = \frac{1}{\rho} \left\{ 1 - \frac{1}{S_\rho(k)} \right\} \quad (46)$$

and $c_\rho(r)$ becomes singular in the event $S_\rho(k) \rightarrow 0^+$ occurs, i.e., when the geometric condition of $S_\rho(k) \geq 0$ is violated. If we make the mild assumption that $B_\rho(r)$ meanwhile remains short ranged so as not to cancel out this singularity, an assumption commonly accepted for the behavior of $B(r)$ in general, then this analysis points once again to the special significance of ρ^* . For the extraction of the salient, long-ranged r dependence that develops in $\beta u_\rho(r)$ in the limit $\rho \rightarrow \rho^{*-}$, one need only look into the inverse Fourier transform of the singular term $\{\rho S_\rho(k)\}^{-1}$ in Eq. (46),

$$\beta u_\rho(r) \sim \frac{1}{\rho} \frac{1}{(2\pi)^3} \int \frac{1}{S_\rho(k)} e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k} \quad (47)$$

or upon angular integrations,

$$\beta u_\rho(r) \sim \frac{1}{\rho} \frac{1}{(2\pi)^3} \int_0^\infty 4\pi k^2 \frac{1}{S_\rho(k)} \frac{\sin rk}{rk} dk. \quad (48)$$

We are now in a position to examine the specific case of square-well $g_0(r)$.

The development of a singularity in $\{S_\rho(k)\}^{-1}$ can be viewed as being due to poles that approach the real axis in

the complex k plane as $\rho \rightarrow \rho^{*-}$. The effect of these poles on the functional form of $\beta u_\rho(r)$ is evaluated by rewriting Eq. (48) in the complex form¹⁷

$$\beta u_\rho(r) \sim \frac{1}{\rho} \frac{1}{8\pi^2 i} \frac{1}{r} \left\{ \int_{-\infty}^\infty \frac{ke^{irk}}{S_\rho(k)} dk - \int_{-\infty}^\infty \frac{ke^{-irk}}{S_\rho(k)} dk \right\}. \quad (49)$$

Focusing on $S_\rho(k)$ around its global minimum allows us to approximate the behavior of the approaching poles in $\{S_\rho(k)\}^{-1}$. Manipulation of Eq. (12) gives

$$S_\rho(k) = 1 + \rho \hat{h}_0(k_{\min}) + \rho \hat{h}_0(k) - \rho \hat{h}_0(k_{\min}) = \left(1 - \frac{\rho}{\rho^*} \right) + \rho \{ \hat{h}_0(k) - \hat{h}_0(k_{\min}) \}, \quad (50)$$

where Eq. (14) has been applied. The next step is to expand $\{ \hat{h}_0(k) - \hat{h}_0(k_{\min}) \}$ around $k=k_{\min}$ and retain only the lowest-order term in $(k-k_{\min})$. The specific formula depends on the sign of α defined by Eq. (17). We examine each case separately.

$\alpha < 0$. This range of α covers the combinations of ϵ and γ for all repulsive-shoulder $g_0(r)$ and some of square-well $g_0(r)$. From Eq. (19) we have $k_{\min}=0$ and $S_\rho(k)$ is approximated by

$$S_\rho(k) \approx \left(1 - \frac{\rho}{\rho^*} \right) + \frac{2\pi\sigma^3}{15} (-\alpha)\rho(k\sigma)^2. \quad (51)$$

The complex integration of Eq. (49) then yields

$$\beta u_\rho(r) \sim \frac{15}{8\pi^2\sigma^6(-\alpha)\rho^2} \frac{\sigma}{r} \exp\left(-\frac{r}{\xi_<}\right), \quad (52)$$

where $\xi_<$ is given, in a form that isolates its singular ρ dependence, by

$$\xi_< = A_< \left(1 - \frac{\rho}{\rho^*} \right)^{-1/2} \quad (53)$$

with the remaining factors subsumed into $A_<$:

$$A_< = \sigma \sqrt{\frac{2\pi\sigma^3}{15} (-\alpha)\rho}. \quad (54)$$

This $\beta u_\rho(r)$ has the form of a screened Coulomb pair potential.^{1,3} In the limit $\rho \rightarrow \rho^{*-}$, the screening length $\xi_<$ diverges with an exponent equal to $-1/2$ and $\beta u_\rho(r)$ represents pure Coulombic repulsion.

$\alpha = 0$. This is the boundary curve of Eq. (23). We again have $k_{\min}=0$ but the term retained in $\hat{h}_0(k)$ is of the order k^4 as opposed to k^2 :

$$S_\rho(k) \approx \left(1 - \frac{\rho}{\rho^*} \right) + \frac{\pi\sigma^3}{210} \alpha_4 \rho (k\sigma)^4 \quad (55)$$

in which we have set

$$\alpha_4 = (e^\theta - 1)(\gamma^7 - 1) - 1 \quad (56)$$

and $\alpha_4 > 0$ according to Eq. (18). Complex integration yields

$$\beta u_\rho(r) \sim \frac{105}{4\pi^2\sigma^6\alpha_4\rho^2} \frac{\xi_+}{\sigma} \frac{\sin(r/\xi_+)}{r/\xi_+} \exp\left(-\frac{r}{\xi_+}\right), \quad (57)$$

where ξ_+ is given by

$$\xi_{\pm} = A \left(1 - \frac{\rho}{\rho^*} \right)^{-1/4} \quad (58)$$

with

$$A = \sigma \left(\frac{2\pi\sigma^3}{105} \alpha_4 \rho \right)^{1/4}. \quad (59)$$

This $\beta u_{\rho}(r)$ has the form of a damped oscillation whose period and decay lengths are both given by ξ_{\pm} . In the limit $\rho \rightarrow \rho^{*-}$, the characteristic length ξ_{\pm} diverges with an exponent equal to $-1/4$.

$\alpha > 0$. Here we have $k_{\min} > 0$ but lack analytical expressions for k_{\min} and $\hat{h}_0(k)$ around $k = k_{\min}$. For the purpose of analysis, we let an undetermined positive parameter D denote a coefficient of expansion and approximate $\{S_{\rho}(k)\}^{-1}$ by

$$\frac{1}{S_{\rho}(k)} \approx \frac{1}{(1 - \rho/\rho^*) + D(k - k_{\min})^2} + \frac{1}{(1 - \rho/\rho^*) + D(k + k_{\min})^2}. \quad (60)$$

It is necessary to include both $(k - k_{\min})^2$ and $(k + k_{\min})^2$ so that $S_{\rho}(k)$ remains an even function of k . In addition, we have approximated $\{S_{\rho}(k)\}^{-1}$ instead of $S_{\rho}(k)$ since it is impossible to assign directly to $S_{\rho}(k)$ a function that is of the order k^2 and at the same time has minima at $k = \pm k_{\min}$: the $\{S_{\rho}(k)\}^{-1}$ above does have maxima at $k = \pm k_{\min}$ for $D > 0$ when $\rho \leq \rho^*$. Carrying out the complex integration yields

$$\beta u_{\rho}(r) \sim \frac{1}{2\pi D \rho} \sqrt{k_{\min}^2 \xi_{>}^2 + 1} \frac{\sin(k_{\min} r + \chi)}{r} \exp\left(-\frac{r}{\xi_{>}}\right), \quad (61)$$

where the length $\xi_{>}$ is defined as

$$\xi_{>} = \sqrt{D} \left(1 - \frac{\rho}{\rho^*} \right)^{-1/2} \quad (62)$$

and the phase factor χ satisfies

$$\tan \chi = \frac{1}{k_{\min} \xi_{>}} \left(0 < \chi < \frac{\pi}{2} \right). \quad (63)$$

This $\beta u_{\rho}(r)$ has the form of a decaying oscillation. Unlike in the case of $\alpha = 0$, the decay length is given by $\xi_{>}$ whereas the period is given independently of $\xi_{>}$ by $2\pi/k_{\min}$. In the limit $\rho \rightarrow \rho^{*-}$, the length $\xi_{>}$ diverges with an exponent equal to $-1/2$.

These analyses also show why the sequence must terminate at $\rho = \rho^*$ rather than simply pass through this point. For $\alpha < 0$ and $\alpha > 0$, the lengths $\xi_{<}$ and $\xi_{>}$ become imaginary numbers when $\rho > \rho^*$ and the exponential-decay term $\exp(-r/\xi)$ in $\beta u_{\rho}(r)$ is converted into an oscillatory term; for $\alpha = 0$, the length ξ_{\pm} becomes a complex number and generates an oscillatory, nondecaying term out of the product $\sin(r/\xi_{\pm}) \exp(-r/\xi_{\pm})$. Since in three dimensions $u(r)$ must decay faster than r^{-3} as $r \rightarrow \infty$ if a well-behaved system is to be produced in the thermodynamic limit, and since $\beta u_{\rho}(r)$ would decay only as fast as r^{-1} in all three cases if $\rho > \rho^*$, the mathematical solutions obtained thereby must be rejected on physical grounds and the equi- $g(r)$ sequence terminated.

V. BEHAVIOR OF PRESSURE AROUND THE LIMITS $\rho \rightarrow 0$ AND $\rho \rightarrow \rho^*$

Once $\beta u_{\rho}(r)$ and its ρ dependence are derived, all the properties of the systems within the sequence follow. As a representative example, we build upon the results of the last section to examine how the pressure, p , varies with ρ close to the limits $\rho \rightarrow 0$ and $\rho \rightarrow \rho^*$.

The virial expansion of p of an imperfect gas with fixed $u_0(r)$ is well known⁵

$$\begin{aligned} \frac{p}{k_B T} = & \rho - \frac{\rho^2}{2V} \int \int f_0(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \\ & - \frac{\rho^3}{3V} \int \int \int f_0(r_{12}) f_0(r_{23}) f_0(r_{31}) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ & \dots \end{aligned} \quad (64)$$

Here V is the volume of the system and $f_0(r)$ the Mayer function defined by Eq. (41). The corresponding virial expansion for equi- $g(r)$ sequence is readily obtained from this standard expression. For economy of presentation, we introduce a shorthand notation for the density expansion of $\beta u_{\rho}(r)$,

$$\begin{aligned} \beta u_{\rho}(r) = & \beta u_0(r) + \rho \beta u_1(r) + \frac{\rho^2}{2} \beta u_2(r) + \frac{\rho^3}{6} \beta u_3(r) + \dots \\ = & \sum_{n=0}^{\infty} \frac{\rho^n}{n!} \beta u_n(r). \end{aligned} \quad (65)$$

We presume this series has a positive radius of convergence. Explicit expressions for the coefficient functions $\{\beta u_n(r)\}$ in terms of $g_0(r)$ follow from Eq. (39); for example, the first three are given by

$$\beta u_0(r_{12}) = -\ln\{g_0(r_{12})\}, \quad (66)$$

$$\beta u_1(r_{12}) = \int h_0(r_{13}) h_0(r_{32}) d\mathbf{r}_3, \quad (67)$$

$$\begin{aligned} \beta u_2(r_{12}) = & 2 \int \int h_0(r_{13}) h_0(r_{34}) h_0(r_{42}) \\ & \times \left\{ \frac{1}{2} h_0(r_{14}) h_0(r_{32}) - 1 \right\} d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \quad (68)$$

The density expansion of the Mayer function, $f_{\rho}(r)$, of $\beta u_{\rho}(r)$ is then derived to be

$$\begin{aligned} f_{\rho}(r) = & \exp\{-\beta u_{\rho}(r)\} - 1 \\ = & f_0(r) - \rho\{1 + f_0(r)\}\beta u_1(r) \\ & + \frac{\rho^2}{2}\{1 + f_0(r)\}[\{\beta u_1(r)\}^2 - \beta u_2(r)] - \dots \end{aligned} \quad (69)$$

The virial expansion we seek is obtained by inserting Eq. (69) into Eq. (64), collecting terms of like order in ρ , and recalling Eq. (43):

$$\begin{aligned} \frac{\bar{p}}{k_B T} &= \rho - \frac{\rho^2}{2V} \int \int f_\rho(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 - \frac{\rho^3}{3V} \int \int \int f_\rho(r_{12}) f_\rho(r_{23}) f_\rho(r_{31}) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 - \dots \\ &= \rho - \frac{\rho^2}{2V} \int \int h_0(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 - \frac{\rho^3}{3V} \left[\int \int \int h_0(r_{12}) h_0(r_{23}) h_0(r_{31}) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \right. \\ &\quad \left. - \frac{3}{2} \int \int \{1 + h_0(r_{12})\} \beta u_1(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \right] - \dots \end{aligned} \tag{70}$$

We have chosen to denote the pressure of an equi- $g(r)$ sequence by the symbol \bar{p} rather than by p in order to emphasize a distinction: while p refers to a single system defined by a fixed $u_0(r)$, \bar{p} refers to a family of systems, one at each ρ with a different pair potential.

A term-by-term comparison between Eqs. (70) and (64) reveals that the two virial expansions differ from each other at order ρ^3 ,

$$\begin{aligned} \frac{\bar{p}}{k_B T} - \frac{p}{k_B T} &= \frac{\rho^3}{2V} \int \int \{1 + h_0(r_{12})\} \beta u_1(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 + \dots \\ &= \frac{\rho^3}{2V} \int \int \int \{1 + h_0(r_{12})\} h_0(r_{13}) \\ &\quad \times h_0(r_{32}) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 + \dots \end{aligned} \tag{71}$$

The ρ^2 term, the lowest-order term that captures non-ideal-gas behavior, is identical for \bar{p} and p because the same form of pair potential is initially shared: it is only in the subsequent terms that the different effects of what is being held fixed are manifested. It is straightforward to derive higher-order terms of \bar{p} beyond what appears in Eq. (70). Given square-well $g_0(r)$, one can also evaluate the integrals to derive analytical expressions for the coefficients in terms of ε and γ based on those obtained for imperfect-gas p .^{15,16}

For \bar{p} in the other limit $\rho \rightarrow \rho^{*-}$, we employ the pressure equation⁵ presented in notations tailored for equi- $g(r)$ sequence,

$$\frac{\bar{p}}{k_B T} = \rho - \frac{\rho^2}{6} \int_0^\infty 4\pi r^3 \frac{d\{\beta u_\rho(r)\}}{dr} g_0(r) dr. \tag{72}$$

For square-well $g_0(r)$, the sign of α determines the form of $\beta u_\rho(r)$ and hence \bar{p} . Since our sole interest is in if and how \bar{p} diverges as $\rho \rightarrow \rho^{*-}$, we simplify this equation by first inserting the square-well $g_0(r)$:

$$\begin{aligned} \frac{\bar{p}}{k_B T} &= \rho - \frac{\rho^2}{6} \int_\sigma^{\gamma\sigma} 4\pi r^3 \frac{d\{\beta u_\rho(r)\}}{dr} e^\theta dr \\ &\quad - \frac{\rho^2}{6} \int_{\gamma\sigma}^\infty 4\pi r^3 \frac{d\{\beta u_\rho(r)\}}{dr} dr. \end{aligned} \tag{73}$$

A divergence in \bar{p} , if it does indeed diverge, can come only from the third term and so we approximate \bar{p} by

$$\frac{\bar{p}}{k_B T} \approx - \frac{\rho^2}{6} \int_0^\infty 4\pi r^3 \frac{d\{\beta u_\rho(r)\}}{dr} dr. \tag{74}$$

An additional simplification of changing the lower limit from $\gamma\sigma$ to 0, which will not affect the divergence, has also been made.

$\alpha < 0$. From Eq. (52), we have

$$\beta u_\rho(r) \sim B_{<} \frac{1}{\rho^2} \frac{\sigma}{r} \exp\left(-\frac{r}{\xi_{<}}\right), \tag{75}$$

where $B_{<}$ is a positive constant whose actual formula need not concern us. Inserting this into Eq. (74) yields

$$\frac{\bar{p}}{k_B T} \sim - \frac{B_{<}}{6} \int_0^\infty 4\pi r^3 \frac{d}{dr} \left\{ \frac{\sigma}{r} \exp\left(-\frac{r}{\xi_{<}}\right) \right\} dr. \tag{76}$$

By changing the variable of integration from r to $y = r/\xi_{<}$, we obtain

$$\frac{\bar{p}}{k_B T} \sim \xi_{<}^2 (-1) \frac{\sigma B_{<}}{6} \int_0^\infty 4\pi y^3 \frac{d}{dy} \left\{ \frac{1}{y} \exp(-y) \right\} dy. \tag{77}$$

The integral over y is independent of ρ and is calculated to be -12π . Finally, by inserting the expression for $\xi_{<}$ from Eq. (53) and ignoring the constant factors, we arrive at

$$\frac{\bar{p}}{k_B T} \propto \left(1 - \frac{\rho}{\rho^*}\right)^{-1}. \tag{78}$$

Thus, for the combinations of ε and γ that satisfy $\alpha < 0$, the pressure \bar{p} diverges in the limit $\rho \rightarrow \rho^{*-}$ with an exponent equal to -1 .

$\alpha = 0$. Here Eq. (57) gives

$$\beta u_\rho(r) \sim B_{=} \frac{1}{\rho^2} \frac{\xi_{=}}{\sigma} \frac{\sin(r/\xi_{=})}{r/\xi_{=}} \exp\left(-\frac{r}{\xi_{=}}\right) \tag{79}$$

with $B_{=}$ denoting a positive constant. Combining this expression with Eq. (74) leads to

$$\begin{aligned} \frac{\bar{p}}{k_B T} &\sim - \frac{B_{=}}{6} \frac{\xi_{=}}{\sigma} \int_0^\infty 4\pi r^3 \frac{d}{dr} \left\{ \frac{\sin(r/\xi_{=})}{r/\xi_{=}} \right. \\ &\quad \left. \times \exp\left(-\frac{r}{\xi_{=}}\right) \right\} dr. \end{aligned} \tag{80}$$

Change of variable from r to $y = r/\xi_{=}$ for the integration yields

$$\frac{\bar{p}}{k_B T} \sim \xi_{=}^4 (-1) \frac{B_{=}}{6\sigma} \int_0^\infty 4\pi y^3 \frac{d}{dy} \left\{ \frac{\sin y}{y} \exp(-y) \right\} dy. \tag{81}$$

The integral over y is -6π . By recalling Eq. (58) for $\xi_{=}$, we have

$$\frac{\bar{\rho}}{k_B T} \propto \left(1 - \frac{\rho}{\rho^*}\right)^{-1} \quad (82)$$

and again $\bar{\rho}$ diverges with an exponent equal to -1 : despite the different functional forms of $\beta u_\rho(r)$ that develop in the limit $\rho \rightarrow \rho^{*-}$, the two cases $\alpha < 0$ and $\alpha = 0$ yield the same exponent.

$\alpha > 0$. The analysis becomes more involved for $\alpha > 0$. We start by rewriting Eq. (61),

$$\beta u_\rho(r) \sim \frac{\sqrt{k_{\min}^2 \xi_{>}^2 + 1}}{\xi_{>}} B_{>} \frac{1}{\rho} \times \frac{\sin(k_{\min} r + \chi)}{r/\xi_{>}} \exp\left(-\frac{r}{\xi_{>}}\right) \quad (83)$$

with $B_{>}$ representing a positive constant of no interest. Inserting this expression into Eq. (74) gives

$$\frac{\bar{p}}{k_B T} \sim \frac{\sqrt{k_{\min}^2 \xi_{>}^2 + 1}}{\xi_{>}} (-1) \rho \frac{B_{>}}{6} \int_0^\infty 4\pi r^3 \times \frac{d}{dr} \left\{ \frac{\sin(k_{\min} r + \chi)}{r/\xi_{>}} \exp\left(-\frac{r}{\xi_{>}}\right) \right\} dr. \quad (84)$$

By changing the variable of integration from r to $y = r/\xi_{>}$, one obtains

$$\frac{\bar{p}}{k_B T} \sim \lambda^2 \sqrt{\lambda^2 + 1} (-1) \rho \frac{B_{>}}{6 k_{\min}^2} \int_0^\infty 4\pi y^3 \times \frac{d}{dy} \left\{ \frac{\sin(\lambda y + \chi)}{y} \exp(-y) \right\} dy, \quad (85)$$

where we have set

$$\lambda = k_{\min} \xi_{>}. \quad (86)$$

The phase factor χ is related to λ , according to Eq. (63), by

$$\chi = \tan^{-1} \frac{1}{\lambda} \quad \left(0 < \chi < \frac{\pi}{2}\right). \quad (87)$$

Since $k_{\min} > 0$ when $\alpha > 0$, the problem is reduced to examining the behavior of \bar{p} in the limit $\lambda \rightarrow \infty$. Here, however, the integral over y in Eq. (85) does not allow a simple extraction of its λ dependence and must be evaluated analytically. Straightforward calculation of this integral, I , yields

$$I = \int_0^\infty 4\pi y^3 \frac{d}{dy} \left\{ \frac{\sin(\lambda y + \chi)}{y} \exp(-y) \right\} dy = 12\pi \frac{(\lambda^2 - 1) \sin \chi - 2\lambda \cos \chi}{(\lambda^2 + 1)^2}. \quad (88)$$

Using Eq. (87), we expand $\cos \chi$ and $\sin \chi$ around $\lambda^{-1} = 0$,

$$\cos \chi = 1 - \frac{1}{2} \frac{1}{\lambda^2} + \frac{3}{8} \frac{1}{\lambda^4} - \dots \quad (89)$$

and

$$\sin \chi = \frac{1}{\lambda} - \frac{1}{2} \frac{1}{\lambda^3} + \frac{3}{8} \frac{1}{\lambda^5} - \dots \quad (90)$$

It then follows that

$$I \simeq \frac{-12\pi}{\lambda^3} \quad (\lambda \gg 1) \quad (91)$$

and in the limit $\rho \rightarrow \rho^{*-}$,

$$\frac{\bar{p}}{k_B T} \sim \rho^* \frac{2\pi B_{>}}{k_{\min}^2}. \quad (92)$$

Thus, \bar{p} reaches only a finite value for $\alpha > 0$ and does not diverge as the terminal point is approached. It is easily shown that the first derivative ($\partial \bar{p} / \partial \rho$) also remains finite in the same limit.

For square-well $g_0(r)$, the terminus is not characterized by a divergence in \bar{p} when $k_{\min} > 0$. This is because pressure reflects the mechanical property of a system only at $k = 0$. If one extends the pressure equation to define a k -dependent pressure, for example, by

$$\frac{\bar{p}(k)}{k_B T} = \rho - \frac{\rho^2}{6} \int_0^\infty 4\pi r^3 \frac{d\{\beta u_\rho(r)\}}{dr} g_0(r) \frac{\sin kr}{kr} dr, \quad (93)$$

then this $\bar{p}(k)$ will recapture the divergence at $k = k_{\min}$ as $\rho \rightarrow \rho^{*-}$ regardless of the sign of α . We believe the entropy \bar{S} , on the other hand, should be able to reflect the terminality without such extension to nonzero k .

VI. DISTINCTION BETWEEN Equi- $g(r)$ SEQUENCES AND Iso- $g^{(2)}$ PROCESSES

Equi- $g(r)$ sequence is closely related to the recently introduced "iso- $g^{(2)}$ process."³ This is a process in which, as ρ is varied, the constancy of $g(r)$ is maintained by a single system rather than by a family of systems. An iso- $g^{(2)}$ system achieves this condition by a pair potential, denoted by $u(r; \rho)$, that has a direct dependence on ρ as opposed to the indexed dependence of $u_\rho(r)$. Although $u(r; \rho)$ and $u_\rho(r)$ formally share the same functional form for a given $g_0(r)$, differences arise in the properties of the systems. For example, the pressure of a system governed by $u(r; \rho)$ is given by^{18,19}

$$\frac{p}{k_B T} = \rho - \frac{\rho^2}{6} \int_0^\infty 4\pi r^3 \frac{\partial\{\beta u(r; \rho)\}}{\partial r} g(r) dr + \frac{\rho^3}{2} \int_0^\infty 4\pi r^2 \frac{\partial\{\beta u(r; \rho)\}}{\partial \rho} g(r) dr. \quad (94)$$

The third term, which vanishes for $u_\rho(r)$, represents the effect of the direct ρ -dependence contained in $u(r; \rho)$. Further discussion on the distinction between $u(r; \rho)$ and $u_\rho(r)$ and its consequences is presented elsewhere.²⁰

VII. CONCLUSIONS

We have introduced the idea of equi- $g(r)$ sequence. This is defined by a family of systems which share the same functional form $g_0(r)$ for the pair correlation function at various ρ . Each system is specified by a density-indexed pair potential $u_\rho(r)$. The sequence in general terminates at a finite density ρ^* or packing fraction η^* due to the non-negativity condition on the structure factor $S(k)$, and we have evaluated η^* for the specific choice of $g_0(r)$ derived from square-

well potential in the limit $\rho \rightarrow 0$. Observation of η_{\max}^* , the maximum possible η^* , for this test case has suggested the approach of deducing the limiting packing structure of hard spheres via functional optimization of $g_0(r)$.

An expression for $u_\rho(r)$ has been derived in the two limits $\rho \rightarrow 0$ and $\rho \rightarrow \rho^*$. In the former, virial expansion leads to the physically reasonable interpretation that features develop in $u_\rho(r)$ so as to suppress a change in $g(r)$ that would otherwise occur if $u(r)$ remained unchanged. In the latter, simple analyses show that $u_\rho(r)$ develops a singular behavior as $\rho \rightarrow \rho^{*-}$ because of the imminent violation of the condition $S(k) \geq 0$. For square-well $g_0(r)$, the singularity is characterized by a length constant ξ that diverges with an exponent equal to $-1/2$ when $\alpha \neq 0$ and $-1/4$ when $\alpha = 0$.

The expressions for $u_\rho(r)$ thus obtained have allowed us to compute the pressure \bar{p} . A term-by-term comparison of the virial expansions reveals that p of imperfect gas and \bar{p} deviate from each other at order ρ^3 . In the limit $\rho \rightarrow \rho^{*-}$, \bar{p} for square-well $g_0(r)$ diverges with an exponent equal to -1 only when $\alpha \leq 0$, that is, when $k_{\min} = 0$. We have suggested an extended definition of pressure to nonzero k so that the divergence is recaptured when the terminality is due to a nonzero k_{\min} . Finally, we have discussed the distinction between equi- $g(r)$ sequence and the related iso- $g^{(2)}$ process and presented the different forms of the pressure equation that apply to each case.

As acknowledged earlier, we have assumed that Eq. (14) determines the equi- $g(r)$ terminal density ρ^* . Strictly speaking, the expression should be interpreted only as an upper bound to that terminal density. If a case could be identified in which Eq. (14) actually exceeded the terminal density, that observation would constitute discovery of a new constraint on the family of $g(r)$'s that are indeed realizable.⁸ At present, no evidence exists for the existence of such a constraint, and so it is reasonable to suppose that Eq. (14) as written is a proper relation for determining the terminal density ρ^* . Nevertheless, the need to eliminate the remaining ambiguity about the interpretation of Eq. (14) is an important objective for future research, and in particular properly designed computer simulations could play a significant role.

In future work, we will seek to obtain configurations that realize the "square-well" $g(r)$ for the possible range of densities. This will be done using efficient stochastic optimization techniques to reconstruct realizations of atomic systems²¹ and digitized heterogeneous media.²²

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