Density fluctuations in many-body systems

Thomas M. Truskett,[1] Salvatore Torquato,[2,3,*] and Pablo G. Debenedetti[1]
[1]*Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544*
[2]*Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544*
[3]*Department of Civil Engineering and Operations Research, Princeton University, Princeton, New Jersey 08544*
(Received 7 August 1998)

The characterization of density fluctuations in systems of interacting particles is of fundamental importance in the physical sciences. We present a formalism for studying local density fluctuations in two special subvolumes (centered around either a reference particle or some arbitrary point in the system) termed *particle* and *void* regions, respectively. We present formal expressions for the probability, as well as the moments, associated with finding exactly n particles inside of either of these subvolumes. Furthermore, we derive the relationship between the probability functions and closely related quantities of interest, such as the nth nearest-neighbor distribution functions and the n-particle conditional pair distribution functions associated with each region. We solve for these quantities exactly in the one-dimensional hard-rod system. The methods developed for studying the hard-rod fluid are applicable for studying a wide class of one-dimensional systems. [S1063-651X(98)06012-7]

PACS number(s): 61.20.Gy

I. INTRODUCTION

Spontaneous fluctuations give rise to rich and complex behavior in many-body systems. Of particular interest are the local fluctuations that occur within a given subset of a system's total volume. For instance, it is instructive to ask the following question: What is the probability of finding *exactly* n particle centers within a spherical region $\Omega_V(r)$ of radius r, centered at an arbitrary point in the system? The answer to this question is given by the n-particle *void probability function* $E_V(r;n)$, a quantity that contains a wealth of thermodynamic and structural information about the system [1–5]. A connection can be made with equilibrium thermodynamics through the second central moment, or variance, of this distribution, provided that the subvolume is allowed to pass to the thermodynamic limit $[\langle n\rangle\to\infty, r\to\infty, \langle n\rangle/\Omega_V(r)\to\text{finite}]$. That is, the fluctuations in particle number are related to the isothermal compressibility κ_T via

$$\frac{\langle n^2\rangle-\langle n\rangle^2}{\langle n\rangle}=\rho kT\kappa_T, \tag{1.1}$$

where ρ is the bulk number density, k is Boltzmann's constant, and T is the temperature.

In the case of the *equilibrium* D-dimensional hard-sphere fluid, the excess chemical potential can be determined from the $n=0$ limit of the void probability function

$$\mu_{\text{ex}}=-kT\ln[E_V(\sigma;0)] \tag{1.2}$$

where σ is the hard-sphere diameter. From a geometric viewpoint, the quantity $E_V(r;0)$ represents the fraction of space available for the addition of another hard sphere of radius $r-\sigma/2$ into the system (commonly referred to as the system's *available space*). It is closely related to the first $(n=1)$ *nearest-neighbor distribution function* $H_V(r;1)$,

$$H_V(r;1)=-\frac{\partial E_V(r;0)}{\partial r}, \tag{1.3}$$

which is the probability density associated with finding the nearest particle a radial distance r away from a given point [6]. It follows that the nearest-neighbor distribution function is equivalent to the area of the surface bounding the available space, normalized by the total volume.

Reiss, Frisch, and Lebowitz [6] derived an exact analytical series representation for $E_V(r;0)$ in terms of the so-called n-particle probability density functions $\rho_1,\rho_2,\ldots,\rho_n$ in their studies of the scaled-particle theory of liquids. Furthermore, both formal series representations [7] and approximations [8,7,9] for D-dimensional hard-sphere fluids have been obtained for the lowest-order versions of these functions, namely, $E_V(r;0)$ and $H_V(r;1)$. The most recent approximations [9] are accurate even for the *metastable* extension of the fluid branch, which is conjectured to end in a *random close-packed* state.

In the case of the general n-particle probability function $E_V(r;n)$, a formal series representation has been obtained [10]; however, a limited knowledge of the n-particle density functions precludes its systematic determination in model systems. Recent simulation studies of liquid water [3] and the three-dimensional hard-sphere fluid [4] suggest that $E_V(r;n)$ may be approximately Gaussian in n, a feature that is closely related to the Gaussian field model of liquids [11] and the Pratt-Chandler theory of hydrophobicity [12]. In this work, we develop a connection between the void probability function and the void nth nearest-neighbor distribution function $H_V(r;n)$. Furthermore, we derive an exact solution for $E_V(r;n)$ and $H_V(r;n)$ in the hard-rod fluid.

Torquato and co-workers [7,9] studied related quantities when there is a particle center at the origin of the subvolume, referred to as the ''particle'' quantities. In particular,

*Electronic address: torquato@matter.princeton.edu

$E_P(r;0)$ is the probability that a cavity of radius r surrounding the reference particle is free of other particle centers. The central particle's nearest-neighbor distribution function is related to $E_P(r;0)$ via

$$H_P(r;1) = -\frac{\partial E_P(r;0)}{\partial r}. \tag{1.4}$$

Knowledge of the nearest-neighbor distribution function is of importance in a variety of problems, including stellar dynamics [13], liquids and glasses [14–19], biological systems [20,21], processing of ceramics [22], transport in heterogeneous materials [23–25], and surface adsorption [26]. MacDonald [27] put forth simple approximations for the particle nearest-neighbor distribution function in hard-sphere systems, and more accurate approximations have since been derived [7,9,28] for general interpenetrable-sphere models for both monodisperse and polydisperse systems.

In this paper, we investigate generalizations of the aforementioned particle quantities. Specifically, we introduce the *particle probability function* $E_P(r;n)$, defined as the probability of finding *exactly* n additional particle centers within a radial distance r of a given reference particle center. Similarly, we can define a ''particle'' nth nearest-neighbor distribution function $H_P(r;n)$, representing the probability density associated with finding the center of the nth nearest neighbor to a reference particle a distance r away from the reference particle center. In Sec. II of this paper, we derive formal expressions for the particle probability function $E_P(r;n)$ and its moments. Furthermore, we derive general representations for the nth nearest-neighbor distribution functions $H_V(r;n)$ and $H_P(r;n)$ and the n-particle conditional pair distribution functions $G_V(r;n)$ and $G_P(r;n)$. Since these quantities depend, generally, on all of the n-particle probability density functions, their explicit evaluation is restricted to the simplest of models. In Sec. III we evaluate, exactly, the void and particle quantities for an equilibrium fluid of hard rods ($D=1$), the most fundamental, nontrivial many-body system.

II. DEFINITIONS AND GENERAL RELATIONS

We consider systems of interacting D-dimensional spheres of diameter σ spatially distributed in a volume V according to the N-particle probability density $P_N(\mathbf{R}^N)$. Specifically, $P_N(\mathbf{R}^N)$ is the probability density associated with finding particles $1,2,\ldots,N$ in a particular configuration $\mathbf{R}^N \equiv \{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N\}$. As can be seen, $P_N(\mathbf{R}^N)$ normalizes to unity. The reduced n-particle probability density ρ_n ($n<N$) is given by

$$\rho_n(\mathbf{R}^n) = \frac{N!}{(N-n)!}\int P_N(\mathbf{R}^N)d\mathbf{R}^{N-n}, \tag{2.1}$$

where $d\mathbf{R}^{N-n}$ represents $d\mathbf{R}_{n+1}\cdots d\mathbf{R}_N$. The reduced n-particle probability density $\rho_n(\mathbf{R}^n)d\mathbf{R}^n$ characterizes the probability of simultaneously finding the center of any n particles at $\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_n$. With this in mind, the ensemble average of any function $F(\mathbf{R}^N)$ that depends on the spatial distribution of the particles is given by

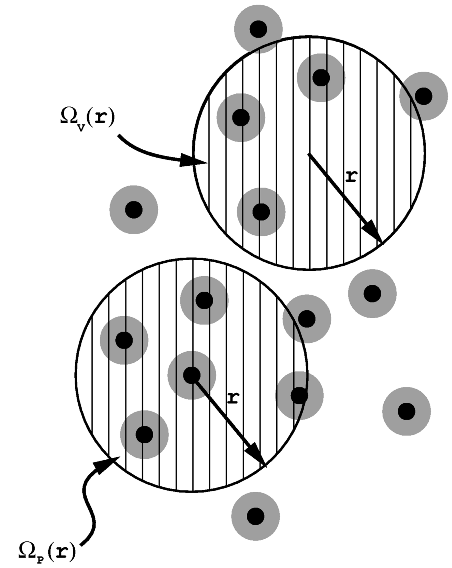

FIG. 1. Schematic representation of regions $\Omega_V(r)$ and $\Omega_P(r)$. The subvolume $\Omega_P(r)$ is centered on some reference particle, while $\Omega_V(r)$ is centered on an arbitrary point in the system.

$$\langle F(\mathbf{R}^N)\rangle = \int F(\mathbf{R}^N)P_N(\mathbf{R}^N)d\mathbf{R}^N. \tag{2.2}$$

If the system is statistically homogeneous, the $\rho_n(\mathbf{R}^n)$ depend on the relative displacements $\mathbf{R}_2-\mathbf{R}_1,\mathbf{R}_3-\mathbf{R}_1,\ldots,\mathbf{R}_n-\mathbf{R}_1$. Throughout this work, it should be understood that the thermodynamic limit has been taken, i.e., $N\rightarrow\infty$ and $V\rightarrow\infty$, where $\rho\equiv N/V$ remains some finite constant.

In order to study fluctuations on a local scale, it is necessary to define the subvolume of interest. We focus on the so-called ''void'' and ''particle'' regions (see Fig. 1). The void region $\Omega_V(r)$ is a D-dimensional spherical region of radius r that is centered at an arbitrary position in the medium. Likewise, a particle region $\Omega_P(r)$ is a spherical region of radius r that is centered on a given reference particle. As is standard practice, we define a characteristic function for the void region by

$$C_V(\mathbf{x};r) = \begin{cases} 1, & \mathbf{x}\in\Omega_V(r) \\ 0, & \mathbf{x}\notin\Omega_V(r). \end{cases} \tag{2.3}$$

Similarly, a characteristic function can be defined for the region surrounding the reference particle

$$C_P(\mathbf{x};r) = \begin{cases} 1, & \mathbf{x}\in\Omega_P(r) \\ 0, & \mathbf{x}\notin\Omega_P(r). \end{cases} \tag{2.4}$$

The characteristic functions are created for mathematical convenience and will prove useful in deriving formal representations of the quantities of interest.

A. Exact integral equations for the void and particle probability functions

In this section we will present formal expressions for two special types of probability functions, $E_V(r;n)$ and $E_P(r;n)$ defined as follows:

$$E_V(r;n)=[\text{probability of finding a region } \Omega_V(r), \text{which is a } D\text{-dimensional sphere of radius } r \text{(centered at some arbitrary point), containing exactly } n \text{ particle centers}]. \tag{2.5}$$

$$E_P(r;n)=[\text{probability that, given a } D\text{-dimensional sphere of diameter } \sigma \text{ at some position in the system, the region } \Omega_P(r), \text{ which is a sphere of radius } r \text{ encompassing this central particle, contains exactly } n \text{ additional sphere centers.}] \tag{2.6}$$

Refer to Fig. 1 for a schematic of the regions $\Omega_V(r)$ and $\Omega_P(r)$.

Vezzetti [10], within the framework of the canonical ensemble, previously derived an expression for the general void probability function $E_V(r;n)$ in terms of the n-particle probability density functions. Specifically, he showed

$$E_V(r;n)=\sum_{i=n}^{N}\frac{(-1)^{i-n}}{(i-n)!n!}\int_{\Omega_V(r)}\rho_i(\mathbf{R}_1\cdots\mathbf{R}_i)d\mathbf{R}^i. \tag{2.7}$$

Following a similar development, we will derive a formal integral equation for the particle probability function $E_P(r;n)$.

The probability of finding zero particles in a region $\Omega_P(r)$ surrounding a given reference particle can be written in terms of the characteristic function for that region,

$$E_P(r;0)=\left\langle \prod_{i=1}^{N-1}(1-C_P(\mathbf{x}_i;r))\right\rangle, \tag{2.8}$$

where particle N is taken as the reference and $\langle\cdots\rangle$ denotes an ensemble average. If the product in Eq. (2.8) is expanded, one obtains

$$E_P(r;0)=1-\sum_{i=1}^{N-1}\langle C_P(\mathbf{x}_i;r)\rangle+\sum_{\{i,j\}}^{N-1}\langle C_P(\mathbf{x}_i;r)C_P(\mathbf{x}_j;r)\rangle-\sum_{\{i,j,k\}}^{N-1}\langle C_P(\mathbf{x}_i;r)C_P(\mathbf{x}_j;r)C_P(\mathbf{x}_k;r)\rangle+\cdots \tag{2.9}$$

$$=1+\sum_{i=1}^{N-1}\frac{(-1)^i(N-1)!}{i!(N-1-i)!}\langle C_P(\mathbf{x}_1;r)\cdots C_P(\mathbf{x}_i;r)\rangle, \tag{2.10}$$

where $\{\cdots\}$ indicates a sum over all pairs, triplets, etc., and the reference particle is excluded from all sums. When the averages in the canonical ensemble are shown explicitly, this becomes

$$E_P(r;0)=1+\sum_{i=1}^{N-1}\frac{(-1)^i}{\rho_1(\mathbf{R}_N)i!}\times\int_{\Omega_P(r)}\rho_{i+1}(\mathbf{R}_1,\ldots,\mathbf{R}_i,\mathbf{R}_N)d\mathbf{R}^i \tag{2.11}$$

which is precisely the result derived by Torquato, Lu, and Rubinstein [7]. Using this formalism, the extension to the general particle probability function $E_P(r;n)$ is straightforward. In terms of the characteristic functions, the probability is given by

$$E_P(r;n)=\frac{(N-1)!}{(N-1-n)!n!}\times\left\langle\prod_{i=1}^{n}C_P(\mathbf{x}_i;r)\prod_{j=n+1}^{N-1}(1-C_P(\mathbf{x}_j;r))\right\rangle. \tag{2.12}$$

Expanding the products, and showing the averages explicitly, yields the desired integral relation

$$E_P(r;n)=\sum_{i=n}^{N-1}\frac{(-1)^{i-n}}{(i-n)!n!\rho_1(\mathbf{R}_N)}\times\int_{\Omega_P(r)}\rho_{i+1}(\mathbf{R}_1\cdots\mathbf{R}_i,\mathbf{R}_N)d\mathbf{R}^i. \tag{2.13}$$

It is worth noting that both the void and the particle probability functions depend on all of the n-particle probability density functions $\rho_1,\rho_2,\ldots,\rho_n$.

B. Moments

Using a generating function approach, Ziff [1] was able to derive an expression for the *moments* of the void probability function $E_V(r;n)$. In particular, he was able to show that

$$\left\langle\frac{n!}{(n-k)!}\right\rangle_{\Omega_V(r)}=\int_{\Omega_V(r)}\rho_k(\mathbf{R}_1\cdots\mathbf{R}_k)d\mathbf{R}^k, \tag{2.14}$$

where $\langle\cdots\rangle_{\Omega_V(r)}$ represents an average in the subvolume $\Omega_V(r)$. This should not be confused with a similar relationship involving the n-particle densities that appear in the grand canonical ensemble $\rho_n^{\mathrm{gr}}(\mathbf{R}_1\cdots\mathbf{R}_n)$, which obey the normalization

$$\left\langle\frac{N!}{(N-k)!}\right\rangle_{\mathrm{gr}}=\int_{V^{\mathrm{gr}}}\rho_k^{\mathrm{gr}}(\mathbf{R}_1\cdots\mathbf{R}_k)d\mathbf{R}^k, \tag{2.15}$$

where V^{gr} is the volume, N is the number of particles in the system, and $\langle \cdots \rangle_{\mathrm{gr}}$ indicates an average in the grand canonical ensemble. Equations (2.14) and (2.15) become asymptotically equivalent only as the thermodynamic limit is approached in both systems, i.e., at a fixed density both $\Omega_V(r)\rightarrow\infty$ and $V^{\mathrm{gr}}\rightarrow\infty$.

Following an approach similar to that of Ziff [1], we will proceed to derive a relationship for the moments of the particle probability function $E_P(r;n)$. It is convenient to recast $E_P(r;n)$, of Eq. (2.13), in the following form:

$$E_P(r;n)=\frac{1}{n!}\left[\left(\frac{\partial}{\partial t}\right)^n\left(1+\sum_{i=1}^{N-1}\frac{t^i}{i!\rho_1(\mathbf{R}_N)}\int_{\Omega_P(r)}\rho_{i+1}(\mathbf{R}_1\cdots\mathbf{R}_i,\mathbf{R}_N)d\mathbf{R}^i\right)\right]_{t=-1}. \tag{2.16}$$

Using Eq. (2.16) and the binomial theorem, it is simple to show that

$$\sum_{n=0}^{N-1}\xi^n E_P(r;n)=1+\sum_{i=1}^{N-1}\frac{(\xi-1)^i}{i!\rho_1(\mathbf{R}_N)}\int_{\Omega_P(r)}\rho_{i+1}(\mathbf{R}_1\cdots\mathbf{R}_i,\mathbf{R}_N)d\mathbf{R}^i. \tag{2.17}$$

From Eq. (2.17), it follows that

$$\left[\left(\frac{\partial}{\partial\xi}\right)^k\sum_{n=0}^{N-1}\xi^n E_P(r;n)\right]_{\xi=1}=\sum_{n=k}^{N-1}\frac{n!}{(n-k)!}E_P(r;n)=\left\langle\frac{n!}{(n-k)!}\right\rangle_{\Omega_P(r)}=\frac{1}{\rho_1(\mathbf{R}_N)}\int_{\Omega_P(r)}\rho_{k+1}(\mathbf{R}_1\cdots\mathbf{R}_k,\mathbf{R}_N)d\mathbf{R}^k, \tag{2.18}$$

yielding the desired moment relation for $E_P(r;n)$. Notice that while both $E_V(r;n)$ and $E_P(r;n)$ depend on all of the n-particle probability density functions, the kth moment of either distribution depends only on $\rho_1,\rho_2,\ldots,\rho_k$.

C. *N*th nearest-neighbor distribution functions

In this section we discuss two general types of neighbor distribution functions, $H_V(r;n)$ and $H_P(r;n)$, defined as follows:

$$H_V(r;n)dr=(\text{probability that at an arbitrary point in the system the center of the } n\text{th nearest particle lies at a distance between } r \text{ and } r+dr), \tag{2.19}$$

$$H_P(r;n)dr=(\text{probability that, given a } D\text{-dimensional sphere of diameter } \sigma \text{ at some position in the system, the center of the } n\text{th nearest particle lies at a distance between } r \text{ and } r+dr). \tag{2.20}$$

The functions $H_V(r;n)$ and $H_P(r;n)$ will be referred to as the void and particle nth nearest-neighbor distribution functions, respectively.

The neighbor functions $H_V(r;n)$ and $H_P(r;n)$ are intimately related to the void and particle probability functions $E_V(r;n)$ and $E_P(r;n)$ discussed earlier. In fact, the relationship can be seen from simple counting arguments. Consider a particular subvolume $\Omega_V(r)$. The probability that the region contains at least n particles is given by $\int_0^r H_V(r;n)dr$. The only other possibility is that there are less than n particles in the region, and thus the relationship can be expressed

$$\sum_{i=0}^{n-1}E_V(r;i)=1-\int_0^r H_V(r;n)dr. \tag{2.21}$$

An identical argument can be invoked to arrive at the particle expression

$$\sum_{i=0}^{n-1}E_P(r;i)=1-\int_0^r H_P(r;n)dr. \tag{2.22}$$

Differentiation with respect to r gives

$$H_V(r;n)=-\sum_{i=0}^{n-1}\frac{\partial E_V(r;i)}{\partial r} \tag{2.23}$$

and

$$H_P(r;n)=-\sum_{i=0}^{n-1}\frac{\partial E_P(r;i)}{\partial r}. \tag{2.24}$$

For statistically homogeneous media, it is convenient to write the neighbor functions as a product of two different correlation functions. Specifically, for D-dimensional particles let

$$H_V(r;n)=\rho s_D(r)G_V(r;n-1)E_V(r;n-1) \quad (2.25)$$

and

$$H_P(r;n)=\rho s_D(r)G_P(r;n-1)E_P(r;n-1), \quad (2.26)$$

where s_D is the surface area of a D-dimensional sphere of radius r. For example, $s_D=2,2\pi r,4\pi r^2$ for $D=1$, 2, and 3, respectively. Given definitions (2.5), (2.6), (2.19), and (2.20), the n-particle conditional pair distribution functions $G_V(r;n)$ and $G_P(r;n)$ must have the following definitions:

$$\rho s_D(r)G_V(r;n)dr=[\text{probability that, given a region } \Omega_V(r) \text{ containing } n \text{ particle centers, particle centers are contained in the spherical shell of volume } s_D dr \text{ encompassing the region}], \quad (2.27)$$

$$\rho s_D(r)G_P(r;n)dr=[\text{probability that, given a region } \Omega_P(r) \text{ containing } n \text{ particle centers (in addition to the central particle), particle centers are contained in the spherical shell of volume } s_D dr \text{ surrounding the central particle}]. \quad (2.28)$$

Note that $G_V(r;0)$ is simply the contact value of the radial distribution function for a test particle of radius $r-\sigma/2$ and a particle of radius $\sigma/2$. Furthermore, when $r=\sigma$, then $G_V(\sigma;0)=G_P(\sigma;0)$ is just the contact value of the radial distribution function $g_2(\sigma)$ for identical spheres of diameter σ. For an equilibrium distribution of spheres, $g_2(\sigma)$ can be related to the pressure of the system [29]. In addition, as $r\to\infty$, the sphere of radius r may be regarded as a plane rigid wall relative to the particles, hence $G_V(\infty,n)=G_P(\infty,n)$.

Finally, we can write down an expression for the ''mean nth nearest-neighbor distance'' $l(n)$ between particles as follows:

$$l(n)=\int_0^\infty rH_P(r;n)dr. \quad (2.29)$$

For the case of impenetrable spheres, Eq. (2.29) provides an operational definition for the random close-packed state. In particular, one can define [9] the random close-packed density to be the maximum packing fraction over all ergodic, isotropic ensembles at which $l(1)=\sigma$.

D. Fully penetrable particles: ideal gas limit

We now consider the case of spatially uncorrelated spheres. Since this simple model represents randomly centered points, the n-particle probabilities become trivial, i.e., $\rho_n=\rho^n$. In this limit, first considered by Hertz [30], we find, via Eqs. (2.7) and (2.13),

$$E_V(r;n)=E_P(r;n)=\frac{(\rho v_D(r))^n}{n!}\exp(-\rho v_D(r)), \quad (2.30)$$

where $v_D(r)$ is the volume of a D-dimensional sphere,

$$v_D(r)=\frac{rs_D(r)}{D}. \quad (2.31)$$

Note that there is no distinction between particle and void quantities in the absence of correlations. The moments of the distribution are given by

$$\left\langle \frac{n!}{(n-k)!}\right\rangle_{\Omega_V(r)}=\left\langle \frac{n!}{(n-k)!}\right\rangle_{\Omega_P(r)}=(\rho v_D(r))^k. \quad (2.32)$$

From Eqs. (2.21), (2.22), (2.25), and (2.26), it is simple to show that

$$H_V(r;n)=H_P(r;n)=\rho s_D(r)\sum_{i=0}^{n-1} E_V(r;i)\left[1-\frac{i}{\rho v_D(r)}\right] \quad (2.33)$$

and

$$G_V(r;n)=G_P(r;n)=\sum_{i=0}^{n}\frac{(\rho v_D(r))^{i-n}n!}{i!}\left[1-\frac{i}{\rho v_D(r)}\right]=1. \quad (2.34)$$

When discussing the ideal gas limit, it is appropriate to assign a diameter σ to the particles, where it is understood that they are fully penetrable. Here $E_V(\sigma/2;0)=\exp(-\rho v_D(\sigma/2))$ is the void fraction. This stands in contrast to totally impenetrable (hard) spheres, where the void fraction is $1-\rho v_D(\sigma/2)$.

E. Totally impenetrable particles: hard-sphere limit

In a system of D-dimensional, mutually impenetrable particles of diameter σ, very few exact results are known. This is due to the fact that it is generally impossible to formulate expressions for the infinite set of n-particle density functions $\rho_2,\ldots,\rho_n(n\to\infty)$. For small ranges of r, some exact results are available. For instance, it is clear from definitions (2.6) and (2.20) that

$$E_P(r;0)=1 \quad \text{for} \quad 0\leq r\leq\sigma, \quad (2.35)$$

$$H_P(r;0)=0 \quad \text{for } 0\leqslant r\leqslant \sigma \tag{2.36}$$

due to impenetrability. Further, it follows from Eq. (2.26) that

$$G_P(r;0)=0 \quad \text{for } 0\leqslant r\leqslant \sigma. \tag{2.37}$$

For the void quantities, a spherical cavity can contain at most one particle center for $r\leqslant\sigma/2$. Thus we have

$$E_V(r;0)=1-\rho\frac{rs_D(r)}{D} \quad \text{for } 0\leqslant r\leqslant\sigma/2, \tag{2.38}$$

and since $\Omega_V(r)$ must contain one or zero particles for this range of r, it follows that

$$E_V(r;1)=\rho\frac{rs_D(r)}{D} \quad \text{for } 0\leqslant r\leqslant\sigma/2. \tag{2.39}$$

It is also simple to show from Eq. (2.23) that

$$H_V(r;n)=\rho s_D(r) \quad \text{for } 0\leqslant r\leqslant\sigma/2, \quad n=1 \tag{2.40}$$

$$=0 \quad \text{for } 0\leqslant r\leqslant\sigma/2, \quad n>1. \tag{2.41}$$

For $r=\sigma/2$, the $n=0$ void probability function

$$E_V(\sigma/2;0)=1-\rho v_D(\sigma/2)=1-\eta \tag{2.42}$$

is equal to 1 minus the reduced density η, or equivalently, the void fraction in this system. It follows that the $n=0$ limit of the void conditional pair correlation function is given by

$$G_V(r;0)=\frac{1}{1-\rho rs_D(r)/D} \quad \text{for } 0\leqslant r\leqslant\sigma/2. \tag{2.43}$$

Although the $n=0$ void and particle quantities are not the same for $r<\sigma$, they are related to one another for $r\geqslant\sigma$ in the case of an *equilibrium* ensemble of hard spheres. In particular, we have

$$E_P(r;0)=\frac{E_V(r;0)}{E_V(\sigma;0)} \quad \text{for } r\geqslant\sigma. \tag{2.44}$$

This conditional probability can be understood by realizing that a cavity of radius σ is structurally equivalent to a hard sphere in an equilibrium system. For general nonequilibrium packings, Eq. (2.44) will not be true (see, e.g., Ref. [26]). Nevertheless, Eq. (2.44) implies

$$H_P(r;1)=\frac{H_V(r;1)}{E_V(\sigma;0)} \quad \text{for } r\geqslant\sigma \tag{2.45}$$

and

$$G_P(r;0)=G_V(r;0) \quad \text{for } r\geqslant\sigma \tag{2.46}$$

for the equilibrium hard-sphere fluid. Finally, we note that, for equilibrium hard-sphere systems,

$$G_V(\infty;0)=G_V(\sigma;0) \quad \text{for } D=1, \tag{2.47}$$

$$G_V(\infty;0)=1+2\eta G_V(\sigma;0) \quad \text{for } D=2, \tag{2.48}$$

$$G_V(\infty;0)=1+4\eta G_V(\sigma;0) \quad \text{for } D=3, \tag{2.49}$$

which are simply the scaled equations of state.

Exact conditions on the quantity $G_V(r;n)$, which arise due to the packing of hard cores, can be determined. For instance, there is a D-dimensional sphere of radius $r_c(n)$ $(n>0)$ which is the largest sphere that cannot contain $n+1$ particle centers. Clearly,

$$G_V(r;n>0)=0 \quad \text{for } r<r_c(n). \tag{2.50}$$

Many other exact conditions can be derived. For instance, in $D=3$ it can be shown that

$$\frac{\partial^k G_V}{\partial r^k}(\sigma/2;1)=0 \quad \forall k. \tag{2.51}$$

Such conditions could provide a starting point for extending the scaled-particle theory of fluids.

For the lowest order cases ($n=0$ for E_V, E_P, G_V, and G_P; $n=1$ for H_V and H_P), exact results have previously been obtained for the equilibrium hard-rod fluid ($D=1$); see, e.g., Refs. [31,32,7]. For $D>1$, accurate, approximate expressions for the void and particle quantities have been derived for the lowest order cases [7,9]. In Sec. III of this work we solve for the general quantities, exactly, in the case of an equilibrium hard-rod fluid.

III. EXACT SOLUTION FOR THE HARD-ROD FLUID

In this section, we will address the statistical geometry of the *equilibrium* hard-rod fluid. For convenience, we choose to work with the dimensionless distance $x=r/\sigma$ and the reduced density $\eta=\rho\sigma$. Recall that $1-\eta$ is equivalent to the void fraction in systems comprising impenetrable particles. The void and particle subvolumes $\Omega_V(x)$ and $\Omega_P(x)$ for the one-dimensional system are shown in Fig. 2.

The hard-rod fluid is unique in two respects, which makes it amenable to theoretical analysis. First, the presence of an intervening particle, and the lack of any long-range interaction, render second neighbors totally ''unaware'' of each other. Secondly, the *chord*-length or gap-size distribution function $p(h)$ for this system is known exactly [31,33]:

$$p(h)=\frac{\eta}{1-\eta}e^{-[\eta/(1-\eta)]h}, \tag{3.1}$$

where $p(h)dh$ represents the probability that the distance between two neighboring particle centers is between $1+h$ and $1+h+dh$. It will be shown that these two features of the statistical geometry are sufficient to characterize the general quantities E_V, E_P, H_V, H_P, G_V, and G_P in the equilibrium hard-rod system.

A. Void quantities

To study the void probability function $E_V(x;n)$, it is convenient to appeal to the following geometric interpretation:

$E_V(x;n) = $ (the fraction of space in the system inside of which the center of a spherical window could be placed such that it would contain exactly n particle centers). (3.2)

This definition is compelling for the hard-rod fluid because it suggests a simple thought experiment. Specifically, one could scan the entire length of the line with a window of length $2x$, and simply record the fraction of space inside of which the center could be placed such that the window would contain exactly the prescribed number of particle centers.

Moreover, this procedure can be greatly simplified because of the topology of the hard-rod system. In particular, the system may be considered a repeating unit cell (that spans from one particle center to the next), with the only difference between neighboring unit cells being the width of the gap separating the particles as shown in Fig. 3. Furthermore, the probability density associated with observing two neighboring particles separated by a distance h is given by Eq. (3.1), quite independent of neighboring gaps.

Consider the quantity $E_V(x;0)$, equal to the fraction of space inside of which the center of the window can be placed such that no particle centers are inside of it. From Eq. (2.42), we know that

$$E_V(x;0) = 1 - 2\eta x \quad \text{for } x < 1/2. \tag{3.3}$$

For $x \geqslant \frac{1}{2}$, we return to the unit cell picture. For instance, one could start with the leftmost edge of the window on a particle center, and then translate the window to the right until the leftmost edge of the window is at the neighboring particle center. The volume of space in the unit cell that contributes to the available space is $h_1 + 1 - 2x$. In what follows, h_1 is the length of the gap in the unit cell and $h_2, \ldots, h_n$ are the lengths of the next $n-1$ gaps to the right of the cell. To calculate $E_V(x;0)$ we simply integrate over the number of gaps per unit length that have size $h_1 > 2x - 1$:

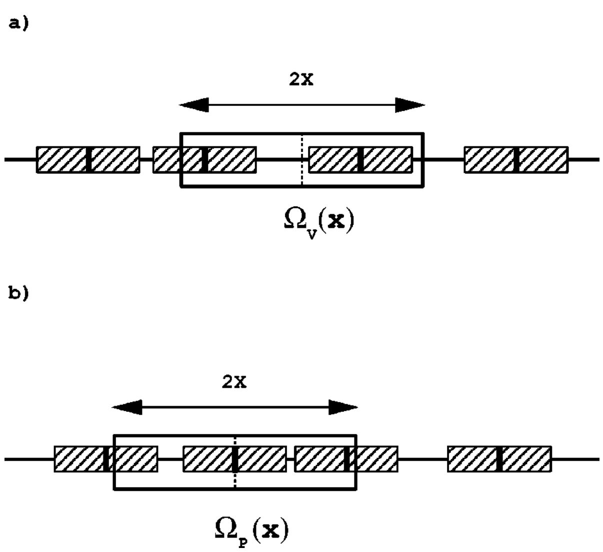

FIG. 2. Schematic representation of (a) $\Omega_V(x)$ and (b) $\Omega_P(x)$ in the one-dimensional hard-rod fluid.

$$\begin{aligned} E_V(x;0) &= \int_{2x-1}^{\infty} (h_1 + 1 - 2x)\,\eta p(h_1)\,dh_1 \\ &= (1-\eta) e^{-[2\eta/(1-\eta)](x-1/2)} \quad \text{for } x \geqslant \tfrac{1}{2}. \end{aligned} \tag{3.4}$$

Since, at most, one particle center can fit inside of a window of radius $x < \frac{1}{2}$, we have

$$E_V(x;1) = 2\eta x \quad \text{for } x < \tfrac{1}{2}. \tag{3.5}$$

For the interval $\frac{1}{2} \leqslant x < \frac{3}{4}$, the fraction of space in the unit cell contributing to the $E_V(x;1)$ is equal to $2(h_1 + 1 - x)$ if $h_1 < 2x - 1$, and is equal to $2x$ otherwise, leaving

$$\begin{aligned} E_V(x;1) &= \int_0^{2x-1} 2(h_1 + 1 - x)\,\eta p(h_1)\,dh_1 \\ &\quad + \int_{2x-1}^{\infty} 2x\,\eta p(h_1)\,dh_1 \\ &= 2\left(1 - \eta x - (1-\eta) e^{-[2\eta/(1-\eta)](x-1/2)}\right) \\ &\quad \text{for } \tfrac{1}{2} \leqslant x < \tfrac{3}{4}. \end{aligned} \tag{3.6}$$

It is easily verified that Eq. (3.6) also holds for the region $\frac{3}{4} \leqslant x < 1$. For $x \geqslant 1$ one must also integrate over all possible gap sizes of h_2, yielding

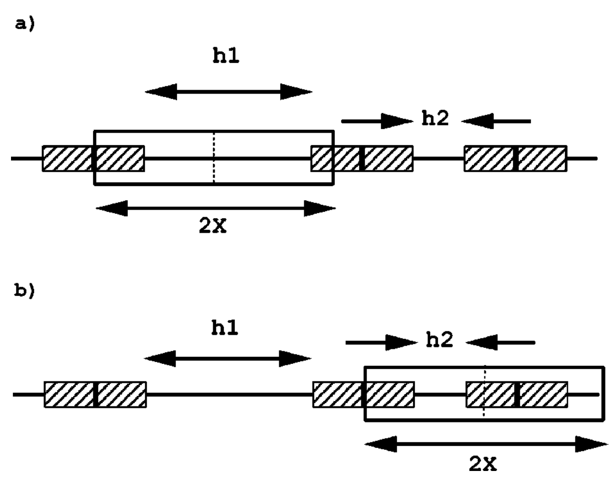

FIG. 3. As the window of size $2x$ moves from (a) to (b) it sweeps out one complete unit cell. The number of cells per unit length that have a gap of size h_1 and gaps of size $h_2, \ldots, h_{n-1}$ to the right is given by p_{n-1} in Eq. (3.9).

TABLE I. First five polynomials $f_n(x;\eta)$ defined by Eq. (3.8) used in determining the void probability function $E_V(x;n)$ for hard rods.

n	$f_n(x;\eta)$
1	0
2	$1-\eta$
3	$2(1-2\eta+\eta x)$
4	$(6-24\eta+27\eta^2+8\eta x-20\eta^2 x+4\eta^2 x^2)/[2(1-\eta)]$
5	$2(6-36\eta+78\eta^2-64\eta^3+9\eta x-42\eta^2 x+57\eta^3 x+6\eta^2 x^2 -18\eta^3 x^2+2\eta^3 x^3)/[3(1-\eta)^2]$

$$E_V(x;1)=2(1-2\eta+\eta x)e^{-[2\eta/(1-\eta)](x-1)} -2(1-\eta)e^{-[2\eta/(1-\eta)](x-1/2)} \quad \text{for } x\geq 1. \tag{3.7}$$

If one proceeds along these lines, the following general form for $E_V(x;n)$ in the region $(n-1)/2\leq x<n/2$ can be deduced:

$$\begin{aligned} E_V(x;n)&=\prod_{j=1}^{n-1}\int_0^{2x-(n-1)-\sum_{i=1}^{j-1}h_i}dh_j\left\{2x-(n-1)-\sum_{k=1}^{n-1}h_k\right\}p_{n-1}(h_1,\ldots,h_{n-1})\\ &=2\eta x-(n-1)+f_n(x;\eta)\times\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n-1}{2}\right)\right],\\ &\text{for } (n-1)/2\leq x<n/2. \end{aligned} \tag{3.8}$$

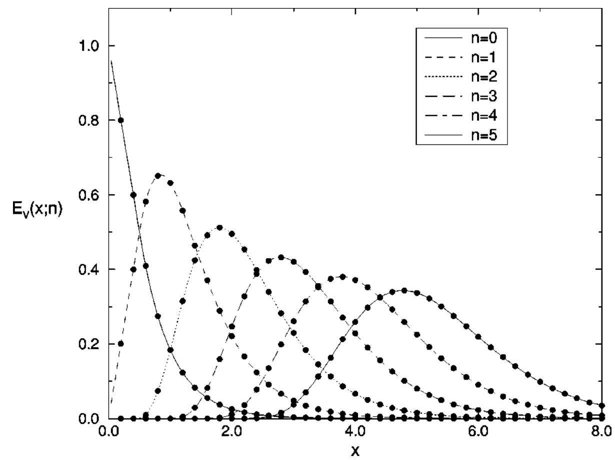

FIG. 4. Void probability function $E_V(x;n)$ for the hard-rod fluid at a volume fraction $\eta=0.5$. The lines indicate the exact solution obtained from Eq. (3.10), and the black dots represent Monte Carlo simulation data.

The quantity $p_{n-1}(h_1,\ldots,h_{n-1})dh_1\cdots dh_{n-1}$ is the number of gaps of size h_1 per unit length which have gaps of sizes $h_2,\ldots,h_{n-1}$ directly to the right:

$$p_{n-1}(h_1,\ldots,h_{n-1}) =\frac{\eta^n}{(1-\eta)^{n-1}}e^{-[\eta/(1-\eta)]h_1}\cdots e^{-[\eta/(1-\eta)]h_{n-1}}. \tag{3.9}$$

$f_n(x;\eta)$ are polynomials in x that can be easily determined analytically from the integral in Eq. (3.8). For convenience, we have given the first several in Table I. In terms of $f_n(x;\eta)$, the full expression for $E_V(x;n)$ can be written

$$\begin{aligned} E_V(x;n)&=0 \quad \text{for } x<(n-1)/2\\ &=2\eta x-(n-1)+f_n(x;\eta)\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n-1}{2}\right)\right], \quad \text{for } (n-1)/2\leq x<n/2\\ &=(n+1)-2\eta x+f_n(x;\eta)\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n-1}{2}\right)\right]-2f_{n+1}(x;\eta)\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n}{2}\right)\right],\\ &\quad \text{for } n/2\leq x<(n+1)/2\\ &=f_{n+2}(x;\eta)\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n+1}{2}\right)\right]-2f_{n+1}(x;\eta)\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n}{2}\right)\right]+f_n(x;\eta)\exp\left[-\frac{2\eta}{1-\eta}\left(x-\frac{n-1}{2}\right)\right]\\ &\quad \text{for } x\geq(n+1)/2. \end{aligned} \tag{3.10}$$

The exact results for $E_V(x;n)$ are shown in Fig. 4 along with Monte Carlo simulation data at a packing fraction of $\eta=0.5$.

Once an analytical expression for the void probability function has been obtained, all of the related void quantities can be determined. For example, the general nth nearest-neighbor distribution function $H_V(x;n)$ and the n-particle conditional pair correlation function $G_V(x;n)$, shown in Figs. 5 and 6, can be calculated using Eqs. (2.23) and (2.25), respectively. Notice that the void quantities vary relatively smoothly in x, a feature that is not shared by the particle quantities calculated in Sec. III B.

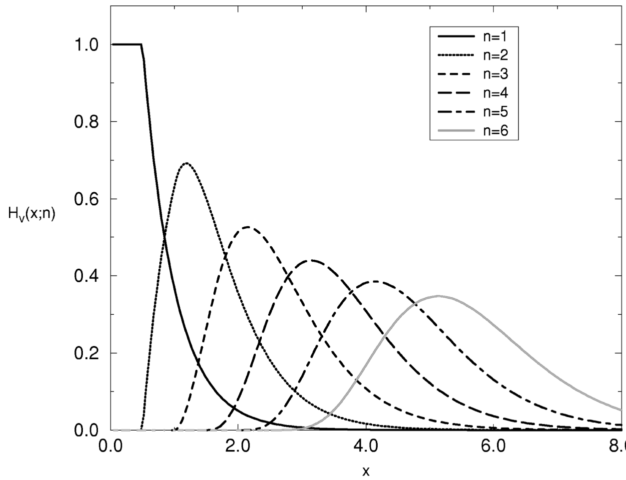

FIG. 5. Void nth nearest-neighbor distribution function $H_V(r;n)$ for the hard-rod fluid at a volume fraction $\eta=0.5$. Results are obtained from Eqs. (2.23) and (3.10).

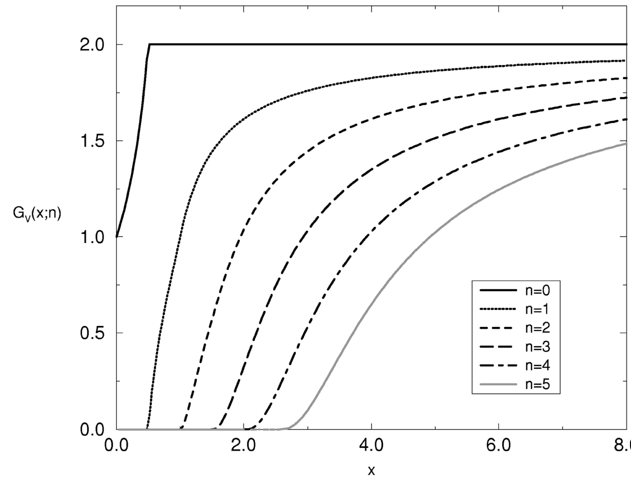

FIG. 6. Void n-particle conditional pair distribution function $G_V(r;n)$ for the hard-rod fluid at a volume fraction $\eta=0.5$. Results are obtained from Eqs. (2.25), (2.23), and (3.10).

B. Particle quantities

A different approach is needed for studying fluctuations about a reference particle in the one-dimensional equilibrium hard-rod fluid. Specifically, symmetry suggests that the problem need only be solved on one side of the reference particle; hence we introduce the *one-sided particle probability function* $E_P^{(1)}(x;n)$ defined in the following manner:

$$E_P^{(1)}(x;n)=(\text{probability that exactly } n \text{ sphere centers are within a distance } x \text{ to the right of the reference particle center.}) \tag{3.11}$$

To be concrete, let us consider the one-sided function $E_P^{(1)}(x;0)$, the probability that no particles are within a distance x to the right of the reference particle center. Given the chord-length distribution function defined by Eq. (3.1), this can be written

$$E_P^{(1)}(x;0)=\int_x^\infty \frac{\eta}{1-\eta} e^{-[\eta/(1-\eta)](y-1)}dy=e^{-[\eta/(1-\eta)](x-1)} \quad \text{for } x\geqslant 1. \tag{3.12}$$

Since events to the left and right of the central particle are uncorrelated, we can form the quantity $E_P(x;0)$ by squaring the one-sided result

$$E_P(x;0)=[E_P^{(1)}(x;0)]^2=e^{-[2\eta/(1-\eta)](x-1)} \quad \text{for } x\geqslant 1. \tag{3.13}$$

Moving on to the $n=1$ case, we note that

$$E_P^{(1)}(x;1)=0 \quad \text{for } x<1 \tag{3.14}$$

due to the hard-core interaction. Only one particle center can fit in the region $1\leqslant x<2$ to the right of the reference particle, yielding

$$E_P^{(1)}(x;1)=\frac{\eta}{1-\eta}\int_1^x e^{-[\eta/(1-\eta)](y-1)}dy=1-e^{-[\eta/(1-\eta)](x-1)} \quad \text{for } 1\leqslant x<2. \tag{3.15}$$

When considering distances $x\geqslant 2$, there are two contributions to $E_P^{(1)}(x;1)$:

$$\begin{aligned}E_P^{(1)}(x;1)&=\left(\frac{\eta}{1-\eta}\right)^2\int_1^{x-1}\int_{x-y}^\infty (e^{-[\eta/(1-\eta)](y-1)})(e^{-[\eta/(1-\eta)](z-1)})dz\,dy+\left(\frac{\eta}{1-\eta}\right)\int_{x-1}^x e^{-[\eta/(1-\eta)](y-1)}dy\\&=\left(\frac{\eta}{1-\eta}(x-2)+1\right)e^{-[\eta/(1-\eta)](x-2)}-e^{-[\eta/(1-\eta)](x-1)} \quad \text{for } x\geqslant 2.\end{aligned} \tag{3.16}$$

The first integral in Eq. (3.16) represents the contribution from configurations when the first particle center to the right is closer than $x-1$ to the reference particle center, and the second particle center to the right is no closer than x to the reference center. The second integral accounts for configurations in which the first particle is between $x-1$ and x to the right of the reference center, irrespective of the second particle's position.

We can have exactly one particle within x of the reference center by either having one on the left of the central particle and none on the right or vice versa, leaving

$$
\begin{aligned}
E_P(x;1) &= 2(E_P^{(1)}(x;1))(E_P^{(1)}(x;0)) = 2e^{-[\eta/(1-\eta)](x-1)}[1-e^{-[\eta/(1-\eta)](x-1)}] \quad \text{for } 1\leqslant x<2 \\
&= 2e^{-[\eta/(1-\eta)](x-1)}\left[\left(\frac{\eta}{1-\eta}(x-2)+1\right)e^{-[\eta/(1-\eta)](x-2)}-e^{-[\eta/(1-\eta)](x-1)}\right] \quad \text{for } x\geqslant 2.
\end{aligned}
\tag{3.17}
$$

Following these arguments, one can arrive at a general form for the one-sided probability function $E_P^{(1)}(x;n)$:

$$
\begin{aligned}
E_P^{(1)}(x;n) &= 0 \quad \text{for } 0\leqslant x<n \\
&= 1-\sum_{i=0}^{n-1}\left(\frac{\eta}{1-\eta}\right)^i\frac{(x-n)^i}{i!}e^{-[\eta/(1-\eta)](x-n)} \quad \text{for } n\leqslant x<n+1 \\
&= \left(\frac{\eta}{1-\eta}\right)^n\frac{[x-(n+1)]^n}{n!}e^{-[\eta/(1-\eta)][x-(n+1)]}+\sum_{i=0}^{n-1}\left(\frac{\eta}{1-\eta}\right)^i\left[\frac{[x-(n+1)]^i}{i!}e^{-[\eta/(1-\eta)][x-(n+1)]}\right. \\
&\quad \left. -\frac{[x-n]^i}{i!}e^{-[\eta/(1-\eta)][x-n]}\right] \quad \text{for } x\geqslant n+1.
\end{aligned}
\tag{3.18}
$$

The full particle probability function $E_P(x;n)$ is then determined from the simple relation

$$E_P(x;n)=\sum_{i=0}^{n}E_P^{(1)}(x;i)E_P^{(1)}(x;n-i) \tag{3.19}$$

which counts all "left-side, right-side" combinations which sum to the desired result. Figure 7 shows the exact results along with a comparison with Monte Carlo simulation data. Notice that the peak in the $E_P(x;2)$ curve is higher than the peak in the $E_P(x;1)$ curve for reduced density $\eta=0.5$. This feature is a manifestation of the natural packing symmetry that develops about the reference particle in one dimension. In other words, the coordination shell consists of a pair of particles, one to the left and one to the right. As the packing fraction is increased, the peaks in the even number curves ($n=2,4,6,\ldots$) become extremely pronounced, as compared to their odd counterparts (see Fig. 8).

Recent computer simulations of liquid water [3] and the three-dimensional hard-sphere fluid [4] suggest that the quantity $E_V(x;n)$ in simple fluids may be accurately approximated by a Gaussian distribution in n, at least far away from very high or very low densities. In Fig. 9 we plot the particle probability function $E_P(x;n)$ versus n for several window sizes at a packing fraction of $\eta=0.5$. The points generated

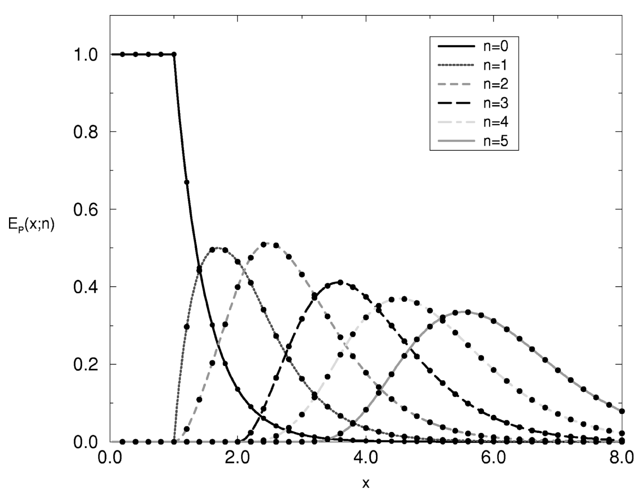

FIG. 7. Particle probability function $E_P(x;n)$ for the hard-rod fluid at a volume fraction $\eta=0.5$. The lines indicate the exact solution obtained from Eqs. (3.18) and (3.19), while the black dots represent Monte Carlo simulation data.

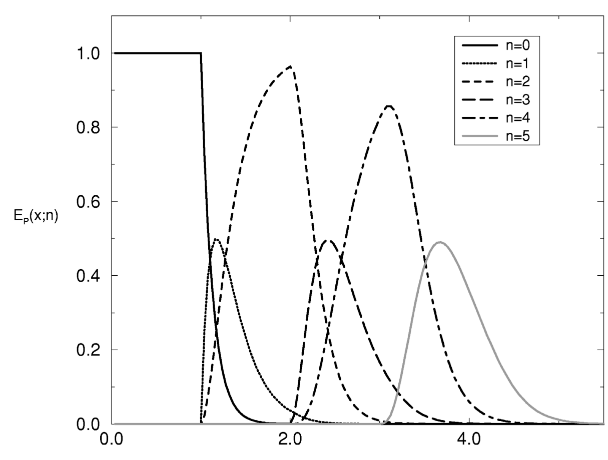

FIG. 8. Particle probability function $E_P(x;n)$ for the hard-rod fluid at a volume fraction $\eta=0.8$, illustrating the pronounced peak heights for even values of n. This feature is related to a packing symmetry described in the text.

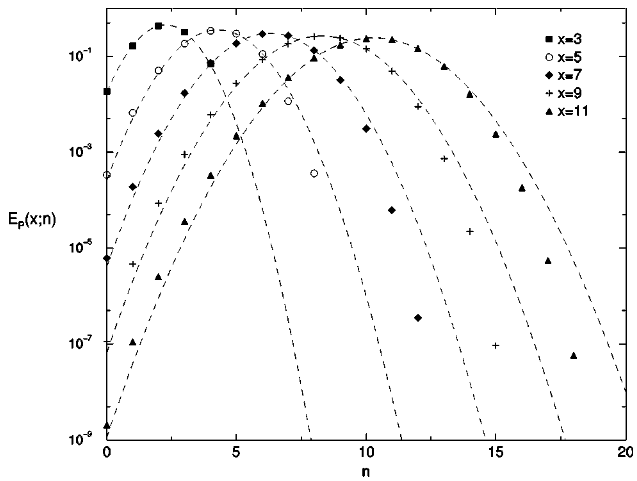

FIG. 9. Particle probability function $E_P(x;n)$ plotted vs n for various window sizes x at volume fraction $\eta=0.5$. The points represent the exact solution obtained from Eqs. (3.18) and (3.19). The lines are fits to the Gaussian form $E_P(x;n)=\exp(A+Bn+Cn^2)$, where A, B, and C are constants of the nonlinear regression.

from Eq. (3.19) were fit to Gaussian curves to test this approximate form for the particle version of the probability function. Although the function $E_P(x;n)$ is nearly Gaussian in n near the peak, significant deviations can be seen in the tails of the distribution. This should be expected, as it is known that both $E_V(x;n)$ and $E_P(x;n)$ depend on all of the n-particle density functions, and thus on all higher moments.

Using relations (2.24) and (2.26), one can determine the particle nth nearest-neighbor distribution function $H_P(r;n)$ (Fig. 10) and the n-particle conditional pair distribution function $G_P(r;n)$ (Fig. 11), respectively. Note the appearance of a kink in the second nearest-neighbor distribution function $H_P(r;n)$. This abrupt change, occurring at $x=2$, corresponds to the first distance at which the second nearest neighbor can occur on the same side of the reference particle as the nearest neighbor. Such anomalies in the particle quantities are expected because the origin is fixed in the center of a reference particle, unlike the void quantities which are averaged uniformly over all possible origins in the system.

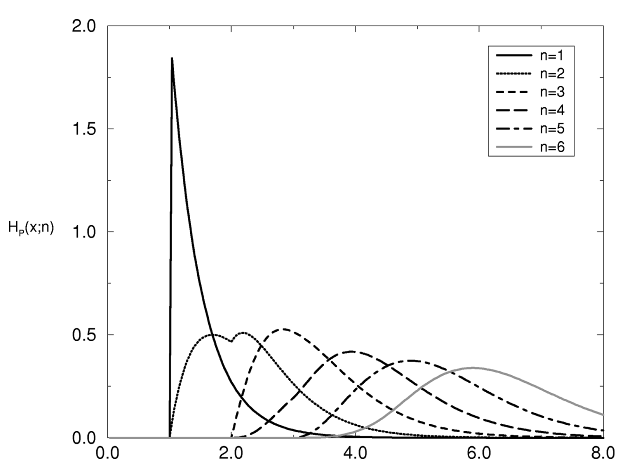

FIG. 10. Particle nth nearest-neighbor distribution function $H_P(r;n)$ for the hard-rod fluid at a volume fraction $\eta=0.5$. Results are obtained from Eqs. (2.26), (2.24), (3.18), and (3.19).

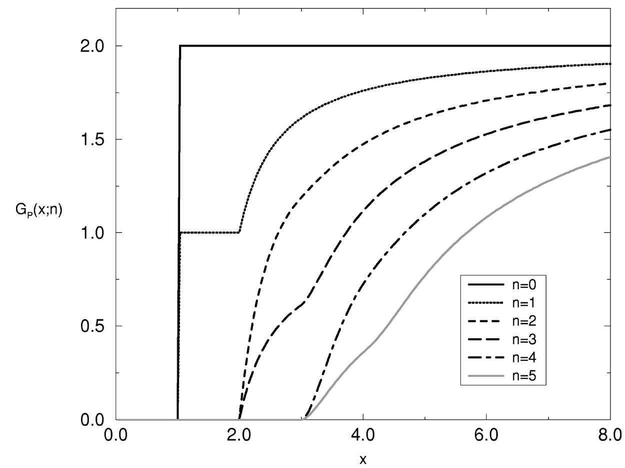

FIG. 11. Particle n-particle conditional pair distribution function $G_P(r;n)$ for the hard-rod fluid at a volume fraction $\eta=0.5$. Results are obtained from Eqs. (2.26), (2.24), (3.18), and (3.19).

It is worth noting that the starting point of our derivation was the one-sided particle probability distribution $E_P^{(1)}(x;n)$. We could have just as well chosen as our starting point the one-sided nth nearest-neighbor distribution $H_P^{(1)}(x;n)$, a quantity evaluated by Elkoshi, Reiss, and Hammerich [32] for both constrained and unconstrained hard-rod systems. This quantity is related to the conventional pair correlation via

$$\rho g(x)=\sum_{i=1}^{\infty} H_P^{(1)}(x;i). \tag{3.20}$$

Although we studied the equilibrium hard-rod system in this work, the methods developed are quite general. In fact they will carry over to *any* one-dimensional system provided that there are no second neighbor interactions and that the chord-length distribution $p(h)$ can be characterized.

IV. CONCLUSIONS

In this paper we present analytical series representations for the general probability functions $E_V(r;n)$ and $E_P(r;n)$ which describe density fluctuations in many-body systems. Furthermore, we have developed equations for their central moments in terms of the n-particle reduced density functions $\rho_1,\rho_2,\ldots,\rho_n$. The results concerning the particle quantities are new, to our knowledge. We have derived relationships for the void and particle nth nearest-neighbor distribution functions $H_V(r;n)$ and $H_P(r;n)$, and the n-particle conditional pair distribution functions $G_V(r;n)$ and $G_P(r;n)$. In the case of the equilibrium hard-rod fluid, we solve for the generalized version of the quantities E_V, E_P, H_V, H_P, G_V, and G_P exactly. We believe the results are the first of this type for a hard-particle system. Furthermore, the methods used to solve the hard-rod problem are quite general, and can be used to address other one-dimensional systems of interacting particles. We are currently developing approximation formulas for the nearest-neighbor quantities for systems of spheres in higher dimensions.

ACKNOWLEDGMENTS

S.T. gratefully acknowledges the support of the U.S. Department of Energy, Office of Basic Energy Sciences (Grant No. DE-FG02-92ER14275). P.G.D. gratefully acknowledges support of the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences (Grant No. DE-FG02-87ER13714), and of the donors of the Petroleum Research Fund, administered by The American Chemical Society. T.M.T. acknowledges the financial support of The National Science Foundation.

[1] R. M. Ziff, J. Math. Phys. **18**, 1825 (1977).
[2] R. M. Ziff, G. E. Uhlenbeck, and M. Kac, Phys. Rep., Phys. Lett. **32C**, 169 (1977).
[3] G. Hummer *et al.*, Proc. Natl. Acad. Sci. USA **93**, 8951 (1996).
[4] G. E. Crooks and D. Chandler, Phys. Rev. E **56**, 4217 (1997).
[5] G. Soto-Campos, D. S. Corti, and H. Reiss, J. Chem. Phys. **108**, 2563 (1998).
[6] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).
[7] S. Torquato, B. Lu, and J. Rubinstein, Phys. Rev. A **41**, 2059 (1990).
[8] H. Reiss and R. V. Casberg, J. Chem. Phys. **61**, 1107 (1974).
[9] S. Torquato, Phys. Rev. E **51**, 3170 (1995).
[10] D. J. Vezzetti, J. Math. Phys. **16**, 31 (1975).
[11] D. Chandler, Phys. Rev. E **48**, 2898 (1993).
[12] L. R. Pratt and D. Chandler, J. Chem. Phys. **67**, 3683 (1977).
[13] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[14] L. Finney, Proc. R. Soc. London, Ser. A **319**, 479 (1970).
[15] J. G. Berryman, Phys. Rev. A **27**, 1053 (1983).
[16] H. Reiss and A. D. Hammerich, J. Phys. Chem. **90**, 6252 (1986).
[17] U. F. Edgal, J. Chem. Phys. **94**, 8191 (1991).
[18] J. R. MacDonald, J. Phys. Chem. **96**, 3861 (1992).
[19] S. H. Simon, V. Dobrosavljevic, and R. M. Stratt, J. Chem. Phys. **94**, 7360 (1991).
[20] C. H. Chothia, Nature (London) **248**, 338 (1974).
[21] J. G. McNally and E. C. Cox, Development (Cambridge, U.K.) **105**, 323 (1989).
[22] I. A. Aksay, Ceram. Int. **17**, 267 (1991).
[23] J. B. Keller, L. A. Rubenfeld, and J. E. Molyneux, J. Fluid Mech. **30**, 97 (1967).
[24] J. Rubinstein and S. Torquato, J. Chem. Phys. **88**, 6372 (1988).
[25] J. Rubinstein and S. Torquato, J. Fluid Mech. **206**, 25 (1989).
[26] M. D. Rintoul and S. Torquato, J. Chem. Phys. **105**, 9258 (1996).
[27] J. R. MacDonald, Mol. Phys. **44**, 1043 (1981).
[28] B. Lu and S. Torquato, Phys. Rev. A **45**, 5530 (1992).
[29] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
[30] P. Hertz, Math. Ann. **67**, 387 (1909).
[31] R. J. Speedy, J. Chem. Soc., Faraday Trans. 2 **76**, 693 (1980).
[32] Z. Elkoshi, H. Reiss, and A. D. Hammerich, J. Stat. Phys. **41**, 685 (1985).
[33] S. Torquato and B. Lu, Phys. Rev. E **47**, 2950 (1993).