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*n*th-nearest-neighbor distribution functions of an interacting fluid from the pair correlation function: A hierarchical approach

Biplab Bhattacharjee*
Department of Chemistry, Physical Chemistry Section, Jadavpur University, Kolkata-700032, India

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The paper presents a general formalism for the nth-nearest-neighbor distribution (NND) of identical interacting particles in a fluid confined in a ν-dimensional space. The nth-NND functions, $W(n,\overline{r})$ (for $n=1,2,3,\ldots$) in a fluid are obtained hierarchically in terms of the pair correlation function and $W(n-1,\overline{r})$ alone. The radial distribution function (RDF) profiles obtained from the molecular dynamics (MD) simulation of Lennard-Jones (LJ) fluid is used to illustrate the results. It is demonstrated that the collective structural information contained in the maxima and minima of the RDF profiles being resolved in terms of individual NND functions may provide more insights about the microscopic neighborhood structure around a reference particle in a fluid. Representative comparison between the results obtained from the formalism and the MD simulation data shows good agreement. Apart from the quantities such as nth-NND functions and nth-nearest-neighbor distances, the average neighbor population number is defined. These quantities are evaluated for the LJ model system and interesting density dependence of the microscopic neighborhood shell structures are discussed in terms of them. The relevance of the NND functions in various phenomena is also pointed out.

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I. INTRODUCTION

For studying the properties of a many-body system of interacting particles, the question of fundamental importance often is to know, how the nearest-neighbor (NN) particles influence some reference particle of interest in the system. An answer to this question as well as an estimate of an important quantity, the mean NN distance requires knowledge of the nearest-neighbor distribution (NND) functions. Microscopic structural informations of a fluid are usually obtained mainly from the pair correlation functions determined either through experiments [1], or estimated from various theoretical schemes [2] or from computer simulation studies [3]. However, the maxima and minima of these functions, although collectively contain significant and quite useful structural information, they cannot provide further detailed microscopic information directly in terms of first-, second- or higher-order neighbors distributed around a central particle in a fluid.

The question of finding NND functions has been studied with considerable success in recent past particularly for hard sphere systems [4,5]. Appropriate derivation of equation of states for fluids may require knowledge of such functions [6,7]. Local field distribution for a correlated system has been recognized to depend significantly on the NND functions [8]. Various transport phenomena in heterogeneous media [9–11] (e.g., electron mobility in insulating fluid [9], diffusion limited rate constants [10], etc.) are also influenced considerably by the immediate neighboring particle distributions. NND functions (though not used directly very often) are also likely to be of particular importance in understanding the nucleation processes [12] (in homogeneous systems and also in case of electrochemical phase formations [13]) as well as in the spectroscopic studies [14] of quenching of photoexcitations (by intermolecular collisions) and solvent relaxation processes [15] (often studied by Raman or Rayleigh light scattering processes which arise from the fluctuations of the system polarizabilities). This is expected as such processes are mainly associated with the static and dynamic influences of the predominantly interacting neighboring solute and solvent particles around the reference particles of interest in an interacting fluid system. Knowledge of the nearest-neighbor distances have also found importance in diverse other fields such as, for example, in controlling of ceramics structures [16], in the case of nucleation of pits on stainless steel [17], and also in biological systems to characterize spatial patterns of the populations in animals, plants, and organisms [18].

Paul Hertz [19] was first to work on the NND function (to be referred to as the *first* NND function in this paper) and NN distance of randomly distributed particles. Assuming ideally random stellar distribution, Chandrasekhar [20] used these results for studying stellar dynamics and showed that the force acting on an individual star was largely due to its NN.

The first NND functions for irreversible deposition phenomena at far from equilibrium [21,22] have also been studied recently, which comes under the vast area of studies named after random sequential adsorption (RSA) models [23–28] associated with the clustering, aggregation, and growth processes. Such studies, however, were essentially motivated by the significant amount of work undertaken by Torquato and others [4,5,29,30] in the last decade to understand the first NND functions under equilibrium in the fluids. Two different types of first NND functions viz., void and particle probability densities for the many-body systems were obtained by Torquato, Lu, and Rubinstein [4]. Interest-

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*Electronic address: bbiplab_juchem@hotmail.com ing analytical expressions for essential quantities like *conditional* pair distribution functions necessary for obtaining the first NND were derived for hard sphere system, in particular, using low density expansion. However, obtaining such analytic expressions for interacting systems, in general, and for those having attractive interaction components, in particular, seems to be extremely difficult if not impossible.

A general formalism for obtaining the first as well as higher-order NND functions particularly for an interacting many-body system would thus be of considerable interest. Efforts have been made by several authors [31–33] to address this issue in recent past. As in the first NN case [4], the nth-NND functions (for $n>1$) are also expected to be related to the n-particle correlation function for the many-body systems. In the low density limit the n-particle correlation function, $\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$ (for $n>1$) may be expressed as the product of the pair correlation functions. With such considerations Mazur [31] attempted to evaluate the nth NND under low density condition. An approximate scheme, more appropriate for low density, to take care of the excluded volume effect of the $(n-1)$ neighbors in the interior on the nth NN was used and illustrated particularly in the context of hard sphere system. However, the question that still remains to be answered is the following : How to find a general formalism for obtaining nth-NND functions (with $n=1,2,3,\ldots,$ etc.) that can be conveniently used for an interacting fluid system with more realistic interparticle interaction and is not restricted to the hard sphere system alone?

With a view to answer the question posed above, we present here, a general, hierarchical formalism which under certain reasonable approximations become quite accurate for the interacting single component fluid systems. It is shown that, given the pair correlation function for a fluid (obtained experimentally, theoretically, or by simulation studies), the nth-NND functions become easily computable for all n $(1,2,3,\ldots,$ etc.) at larger range of density. The hierarchical relation involves $(n-1)$th-NND function alone unlike in Ref. [31] where all lower-order NND functions up to $n=1$ are required simultaneously. The formalism also provides a way to resolve the pair correlation function of the fluid in terms of all higher-order NND functions. The present approach bypasses difficulties encountered in other approaches in an interesting and subtle way while keeping the formalism quite general and simple with closed form hierarchical solutions amenable for easy computation leading to significant insights about the fluid (of interacting particles not restricted to hard spheres alone) structure. Representative comparison of the predictions from the present formalism with simulation data [obtained for Lennard-Jones (LJ) system], as will be discussed later, shows very encouraging results.

A brief review of the n-particle distribution function is presented in Sec. II. The formalism to obtain the nth-NND functions for a ν-dimensional system of identical interacting particles with number density ρ is presented in Sec. III. Various relevant quantities derived from the formalism are also described in the section. In Sec. IV the details of molecular dynamics simulation and computational methodologies are presented. Results obtained for the LJ fluid are discussed in Sec. V followed by our concluding remarks in Sec. VI.

II. *n*-PARTICLE DISTRIBUTION FUNCTION

Considering a system of N identical, interacting particles distributed isotropically in a ν-dimensional space of volume V, the reduced n-particle probability density $\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$, for $n<N$, is defined by [2]

$$\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n}) = \frac{N!}{(N-n)!Z_N}\int_0^V\cdots\int_0^V e^{-\beta U_N(\overline{r_1},\overline{r_2},\ldots\overline{r_N})} \times d^\nu\overline{r}_{n+1}d^\nu\overline{r}_{n+2}\cdots d^\nu\overline{r}_N. \tag{1}$$

The positional vector of the ith particle is represented as $\overline{r_i}$ and the n-particle correlation function $g^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$ is defined as

$$\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})=\rho^n g^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n}). \tag{2}$$

In the above equation ρ is the bulk number density of the system with volume V and Z_N, the configurational integral is given by

$$Z_N=\int_0^V\cdots\int_0^V e^{-\beta U_N(\overline{r_1},\overline{r_2},\ldots\overline{r_N})}d^\nu\overline{r_1}d^\nu\overline{r_2}\cdots d^\nu\overline{r_N}. \tag{3}$$

The quantity $\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})d^\nu\overline{r_1}d^\nu\overline{r_2}\cdots d^\nu\overline{r_n}$ therefore gives the probability of simultaneously finding the center of a particle in volume element $d^\nu\overline{r_1}$ about $\overline{r_1}$, the center of a second particle in volume element $d^\nu\overline{r_2}$ about $\overline{r_2}$ etc. up to finding the nth particle in volume element $d^\nu\overline{r_n}$ about $\overline{r_n}$ irrespective of the positions of the rest of the $(N-n)$ particles. For an uncorrelated system, $\rho^{(n)}=\rho^n$ and the n-particle correlation function $g^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$ becomes unity. Let us now, for example, consider a configuration of a hard sphere system where n particles are placed so that a few among them overlap. Such overlaps in the excluded volume regions for the hard spheres would lead to $U_N(\overline{r_1},\overline{r_2},\ldots\overline{r_N})$ in the integral above to be almost infinitely large and thus $\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$ will be virtually zero for such a configuration. Therefore, the excluded volume effect is incorporated in the definition of $\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$ through the interparticle potential $U_N(\overline{r_1},\overline{r_2},\ldots\overline{r_N})$. It is also to be noted in Eq. (1) that the other $(n+1)$ to N particles, the positions of which are integrated or averaged out, will also influence the value of $\rho^{(n)}(\overline{r_1},\overline{r_2},\ldots,\overline{r_n})$ in a mean field sense for the similar reason.

III. NEIGHBOR DISTRIBUTIONS FOR INTERACTING PARTICLES

A. *n*th-nearest-neighbor distribution

The nth-NND function, $W(n,\overline{r})$ of a ν-dimensional system with N identical particles is defined such that, given a reference particle present at the origin, $W(n,\overline{r})d^\nu\overline{r}$ gives the probability of finding its nth NN (for $n=1,2,3,\ldots,$ etc.) in the volume element $d^\nu\overline{r}$ between $\overline{r}$ and $\overline{r}+d^\nu\overline{r}$. Our definition of the NN is consistent with the earlier works on the NND functions and it is considered that there must be one and only one nth neighbor as pointed out in Ref. [31]. Consequently, it can be shown that all the NND functions are strictly normalized, and may therefore be specifically referred to as normalized NND (NNND) functions. However, for the rest of the paper the name NND will be used instead of NNND to keep it short and simple for convenience.

In the present formalism, it is to be noted that the nearest neighbors of a particle in the fluid are assumed never to be degenerate, that is, these neighbors are never located at exactly the same distance from the center of the particle. Degenerate neighbors may definitely arise, for example, as a limiting case like the close packed or jammed situation of a hard sphere system. Present formalism does not, however, address directly to such a situation which essentially represents a solid phase wherein a reference particle is expected to have m (say) equidistant neighbors with $m>1$ in contact with the particle. Use of NND functions defined above for such a situation requires careful interpretation of m such neighbors. For example, in case of a fluid, if the centers of m such neighbors beyond the $(n-1)$th neighbor of a reference particle becomes exactly degenerate, which is extremely unlikely in a fluid, those neighbors may be arbitrarily labeled as nth neighbor, $(n+1)$th neighbor, up to $(n+m-1)$th neighbor without any loss of generality. However, further discussions related to such degenerate neighbor situation is specifically excluded from this paper to focus mainly on the general nature of the formalism proposed here.

The probability, $W(n,\overline{r})d^\nu\overline{r}$, defined above is now expressed as a conditional probability that out of possible $(N-1)$ neighbor particles of a reference particle in the system, $(n-1)$ particles remain in the interior of spherical volume $\Omega(\overline{r})$ of radius $\overline{r}$ around the reference particle placed at the center, the nth particle remains within volume element $d^\nu\overline{r}$ between $\overline{r}$ and $\overline{r}+d^\nu\overline{r}$ and the remaining $(N-n-1)$ particles occupy the rest of the volume. Therefore, the probability, in general, can be written formally as

$$W(n,\overline{r})d^\nu\overline{r}=\rho^{-1}\int_0^{\Omega(\overline{r})}d^\nu\overline{r}_1\cdots\int_0^{\Omega(\overline{r})}d^\nu\overline{r}_{n-1}\times\left\{\int_{\Omega'(\overline{r})}^{V}d^\nu\overline{r}_{n+1}\cdots\int_{\Omega'(\overline{r})}^{V}d^\nu\overline{r}_{N-1}\times\rho^{(N)}(\overline{r}_1,\ldots\overline{r}_{n-1},\overline{r},\overline{r}_{n+1}\cdots\overline{r}_{N-1})d^\nu\overline{r}\right\}. \quad (4)$$

A particle being chosen at the origin for a homogeneous system is reflected through the factor ρ^{-1} and all the distances are measured with respect to its position at the origin. The lower limit of $\Omega'(\overline{r})$ ensures the exclusion of volumes $\Omega(\overline{r})$ and $d^\nu\overline{r}$ from being occupied by any of the $(n+1)$ to $(N-1)$ particles. Obviously, any function of interest for a bulk system of interacting particles involving N-particle correlation function is not of much use without further simplification. In a similar spirit as the earlier approaches for the first NND [19,20], the condition of excluding the nth and higher-order neighbors from the interior of volume $\Omega(\overline{r})$ is solely taken care of by introducing $W(n,\overline{r})$ itself in the right-hand side of Eq. (4) and the equation for $W(n,\overline{r})$ is rewritten as

$$W(n,\overline{r})d^\nu\overline{r}=\left(1-\int_0^{\Omega(\overline{r})}W(n,\overline{\tau})d^\nu\overline{\tau}\right)\times\left\{\left[\rho^{-1}\int_0^{\Omega(\overline{r})}\cdots\int_0^{\Omega(\overline{r})}\rho^{(n+1)}(\overline{r}_1\overline{r}_2\cdots\overline{r}_{n-1},\overline{r})\times d^\nu\overline{r}_1d^\nu\overline{r}_2\cdots d^\nu\overline{r}_{n-1}\right]d^\nu\overline{r}\right\}. \quad (5)$$

The first factor in the above expression, which introduces nonlinearity explicitly into the problem, by definition ensures the absence of the nth neighbor [and thus rest of the $(N-n-1)$ higher-order neighbors also] within the spherical volume $\Omega(\overline{r})$ around the central particle. The second term now gives the conditional probability of finding the centers of the particles 1 to $(n-1)$ within the spherical volume $\Omega(\overline{r})$ around a reference particle at the origin and the nth particle within the volume element $d^\nu\overline{r}$ between $\overline{r}$ and $\overline{r}+d^\nu\overline{r}$, irrespective of the positions of the rest of the $(N-n-1)$ particles. Here we have ignored any explicit dependence of the second factor on the spatial positions of higher-order neighbors and the $(n+1)$-particle correlation function is influenced by the higher neighbors in a mean field sense. For the spherically symmetric homogeneous system with bulk number density ρ and with $\rho^{(2)}(\overline{r})=\rho^2g^{(2)}(\overline{r})$, from Eq. (5) the expression for the first NND, $W(1,\overline{r})$ becomes

$$W(1,\overline{r})d^\nu\overline{r}=\left(1-\int_0^{\Omega(\overline{r})}W(1,\overline{\tau})d^\nu\overline{\tau}\right)\{\rho g^{(2)}(\overline{r})d^\nu\overline{r}\}. \quad (6)$$

The factor $\rho g^{(2)}(\overline{r})$ here may be also referred to as the local density [2]. The above equation for the first NND can be exactly solved and will be discussed later in Sec. III B.

For higher-order neighbors (i.e., $n>1$), finding a closed form exact solution even for Eq. (5) for an interacting system becomes very complicated for involving many particle correlation functions. We therefore reformulate the equation into an exactly solvable hierarchical equation for $W(n,\overline{r})$, wherein the second factor in Eq. (5) is further rewritten, in a similar spirit as before, in terms of the $(n-1)$th NND, $W(n-1,\overline{r})$, and the pair correlation function. In the final proposition of the present formalism, the probability that the nth NN to a reference particle kept at origin, occurs between $\overline{r}$ and $\overline{r}+d^\nu\overline{r}$, is thus equated with the product of three factors as follows,

$$W(n,\overline{r})d^{\nu}\overline{r}=\left(1-\int_0^{\Omega(\overline{r})}W(n,\overline{\tau})d^{\nu}\overline{\tau}\right)\times\left(\int_0^{\Omega(\overline{r})}W(n-1,\overline{\tau})d^{\nu}\overline{\tau}\right)(\rho^{-1}\rho^{(2)}(\overline{r})d^{\nu}\overline{r}). \tag{7}$$

In the above equation, the first factor ensures that no nth neighbor exists interior to $\overline{r}$ [having volume $\Omega(\overline{r})$], and the second factor ensures that the $(n-1)$th neighbor (and thus all lower order neighbors) does exist interior to $\overline{r}$. In the third factor, the term $\rho^{-1}\rho^{(2)}(\overline{r})d^{\nu}\overline{r}$, is used as the probability of finding a particle (which eventually becomes the nth neighbor) within a volume element of $d^{\nu}\overline{r}$ in a ν-dimensional space at a distance $\overline{r}$ from the central reference particle irrespective of the positions of the rest of the particles.

In the present formalism, the excluded volume effect gets incorporated hierarchically through the function $\rho^{(2)}(\overline{r})$, which would be replaced by $\rho^2 g^{(2)}(\overline{r})$. $g^{(2)}(\overline{r})$ being the pair correlation function, its oscillating nature as obtained either from experiments or from theory, or from simulation studies of interacting fluid systems, already reflects the excluded volume effect due to the finite size of the particles and their interactions in the fluid. Therefore, although m-particle correlation function for $1\leqslant m\leqslant(n-1)$ is not explicitly utilized at the outset in the formalism of the nth-NN distribution, the higher-order correlation gets incorporated hierarchically into the formalism through the nontrivial nonlinear dependence of $W(n,\overline{r})$ on $g^{(2)}(\overline{r})$ and $W(n-1,\overline{r})$ alone. The basic input being the pair correlation function $g^{(2)}(\overline{r})$ which gets suitably modified as the density or the temperature changes for a system, the proposed formalism for obtaining $W(n,\overline{r})$ hierarchically is expected to be very accurate for thermodynamic systems at arbitrary densities and temperatures. For this hierarchical nature, this approach is likely to give rise to a very good upper bound estimate for the nth-NND functions as $g^{(2)}(\overline{r})$ is influenced by the many-body effect in a mean field sense (cf. Sec. II). The representative comparison of the results with the simulation data also show good agreement.

For a homogeneous system of spherically symmetric identical particles, the pair correlation function depends only on the magnitude of the interparticle separation, r. The superscript of $g^{(2)}(\overline{r})$ and the bar over r will be ignored for notational simplicity in the subsequent discussions and it will also be referred to as the radial distribution function (RDF). By replacing the volume element $d^{\nu}\overline{r}$ by $4\pi r^2 dr$ for the three-dimensional system, Eq. (7) becomes

$$W(n,r)=\left[1-\int_0^r W(n,\tau)4\pi\tau^2 d\tau\right]\times\left[\int_0^r W(n-1,\tau)4\pi\tau^2 d\tau\right]\rho g(r). \tag{8}$$

From the above equation we derive

$$\frac{d}{dr}\left(\frac{W(n,r)}{[F(n-1,r)]\rho g(r)}\right)=-\left(\frac{W(n,r)}{[F(n-1,r)]\rho g(r)}\right)\times F(n-1,r)\rho g(r)4\pi r^2, \tag{9}$$

where

$$F(n,\lambda)=\int_0^{\lambda}W(n,\tau)4\pi\tau^2 d\tau. \tag{10}$$

Hence, on integration Eq. (9) gives

$$W(n,r)=\rho g(r)F(n-1,r)\times\exp\left[-\int_0^r \rho g(\tau)F(n-1,\tau)4\pi\tau^2 d\tau\right], \tag{11}$$

since according to Eq. (8), the term within the bracket in the left-hand side of Eq. (9) becomes unity as $r\rightarrow 0$. Equation (11) represents the exact hierarchical solution of the nth NND in terms of $(n-1)$th NND and the $g(r)$. For the first NND the solution becomes even simpler as shown below.

B. First nearest-neighbor distribution

The probability that the NN (to be referred to as the first NN) to a particle, kept at origin, occurs between $\overline{r}$ and $\overline{r}+d^{\nu}\overline{r}$ is denoted by $W(1,\overline{r})d^{\nu}\overline{r}$. This probability must be clearly equal to the probability that no particle exists interior to $\overline{r}$ times the probability that a particle does exist between $\overline{r}$ and $\overline{r}+d^{\nu}\overline{r}$. Accordingly, for spherically symmetric particles, $W(1,r)$ must satisfy the relation, as can also be obtained from Eq. (6),

$$W(1,r)=\left(1-\int_0^r W(1,\tau)4\pi\tau^2 d\tau\right)\rho g(r). \tag{12}$$

From the above equation one can derive

$$\frac{d}{dr}\left(\frac{W(1,r)}{\rho g(r)}\right)=-\left(\frac{W(1,r)}{\rho g(r)}\right)\rho g(r)4\pi r^2. \tag{13}$$

Hence, on integrating,

$$W(1,r)=\rho g(r)\exp\left[-\int_0^r \rho g(\tau)4\pi\tau^2 d\tau\right], \tag{14}$$

since according to Eq. (12), $W(1,r)\rightarrow\rho g(r)$ as $r\rightarrow 0$. Therefore, Eq. (14) gives the expression for the first NND for an interacting fluid. Representative comparison between this result and the simulation data for Lennard-Jones fluid shows very good agreement and will be discussed later. For spatially uncorrelated systems $g(r)$ being unity, Eq. (14) leads to Hertz's solution [19,20] for Poisson distributed points (also for randomly distributed fully penetrable spheres) with number density ρ. Equation (14) for the first NND function is also similar as that obtained in Refs. [4,31] for hard spheres except that instead of $4\pi r^2\rho g(r)$ they involved *conditional* pair distribution function, $G(\mathrm{r})$. Use of analytic expressions of such functions obtained for hard sphere systems

[4,29] under various approximation schemes led to very good agreement with the Monte Carlo simulation results for the first NND functions. To the best of our knowledge, however, we have not come across any comparative study to show how the results of first NND function obtained using appropriately the RDF obtained from the computer simulation of hard sphere model system differs from that obtained using analytical expression for the *conditional* pair distribution function. Preliminary studies [34] using Percus-Yevick RDF for hard sphere model, which is not quite accurate at higher densities, calculated $W(1,r)$ according to Eq. (14) matched quite well particularly at lower densities with the results of Torquato and Lee [29] using the *conditional* pair distribution function expression obtained from the Carnahan-Sterling approximation. We intend to undertake shortly such comparative studies for hard sphere model system by obtaining reliable RDF functions at arbitrary densities using molecular dynamics simulation.

In the present formalism Eqs. (11) and (14) therefore give us the complete solution of the nth NND in terms of hierarchy of equations. It is also to be noted that Eq. (14) can be obtained from Eq. (11) by substituting $F(0,r)=1$ in it, reflecting the presence of the central reference particle. In view of this, Eq. (11) may be considered to give the complete solution of the problem (for all n) in the present formalism. The first NND, $W(1,r)$ is obtained from Eq. (14) using the knowledge of $g(r)$ obtained either from experimental, theoretical, or computer simulation studies. All other nth-NND functions, $W(n,r)$ for $n=2,3,4,\ldots,(N-1)$ are obtained from the knowledge of $g(r)$ and only the numerically already obtainable $W(n-1,r)$ function alone instead of requiring simultaneously all the $W(m,r)$ functions with $1\leqslant m \leqslant(n-1)$ as required according to the earlier work of Mazur [31].

C. Normalization check for $W(n,r)$

The probability of finding the nth NN within the sphere of radius r around a particle kept at the center is given by $F(n,r)$ [cf. Eq. (10)]. According to the definition of $W(n,r)$, the function $F(n,r)$ should become unity for any $n\leqslant(N-1)$ as $r\rightarrow\infty$. This can be tested by evaluating the following integral,

$$I=\int_0^\infty W(n,r)4\pi r^2 dr. \tag{15}$$

Above integral can be rewritten as

$$I=\int_0^\infty -\left(\frac{d}{dr}[Y(n-1,r)]\right)dr,$$

which gives

$$I=-Y(n-1,r)|_0^\infty, \tag{16}$$

where

$$Y(n-1,r)=\exp\left[-\int_0^r \rho g(\tau)F(n-1,\tau)4\pi\tau^2 d\tau\right]. \tag{17}$$

The integral in the exponent above, in the thermodynamic limit, will be infinitely large as $r\rightarrow\infty$, since $g(\tau)$ and $F(n-1,\tau)$ have non-negative finite values in the range $\tau>0$. Thus, from Eq. (16),

$$I=-e^{-\infty}+e^0=1.$$

The above result indicates, as mentioned earlier, that the nth-NND functions are normalized for all values of $n=1,2,3,\ldots,(N-1)$. Also note that having τ as the upper limit instead of infinity, from Eq. (15) $I=F(n,\tau)$, and Eq. (16) leads to $F(n,\tau)=1-Y(n-1,\tau)$, relating $F(n,\tau)$ with $F(n-1,\tau)$.

D. Average *n*th-nearest-neighbor distance

The general definition for the average nth-NN distance is as follows,

$$\langle r_n\rangle=\int_0^\infty rW(n,r)4\pi r^2 dr, \tag{18}$$

which can be rewritten as

$$\langle r_n\rangle=\int_0^\infty -r\left\{\frac{d}{dr}[Y(n-1,r)]\right\}dr, \tag{19}$$

where $Y(n-1,r)$ is defined in Eq. (17). By doing integration by parts we get

$$\langle r_n\rangle=-rY(n-1,r)|_0^\infty+\int_0^\infty Y(n-1,r)dr. \tag{20}$$

The first term in the above equation becomes zero as in the thermodynamic limit the exponent in $Y(n-1,r)$ [cf. Eq. (17)] will diverge as $r\rightarrow\infty$. Therefore, we obtain the final expression as

$$\langle r_n\rangle=\int_0^\infty Y(n-1,r)dr. \tag{21}$$

The above expression shows that the average nth-NN distance completely depends on the $(n-1)$th-NND function and the RDF $g(r)$.

The difference between the successive mean nearest-neighbor distances can now be written as

$$\begin{aligned}\langle r_{n+1}\rangle-\langle r_n\rangle&=\int_0^\infty [Y(n,r)-Y(n-1,r)]dr\\&=\int_0^\infty dr Y(n,r)\left\{1-\exp\left[-\int_0^r \rho g(\tau)\right.\right.\\&\qquad\left.\left.\times[F(n-1,\tau)-F(n,\tau)]4\pi\tau^2 d\tau\right]\right\}.\end{aligned}$$

Considering the definitions of the nth-NND functions [$W(n,r)$] and $F(n,r)$ [cf. Eq. (10)], it is expected that the probability of finding $(n-1)$ neighbors would be greater than finding n neighbors within a radial distance r around a reference particle for an interacting system. Thus one can argue (also may be easily confirmed for $n=1,2,3,\ldots$, etc., from the relation of $F(n,\tau)$ with $F(n-1,\tau)$ mentioned in Sec. III C and $F(0,r)=1$, mentioned in Sec. III B) that $[F(n-1,r)-F(n,r)]\geqslant 0$ (equality corresponds to the degenerate situation, not considered here) for any values of n at any value of r. $Y(n,r)$ being always a positive quantity [cf. Eq. (17)], this inequality thus suggests from the above relation that $[\langle r_{n+1}\rangle-\langle r_n\rangle]\geqslant 0$ for any value of n. This nondecreasing as well as nonlinear (particularly pronounced at higher densities) dependence of the mean nth-NN distances on n is also demonstrated in the results obtained from the simulation data (cf. Sec. V).

E. Average neighbor population in the spherical neighborhood

It is to be noted that $F(n,r)$ as defined in Eq. (10), gives the probability of finding central particles having n neighbors within the spheres of radius r around them. So the number of particles having nth NN within spheres of radius r around them is $NF(n,r)$, where N is the total number of particles in the bulk system. The fraction of particles having n neighbors within spheres of radius r around them is thus $[F(n,r)/\Sigma_{i=1}^{N-1}F(i,r)]$. The average neighbor population $\langle n_r\rangle$, i.e., the average number of neighbors likely to be present within a sphere of radius r around any particle taken as the central particle in a fluid is thus expressed for the first time as the following quantity,

$$\langle n_r\rangle=\sum_{n=1}^{N-1}\frac{n\cdot F(n,r)}{\sum_{i=1}^{N-1}F(i,r)}. \tag{22}$$

Density dependence of this quantity and its relevance particularly in the context of neighborhood shell structures will be discussed for the LJ fluid in Sec. V.

IV. SIMULATION AND COMPUTATIONAL DETAILS

For some preliminary representative comparison between the results obtained from the present formalism and that from the simulation directly, molecular dynamics (MD) simulation [3] of spherically symmetric interacting model system was undertaken. All MD simulation studies reported here have been carried out in the microcanonical ensemble with cubic boundary conditions. The particle-particle interaction was modeled as Lennard-Jones (LJ) potential, $u(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. The LJ parameters ϵ and σ corresponding to argon ($\epsilon=120k_B$ and $\sigma=3.41A$) were used and the particle mass was taken to be 39.95 (Ar). A $(5\times5\times5)$ cell was considered for each of the simulation run involving 500 particles. Time steps of 10 fs were used for integration. Integrations in the simulation were carried out using the velocity verlet scheme [3]. Simulations were carried out for a total period of 500 ps. The equilibrium periods were of 200 ps during which the velocities were scaled to obtain the desired temperature. The densities were varied by appropriately modifying the size of the unit cells. The desired temperatures were also suitably chosen so that the average temperatures during the MD runs for the systems at different densities were comparable and at lower than the room temperature.

For the computation of the relevant quantities, the results of the preceding section were converted into corresponding nondimensional forms. The probability of finding the nth NN within a spherical shell volume of $4\pi r^2dr$ around a particle at the origin is given by $W(n,r)\times 4\pi r^2dr$. In terms of a nondimensional variable $x(=r/\sigma)$, this probability is redefined as $P(n,x)dx$ with $P(n,x)=\sigma^3W(n,x\sigma)4\pi x^2$. The $P(n,x)$ functions are obtained from the expression of $W(n,r)$ in Eq. (11) as follows,

$$P(n,x)=\rho^*4\pi x^2g(x)\Phi(n-1,x)\times\exp\left[-\int_0^x\rho^*g(\tau)\Phi(n-1,\tau)4\pi\tau^2d\tau\right] \tag{23}$$

with $\rho^*=\rho\sigma^3$ and the integrated nth-NND function [cf. Eq. (10)],

$$\Phi(n,x)=\int_0^xP(n,\tau)d\tau. \tag{24}$$

Results are discussed in the following section in terms of the nth-NND functions, $P(n,x)$ calculated according to Eq. (23). The probability of finding the nth NN within the spherical volume of radius $x\sigma$ around a central reference particle is computed according to Eq. (24). The average nth-NN distances are computed by rewriting Eq. (18) as

$$\langle X_n\rangle=\int_0^\infty xP(n,x)dx \tag{25}$$

so that $\langle r_n\rangle=\langle X_n\rangle\sigma$. The average neighbor population within a sphere of radius $x\sigma$ around an arbitrary reference particle [cf. Eq. (22)] is evaluated as

$$\langle n_x\rangle=\sum_{n=1}^{N-1}\frac{n\cdot\Phi(n,x)}{\sum_{i=1}^{N-1}\Phi(i,x)}. \tag{26}$$

For some representative comparison the $P(n,x)$ values were also determined directly from the simulation data during MD run as follows,

$$P(n,x)\Delta=\frac{1}{\tau}\sum_{i=1}^{\tau}\frac{N_{s,n}(x,i)}{N_s(i)}. \tag{27}$$

In the above, τ is the number of MD time steps and $N_s(i)$ is the number of particles sampled at the ith MD time step. Among these $N_s(i)$ particles, $N_{s,n}(x,i)$ is the number of such sampled particles in the ith MD time step, each of which having $(n-1)$ neighbors within a sphere of radius x around them also has at least one or more particles present within a spherical shell of thickness Δ between the spheres of radius x and $x+\Delta$. In our studies, $N_s(i)$ is same as the total number

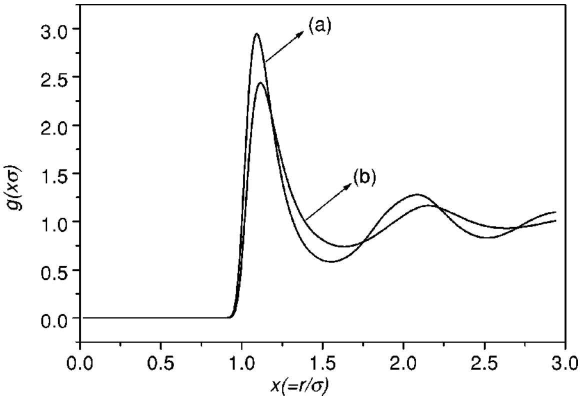

FIG. 1. Radial distribution function (RDF) profiles $g(x\sigma)$ obtained from the MD simulation of Lennard-Jones fluid against radial distance $x(=r/\sigma)$ at the densities $\rho^*=0.8564$ (a), 0.6422 (b) at comparable temperatures $T(\mathrm{K})=98.0762\pm2.3927$ (a) and 98.5407 ±2.2084 (b).

of particles used for the simulation. To get better accuracy in the calculation of $P(n,x)$, τ and $N_s(i)$ must be very large and Δ must be chosen very small. For our estimation of $P(n,x)$ we have chosen $\Delta=0.0025$.

For the discussion in the following section, the relevant quantities in the above equations were computed using the extended Simpson's rule [35] for numerical integrations and the cubic spline interpolation method [36].

V. DISCUSSION

It is understood that the RDF profiles contain considerable amount of microscopic information according to the classical theory of fluid. It is also of great advantage that these profiles are obtainable experimentally, theoretically, or by suitable computer simulation studies. The RDF profiles obtained from the MD simulation of the LJ fluid at two different densities having comparable system temperatures are shown in Fig. 1. In both the cases the sharp rise of $g(x\sigma)$ before $x(=r/\sigma)=1.0$ indicates softness of the LJ fluid. At lesser density the peak positions of the $g(r)$ profiles appears at higher values of x and the peaks are broadened reflecting, in an average sense, more diffused structures ("neighborhood shells") around the particles in the fluid. However, further detailed insight in terms of nearest-neighbors around a reference particle is not very apparent from these RDF profiles. For example, from the RDF profiles, it is virtually impossible to comment on the most probable position of the first NN of a central reference particle in a fluid. This position, in general, should not be associated with the first maxima of the RDF profiles as will be demonstrated below. An important emphasis of the present work is therefore, in a way, to resolve the full microscopic structural information content of the RDF profiles into individual NND functions.

Before discussing the nth-NND function, $P(n,x)$ in detail, some representative comparisons between these functions obtained according to the proposed formalism [cf. Eq. (23)] and the simulation studies [cf. Eq. (27)] are shown in Figs. 2(a) and 2(b). Such analysis of higher-order neighbors for an interacting system has been done here. Very good agreements between the computed $P(n,x)$ profiles and the simulation results (shown for $n=1,2,3$) at both the densities studied is indicative of the reasonable assumptions incorporated into our present formalism. The deviations between the computed $P(n,x)$ and the simulation data for higher n values, in particular, are not completely unexpected and may be due to two reasons. One obvious reason being that such deviations at higher n as well as small deviations around maxima, for example, for $n=3$ in Figs. 2(a) and 2(b) are likely to narrow down with the simulation results obtained from even larger system size and with longer MD simulation run with smaller Δ values [cf. Eq. (27)]. An elaborate simulation study on an even larger system, particularly to study the hard sphere neighbor distributions is intended in near future to have better insights into such neighbor distribution problems. The other possible reason for the deviations for higher n values may be associated with the assumptions in the formalism leading to a certain degree of over estimation and an attempt for further improvement of the formalism is being looked into. However, considering that the RDF of the interacting system is the only input into the proposed formalism, the results reported here are also quite useful due to the simplicity of the approach and the agreement in the representative comparison between the formalism results and the

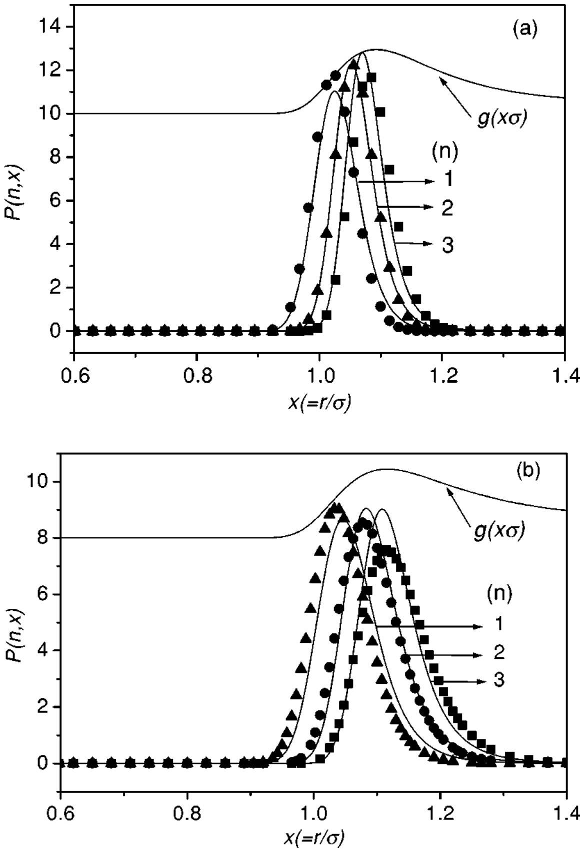

FIG. 2. (a),(b) Representative comparison of nth-NND functions, $P(n,x)$ vs $x(=r/\sigma)$ curves (solid lines) with corresponding simulation data (symbols) for $n=1,2,3$ at densities $\rho^*=0.8564$ (a), 0.6422 (b) at corresponding comparable temperatures as in Fig. 1. The corresponding RDF $g(x\sigma)$ shifted by constant values [10.0 for 2(a) and 8.0 for 2(b)] are also shown.

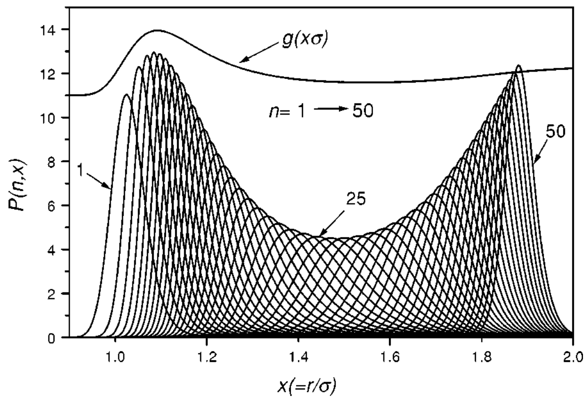

FIG. 3. nth-NND functions, $P(n,x)$ of the Lennard-Jones fluid plotted against radial distance $x(=r/\sigma)$ at density $\rho^*=0.8564$ and temperature $T(K)=98.0762\pm0.2.3927$ for $n=1-50$. Corresponding RDF $g(x\sigma)$ shifted by a constant value 11.0, is also shown.

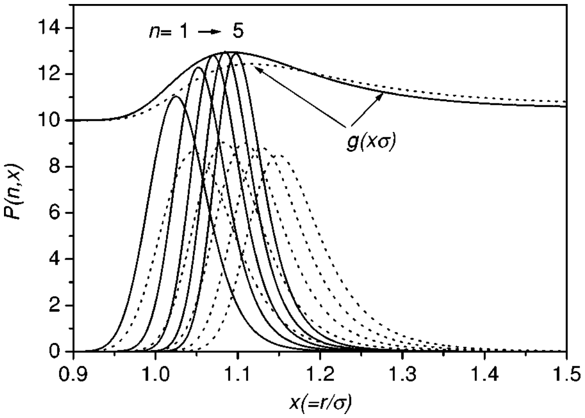

FIG. 4. Relative comparison of nth-NND functions, $P(n,x)$ plotted against radial distance $x(=r/\sigma)$ for $n=1-5$ at densities $\rho^*=0.8564$ (solid lines) and $\rho^*=0.6422$ (dotted lines) with respective temperatures as in Fig. 1. Corresponding RDF, $g(x\sigma)$ profiles, shifted by a constant value 10.0 are also shown.

simulation data as seen in Figs. 2(a) and 2(b).

The rest of the discussions in this section will be based on the results for the LJ fluid computed from the $P(n,x)$ profiles obtained following Eq. (23). In Fig. 3, at the highest density considered, the $P(n,x)$ functions for $n=1-50$ are plotted along with the RDF, $g(r)$ shifted vertically by a constant amount for suitable visual comparison. Conventionally, the first peak of the RDF is associated with the first neighbor shell for any reference particle in a fluid and the first shell is considered to be extended up to the first minimum of the RDF. The $P(n,x)$ plots, however, indicate that the maximum of the first NN appears at a distance closer than the first peak position of the corresponding RDF. This indicates that for almost all the particles their first NN remains at a closer proximity than the distance at which the first peak of $g(r)$ appears. The first minimum of the RDF appears at nearly $r=1.5\sigma$ for the density $\rho^*=0.8564$ (cf. Fig. 1). It is seen from the $P(n,x)$ plots in the figure that several neighbors are present within that range and there the $P(n,x)$ is maximum for $n=27$. From simple spatial arrangement considerations this suggests that the conventional first neighbor shell is likely to consist of more than the immediate neighbors. Such neighbors are therefore not equivalent in terms of their proximities with respect to the central reference particles and they would behave differently physicochemically compared to, for example, the first NN. The figure also shows that at around $r=1.1\sigma$, while many particles are surrounded by eight or less neighbors there is virtually no particle surrounded by 12 or more neighbors. The significantly larger overlap between $P(1,x)$ and $P(8,x)$ as compared to that between $P(1,x)$ and $P(12,x)$, at the highest density considered is also possibly an indication of the fact, as the voronoi analysis suggested earlier [37], that the bcc clusters are the probable nuclei for the crystallization of the soft spheres. The sharper and more symmetric $P(n,x)$ profiles having smaller width for smaller n (5, say) are because of the neighbors in the immediate vicinity of the central particles which are more strongly held. The smaller peak height with larger width of the $P(n,x)$ profiles for intermediate values of n indicate that the population of such neighbors are also relatively smaller and distributed over a larger range due to more pronounced excluded volume effect in the region where minima of $g(r)$ occurs.

The relative comparison of the $P(n,x)$ profiles at two densities shown in Fig. 4 indicate the dependence of the neighborhood structures on the densities at comparable temperatures. It is clear that compared to the $g(x\sigma)$ plots as shown in the same figure, remarkable differences in the $P(n,x)$ profiles for $n=1-5$ leads to better insights about the neighborhood structures in a fluid. The peaks at lower density are smaller in height, relatively wider and shifted to higher values of x indicating relatively more diffused neighborhood structures. Smaller separations of the successive $P(n,x)$ peaks at the larger density reflect more compact neighborhood.

In Fig. 5, the probabilities of finding the nth NN within a sphere of radius $r(=x\sigma)$, is plotted in terms of the integrated nth-NND functions, $\Phi(n,x)$ [cf. Eq. (24)] for two different densities. For both the densities, $\Phi(n,x)\rightarrow1$ at higher values of x for all n indicates strict normalization

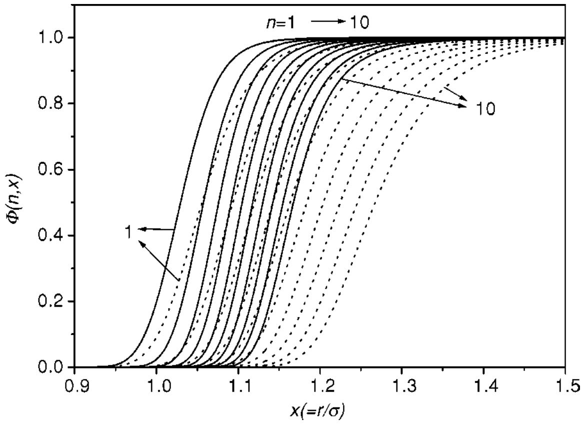

FIG. 5. Integrated nth-NND functions, $\Phi(n,x)$ plotted against radial distance $x(=r/\sigma)$ for $n=1-10$ at densities $\rho^*=0.8564$ (solid lines) and $\rho^*=0.6422$ (dotted lines) at respective comparable temperatures as in Fig. 1.

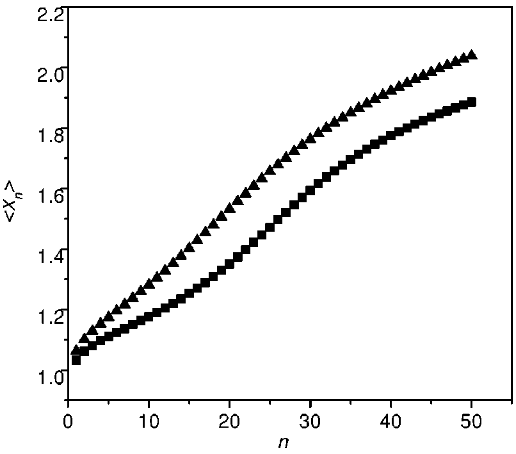

FIG. 6. Average *n*th-NN distance plotted against *n* for two densities $\rho^* = 0.8564$ (squares) and $\rho^* = 0.6422$ (triangles) at respective comparable temperatures as in Fig. 1.

property. The $\Phi(n,x)$ curves reaching unity more slowly for the lower density reflect relatively more diffused neighbor structures.

The average *n*th-NN distances, $\langle X_n \rangle$ obtained according to Eq. (25), for different values of *n* (showing their nondecreasing dependence on *n*) at the two densities considered are shown in Fig. 6. The points for the lower density show an almost linear dependence with *n* in the initial range indicating that the successive neighbors are almost evenly distributed. The dependence is relatively nonlinear for the higher density. This nonlinearity is likely to be more pronounced with further increase in density. More rigid structuredness in the immediate vicinity of any central particle is reflected in the slower variation of the $\langle X_n \rangle$ for smaller *n* values at the higher density. At further higher densities, close to the close-packing density, this region is likely to be like a plateau indicating almost equidistant and nearly equivalent neighbors of the first shell in the immediate vicinity of any particle taken as the central reference particle.

These points are further illustrated in terms of another new quantity, the average neighbor population $\langle n_x \rangle$ around an arbitrary reference particle, calculated according to Eq. (26). At $x \to 0$ limit both the numerator and the denominator of Eq. (26) becomes zero giving rise to the limiting value of $\langle n_x \rangle$ to be unity. So the deviation of $\langle n_x \rangle$ from unity, i.e., $\langle n_x \rangle - 1$ indicates the average neighbor population. The plot of $\langle n_x \rangle$ against the nondimensional radial distance *x* is shown in Fig. 7. Figure 7(a) at the higher density is significantly nonlinear indicating prominent neighborhood shell structure. For example, the point at which the slope significantly decreases (near $x = 1.32$ and $\langle n_x \rangle = 7.4$), shown approximately as *p* on Fig. 7(a) qualitatively indicates that the neighbors within $x \leqslant 1.32$ (say) would behave differently physicochemically than those at $x > 1.32$. The value of $\langle n_x \rangle$ at the point indicates that most particles will be surrounded by six to seven neighbors within that spherical radius of $r = 1.32\sigma$. The first inflexion point observed in Fig. 7(a) for the higher density would be even sharper at further higher density and may possibly be associated with the first neighbor shell. Figure 7(b), however, shows almost linear dependence indicating that the neighbors around any central particle are evenly distributed. The slope change at the point *q* occurs at higher value of *x* and is also not so sharp indicating that the neighborhood shell structure is more diffused at the lesser densities. From these considerations, $\langle n_x \rangle$ may be a more suitable quantity for defining the shell boundaries which will be prominent particularly at higher densities.

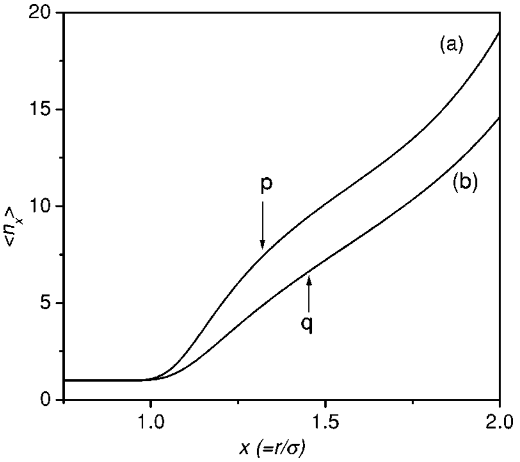

FIG. 7. Average NN population within a sphere around a central particle plotted against the radial distance $x(=r/\sigma)$ at densities $\rho^* = 0.8564$ (a) and $\rho^* = 0.6422$ (b) at respective comparable temperatures as in Fig. 1. The points around which the slope of the curves decreases is indicated by *p* [for (a)] and *q* [for (b)].

VI. CONCLUSION

In the general formalism presented here, the *n*th-NND function of an isotropic interacting fluid is expressed in terms of pair correlation function and the $(n-1)$th-NND function alone. The resulting nonlinear relationship introduces *n*-particle correlations into the problem in a hierarchical manner. Similar approach may be of importance in other areas of interest too for handling higher-order correlations. These NND functions apart from providing interesting detailed insights about the neighborhood structure (not otherwise directly available) are also likely to make one appreciate the RDF profiles of a fluid even better from microscopic structural point of view. The radial distribution functions being relatively easily obtainable either from experiments, theoretical or simulation studies, the present formalism provides a quite general closed form solution for the neighbor functions which could be computed without much difficulties for interacting systems, and is likely to work for systems at arbitrary densities and temperatures.

The comparative studies of the *n*th-NND functions obtained from the formalism match very well with the MD simulation data, particularly for smaller values of *n* indicating the approximations associated with the present formalism to be quite reasonable. From the results analyzed for the LJ-fluid system, it is observed that significant details of the neighborhood structures are revealed by the neighbor distribution functions which are not directly obtainable from the

RDF profiles alone. For example, relevant information about the microstructures may be obtained in terms of the average *n*th-NN distances. These quantities apart from demonstrating their nondecreasing dependence on *n* also show significant nonlinear variation with *n* particularly at higher densities. A newly defined quantity, the average neighbor population number within a sphere of radius *r* around a central particle leads to important insights about the neighborhood (''shell'') structures around a reference particle in a fluid, as discussed in the preceding section.

We intend to undertake extensive MD simulation study of particularly hard spheres and other interacting model systems with even larger system size in near future to study the formalism further. Extension of the present work for the multicomponent systems as well as incorporating time dependence into the formalism would be our next aim. The local field distributions around a reference particle in a fluid being significantly influenced by the NN particles, appropriate use of the NND functions may be of significant importance for better understanding of various phenomena involving nucleation and growth processes as well as in the formulation of dynamic processes associated with the quenching (by neighboring particle collision) and solvent relaxation of photoexcited molecules in a fluid.

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