*n*th-Nearest neighbour distribution functions of a binary fluid mixture[†]

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Abstract.   For obtaining microscopic structural information in binary mixtures, often partial pair correlation functions are used. In the present study, a general approach is presented for obtaining the neighbourhood structural information for binary mixtures in terms of *n*th nearest neighbour distribution (NND) functions (for *n* = 1, 2, 3, …). These functions are derived from the partial pair correlation functions in a hierarchical manner, based on the approach adopted earlier by us for single component fluids. Comparison of the results with MD simulation for Lennard–Jones binary mixtures is also presented. NND functions show reasonable matching for smaller n values particularly at higher density. The average *n*th nearest neighbour distance shows interesting feature.

Keywords.   Nearest neighbour distribution; binary mixture.

1.   Introduction

Properties of an interacting many-particle system often depends fundamentally on the influence of the nearest neighbour (NN) particles around a reference particle of interest in pure as well as multi-component fluid systems. For microscopic structural studies, an estimate of quantities like the mean NN distance as well as the microscopic neighbourhood population around any reference particle require knowledge of the nearest neighbour distribution (NND) functions. General interest in the subject has been there for quite some time[1] mainly because of its relevance in various fields of science.[2–4]

Microscopic structural information at equilibrium for fluids are usually obtained mainly from the pair correlation functions (PCFs) evaluated experimentally,[5] theoretically[6] or from simulation[7] studies. In recent times considerable efforts have been made to obtain more detailed studies of NND functions, particularly for hard sphere fluids.[8] Efforts have also been made earlier to obtain the NND functions for interacting single component systems.[9] Similar questions are also of interests in the field of material science as well.[10] With increased interests in complex multi-component systems, fundamental studies on the binary mixtures are gathering a lot of importance at present. Significant studies on the influence

of composition on both structural[11] as well as dynamical properties of binary mixtures[12] in particular have attracted a lot of attention in recent times.

For better understanding of the microscopic neighbourhood structures around a reference particle in a binary mixture, knowledge of NND functions are essential. In the present work, *n*-particle distribution function is briefly reviewed in section 2. In section 3, we extend our earlier approach,[13] for obtaining the NND functions for single component fluids, to binary fluid mixtures. The MD simulation and computation details are presented in section 4. Results are elaborated in section 5 and conclusions are provided in section 6.

2.   *n*-Particle distribution function

Considering a binary system of N_α and N_β particles of α and β type respectively, distributed isotropically in a ν-dimensional space of volume V, the reduced $(n_\alpha + n_\beta)$ particle probability density for two component fluid with $n_\alpha < N_\alpha$ and $n_\beta < N_\beta$, is defined by

$$\rho^{(n_\alpha+n_\beta)}(\bar{R}_{\alpha,n_\alpha},\bar{R}_{\beta,n_\beta}) = \frac{N_\alpha!}{(N_\alpha - n_\alpha)} \times \frac{N_\beta!}{(N_\beta - n_\beta)}$$

$$\times \frac{\int\limits_0^V\int\limits_0^V e^{-\beta U_{(N_\alpha+N_\beta)}(\bar{R}'_{\alpha,N_\alpha},\bar{R}'_{\beta,N_\beta})} d^\nu \bar{R}'_{\alpha,N_\alpha} d^\nu \bar{R}'_{\beta,N_\beta}}{Z_{(\alpha+\beta)}}, \quad (1)$$

with $\bar{R}_{i,N_\alpha} \equiv (\bar{r}_{i,1}, \bar{r}_{i,2},...,\bar{r}_{i,n})$; $i = \alpha, \beta$. and the ν-dimensional volume elements are, $d^\nu \bar{R}_{i,N_\alpha} \equiv d^\nu \bar{r}_{i,1} d^\nu \bar{r}_{i,2}...d^\nu \bar{r}_{i,N_\alpha}$; $i = \alpha, \beta$. The configurational integral,

$$Z_{(N_\alpha + N_\beta)} = \iiint_V e^{-\beta U_{N_\alpha + N_\beta}(\bar{r}_{\alpha,1}...,\bar{r}_{\alpha,N_\alpha},\bar{r}_{\beta,1}...,\bar{r}_{\beta,N_\beta})}$$
$$d^\nu \bar{r}_{\alpha,1}...d^\nu \bar{r}_{\alpha,N_\alpha}.d^\nu \bar{r}_{\beta,1}...d^\nu \bar{r}_{\beta,N_\beta}. \quad (2)$$

The quantity $\rho_{\alpha\beta}^{(n_\alpha + n_\beta)}(\bar{R}_{\alpha,n_\alpha}, \bar{R}_{\beta,n_\beta}) d^\nu \bar{r}_{\alpha,1}... d^\nu \bar{r}_{\alpha,n_\alpha}.$ $d^\nu \bar{r}_{\beta,1}...d^\nu \bar{r}_{\beta,n_\beta}$ therefore gives the probability of simultaneously finding the centers of n_i ($i = \alpha$ and β) particles in their respective volume elements $d^\nu \bar{r}_{i,1}, d^\nu \bar{r}_{i,2},...d^\nu \bar{r}_{i,n_i}$ ($i = \alpha$ and β) at respective distances from the origin, irrespective of the positions of the rest of the ($N_\alpha - n_\alpha$) α-type particles and the ($N_\beta - n_\beta$) β-type particles. It is to be noted that the excluded volume effect is taken care of by the presence of inter-particle potential, $U_{N_\alpha + N_\beta}$ $(\bar{r}_{\alpha,1}...\bar{r}_{\alpha,N_\alpha}, \bar{r}_{\beta,1}...\bar{r}_{\beta,N_\beta})$. For an uncorrelated system, $\rho_{\alpha\beta}^{(n_\alpha + n_\beta)}(\bar{R}_{\alpha,n_\alpha}, \bar{R}_{\beta,n_\beta}) = \rho_\alpha^{n_\alpha} \rho_\beta^{n_\beta}$ with ρ_α and ρ_β being the bulk densities of the individual components of the binary mixtures. Thus, the ($n_\alpha + n_\beta$) particle partial (cross) correlation function, $g_{\alpha\beta}^{(n_\alpha + n_\beta)}(\bar{R}_{\alpha,n_\alpha}, \bar{R}_{\beta,n_\beta})$ is defined as,

$$\rho_{\alpha\beta}^{(n_\alpha + n_\beta)}(\bar{R}_{\alpha,n_\alpha}, \bar{R}_{\beta,n_\beta}) = \rho_\alpha^{n_\alpha} \rho_\beta^{n_\beta}.g_{\alpha\beta}^{(n_\alpha + n_\beta)}(\bar{R}_{\alpha,n_\alpha}, \bar{R}_{\beta,n_\beta}). \quad (3)$$

Therefore, the partial pair (two particle) correlation function, $g_{\alpha\beta}^{(1+1)}(\bar{r}_\alpha, \bar{r}_{\beta,1}) d^\nu \bar{r}_{\alpha,1} d^\nu \bar{r}_{\beta,1}$ is associated with the probability of finding one particle of α-type between $\bar{r}_{\alpha,1}$ and $\bar{r}_{\alpha,1} + d^\nu \bar{r}_{\alpha,1}$ and another β-type particle between $\bar{r}_{\beta,1}$ and $\bar{r}_{\beta,1} + d^\nu \bar{r}_{\beta,1}$, irrespective of the other particles.

3. Neighbour distribution functions for interacting binary systems

3.1 *nth nearest neighbour distribution functions*

The nth NND function, $W_{\alpha\beta}(n_\beta, \bar{r})$ of a ν-dimensional binary system with N_α particles of α-type and N_β particles of β-type is defined such that given a reference particle of α-type present at the origin, $W_{\alpha\beta}(n_\beta, \bar{r}) d^\nu \bar{r}$ gives the probability of finding its β-type n_βth nearest neighbour ($n_\beta = 1, 2, ...$ etc.) in the volume element $d^\nu \bar{r}$ between $\bar{r}$ and $\bar{r} + d^\nu \bar{r}$. As in single component case,[13] extending similar explanation, we express the nearest neighbour distribution functions for the binary mixtures, in general, as

$$W_{\alpha\beta}(n_\beta, \bar{r}) d^\nu \bar{r} = \left(1 - \int_0^{\Omega(\bar{r})} W_{\alpha\beta}(n_\beta, \bar{\tau}) d^\nu \bar{\tau}\right)$$
$$\times \left\{\left(\rho_\alpha^{-1} \int_0^{\Omega(\bar{r})} ... \int_0^{\Omega(\bar{r})} \rho_{\alpha\beta}^{(1+n_\beta)}(\bar{R}_{\beta,n_\beta-1}, \bar{r}) d\bar{R}_{\beta,n_\beta-1}\right) d^\nu \bar{r}\right\}. \quad (4)$$

The first factor in the right hand side of the above expression excludes the n_βth and higher order β-type neighbours from the interior of volume $\Omega(\bar{r})$. The second term gives the conditional probability of finding the centers of β-type particles 1 to ($n_\beta - 1$) within the spherical volume $\Omega(\bar{r})$ around a α-type reference particle at the origin and the n_βth β-type particle within the volume element $d^\nu \bar{r}$ between $\bar{r}$ and $\bar{r} + d^\nu \bar{r}$, irrespective of the positions of the rest of the ($N_\alpha - 1$) α-type and ($N_\beta - n_\beta$) β-type particles. However, the above expression also involves many particle distribution function and thus difficult to work with. Incorporating similar approximation further, as in the single component case,[13] an exactly solvable hierarchical equation for $W_{\alpha\beta}(n_\beta, \bar{r})$ may be expressed as,

$$W_{\alpha\beta}(n_\beta, \bar{r}) d^\nu \bar{r} = \left(1 - \int_0^{\Omega(\bar{r})} W_{\alpha\beta}(n_\beta, \bar{\tau}) d^\nu \bar{\tau}\right)$$
$$\times \left(\int_0^{\Omega(\bar{r})} W_{\alpha\beta}(n_\beta - 1, \bar{\tau}) d^\nu \bar{\tau}\right).(\rho_\alpha^{-1} \rho_{\alpha\beta}^{(1+1)}(\bar{r}) d^\nu \bar{r}). \quad (5)$$

In the right hand side of the above expression, the first factor ensures that no n_βth neighbour of β-type exists interior to $\bar{r}$ (having volume $\Omega(\bar{r})$) and the second factor ensures that the ($n_\beta - 1$)th neighbour (and thus all lower order neighbours) of β-type particles) does exist interior to $\bar{r}$. The third factor is used as the probability of finding a β-type particle (which becomes the n_βth neighbour of β-type) within a ν-dimensional space volume element $d^\nu \bar{r}$ between $\bar{r}$ and $\bar{r} + d^\nu \bar{r}$, keeping a α-type particle at the origin.

For a homogeneous binary mixture in a three-dimensional space, the exact solution of the above expression gives the NND functions as

$$W_{\alpha\beta}(n_\beta, \bar{r}) = \rho_\beta g_{\alpha\beta}^{(1+1)}(\bar{r}) F_{\alpha\beta}(n_\beta - 1, \bar{r})$$
$$\exp\left\{-\int_0^{\bar{r}} \rho_\beta g_{\alpha\beta}^{(1+1)}(\tau) F_{\alpha\beta}(n_\beta - 1, \bar{\tau}) d^3 \bar{\tau}\right\}, \quad (6)$$

with

$$F_{\alpha\beta}(n,\bar{r}) = \int_0^{\bar{r}} W_{\alpha\beta}(n_\beta, \bar{\tau}) d^3\bar{\tau} \; .$$

For the spherically symmetric molecules in a three-dimensional space (6) becomes

$$W_{\alpha\beta}(n_\beta, r) = \rho_\beta g_{\alpha\beta}^{(1+1)}(r) F_{\alpha\beta}(n_\beta - 1, r)$$

$$\exp\left\{ -\int_0^r \rho_\beta g_{\alpha\beta}^{(1+1)}(\tau) F_{\alpha\beta}(n_\beta - 1, \tau) 4\pi\tau^2 d\tau \right\}, \quad (7)$$

with

$$F_{\alpha\beta}(n,r) = \int_0^r W_{\alpha\beta}(n_\beta, \tau).4\pi\tau^2 d\tau.$$

3.2 *Average nth nearest neighbour distance*

The general definition for the average distance between a α-type particle and its n_βth neighbour of β-type particle can be expressed as

$$\langle r_{\alpha\beta}(n_\beta) \rangle = \int_0^\infty r W_{\alpha\beta}(n_\beta, r) 4\pi r^2 dr. \quad (8)$$

4. Simulation and computational details

Results of the NND functions for the binary systems presented in the previous section were compared with the molecular dynamic (MD) simulation of Lennard–Jones binary mixtures. MD simulation was performed in a constant energy microcanonical (N, V, E) ensemble with usual periodic boundary conditions. The model binary system consisted of total 500 (α-type and β-type) particles interacting in pairs according to Lennard–Jones (LJ) potential

$$U_{\alpha\beta}(r_{\alpha\beta}) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^6 \right].$$

The system taken was an equimolecular binary mixture of two types of particles resembling Ne (α-type) and Kr (β-type). The LJ parameters used were $\sigma_{\alpha\alpha} = 2.86$ Å, $\sigma_{\beta\beta} = 3.827$ Å, $\varepsilon_{\alpha\alpha}/k_B = 34.2°$K, $\varepsilon_{\beta\beta}/k_B = 164.0°$K. Mass of the particles taken were

$m_{Ne} = 20.183$ amu and $m_{Kr} = 83.80$ amu. The cross interaction parameters are determined by Lorentz–Berthelot rules:

$$\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_\alpha.\varepsilon_\beta} \text{ and } \sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2.$$

The time steps were set to be 10 fs and the temperature was set at 170°K. MD simulation data reported here are at reduced densities, $\rho^* = 0.4$ and 0.5, where $\rho^* = P\cdot\rho_\alpha^3 = N_{total} \times \sigma_\alpha^3/V_{simbox}$) with N_{total} ($= N_\alpha + N_\beta$) total no of molecules, V_{simbox} being the simulation box volume. The MD runs of 1×10^5 time steps were taken to equilibrate the system and further 1×10^5 time steps were used to evaluate time average statistical properties. Velocity Verlet algorithm was used for integrating the equation of motion. Systems at higher ρ^* were not studied to avoid any possibility of phase separation.

For comparison of the result the nth NND functions are computed as $P_{\alpha\beta}(n,x)[= \sigma_\alpha^3 W_{\alpha\beta}(n_\beta, x\sigma_\alpha) 4\pi x^2]$ and compared with the corresponding MD simulation data obtained as described in our earlier work.[13] Using MD simulation data, the average NN distance, $\langle r_{\alpha\beta}(n_\beta) \rangle$ is computed using (8) after dividing by σ_α and the non-dimensional $X_{\alpha\beta}(n_\beta)$, is plotted

5. Discussions

The partial pair correlation functions (PCFs), while are obtainable for various systems experimentally, theoretically or from simulation, the precise microscopic neighbourhood information essentially embedded in such functions are not quite obvious. Typical partial PCFs for a binary mixture at two different reduced densities, ρ^* obtained from MD simulation at comparable average temperatures are shown in figure 1.

At lower density, the relatively broadened peaks shifted at higher x ($= r/\sigma_\alpha$) and of lesser peak height for all the partial PCFs indicate more diffused structures around the particles in the fluid. The shifts in the starting of $g_{\alpha\beta}^{(1+1)}(x)$ reflects the size difference in the to components of the binary mixture. Although the peaks and troughs in the $g_{\alpha\beta}^{(1+1)}(x)$ profiles are indicative of the structuredness around the reference particle α, the nature of distributions of the nearest neighbours is not quite apparent. For example, the most probable position of the first nearest neighbour of β-type (say) around a α-type particle at the origin

should not be, in general, assigned to the first peak of the respective partial PCFs. Present approach, in a way, resolves full microscopic structural information contained in PCFs in terms of the hierarchically derived NND functions.

Some representative comparison between $P_{\alpha\beta}(n, x)$ obtained from the proposed methodology and that obtained from the MD simulation are shown in figures 2–4. Reasonable agreement for smaller n values at higher densities is observed. The agreement is relatively lesser at the lower density studied, as seen in figure 3. Similar comparison for pure fluid[13] showed even better matching at higher densities, up

to which we cannot reach here for the binary mixtures to avoid the problem of phase separation. The trends of the graphs in figure 4 shows that the deviation increases for higher neighbours even for $\rho^* = 0.5$. These results indicate that the correlation effects neglected here, has to be incorporated further for better improvement. Efforts are being made in this direction.

A typical plot of the profiles of the nth NND functions up to $n = 20$ for finding β-type neighbours keeping a α-type neighbour at the origin, obtained from the MD simulation is shown in figure 5, along with the corresponding partial PCF profile to show
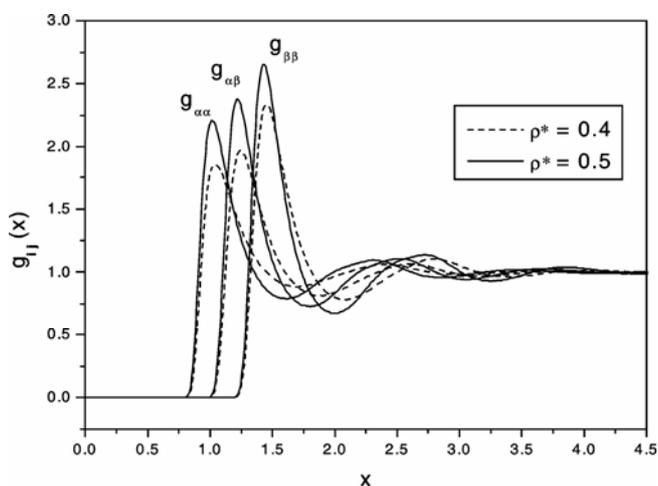
Figure 1. MD simulation data for the partial pair correlation functions for the binary mixture of Ne, Kr at comparable temperatures with $\rho^* = 0.4$ ($T(K) = 172.25 \pm 3.25$) and $\rho^* = 0.5$ ($T(K) = 168.97 \pm 3.73$).
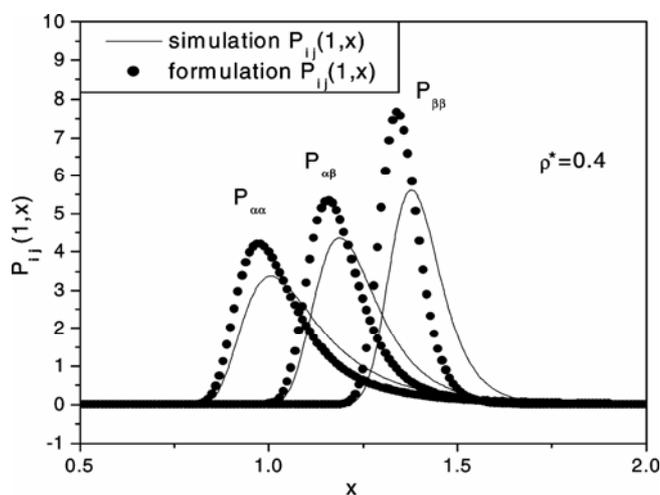
Figure 3. Comparison of the first NND functions for the binary mixture at $\rho^* = 0.4$ at temperature mentioned in figure 1.
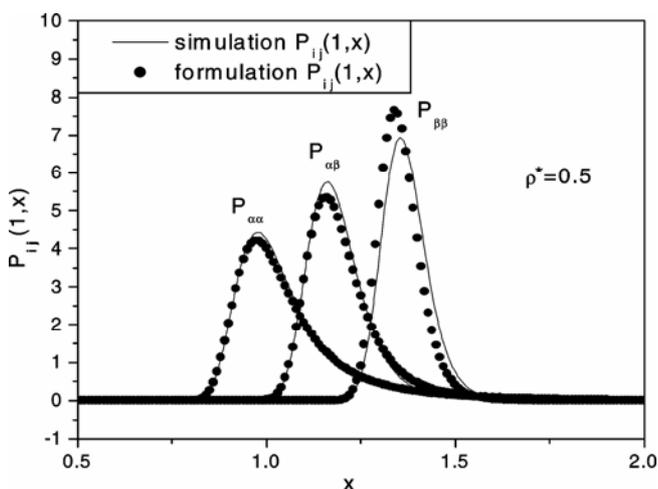
Figure 2. Comparison of the first NND functions for the binary mixture at $\rho^* = 0.5$ at temperature mentioned in figure 1.
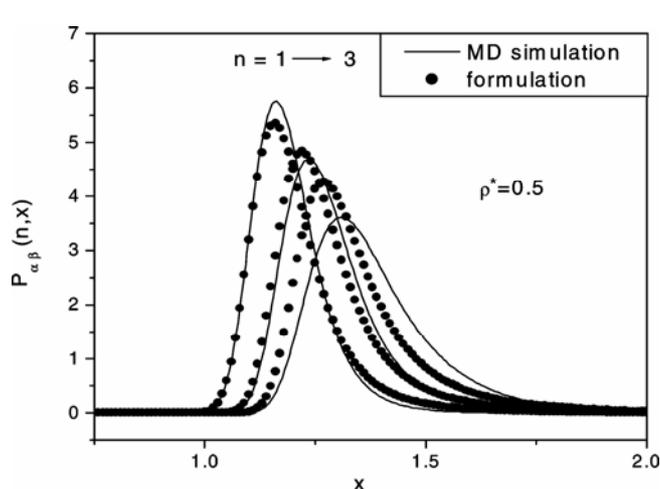
Figure 4. Comparison of the nth-NND functions ($n = 1$, 2, 3) for the binary mixture at $\rho^* = 0.5$ at temperature mentioned in figure 1.

how the most probable positions of the respective neighbours are embedded in the overall partial PCF profiles. Average nth NN distance for mono-dispersed spheres has been computed recently by others in a different context.[10] Here, a typical plot of variation of the average NN distance, obtained MD simulation data for the binary mixture with various n, is shown in figure 6. The distinct change of slope of the graphs around eighth to tenth neighbour is possibly an indication of the end of the first shell structure.

An Improved theoretical prescription for computing the nth NND functions is still being looked into. Further studies of these functions in greater detail,
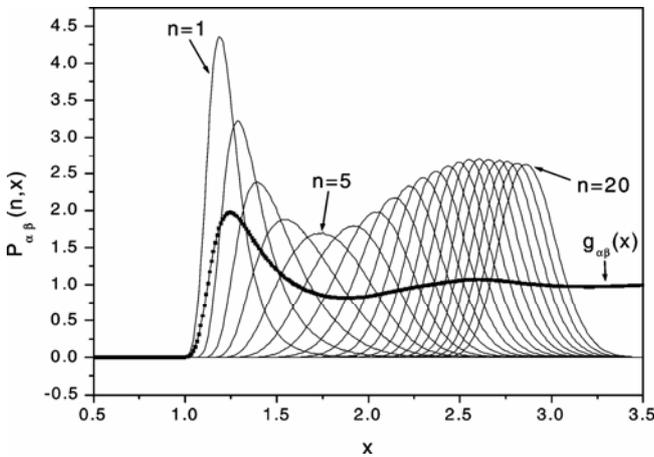
Figure 5. nth-NND functions for first 20 β-type neighbours around a α-type particle at the origin obtained from MD simulation for the binary mixture at $\rho^* = 0{\cdot}5$ at temperature mentioned in figure 1.
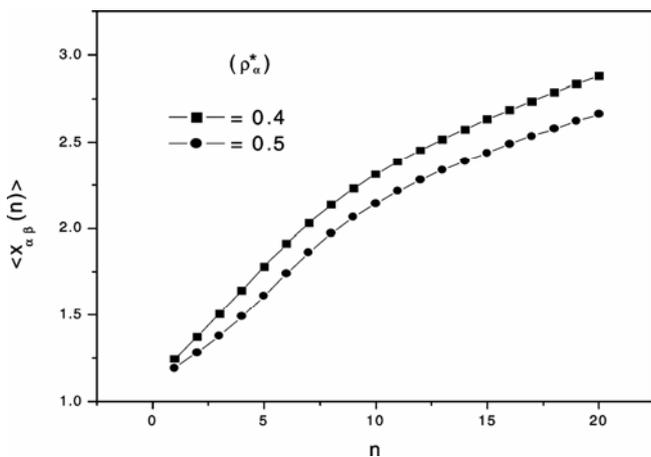
Figure 6. Variation of the average nth-NN distance with n obtained from MD simulation for the binary mixture of Ne, Kr at $\rho^* = 0{\cdot}5$ and $0{\cdot}4$ at temperature mentioned in figure 1.

particularly for the binary mixtures with composition variations, is likely to provide many insights into the microscopic neighbourhood structures both for static and dynamic phenomena.

6. Conclusion

In the general methodology presented here, the nth-NND functions of a homogeneous interacting binary fluid mixture is expressed in terms of partial pair correlation functions and the $(n-1)$th-NND functions and can be computed in a hierarchical manner. These functions, although obtained via partial PCFs (obtainable from experiments, simulation or theoretical approximation schemes), provide interesting microscopic insights about neighbourhood structures in a binary mixture. Such insights are usually not directly available from the profile of partial PCFs. For example, the most probable position and the average distance of the nth neighbour of one type of component around another component is not easily obtainable from the partial PCF profiles. The comparisons of the computed NND functions with simulation data show reasonable matching particularly for smaller n values at higher density. The NND profiles for higher n values obtained from the MD simulation demonstrate detailed features consistent with the partial PCF profile. The nth NN distances for the individual components computed using simulation data show interesting variations in the slopes around some intermediate values of n, a possible criterion for locating the shell structures.

Extensive MD simulation study particularly of composition dependence and parametric dependence of the interaction potentials on the NND functions for binary mixtures is underway. At lower densities the results show that the computed NND functions seem to over estimate the values. Further improvement in the formulation to take care of the correlation effect even more accurately while simplifying (4) is being attempted. An improvement, following the approach by Mazur,[9] is also being looked into and will be presented elsewhere.

Acknowledgement

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