A Note on the Self Consistent Approximation Method for the Evaluation of Radial Distribution Functions of Simple Fluids

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The self consistent approximation of Rowlinson, Carley and Lado has been applied to calculate the radial distribution functions of simple fluids (Neon, Krypton and Xenon) interacting with a Lennard-Jones 6:12 potential. It has been found that in general the self consistent values are nearer to the exact values than other values.

Introduction

The virial coefficients can be calculated either from the pressure equation

$$\frac{p\,v}{N\,k\,T} = 1 - \frac{2\,\pi\,\varrho}{3\,k\,T}\int_0^\infty g(r)\,\frac{\mathrm{d}u}{\mathrm{d}r}\,r^3\,\mathrm{d}r \qquad (1)$$

or from the compressibility equation

$$k\,T\left(\frac{\partial\varrho}{\partial p}\right)_\mathrm{T} = 1 - 4\,\pi\,\varrho\int_0^\infty c(r)\,r^2\,\mathrm{d}r\,. \qquad (2)$$

The virial coefficients as calculated from the above two equations of state are different because of the approximate expressions used for the radial distribution function $g(r)$. However, it has been shown that an exact expression for $g(r)$ should give the same virial coefficients [1]. Hence Rowlinson [2], and Carley and Lado [3] (R-C-L) proposed a self consistent approximation (SCA) so as to achieve the same virial coefficients. Such SCA theories yield much better results than the individual theories such as that of Percus-Yevick (PY) or the convolution hypernetted chain (CHNC) approximations [4–8]. These SCA theories, when extended to the so-called PY 2 and CHNC 2, better agreement with the exact theory is obtained [5]. It is worthwhile noting here that Stell [9] recently has derived the R-C-L approximation from the functional formalism by taking a linear combination of the functionals F_PY and F_CHNC. In this note it is proposed to apply the R-C-L approximation to derive the $g(r)$ of some simple fluids.

According to R-C-L the direct correlation function (DCF) can be written as

$$c(r) = f(r)\,y(r) + \varphi[y(r) - 1 - \ln y(r)]\,. \qquad (3)$$

Here

$$f(r) = e^{-\beta u(r)} - 1\,,$$
$$y(r) = g(r)\,e^{\beta u(r)}\,,$$

and

$$\beta = (k_\mathrm{B}\,T)^{-1}\,,$$

where $u(r)$ is the pair potential, k_B the Boltzmann constant and T the absolute temperature. It may be noted here that for $\varphi = 0$ Eq. (3) reduces to the PY equation while it reduces to the CHNC equation for $\varphi = 1$. Equation (3) gives consistent values up to the fourth virial coefficient only, and the consistency is lost from the fifth virial coefficient onwards. In order to achieve self consistency between the virial coefficients to any order Rowlinson expanded the parameter φ in terms of the density, namely

$$\varphi(C, T) = \sum_{n=4}^{\infty} C^{n-4}\,\varphi_n(T) \qquad (4)$$

where φ_4 and φ_5 are evaluated from the conditions

$$B_4(\mathrm{P}) = B_4(\mathrm{C})$$

and

$$B_5(\mathrm{P}) = B_5(\mathrm{C})\,. \qquad (5)$$

Here $B_4(\mathrm{P})$, $B_5(\mathrm{P})$, $B_4(\mathrm{C})$ and $B_5(\mathrm{C})$ are the fourth and fifth virial coefficients as calculated from the pressure equation of state and the compressibility equation of state, respectively.

Similar SCA theories have been proposed by several authors [10–12].

The expressions for $B_4(\mathrm{P})$, $B_4(\mathrm{C})$, $B_5(\mathrm{P})$ and $B_5(\mathrm{C})$ and the topological meaning of the diagrams involved therein have been given elsewhere [7, 8]. The

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various diagram contributions are taken from literature[13–16].

The above SCA has been utilised to calculate the $g(r)$ of inert gas liquids interacting with a Lenard-Jones (LJ) 6:12 potential function employing the well known density expansion of $g(r)$[17]. The density expansion of $g(r)$ has been utilised up to $g_3(r)$ in the present calculations.

Results and Discussion

The radial distribution functions of Neon, Krypton and Xenon have been computed with LJ 6:12 potentials at the temperature $T^*(=kT/\varepsilon)=1.2$ and at the densities $\varrho=2.0\times10^{-2}/\text{Å}^3$, $0.75\times10^{-2}/\text{Å}^3$ and $1.4162\times10^{-2}/\text{Å}^3$, respectively, cf. Figures 1 – 3.

In all these computations $g(r)$ has been compared with exact, PY and CHNC values. In the case of Ne the PY and SCA values agree with the exact values while CHNC gives a higher peak. Both the molecular dynamics (MD)[18] and experimental values lie below the computed values. The exact values lie closest to both these curves. The discrepancy between the MD and experimental values is due to the fact that the MD values are not available exactly at the same density and temperature at which the computations were performed. The discrepancy between the experimental and the computed curves may be considered as satisfactory from the fact that Ne is a quantum mechanical liquid.

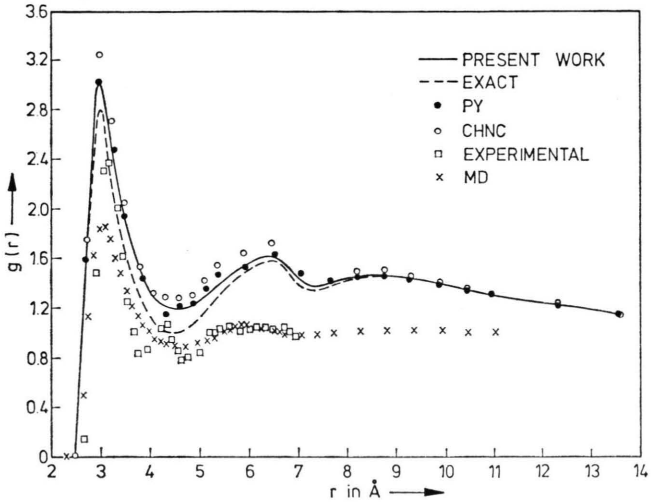

Fig. 1. Radial distribution function $g(r)$ vs. r in Å of liquid Neon at $T^*(=kT/\varepsilon)=1.2$ and $\varrho=2.0\times10^{-2}$ atoms/Å^3.

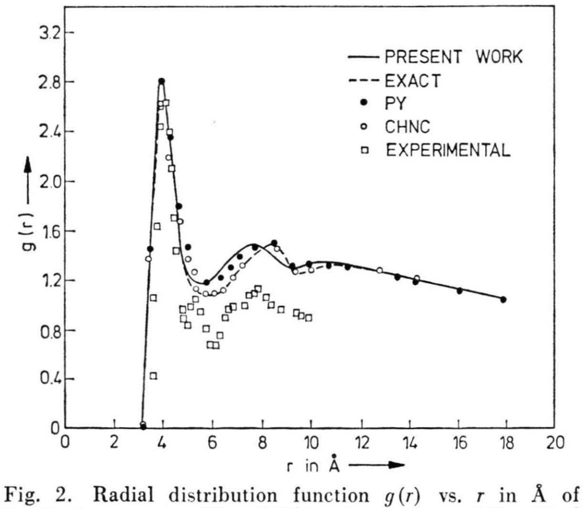

Fig. 2. Radial distribution function $g(r)$ vs. r in Å of liquid krypton at $T^*(=kT/\varepsilon)=1.2$ and $\varrho=0.75\times10^{-2}$ atoms/Å^3.

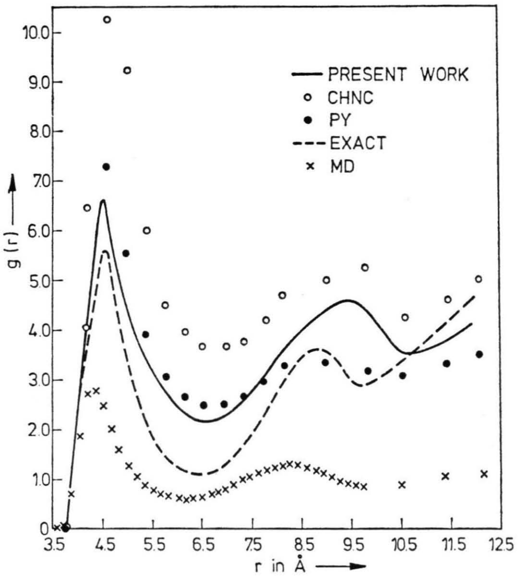

Fig. 3. Radial distribution function $g(r)$ vs. r in Å of liquid Xenon at $T^*(=kT/\varepsilon)=1.2$ and $\varrho=1.4162\times10^{-2}$ atoms/Å^3.

All the three approximations are in good agreement with the exact values in the case of Kr. However it may be pointed out in this context that CHNC fares better than the other approximations at medium interparticle distances. All the computed curves, however, along with the exact ones lie much above the experimental values. Khan[19], while comparing his structure factor computations in the case of Kr at $T=210\ ^\circ\text{K}$ and $\varrho=0.75\times10^{-2}/\text{Å}^3$ with experimental neutron diffraction values pointed out that the experimental measurements at this critical region are in error and hence the theoretical computations are more reliable. Such might be true in the present case also.

In the case of Xe the SCA values are in better agreement with the exact values than the PY and CHNC values, the latter being considerably higher. It may be pointed out here that the peak value of 6.9 for $g^{\mathrm{SCA}}(r)$ is considerably higher than the exact value of 5.7 while both the CHNC and PY values are very high compared to the exact values. However, all these values are higher than the MD values. This divergence of MD values is to be expected at the density ϱ^* of the fluid at which the computations performed is rather high. Thus it is instructive to include the high density calculations which clearly demonstrate the usefulness of the density expansion of $g(r)$ at low densities. Thus, as can be seen from the graph the agreement becomes poorer as the density of the fluids becomes higher. As the X-ray diffraction measurements were reported to be wrong by Khan and Broyles for this liquid we did not give the experimental values for comparison.

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