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## The static structure factor of monatomic liquids using an analytical expression for the hard-sphere correlation function

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### ABSTRACT

In this work, we investigated the behavior of the static structure factor,  $S(k)$ , for a dense classical insulating liquid based on an analytical expression for the hard-sphere radial distribution function (HS-RDF). Although HS-RDF gives a good description for the large angle behavior of  $S(k)$  over a wide range of densities, it fails to predict the low angle behavior of  $S(k)$  at low densities. A correction to the DCF for HS fluids, originally suggested by Henderson *et al.*, is given, which removes this shortcoming. The applied DCF involves a reliable interaction, and allows one to obtain a good accuracy for the low- $k$  behavior of  $S(k)$  over low densities. The closure considered here provides very well the Ornstein-Zernike (OZ) behavior of  $S(k)$  at low- $k$  for monatomic fluids, and shows the regularity that a minimum  $S(k)$  varies linearly with density, which is correct just for insulator fluids. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

Hard-sphere;  
Radial distribution function;  
Direct correlation function;  
Structure factor;  
Ornstein-Zernike equation.

### INTRODUCTION

The classical theories suggested for the structures and thermodynamic properties of hard-sphere (HS) fluids have been stabilized in the 1960s and early 1970s on the basis of two parallel but complementary approaches: the scaled-particle theory and the integral equation theory<sup>[1,2]</sup>. The first theory was developed by interpolating classical and statistical considerations on the free energy for the creation of spherical cavities (scaled particles) in a HS fluid. Thermodynamic properties and the contact values for the pair distribution functions from this approach are in good agreement with the simulation results. The integral equation theory, on

the other hand, is primarily based upon the Ornstein-Zernike (OZ) equation coupled with the Percus-Yevick (PY) closure<sup>[3-6]</sup>. Analytical solution to the PY equation was first developed by Thiele<sup>[7]</sup>, and independently by Wertheim for uniform HSs<sup>[8]</sup>, and by Lebowitz and Rowlinson for HS mixtures<sup>[2]</sup>. The pair distribution function in the PY equation is in good agreement with the simulation results (except for near-contact) but the thermodynamic properties derived from different routes do not always agree with each other.

The radial distribution function (RDF) and the direct correlation function (DCF) with its close relative, the static structure factor  $S(k)$ , are the basic quantities used to discuss the thermodynamic properties and structure of a liquid<sup>[9-13]</sup>. The importance of correlation func-

tions arise from the fact that, given the form of potential of the intermolecular forces, if the RDF is known as a function of the density  $\rho$  and temperature  $T$ , the standard methods of statistical mechanics allow for the determination of all the equilibrium properties of the fluid. The quantity of  $S(k)$ , as one of the important properties characterizing a liquid, is a measure of interparticle correlations in the reciprocal space. An accurate knowledge of this quantity is crucial for studying numerous thermodynamic and transport properties of any fluid system. The static structure factor is experimentally measured by the use of the neutron and X-ray scattering techniques<sup>[14]</sup>.

It is clear that prediction of the structural and thermodynamic properties of dense fluids requires an accurate knowledge concerning the interatomic potential<sup>[15,16]</sup>. The most direct probe of a realistic potential is in the experimental observation of the static structure factor closely related to density fluctuations, and contains useful information about short- and long-range parts of the pair and higher-order potentials. Clearly, the short-range part of interaction potential is better understood than the long-range one, and the outcome of the structural properties cannot be fully attributed to the effect of the two-body interactions alone because such a description is not strictly valid since the interaction between two particles is disturbed by the presence of a close third particle. Therefore, a correction to the pair potential established at an electronic level and suspected to be the three-dipole dispersion interaction is required. The importance of a quantitative investigation of the long-range part of interaction potential, including two- and three-body dispersion forces, has been emphasized for long time<sup>[12-20]</sup>.

In this work, we used an analytical expression for HS-RDF to calculate  $S(k)$  over a wide range of  $k$  for real monatomic liquids. The applied HS-RDF model can not satisfy the thermodynamic states with low densities<sup>[21]</sup>. Thus we considered another approach for this region. It is based on a known definition of the DCF by Henderson *et al.*<sup>[22]</sup> which may be used to predict the behavior of  $S(k)$  for monatomic fluids at low densities. In this model, a linear combination of the PY function, applied for the core of the DCF, and a non-linear expression for its tail is used. Also, this model improved under an effective intermolecular parameter. In this way,

we investigated the behavior of  $S(k)$  for a wide range of thermodynamic states.

This paper is organized as follows. In Sec. 2, we start by briefly describing the method used to indicate the analytical expression for the HS-RDF model in order to predict the behavior of  $S(k)$  for the argon and xenon liquids at high densities. In Sec. 3, the low- $k$  behavior of  $S(k)$  is evaluated for low densities using a known definition of the DCF. Moreover, we attempt to assess that the first minimum  $S(k)$  varies linearity with density, as a regularity, in monatomic fluids. The paper is closed in Sec. 4, where we review our findings, and provide some concluding remarks.

## PREDICTION OF $S(k)$ OVER HIGH DENSITIES

Since the HS-RDF model is frequently used to provide reference fluid properties in the perturbation theories for simple liquids, we used an expression for HS-RDF presented by Smith and Henderson<sup>[21]</sup> in order to predict the behavior of  $S(k)$  versus wave vector  $k$  for monatomic fluids. This model includes the following formula for spherical particles of uniform size,  $\sigma$ , with the scaled distance variable  $x = r/\sigma$ :

$$g(x) = \sum_{n=1}^{\infty} H(x-n)g_n(x) \quad (1)$$

where  $H(x-n)$  is the Heaviside step function, as:

$$H(x-n) = \begin{cases} 0 & x < n \\ 1 & x \geq n \end{cases} \quad (2)$$

The functions  $g_n(x)$  are piecewise continuous components of RDF, defined as:

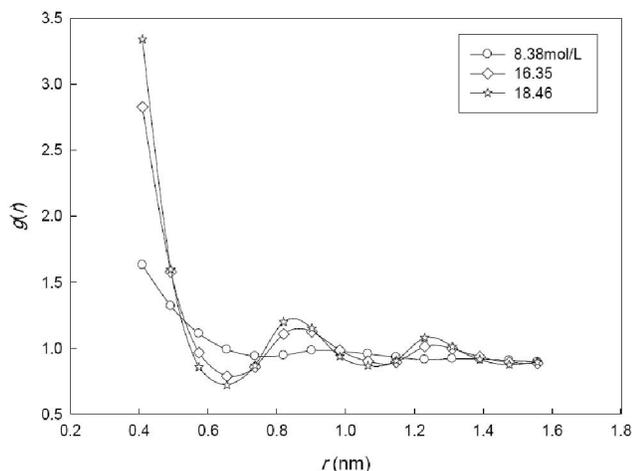
$$xg_n(x) = \frac{(-12\eta)^{n-1}}{(n-1)!} \sum_{i=0}^2 \lim_{t \rightarrow t_i} \frac{d^{n-1}}{dt^{n-1}} \left[ (t-t_i)^n t \left( \frac{L(t)}{S(t)} \right)^n \exp[t(x-n)] \right] \quad (3)$$

where  $\eta$  is the packing fraction, and the functions  $t_i$ ,  $S(t)$  and  $L(t)$  have the same definitions as in Ref. <sup>[21]</sup>. In summary, the calculated algorithm for HS-RDF (Eq. 3) is fully described in Refs<sup>[21,23]</sup>.

The results obtained for the HS-RDF calculations for liquid Xe at the three densities 8.38, 16.35, and 18.46 mol/L are shown in Figure 1. For the three first shells in Figure 1, we considered that the RDF values increase with density, which is expected.

We may use the HS-RDF model to calculate the

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**Figure 1 :** Hard-sphere radial distribution function,  $g(r)$ , versus  $r$  for Xe liquid at several densities: 8.38 (●), 16.35 (◆) and 18.46 mol/L (★).

structure factor  $S(k)$  from a Fourier transform as:

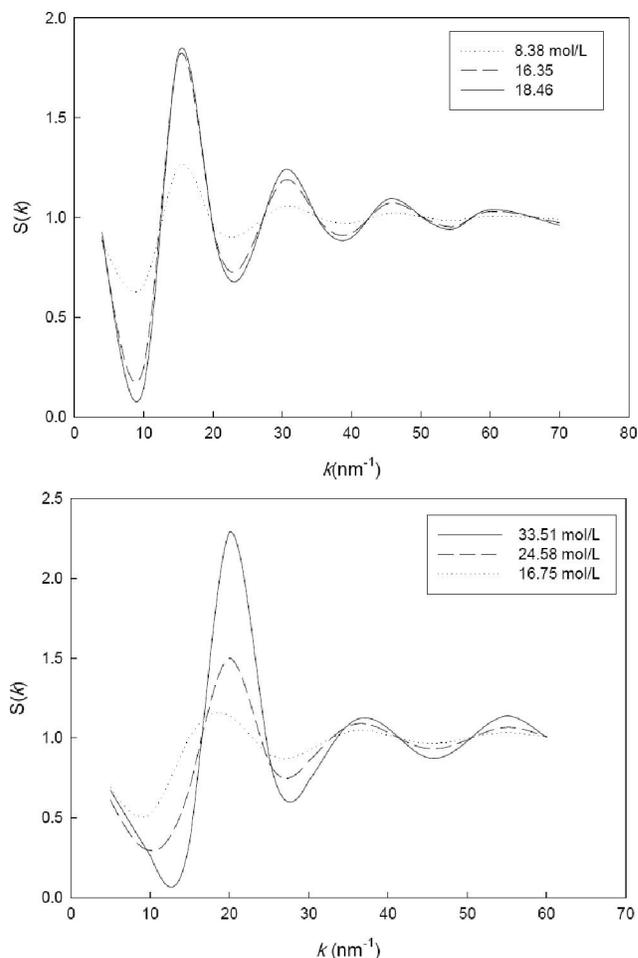
$$S(k) = 1 + 4\pi\rho \int_0^{\infty} [g(r) - 1] \frac{\sin kr}{kr} r^2 dr \quad (4)$$

Figure 2 shows the calculated results for the behavior of  $S(k)$  at a wide range of  $k$  for liquid Xe at the densities similar to those in figure 1 (upper part of Figure 2), and for liquid Ar at the three densities 16.75, 24.58, and 33.51 mol/L (lower part of Figure 2). According to Figure 2, the qualitative behavior of  $S(k)$  is correctly generated, and the numbers and heights of bumbings are increased with density, which is expected<sup>[17]</sup>.

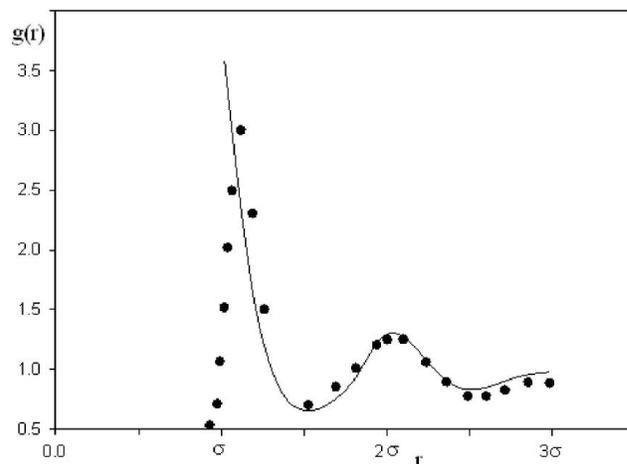
Figure 3 gives a comparison between the RDF calculated on the basis of this model and the Yarnel's molecular dynamic calculations on a Lennard-Jones (LJ) fluid<sup>[24]</sup>. It is clear that the agreement is rather good over a wide range of  $r$ , where  $r > \sigma$ .

The results obtained for the HS-RDF calculations at low-densities such as reduced density  $\rho^* = 0.01$  is shown in Figure 4. According to this figure, at low densities, the shape of  $g(x)$  seems much poorer around the shell positions, and the results may be meaningless around the first shell.

Figure 5 shows the behavior of  $S(k)$  for similar features in Figure 4. Clearly, while the shape of  $S(k)$  seems the same as that at high densities, the qualitative feature for the OZ behavior of  $S(k)$  can not be claimed for the low- $k$  region. However, although the applied HS-RDF gives useful results for  $g(r)$  and  $S(k)$  for simple fluids at high-densities, it fails to describe the structure factor at low-densities, most noticeably at low- $k$ , where attrac-



**Figure 2 :** Structure factor  $S(k)$  in wide range of  $k$  for Xe liquid at several densities: 8.28 (...), 16.35 (—) and 18.64 mol/L (—), upper part, and for Ar liquid at several densities: 16.75 (...), 24.58 (—) and 33.51 mol/L (—), lower part.



**Figure 3 :** Comparison of the theoretical (line) and Yarnel's molecular dynamic<sup>[24]</sup> calculations (symbol) for HS-RDF.

tive forces are important, and a HS repulsion alone seems to be unable to describe this feature correctly.

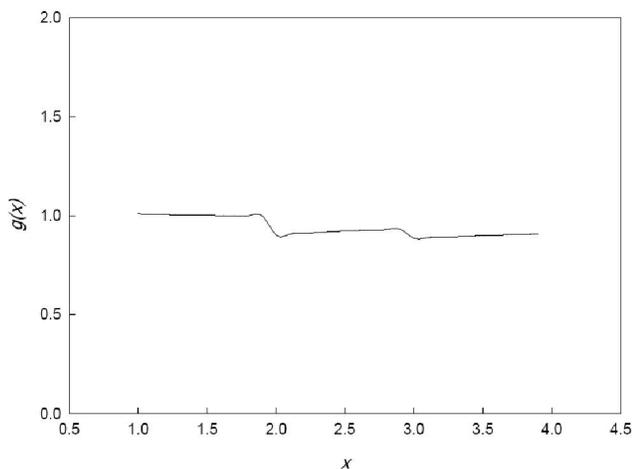


Figure 4 : Hard-sphere radial distribution function,  $g(x)$ , versus reduced distance at low reduced density  $\rho^* = 0.01$ .

The next section is concerned with how the HS model can be improved so as to remove this discrepancy.

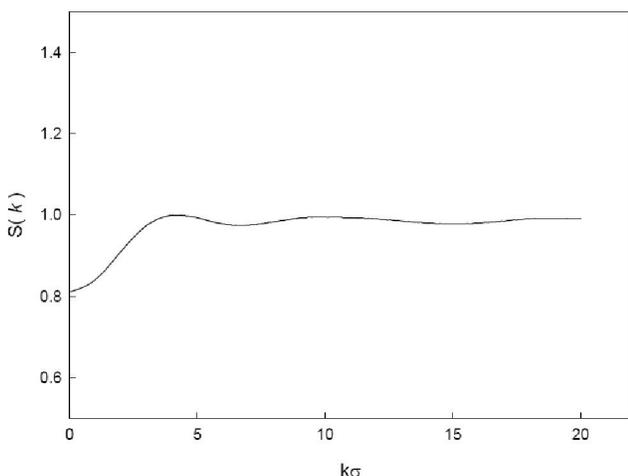


Figure 5 : Behavior of the structure factor for the same feature of figure 4.

### PREDICTION OF $S(k)$ OVER LOW DENSITIES

As mentioned earlier, different paths have been followed to obtain an improved expression for the structure and thermodynamic properties of HS fluids. The main approach is focused on the integral equation theory. This theory is primarily based on the OZ equation as:

$$g(\mathbf{r}) - 1 = c(\mathbf{r}) + \rho \int_0^\infty h(\mathbf{r}') c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (5)$$

where  $\rho$  is the number density, and  $h(r) = g(r) - 1$  is the total correlation function. Henderson *et al.*<sup>[23]</sup> have improved more accurate representation of the HS-RDF

model so that the equation of state derived from the Virial theorem and the fluctuation theorem consisted each other. They obtained the following expression for the DCF:

$$c(\mathbf{r}) = \begin{cases} c_{PY}(\mathbf{r})(1 - 0.127\rho^{*2}) & r < \sigma \\ B \exp[20(1 - r/\sigma)]/r & r > \sigma \end{cases} \quad (6)$$

where  $c_{PY}(r)$  is the DCF of the HS reference fluid that is expressed by the PY equation for the HS fluid,  $\rho^* = \rho\sigma^3$  is the reduced density, and  $B$  is chosen to give the correct discontinuity of the DCF at  $r = \sigma$ . We considered a similar term in Eq. 6 to predict the  $S(k)$  behavior at low densities. We merely claim that it may be sufficiently accurate to permit reliable of the DCF for more realistic systems with attractive forces. We obtained parameter  $B$  in Eq. 6 under the consistency in thermodynamic conditions using the  $pV/T$  data as:

$$B_r = \frac{1}{k_B T} \left( \frac{\partial P}{\partial \rho} \right)_T = 1 - 4\pi\rho \int_0^\infty c(\mathbf{r}) r^2 d\mathbf{r} \quad (7)$$

where  $B_r$  denotes the reduced bulk modulus,  $P$  is the pressure, and  $k_B$  is the Boltzmann's constant. On the other hand, parameter  $B$  (eq. 6) is a state-dependent quantity that can be calculated in any thermodynamic state.

As mentioned above, by obtaining parameter  $B$ , we may calculate the  $c(r)$  function at all the range for  $r$ , and then calculate  $c(k)$  and  $S(k)$  using the following equations:

$$c(\mathbf{k}) = 4\pi\rho \int_0^\infty c(\mathbf{r}) \frac{\sin \mathbf{k}\mathbf{r}}{\mathbf{k}\mathbf{r}} r^2 d\mathbf{r} \quad (8)$$

where  $c(k)$  is the Fourier transform of DCF, and:

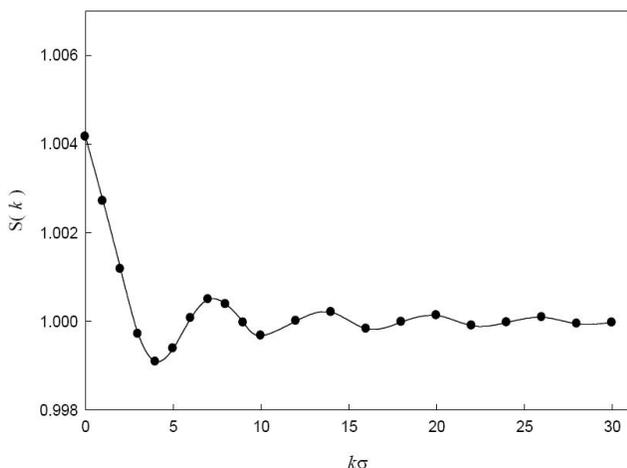
$$S(k) = (1 - \rho c(k))^{-1} \quad (9)$$

It is clear that all the approximations used in the model may be exaggerated in the Fourier transform. Therefore, we evaluated accuracy of the model via prediction of the behavior of  $S(k)$ .

In Figure 6, we present the behavior of  $S(k)$  at a wide range of  $k$  for fluid Xe at the density 0.33 mol/L. Our results showed that the qualitative behavior of  $S(k)$  was correctly generated at the low density region. According to Figure 6, our calculations are capable of predicting the OZ behavior of  $S(k)$  at the low- $k$  region with a minimum value of  $S(k)$ . This behavior verifies

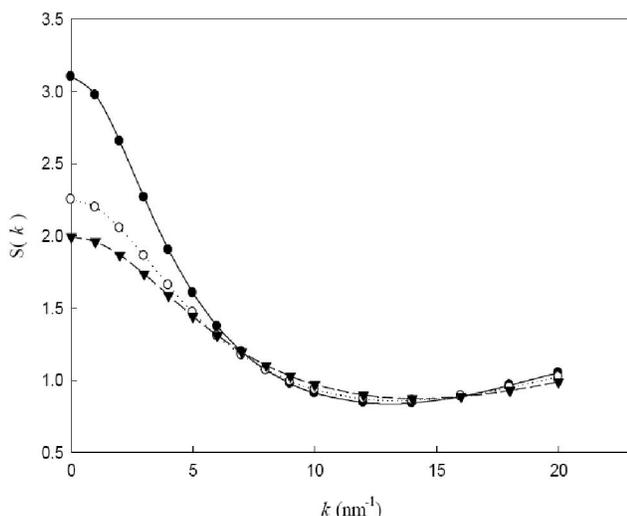
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that the long-range attraction forces have correctly been taken into account in the DCF model (Eq. 6).



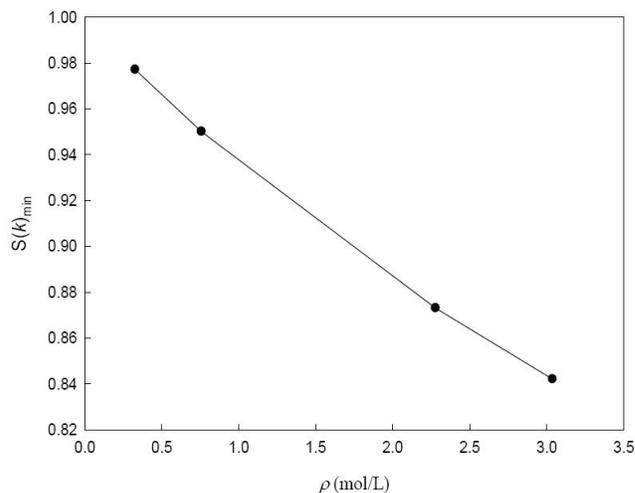
**Figure 6 :** Behavior of the structure factor at wide range of reduced wave factor ( $k\sigma$ ) for Xe fluid at density  $\rho = 0.33$  mol/L.

However, our calculations denote good qualitative results at a wide range of  $k$  over low densities but the prediction of low- $k$  behavior of  $S(k)$  is a considerable result. In this way, we showed the low- $k$  behavior of  $S(k)$  for fluid Xe along the isochor 2.28 mol/L in Figure 7. As we can observe in this figure, when the temperature reduces and approaches the thermodynamic state with low repulsion interactions (or considerable long-range attractions), the values for  $S(k)$  diverge at  $k \rightarrow 0$ . This is expected because the thermal density fluctuations of atoms or molecules in a system increase, where the long-range correlation length increases<sup>[25-30]</sup>.



**Figure 7 :** Small- $k$  behavior of  $S(k)$  for Xe fluid along the isochor 2.28 mol/L: 260 (●), 285 (○) and 300 K (▼).

Furthermore, in order to evaluate the behavior of the first minimum  $S(k)$ , we calculated the small-angle structure factor for Xe at  $T = 300$  K over the range of low densities. The results obtained show that our model is capable of giving a good qualitative description of the OZ behavior for  $S(k)$  at low- $k$ , in which there is an observable minimum of  $S(k)$  whose values and positions vary with the thermodynamic states. In Figure 8, we plotted the variation of  $S(k)_{min}$  versus  $\rho$  at  $T = 300$  K. According to this figure, the values for  $S(k)_{min}$  vary with a linear relation with density. It seems that the values for  $S(k)_{min}$  are related to the range and values of the attraction forces, and so they should be decreased with increase in density. In fact, the long-range attractive contribution was accurately taken into account by computing a state-dependent parameter  $B$  (eq. 6) in our closure.



**Figure 8 :** Linear behavior of  $S(k)_{min}$  versus  $\rho$  for Xe at  $T = 300$  K.

## CONCLUSION

This article is concerned with the structural properties of argon-like fluids at a wide range of densities. In this study, we used an analytical expression for the HS-RDF model to calculate the structure factor at high densities. Since the values for  $S(k)$  at a low wave factor is very sensitive to the attractive forces, which are important at low densities, the HS-RDF model fails in these thermodynamic states. Thus we applied a modified DCF model based on the thermodynamic consistency for predicting the behavior of  $S(k)$  at low densities. In this

model, a PY expression for the DCF inside the repulsive core ( $r < \sigma$ ) was softened with a long-ranged interaction by a non-linear expression.

It was found that our closure provided very well the OZ behavior of  $S(k)$  at low- $k$ . Furthermore, it was found that there is a minimum  $S(k)$  at low- $k$  for a wide range of thermodynamic states in simple fluids, in which the positions and values for this minimum vary linearly with density. This behavior was also observed in the experimental measurements.

### ACKNOWLEDGEMENT

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