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MOLECULAR DYNAMICS CALCULATION OF THE DENSITY DEPENDENCE OF S(K) OF KRYPTON

F. Barocchi*, G. Spinelli* and R. Magli**

* *Dipartimento di Fisica, Università di Firenze, Largo Enrico Fermi, 2 50100 Firenze, Italy*

***Dipartimento di Energetica, Università di Firenze, Via S. Marta, 3 50139 Firenze, Italy*

Abstract - We have performed a computer simulation "experiment" and produced a set of S(k) for Krypton at room temperature as function of the density between $1.3\text{x}10^{27}$ and $6.5\text{x}10^{27}$ atoms/m^3 . An analysis of the density behaviour of the computer "experimental" S(k) is then performed with the same procedure used for the real experimental data [2] . The results of the analysis show the possibilities and limitations of the method together with the useful range of density and k values for real experiments.

The measurement of the structure factor S(k) in monoatomic fluids as a function of the density ρ can, in principle, provide informations on the pair-potential and on the three-body contribution to the pair distribution function g(r). Recent experimental data of the S(k) of Krypton at room temperature as a function of ρ between $0.25\cdot10^{27}$ and $6.2\cdot10^{27}$ atoms/m^3 have been analyzed in order to extract the before mentioned informations [1,2] . However, it is well known that there are difficulties in extracting informations from virial expansions of measured properties,particularly if one deals with three-body properties, since the three-body contribution must be small, in order to ensure the fast convergence of the virial series, but also measurable with good precision even when higher order terms in the series expansion are neglected. This is even a more difficult problem for the density expansion of the S(k) since the convergence is not, in principle, the same for the various k values. Due to those difficulties it is therefore desiderable to test in a known system the procedures used for the derivation of the two- and three-body properties from the S(k). In order to perform this test we have produced a set of "experimental" S(k) by means of computer Molecular Dynamics simulation for nine densities between $1.3\cdot10^{27}$ and $6.74\cdot10^{27}$ atoms/m^3 for Krypton at temperature T = (297 ± 3) °K. The potential used in the simulation is the pair-potential of Barker et al.[3] . The simulation has been performed with standard Molecular Dynamics techniques for a system of 500 particles. At each density the averages have been performed over a set of 5000 time steps. The errors of these "experimental" S(k) are of the order of 2% for each point, these have been estimated from the statistics of the values and correspond to the effect of temperature fluctuations which are present in the microcanonical ensemble.
Fig.1 shows the behaviour of the "experimental" S(k) for two densities while Fig.2 gives the behaviour of $(S(k)-1)/\rho$ versus ρ for three different values of k where:

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$$\frac{S(k)-1}{\rho} = S_0(k) + \rho \cdot S_1(k) + O(\rho^2) \qquad (1)$$

$$S_0(k) = \int d\underline{r}\ \exp(-i\underline{k}\cdot\underline{r}) \cdot (g_0(r) - 1) \qquad (2)$$

$$S_1(k) = \int d\underline{r}\ \exp(-i\underline{k}\cdot\underline{r}) \cdot g_1(r) \qquad (3)$$

where $g_0(r)$ and $\rho \cdot g_1(r)$ are the pairs and triplets contributions to the g(r), respectively. The theoretical expressions for $g_0(r)$ and $g_1(r)$ are known and are given by[4] :

$$g_0(r) = \exp(-U(r)/K\cdot T) \qquad (4)$$

$$g_1(r) = g_0(r) \cdot \left[\int (\exp(-U(s)/K\cdot T - 1) \cdot (\exp(-U(|\underline{r}-\underline{s}|)/K\cdot T - 1) \right] d\underline{s} \qquad (5)$$

where U(r) is the pair-potential, $\underline{r}$ is the displacement between a given pair of atoms, $\underline{s}$ is the displacement between one of these atoms and a third atom, K is Boltzmann's constant, $\underline{k}$ is the wave vector.

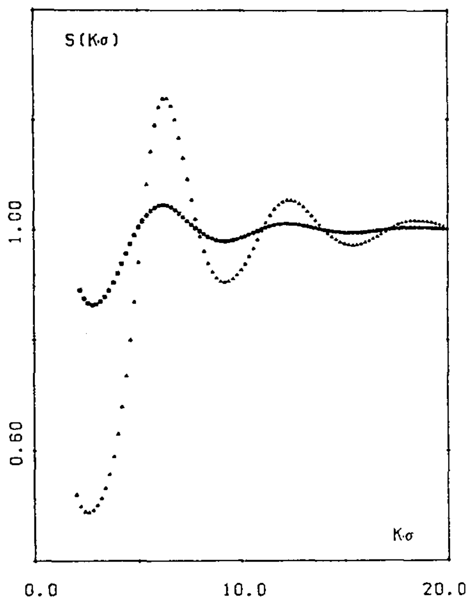

Fig.1 S(k) from our M.D.calculation for Kr at 1.3×10^{27} (squares) and 6.5×10^{27} atoms/m^3 (triangles). Pair-potential from ref. [3] ; σ = 3.573 Å; T = 297 °K.

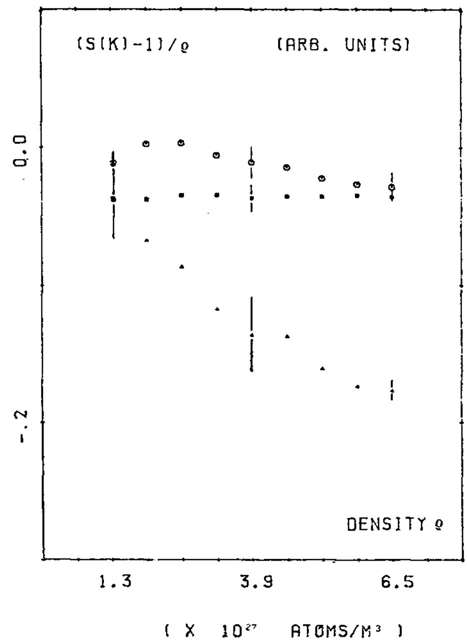

Fig.2 (S(k)-1)/ρ versus ρ for k = .42Å^{-1} (triangles), k= 1.4 Å^{-1} (dots), k = 2.8Å^{-1} (squares). Density ρ between 1.3×10^{27} and 6.5×10^{27} atoms/m^3 . Typical error bars are shown.

From the density behaviour of S(k) one can derive with a least squares fit procedure S_0 (k) and S_1 (k). The "experimental" S_0 (k) and S_1 (k) derived from our set of simulated S(k) values are given in Fig. 3 and 4, together with theoretical values calculated directly from eqs.(2),(3),(4) and (5) by means of the use of the Barker potential of Krypton.

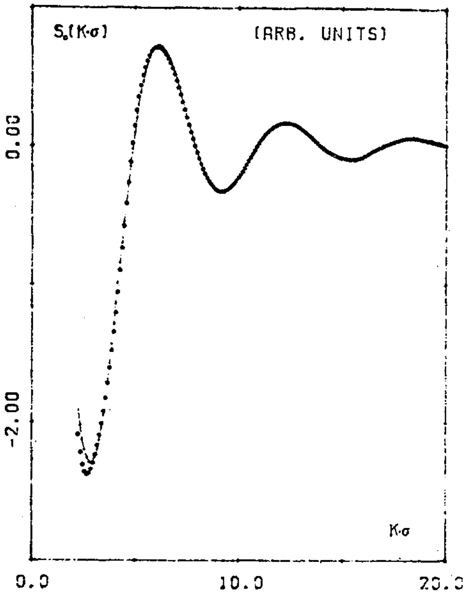

Fig.3 S_0(k) from eq.(2) (continuous line) and from our M.D.calculation (dots).

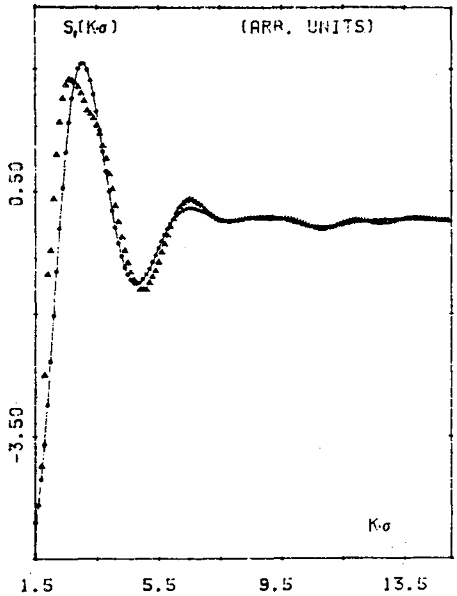

Fig.4 S_1(k) from eq.(3) (dots) and from our M.D.calculation (triangles). Continuous line serves as a guide to the eye.

With a procedure analogous to the one used in ref.[2] we can now derive an "experimental" pair-potential from the S_0(k). Fig.5 shows this "experimental" pair-potential compared to the Barker et al. one from which the experiment started. The agreement in the compared range is at worst of the order of few percent which demonstrate the possibility of extracting good pair isotropic potentials from S(k) density behaviour "experimental" data which are affected by errors of the order of 2%.

The comparison for $S_1(k)$ is less encouraging for $k \cdot \sigma < 3$ i.e. for $k < .8$ Å^{-1} while is good for $k \cdot \sigma > 3$. This could be due either to an insufficient precision of our S(k) for $k \cdot \sigma < 3$ or to inadequacies of our procedure for the determination of S_1 (k) in that range of k values. There are in facts regions of k values in which the virial expansion of S(k) should be used very carefully as it is shown by Fig.6 where we have plotted the theoretical values $S_0 / \rho \cdot S_1$ for a density $\rho = 6.5 \times 10^{27}$ atoms/m^3 .

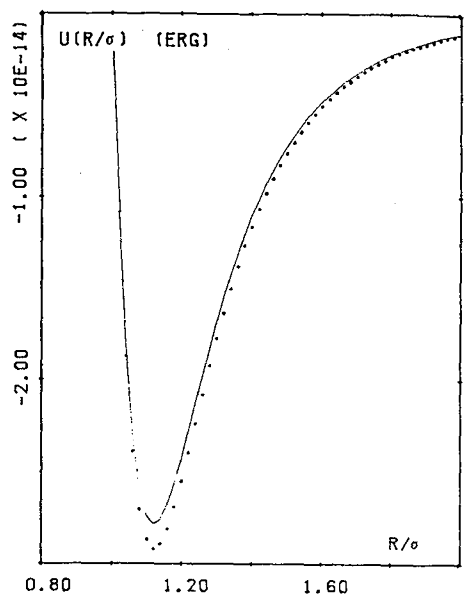

Fig.5 Pair-potential from Barker et al.[3] (continuous line) and from our M.D. calculation (dots).

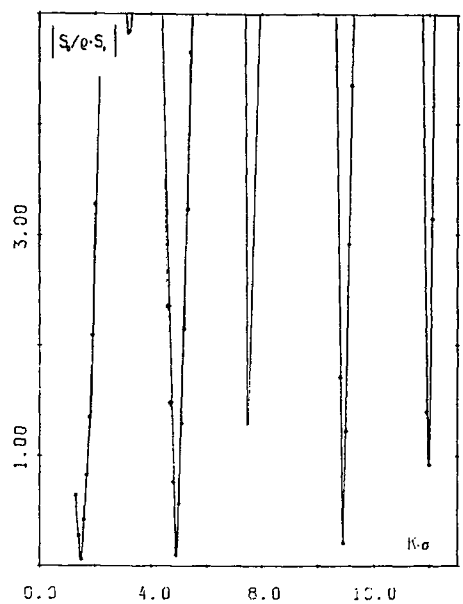

Fig.6 Absolute value of $S_0(k)/\rho \cdot S_1(k)$ from eqs.(2) and (3) at density $\rho = 3.9 \times 10^{27}$ atoms/m^3.

From Fig.6 it appears that there are large regions for $k \cdot \sigma < 6$ where the ratio $S_0/\rho \cdot S_1$ is smaller than 3 showing that the contribution of $\rho \cdot S_1$ to eq. (1) is conspicuous. Therefore derivation of S_1 in those regions of $k \cdot \sigma$ neglecting the terms $O(\rho^2)$ in (1) can lead to considerable errors when densities of about 3.9×10^{27} atoms/m^3 are used. For $k \cdot \sigma > 6$ there are less problems even though also here we have sharp regions in which analogous difficulties appear.

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