Experimental Determination of the Long-Range Potential of Argon Pairs by Means of Small-Angle Neutron Diffraction

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We have experimentally determined the static structure factor $S(k)$ in low density argon gas for $1.0 < k < 3.5\ \text{nm}^{-1}$, by means of the small-angle neutron scattering diffractometer PAXE at Laboratoire Léon Brillouin in Saclay. The experiment has been performed at three number densities between 1.51×10^{27} and $2.30 \times 10^{27}\ \text{m}^{-3}$ along the $T = 138.75$ K isotherm. From the data the small-k dependence of the Fourier transform $c(k)$ of the direct correlation function $c(r)$ has been derived and the existence of the $|k|^3$ term in the behavior of $c(k)$ experimentally demonstrated. The experiment has allowed the first direct measurement of the coefficient C_6 of the London dispersion interaction in the pair potential of argon. [S0031-9007(96)00761-2]

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It is commonly accepted that the London dispersion energy determines the form of the long-range r^{-6} interaction potential between two electronic ground state atoms, where r is the interatomic distance [1]. However, no direct experimental determination of this behavior in the potential has ever been performed. Only indirect experimental evidence of the correctness of this theoretical prediction has been accomplished up to now through the modeling of interatomic pair potential with various techniques [2].

One possibility for a direct assessment of the r^{-6} long-range interaction among the particles of a fluid is given by the connection between the small-k behavior of the static structure factor $S(k)$ and the long-range microscopic force. This connection was pointed out for the first time long ago by Enderby, Gaskell, and March [3]. The main result of that work is that for classical fluid insulators, such as noble gases, $S(k)$ is expected to have at small k a nonanalytic $|k|^3$ term directly related to the r^{-6} tail of the microscopic van der Waals interaction potential in the fluid. Several papers have been devoted to this subject [4–6] and recently this matter has been discussed in detail by Reatto and Tau [7]. In particular, these authors take into account in the theory also the effects of the three-body long-range potential and of retardation, and show that, from an experimental point of view, it is preferable to perform the data analysis of terms of the Fourier transform $c(k)$ of the direct correlation function $c(r)$ than in terms of $S(k)$ itself.

Measurements of the $|k|^3$ behavior of $c(k)$ can therefore give in principle an experimental direct verification of the r^{-6} power law together with the experimental determination of the van der Waals constant related to r^{-6}. In particular in the zero-density limit this last constant coincides with the C_6 coefficient of the London dispersion force.

Neutron diffraction measurements, when possible, have been proven to be a direct method for the determination of the interaction potential between pairs in gases [8–10]. In particular, the experimental determination of the $|k|^3$ dependence of $c(k)$ has been attempted in a previous experiment and preliminary results were published [11]; however, the k range used in that case was not sufficiently low to ensure the determination of the correct behavior of $c(k)$.

By means of theoretical calculations of $c(k)$ performed with the modified hypernetted chain equation, Reatto and Tau [7] have shown that, in low density noble gases, the k range useful for the determination of the $|k|^3$ dependence is the one for which $k \leq 3\ \text{nm}^{-1}$. This range is experimentally accessible with small-angle neutron scattering (SANS) instrumentations.

In the theory of simple fluids, the static structure factor $S(k)$ and the Fourier transform $c(k)$ of the direct correlation function $c(r)$ are defined by

$$S(k) = 1 + n \int d\boldsymbol{r} \exp(i\boldsymbol{k} \cdot \boldsymbol{r})[g(r) - 1], \quad (1)$$

$$c(k) = \int d\boldsymbol{r} \exp(i\boldsymbol{k} \cdot \boldsymbol{r}) c(r), \quad (2)$$

where $g(r)$ is the pair correlation function and $c(r)$ is given by the Ornstein-Zernike relation

$$h(r) = c(r) + n \int d\boldsymbol{r}' \, c(r') h(|\boldsymbol{r} - \boldsymbol{r}'|), \quad (3)$$

with

$$h(r) = g(r) - 1. \quad (4)$$

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$S(k)$ is an experimentally accessible quantity and $c(k)$ can be derived from $S(k)$ by using the relationship obtained from Eqs. (1)–(4):

$$c(k) = [S(k) - 1]/nS(k). \quad (5)$$

Here we report the results of a measurement of $S(k)$ in argon gas at low density and at small k, performed by means of SANS with the PAXE diffractometer at the Laboratory Léon Brillouin in Saclay, from which the $|k|^3$ behavior is experimentally detected for the first time and the C_6 coefficient of the microscopic pair potential of argon measured.

The experiment has been performed along the 138.75 K isotherm at three low densities chosen in such a way as to ensure minimization of many-body effects in the fluid as in a previous experiment [9,11], i.e., $n = 1.51 \pm 0.03$, 1.99 ± 0.06, and 2.30 ± 0.07 nm^{-3}, where n is the number density. Also in the present case the ^{36}Ar isotope has been used in order to benefit from its large coherent neutron scattering cross section. The sample gas was kept in a low temperature flat cell of 0.65 cm thickness and with quartz windows capable to withstand pressure up to 50 bars. The cell was mounted in a cryostat with temperature stability within 0.2 K.

The experiment has been performed with neutron wavelength of 4.0 Å and the distance between the sample and the two dimensional BF_3 gas detector was 150 cm. The choice of these values has allowed the $0.1 < k < 3.5$ Å^{-1} range to be covered with an overall resolution $\Delta k/k \sim 10\%$.

The neutron intensity data were corrected for the effect of background, self-shielding, multiple and inelastic scattering, and detector efficiency. The absolute normalization of the data has been accomplished extrapolating the data to the compressibility limit $S(0) = nk_BT\chi_T$, where k_B is the Boltzmann constant, T the absolute temperature, and χ_T the isothermal compressibility, thus obtaining the static structure factors $S(k)$. We estimate that this data analysis procedure leads to a final uncertainty on the absolute scale of $S(k)$ which ranges from 1.4% for the higher density to 1.8% for the lower one.

The $c(k)$'s were then derived from the $S(k)$'s by means of Eq. (5).

Figure 1 shows the low-k $c(k)$'s at the measured densities together with $c(k=0)$ values derived combining Eq. (5), the compressibility relation, and the thermodynamical data of Ref. [12].

In low density systems the interaction law can be written retaining only the pair and the triplet contributions and it has been demonstrated [7] that the asymptotic behavior of $c(r)$ is given by

$$c(r) \underset{r\to\infty}{\sim} b\phi(r) + C(r), \quad (6)$$

where $\phi(r)$ and $C(r)$ are the long-range pair potential and dressed three particle vertex, respectively. When in

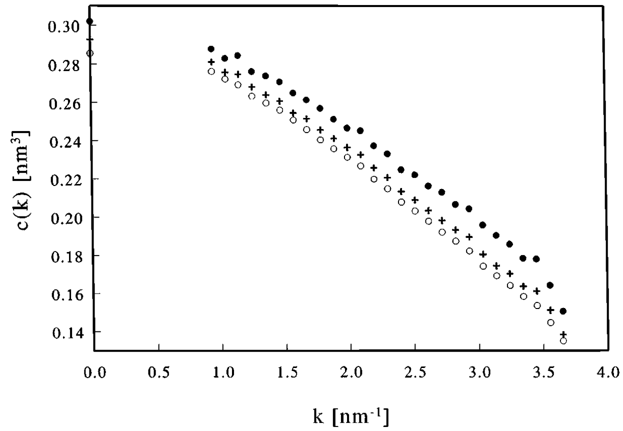

FIG. 1. Experimental $c(k)$ at $T = 138.75$ K. From top to bottom: $n = 1.51$, 1.99, and 2.30 nm^{-3}. The statistical uncertainties are within the size of the symbols. The $k = 0$ values are obtained from Ref. [11] data.

the long-range pair potential the dispersion term is the dominant one and the irreducible three-body interaction is assumed to be of the triple dipole Axilrod-Teller (AT) form we can write

$$\phi(r) \underset{r\to\infty}{\sim} -C_6/r^6, \quad (7)$$

$$C(r) \underset{r\to\infty}{\sim} (8\pi/3)\beta n\nu/r^6. \quad (8)$$

Here $\beta = 1/k_BT$, where ν is the strength of the AT potential.

By using expressions (6)–(8) and asymptotic Fourier analysis it can be shown [7] that the small-k expansion of $c(k)$ is given by

$$c(k) \underset{k\to 0}{\sim} c(0) + c_2k^2 + c_3|k|^3, \quad (9)$$

where the $|k|^3$ term is due to the r^{-6} two- and three-body potential tails in direct space and the c_3 coefficient is given by

$$c_3 = (\pi^2/12)(C_6 - 8\pi n\nu/3)/k_BT. \quad (10)$$

We have therefore performed a least squares fit of the three parameters function (9) to our experimental $c(k)$ at the three measured densities; in all cases the reduced χ^2 was of the order of unity. In order to display the $|k|^3$ dependence of the experimental $c_{\exp}(k)$ it is more convenient to plot the quantity $\lambda(k)$ defined as

$$\lambda(k) \underset{k\to 0}{=} [c(k) - c(0)]/k^2 \sim c_2 + c_3|k|. \quad (11)$$

Figure 2 shows the experimental results $\lambda_{\exp}(k)$ for argon at $T = 138.75$ K for the three different measured densities, together with the function $\lambda_{\exp}(k)$ given by Eq. (11)

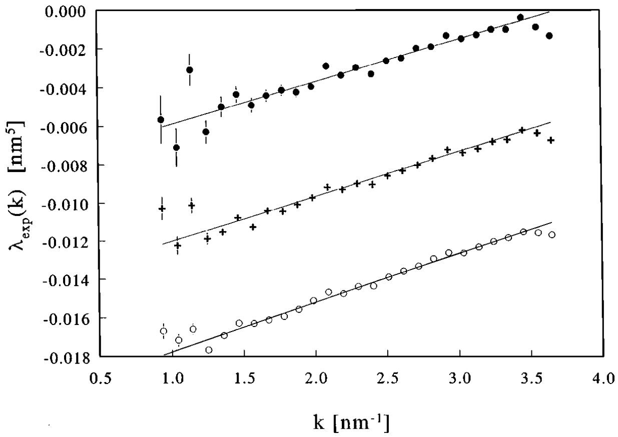

FIG. 2. Experimental results for $\lambda(k)$ (see text). Symbols as in Fig. 1. $n = 1.99$ and 1.51 nm^{-3} data are shifted upward by 0.005 and 0.01, respectively. Straight lines represent the results obtained with the least squares fitting procedure [see text, Eq. (9)].

and where $c(0)$, c_2, and c_3 are the coefficients derived from the least squares fit performed on $c_{\text{exp}}(k)$ with the polynomial function (9). From this figure the $|k|$ dependence of $\lambda_{\text{exp}}(k)$ and therefore the $|k|^3$ dependence of $c_{\text{exp}}(k)$ are confirmed leading to the experimental demonstration of the r^{-6} behavior of the interaction potential among argon pairs.

No density dependence of $c_3(n)$ can be extracted from our data within the experimental uncertainties. The average value of c_3 can be evaluated and then, using Eq. (10), the experimental determination of C_6 which gives $C_6 = (5.54 \pm 0.83) \times 10^{-78}\ \text{J m}^6$. The present experimental result compares rather well with the estimated values given by Standard and Certain [13], that is, $6.42 \times 10^{-78}\ \text{J m}^6$ and by Kumar and Meath [14], that is, $6.16 \times 10^{-78}\ \text{J m}^6$. The smallness, at these low densities, of the three-body contribution does not give the possibility of deriving a value for ν from the present experimental results.

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