Pair Potential from Neutron Diffraction on Argon at Low Densities

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We report the results of measurements of the static structure factor $S(\kappa)$ for gaseous ^{36}Ar at 140 K and four (subcritical) low densities from which, for the first time, we derive the well of the isotropic pair potential directly by means of a simple Fourier transform inversion.

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The determination of the precise form of the interaction potential in simple monatomic systems, like noble gases, has been a matter of study for many years. The joint use of a large amount of experimental data on various physical quantities, like second virial coefficients, transport coefficiencies in low-density gases, atomic collision scattering cross sections, spectroscopic properties of dimers, and properties of solids led to parametrized functions that are accepted as good representations of the pair potential of noble gases.[1-3] However, none of these physical quantities by itself yields directly, or by a simple inversion scheme, without additional information on the pair potential. As an example, compare the calculations of the potential curve of the ground state of Ar_2 by Colbourn and Douglas[4] from their accurate spectroscopic data, together with information from long-range forces and information from the second virial coefficient. As far as inversion schemes are concerned, the best possibility is found in atomic scattering experiments, where the deflection angle is inverted to the pair potential.[5] Recently McLean, Liu, and Barker[6] reported *ab initio* calculations that yield in the repulsive region probably the best available estimate of the argon pair potential. They expect that empirical potentials are more accurate in the region of the attractive well and therefore they constructed a composite potential that agrees with their calculations for $r < 0.343$ nm and with the empirical pair potential of Aziz and Slaman[3] for $r > 0.343$ nm. The experimental quantity that, in principle, is most directly connected to the interaction potential is the zero-density limit of $H(\kappa) = [S(\kappa) - 1]/n$, where n is the number density and $S(\kappa)$ is the structure factor, which is measured in neutron-diffraction experiments. This has already been shown to be possible for krypton,[7] where experimental data of Teitsma and Egelstaff[8] were used. In that case the accuracy of the data at densities below 2 atoms/nm^3 and the limited κ range, which was restricted to the maximum value $\kappa = 40$ nm^{-1}, did not permit a satisfactory and precise derivation of the pair potential. An earlier attempt to derive the pair potential of argon from neutron scattering data at low density was made by Andriesse and Legrand.[9,10] In that case the κ range and precision were limited also. Moreover the measurement was performed at one density only, not low enough to neglect many-body contributions. Karnicky, Reamer, and Pings[11] derived the pair potential of argon from x-ray scattering data at several densities, in a limited κ range. They applied an integral-equation theory to correct for many-body contributions.

In our method it is of fundamental importance to determine the density dependence of $S(\kappa)$, from which the zero-density limit is derived. In fact, the quantity $H(\kappa)$ is the (three-dimensional) Fourier transform of the total correlation function $h(r) = g(r) - 1$ of the monatomic fluid, where $g(r)$ is the radial distribution function, i.e.,

$$H(\kappa) = \int h(r) \exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}) d\mathbf{r} . \quad (1)$$

For a low-density microscopically isotropic gas at temperature T, the virial expansion yields

$$h(r) = h_0(r) + n h_1(r) + O(n^2) , \quad (2)$$

where in the classical limit,

$$h_0(r) = \exp[-\beta U_2(r)] - 1 . \quad (3)$$

$h_1(r)$ is the coefficient of the first density correction, $\beta = 1/k_B T$, and $U_2(r)$ is the pair potential between two particles at a distance r. Substitution of Eq. (2) into Eq. (1) yields

$$H(\kappa) = H_0(\kappa) + nH_1(\kappa) + O(n^2), \quad (4)$$

where $H_0(\kappa)$ and $H_1(\kappa)$ are the Fourier transforms of $h_0(r)$ and $h_1(r)$, respectively [cf. Eq. (1)]. From the experimental values of $S(\kappa)$ the values of $C(\kappa)$, the Fourier transform of the direct correlation function $c(r)$, which is defined by the Ornstein-Zernike integral equation,[12] can be derived as follows:

$$C(\kappa) = [S(\kappa) - 1]/nS(\kappa)$$
$$= H(\kappa)/[1 + nH(\kappa)]. \quad (5)$$

Therefore also $C(\kappa)$ can be given by a virial expansion, similar to Eq. (4):

$$C(\kappa) = C_0(\kappa) + nC_1(\kappa) + O(n^2). \quad (6)$$

It is straightforward to show that

$$C_0(\kappa) = H_0(\kappa), \quad (7)$$

$$C_1(\kappa) = H_1(\kappa) - [H_0(\kappa)]^2. \quad (8)$$

Equations (4) and (6) show that $H_0(\kappa)$, $H_1(\kappa)$, $C_0(\kappa)$, and $C_1(\kappa)$ can be determined from the experimental density dependence of $H(\kappa)$ and/or $C(\kappa)$, in a range of densities where terms of order n^2 may be neglected, with the size of the $O(n^2)$ terms as the theoretical limit to the precision. Equations (4) and (6) represent series expansions of two different quantities whose terms are connected. Therefore both can be used to extract information on $H_0(\kappa) = C_0(\kappa)$, $H_1(\kappa)$, and $C_1(\kappa)$. Here we will only give a detailed discussion of the experimental results for $C_0(\kappa)$. The terms $C_1(\kappa)$ and $H_1(\kappa)$ will be discussed separately. The determination of $H_0(\kappa)$ and $C_0(\kappa)$ from Eqs. (4), (6), and (7) in a wide range of κ values permits the derivation of $h_0(r)$ by means of the Fourier transform

$$h_0(r) = (2\pi)^{-3} \int H_0(\kappa) \exp(i\boldsymbol{\kappa}\cdot\mathbf{r}) d\mathbf{r} \quad (9)$$

and of the isotropic pair potential

$$U_2(r) = -k_B T \ln[h_0(r) + 1]. \quad (10)$$

High-precision data for $H_0(\kappa)$ over a wide range of κ values are required to perform this program, since noise on and truncation of $H_0(\kappa)$ are the final limits for the precision of the Fourier inversion for the determination of $h_0(r)$ and in turn of $U_2(r)$. This implies that $S(\kappa)$ should be determined in the low-density gas over a wide κ range, $0 < \kappa < 100$ in our case (κ is given in nm^{-1} throughout this Letter), with a higher precision the lower the density.

Our measurements of $S(\kappa)$ in ^{36}Ar, chosen for its large coherent scattering cross section [78 b/atom (Ref. 13)], were performed at four densities, $n = 0.902$, 1.399, 1.900, and 2.393 atoms/nm^3, at $T = 140$ K for $2.4 < \kappa < 100$ at the D4B diffractometer of the Institute Laue-Langevin (ILL) in Grenoble. The ^{36}Ar was kept in a thin walled cylindrical vanadium container (height 60 mm, inner radius 5.75 mm, and wall thickness 0.1 mm), mounted on an ILL "orange cryostat" at $T = 140.0 \pm 0.1$ K. The temperature and density (pressure) were measured continuously and turned out to be stable to at least one part per thousand. The accuracy of $S(\kappa)$, from counting statistics, varied between six parts per ten thousand at the lower density and two parts per thousand at the higher density, for each κ value. The incident wavelength was $\lambda = 0.0703$ nm and the scattering percentage from the samples varied between six and fourteen percent. Two ^{3}He gas multidetectors were used, one at a distance of 2.92 m for measurements at low κ ($2.4 < \kappa < 15$), and the other one at 0.73 m for measurements at higher κ ($10 < \kappa < 100$). The measurements were taken in repeated runs to judge the stability of the experimental setup. "Background" measurements, including scattering from the container and the vanadium tail of the cryostat (approximately 1.5% scattering), were done with such amounts of ^{3}He in the container that the macroscopic total cross sections of the ^{36}Ar samples and the corresponding absorption cross section of the ^{3}He were equal. This allowed us to subtract properly the background scattering. The time apportionment between sample and corresponding background was chosen to minimize the statistical inaccuracy on $H(\kappa)$. The total measuring time spent on each density was such that after correction for the background all $H(\kappa)$'s should have approximately the same statistical accuracy. The data were corrected for background, multiple scattering (including scattering between the sample and the container and the tail of the cryostat), attenuation effects, and effects for inelastic scattering.[14] Finally we applied a correction to replace the nominal scattering angle by the average scattering angle (the difference is due to the finite sizes of the sample and the detector cells). Then

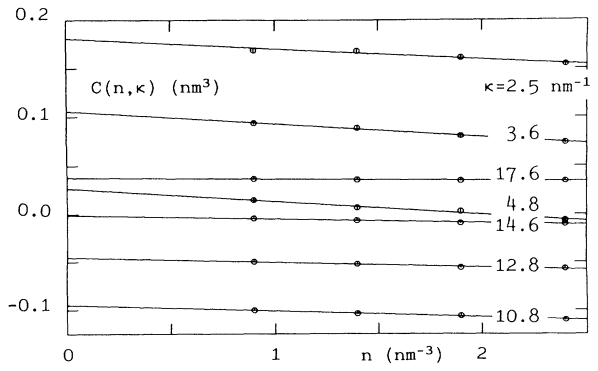

FIG. 1. Experimental $C(n,\kappa)$ at various κ values (symbols) and weighted linear fits to the data (lines).

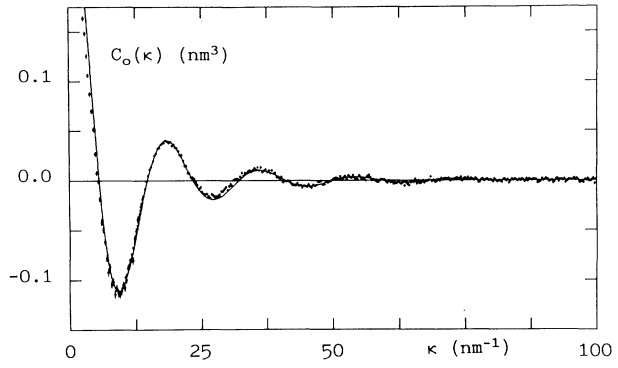

FIG. 2. $C_0(\kappa)$ from extrapolation of $C(n,\kappa)$ to $n=0$ (symbols) and calculated from pair potentials taken from the literature (Refs. 2 and 3) (line).

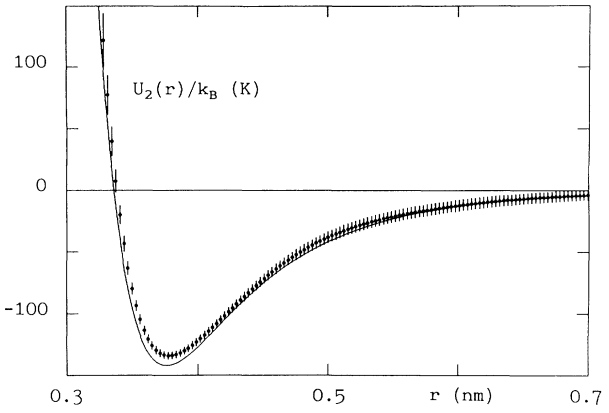

FIG. 3. Pair potential from this experiment (symbols) and taken from the literature (Refs. 2 and 3) (line).

the data taken with the two detectors were matched in the overlap region. We normalized the data using the fact that $S(n,\kappa) \rightarrow 1$ for high-κ values.

From the four experimental structure factors $S(n,\kappa)$ we determined $H(n,\kappa)$ and $C(n,\kappa)$, including estimates of the statistical inaccuracy based on counting statistics. We calculated the values of $H(n,\kappa)$ and $C(n,\kappa)$ at $\kappa=0$ for the compressibility theorem[15]

$$S(n,\kappa=0)=k_BT/(dp/dn)_T \qquad (11)$$

for the four experimental densities, using the equation of state of Stewart *et al.*[16] It turned out that $C(n,\kappa=0)$ could be represented extremely well by a linear function of the density, with the correct $C(n=0,\kappa=0)$ limit, whereas for $H(n,\kappa=0)$ this was not the case.

For each value of κ we estimated $H_0(\kappa)$, $H_1(\kappa)$, $C_0(\kappa)$, and $C_1(\kappa)$ from a weighted least-squares fit to the data, taken at four densities, of a function linear in the density. In Fig. 1 we show the typical density dependence of $C(\kappa)$ at various κ values, characteristic for different κ ranges. In the κ range we explored, both the $H(n,\kappa)$ and $C(n,\kappa)$ data could be represented within the experimental accuracy by a linear function of density, in agreement to first order with Eqs. (4) and (6). The result for $C_0(\kappa)$ is plotted in Fig. 2, together with the theoretical prediction based on the pair potential of either Ref. 2 or 3. [The differences between $C_0(\kappa)$'s, calculated from these two pair potentials, are for our purpose negligible.] Within the experimental accuracy, the relations between the coefficients given by Eqs. (7) and (8) were verified.

At the lower κ values, measured with detector 1 at 2.92 m, we observe relatively large deviations, up to 30%, of the experimentally determined values of $C_0(\kappa)$, compared to the theoretical prediction. The values determined from the experiment are systematically less than the ones predicted by the pair potential taken from the literature.

In the range $25 < \kappa < 35$, measured with detector 2 at 0.73 m, the experimental values are larger than the predicted ones. These deviations are significantly in excess of the (statistical) inaccuracy, estimated from counting statistics (cf. Fig. 2). Note that at higher κ values, measured mainly with detector 2, the statistical accuracy is better due to the higher count rate of this setting.

From Fourier transformation of $C_0(\kappa)$ we determined $c_0(r)=h_0(r)$ and $U_2(r)$ using Eq. (10). We verified that truncation of the experimental $C_0(\kappa)$ at low κ (<2.4) and at high κ (>100) affects $c_0(r)$ by an amount of approximately 1% in the region of the peak. Quantum corrections to $h_0(r)$ amount to less than 1% in the region of the peak.[17] In Fig. 3 we show the pair potential for ^{36}Ar as derived from the present experiment together with the pair potential of Ref. 2 or 3. The value of r where the experimental pair potential equals zero is $\sigma=0.338\pm0.001$ nm and the well depth is $\epsilon/k_B=134$ K. We estimate the accuracy of the pair potential determined this way to be approximately $\Delta U_2(r)/k_B=3$ K from propagation of errors.

We have shown that in the favorable case of ^{36}Ar, due to its large coherent neutron scattering cross section, it is possible to obtain experimentally direct access to the pair potential.

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