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Density analysis of the neutron structure factor and the determination of the pair potential of krypton

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We propose a method of analysis of the density behavior of the experimental neutron scattering structure factor which permits us to derive directly from the experimental results an "experimental" pair potential. We apply the method to the recent results of Teitsma and Egelstaff in krypton gas and derive a pair potential which is in good agreement with the empirical potential of Barker *et al.* Some discrepancies in the range $4 < r < 8$ Å are noted.

It is well known that the pair distribution function $g(r)$ of a monatomic gas at low density can be expressed as a series expansion with respected to the density.[1] For the case of an homogeneous low-density gas system at temperature T, $g(r)$ assumes the form

$$g(r) = g_0(r) + \rho g_1(r) + O(\rho^2) \ , \tag{1}$$

where

$$g_0(r) = \exp[-\beta U_2(r)] \tag{2}$$

and $g_1(r)$ is the coefficient of the first density correction, which depends on both the two- and three-body potentials. In expression (2) $\beta = 1/k_B T$, $U_2(r)$ is the pair potential, and r is the distance of a generic pair of atoms.

The static structure factor $S(k)$ of a fluid, which can be measured precisely by means of neutron scattering, is directly related to the Fourier transformation of $g(r)$ as

$$S(k) = 1 + \rho \int [g(r) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \ . \tag{3}$$

Therefore, the $S(k)$ of a low-density gas can also be written from Eqs. (1) and (3) as a power series with respect to ρ, i.e.,

$$S(k) = 1 + S_0(k)\rho + S_1(k)\rho^2 + O(\rho^3) \ , \tag{4}$$

where

$$S_0(k) = \int [g_0(r) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \ , \tag{5}$$

$$S_1(k) = \int g_1(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \ . \tag{6}$$

From Eq. (4) it is clear that a measurement of $S(k)$ in a gas as a function of density ρ at fixed T would permit a direct measurement of $S_0(k)$ and $S_1(k)$ if the density region which is explored is such that terms of order $O(\rho^3)$ are either small or even negligible.

The experimental measurement of $S_0(k)$ would then permit the determination of $g_0(r)$ by means of the simple Fourier transformation

$$g_0(r) = 1 + \frac{1}{(2\pi)^3} \int S_0(k) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k} \tag{7}$$

and, therefore, the determination from the experiment, of the isotropic pair potential

$$U_2(r) = -k_B T \ln g_0(r) \ . \tag{8}$$

Andriesse and Legrand have performed a measurement of $S(k)$ in a limited range of k values at low density (2.52×10^{27} atoms/m^3) in ^{36}Ar and derived a pair potential.[2,3] However, their density was not low enough to allow the many-body contributions to be neglected; therefore they were obliged to apply a correction based on the hypernetted chain (HNC) and Percus-Yevick (PY) approximated theories. Moreover, they performed a termination of $S(k)$ to high-k values based on an arbitrary smoothing procedure.

Here we will demonstrate that the derivation of a pair potential, from density measurements of $S(k)$ alone, is possible if accurate data are available. Only recently Teitsma and Egelstaff[4(a)] have performed an experiment which allows the application of this procedure. They have measured $S(k)$ for $0.2 \leq k \leq 4$ Å^{-1} of krypton gas at room temperature ($T = 298$ K) with high precision and for 15 densities. However, in the analysis of the data they focused attention on the determination of the importance, for the quantity $S_1(k)$, of the three-body irreducible potential $U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ assuming a known form for the pair potential $U_2(r)$. Egelstaff, Teitsma, and Wang[4(b)] have extracted $S_0(k)$ by extrapolating $c(k) = [1 - 1/S(k)]/\rho$ to $\rho = 0$, but they used a theoretical form for $S_0(k)$ for $k > 4$ Å^{-1}. In this Brief Report, we will show that the krypton data of $S(k)$ permit the application of the before-mentioned procedure, in order to extract $S_0(k)$, and consequently $U_2(r)$, directly from the experiment.

For our purposes it is convenient to analyze the behavior of the quantity $[S(k) - 1]/\rho$, see Eq. (4), as a function of

ρ. The procedure is the following. Since the experimental $S(k)$, as given in Ref. 4(a), have an average accuracy better than 0.5%, we have assumed this accuracy as a constant relative error. We have performed a weighted least-squares fit of the experimental data, at fixed k, of $[S(k)-1]/\rho$ to polynomials in ρ of zeroth, first, and second order. Then we have chosen, for each k value, the polynomial which gave the highest degree of likelihood based on the value of χ^2. The choice, based on this criterion, shows that the data for $1.7 < k < 4$ Å^{-1} are best fitted by a constant (zeroth-degree polynomial), the data for $0.65 < k < 1.7$ Å^{-1} are best fitted by a linear function (first-order polynomial), and the data for $0.2 < k < 0.65$ Å^{-1} are best fitted by a quadratic form (second-order polynomial). Figure 1 shows the quality of the fit for a value of k in each of the three regions. This behavior of the degree of the fitting polynomial versus k is similar to what has been found in the depolarized interaction-induced light scattering (DILS)[5] where the scattering cross section in gases has the same property with respect to the frequency ν and the density ρ.

This fact indicates that within the experimental errors, in the range of densities studied, for values of $1.7 < k < 4$ Å^{-1} $S(k)$ is determined only by two-body correlations; in the region where $0.65 < k < 1.7$ Å^{-1} three-body correlations are also important, while for $0.2 < k < 0.65$ Å^{-1} correlations of higher order that three must be considered if the range $0 < \rho < 6\times10^{27}$ atoms/m^3 is used. [The second region extends to lower k if $c(k)$ is used in place of $S(k)$.] This is the counterpart, in k space, of a property that also the $g(r)$, represented by Eq. (1), has with respect to r and ρ. In fact, the larger the value of r that one considers in Eq. (1) the larger the number of terms that one must retain in the series expansion.

Figure 2 shows the behavior of $S_0(k)$ that we have extracted from the experimental data of krypton with the above-mentioned fitting procedure and turns out to be very similar to the one already obtained by Egelstaff, Teitsma, and Wang[4(b)] with a similar fitting procedure. The second step is now to perform the Fourier transform of $S_0(k)$ and derive $g_0(r)$. $S_0(k)$ is extracted from the experiment in a finite range of k; therefore, some kind of extrapolation must be applied to $S_0(k)$, both toward zero and high-k values, in order to perform a reliable Fourier transform.

The interpolation toward the zero-k value is readily done, since the value of $S_0(k=0)$ is known from the equation-of-state data[6] and also the form of $S_0(k)$ between $k=0$ and $k=0.2$ Å^{-1} does not appreciably affect the values of $g_0(r)$ in the region of the peak, which is of interest here. We have performed this interpolation by means of a parabola in k^2 which fits the data between 0 and 0.4 Å^{-1}.

The extrapolation toward high-k values is more important and must be discussed in some more detail. The Fourier transform of a structure factor (truncated at $k=k_t$) for which the $S_0(k)$ is different from zero for $k > k_t$, is appreciably affected by this truncation, giving rise to a $g_t(r)$ which shows a lowering in the maximum and spurious oscillations at high r in comparison to the true $g(r)$. [Here we have indicated with $g(r)$ the Fourier transform of the full $S(k)$ while $g_t(r)$ is the Fourier transform of the truncated $S(k)$.] This is easily verified performing a calculation on a

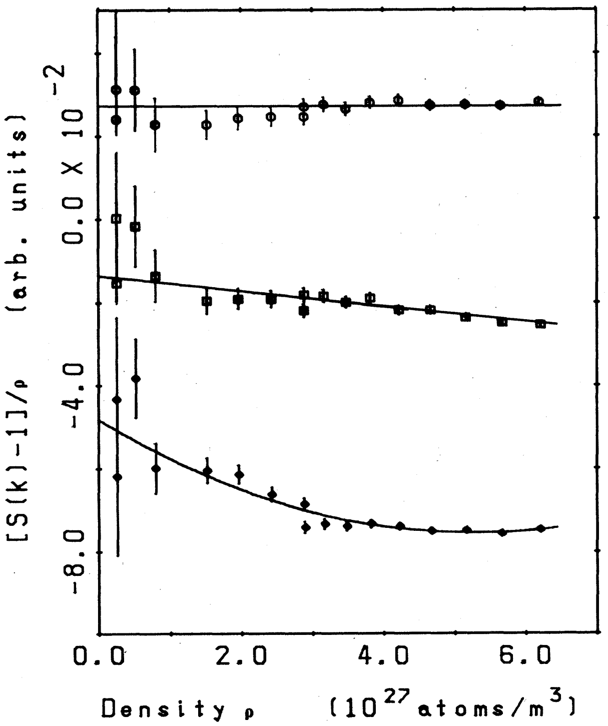

FIG. 1. Experimental values and best-fit line as a function of density, of the function $[S(k)-1]/\rho$ for three different values of k: 1.9 Å^{-1} (circles); 1.3 Å^{-1} (squares); 0.55 Å^{-1} (diamonds).

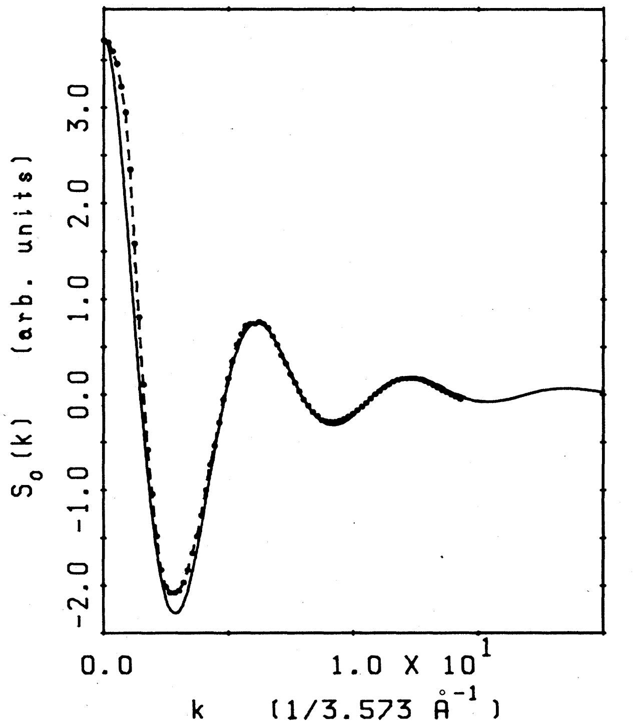

FIG. 2. The behavior of $S_0(k) = \lim_{\rho\to0}[S(k)-1]/\rho$ as a function of k. All the points but the first three are derived by the fitting procedure described in the text. The low-k points have been derived by interpolating the behavior of $S_0(k)$ by means of its $k=0$ value (compressibility) as explained in the text. Dots are the experimental data, the solid line refers to the Barker *et al.* potential, and the broken lines refer to our potential (see text).

model $g(r)$ and $S(k)$, for example, for a Lennard-Jones (LJ) potential.

In Refs. 4(a) and 4(b) an extrapolation procedure of the experimental structure factors, based on a known pair potential, was adopted in order to derive information on the pair and triplet potentials.

Here, since our primary purpose is to demonstrate that we can extract a good potential by using only the experimental results of $S_0(k)$, we will not assume any known potential of krypton and will adopt an iterative procedure starting only from the experimental results. This procedure is based on the following observation. If the experimental data do extend to sufficiently high k (in the case of krypton, for which measurements have been performed up to $k \sim 4$ Å^{-1}) even though the data do not allow a direct inversion procedure, almost complete information on the $g_0(r)$, and consequently on the pair potential, is contained in the truncated experimental results for $r \geqslant 2\pi/k_t$. Here, k_t indicates the value of k for which the experimental $S_0(k)$ is truncated, for example, in the case of the experiment on krypton $2\pi/k_t = 1.57$ Å.

We need then to find a model-independent general procedure with which to extrapolate the truncated $S_0(k)$ in order to properly extract a $g_0(r)$; this procedure will damp down the Fourier oscillations and increase the magnitude of the peak of $g_t(r)$.

The procedure we propose, is the following.

(1) We Fourier transform the truncated experimental $S_0(k)$ and derive a zeroth order $g^{(0)}(r) = g_t(r)$.

(2) From this $g^{(0)}(r)$ we define two parameters σ_0 and ϵ_0 as follows. σ_0 is the value of r for which $g^{(0)}(r) = 1$, while ϵ_0 is $-k_B T \ln g_{\max}^{(0)}$, where $g_{\max}^{(0)}$ is the peak value of $g^{(0)}(r)$.

(3) We use a model potential parametrized by σ_0 and ϵ_0 to construct a pair distribution function whose Fourier transform is used to extrapolate the experimental $S_0(k)$ and obtain an $S_0^{(1)}(k)$.

(4) We Fourier transform this $S_0^{(1)}(k)$ to derive a first order $g^{(1)}(r)$.

(5) We repeat points (2)–(4) starting from $g^{(1)}(r)$ and iterate the procedure until $g^{(n)}(r) = g^{(n-1)}(r)$.

(6) At this point we identify the pair distribution function $g^{(n)}(r)$ with the true, low-density $g_0(r)$ and derive the experimental pair potential from Eq. (8).

The above-mentioned iteration procedure has been applied starting from the $S_0(k)$ of krypton with three different model forms for the potential, namely, the 9-6 and 12-6 Lennard-Jones potentials given by

$$U_{9\text{-}6}(r) = \frac{27}{4}\epsilon\left[\left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^6\right] , \qquad (9)$$

$$U_{12\text{-}6} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] , \qquad (10)$$

and the multiparameter potential of Barker *et al.*[7] defined as

$$U_B(r) = \epsilon U_B^*(r) \qquad (11)$$

with

$$r_m = 1.121\sigma ,$$

where the various constants in U_B^* were taken from Ref. 7 and σ and ϵ are the parameters used in the iteration procedure. A plot of the three potentials (9), (10), and (11) on the same scale (i.e., in units $\sigma = \epsilon = 1$) would show the large differences of their attractive parts.

Figure 3 shows, as an example, the behavior of the $g^{(0)}(r)$, which is our starting point together with the successive $g^{(1)}(r)$, $g^{(2)}(r)$ when Eq. (10) is used for the model potential. On the same plot $g^{(3)}(r)$ would be coincident with $g^{(2)}(r)$. From the figure the fast convergence of the procedure is also clear.

Figure 4 shows the three potentials as they result from the iteration procedures performed with the three different model forms. They are shifted for convenience and each one is compared with the empirical potential due to Barker *et al.*[7] On the scale of the figure, if plotted together the three potentials would be hardly distinguishable except in the region of the bottom of the well. Their behavior is similar to that of the Barker *et al.*[7] potential, which was derived from a completely different large set of experimental results. If one would plot the relative differences of our three experimental potentials with respect to the empirical one, it would be found that the relative differences for $1.0 < r/\sigma < 1.9$ show that the "experimental" potentials are always within a few percent in agreement. In addition they agree with the Barker *et al.* potential within $\sim 5\%$ in the lower part of the well, while they show a discrepancy of the order of $\sim 3\%$ of ϵ in the region around 1.6σ. This is $\sim 15\%$ of $U_B(r = 1.6\sigma)$, and this discrepancy is observed also in comparison with the Aziz potential.[8]

In Fig. 2 we also compare the experimental behavior of $S_0(k)$ with that derived by means of the Barker *et al.* potential and by means of our three experimental potentials. The three $S_0(k)$ derived from our three experimental potentials are not distinguishible from one another on the plot while the one derived with the Barker *et al.* potential differs from

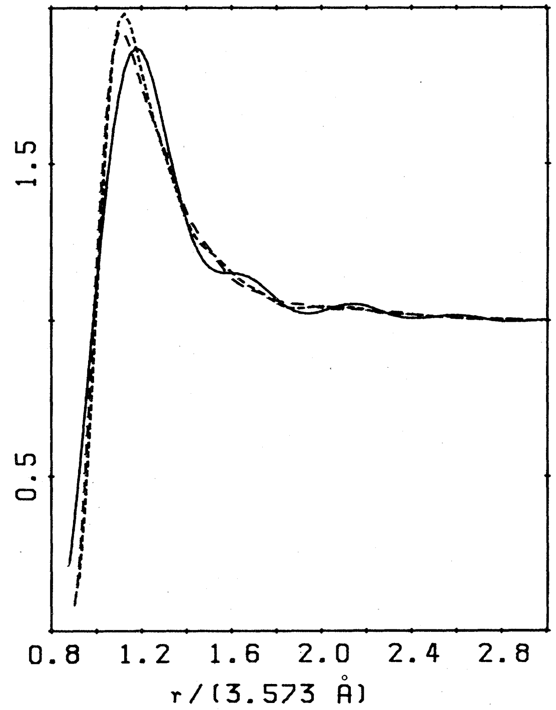

FIG. 3. The behavior of the various $g^{(n)}(r)$ for the case of the 12-6 LJ extrapolation, the solid line is the Fourier transform of the "crude" experimental $S_0(k), g^{(0)}(r)$. The dashed line is the first iteration $g^{(1)}(r)$ and the dotted line is the second iteration $g^{(2)}(r)$. The following iteration, $g^{(3)}(r)$, would be undistinguishible from $g^{(2)}(r)$ on the scale of the figure.

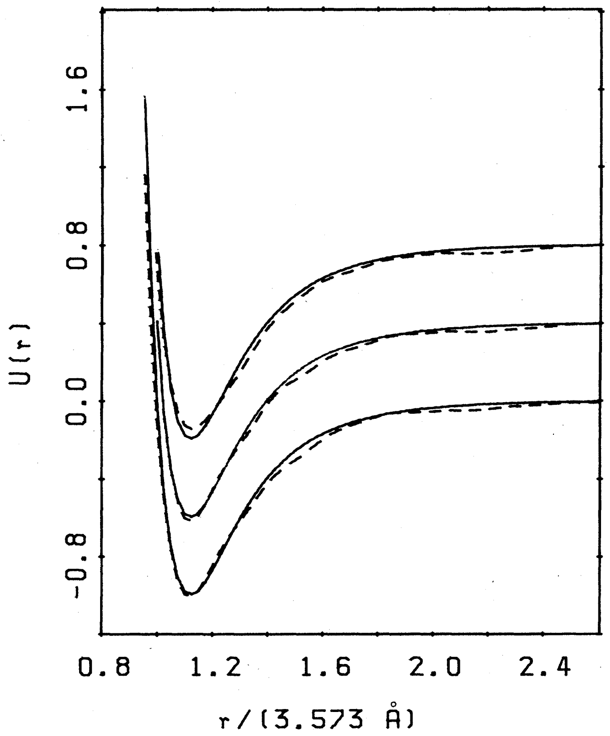

FIG. 4. The three experimental potentials derived by neutron scattering data are shown on the figure (dotted line). Each one is compared with the theoretical Barker *et al.* potential (solid line). The plots are shifted for clarity and represent (from top) the potential obtained by using the 9-6 LJ potential model for extrapolation of $S_0(k)$, the one obtained by using the 12-6 LJ, and the one obtained by using the Barker *et al.* potential model.

the experimental data at low-k values.

As a conclusion we can summarize the results of our analysis as follows.

(1) A pure two-body structure factor $S_0(k)$ which is related only to the pair potential can be derived from experiments in low-density gas phases.

(2) The high-k extrapolation procedure of the experimental $S_0(k)$, which is necessary in order to derive a $g_0(r)$ from the Fourier transformation, can be performed starting only from the experimental $S_0(k)$ data and a model form for a potential which is used for the extrapolation.

(3) When an iteration procedure is applied in order to derive $g_0(r)$ and $U(r)$ from $S_0(k)$, the final result for $U(r)$ in the region of the well is practically independent on the model form used for the potential from which we start the iteration, if the experimental $S_0(k)$ is extended towards sufficiently high-k values.

(4) We have shown that our procedure, when applied to the experimental $S_0(k)$ of krypton, gives a pair potential which agrees reasonably well with the one derived by Barker *et al.* from a large set of different physical quantities.

(5) The advantage of our method is that it does *not* depend upon either an assumed mathematical form for the potential or on fitting constants to experimental data. This is especially important over the intermediate range (4–8 Å) of r, where the long- and short-range expressions for $U(r)$ are joined together in the conventional method. It is not surprising, therefore, to find the largest relative discrepancy between our results and previous potentials over this range.

We conclude that the experimental determination of the structure factor in low-density gases and the analysis of its density behavior can become a new experimental method for the direct determination of pair potentials in atomic systems and isotropic "effective" pair potential for simple homonuclear molecules.

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