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Structure of krypton gas: Monte Carlo results, virial expansions, and real experimental data

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We have made Monte Carlo calculations of the pair correlation function $g(r)$ of a dense gas along the 297 K isotherm using a published pair potential for krypton. Eleven states were simulated, and then, using the pair potential plus the Axilrod-Teller triple-dipole potential, seven states were simulated. The effect of the triplet potential was very small except near the principal peak of $g(r)$. We compare, in real and Fourier space, these results to the virial expansion of $g(r)$ at low densities to test its range of validity. This work provided the background for the interpretation of the experimental data of Teitsma and Egelstaff on real krypton gas, and examples are given involving the extraction of the pair- and triplet-potential terms.

I. INTRODUCTION

The computer-simulation method has been used widely to study model fluids.[1] In this paper we report calculations of the pair-correlation function $g(r)$ for a dense gas as a function of density along an isotherm. This program had several empirical objectives, namely, to discover the useful range of the virial expansion[2] for $g(r)$ if it was cut off at several terms, and to investigate the effect of the long-range three-body (Axilrod-Teller[3]) potential on the short-range part of $g(r)$. In addition we have carried out parallel investigations in Fourier space in order to design diffraction experiments and to interpret experimental data.[4,5]

We have employed the krypton potential of Barker *et al.*,[6] but the difference between this potential and other possible choices[7,8] is not significant for our purposes. For later comparison with experiment[4,5] we chose an isotherm at 297 K and densities between 2 and 15×10^{27} atoms m^{-3} (the critical density of real krypton is 6.5×10^{27} atoms m^{-3}). This range covers the virial expansion region, densities comparable to the critical density, and a density range where hard-core interactions are important.

Section II outlines our Monte Carlo calculations and summarizes the data reduction. Sections III and IV compare the data with the virial expansions in real and Fourier space, and have provided the background against which the diffraction data on real krypton gas has been analyzed.[4,5] An example showing the extraction of the leading pair- and triplet-potential terms from the experimental data is discussed.

II. MONTE CARLO CALCULATIONS

The calculations using the pair potential were carried out with a 128-particle system located in a dodecahedral cell to minimize the excess volume.[9] An N.V.T. ensemble[1] and periodic boundary conditions were used, and the program was run on a Nova 2 minicomputer. The initial locations were on an fcc lattice; a run of $\sim10^5$ configurations being used to equilibrate them to the initial fluid configuration. For significant changes in density a short run of 10^4 configurations was made, starting from an acceptable configuration for the old density in order to find a starting configuration for the new density. Eleven states having densities between 2 and 15×10^{27} atoms m^{-3} (Table I) and a temperature of 297.5 K were simulated, using the pair potential of Barker *et al.*[6] Barker *et al.* deduced the constants in an empirical function for

TABLE I. Linear corrections applied to the first series of Monte Carlo calculations. The formula used was $g(r^*)=g(r^*)_{\mathrm{MC}}/(a+b\,r^*)$, where r^* was in reduced units of $r^*=1$ corresponding to $r=4.0067$ Å^{-1}.

ρ	a	b
2.0	0.993	−0.0038
3.0	0.992	−0.0045
4.0	0.991	−0.0051
5.0	0.992	−0.0056
6.0	0.995	−0.0061
7.0	0.997	−0.0065
8.0	0.999	−0.0069
9.0	1.002	−0.0073
10.0	1.003	−0.0077
12.5	1.007	−0.0086
15.0	1.008	−0.0094

the pair potential by fitting to all the experimental data on krypton available to them. The agreement between their results and those of others[7,8] tends to confirm that this potential is close to the real two-body potential. We refer to these as the first series of runs.

In a second series of runs at densities of 3, 4.5, 6, 8, 10, 12.5, and 15×10^{27} atoms m^{-3}, the Axilrod-Teller[3] potential was added to the potential of Barker *et al.* using their parameters (for $\rho=6$ we did a run at the beginning and another at the end of this series). For these calculations we used the N.V.T. ensemble, a dodecahedral cell and a 64-particle system, using a program written for an IBM 370 computer. The two- and three-body potentials are cut off at a distance r_m which represents the radius of the largest sphere which can be fitted inside the dodecahedral cell. For three-body potential runs a list of particles within r_m of particle i is kept to speed up the calculation of the three-body potential. Still, the three-body potential runs are about three times slower compared to two-body runs. At each density of this series two runs were made, one using the pair plus triplet potentials and one using the pair alone. The number of configurations run for each case was between 1 and 1.5×10^5, and the significant results are the differences between each pair of calculations in this series; that is, we use the second series to test for the changes caused by adding the Axilrod-Teller potential, and we use the first series for the best data on $g(r)$.

We observed that the oscillations in $g(r)$ were damped to a level comparable to the statistical fluctuations at $r\sim\frac{1}{2}$ (box size), except for $\rho\geq 10\times10^{27}$ atoms m^{-3}. The values of $g(r)$ were smoothed by fitting the function $y(r)$, where $y(r)=e^{\beta u(r)}g(r)$ and $u(r)$ is the pair potential, to an nth-order polynomial where n was chosen so that deviations from the polynomial were due to statistical fluctuations only. Two corrections were required to these data. First, for all runs except the final four of the second series, there was an error in the application of the periodic boundary conditions, which had the effect of delaying by one cycle the return of those particles which left by the corners of the dodecahedron. We believe this did not affect low values of r but led to a small depression in the values of $g(r)$ at large r; and we noted that the observed limiting value of $g(r)$ showed almost the same deviation from unity for all runs except the final four. Secondly, for an N.V.T. ensemble the limiting value of $g(r)$ at high r should be $(kT/N)\,(\partial\rho/\partial P)|_T$, where ρ and P are the number density and pressure, respectively. The value of the compressibility was taken from the virial series[10,11] for $\rho<4\times10^{-27}$ atoms m^{-2} and from real experimental data for krypton for larger values of ρ. We have assumed that the latter correction may be applied for all values of r, but that it is masked by the first correction at high r. Thus we combined both corrections into a factor $(a+br)$ which varied linearly with r, and chose the two parameters (a and b) by fitting to the first correction at high r and to the second correction at r corresponding to the major peak in $g(r)$. These coefficients are shown in Table I, for the first series of runs, and it can be seen that the parameters behave systematically and are close to their ideal values ($a=1$ and $b=0$).

Examples of the results obtained in this way are shown in Fig. 1, where data for $\rho=3$, 6, 8, and 10×10^{-27} atoms m^{-3} are plotted. The first series of runs are shown by the full lines, and when the differences observed in the second series of runs were added to these data we obtained the dashed lines (both lines are drawn by "eye" through the Monte Carlo points). We note that the average effect of the Axilrod-Teller term is "repulsive" and is largest near the major peak in $g(r)$ for $\rho\sim6\times10^{27}$ atoms m^{-3}. The maximum effect is only ~5%.

The maximum value of r was a function of density since N was fixed and the volume of the cell

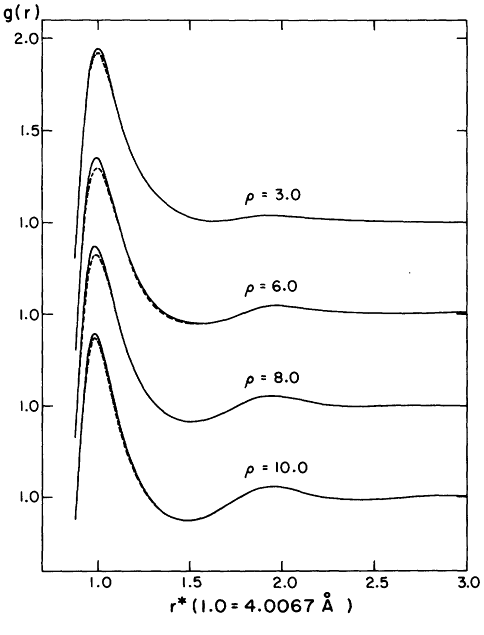

FIG. 1. Examples of the pair-distribution function $g(r)$ from the two series of calculations. The full lines are the series-one pair-potential calculation, and the dashed lines show the effect of adding the differences between calculations using pair and pair plus Axilrod-Teller potentials from series two. Results are shown for 3, 6, 8, and 10×10^{27} atoms m^{-3}.

was varied. Values of $g(r)$ larger than this limit were set to 1.0; an approximation which was good at low densities but poor at high densities. The resulting numerical functions were Fourier transformed to find the structure factor $S(Q)$, where

$$S(Q)=1+\rho\int e^{i\vec{Q}\cdot\vec{r}}[g(r)-1]d\vec{r}.$$

The numerical errors in the transformed data were estimated to be ~0.01 for $Q\sim 5\ \mathrm{nm}^{-1}$ and less at higher-Q values. Because of the small box size, data on $S(Q)$ for $Q<5\ \mathrm{nm}^{-1}$ were not reliable.

III. COMPARISON WITH A CUT-OFF VIRIAL EXPANSION IN *r* SPACE

The virial expansion for $g(r)$ in a system of particles interacting with a pair of potential $u(r)$ is

$$g(r)=f(r)+1 +\rho[f(r)+1]\int f(|\vec{r}-\vec{s}|)f(s)d\vec{s}+O(\rho^2), \tag{1}$$

where $f(r)=e^{-\beta u(r)}-1$. We shall write this series in the form

$$g(r)=\sum_{m=0}^{\infty}\rho^m g_m(r). \tag{2}$$

The terms up to $m=2$ have been evaluated by Groome[10] for the Barker *et al.*[6] potential. A comparison between the virial series cut off at $m=1$ and 2 with the $g(r)$ data for $\rho=2\text{–}6\times 10^{27}$ atoms m^{-3} is given in Fig. 2. It can be seen that the two-term virial series is satisfactory for densities $\leqslant 3$, and the three-term virial series is satisfactory for densities $\leqslant 4$ but becomes less satisfactory at $\rho=6$. At higher densities we noted significant deviations from the three-term virial.

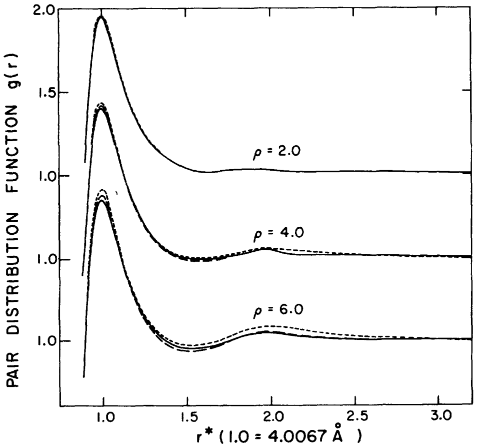

FIG. 2. Comparison of the Monte Carlo calculations to the virial expansion of $g(r)$ for two and three terms. The full line is the Monte Carlo calculation; the short dashed line is the virial expansion for two terms, and long dashes indicate the virial expansion for three terms.

If the Axilrod-Teller potential[3] is added to the system then terms $g_1(r)$ and higher must be modified. The correction to the $g_1(r)$ term, which we write as g_c, is

$$g_c(r)=\int[f(r)+1][f(s)+1] \times[f(|\vec{r}-\vec{s}|)+1]e^{-\beta u_3(\vec{r},\vec{s})}d\vec{s}, \tag{3}$$

where $u_3(\vec{r},\vec{s})$ is the three-body potential. This term, using the Axilrod-Teller potential, has been evaluated by Groome.[10] We compare it to the difference between the pairs of results from the second series of data in Fig. 3. Since the magnitude of this term, compared to the leading term of Eq. (2), is small at low ρ we observed only small differences, and because of poor statistics on these small differences we neglected the lowest two densities and have averaged the two

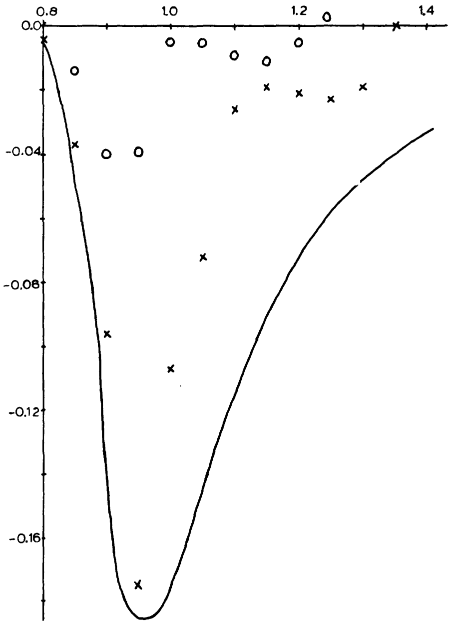

FIG. 3. Comparisons between the Axilrod-Teller term [Eq. (3)] given by the full line, and the differences $[\Delta g(r)/\rho]$ between the series-two calculations. The averages of three runs at $\rho=6$, 6, and 8×10^{27} atoms m^{-3} are shown by the crosses and the averages of three runs at $\rho=10$, 12.5, and 15×10^{27} atoms m^{-3} are shown by the open circles. The data taken at $\rho=3$ and 4.5×10^{27} atoms m^{-3} showed a small difference, with relatively large errors, which were enlarged when dividing out the factor ρ in the quantity $\Delta g(r)/\rho$. Thus these data were not meaningful and are not shown.

runs at $\rho = 6$ with the single run at $\rho = 8$ to give a mean at $\rho = 6.7$. Also we averaged the runs at $\rho = 10$, 12.5, and 15 to give a mean at $\rho = 12.5$. It can be seen from Fig. 3 that terms with $m > 1$ must reduce significantly the $g_c(r)$ term for $\rho = 12.5$, and some reduction occurs at higher r for $\rho = 6.7$. In addition, in order to extract the $g_c(r)$ term from experimental data it would be necessary to work with $\rho < 5 \times 10^{27}$ atoms m^{-3}.

IV. COMPARISON WITH VIRIAL EXPANSION IN FOURIER SPACE

In Fig. 4 we have plotted the results of Fourier transforming the pair distribution functions for the five densities (lettered a–e) 2, 3, 4, 5, and 6×10^{27} atoms m^{-3}. We see that the transform of the $g(r)$ virial series is inadequate for $\rho > 4 \times 10^{27}$ atoms m^{-3} for values of Q less than 0.8 Å^{-1}, as expected from the discussion of Fig. 2. Also shown on this figure, for the three densities 4, 5, and 6×10^{27} atoms m^{-1}, are $S(Q)$ values obtained through the virial series of the direct correlation function $c(Q)$:

$$S(Q) = 1/[1 - \rho c(Q)], \quad \text{with} \quad c(Q) = \sum_{m=0} \rho^m c_m(Q). \tag{4}$$

This series was truncated at $m = 1$, where

$$c_0(Q) = \int f(r) e^{i\vec{Q}\cdot\vec{r}} d\vec{r},$$

and

$$c_1(Q) = \int\int f(r) f(s) f(|\vec{r} - \vec{s}|) e^{i\vec{Q}\cdot\vec{r}} d\vec{s}\, d\vec{r}.$$

[The three-body correction to $c_1(Q)$ is given by the Fourier transform of Eq. (3).] These two functions were computed for two model potentials[6,7] by Wertheim,[11] and it can be seen that they fit $S(Q)$ reasonably well over the range shown in the figure. For $Q > 2.5$ Å^{-1} only the $c_0(Q)$ term was found to be significant.

To demonstrate the density range over which Eq. (4) and the Monte Carlo results are in agreement, we show in Fig. 5, the variation of $c(Q)$ with density for several values of Q. The full line corresponds to the potential of Barker *et al.*,[6] but if the Aziz potential[7] is used, only minor changes are found. For $\rho < 5 \times 10^{27}$ atoms m^{-3} the data lie along the line within the errors shown but fall away at higher ρ especially for the lower-Q values. The function shown by the full line in Fig. 3 has been Fourier transformed yielding a curve which has a maximum at $Q = 0$, and which falls to about $\frac{1}{10}$ of the maximum value at $Q = 0.56$ and passes through zero at 0.65 Å^{-1}. These data give the change of slope expected from the Axilrod-Teller term, and for $Q = 0.5$ Å^{-1} we show by the dashed line, the effect of adding this term to Wertheim's[11] results for $c(Q)$. The series-two Monte Carlo data are consistent with the new slope for $\rho < 5 \times 10^{27}$ atoms m^{-3} although the precision is worse by a factor of 2 than the series-one comparison.

The experimental results for real krypton[5] are shown by the circles in Fig. 5, and their errors are similar to those of the series-one Monte Carlo data. It is clear that for several of the cases shown these data do not agree with the

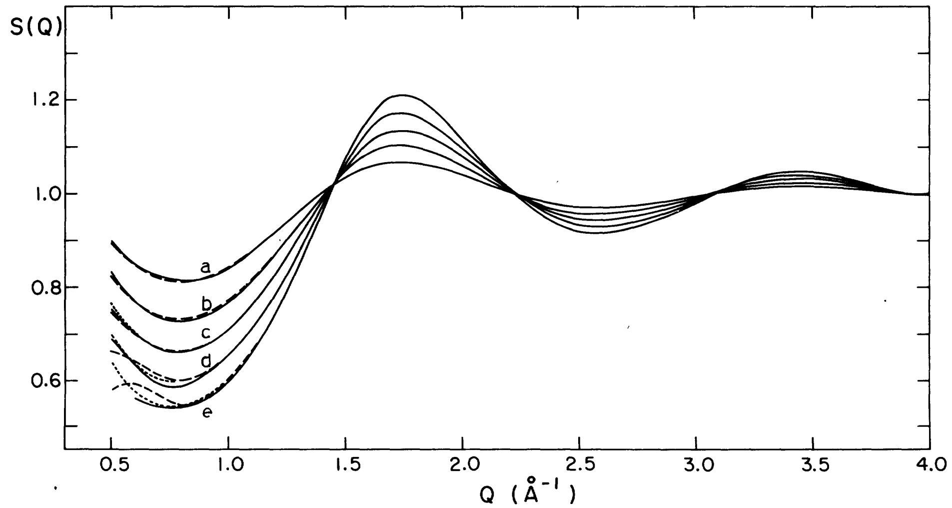

FIG. 4. The structure factors obtained from Fourier transforming the pair-distribution-function calculations obtained from the Monte Carlo calculations (because of the small box size the data are valid for $Q > 0.5$ Å^{-1} only). Also shown are the results of transforming the virial expansion of $g(r)$ (dashed lines) and results of calculating the first two terms of $c(Q)$ (dotted lines).

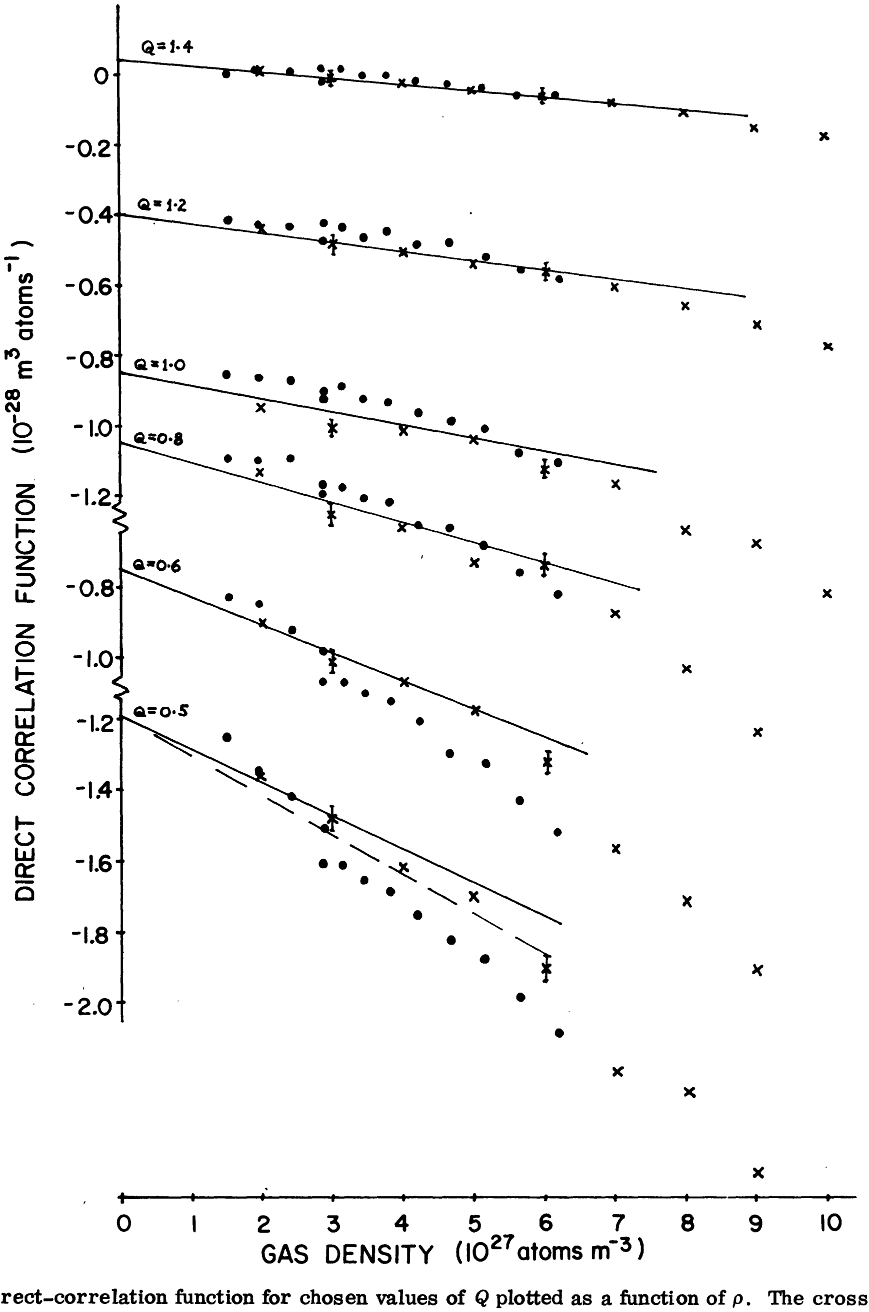

FIG. 5. The direct-correlation function for chosen values of Q plotted as a function of ρ. The crosses are the Monte Carlo data and the circles are the experimental results, with error bars corresponding to an error of ± 0.005 in $S(Q)$. The full line is the expression $c_0(Q)+\rho c_1(Q)$ and the dashed line for $Q=0.5$ Å^{-1} is this expression plus the Axilrod-Teller term (obtained from the Fourier transform of the full line in Fig. 3).

Monte Carlo data, even after the Axilrod-Teller term has been included. Experimental intercepts at $\rho \rightarrow 0$ were obtained by extrapolation over the linear range (defined above) and are shown in Fig. 6 as a function of Q. They are close to the predictions of either the Aziz[7] or Barker *et al.*[6] potentials, but significant differences are seen especially for Q values near 0.7 Å^{-1}. These may arise through the inability of the analytic representations of $u(r)$ to cover adequately the merging of an r^{-n} expansion, valid at large r, into another function at $r \sim 6$ Å. The slopes of the experimenal data give the transform of Eq. (3) and have been discussed in Ref. 5. Since they differ from the slopes obtained above there must be a significant contribution from shorter-ranged three-body forces,

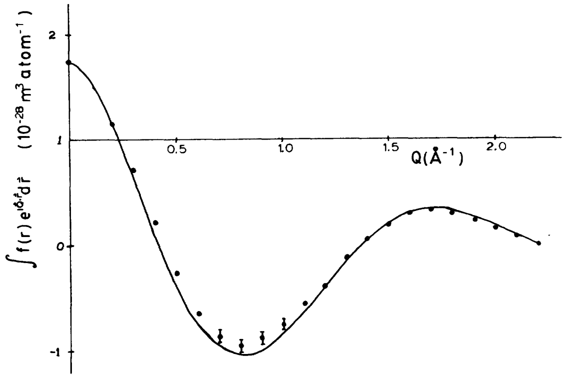

FIG. 6. The Fourier transform of the Mayer $f(r)$ function for krypton at room temperature. The experimental points were obtained by extrapolating the neutron diffraction data (Ref. 5) to $\rho \rightarrow 0$, and the line was calculated using the Aziz potential.

especially for $Q \sim 0.7$ Å^{-1}.

We have noticed that the Monte Carlo data for $c(Q)$ are linear in ρ to $\rho > 10 \times 10^{27}$ atoms m^{-3} for $Q > 1.5$ Å^{-1}, and that for $Q > 2$ Å^{-1} they are almost independent of ρ. The departures from linearity between $\rho = 5$ and 10, are most noticeable at the principal minimum of $S(Q)$ where $|S(Q) - 1|$ is large.

The Monte Carlo structure factors at densities of 5, 8, 10, 12.5, and 15×10^{27} atoms m^{-3} are shown in Fig. 7. At the highest density the truncation of $g(r) - 1$ is expected to give rise to significant errors, the effect of which can be observed near $Q = 2.5$ Å^{-1}. In this density range the major peak in $S(Q)$ shifts to higher Q, in contrast to lower densities (Fig. 4) where its location is constant. This is due to the movement of the peak in $g(r)$ to smaller r corresponding to the onset of "liquidlike" behavior.

V. SUMMARY

We have made Monte Carlo simulations of a system of atoms at room temperature interacting with the krypton pair potential, and the Axilrod-Teller triple-dipole potential. The object has been to provide data against which to test virial expansions of the pair-correlation function, to determine the magnitude of the triple-dipole contribution to $g(r)$ and $c(Q)$ and to interpret experimental structure factor data.

The triple-dipole term lowers the major peak in $g(r)$, and for low densities this effect is a few percent of the peak value. At higher densities it has a relatively smaller effect. In Fourier space it gives a significant contribution at $Q = 0$ but this falls away rapidly with increasing Q and is difficult to detect at the Q values at which good Monte-Carlo data were obtained by us.

We have found that a three-term virial series for $g(r)$ works quite well for densities below 4×10^{27} atoms m^{-3} but is poor at higher density. In addition, we examined numerical calculations of the structure factor obtained from Fourier, transforming the sum of the first three terms of Eq. (2), or using Eq. (4) for the direct-correlation function. A comparison of Monte Carlo data and the expansions confirmed that (4) is more satisfactory as expected. It is illuminating to compare the conclusions drawn from Figs. 2 and 4 for

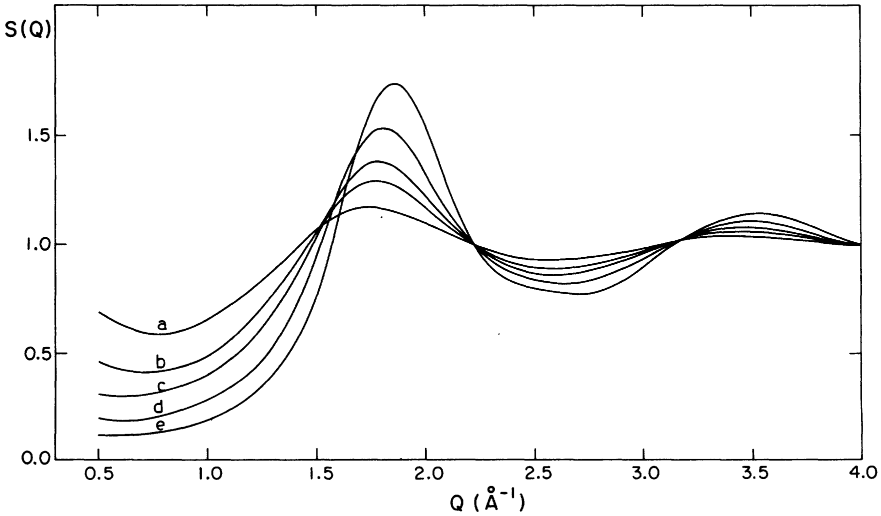

FIG. 7. The structure factor from the series-one data for densities 5, 8, 10, 12.5, and 15×10^{27} atoms m^{-3} labeled a, b, c, d, and e, respectively. The truncation of $g(r)$ by the finite box size has an increasing effect as ρ is increased and probably accounts for the anomalous shape near $Q = 2.5$ Å^{-1}.

$\rho = 6$, since the errors in $g(r)$ accumulate at the lower-Q range in $S(Q)$.

The above data were used to show that the direct-correlation function over a Q range of interest in a diffraction experiment is linear in ρ for densities extending up to 5×10^{27} atoms m^{-3}, to within the precision of the Monte Carlo data. This is an important conclusion which has already been used in the interpretation of diffraction data[4,5] and was used here to extract the transform of the Mayer function from the experimental data. Also we have shown that for any of our densities a simple virial expansion of $c(Q)$, using only the leading term in Eq. (4) works satisfactorily at high Q. The work reported in this paper is an example of the way the Monte Carlo technique for the study of the structure of fluids can be used to design and interpret real experiments on a dense gas.

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