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Structure of gaseous Kr in the low-q region by neutron scattering and interaction potentials

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Accurate experimental information on the long-range triplet interactions in noble fluids, as well as on the two-body potential, can be obtained from the low-density behavior of the static structure factor $S(q)$ in the small-q region. The results here reported of a recent low-q neutron diffraction investigation in Kr, devoted to undercritical densities in the range $2.4 < n/\mathrm{nm}^{-3} < 4.3$, provide important indications on the pair interactions and allow also a reliable analysis of irreducible three-body potential effects on the measured structure, from which the triple-dipole Axilrod-Teller strength is extracted with unprecedented accuracy.
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I. INTRODUCTION

Neutron diffraction measurements have turned out to be quite effective in determining the pair interaction law in low-density gases [1–4]. In the last few years neutron experiments have been extended to small-angle investigations to study two- and three-body dispersion forces in classical monatomic fluids [5–8], taking advantage of the connection between the low-q behavior of the static structure factor $S(q)$ and the long-range interactions. In particular, a special feature of $S(q)$, namely, the q^3 term in its low-q expansion [9–11], allows a direct experimental access to the long-range pair and triplet dipolar interactions in noble fluids.

Small-q ($1 < q/\mathrm{nm}^{-1} < 4$) neutron diffraction on low-density ($n < 2.5\,\mathrm{nm}^{-3}$) Ar, Kr, and Xe was then profitably employed to measure the dipole-dipole van der Waals constant C_6 of these systems [5–7], and also provided the first determination of the triple-dipole Axilrod-Teller (AT) forces in Xe [7]. Conversely, the weak intensity of three-body long-range interactions in less polarizable systems, such as Ar and Kr, could not be extracted from the cubic low-q dependence of the first available $S(q)$ data in the dilute gas phase [5,6].

In the case of Kr, it was proved very recently that the strength ν of the AT potential can indeed be measured by the above method if small-q structure factor determinations are performed in a wide density range [12], varying from the dilute gas up to liquid densities. However such a direct access to the AT interaction is generally affected by considerable experimental uncertainties (more than 50%), both because the q^3 term gives a very weak contribution to the measured low-q structure and because few densities have been studied so far by small-angle investigations in noble systems, especially in the dense fluid region.

Actually, a different method to derive much more accurate experimental estimates of the AT dispersion energy of simple fluids exists, and it is based on the density analysis of the total $S(q)$ of dilute gases at small q values. Its application to the low-density Kr data previously mentioned [6] allowed the first determination of the AT triple-dipole interaction constant for this system, providing a ν value with about 20% experimental uncertainty [8].

However, such a method requires the use of a model for the total pair potential, and its overall accuracy critically depends on the agreement between the experimental two-body properties of the fluid and the model assumed. In this respect, no clear indications have ever been obtained either from wide- [13] or small-angle [8] neutron data on the structure of low-density Kr. For instance, in the case of the first low-q results [8], only partial agreement was found between the experimental pure two-body structural quantities and the descriptions provided by the best available realistic models for the pair potential of Kr (some deviation being observed for $q > 2\ \mathrm{nm}^{-1}$), while in the case of the pioneering neutron experiment of Teitsma and Egelstaff on Kr [13] discussion on this important aspect was not quantitatively deepened.

In this paper we describe in detail low-density Kr data, which were already used and briefly discussed in Ref. [12], obtained from a recent low-q neutron diffraction measurement. In particular, the virial expansion (to first order in density) of the experimental $S(q)$ is determined here and a careful analysis is performed, aimed both at gaining valuable experimental information on the pair potential and at achieving a much more accurate determination of the AT contribution to the total interaction.

The opportunity was also taken to compensate partly for the lack of information on the low-q structure of Kr by devoting our measurements to higher undercritical densities, unexplored so far by small-angle diffraction, and by covering a slightly wider q range (up to 5.5 nm^{-1}). Five thermodynamic states of natural Kr were studied at room temperature and densities in the range $2.4 < n/\mathrm{nm}^{-3} < 4.3$, reproducing some of the states Teitsma and Egelstaff [13] investigated by standard neutron diffraction at higher q values. We tried to improve the overall quality of the data, not only by increasing the count statistics, but also by adopting new accurate experimental techniques, such as the use of dilute hydrogen as a reference sample for normalization purposes.

The paper is organized as follows. Section II summarizes the theoretical background. In Sec. III the experimental setup is described in some detail, while Sec. IV is devoted to the data treatment. The results of this experiment are discussed in Sec. V and, finally, in Sec. VI we draw our conclusions.

II. REVIEW OF THE THEORY

Interaction properties in monatomic fluids can be studied through accurate determinations of the static structure factor $S(q)$. In fact $S(q)$ is related, via Fourier transformation, to the pair distribution function $g(r)$,

$$S(q) = 1 + n \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}[g(r) - 1], \tag{1}$$

which, in turn, depends on the interaction potential in a fluid composed of N particles:

$$V(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \sum_{i<j} V_2(r_{ij}) + \sum_{i<j<k} V_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) + \cdots,$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|, \tag{2}$$

where V_2 is the (central) pair potential, V_3 the irreducible three-body potential and $\mathbf{r}_i$ is the position vector of atom i. In what follows we shall neglect fourth- and higher-order many-body terms.

Another important quantity in the theory of fluids is the direct correlation function $c(r)$, related to the total correlation function $h(r)$ through the Ornstein-Zernike equation

$$h(r) = g(r) - 1 = c(r) + n \int d\mathbf{r}'\, c(r')\, h(|\mathbf{r} - \mathbf{r}'|) \tag{3}$$

whose Fourier transform is $H(q) = [S(q) - 1]/n = c(q) + nc(q)H(q)$, and leads to

$$c(q) = \frac{1}{n}\left[1 - \frac{1}{S(q)}\right]. \tag{4}$$

Both the total and the direct correlation functions are related to the thermodynamic properties of the fluid. For instance, the well-known compressibility equation

$$\frac{n\chi_T}{\beta} = 1 + n \int d\mathbf{r}\, h(r) = S(0) \tag{5}$$

links the isothermal compressibility χ_T to $S(q=0)$. In Eq. (5) $\beta = 1/(k_B T)$, where T is the temperature of the fluid and k_B is the Boltzmann constant.

Several methods provide useful information on the interaction law starting from structural data. The one we deal with in this paper is based on the density behavior of $S(q)$ in dilute gases, which has been profitably used in the past to obtain important indications on the two-body interactions in classical [1–3] and quantum fluids [4], as well as about three-body effects in noble gases [13–16].

It is well known [17,18] that density expansions analogous to the virial series for the pressure p hold for all the correlation functions previously introduced and for their Fourier transforms. Particularly useful to our purposes is the low-density behavior of $c(q)$, which can be written as

$$c(q) = c_0(q) + nc_1(q) + O(n^2), \tag{6}$$

where the zero-density term $c_0(q)$ depends only on V_2, since

$$c_0(q) = \int d\mathbf{r}\, \exp(i\mathbf{q}\cdot\mathbf{r})\{\exp[-\beta V_2(r)] - 1\}, \tag{7}$$

while the first-order term $c_1(q)$ can be split in two contributions $c_1^{(2)}(q) + c_1^{(3)}(q)$, the latter depending also on V_3, according to

$$c_1^{(2)}(q) = \int d\mathbf{r}_{12}\, d\mathbf{r}_{13}\, \exp(i\mathbf{q}\cdot\mathbf{r}_{12}) f_{12} f_{13} f_{23},$$

$$c_1^{(3)}(q) = \int d\mathbf{r}_{12}\, d\mathbf{r}_{13}\, \exp(i\mathbf{q}\cdot\mathbf{r}_{12})(1 + f_{12})(1 + f_{13}) \times (1 + f_{23}) f_{123} \tag{8}$$

where $f_{ij} = \exp[-\beta V_2(r_{ij})] - 1$ is the Mayer function and $f_{123} = \exp[-\beta V_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)] - 1$.

It is useful to note that the experimentally accessible quantity $S(q)$, as well as the derived quantity $c(q)$, probe two-body correlations. If irreducible three-body forces are also present, obviously $S(q)$ and $c(q)$ measure pair correlations which depend on the features of the triplet potential too, as expressed, to first order in density, by the second relation in Eqs. (8).

It is also clear, from Eqs. (7) and (8), that reliable models for the pair and the triplet potentials can be used to calculate c_0 and c_1. On the other hand, isothermal structure factor measurements, if performed at densities low enough so that n^2 and higher-order terms are negligible in Eq. (6), provide, through a linear density fit to $c(q)$, an experimental determination of c_0 and c_1. The comparison between calculated and experimental quantities thus allows a stringent test on the pair and triplet potential models assumed.

The effects of nonadditive three-body interactions on fluid structure are known to be considerable especially in the low-q region [14–16]. Therefore, the experimental behavior of $c_1(q)$ at small q values ($q \lesssim 5\ \mathrm{nm}^{-1}$) gives important information about the role played by triplet forces and on the adequacy of the model typically assumed to describe them, i.e. the AT triple-dipole interaction [19]

TABLE I. Thermodynamical coordinates of the Kr states considered in this work according to the equation of state of Ref. [22]. $S(0)$ values, as obtained from compressibility calculations [see Eq. (5)] are also shown.

State No.	T (K)	p (bar)	n (nm^{-3})	$S(0)$
1	300.4 ± 0.09	84.04 ± 0.04	2.4214 ± 0.0003	1.42
2	298 ± 1	95.8 ± 0.7	2.875 ± 0.002	1.49
3	297 ± 1	111.1 ± 0.9	3.455 ± 0.003	1.55
4	297 ± 1	121.1 ± 0.9	3.847 ± 0.002	1.58
5	297.2 ± 0.5	132.5 ± 0.5	4.277 ± 0.002	1.59

$$V_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \nu \frac{1+3\cos\theta_1\cos\theta_2\cos\theta_3}{(r_{12}r_{23}r_{13})^3}, \tag{9}$$

where the angles θ_i and the sides r_{ij} define the triangle formed by the three particles and the strength ν depends on the system in consideration. Computational methods based on dynamic polarizability evaluations have been developed to obtain numerical results for the interaction constant ν of various systems [20]. These estimates are often referred to as ‘‘semiempirical,’’ since the dynamic dipole polarizability obtained from index of refraction data is used to calculate ν.

III. EXPERIMENTAL DETAILS

The experiment was carried out at the Orphée reactor of Laboratoire Léon Brillouin, Saclay, using the small-angle diffractometer PAXE with a monochromatic neutron beam of wavelength $\lambda_0 = 0.4\,\mathrm{nm}$. The latter is the shortest wavelength that can be selected on PAXE, and it was chosen both to minimize neutron absorption from natural Kr and to exploit the instrument maximum flux. The width of the wavelength distribution around the chosen value is estimated to be about 10% of λ_0. However, the consequent limited resolution in q has negligible effect in our case, since $S(q)$ is a slowly decreasing function at small q values.

The incident beam, of circular shape, was defined by means of a cadmium diaphragm of 0.9-cm diameter, suited to the sample container dimensions. The latter is the same slab container, with single-crystal sapphire windows, used in a recent experiment on dilute Kr [6,8] and was kindly provided by the IRI [21] neutron group. The sample (whose shape is a truncated cone of 3.48-cm height) was positioned with its central axis along the incident neutron beam. To take advantage of a completely symmetrical configuration, the $^{10}BF_3$ detector (a square matrix of 64×64 cells, $1 \times 1\,\mathrm{cm}^2$ each) was centered on the transmitted beam. A sample-detector distance of 99.5 cm was chosen. As a result of the above setup, the explored q range was $0.8 < q/\mathrm{nm}^{-1} < 5.5$.

A capillary tube, screwed to the container, was connected through a high-pressure gas-handling system to the sample gas bottle in order to fill the container at the desired pressure. The five thermodynamic states of natural Kr (pure within 99.995%) studied at room temperature are reported in Table I, together with the corresponding $S(0)$ values obtained from the isothermal compressibilities [see Eq. (5)]. The equation-of-state data of Jůza and Šifner [22] were used to calculate $S(0)$ and the number density of each state, taking into account temperature and pressure fluctuations to evaluate the uncertainties. States are labeled as shown in the first column.

To extract the structure factor from diffraction data, additional measurements for background evaluation and for instrumental calibration need to be performed. The former requires empty beam, empty container, and cadmium-covered container measurements, while the latter is discussed in the subsection below. The counting time for each of these measurements was adjusted (according to scattering power and absorption calculations) in order to obtain comparable errors on all the experimental $c(q)$'s, almost independently of the density. An exception is made for state No. 1 in Table I, whose short measurement was performed as a check against the previous low-q experiment on Kr [6,8].

A new normalization standard: H_2

The relation between $S(q)$ and the single scattering intensity from the sample, $I_s^{(1)}$, can be written as

$$I_s^{(1)}(q) = NF(q)\left[\frac{\sigma_{\mathrm{coh}}}{4\pi}S(q) + \frac{\sigma_{\mathrm{inc}}}{4\pi} + P(q)\right], \tag{10}$$

where N is the number of atoms exposed to the beam, σ_{coh} and σ_{inc} are the coherent and incoherent scattering cross sections, respectively, $P(q)$ represents the inelastic scattering contribution (in units of barn/sr), and $F(q) = \Phi\Delta\Omega\varepsilon(k_0)$ is an instrumental factor, depending on incident flux Φ, solid angle $\Delta\Omega$, and detector efficiency at the incident neutron wave vector $\varepsilon(k_0)$. It is clear from Eq. (10) that the determination of $F(q)$ allows instrumental calibration and data normalization to absolute units. This important step in the data treatment usually requires an extra measurement on a reference incoherent sample, such as vanadium or water. However, the unavoidable differences in the geometry between fluid samples and such standards can lead to severe normalization errors.

Recently low-density CH_4 was used as a new reference sample for normalization purposes [8,23], both because the double differential cross section for methane (when close to perfect gas conditions) can be computed rather well and because hydrogen is a strongly incoherent neutron scatterer. The great advantage with such a gaseous standard is that the same container can be used both for the sample and for CH_4, thus leaving the geometry unchanged.

In this respect, however, another, even better, calibration sample is dilute hydrogen. In fact, its double differential cross section can be calculated exactly (to the extent that vibration-rotation coupling can be neglected) developing the quantum-mechanical model for a diatomic ideal gas of freely rotating harmonic oscillators [24–26]. Moreover, for a given number of H atoms, low-density hydrogen [27] is closer to ideal gas conditions than methane [28]. Hydrogen has thus been used as a reference sample, at the very low density of $n = 0.0979\,\mathrm{nm}^{-3}$.

Since the single scattering intensity from H_2 can be written as

$$I^{(1)}_{\mathrm{H}_2}(q)=F(q)N_{\mathrm{H}_2}\int_{-\infty}^{\omega_0}d\omega\,\frac{\varepsilon(k_1)}{\varepsilon(k_0)}\frac{d^2\sigma}{d\Omega\,d\omega}\bigg|_{\mathrm{H}_2}, \qquad (11)$$

the instrumental factor $F(q)$ follows immediately from the measured intensity with the hydrogen sample (once corrected for attenuation and multiple scattering) and from the frequency integration, at constant scattering angle, of the model for the double differential cross section of hydrogen.

IV. DATA TREATMENT

To extract the single scattering intensity from the raw neutron data, corrections for background, container scattering, attenuation effects and multiple scattering are required. Taking all these corrections into account, $I_s^{(1)}$ can be expressed in terms of the experimental quantities as [8]

$$I_s^{(1)}=\frac{I_{\mathrm{sc}}^{\mathrm{expt}}-I_{\mathrm{Cd}}-T_{\mathrm{sc}}(I_{\mathrm{eb}}-I_{\mathrm{Cd}})-\dfrac{A_{c,\mathrm{sc}}}{A_{\mathrm{c,c}}}[I_{\mathrm{c}}^{\mathrm{expt}}-I_{\mathrm{Cd}}-T_c(I_{\mathrm{eb}}-I_{\mathrm{Cd}})]}{A_{s,\mathrm{sc}}(1+m_s)} \qquad (12)$$

where the dependence on the scattering angle has been omitted and the subscript to the intensities I refers to the sample + container (sc) or to the empty container (c) or to the cadmium-covered container (Cd) or, finally, to the empty-beam (eb) runs. The same meaning have the subscripts to the transmission T factors, the latter accounting for the background neutrons attenuation.

The attenuation from sample and container is taken into account by the well known Paalman-Pings coefficients $A_{\alpha,\beta}$, with α denoting where scattering takes place and β indicating where attenuation occurs. Their angular dependence is typically weak, even more at small angles and in narrow angular ranges, and was negligible in our case.

The fraction of multiple to single scattering from the sample, m_s, has been evaluated, in the isotropic approximation, by calculating the double-to-single intensity ratio through multidimensional Monte Carlo integrations and using the Sears formula [29]. The values obtained for m_{s} were found to range from 2.5% to 4% with increasing density.

Using Eqs. (10)–(12), $S(q)$ can be obtained, provided the inelastic scattering contribution $P(q)$ is evaluated. To perform this last correction we assumed the ideal gas (i.g.) model and calculated $P(q)$ as:

$$P(q)=\frac{1}{\varepsilon(k_0)}\int_{-\infty}^{\omega_0}d\omega\,\varepsilon(k_1)\,\frac{d^2\sigma}{d\Omega\,d\omega}\bigg|_{\mathrm{i.g.}}-\frac{\sigma_{\mathrm{scat}}}{4\pi}, \qquad (13)$$

where $\sigma_{\mathrm{scat}}=\sigma_{\mathrm{coh}}+\sigma_{\mathrm{inc}}=7.68\,\mathrm{b}$ is the total scattering cross section of Kr [30]. Since Kr is a relatively heavy element, this correction turned out to be quite small (less than 0.022 b/sr), as expected. However, it is of the same order of magnitude of $\sigma_{\mathrm{inc}}/(4\pi)$, where $\sigma_{\mathrm{inc}}=0.2\,\mathrm{b}$ is the incoherent cross section of Kr (see, for example, Ref. [13]).

The structure factors thus obtained are shown in Fig. 1, with the labeling of Table I. Error bars are smaller than the size of the symbols. The average relative error is about 0.3% for each state. The agreement with thermodynamical data at $q=0$ is qualitatively good. However a closer inspection can be performed, taking advantage of the small-q behavior of the structure factor of simple liquids [9,11] experimentally confirmed in Refs. [5–7,12]. Thus by fitting the model function $S(q)=s_0+s_2q^2+s_3q^3+s_4q^4$ to the measured $S(q)$, an "experimental" $S(0)$ value s_0, could be derived and compared with the thermodynamical one (Table I) at each density. A ratio $s_0/S(0)$ ranging from 0.96 to 0.97 was found for the various states, with no evident correlation with density. In order to remove even these small differences, a final correction on the measured $S(q)$ was performed using the renormalization factors $S(0)/s_0$.

From these renormalized structure factors we derived, through Eq. (4), the corresponding $c(q)$'s shown in Fig. 2. Here the results are compared with calculations [to first order in density, see Eqs. (6)–(8)] based on model potentials. In particular, the two-body Hartree-Fock dispersion [31] potential of Aziz and Slaman [32], which is known to be an accurate model for pair interactions in Kr [14], and the AT triplet potential of amplitude $\nu=2.22\times10^{-26}\,\mathrm{J\,nm}^9$, the latter being a weighted mean of the semiempirical estimates for this constant in Kr [20], were taken. The data for state 1 agree quite well with those of the previous low-density experiment on Kr [6,8], also shown in the plot. Good overall agreement is found between data and calculations. Generally speaking, this indication is not enough to assess the validity of the model potentials used in the calculations. In fact, the total $c(q)$ is not particularly sensitive to the interaction details, since it represents a com-

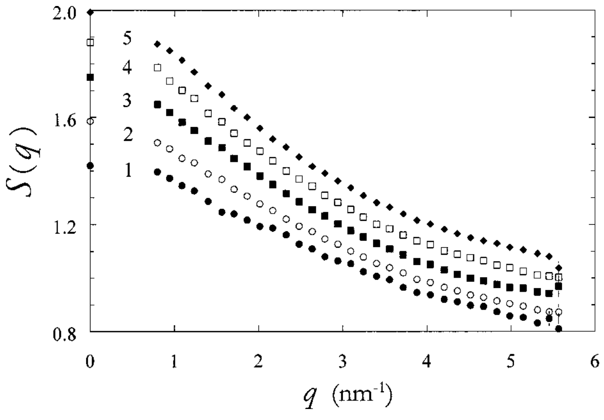

FIG. 1. Experimental structure factor $S(q)$ for the five densities of Table I. Data for states 2–5 have been shifted upwards by 0.1, 0.2, 0.3, and 0.4, respectively. The corresponding thermodynamical $S(0)$ values [22], shifted by the same amounts, are also shown.

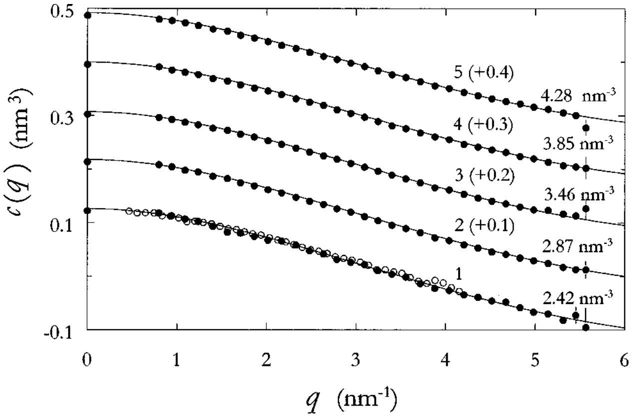

FIG. 2. Experimental $c(q)$ (dots with error bars) for the five states of Kr studied in this work, shifted by the amounts shown in brackets. The density of each state is also reported. Data are compared with the corresponding quantities as calculated from Eqs. (6)–(8) (solid curves) using the pair potential of Ref. [32] plus the AT three-body interaction with the average literature amplitude $\nu = 2.22 \times 10^{-26}$ J nm^9 [20]. The data for state 1 obtained from the only previous experiment on the low-q structure of Kr [6,8] are also shown (open circles). Data at $q=0$ are thermodynamical values [22].

bination of two- and many-body effects. To obtain reliable information on pair and triplet interactions one must refer to the single quantities $c_0(q)$ and $c_1(q)$, which are discussed in Sec. V.

V. RESULTS AND DISCUSSION

A. Density analysis

The density dependence of the experimental $c(q)$, at various q values, is shown in Fig. 3, together with the least-squares fit lines. The $q=0$ values, as obtained from the *PVT* data of Jůza and Šifner [22] are also reported with different symbols. The errors on $c(0)$ were estimated (0.45% on average in the density range here considered) on the basis of the equation-of-state accuracy and are much smaller than the size of the symbols. Both structural and thermodynamical data show a linear behavior in density. The absence of n^2 and higher-order terms excludes higher than three-body contributions within the experimental uncertainties. Therefore, in the density range considered here, $c_0(q)$ and $c_1(q)$ can be determined from the intercept and the slope of each regression line [see Eq. (6)] and the results are shown in Figs. 4 and 5, compared with the calculated quantities.

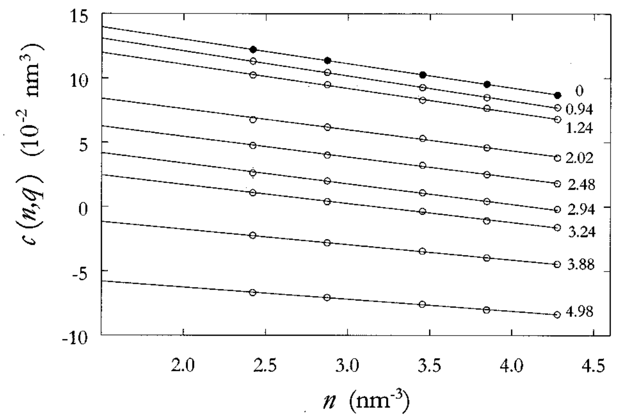

FIG. 3. Density behavior of the experimental $c(q)$ (open circles with error bars) at some of the investigated q values, specified in the plot (nm^{-1}). The thermodynamical [22] $c(0)$ data are also reported (dots) as a function of density. The solid lines represent the least squares linear fits to the data according to Eq. (6).

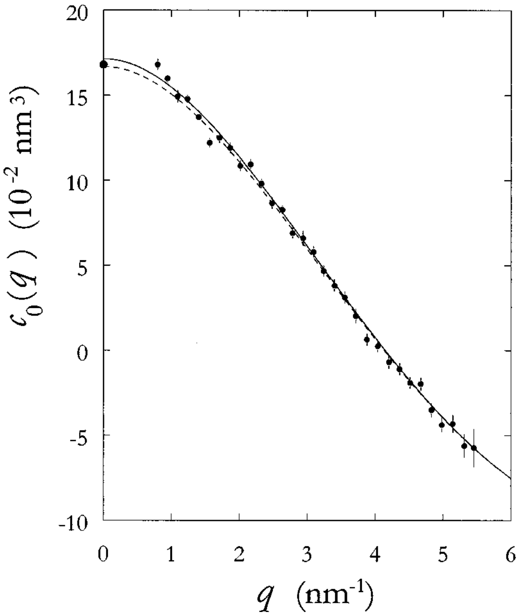

FIG. 4. Experimental $c_0(q)$ (dots with error bars), as obtained from the various intercepts of the density fits to the measured $c(q)$'s. Calculations [see Eq. (7)] with the pair potential models of Refs. [32] (solid curve) or [33] (dashed curve) are compared to the data.

The pair potential of Ref. [32] reproduces a pure two-body property like $c_0(q)$ remarkably well. In the whole q range covered in this low-q investigation, no deviation is observed from the calculated shape, not even at higher q values, as was found in [8]. This might be due to the different calibration samples used in the two experiments, and to a different accuracy in the modeling of the respective double differential cross sections.

The calculation based on another realistic potential for the two-body interactions in Kr, i.e., the well-known one of Barker *et al.* [33], gives a similarly very good description of the experimental $c_0(q)$ and is in better agreement with thermodynamics $(q=0)$, though the mean square deviation from the structural data was found to be slightly higher than for the result of Ref. [32], therefore, we shall mainly refer to the latter hereinafter.

As it is clear from Fig. 5, pair interactions alone cannot account for the experimental behavior of $c_1(q)$, which can be explained only including irreducible three-body interactions too. An additional triplet potential of the AT type gives a good description of the experimental data for $c_1(q)$, though calculations slightly miss the thermodynamical $(q=0)$ value. However, this small difference between thermodynamics and calculations appears to be independent of the pair potential assumed since, for instance, the models of Refs. [32] and [33] give equal results for $c_1^{(2)}(q)$ to within 0.2% at most, and calculations of $c_1^{(3)}(q)$ are found to be

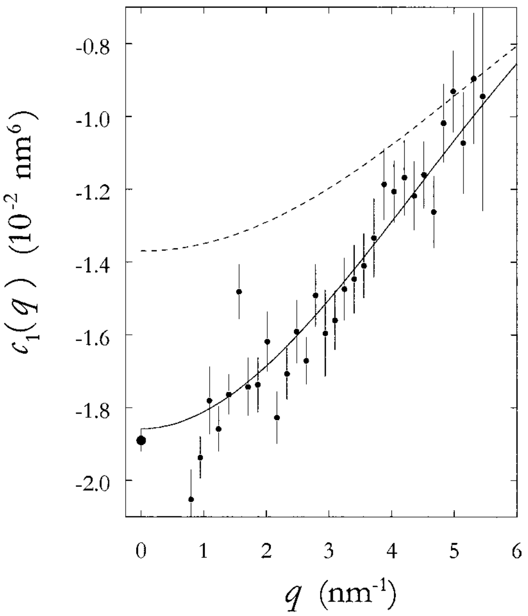

FIG. 5. Experimental $c_1(q)$ (dots with error bars), as obtained from the slopes of the linear density fits, compared with calculations [see Eq. (8)] performed using the pair potential of Ref. [32] and with (solid curve) or without (dashed curve) irreducible three-body AT interactions of amplitude $\nu = 2.22\times 10^{-26}\,\mathrm{J\,nm}^9$ [20]. Equal results for $c_1(q)$ and $c_1^{(2)}(q)$ are obtained by modeling the two-body interactions with Barker *et al.*'s [33] potential.

even less sensitive to the two-body potential used, as already observed in Ref. [14], and for this reason, the results of Refs. [32] and [33] are undistinguishable on the scale of Fig. 5. Therefore, only the features of the triplet interaction seem to have, through $c_1^{(3)}(q)$, a decisive influence on the resulting $c_1(q)$ in the low-q region.

It is worth noting that, since the linear density term in Eq. (6) is quite a bit smaller than $c_0(q)$, precise experimental determinations of $c_1(q)$ by means of a fitting procedure generally require extremely accurate structural data. This problem has prevented one, so far, from obtaining for most systems [3,8,15,16], quantitative information on three-body forces directly from the experimental behavior of $c_1(q)$, even when the most appropriate q region to detect triplet potential effects (i.e., the low-q one) was probed in detail, as it was done for Kr in Ref. [8]. The situation appears to be different with the present small-q results on Kr (Fig. 5), which show a rather good accuracy, and whose nearly regular trend can indeed be taken as an indication of the high quality of our data.

B. Accurate determination of Axilrod-Teller triple-dipole forces

In Sec. V A, clear evidence was obtained of the validity of the pair potentials of Refs. [32] and [33] in reproducing the experimental pure two-body correlations in the fluid, together with a first indication of the overall adequacy of the AT triplet potential to explain the observed three-body interaction effects on the measured structure. The important information gained on the pair interactions allows a further analysis on three-body interactions in Kr, since one of the above two-body models can rightly be used to isolate $c_1^{(3)}(q)$, i.e., the quantity depending on the irreducible triplet potential, from the experimental $c(q)$. For instance, an "experimental" $c_1^{(3)}(q)$ can be determined from the data, as was done in Ref. [8], through

$$c_1^{(3),\mathrm{expt}}(q) = \frac{1}{n}\left[c^{\mathrm{expt}}(q) - c_0^{\mathrm{calc}}(q) - n c_1^{(2),\mathrm{calc}}(q)\right], \quad (14)$$

i.e., exploiting the calculated two-body structural quantities, $c_0(q)$ and $c_1^{(2)}(q)$, and the full experimental quantity $c(q)$.

However, while small differences between the results of Refs. [32] and [33] for $c_0(q)$ can be observed especially at low-q values (see Fig. 4), calculations of $c_1^{(2)}$ are insensitive to which of the above pair potentials is used. It is clear then that, once the overall reliability of the two-body model is established, the most appropriate way to extract $c_1^{(3)}(q)$ from the structural data is

$$c_1^{(3),\mathrm{expt}}(q) = c_1^{\mathrm{expt}}(q) - c_1^{(2),\mathrm{calc}}(q), \quad (15)$$

which has the advantage of being a nearly model-independent determination, though intrinsically affected by larger errors. In fact, the main difference between Eqs. (14) and (15) is that the latter avoids the use of the calculation of c_0, which is the only one showing a weak but detectable dependence on the choice of the pair potential model, and allows one to determine $c_1^{(3)}$ as if subtracting the experimental c_0 from the total $c(q)$. Obviously, if the experimental c_0 is far from consistent with a given two-body model, the use of $c_1^{(2)}$ calculated with the same pair potential is not justified to confidently derive $c_1^{(3)}$ from Eq. (15).

Provided this is not the case, as for the present data, the comparison between experimental [Eqs. (14) or (15)] and calculated $c_1^{(3)}(q)$ allows a quantitative study on the strength of the AT potential. In fact, using the second equation in Eq. (8) and assuming an AT triplet interaction, $c_1^{(3),\mathrm{calc}}(q)$ is found to be proportional, within 0.2% in the whole q range of our measurements, to the ν value ($\nu < 3\times 10^{-26}\,\mathrm{J\,nm}^9$) used in the calculations. Thus the amplitude ν which, if chosen to calculate $c_1^{(3)}$, would reproduce at best the experimental data can be fitted by means of

$$c_1^{(3),\mathrm{expt}}(q) = \nu\left(\frac{c_1^{(3),\mathrm{calc}}(q,\nu_0)}{\nu_0}\right), \quad (16)$$

where ν_0 represents the AT strength used to evaluate the fitting function, for instance the average semiempirical value $2.22\times 10^{-26}\,\mathrm{J\,nm}^9$ [20], and ν is the only free parameter.

Since our data provided an accurate determination of $c_1(q)$, the more appropriate Eq. (15) could be employed to derive $c_1^{(3)}$, and the results (dots with error bars) are shown in Fig. 6, compared with the corresponding calculation performed using the two-body potential of Refs. [32] and [33] plus an AT three-body interaction of strength $\nu_0 = 2.22\times 10^{-26}\,\mathrm{J\,nm}^9$. The best fit according to Eq. (16), also reported in Fig. 6 (dashed curve), provided the value

$$\nu = (2.39\pm 0.09)\times 10^{-26}\,\mathrm{J\,nm}^9,$$

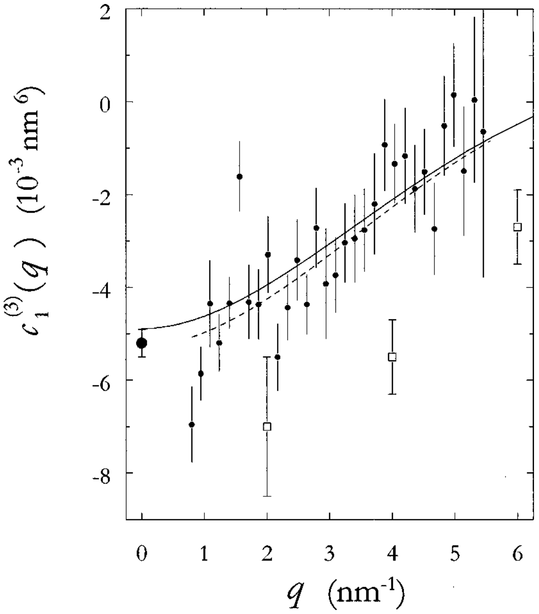

FIG. 6. Experimental $c_1^{(3)}(q)$ (dots with error bars) as obtained from Eq. (15). The solid curve corresponds to the calculation performed with Aziz and Slaman's potential [32] plus three-body AT potential. The best fit to the data according to Eq. (16) (dashed curve) provided $\nu = 2.39\times10^{-26}$ J nm^9. Open squares are the Teitsma and Egelstaff standard neutron diffraction results [13] relevant to the q range explored in this work.

on which we estimate an additional systematic error of the order of 0.1×10^{-26} J nm^9, related to the final renormalization of the experimental $S(q)$ to the thermodynamical data.

Our result agrees remarkably well with the previous evaluation of ν obtained from the first low-q experiment on dilute Kr [8], $\nu = (2.40\pm0.21)\times10^{-26}$ J nm^9, on which, according to the authors' estimates, a systematic error of 0.25×10^{-26} J nm^9 must also be considered. Differently from the new determination, the value of Ref. [8] was derived using Eqs. (14) and (16) and modeling the two-body interaction with the potential of Ref. [32]. Indeed, the present data allowed a strong reduction of the experimental uncertainty on the AT potential amplitude of Kr. This is an evidence of the good quality of the new measurements since, though dealing with a more appropriate but less accurate quantity like $c_1(q)$, the error on the fitted parameter ν is anyway halved with respect to the previous determination based on the total $c(q)$ [8].

However, both low-q investigations appear to give a mean ν value slightly larger than all existing semiempirical estimates for Kr [20], though consistency is reached within the errors (the upper bound predicted for this interaction constant by the computational methods is 2.275×10^{-26} J nm^9 [20]). Our results show that such an effect cannot be ascribed to possible subtle dependencies on the pair potential model used to extract the experimental $c_1^{(3)}(q)$ or to deviations between the experimental and calculated pure two-body correlations, since both these difficulties are overcome by the use of Eq. (15) and by the remarkable agreement found between calculations and experimental data for $c_0(q)$. Thus the consistency found between the results of both low-q structural measurements, though different and independent of each other, appears to be significant.

We found it interesting to perform the same analysis at $q=0$, using Eq. (15) to derive the experimental $c_1^{(3)}(0)$ from the slope of the density fit to the *PVT* data (dots in Fig. 3) and applying Eq. (16) (with $q=0$) to evaluate ν. This provides $\nu = (2.36\pm0.14)\times10^{-26}$ J nm^9, which agrees rather well with our result obtained above by fully exploiting the information contained in the q dependence of $c_1^{(3)}$. Therefore, both thermodynamical data, which are generally more accurate but limited to the single $q=0$ value, and structural measurements, in the whole q range where three-body effects are important, lead approximately to the same value for the AT strength, indicating that a different ν (at least 6% higher than the mean semiempirical one [20]) should be used in the calculations to properly account for the experimental results.

For the sake of completeness, Fig. 6 also reports the $c_1^{(3)}(q)$ data, limited to the q range considered here, derived by Teitsma and Egelstaff from the early wide-angle neutron diffraction experiment on Kr [13] and successively further analyzed in Ref. [14]. The same method used in this paper [see Eq. (15)] was first applied by the above authors to extract $c_1^{(3)}(q)$ from the experimental $c_1(q)$, taking advantage of the calculation of $c_1^{(2)}(q)$ with the pair potential of Barker *et al.* [33].

Although standard diffraction provided only few experimental points in the q region which is more suited to inquiries on three-body potential effects ($q<6$ nm^{-1}), it is anyway quite clear that very different results were obtained by Teitsma and Egelstaff with respect to the recent low-q ones. It is also evident why the first data of [13] raised naturally questions on the adequacy of the AT long-range interaction to effectively account for three-body forces in real fluids. However, neither the low-q data of [8], nor the even more accurate ones of this work, provide any convincing evidence of different from AT three-body interactions.

On the other hand, the $c_1^{(3)}$ of Ref. [13] seems to deviate largely (more than 35%) from the thermodynamical limit. The authors of Ref. [13] did not comment on this discrepancy, which is not found in our data. We already noted, however, that $c_1^{(3)}$ is sensitive to discrepancies between experimental and modeled pure two-body correlations, and can be consistently determined only if good agreement exists, as in the present work, between the fitted c_0 and the corresponding result provided by the chosen pair potential model. We also think that the normalization procedure is a crucial problem for such delicate investigations. In this respect, an important improvement was obtained by the use of low-density hydrogen or methane [8,23] calibration samples in place of the vanadium normalization.

Finally we note that the result obtained for ν might be slightly different if other terms in the long-range multipolar expansion of the three-body potential are taken into account. Tau *et al.* [14] calculated $c_1^{(3)}(q)$ for room temperature Kr, adding to the triple-dipole (DDD) AT term the quadrupolar terms DDQ, DQQ, and QQQ. The use of such a triplet interaction, in place of the AT potential alone, was shown [14] to improve the agreement of the calculation with thermodynamics, but its effect is negligible compared to the deviation of the Teitsma and Egelstaff results from *PVT* data. Concerning the low-q data of this work, we estimated that, by subtracting the effect of the above three-body quadrupolar contributions from the experimental $c_1^{(3)}$, and fitting the amplitude of the residual pure AT part, the resulting ν would be 2% smaller than the value obtained by neglecting such effects. However, there is some indication that an effective cancellation might exist between the above quadrupolar terms (DDQ, DQQ, and QQQ) and the triple-dipole term resulting from fourth-order perturbation theory [usually indicated as $(\mathrm{DDD})_4$ to distinguish it from the third-order AT one] [34]. This has been shown, for instance, for the lattice energy of rare gas crystals at 0 K [35]. For this reason, the inclusion of quadrupolar three-body terms only does not necessarily lead to a more correct determination of ν and we decided not to consider it. On the other hand, we note that, to third order in perturbation theory, terms including octopole moments might have a small effect on $c_1^{(3)}(q)$. Among these the dipole-dipole-octopole (DDO) one should be first quantitatively checked.

VI. CONCLUSIONS

Three-body forces mainly affect the structure factor at small-q values, therefore conclusions on their effects can reliably be drawn only through low-q measurements. The data presented in this paper provide important information on both the pair and triplet interactions in Kr, since accurate experimental determinations of $c_0(q)$ and $c_1(q)$ in the range $0.8 < q/\mathrm{nm}^{-1} < 5.5$ are obtained.

Our data provide not only clear evidence of irreducible three-body effects on the structure of fluid Kr but, in addition, reveal that, together with a reliable model for the pair potential, the long-range triple-dipole AT interaction is both absolutely necessary and, on the whole, sufficient to explain the experimental behavior of $c_1(q)$ within the uncertainties. Thus the results of this work represent convincing proof that the AT potential alone properly accounts for three-body interaction effects on the structure of noble gases.

The remarkable agreement of the experimental $c_0(q)$ with the corresponding calculations based on realistic pair potentials for Kr (those of Refs. [32] and [33]) confirms the validity of the quoted models. This represents the basic condition, allowing one to extract a reliable $c_1^{(3)}(q)$ from the experimental data and further to investigate the three-body interactions quantitatively. The method described here to determine the strength of the AT potential appears to be applied properly, since $c_1^{(3)}(q)$ is derived directly from the experimental $c_1(q)$ and is nearly model independent.

The high quality of our data thus led to the most accurate (8%) determination of the AT potential amplitude of Kr from structure factor measurements, to our knowledge. This determination is also, more generally, the best experimental result for three-body AT forces in noble gases. We believe that the choice of hydrogen as a reference sample for data normalization had an important role in increasing both the accuracy and the reliability of the results.

The optimal ν value that adequately describes both structural and thermodynamical data is found to be slightly higher than, though consistent with, the published values of ν calculated for Kr by the semiempirical approach [20]. Such an indication is also qualitatively confirmed by the very recent direct measurement of ν for Kr [12], a result which, though not very accurate, was obtained by exclusively probing the dipolar interactions [11] and independently of any assumption on the two-body properties of the fluid. Indirectly, all the results of this work prove that accurate low-q neutron data can be very helpful to develop realistic models for the interaction law in simple fluids, even at the level of three-body interactions.

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