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Long-range interactions in xenon

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The small-k behavior of the static structure factor $S(k)$ in a noble gas fluid is related to the two- and three-body part of the long-range interatomic potential, the London and Axilrod-Teller interaction, respectively. We have measured the $S(k)$ of xenon at room temperature and four low densities by means of a small angle neutron diffractometer. A careful data analysis has allowed the determination of the strength of the long-range pair potential as well as the clear detection of the three-body effect, whose intensity has been directly obtained. [S1063-651X(98)01508-6]

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In the experimental investigation of microscopic properties like the interparticle interaction law of fluids, the static structure factor $S(k)$ plays a major role. This can be easily understood looking at the integral equation relating the $S(k)$, an experimental quantity, to the pair distribution function $g(r)$, which describes the microscopic properties of the fluid:

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

where ρ is the number density, $\mathbf{k}$ is the exchanged wave vector, and $\mathbf{r}$ is the interparticle distance vector.

The long-range interaction features are in particular related to the k functional dependence of $S(k)$. Enderby, Gaskell, and March [1] demonstrated that, in classical noble gases, the presence of the van der Waals pair potential tail r^{-6} induces, in the small-k expansion of $S(k)$, the appearance of a k^3 term simply related to the pair potential intensity [see Eq. (5) below]:

$$S(k)=S(0)+S_2k^2+S_3|k|^3+S_4k^4+\cdots, \tag{2}$$

where $S(0)=\rho k_BT\chi_T$ is given by the *compressibility equation*, k_B is the Boltzmann constant, T the absolute temperature and χ_T the isothermal compressibility. Casanova *et al.* [2] and Reatto and Tau [3] have carefully analyzed the effect of the long-range interaction given by the dipole-dipole dispersion energy [4] plus a triple-dipole contribution of the Axilrod-Teller (AT) type [5] on the $S(k)$ behavior. In Ref. [3] was also shown that it is convenient to study the direct correlation function $c(k)$ defined by the Ornstein and Zernike relation [6] according to

$$c(k)=\frac{S(k)-1}{\rho S(k)}. \tag{3}$$

Analogously to $S(k)$, also $c(k)$ admits the small-k expansion

$$c(k)=c(0)+\gamma_2k^2+\gamma_3|k|^3+\gamma_4k^4+\cdots, \tag{4}$$

where $c(0)=[S(0)-1]/\rho S(0)$. While the $c(0)$, γ_2 and γ_3 coefficients all depend on the two- and three-body interactions, only for the latter an analytical expression is known [3], which reads

$$\gamma_3=\frac{\pi^2}{12}\beta\left(B-\frac{8\pi}{3}\rho\nu\right), \tag{5}$$

where $\beta=1/k_BT$, B and ν are the strengths of the London dispersion energy and of the AT interaction, respectively. The next terms of order higher than three in the expansion (4) will be neglected.

Reatto and Tau solved the modified hypernetted equation for low density noble gases system [3] and pointed out that the appropriate k range to study the expansion (4) up to k^3 was approximately $1\lesssim k\lesssim 4\ \mathrm{nm}^{-1}$; the lower limit of this range is due to retardation effects in the interaction propagation, while the upper one is a limit above which higher order contributions begin to become important.

Therefore the measurements of $S(k)$ of a noble gas fluid as a function of the density in the k range accessible by means of small angle neutron scattering (SANS), and the detection of a cubic behavior in the $c(k)$ give the possibility of experimentally demonstrating the existence of the long-range r^{-6} tail and measuring the B and ν strengths.

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These theoretical predictions have been recently confirmed for the first time through SANS experiments on gaseous argon [7] and krypton [8], thus demonstrating that this technique currently represents a unique way to have a direct access to long-range forces. However, in the argon and krypton cases, the density behavior of Eq. (5) has not been measured nor used to derive ν since this effect is too small in these systems.

Here we report the main results of a SANS experiment on low density xenon, i.e., a system with a higher polarizability than argon and krypton and, consequently, with an expected enhancement of the investigated effects, thus allowing the use of Eq. (5) to measure the two- and three-body long-range interaction strengths. A brief description of some results of this experiment has been presented in [9]. The experiment has been performed at the PAXE diffractometer of the Laboratoire Léon Brillouin in Saclay.

The sample was natural xenon, which has $\sigma_{\text{coh}}=3.1(1)$, $\sigma_{\text{inc}}=1.3(1)$ and $\sigma_{\text{abs}}(\lambda=0.18\text{ nm})=53.1(2.5)$ barn for the coherent, incoherent, and absorption neutron cross section, respectively [10,11]. The experiment has been performed along the isotherm $T=297.6\pm1$ K at four densities, namely, $\rho_{\text{exp}}=(0.158,\ 0.227,\ 0.28,\ 0.32)\rho_{\text{cr}}$, where $\rho_{\text{cr}}=5.04\text{ nm}^{-3}$ is the critical density; the values of the experimental densities have been computed using data of Ref. [12] and we estimate the relative accuracy on their determination to be within 0.5%. The experimental setup analogous to what is described in [8] will not be discussed here. The measured intensity patterns were corrected for background, attenuation, multiple, and inelastic effects. Then the relative and absolute calibration were applied. The final $S(k)$ data for the four experimental densities are reported in Fig. 1 together with the corresponding compressibility values at $k=0$ [12].

In order to investigate the $k\to0$ behavior an analytical representation $S_{\text{an}}(k)=s_0+s_2k^2+s_3k^3$ has been fitted to the experimental data. The results of the fitting procedure have been carefully evaluated by increasing the number of considered experimental points and looking for the stability of the fitting parameters and the minimum of the reduced χ_r^2 defined as

$$\chi_r^2=\frac{1}{(N-N_p)}\sum_{i=1}^{N}\frac{|S_{an}(k_i)-S(k_i)|^2}{s_i^2}, \tag{6}$$

where N is the number of fitted points, $N_p=3$ is the number of parameters of the model function $S_{\text{an}}(k)$ and s_i is the estimated standard deviation of $S(k_i)$ at $k=k_i$. For all the four investigated states, the two conditions have been fulfilled extending the fit up to a maximum value of $k\sim3.5$ nm^{-1}, with a reduced χ_r^2 always of the order of the unity. The values of s_0 obtained in this way are reported in Table I together with the corresponding values of $S(0)$. It can be seen that an excellent agreement has been obtained, always within 0.5% and within the experimental error. This represents a very valuable test of the quality of the whole experimental procedure and data analysis.

We have also fitted to the experimental data a polynomial of higher order, i.e., including a k^4 term in the analytical representation $S_{\text{an}}(k)$, without obtaining any real improvement of the results, and thus confirming the goodness of our assumption.

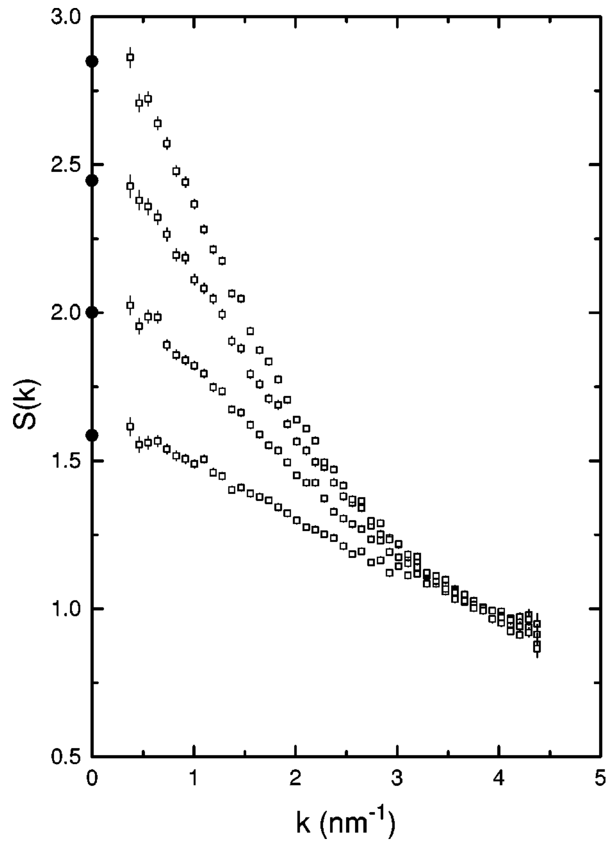

FIG. 1. Experimental S(k) for xenon at $T=297.6$ K. From bottom to top: $\rho=0.95$, 1.37, 1.69, and 1.93 nm^{-3}. The filled circles are the $k=0$ values calculated from PVT data of Ref. [12].

The experimental $c(k)$'s have been calculated from $S(k)$'s according to Eq. (3). At low density $c(k)$ can be expressed through the virial expansion

$$c(k)=c_0(k)+\rho c_1(k)+o(\rho^2), \tag{7}$$

where the zero density limit $c_0(k)$ depends only on the pair potential, while $c_1(k)$ depends also on the three-body interaction [13]; in this relation and in the following, the subscript n refers to the nth order of the virial expansion. By fitting to the four measured $c(k)$'s, for each k value, a function linear with respect to the density, the experimental $c_0(k)$ has been evaluated. Also for $c_0(k)$ the small-k expansion (4) holds, i.e.,

$$c_0(k)=c_0(0)+\gamma_{2,0}k^2+\gamma_{3,0}|k|^3+\cdots, \tag{8}$$

with

TABLE I. s_0 is the limit $S(k=0)$ obtained by a cubic fit to the experimental $S(k)$ as discussed in the text, while $S(0)$ has been calculated from PVT data of Ref. [12].

ρ (nm^{-3})	s_0	$S(0)$
0.95	1.585 ± 0.006	1.584 ± 0.005
1.37	2.000 ± 0.007	2.010 ± 0.007
1.69	2.44 ± 0.01	2.445 ± 0.008
1.93	2.85 ± 0.01	2.86 ± 0.01

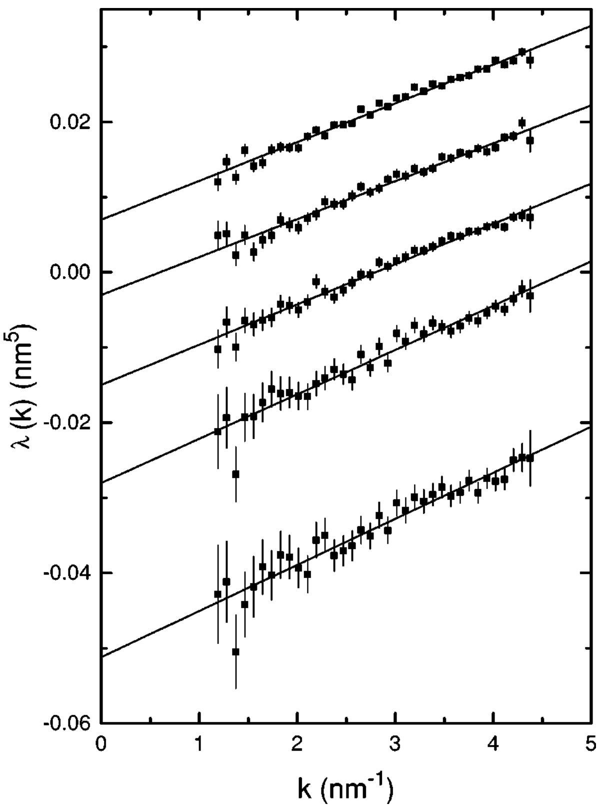

FIG. 2. Experimental values of $\lambda(k)$ and $\lambda_0(k)$. From bottom to top: $\lambda_0(k)$ and the four $\lambda(k)$'s: $\rho=0.95$ (shifted upwards by 0.02), 1.37 (+0.03), 1.69 (+0.04), and 1.93 (+0.05) nm^{-3}. The lines represent the result of a linear fit to the data, as discussed in the text.

$$\gamma_{3,0}=\frac{\pi^2}{12}\beta B, \tag{9}$$

which depends only on the pair interaction amplitude B and on the temperature T. In order to experimentally determine the k^3 coefficient in Eqs. (4) and (8) it is convenient to look at the quantities

$$\lambda(k)=\frac{c(k)-c(0)}{k^2}=\gamma_2+\gamma_3|k|+\cdots, \tag{10}$$

$$\lambda_0(k)=\frac{c_0(k)-c_0(0)}{k^2}=\gamma_{2,0}+\gamma_{3,0}|k|+\cdots. \tag{11}$$

The $\lambda(k)$'s at the four different densities and $\lambda_0(k)$, shown in Fig. 2, exhibit a nearly linear behavior as function of k, thus demonstrating, within the experimental errors, the existence of the k^3 terms in the expansions (4) and (8), and the correctness of the assumed long-range dipole-dipole London and triple-dipole AT interactions.

In Fig. 2 also the lines obtained with a linear fit to the data are reported. The slopes of these straight lines represent the γ_3 and $\gamma_{3,0}$ coefficients of Eqs. (10) and (11), respectively.

In the case of $\lambda_0(k)$, the experimental determination of $\gamma_{3,0}$ gives directly the value of B by means of Eq. (9). The resulting value of B for xenon is reported in Table II together with literature values obtained by means of semiempirical methods [14–16]. We observe a very good agreement between the present experimental result and the existing estimates of B.

TABLE II. Comparison of present work results with values found in literature.

	B (10^{-58} erg cm^6)	ν (10^{-82} erg cm^9)
Present work	2.82 ± 0.22	8 ± 4
Ref. [14]	2.74[a]	7.91[b]
Ref. [15]	2.86 ± 0.25	7.87 ± 0.08
Ref. [16]	2.78[a]	7.95[b]

[a]The estimated error is ~1%.
[b]The estimated error is ~1–2%.

A similar linear fit to $\lambda(k)$'s has provided the values of γ_3 at the four experimental densities, which are shown in Fig. 3 as function of ρ. In this figure the value at $\rho=0$ as well as the straight line have been obtained inserting the literature average values of B and ν, i.e., $B=(2.80\pm0.07)10^{-58}$ erg cm^6 and $\nu=(7.91\pm0.03)10^{-82}$ erg cm^9, obtained by means of semiempirical methods (see Table II), in Eq. (9) and in Eq. (5), respectively.

We have then extracted the experimental value of ν by using a linear fit to the data shown in Fig. 3, including also the semiempirical value at zero density. The obtained value is $\nu=8\pm4$ and is also reported in Table II along with the previously published semiempirical values.

Although not very accurate, we stress that we believe that this is the first direct experimental determination of the

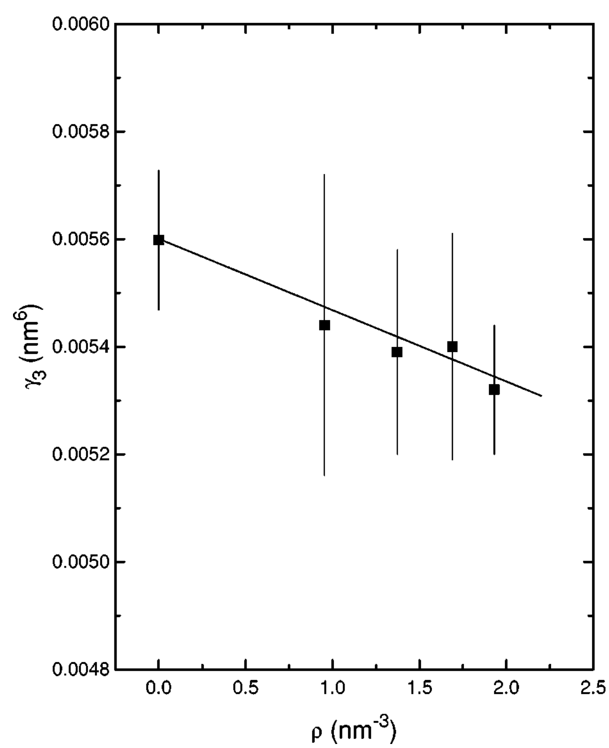

FIG. 3. The values of γ_3 as obtained from a linear fit to the four $\lambda(k)$'s, while the data at $\rho=0$ and the lines have been calculated inserting the semiempirical values of B and ν in Eqs. (9) and (5), respectively.

triple-dipole Axilrod-Teller interaction. Also Fig. 3 shows the first experimental evidence of the density behavior of γ_3, which we have been able to obtain in xenon because of the larger value of ν compared to the ones of argon and krypton.

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