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Interatomic dispersion forces and small angle scattering from rare gas fluids

L Reatto† and M Tau‡

† Dipartimento di Fisica dell' Università via Celoria 16, I20133 Milano, Italy
‡ Dipartimento di Fisica dell' Università viale delle Scienze, I43100 Parma, Italy

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Abstract. The structure factor $S(q)$ and the direct correlation function $\tilde{c}(q)$ of rare gases are expected to have a non-analytic $|q|^3$ term at small q. This term is due, in addition to the well known long-range r^{-6} tail of the two-body interaction, also to the three-body Axilrod–Teller (AT) interaction. The coefficient $\tilde{c}_3$ of the $|q|^3$ term of $\tilde{c}(q)$ has a particularly simple state dependence, T^{-1} in temperature and linear in density, when the AT interaction is present. If no three-body interaction is present $\tilde{c}_3$ is density independent. Therefore the experimental determination of the density dependence of $\tilde{c}_3$ will give unequivocable evidence of three-body forces. On the basis of the integral equation method we determine that it will be easier to detect the $|q|^3$ term if the scattering data are analysed in term of $\tilde{c}(q)$ and for measurements at density and temperature not far from the critical point. Under these favourable conditions scattering measurements in the range 1–4 nm^{-1} will give a precise determination of the $|q|^3$ term. The role of retardation, which changes the r^{-6} tail into r^{-7}, on the small-q behaviour of $S(q)$ and $\tilde{c}(q)$ is also evaluated and this effect is predicted to be measurable for $q \lesssim 0.5$ nm^{-1}.

1. Introduction

The static structure factor $S(q)$ of a fluid is a quantity of fundamental interest because it gives information on the spontaneous density fluctuations and on the local order which is present in the system. In addition in the case of a monoatomic fluid $S(q)$ in principle uniquely determines the interatomic interaction $\varphi(r)$ if this interaction is pairwise additive (for a review see [1]). If many-body forces are also present then $S(q)$ determines an effective pair interaction. If this scheme to deduce $\varphi(r)$ from $S(q)$ is simple, in principle, it is well known that the inversion of $S(q)$ is, in practice, very demanding both experimentally and theoretically because of the high sensitivity [2] of the extracted interaction to the accuracy and q-range of the data and to the approximations of the theory which are used in the inversion of $S(q)$.

In the case of rare gases there is one feature of $\varphi(r)$ which, in principle, can be extracted from $S(q)$ without any ambiguity—its long-range r^{-6} tail. As a result of this long-range tail due to dispersion forces, $S(q)$ is non-analytic at $q = 0$ and its small-q expansion displays a $|q|^3$ term with a coefficient simply related to the amplitude of the r^{-6} tail [3]. Here the only problem is how small q has to be in order for the $|q|^3$ term to be unravelled from the other terms. We are not aware that any measurement of $S(q)$ has detected this $|q|^3$ term yet.

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A number of articles [4–6] have been specifically devoted to the question of the small-q behaviour of $S(q)$ after the pioneering work by Enderby *et al* [3] and we address this problem again for several reasons. First we have now available from the theory of fluids, schemes based on the integral equation for the radial distribution function $g(r)$ which are very accurate [7, 8] over most of the phase diagram and describe both the short- and long-range behaviour of $g(r)$ starting from realistic models of the interatomic interaction. Previous studies [4, 5] were based on schemes which were only accurate in the very dense regime, which were specific to small-q or have been limited [6] to the Lennard–Jones potential (LJ). On the basis of previous studies one cannot completely answer the questions we have in mind: in which q should range experimentalists expect to find the $|q|^3$ term and which region of the phase diagram is most favourable for its detection. The second reason is that we find that the triple dipole Axilrod–Teller (AT) interaction also contributes to the $|q|^3$ term. Fortunately we have already extended [7] the integral equation we use, a modified hypernetted chain (MHNC) equation [9], to the case when a three-body interaction is present so that we can analyse this question. Finally the r^{-6} tail of the interatomic interaction does not extend to arbitrarily large distances and retardation due to the finite velocity of light modifies the asymptotic behaviour of $\varphi(r)$ giving a r^{-7} tail. Therefore the $|q|^3$ term does not extend to arbitrary small-q but this question has not been examined in the literature. Here we also study how retardation modifies the small-q behaviour of $S(q)$ and $\tilde{c}(q)$ and the thermodynamic properties.

The contents of the article are as follows. In section 2 we discuss the integral equation we are using in the case of pair forces and pair plus triplet forces. In section 3 we consider the small-q behaviour of $S(q)$ and of the Ornstein–Zernike direct correlation function $\tilde{c}(q)$ given by our equation. Then we present the result of a numerical solution to the equation for an interatomic interaction appropriate to argon; we display the q region where the $|q|^3$ term should be detectable both for $S(q)$ and $\tilde{c}(q)$ and we discuss the range of density and temperature more favourable for the detection of the $|q|^3$ term. In section 4 we discuss the effects of retardation on the properties of the fluid. A discussion of our results is given in section 5.

2. The integral equation scheme

We assume that the interatomic interaction consists of a central pair potential plus a three-body potential,

$$U(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)=\sum_{i<j}\varphi(r_{ij})+\sum_{i<j<k}\phi^{(3)}(\boldsymbol{r}_i,\boldsymbol{r}_j,\boldsymbol{r}_k),\qquad r_{ij}=|\boldsymbol{r}_j-\boldsymbol{r}_i| \tag{1}$$

and that quantum effects can be neglected. The first equation we use is the modified hypernetted chain (MHNC) equation extended to include three-body forces [7]. This reads

$$g(r)=\exp[-\beta\varphi(r)+\theta(r)+C(r)+E_{\mathrm{HS}}(r;d)] \tag{2}$$

$$\theta(r)=g(r)-1-c(r)=h(r)-c(r) \tag{3}$$

where the direct correlation function $c(r)$ is related to $g(r)=1+h(r)$ by the Ornstein–Zernike (OZ) relation

$$h(r)=c(r)+\rho\int \mathrm{d}^3r'c(r')h(|\boldsymbol{r}-\boldsymbol{r}'|) \tag{4}$$

and $C(r)$ is the dressed three-particle vertex

$$C(r_{12}) = \rho \int \mathrm{d}^3 r_3\, g(r_{13}) g(r_{23}) \{\exp[-\beta\phi^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)] - 1\}. \tag{5}$$

If in (2) E_{HS} were the exact bridge function of the system including diagrams with three-body plaquettes, equation (2) would be exact. The approximation resides in replacing this unknown bridge function with that of hard spheres of diameter d in which the optimal choice of d is determined by the equation

$$I(d) = \int \mathrm{d}^3 r\, [g(r) - g_{\mathrm{HS}}(r;d)] \frac{\partial E_{\mathrm{HS}}(r;d)}{\partial d} = 0. \tag{6}$$

If only two-body forces are present one has simply to drop the term $C(r)$ in equation (2).

We also consider a related equation [10], a cross-over hypernetted chain equation (CRS–MHNC), which differs from equation (2) in the substitution of the hard sphere bridge function E_{HS} for the cross-over form

$$E_{\mathrm{CRS}}(r) = \{1 - l(r)\} E_{\mathrm{HS}}(r;d) + l(r)[1 - g(r) + \ln g(r)]. \tag{7}$$

The term in square braket represents the functional form corresponding to the mean spherical approximation (MSA), i.e. it is such that $c(r) = -\beta\varphi(r)$ where $l(r) = 1$. The cross-over function $l(r)$ vanishes in the core region and is unity at large distances so that $E_{\mathrm{CRS}}(r)$ has the hard sphere form at short distance and the MSA form at large distance. We refer the reader to [7] for the form of $l(r)$ and for the criterion which determines the cross-over parameters.

The accuracy of the MHNC and CRS–MHNC equation is well documented by a number of comparisons with simulation results for different forms of the pair interaction $\varphi(r)$ and in various regions of the phase diagram. The effects of the three-body AT interaction is also accurately represented [8, 11]. The results of the two equations are very similar, if we exclude the immediate neighbourhood of the critical point, the CRS–MHNC being slightly superior.

We consider now the long-range behaviour of $c(r)$ and $h(r)$ and the small-q behaviour of the related functions

$$\widetilde{c}(q) = \int \mathrm{d}^3 r\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} c(r) \tag{8}$$

$$S(q) = 1 + \rho \int \mathrm{d}^3 r\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} [g(r) - 1] \tag{9}$$

when the pair interaction has the tail

$$\varphi(r) \sim -B/r^6 \qquad \text{as } r \to \infty. \tag{10}$$

If $S(0) = \rho k_{\mathrm{B}} T K_T$ is finite, i.e. the system is not at the critical point, a general result by Groeneveld and Stell [12] states that $c(r) \sim -\beta\varphi(r)$ asymptotically as $r \to \infty$. This behaviour is also given by the MHNC equation as can be shown by taking the logarithm of equation (2) and expanding $\ln g = \ln(1 + h) = h - \frac{1}{2}h^2 + \cdots$. When no three-body forces are present we get

$$c(r) \sim -\beta\varphi(r) + A_2 h^2(r) + E_{\mathrm{HS}}(r) + \cdots \qquad \text{as } r \to \infty \tag{11}$$

with $A_2 = \frac{1}{2}$. $E_{\rm HS}(r)$ decays to zero at large distance more rapidly than a power law and from the OZ relationship it follows that $h(r)$ and $c(r)$ decay to zero with the same power law. Thus the result $c(r) \sim -\beta\varphi(r)$ follows. In the case of the CRS-MHNC we have the stronger result $c(r) = -\beta\varphi(r)$ in the range where $l(r) = 1$. We conclude that for both equations the dominant long-range behaviour of $c(r)$ is correct. The subdominant term is not correct, having $A_2 = \frac{1}{2}$ for MHNC and $A_2 = 0$ for CRS-MHNC, whereas the exact A_2 is a state-dependent coefficient related to the thermodynamic properties [12].

The situation is slightly different when a three-body interaction is present because the dressed three-particle vertex $C(r)$ has a long-range tail when $\phi^{(3)}$ has the AT form:

$$\phi^{(3)}_{\rm AT}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \nu \frac{1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3}{r_{12}^3 r_{23}^3 r_{13}^3} \tag{12}$$

where θ_i are the angles of the triangle with vertices at $\boldsymbol{r}_i$, $i = 1, 2, 3$. Casanova *et al* [13] discussed the three-particle vertex (5) in the limit of low density where $g(r)$ becomes equal to the Boltzmann factor $\exp[-\beta\varphi(r)]$. They considered three different pair potentials (hard sphere, square well and Lennard–Jones) for which they obtained the same asymptotic behaviour

$$C(r) \sim -\frac{8\pi}{3}\beta\rho\nu\frac{1}{r^6} \qquad \text{as } r \to \infty \tag{13}$$

and argued that such a result is valid in general for any two-body potential. We would expect that this conclusion would also be valid at arbitrary density if the asymptotic contribution to $C(r = |\boldsymbol{r}_2 - \boldsymbol{r}_1|)$ derives from a region of integration over $\boldsymbol{r}_3$ in equation (5) where $\boldsymbol{r}_3$ is far from $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ so that the g in the integrand can be approximated by unity. We have proved this statement analytically and result (13) under the only condition that $h(r)$ vanishes at least as fast as $r^{-\alpha}$ with $\alpha > 0$ as $r \to \infty$. Therefore result (13) also holds true at the critical point. We arrived at this result by extending the integration in equation (5) over $\boldsymbol{r}_2$ and introducing the delta function $\delta(\boldsymbol{r}_{23} - \boldsymbol{r}_{13} + \boldsymbol{r}_{12})$ as a factor in the integrand. At this point the integrals can be written in Fourier space so that one can apply Fourier asymptotic [14] analysis and after some manipulations we arrive at (13). It is clear from (2) that $-C(r)/\beta$ has the role of an effective two-body interaction which has to be added to $\varphi(r)$ so that

$$c(r) \sim -\beta\varphi(r) + C(r) = \beta(B - (8\pi/3)\rho\nu)/r^6 \qquad \text{as } r \to \infty. \tag{14}$$

From the diagrammatic representation of the bridge function it is found that the diagrams with three-body plaquettes decay to zero faster than $C(r)$ so that (14) has general validity and is not limited to the MHNC equation we are using.

By using asymptotic Fourier analysis [14] it is a simple matter [3] to obtain from (14) the small-q expansion of $\widetilde{c}(q)$ and $S(q)$ with the result

$$\widetilde{c}(q) = \widetilde{c}(0) + \widetilde{c}_2 q^2 + \widetilde{c}_3 |q|^3 + \widetilde{c}_4 q^4 + \cdots \tag{15}$$

$$S(q) = \frac{1}{1 - \rho\widetilde{c}(q)} = S(0) + S_2 q^2 + S_3 |q|^3 + S_4 q^4 + \cdots. \tag{16}$$

The $|q|^3$ terms are due to the r^{-6} tail in direct space and the coefficients read

$$\widetilde{c}_3 = \frac{\pi^2}{12}\left(B - \frac{8\pi}{3}\rho\nu\right) \Big/ k_{\rm B}T \tag{17}$$

$$S_3 = \rho[S(0)]^2 \widetilde{c}_3. \tag{18}$$

$\tilde{c}_3$ has a very simple state dependence, it is inversely proportional to temperature and is a linear function of density due to the AT interaction. For a pure two-body interaction $\tilde{c}_3$ is density independent. Contributions to the three-body interaction of higher order of the triple dipole one do not contribute to $\tilde{c}_3$ so that the result (17) is exact for fluids of apolar molecules. Quadruple dipolar interaction gives rise to a four body interaction which contributes to $\tilde{c}_3$ with a term proportional to ρ^2 but this contribution should remain small even at the highest densities. The state dependence of the coefficient S_3 is much more complex due to the presence of the square of the adimensional isothermal compressibility $S(0)$ as shown in (18).

The q-range most appropriate for detection of the $|q|^3$ terms depends on the value of the coefficients of the higher order terms for which no analytic expression is known. We have determined this q-range from the numerical solution of the integral equations as discussed in the next section.

3. Small-q behaviour of $S(q)$ and the $|q|^3$ term for argon and for other rare gases

We start with the study of argon. For the pair interaction we take the HFD-B2 form of Aziz *et al* [15] and as the amplitude of the AT interaction the value $\nu = 73.39 \times 10^{-84}$ erg cm^{-9} [16]. We solve the MHNC and the CRS-MHNC equation with a standard iterative method and we take a very large cut-off in r space in order to reproduce the long-range tail and the $|q|^3$ terms. We use a step size $\Delta r = 0.025$ with 2^{14} points so that $R_{\text{max}} = 410$ in units of the position r_{m} of the minimum of $\varphi(r)$, $r_{\text{m}} = 0.37565$ nm for the HFD-B2 potential. With the AT interaction $\phi^{(3)}$ it is appropriate to expand the Boltzmann factor in C, equation (5), to linear order in $\beta\phi^{(3)}$ and we rewrite it in the form

$$C(r_{12}) = -\beta\rho \int \mathrm{d}^3 r_3 \, [g(r_{13})g(r_{23}) - E(r_{13} - r_{\text{c}})E(r_{23} - r_{\text{c}})]\phi^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$$
$$- \beta\rho \int \mathrm{d}^3 r_3 \, [E(r_{13} - r_{\text{c}})E(r_{23} - r_{\text{c}})]\phi^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) \qquad (19)$$

where $E(x)$ is the step function, $E(x) = 1$ for $x < 0$, $E(x) = 0$ for $x > 0$. The second integral can be computed analytically and the first is computed numerically with a cut-off on the integration on $\boldsymbol{r}_3$ such that $r_{13}, r_{23} < r_{\text{c}}$ with $r_{\text{c}} = 5\, r_{\text{m}}$. This amounts to neglecting the small difference of $g(r)$ from unity when $r > r_{\text{c}}$ and the value of r_c is such that this approximation has a completely negligible effect on $C(r)$.

In order to extract the coefficients $\tilde{c}_3$ and S_3 from the numerical result we construct the quantities

$$\lambda(q) = \frac{\tilde{c}(q) - \tilde{c}(0)}{q^2} \quad \sim \quad \tilde{c}_2 + \tilde{c}_3|q| + \tilde{c}_4 q^2 + \cdots \qquad \text{as } q \to \infty \qquad (20)$$

$$\mu(q) = \frac{S(q) - S(0)}{q^2} \quad \sim \quad S_2 + S_3|q| + S_4 q^2 + \cdots \qquad \text{as } q \to \infty \qquad (21)$$

so that from the slope at the origin we get $\tilde{c}_3$ and S_3 and the intercept at $q = 0$ gives, respectively, $\tilde{c}_2$ and S_2. In figure 1 we have shown $\tilde{c}_3$ as function of density for the $T = 180$ K isotherm with and without $\phi^{(3)}$ together with the analytical result.

The numerical result agrees with the exact result to better than 1% and this is quite adequate for our purpose. For the HFD-B2 potential for argon plus the AT interaction the coefficient $\tilde{c}_3$ has the value

$$\tilde{c}_3 = [0.3667 - 0.003663\,\rho]/T\ (\mathrm{nm}^6) \tag{22}$$

where ρ is in nm^{-3} and T in Kelvin so that with respect to low density the value of $\tilde{c}_3$ is reduced by about 20% at the density of the triple point due to the three-body AT interaction. The Barker *et al* [17] pair potential gives essentially the same value of $\tilde{c}_3$, i.e. $\tilde{c}_3(\rho = 0) = 0.3673/T\ (\mathrm{nm}^6)$, and the HFD-C [18] pair potential gives a slightly smaller value $\tilde{c}_3(\rho = 0) = 0.3627/T\ (\mathrm{nm}^6)$.

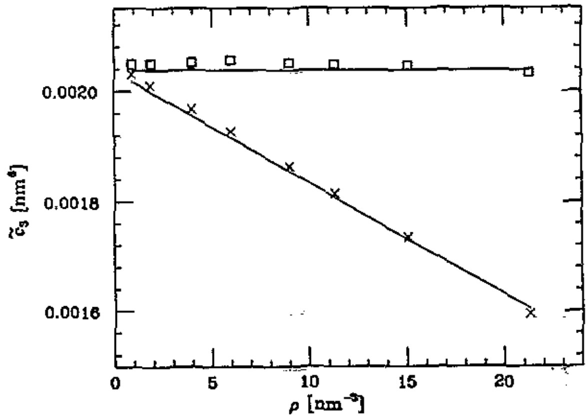

Figure 1. Coefficient $\tilde{c}_3$ of the cubic term of $\tilde{c}(q)$ as function of density from the MHNC equation for argon at $T = 180$ K for the HFD-B2 potential with (×) and without (□) the AT three-body interaction. Full lines represent the analytical result (22) with and without the AT interaction.

As an example of the overall behaviour of $\lambda(q)$ in figure 2 we show $\lambda(q)$ as function of q at $T = 140$ K and at $\rho = 1.9\ \mathrm{nm}^{-3}$ computed with the MHNC equation with and without $\phi^{(3)}$. It is clear from the figure that over an extended range of q of order of $4\ \mathrm{nm}^{-1}$ $\lambda(q)$ is an essentially linear function of q so that it should be possible to extract $\tilde{c}_3$ from the experimental $S(q)$, converted to $\tilde{c}(q)$, if this is measured in the range of order 1–4 nm^{-1}. This is quite an accessible range with available instrumentation. It is interesting to contrast this behaviour of $\lambda(q)$ with the one corresponding to a short-range potential. To this end we have used an empirical pair interaction $\varphi_{em}(r)$ which has been extracted from the measured $S(q)$ at low density by Fredrikze *et al* [19]. $\varphi_{\mathrm{em}}(r)$ has an attractive well similar to that of the HFD-B2 form but beyond a distance of order of 10 Å $\varphi_{\mathrm{em}}(r)$ has weak oscillations around zero and not a r^{-6} tail. This is probably due to some cut-off problem with the experimental data but it gives us a pair interaction of finite range. In fact we truncate $\varphi_{\mathrm{em}}(r)$ and displace it to zero at the position of the first maximum which is at $r \simeq 10$ Å. The resulting $\lambda(q)$ is also shown in figure 2 and the completely different behaviour is clear at small-q.

The q-range where $\lambda(q)$ has an essentially linear behaviour with q depends on T and ρ. In order to display the large quantity of information in compact form we define $q^c_{3\%}$ as the value of q where the percentage deviation of $\lambda(q)$ from the straight line $\tilde{c}_2 + \tilde{c}_3|q|$ is 3%. We take this to be a measure of the q-range where from our theory

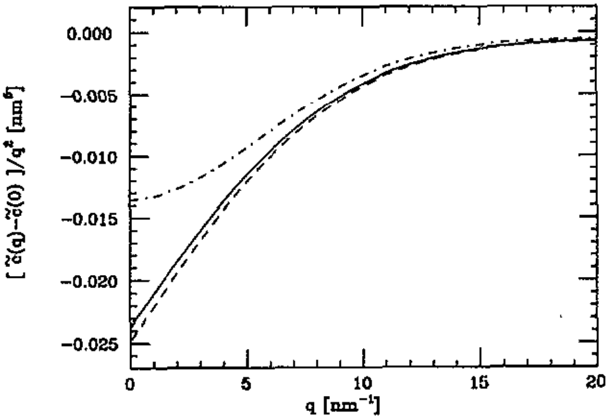

Figure 2. $\lambda(q) = [\tilde{c}(q) - \tilde{c}(0)]/q^2$ as function of q for argon at $T = 140$ K and $\rho = 1.9$ nm^{-3} for the HFD-B2 potential with (full curve) and without (broken curve) the AT interaction and for an empirical (see text) short range pair interaction (chain curve).

the $\tilde{c}_3$ term is 'visible' in $\tilde{c}(q)$ or, more precisely, in $\lambda(q)$. $q^c_{3\%}$ is shown in figure 3 as function of density for the two isotherms $T = 180$ and 140 K when the MHNC equation is used with and without $\phi^{(3)}$. The results from the CRS-MHNC equation, which we do not show, are similar and in general it turns out that $q^c_{3\%}$ is larger by 10–20% than the MHNC result.

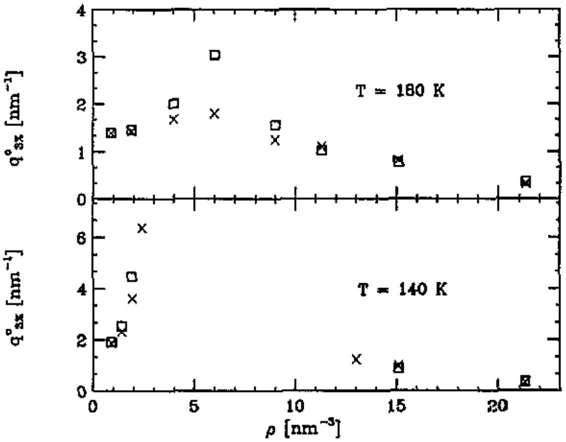

Figure 3. Range $q^c_{3\%}$ of linearity of $\lambda(q)$ for the isotherms $T = 180$ and 140 K of argon for the HFD-B2 potential with (×) and without (□) the AT interaction.

The general comment we can make is that $q^c_{3\%}$ is larger for an intermediate value of the density, roughly in the region of the critical density if $T > T_c$ or on the coexistence line if $T < T_c$, and it becomes small, typically below 1 nm^{-1}, at the density of the triple point. $q^c_{3\%}$ becomes larger for decreasing temperature but at the same time the liquid–vapour coexistence region becomes wider and the detection of $\tilde{c}_3$ is more difficult. For instance at the triple point $q^c_{3\%} = 0.4$ nm^{-1}. The presence of the three-body interaction slightly modifies the shape of $\lambda(q)$ but in general does not alter the region of linearity very much. A large effect on $q^c_{3\%}$ is present if the system is close to the critical point or to the spinodal line where $S(0)$ becomes larger than unity. For instance at $T = 180$ K and $\rho = 6\ \mathrm{nm}^{-3}$ ($T/T_c = 1.19, \rho/\rho_c = 0.74$) $q^c_{3\%}$ drops from *3.0 to 1.8* nm^{-1} *when* $\phi^{(3)}$ *is introduced.* We believe that this is an indirect effect due to the displacement of the critical temperature. In fact the critical temperature T_c changes [11] by about 10% due to the presence of $\phi^{(3)}$ and T_c is substantially larger than experiment if only the two-body interaction is considered. On the other hand empirically we find that there is a relationship between the value of $q^c_{3\%}$ and that of $S(0)$—a large value of $S(0)$ is connected to a large value of $q^c_{3\%}$.

Different behaviour is found with $S(q)$ or, more precisely, with $\mu(q)$ given in equation (21). If we define $q^S_{3\%}$ for $\mu(q)$ in a similar way to $q^c_{3\%}$ we find that $q^S_{3\%}$ never exceeds 1 nm^{-1} and it is smaller at intermediate densities. If $q^S_{3\%}$ for $\mu(q)$ is slightly larger than $q^c_{3\%}$ for $\lambda(q)$ at the density of the triple point, at intermediate density it is an order of magnitude smaller (see figure 4). We can understand this different behaviour as follows. If the relevant q is so small that we can neglect the higher order terms not written in (20) and (21) we easily obtain $q^c_{3\%} = 0.03\,\tilde{c}_3/|\tilde{c}_4|$ and $q^S_{3\%} = 0.03\,\tilde{c}_3/|\tilde{c}_4 + \rho S(0)\tilde{c}_2^2|$. Hence a large value of $S(0)$ leads to a small value of $q^S_{3\%}$ since $\tilde{c}_2$ is a smooth function of T and ρ (see table 1). Only at the lowest temperature in the liquid phase, i.e. at the triple point, is $q^S_{3\%}$ substantially larger than $q^c_{3\%}$ but its value, $q^S_{3\%} = 0.8\ \mathrm{nm}^{-1}$, is still small so it will not be easy to detect.

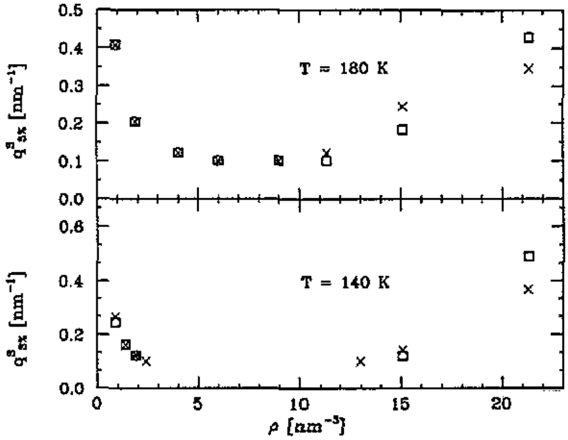

Figure 4. Range $q^S_{3\%}$ of linearity of $\mu(q)$. Symbols have same meaning as in figure 3.

For all the thermodynamic states we have considered the structure factor has an OZ behaviour at small-q, i.e. $S(q)$ has a downward curvature around $q = 0$ so that $S(q)$ has a minimum at a finite q. This minimum is very prominent at intermediate densities and very weak at the highest densities. The position and value at this minimum are given in the table at selected densities at a temperature above T_c, at one below and at the triple point. We also give the value of $S(0)$, $\tilde{c}(0)$ and $\tilde{c}_2$. The value of S_2 (see equation (16)) can be easily obtained from the relationship $S_2 = \rho[S(0)]^2\tilde{c}_2$. There is a substantial agreement of the computed $S(0)$ with the experimental value (last column) deduced from the isothermal compressibility, the typical deviation being of the order of 5%. The percentage deviation becomes somewhat larger for states in the neighbourhood of the critical point as might be expected close to states where $S(0)$ is diverging.

We have also performed some computations with the LJ potential and we give some

Table 1. Fluid argon with two-plus three-body potential (see text): value at $q = 0$ of $\tilde{c}(q)$ and of $S(q)$, of the coefficient $\tilde{c}_2$ (equation (15)), of the position $q_{\rm min}$ of the first minimum of $S(q)$, of $S(q_{\rm min})$ from the triplet MHNC equation. In the last two rows these quantities are given when the Lennard–Jones potential is used with the parameters $\sigma = 0.3405$ nm and $\epsilon/k_{\rm B} = 119.8$ K. In the last column the experimental value of $S(0)$ deduced from a fitted equation of state [20] is given.

T (K)	ρ (nm^{-3})	$\tilde{c}(0)$ (nm^3)	$\tilde{c}_2$ (nm^5)	$S(0)$	$q_{\rm min}$ (nm^{-1})	$S(q_{\rm min})$	$S(0)_{\rm exp}$
180	1.90	0.173	−0.0165	1.49	8.72	0.839	1.48
180	6.00	0.111	−0.0153	3.00	8.29	0.580	2.80
180	11.32	0.0047	−0.0132	1.06	7.47	0.344	1.11
180	21.30	−0.7973	−0.0027	0.0556	1.37	0.0555	0.0529
140	1.90	0.300	−0.0237	2.33	9.13	0.809	2.22
140	15.09	−0.0742	−0.0156	0.47	7.06	0.202	0.54
140	21.30	−0.8556	−0.0049	0.0520	2.16	0.0517	0.0504
85	21.30	−0.8881	−0.0140	0.0502	4.76	0.0465	0.0487
85	21.30	−1.0146	−0.0278	0.0442	4.85	0.0390	0.0487
85	20.91	−0.8973	−0.0288	0.0506	5.08	0.0432	0.0560

results for two states close to the triple point in table 1. The isothermal compressibility is smaller than experiment when the standard values for σ and ϵ are used and the amplitude of the cubic term $\tilde{c}_3$ is more than double the value given by the accurate pair potential plus the AT interaction. In fact we have $\tilde{c}_3 = 0.00723$ nm^6 for the LJ potential at $T = 85$ K ($T^* = 0.7095$) whereas from (22) we get $\tilde{c}_3 = 0.00340$ nm^6. Therefore the LJ potential cannot be used to give a reliable estimate of the low-q behaviour of $S(q)$.

We can also make a comparison with the result of Evans and Sluckin [4] and the state $T = 85$ K, $\rho = 20.91$ nm^{-3} corresponds exactly with one of their states computed within a perturbative approach with the random phase approximation for attractive forces. Their compressibility is substantially smaller than ours, $S(0) = 0.0367$ against our $S(0) = 0.0506$, and this difference is in qualitative agreement with previous comparisons [6] of MHNC with perturbative theory. On the basis of previous comparisons [7, 8] with simulation results we believe that the present result is more accurate. The coefficient $\tilde{c}_3$ is the same in the two approaches and is exact, $\tilde{c}_2$ is roughly the same. The OZ minimum of $S(q)$ obtained by Evans and Sluckin [4] is much shallower than what we find, they get $S(q_{\rm min})/S(0) = 0.95$ with $q_{\rm min} = 2.5$ nm^{-1} whereas we have $S(q_{\rm min})/S(0) = 0.85$ with $q_{\rm min} = 4.3$ nm^{-1}. This indicates that the coefficients of the q^4 and possibly the higher order terms of the power expansion of $S(q)$ are different in the two approximations. Unfortunately we cannot use simulations results as a test of which theory is more accurate in this respect because this would require a simulation with a much larger number of particles than has been currently used.

From the best representation [21, 15, 22] of the interatomic interaction for the other rare gases and from (17) we obtain the following expressions for the coefficient $\tilde{c}_3$ of the cubic term:

$$\text{Ne}: \qquad \tilde{c}_3 = [0.03927 - 0.00009\,\rho]/T\ (\text{nm}^6) \tag{23}$$

$$\text{Kr}: \qquad \tilde{c}_3 = [0.74650 - 0.01100\,\rho]/T\ (\text{nm}^6) \tag{24}$$

$$\text{Xe}: \qquad \widetilde{c}_3 = [1.64681 - 0.03968\,\rho]/T\ (\text{nm}^6). \tag{25}$$

Neon has non-negligible quantum corrections but we conjecture that there is no quantum correction in $\widetilde{c}_3$. This is not true for S_3 because its value depends on $S(0)$.

We have only performed detailed computations of $S(q)$ and $\widetilde{c}(q)$ for argon so that we cannot give a precise estimate of the extension of the linearity of $\lambda(q)$ and $\mu(q)$ for other rare gases . In fact the accurate pair interactions for the different rare gases do not scale one with the other and the law of corresponding states is not satisfied exactly even at the level of the two-body interaction. However the deviations are not very large and we can expect that the value of $q^c_{3\%}$ obtained for argon is indicative of its value for the other rare gases if we consider analogous thermodynamic states in terms of the respective critical or triple points. This is borne out by the few computations we have performed. For instance for Xe at $T = 346$ K and $\rho = 3.8$ nm^{-3}, which corresponds to argon at $T = 180$ K and $\rho = 6$ nm^{-3} in terms of the critical point constants, we obtain $q^c_{3\%} = 2.7$ nm^{-1} which should be compared with $q^c_{3\%} = 1.8$ nm^{-1} for Ar.

4. Retardation effects

The long-range behaviour of the dispersion forces between polarizable entities is affected by the finite velocity of propagation of the electromagnetic field [23]. In the case of non-polar molecules like the rare gases the interaction energy at large distance changes from r^{-6} to r^{-7} and this reduction is due to the fact that this energy does not depend on the istantaneous values of the fluctuating dipole moments of the two atoms but on their values at two different times related to the time interval of propagation of the electromagnetic field from one atom to the other.

The retardated dispersion forces can be written in the form

$$\varphi(r) = -\frac{B}{r^6}G(r) \tag{26}$$

with $G(r) \rightarrow 1$ as $r \rightarrow 0$ and $G(r) \sim 1/r$ as $r \rightarrow \infty$. If the fluctuation of the istantaneous dipole moment is dominated by a unique electronic transition the energy of which we call $h\nu_0$, the retardation factor $G(r)$ for short distances [24] is

$$G(r) = 1 - \frac{1}{3}(q_0 r)^2 + \cdots \qquad (q_0 r \ll 1) \tag{27}$$

and for large distances [23]

$$G(r) \sim \frac{23}{3\pi}\frac{1}{q_0 r} \quad \text{as } r \rightarrow \infty \tag{28}$$

where q_0 is the wavevector corresponding to ν_0:

$$q_0 = \frac{2\pi}{\lambda_0} = 2\pi\nu_0/c. \tag{29}$$

In this same approximation the strength B of the non-retarded interaction is given by

$$B = \tfrac{3}{4}\alpha^2 h\nu_0 \tag{30}$$

where α is the atomic polarizability. $G(r)$ has been computed [23] numerically at intermediate distances and we find that a useful analytical approximant is

$$G(x) = \frac{\alpha}{x}[1 + ax^2 \exp^{-bx}]^{-1} \tanh(x/\alpha) \qquad x = q_0 r \tag{31}$$

with coefficients

$$\alpha = \frac{23}{3\pi} \qquad a = \frac{1}{3} - \frac{3\pi^2}{23^2} \qquad b = 6.11. \tag{32}$$

The values of α and a are such that (31) has the expansions (27) and (28) and the value of b is such that $G(r)$ has the correct value at $x = 0.3$.

When we take retardation into account the small-q expansions (15) and (16) of $\widetilde{c}(q)$ and $S(q)$ are no longer correct and the algebraic $|q|^3$ singularity becomes a logarithmic one. If only two-body forces are present with the large r behaviour (26, 28) the expansion of $\widetilde{c}(q)$ reads

$$\widetilde{c}(q) = \widetilde{c}(0) + \widetilde{c}_2 q^2 + \widetilde{c}_{4\ln} q^4 |\ln |q/q_1|| + \widetilde{c}_4 q^4 + \cdots \tag{33}$$

where

$$\widetilde{c}_{4\ln} = \frac{23}{90} \frac{B}{q_0 k_{\rm B} T} \tag{34}$$

and q_1 is a scale factor which cannot be determined by asymptotic analysis. $S(q)$ has an expansion similar to (33) and the characteristic coefficient is $S_{4\ln} = \rho[S(0)]^2 \widetilde{c}_{4\ln}$.

Since retardation only becomes effective at large distances we might expect that a quantity such as $\lambda(q) = [\widetilde{c}(q) - \widetilde{c}(0)]/q^2$ or $\mu(q) = [\widetilde{S}(q) - \widetilde{S}(0)]/q^2$ has an essentially linear behaviour in q in a window of q values. On one hand we have an upper limit already considered in the previous section beyond which the term q^4 and the higher ones become important. In addition we have now a lower limit q_l below which retardation becomes effective; the appropriate expansion is given by (33) and $\lambda(q)$ should display curvature. In order to determine the size of this window we have performed MHNC computations for argon with the pair interaction

$$\varphi_R(r) = G(r)\varphi(r) \tag{35}$$

where $\varphi(r)$ is the HFD–B2 interaction considered in the previous section and $G(r)$ is the approximant (31). Using the B value of the HFD–B2 interaction and the polarizability of argon ($\alpha = 1.63 \times 10^{-24}$ cm^3) in equation (30), we obtain ν_0 and therefore q_0 from (29) with the result that $h\nu_0 = 19.3$ eV, $q_0 = 0.098$ nm^{-1}, $\lambda_0 = 64$ nm. The $G(r)$ factor in (35) modifies the interaction φ_R only at large distance where $\varphi(r)$ has already reached the asymptotic r^{-6} behaviour so that (35) is a fair representation of the interatomic interaction at all distances.

In figure 5 the effect of retardation on $\lambda(q)$ is shown for the state $T = 140$ K and $\rho = 1.9$ nm^{-3}. In this case the upper limit of linearity of $\lambda(q)$ is rather large, $q^{c}_{3\%} = 4.5$ nm^{-1}, when no retardation is included and as expected there is a window of q values where $\lambda(q)$ is essentially linear in q when retardation is taken into account. However the presence of curvature in $\lambda(q)$ is evident at the smaller q and if we allow for a 3% deviation from linearity we find that the lower limit is $q \simeq 0.5$ nm^{-1} for this

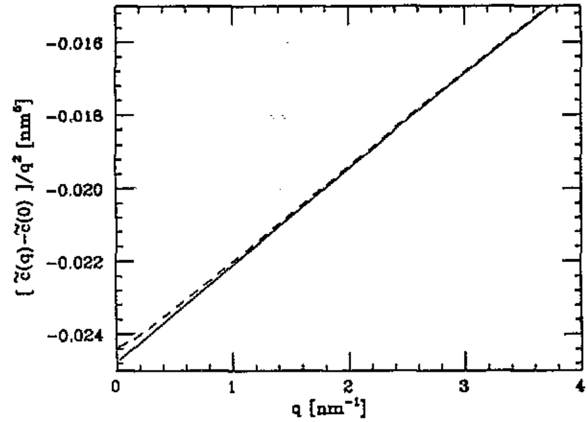

Figure 5. $\lambda(q) = [\tilde{c}(q) - \tilde{c}(0)]/q^2$ as function of q as in figure 2. Here the broken line represents the result for the retarded HFD-B2 potential, equation (35), and the full line for the unretarded one.

thermodynamic state. At higher density where $q^c_{3\%}$ drops below 1 nm^{-1} the window of linearity becomes small or disappears altogether. This last case always applies to $S(q)$ because q has to be so small in order to see linearity in $\mu(q)$ in the unretarded case that the $|q|^3$ behaviour is completely washed out by retardation effects.

Therefore our prediction is that it will only be possible to detect the unretarded $|q|^3$ term under the favourable conditions mentioned in the previous section—an intermediate value of density and analysis of the scattering data in terms of $\tilde{c}(q)$. In other cases the retardation effect washes out the $|q|^3$ term leaving a weaker singularity $q^4 \ln|q|$. Retardation effects should become observable for $q \lesssim 0.5$ nm^{-1}.

In the case of heavier rare gases, for instance xenon, the detection of the $|q|^3$ term should be slightly easier. On one hand the upper limit $q^c_{3\%}$ is somewhat larger than in argon. On the other the characteristic energy $h\nu_0$ is smaller so that also q_0 is smaller by 20–30% in the case of Xe, and the window of linearity of $\lambda(q)$ is larger.

We have considered the effect of retardation on the pair forces only. In a similar manner the large distance behaviour of the three-body AT interaction is affected by retardation and the $|q|^3$ contribution to $\tilde{c}(q)$ and $S(q)$ will disappear at sufficiently small q. However we are not aware of any study of how $\phi^{(3)}_{\rm AT}$ is modified at large distance by retardation.

In general retardation has only a very small effect on the thermodynamic properties of the system but at the highest density the effect is not completely negligible. For instance at $\rho = 21.3$ nm^{-3} and $T = 140$ K, $S(0)$ of argon (two-body forces only) changes from 0.0581 to 0.0562 when retardation is present. This is about one-third of the effect of the AT interaction. However the absolute accuracy of the MHNC is not sufficient to make a comparison with experiment.

5. Conclusions

We have revisited the question of the non-analytic cubic term in the small-q expansion of $S(q)$ of rare gases. On the basis of an accurate integral equation for $g(r)$ and of the best model of the interatomic interaction, included the three-body AT interaction, we find that measurement of $S(q)$ in the range 1–4 nm^{-1} under the most favourable conditions should be able to detect this $|q|^3$ term. Favourable conditions are an intermediate range of density and an analysis of the scattering data in term of $\tilde{c}(q)$ and not $S(q)$. In the region of the triple point the q range needs to be smaller by a factor of five. Existing experimental data for $S(q)$ do not extend to small enough q, for instance the measurement of [8] starts at 2.4 nm^{-1}, and do not allow a clear detection of the $|q|^3$ term. The added range down to 1 or better 0.5 nm^{-1} is essential for this purpose.

We have also considered the effect of retardation of dispersion forces on the correlations in the system. The $|q|^3$ behaviour is modified in $q^4 \ln |q|$ and retardation should affect $S(q)$ and $\tilde{c}(q)$ for $q \lesssim 0.5\ \mathrm{nm}^{-1}$. Therefore detection of retardation effect in the interatomic interaction of rare gases appears to be a feasible experiment. On the other hand this same effect puts limits to the observability of the $|q|^3$ term to the favourable situations mentioned earlier and to the accuracy with which its coefficient can be determined.

The experimental determination of the coefficient $\tilde{c}_3$ of the cubic term of $\tilde{c}(q)$ is of fundamental importance because of the direct and simple relationship between $\tilde{c}_3$ and the large distance behaviour of the interatomic interaction. For a pure two-body interaction $\tilde{c}_3$ is rigorously density independent whereas the presence of the AT interaction leads to a linear ρ dependence. Probably the detection of this density dependence of $\tilde{c}_3$ represents the most unequivocable way of obtaining evidence for the presence of three-body forces in condensed matter, at least in their long-range aspect. Moreover deviation of $\tilde{c}_3$ from linearity in ρ would be evidence for four-body long range interaction. We also point out that the very simple T and ρ dependence of $\tilde{c}_3$ as given by (17) allows for a stringent test of the consistency of an experimentally determined $\tilde{c}_3$. In fact by performing the experiment along two different isotherms the ratio of $\tilde{c}_3$ at the two temperatures but at the same density should be equal to the inverse ratio of the temperatures and this ratio must be independent of density even if many-body forces beyond the three-body ones should be present.

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