DISPERSION FORCES IN SIMPLE FLUIDS PROBED BY NEUTRON DIFFRACTION

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Dispersion forces, acting among the instantaneous electric multipoles arising in each atom of a simple fluid, provide an important contribution to the interaction law $V=V(r_1, \ldots, r_N)$ and represent, in non-polar insulating fluids, the leading term of its long-range tail. Despite the fundamental physical relevance of V, very few (if any) experimental studies of its asymptotic behaviour have been reported in literature until the early nineties. Consequently, this part of V is usually determined using semi-empirical methods which partly rely on experimental data (as polarizabilities, photoabsorption spectra, etc.), while they are heavily based on theoretical calculations [1].

Only quite recently, by taking advantage of the neutron scattering instrumentation and data analysis techniques presently available, it has been experimentally demonstrated that the information contained in the static structure factor $S(k)$ can be profitably used to investigate V and in particular its long-range features. It is worth noting that the search for experimental techniques able to access the asymptotic part of the interaction potential can be of general help, not only to duly verify the computational results and to experimentally constrain the proposed potential models, but also to develop methods of measurement of these fundamental properties in less known or more complicated (e.g., mixtures, conducting fluids, etc.) systems.

In the last decade our group performed a set of experiments on rare gas fluids by means of the Small Angle Neutron Scattering (SANS) diffractometer PAXE (Laboratoire Léon Brillouin, Saclay, France). We shall briefly review some of the results obtained.

For the classical systems considered in the following, we will assume that V can be written as:

$$V(r_1, \ldots, r_N) = S_{i<j} \, V_2(r_{ij}) + S_{i<j<k} \, V_3(r_i, r_j, r_k) + \ldots,$$

$$r_{ij} = |r_i - r_j| \tag{1}$$

where r_i represents the position of the i-th atom. In non-polar insulating fluids, the leading contributions to the long-range part of the pair and triplet interactions are, respectively, the dipole-dipole interaction [2] :

$$V_2(r) \sim - C_6 / r^6 \tag{2}$$

and the triple-dipole one [3] :

$$V_3(r_1, r_2, r_3) \sim ?_{AT}[1+3\cos?_1 \cos?_2 \cos?_3] /$$
$$[r_{12} \, r_{23} \, r_{13}]^3 \tag{3}$$

where r_{12}, r_{23} and r_{13} represent the sides of the triangle formed by three atoms located at r_1, r_2 and r_3, and $?_1$, $?_2$ and $?_3$ are the internal angles of that triangle. For several reasons it is convenient to interpret the results in terms of the direct correlation function $c(r)$ introduced by Ornstein and Zernike in 1914, whose Fourier transform $c(k)$ is connected to the experimentally accessible $S(k)$ via :

$$c(k) = [S(k) - 1] / (n \, S(k)) \tag{4}$$

where n is the number density of the system. Several methods exist for the interpretation of structural data in terms of microscopic forces and they have been applied in various studies [see, for example, Refs. 4, 5 and references therein quoted]. Two examples are here reported.

For classical insulating fluids, the main result of the theory which relates in an analytical way the long-range behaviour of the pair potential to the features of $c(k)$ at small k-values, can be summarized saying that $c(k)$ is expected to have, at small k, a $k^3/$ term directly connected to the strength of the long-range Van der Waals interaction. In formulæ, if Eqs.(2) and (3) are assumed to correctly model V_2 and V_3 at long distance, then for $k ? \ 0$:

$$c(k) \sim c(0) + ?_2 k^2 + ?_3 k^3 + O(k^3) \tag{5}$$

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with :

$$?_3 = p^2 \, \beta \, [C_6 - 8 \, p \, n \, ?_{AT} / 3] / 12 \qquad (6)$$

where $\beta = 1 / k_B T$. A density dependence of the k^3 term in the low-k expansion of $c(k)$ provides a direct way of measuring both the dipolar coefficient C_6 and the strength $?_{AT}$ of the triple dipole interaction and represents a clear-cut evidence of three-body effects. Fig. 1 reports the quantity $?_3/\beta$ as a function of the density for krypton (for comparison, the density of krypton at critical point is 6.55 nm^{-3}) as measured in a set of experiments performed on PAXE [6]. It turns out that, if low-k structural investigations are performed in a wide density range, from the dilute gas case up to densities close to that of the triple point, a significant density dependence of $?_3$ can be detected, thus obtaining $C_6 = (12.5\pm0.6) \, 10^{-78}$ J m^6 and $?_{AT} = (2.3\pm1.6) \, 10^{-107}$ J m^9, in agreement with the semi-empirical estimates present in literature. It is worth noting that this determination of $?_{AT}$, though affected by a large uncertainty, is independent of any assumed model for the pair interaction. More accurate results for $?_{AT}$ can be obtained with other methods, as it has been done for example in [5, 7].
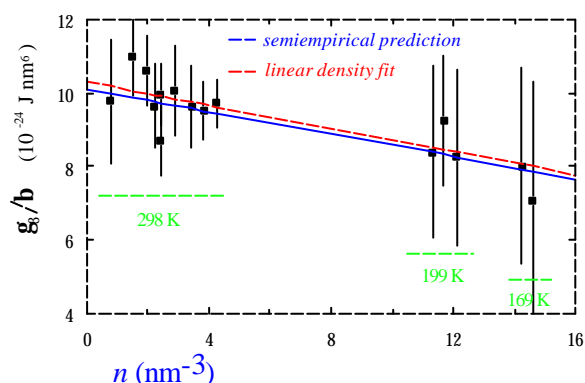

Figure 1. Cubic term $?_3$ in the measured $c(k)$, times $k_B T$, as a function of the density (squares with error bars) for Kr. The solid line represents the theoretical prediction, as calculated from eq. (6) using the averages of the semiempirical estimates for C_6 and $?$ found in the literature. The dashed line is the least-squares fit to all the experimental $?_3 / \beta$ values with the model function $A + B \, n$.

Further knowledge of the microscopic interaction law can be gained comparing the k-dependence of experimental structural quantities with theoretical predictions of reliable liquid state theories, based on different model potentials. In Fig. 2 the experimental density derivatives of $H(k) = [S(k)-1]/n$ are reported for Kr at 169 and 199 K. They

are compared with theoretical results obtained using the MHNC and the SC-HRT theories [see Ref. 8 for details] and three interaction models: a pure two-body (AS, [9]), a two-body plus a usual Axilrod-Teller contribution (AS+AT), and a two-body plus the three-body modification of AT (AS+AT$_{eff}$) required for a good theoretical description of critical-point thermodynamic data [8]. It is seen that deviations of the pure two-body model from the neutron data reach even 100%, while the use of AT and AT$_{eff}$ models greatly improves the agreement. In conclusion, this comparison proved the major role of three-body forces in determining the structure of a simple liquid for k values smaller than the position of the first minimum of $S(k)$, and provided also a convincing evidence of the presence of additional many-body contributions beyond the long-range
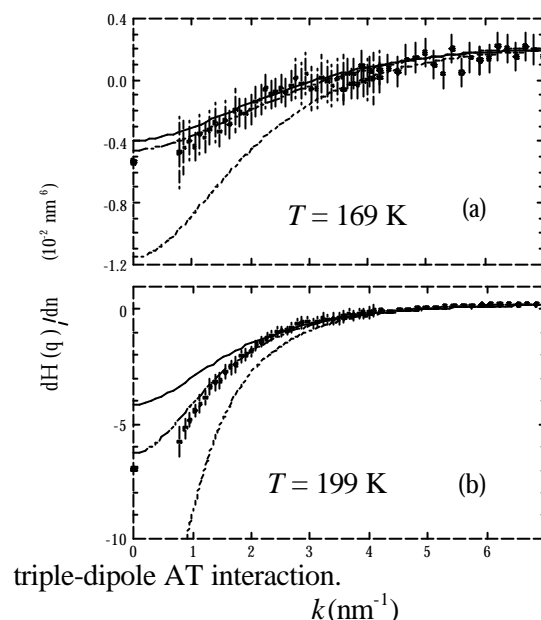

triple-dipole AT interaction.

Figure 2. Experimental density derivative of $H(k)$ (dots with error bars) of liquid Kr. Data at higher k-values (open circles) are from Ref. [10]. The SC-HRT prediction based on the Ref. [9] V_2 pair potential plus (Axilrod-Teller)$_{eff}$ interaction (dash-dotted curve) is shown, together with the MHNC results based on the V_2 (dashed curve) and on the V_2 plus (Axilrod-Teller) interaction (solid curve). Full squares at $k=0$ are the thermodynamic limits. (a) $dH(k)/dn$ at T=169 K and n=14.40 nm^{-3}. (b) $dH(k)/dn$ at T=199 K and n=11.66 nm^{-3}. The derivative from the data of Ref.[10] is at the slightly different density n=11.57 nm^{-3}.

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