Inelastic Neutron Scattering and Molecular Dynamics Determination of the Interaction Potential in Liquid CD_4

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Anisotropic interactions of liquid CD_4 are studied in detail by comparison of inelastic neutron Brillouin scattering data with molecular dynamics simulations using up to four different models of the methane site-site potential. We demonstrate that the experimental dynamic structure factor $S(Q, \omega)$ acts as a highly discriminating quantity for possible interaction schemes. In particular, the Q evolution of the spectra enables a selective probing of the short- and medium-range features of the anisotropic potentials. We show that the preferential configuration of methane dimers at liquid densities can thus be discerned by analyzing the orientation-dependent model potential curves, in light of the experimental and simulation results.

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The still limited knowledge about the intermolecular interactions governing the microscopic behavior of fluids explains the unfading scientific interest in this field. In addition to the experimental and theoretical methods used to access the interaction law [1–3], modern liquid state physics has greatly benefited from the advent of computer simulation techniques [4], which often represent the only possibility for testing model potentials of polyatomic systems against experimental results.

From the experimental side, the accuracy and resolution attainable in neutron scattering determinations of the static, $S(Q)$, and dynamic, $S(Q, \omega)$, structure factors have been crucial to study the interaction in monatomic fluids. Neutron experiments of the last decade, combined with simulations and/or theory, clearly showed that many, even weak, interaction properties (short- and long-range, two- and three-body) can be accessed by exploiting accurate structural and dynamical data, both for rare-gas fluids [5–10] and for liquid metals [11,12].

In the more complex case of molecular systems, static structure neutron measurements and simulations have certainly provided a wealth of useful data both on the average center-center interactions, and on the traces of anisotropic forces [13–20]. Differently, the few existing neutron studies of $S(Q, \omega)$ in simple molecular liquids [21–23] were mainly focused on the experimental characterization of collective modes, neglecting their connection with the interaction law. Thus, the important opportunity to draw deeper, "non–frequency-integrated," information on the interactions in polyatomic liquids from the dynamical quantities has not yet been seized. A dynamical approach to the interaction properties can be much more strictly probing than the static counterpart, since spectral shapes supply more stringent tests of trial potential models.

The totally unexplored "interaction sensitivity" of $S(Q, \omega)$ of molecular fluids is now within reach of molecular dynamics (MD) simulations and high-resolution inelastic neutron scattering (INS) experiments. Thanks to present computing power, accurate collective and self-correlation functions can efficiently be obtained for several potential models. On the other hand, the well-defined coupling of the probe to the nuclei in the system makes the neutron technique the most suited for determinations of spectral intensities on an absolute scale. Thus, joint dynamical neutron measurements and simulations represent a novel method for investigations of the microscopic properties of polyatomic liquids, which we apply here to the study of the interaction potential of methane.

Methane is an interesting representative of the complexity of the interaction problem we encounter in molecular systems: even for this simple classical fluid, composed of nonpolar molecules with high symmetry and low polarizability (i.e., negligible three-body terms and thermodynamic state dependence), several, rather different, site-site interaction potentials have been proposed (e.g., see Refs. [18,24–27]). Such a variety clearly shows that molecular liquids still miss well-assessed and unified criteria for the general modeling of the potential energy function, already at the level of the pair interactions even for the simplest molecules. The case of methane is further intriguing since, on the one hand, some of its properties can qualitatively be described in terms of a monatomic-like behavior; on the other hand, the role of anisotropy, pointed out long ago [28,29], needs to be clarified, in order to discriminate among the available potentials and between contrasting conclusions about the presence of orientational correlations in the fluid phase [18,29].

For these purposes, we probed the dynamics of liquid CD_4 by means of parallel INS experiments and MD simulations in the wave vector range $2 < Q[\mathrm{nm}^{-1}] < 15$, the highest Q reaching about 80% of Q_p, i.e., the position of the main maximum in the static structure factor [30]. The molecular number density of the CD_4 sample is $n = 16.6\ \mathrm{nm}^{-3}$ at $T = 97.7$ K. A brief preliminary account of the neutron measurements, partially analyzed for a discussion of the approximate center-of-mass dynamics, was given in Ref. [31], where the energy and damping of collective modes in CD_4 were compared with those of other mono- and polyatomic fluids. Here we present the total coherent neutron spectra obtained by a complete data analysis, which, after typical corrections for background, attenuation, and multiple scattering, also requires a careful treatment of the incoherent scattering.

Both total and self-dynamics simulations were carried out for the CD_4 sample, using a reasonable selection of existing site-site potentials, i.e., the two empirically derived models of Righini, Maki, and Klein (RMK) [25] and of Strauss *et al.* (SA) [18], and the two *ab initio* based models of Tsuzuki, Uchimaru, and Tanabe (TUT) [26] and of Rowley and Pakkanen (RP) [27].

For each model, constant-*NVE* calculations were performed by following the time evolution of 4000 molecules for more than 300 ps, after a thermalization interval greater than 60 ps. Using a force cutoff distance of 1.5 nm, the equations of motion were integrated as described in Refs. [31,32], with a time step of 2 fs. The simulations finally provided us with the *partial* $S_{\alpha\beta}(Q, \omega)$ (with $\alpha, \beta =$ C, D) and *self*, $S_{\alpha,\mathrm{self}}(Q, \omega)$, dynamic structure factors. The usual definition [33] of $S_{\alpha\beta}(Q, \omega)$ was adopted here.

The INS experiments give instead access to the total double-differential cross section. This, apart from energy resolution and other instrumental effects, is proportional to the sum of coherent and incoherent terms, i.e.,

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \tilde{S}_{\mathrm{coh}}(Q, \omega) + \tilde{S}_{\mathrm{self,inc}}(Q, \omega), \tag{1}$$

where, omitting the (Q, ω) dependence, for CD_4 we have:

$$\tilde{S}_{\mathrm{coh}} = b^{(\mathrm{C})2}_{\mathrm{coh}} S_{\mathrm{CC}} + 4 b^{(\mathrm{C})}_{\mathrm{coh}} b^{(\mathrm{D})}_{\mathrm{coh}} S_{\mathrm{CD}} + 4 b^{(\mathrm{D})2}_{\mathrm{coh}} S_{\mathrm{DD}} \tag{2}$$

$$\tilde{S}_{\mathrm{self,inc}} = b^{(\mathrm{C})2}_{\mathrm{inc}} S_{\mathrm{C,self}} + 4 b^{(\mathrm{D})2}_{\mathrm{inc}} S_{\mathrm{D,self}}, \tag{3}$$

with $b^{(\alpha)}_{\mathrm{coh/inc}}$ the coherent or incoherent neutron scattering lengths of the nuclei in the molecule.

From MD the coherent part of the spectra appears to be more sensitive to the intermolecular potential. Thus, it is convenient to subtract the incoherent component $\tilde{S}_{\mathrm{self,inc}}$ from the neutron data. Such a contribution can be evaluated resorting to simulations of $S_{\alpha,\mathrm{self}}$, performed for consistency with each interaction model, after proper detailed-balance asymmetrization of the classical MD outputs. In our case, the MD self-spectra turn out to be nearly independent of the potential within the instrumental resolution, at all investigated Q values. Therefore, subtraction of the incoherent term from the CD_4 data leads to coherent spectra which superimpose each other within the experimental uncertainties.

Figure 1 compares, at various Q values, the experimental $\tilde{S}_{\mathrm{coh}}(Q, \omega)$ of liquid CD_4 with the asymmetrized MD

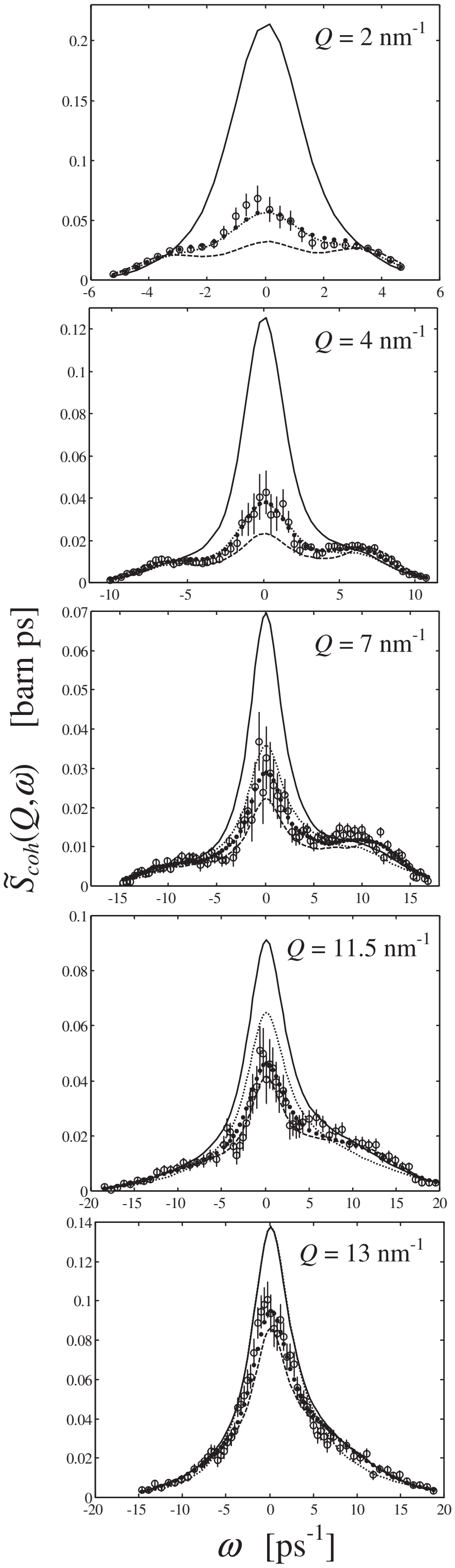

FIG. 1. $\tilde{S}_{\mathrm{coh}}(Q, \omega)$ of liquid CD_4 at selected Q values. Neutron data (circles with error bars) are compared with the MD results, after instrumental resolution broadening, for the SA (dotted line), RMK (solid line), TUT (full dots) and RP (dashed line) potentials. In the lowest frame, the SA and RMK central peaks coincide.

results, broadened according to the experimental resolution, and combined following Eq. (2).

From Fig. 1, it is clear that the TUT model gives a remarkably good description of the experimental data at all Q values, while the RMK potential is hugely inefficient. The RP and SA results show opposite tendencies with varying Q. The former is unable to account for the central peak in the low-Q spectra. The latter, while accounting for the low-Q dynamics very well, becomes more and more inefficient as Q grows, with departures that progressively affect the whole spectral shape.

As to the RMK model, this clearly misses the experimental spectra, with enormous discrepancies affecting the central peak at small Q values. These gross inaccuracies seriously compromise the RMK prediction of the low-Q static structure and, very likely, of the isothermal compressibility, which is related to $S(0)$. In this respect, it is worth recalling that the decisive role of attractive interactions on the low-Q ($\simeq 1$–$2\ \mathrm{nm}^{-1}$) structure of fluids is a well-established achievement of theoretical and experimental research in this field [8–10,34].

Concerning the central Rayleigh line, we note that the RMK and RP predictions display an opposite behavior: the former largely overestimating, the latter underestimating, the experimental low-Q data.

As a fact, we have experimental and MD data that, at low-Q values, point at some equivalence in the TUT and SA potentials, while, at higher-Q values, indicate some similarity in the TUT and RP behaviors. These observations can find a unifying explanation by analyzing the salient features of the various interaction models, for a few representative molecular orientations.

Figure 2 shows the total potential energy curves of the above models, as a function of the CC distance, in three example configurations of the methane dimer: base-vertex (bv), base-base (bb), and vertex-vertex (vv). To show all the details of both the medium- and short-range features of the various potentials, the hard-core region is plotted on a semilogarithmic scale.

Inspection of Fig. 2 quite straightforwardly leads to the conclusion that only bv configurations correspond to potential curves compatible with the results of Fig. 1. Indeed, only bv-like geometries of the dimer show, in different ranges, the close resemblance of TUT with SA, and of TUT with RP that is witnessed by the Q evolution of the spectra.

In particular, in bv-like dimers, TUT and SA display equivalent main features in the attractive-well region, with nearly equal values of the well depth and of the collision parameter. In the same region, RMK and RP show differences of opposite sign from the TUT (or SA) behavior, of large size in the RMK case. All these facts, occurring simultaneously in the bv case only, account for the observed trends in the low-Q spectra, which, actually, are expected to mostly probe the medium-range attractive properties of the potential. The neutron and MD data

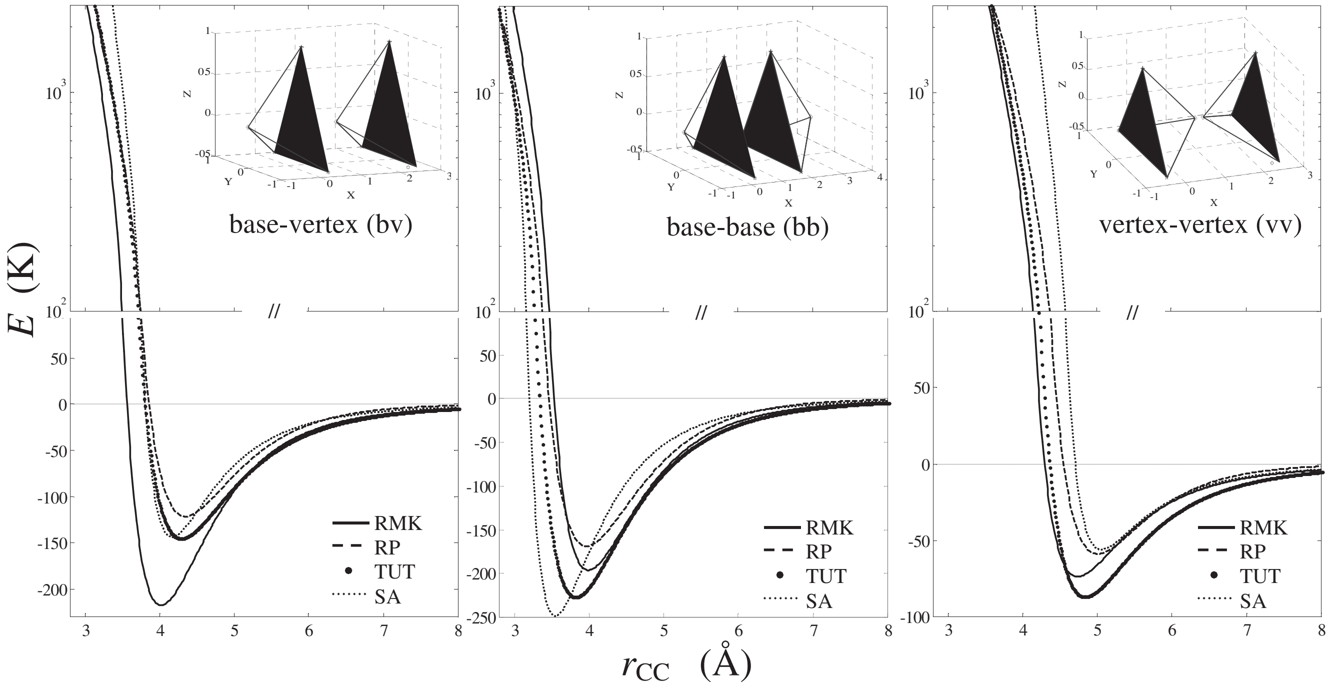

FIG. 2. Three significant configurations of methane dimers (3D graphs in the reference system XYZ, reported as insets) and corresponding total CD_4-CD_4 potential energy, in units of the Boltzmann constant. Different curves refer to the RMK (solid curve), TUT (full circles), RP (dashed curve), and SA (dotted curve) models, plotted as a function of the CC distance along the X axis of the coordinate system. Different energy scales are adopted to enhance, simultaneously, all the details of the attractive well and of the repulsive wall: a linear scale for the former, and a logarithmic scale for the latter.

reveal, in particular, that even small differences in the schematization of attractive forces are magnified in the low-Q dynamics, and mainly affect the correct prediction of the Rayleigh line in the spectra.

On the other side, in bv-like configurations, TUT and RP show nearly coincident hard-core properties. Conversely, SA is clearly characterized by the hardest repulsive behavior. Such features, peculiar of the bv case only, justify the neutron and MD results at intermediate and high-Q values, where the short-range interactions are more and more sensitively probed as Q_p is approached. The data further indicate that different hard-core behaviors modify all portions of the higher-Q spectra.

Our comparison of the experimental and simulated dynamic structure of liquid CD_4 on an absolute scale, combined with the study of the orientation-dependent model potential curves, provides a convincing evidence that bv-like geometry dominates in the short-range arrangement of methane molecules at liquid densities, and probably favors a molecular network at the nanometric scale.

This study proves that neutron dynamical data are extremely selective, not only as far as medium- and short-range anisotropic potential effects are concerned, but also as regards the preferred orientation of the molecules in the liquid. Thus, in this work, we decidedly unveiled the importance of orientational correlations in the dense liquid phase of methane.

The joint use of neutron spectroscopy and computer simulations is shown here to rise to a novel and genuine discriminating method in the investigation of interaction effects in a polyatomic liquid. We believe that such an access to molecular liquids dynamics, though demanding, is of general application, and deserves due efforts. Indeed, these can be rewarded by the remarkable opportunity of performing an interaction analysis which, like the present one, can lead to an unexpectedly rich pool of information.

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