

Direct experimental assessment of the strength of orientational correlations in polar liquids

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The strength of molecular orientational correlations in polar liquids is assessed by means of comparison of the diffuse scattering patterns of a liquid composed by molecules devoid of permanent electric dipole but having a weak quadrupole moment and those for a liquid composed by permanent molecular dipoles. The extent of orientational correlations within the liquid phases is in both cases assessed by comparison of the liquid radial distributions to those present in the rotator-phase (plastic) crystal phases of both compounds. For such disordered-crystal phases, information concerning orientational correlations is directly derived from the experimental scattering patterns by means of analysis of the diffuse scattering background present beneath the Bragg peaks. The results show that rather than long-ranged, orientational correlations in polar or polarizable liquids are confined within distances comprising the second coordination sphere.

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I. INTRODUCTION

The role played by long-range electric multipolar interactions in polar liquids to determine short-ranged space-time correlations has been the issue of numerous research efforts [1]. One of the puzzling issues within the field is the widespread appearance of exponential (Debye) relaxations characteristic of isotropic molecular reorientations within a dielectric continuum [1]. In fact, for liquids composed by particles experiencing strong multipolar interactions one may expect to find significant deviations from exponential relaxation due to dielectric friction as well as due to the onset of collective oscillatory dipole motions [2]. The absence of such deviations in many experimental observations, lead to some [3] to postulate a mechanism able to reconcile this expectancy with experiment attributing the presence of mostly Debye relaxation to the combined effects of molecular translations and rotations. That is, purely rotational motions were expected to give rise to departures from Debye behavior, but these are deemed to be minimal once translational motions set in. An experimental assessment of such a mechanism was reported some time ago in Ref. [4] by means of a comparison of the shape of the dielectric spectra of several liquids to that of the same materials within their rotator-phase crystals (RPC). The results suggested the inability of the model described in Ref. [3] to account for significant experimental evidence since the effects of translational motions on dielectric relaxations within the rotationally disordered crystals are deemed to be minimal and still, the dielectric spectrum shows an exponential shape.

Recent data for materials that can be prepared within liquid and rotationally-disordered crystal phases [5], also show that the dielectric spectrum for both states exhibits close analogies which suggest that molecular orientational correlations within the liquid and rotator-phase crystal share many

common characteristics. Furthermore, the basic phenomena observed on such systems can also be found in simple systems such as hard dipolar ellipsoids that are amenable to detailed microscopic calculations [6]. The adequacy of the RPCs as test benches for studies on orientational correlations is grounded upon the closeness of their thermodynamic stability to that of the molten materials, taken on the Ostwald rule of stages sense.

On general grounds, the quantitative characterization of orientational correlations in liquids constitutes a basic requirement for the understanding of their microscopic dielectric properties, within which the $\epsilon(Q)$ static longitudinal, wave-vector-dependent component of the dielectric tensor $\epsilon_{\alpha\beta}(Q)$ is paramount. In fact, our knowledge about this property heavily relies upon the availability of microscopic information on the charge-density structure factors. These quantities are in principle amenable to experiment by neutron diffraction [7], and in fact estimates for the response function $\chi(Q) = 1 - 1/\epsilon(Q)$ can be obtained from information pertaining a whole set of atomic $g_{ij}(r)$ partial pair distribution functions. Derivation of accurate sets of such functions is however a considerable task. In fact, experimental and theoretical efforts to quantify the strength of orientational correlations date back several decades. A pioneering effort carried out to determine the extent of positional and orientational correlations by direct (i.e., diffraction) means using a combination of neutron diffraction using isotope substitution and x-ray diffraction data was reported by Bertagnolli *et al.* [8] The resulting data which are largely affected by uncertainties due to measurement statistics did provide a set of one-dimensional projections of the static liquid structure in terms of static correlations cast in form of a rotational invariant formalism. Also, progress has also been registered on more recent times on modeling these phenomena with the help of

the integral equation theory [9] as well as numerical simulations. While the calculation of some features characterizing orientational order such as the Q -dependent Kirkwood g factor are now beginning to reach acceptable accuracy, the predictions concerning strong-interacting liquids still are affected by relatively large uncertainties [9].

Here we report on experimental results aiming to shed some light onto these aspects, particularly concerning the issue of how orientational correlations within the rotationally disordered (plastic crystal) state relate to those for the melt. The rationale behind such an endeavor bases itself upon data referred to above [5] which show that data pertaining RPCs provide a good measure of the strength of such correlations within the liquid. For such a purpose we have carried out neutron diffraction studies on two materials, carbon tetrachloride (CCl_4) and tert-butyl chloride $[(\text{CD}_3)_3\text{CCl}]$ that can be studied within the normal liquid phase as well as into high-symmetry fcc rotator-phase crystals. The former sample is composed by molecules with high point-group symmetry T_d and consequently are devoid of permanent electric dipoles, while retaining a weak electric octupole moment ($Q_{el}=15\pm 3 \text{ D \AA}^2$ [10]). In contrast, $(\text{CD}_3)_3\text{CCl}$ molecules show a lower C_{3v} symmetry and this leads to a finite value for its electric dipole moment which has a gas-phase value of $\mu_{elec}=2.14 \text{ D}$ [10].

II. EXPERIMENTS AND DATA ANALYSIS

The measurements were carried out using the D1b diffractometer at the Institut Laue Langevin (Grenoble) employing an incident wavelength $\lambda=1.28 \text{ \AA}$. The preparation of the samples in their liquid or RPC phases was carried out *in situ*, by means of mild thermal treatments. Measurements were performed, on both compounds, at temperatures of 298 K and 240 K corresponding to liquid and RPC phases of CCl_4 and at 298 K and 238 K for those pertaining $(\text{CD}_3)_3\text{CCl}$, respectively. The samples were contained in standard vanadium cans. The diffraction histograms (neutron counts versus detector angle) were fully corrected and converted into absolute scales by means of the CORRECT program package [11] using a vanadium rod as an external reference. The measured quantity is thus the single-differential neutron scattering cross section which contains contributions from spin-incoherent and coherent scattering processes,

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{d\sigma}{d\Omega}\right)_{inc} + \left(\frac{d\sigma}{d\Omega}\right)_{coh}, \quad (1)$$

the latter being also a sum of contributions

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{self} + \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{intra} + \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{inter}, \quad (2)$$

where superscripts denote scattering processes not giving rise to interference, those generated by nuclei within a single molecule and those resulting from nuclei located on different molecules. The latter two are related to sum of all partial structure factors weighted by the respective coherent neutron scattering lengths as

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{dist} = \sum_{\alpha=1}^M \sum_{\beta=1}^M b_{\alpha} b_{\beta} (S_{\alpha\beta}(Q) - 1) \quad (3)$$

and the summations run over molecules within the sample all composed by M atoms.

The static structure factors $S(Q)$ that correspond to the weighted average Eq. (3) for both samples in their liquid and RPC forms are shown in Fig. 1.

To explore the effects of the high- Q truncation of the diffraction pattern previous to Fourier transformation, we carried out several tests inverting the $Q(S(Q)-1)$ interference functions by means of a MaxEnt algorithm [12]. The procedure is free from truncation effects since the prior distribution may be subjected to different constraints [12]. The results were then compared to those already measured for liquid CCl_4 that reach far larger momentum transfers. Most of the effects of truncating the fully corrected structure factor concern the amplitudes of the intramolecular peaks, while those differences pertaining the inter-molecular correlations were found to be comparable to those exhibited by the same material in measurements performed using total-diffraction or reactor-based techniques [13].

Reverse Monte Carlo simulations were performed using a standard package [14]. This method uses a standard Monte Carlo algorithm where the χ^2 statistic calculated from difference between experimental structure factor and that calculated from the particles configuration within the simulation box is taken as the cost function to be minimized instead of the system energy. A number of constraints need to be satisfied which in our case bound the molecules to retain molecular geometries and maximal vibrational displacements not exceeding those given by molecular mechanics calculations. Such a step was found to be necessary to avoid unphysical molecular deformations. While the method does not guarantee the uniqueness of the solution it provides a realistic molecular configuration compatible with the experimental observation. For a recent appraisal of the performance of such methods as well as its range of application the interested reader may consult Ref. [15].

Simulation runs for the liquids were carried out on an ensemble of 1000 molecules. This corresponds to simulation boxes of 54.34 \AA of side for CCl_4 and 55.8 \AA in the case of $(\text{CD}_3)_3\text{CCl}$ compound. Those concerning the RPC phases employed 864 molecules using simulation boxes of 50 \AA and 52 \AA , respectively. In order to increase statistics, averages over different initial configurations were taken.

III. RESULTS

A first pertinent remark that can be made upon a glance to Fig. 1 concerns the close similarity of the diffuse scattering pattern (i.e., the scattering intensity beneath the sharp Bragg peaks), of the liquid and RPC phase of CCl_4 . Indeed, most of the differences between the two diffractograms concern the appearance of a strong Bragg peak corresponding to the $[200]$ reflection [16] at momentum transfers $Q \approx 1.508 \text{ \AA}^{-1}$ that corresponds within the melt to those characteristic of the first sharp diffraction peak (FSDP). Such similitude indicates the existence of a single length-scale for this material that is

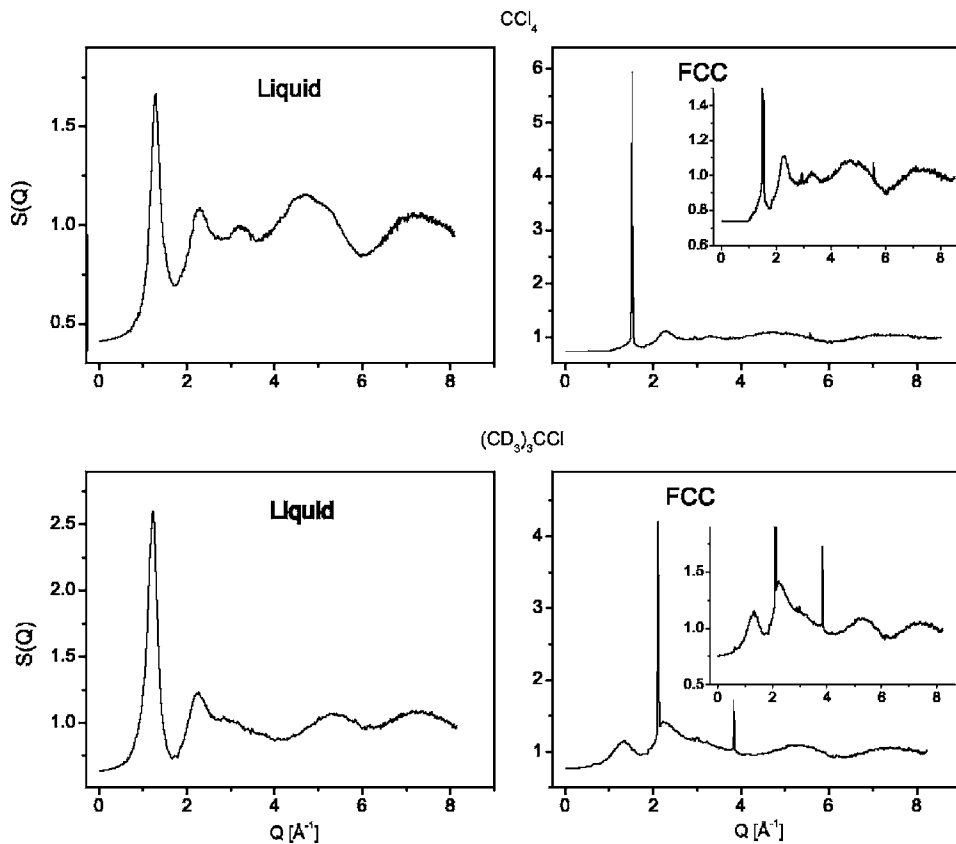


FIG. 1. The upper frame shows the total static structure factors for CCl_4 at 298 K (liquid, left) and 240 K (RPC, right). The lower frames show the corresponding quantities for $(\text{CD}_3)_3\text{CCl}$ at 298 K (liquid) and 238 K (RPC). The inset within the right-hand-side frames are blowups plotted for the ease of comparison with those for the liquids.

composed by globulelike molecules and, in the absence of further information, suggests that packing effects dominate over orientational correlations. Such proximity is not so easily established for $(\text{CD}_3)_3\text{CCl}$ due to the strong texture of the crystals that masks the appearance of a strong peak on top of the lowest-angle diffuse peak as seen in other studies [17]. Positional correlations are here sensed by the Bragg pattern that has its lowest visible [220] reflection at $Q \approx 2.1 \text{ \AA}^{-1}$ [18], sitting close to the second peak of the diffuse diffraction patterns.

Let us start our analysis with the rotator-phase-crystal diffraction data. To put the observations on quantitative grounds, let us recall that $S(Q)$, the static structure factor for the RPC's can be approximately decomposed into a sum of Bragg and diffuse components [19],

$$S(Q) = S_{\text{Bragg}}(Q) + S_{\text{diff}}(Q), \quad (4)$$

where $S_{\text{Bragg}}(Q)$ provides information about the time-averaged crystal structure [19] which in both cases correspond to fcc lattices where the nodes are occupied by the molecular centers of mass. The underlying assumption here concerns the weakness of translation-rotation coupling effects, which are deemed to be small in these materials [20]. The Bragg pattern in turn contains

$$S_{\text{Bragg}}(Q) = \langle |b_Q|^2 \rangle \quad (5)$$

where $\langle \dots \rangle$ denote a thermodynamic average; and

$$b_Q = \sum_j b_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (6)$$

where b_j is the scattering length and \mathbf{r}_j the position of the j th nucleus and the sum runs over all the nuclei in the system. The diffuse scattering part $S_{\text{diff}}(Q)$ arises from the equilibrium thermal fluctuations in b_Q and is formally expressed as $S_{\text{diff}}(Q) = \langle |\delta b_Q|^2 \rangle$. A contribution to such diffuse scattering patterns arises from the molecular form factors, that is the interference effects arising from pairs of nuclei within a molecule composed by M nuclei separated by distances d_{ij} and executing vibrational motions with an amplitude γ_{ij} . These give rise to the contribution $(d\sigma/d\Omega)_{\text{coh}}^{\text{intra}}$ to the total cross section that is responsible for the oscillatory pattern dominating the region of large momentum transfers. Since the molecular geometries are well known, this contribution is easily modeled as

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{\text{coh}}^{\text{intra}} &= f(Q) \\ &= \left(1 / \sum_i b_i \right)^2 \sum_{i \neq j}^M b_i b_j \sin(Qd_{ij}) / (Qd_{ij}) \exp(-\gamma_{ij} Q^2). \end{aligned} \quad (7)$$

Once modeled, this contribution can be subtracted from the total diffraction pattern following well established procedures [21] based upon data concerning the molecular structures and vibration amplitudes. These are either known from previous experiments [22,23] or can be reliably calculated

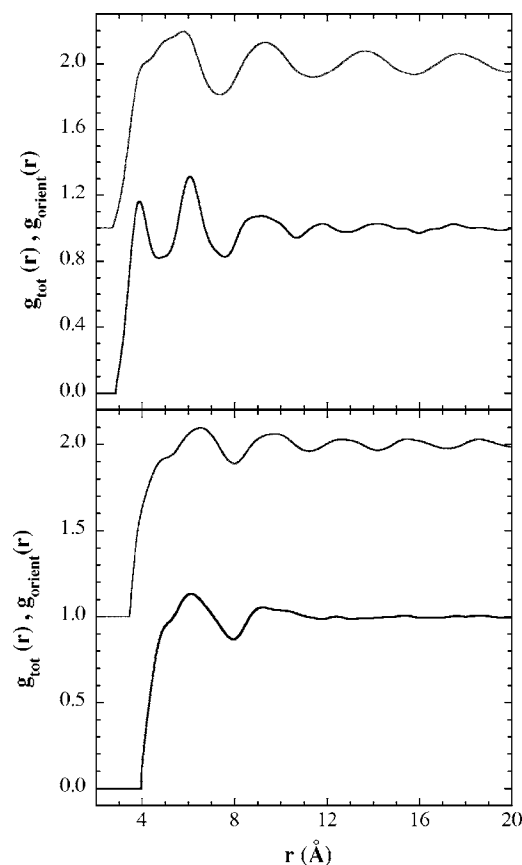


FIG. 2. The upper frame shows a comparison of $g_{orient}(r)$ (lower curve) and the total $g_{tot}(r)$ intermolecular radial distributions (upper curve) for CCl_4 at $T=240$ K in its rotator-phase crystal. The lower frame shows the corresponding quantities for $(\text{CD}_3)_3\text{CCl}$ $T=238$ K (RPC). Notice that the curves for $g_{tot}(r)$ are shifted upwards by one unit.

from theoretical chemistry approaches. In what follows all the structure factors under considerations will regard those where such contribution has been subtracted.

The approximate isolation of the relevant distribution function for orientational correlations is thus carried out by subtracting the Bragg pattern from the measured $S(Q)$, yielding $S_{diff}(Q) = S(Q) - S_{Bragg}(Q)$. The $S(Q)$ and $S_{diff}(Q)$ will thus provide estimates for the real space radial distribution functions,

$$g_{tot}(r) = 1 + \frac{\rho}{2\pi^2} \int_0^{Q_{max}} [S(Q) - 1] \frac{\sin(Qr)}{Qr} Q^2 dQ, \quad (8)$$

$$g_{orient}(r) = 1 + \frac{\rho}{2\pi^2} \int_0^{Q_{max}} [S_{diff}(Q) - 1] \frac{\sin(Qr)}{Qr} Q^2 dQ. \quad (9)$$

Figure 2 depicts a comparison between $g_{tot}(r)$ and $g_{orient}(r)$ as derived for the two RPC's.

Data pertaining $g_{tot}(r)$ for CCl_4 as displayed in Fig. 2 show a periodic oscillation with period ≈ 4.1 Å which

extends up to ≈ 5 Å where the first maximum of such an oscillation appears as a shoulder superposed to other short-range structure. Such an oscillation arises as a result of the strong Bragg peak and from values just given it becomes clear that such an oscillation provides a measure of the radially-averaged distribution of molecular centers of mass $g_{com}(r)$. The $g_{orient}(r)$ curve also displayed there shows, as expected, an aperiodic oscillatory structure extending somewhat beyond 15 Å. Its first narrow peaks at 13.9 Å 6.0 Å indicating very strong orientational correlations at short distances came as a surprise, account made of the absence of permanent molecule dipole moments. In stark contrast, data for $(\text{CD}_3)_3\text{CCl}$ show significantly less marked features. The total $g_{tot}(r)$ shows again an oscillatory pattern up to large distances indicative of crystalline positional ordering. Its narrow period of ≈ 3.1 Å, warns against an over-simple interpretation since such high frequency comes as a consequence of the vanishingly low intensity of the lower angle 1.25 \AA^{-1} reflection due to the growth along the [111] direction of strongly textured crystals. What is here of importance is however the marked contrast between the $g_{orient}(r)$ orientational function for the latter material and that shown by CCl_4 . As seen from the figure, $g_{orient}(r)$ shows significant features confined below ≈ 12 Å and also evidences far less sharp features at short distances. The result is most striking if one considers that such a molecule shows a substantial permanent dipole moment.

The total intermolecular radial distributions for both liquids are shown in Fig. 3.

Data for liquid CCl_4 show visible oscillations up to relatively large distances, which account made of the molecular dimensions tell that correlations persist within the liquid up to about four times the value of the molecular diameter. The extent in distance of such correlations is seen to be comparable to that seen for the RPC, showing oscillations in $g_{orient}(r)$ that last up to some 20 Å. The most remarkable feature is however the perfect match in position of the first two peaks of the disordered crystal $g_{orient}(r)$ to those of the liquid. This unmistakably tells that short-ranged orientational correlations in liquid and RPC share common characteristics, even if those within the liquid are far less marked. In both cases they give rise to the lower-distance peaks in the total radial distributions while those arising from positional correlations only contribute to such quantities as a shoulder appearing at ≈ 5 Å. The results for liquid $(\text{CD}_3)_3\text{CCl}$ show also a remarkable match of the first peaks for both the liquid and RPC radial distribution. The action of the electrostatic forces in both liquid and crystal is here evidenced by the coincidence in peak position and height of the first peak. Notice however that in both cases the structure is less marked than that for CCl_4 and also oscillations persist up to somewhat shorter distances.

The similitude of peaks in $g_{orient}(r)$ for CCl_4 with prominent features in liquid $g_{tot}(r)$ provides an indication of their orientational nature. Such an assertion is also substantiated by results of the density dependence of $g_{tot}(r)$. In fact data from Ref. [24] shows that the liquid FSDP shifts to higher momentum transfers as a consequence of the 13 per cent increase in density, following a non-linear trend. In contrast,

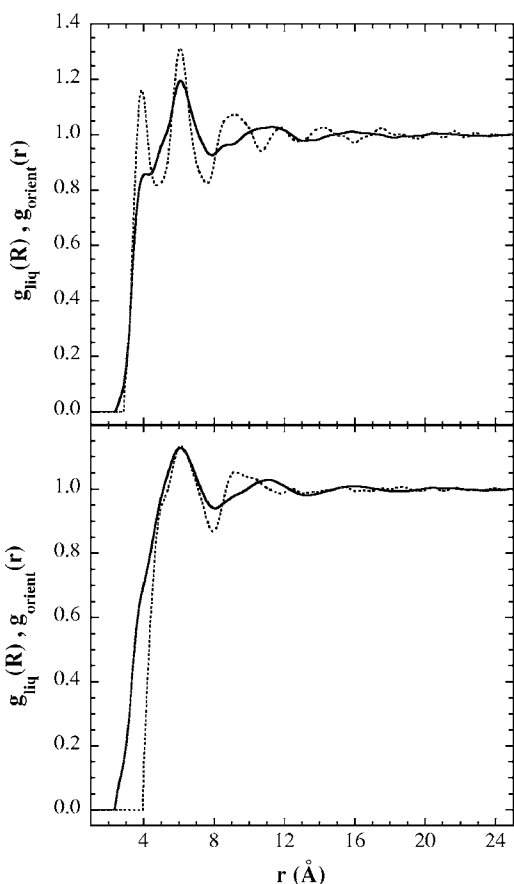


FIG. 3. The upper frame displays $g_{tot}(r)$ for liquid CCl_4 (solid line). Superposed to such curve is shown $g_{orient}(r)$ as derived for the RPC (dotted line). The lower frame shows the corresponding functions for $(\text{CD}_3)_3\text{CCl}$.

the peak seen in $g_{tot}(r)$ at $\approx 3.5 \text{ \AA}$ significantly increases in height and that at about 7.6 \AA sharpens up somewhat but both remain unshifted. Although no study on the density dependence of $S(Q)$ has been reported for liquid $(\text{CD}_3)_3\text{CCl}$, the matching of the position of the main peak of the liquid $g_{tot}(r)$ and that of the RPC $g_{orient}(r)$ can plausibly be understood on the same basis.

IV. DISCUSSION

The experimental findings reported on above have been then analyzed by means of Reverse Monte Carlo (RMC) simulations of the scattering patterns. The carbon-carbon partial radial distribution function $g_{CC}(r)$, for CCl_4 provides a good measure of the distribution function for the molecular centers of mass $g_{com}(r)$ and it is shown in Fig. 4. From there we can infer details about the molecular weighted density distribution

$$\rho(r) = 4\pi\rho_m r^2 g_{com}(r), \tag{10}$$

where ρ_m stands for the macroscopic number density.

Numerical information on molecular coordination numbers (MCN) are then obtained from integrals taken over the

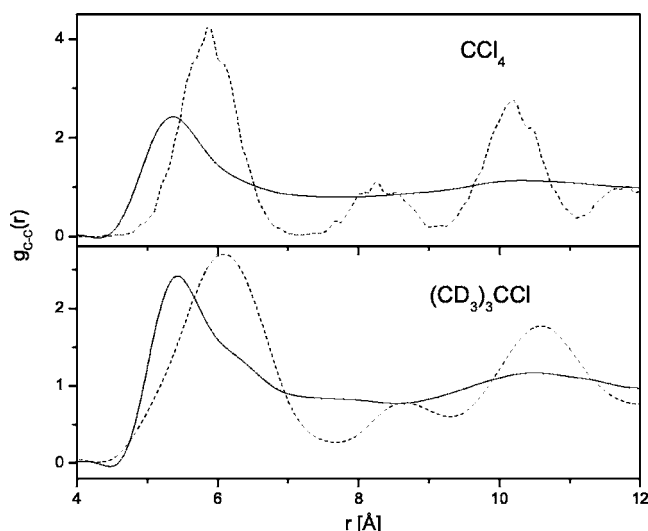


FIG. 4. C—C pair partial correlation functions for both compounds. Solid lines correspond to liquid phases, dashed lines to fcc.

peaks of $\rho(r)$, and it is shown in Fig. 5. Data for the first shell yields ≈ 12 molecules, that is the same as that for the fcc crystal. The result suggests that packing within liquid CCl_4 also shares common characteristics with that for an atomic fluid, a result that comes into line with estimates reported on in Ref. [25], where the liquid structure is described in terms of packing of hard-spheres of diameter $\sigma = 5.041 \text{ \AA}$. This figure compares to that of $\sigma = 5.4 \text{ \AA}$ derived from the position of the peak maximum of g_{com} . The difference between both values is fully accountable if the characteristics of hard-sphere potentials compared to more realistic functions are taken into consideration.

Following the same steps as done for carbon tetrachloride, we can assimilate the shape of the $(\text{CD}_3)_3\text{CCl}$ molecule to

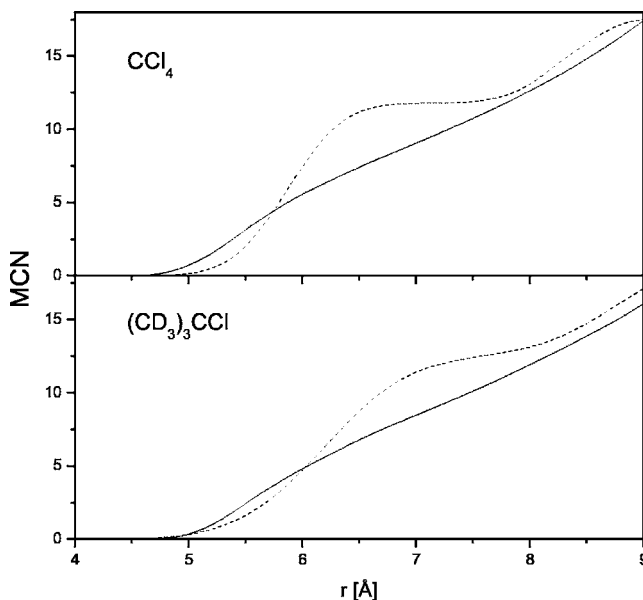


FIG. 5. Integrals taken over the molecular weighted density distributions for both compounds. Solid lines correspond to liquid phases, dashed lines to fcc.

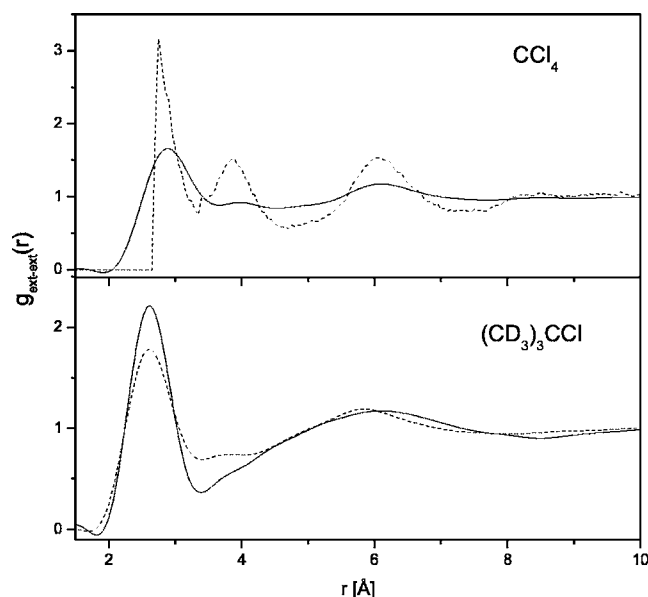


FIG. 6. External-external atoms pair partial correlation functions for both compounds. Solid lines correspond to liquid phases, dashed lines to fcc.

that of a sphere, an approximation warranted by the close values of the van der Waals radii of chlorine and the methyl pseudoatom [26]. Data for the partial $g_{CC}(r)$ as well as for the coordination number are shown in (Figs. 4 and 5). If we disregard the offset of about 0.4 Å from the molecular center of mass and make use of the partial $g_{CC}(r)$ as an estimate for $g_{com}(r)$ we again find a value of $\sigma \approx 5.4$ Å for the sphere diameter. The calculated molecular coordination number now turns to be of 11 molecules. Such a difference points towards the less packed structure of tert-butyl chloride compared to that of CCl_4 , a finding that correlates with the smaller value of the macroscopic density of the former.

A comparison with data pertaining the fcc phases can now be directly made from inspection of graphs shown in Fig. 4 and Fig. 5. From there, one sees that for distances comparable to the values of the estimated diameters quoted above, both liquids are significantly *denser* than the corresponding crystals, even if the macroscopic densities of the latter are higher. The situation is however reversed at somewhat higher distances, where the number of surrounding molecules about a central one in the crystal exceeds that of the liquid.

To infer additional information about orientational correlations, we consider the functions $g_{ext-ext}(r)$ shown in Fig. 6. These are defined as scattering-length weighted averages taken over the “external atoms,” that latter being the four chlorine in CCl_4 [i.e., this definition makes this function equivalent to the $g_{Cl-Cl}(r)$ distribution] and the chlorine plus the methyl groups in $(\text{CD}_3)_3\text{CCl}$. The position of the maximum first peak for liquid and crystal functions in CCl_4 differs by only 0.1 Å in contrasts with the shift of 0.5 Å shown for the center-of-mass functions. Subsidiary maxima for the crystal appearing at about 3.9 Å and 6 Å do also have a correlate in the liquid function. This contrasting behavior of the center-of-mass and external-atom functions is interpreted as a result of the different average orientations present in the

crystal and liquid that involve a rotation of an average angle of 71°.

A comparison with data pertaining tert-butyl chloride now reveals a striking behavior. First, as expected from the higher number of scattering centers in $(\text{CD}_3)_3\text{CCl}$, the crystal and liquid functions display less marked differences, mostly concerning the height of the first peak and the region just above it (centered at ≈ 3.5 Å). Second, the first peak in the liquid shows a higher intensity than that of the disordered crystal and finally, the position of maxima for longer distances shift from ≈ 6.1 Å in the liquid to 5.8 Å within the fcc phase. These results taken together with those regarding the coordination numbers portray a situation where orientational correlations within the liquid appear as *stronger than those for the fcc crystal*. The finding is rationalized by recourse of symmetry arguments. As it is well known, both the molecular symmetry and that of the fcc phase have to be *symmorphic*. This is to say that in order to preserve the average cubic-lattice symmetry, the molecules have to reorient at their lattice sites accordingly. In other words, because of the lower point-group C_{3v} symmetry of $(\text{CD}_3)_3\text{CCl}$ compared to that of T_d for carbon tetrachloride, one may expect the former compound to exhibit within its fcc phases molecular reorientations about more crystal directions than those for the latter. This has to occur in order to preserve the higher symmetry of the cubic crystal. Explicitly [27], one expects T_d molecules to reorient within the cubic crystal along two different axis while 8 different reorientations needed to be executed by a C_{3v} molecule to preserve the crystal symmetry. Support for such a picture comes from spectroscopic measurements [28] which show that dynamics data for $(\text{CD}_3)_3\text{CCl}$ within its “plastic” phase can be explained in terms of nearly isotropic rotational-diffusion models which portray rotational motions taking place within an ensemble of low rotational barriers.

V. FINAL REMARKS

To understand the origin of the findings here reported on, particularly the apparently stronger orientational correlations found for CCl_4 , a nonpolar liquid compared to $(\text{CD}_3)_3\text{CCl}$, we should bear in mind the following considerations. First, liquid CCl_4 is known to be highly polarizable as shown by its strong nonlinear optical properties [29,30]. These unveil the action of microscopic interaction induced phenomena within the liquid resulting from strong higher-order terms in the molecular susceptibility which lead to the appearance of strong induced-dipole absorption [30]. In particular, analysis of experimental spectra reveals a wide distribution of induced dipole moments [30] having a mean value of some 0.26 D and a width of about 0.3 D. Also, molecular interactions in this liquid are known to be particularly strong as revealed by the generation of acoustic waves via the third-order linear polarization or by the presence of split dipole modes in its hyper-Raman spectrum [31]. On such grounds one can expect nonequilibrium friction effects such as those proved by three-pulse polarization anisotropy experiments [32] to be here in operation.

The results reported here, that is the presence of orientational correlations in polar or polarizable liquids which are

confined within the second coordination sphere, compare to previous determinations concerning a stronger polar material such as ethanol in its RPC and glass states [33]. In contrast, calculated data for solutes within a polar solvent or a net polar liquid such as formamide [34] suggest that correlations beyond such a range may there be operative.

Finally the effects of strong orientational correlations are also felt by the single-particle dynamics of these liquids [35] which require a sum of a Gaussian for short times and two exponentials to adequately describe the rotational relaxation functions. Further studies comparing the reorientational dynamics of materials such as those here explored will surely shed new light onto this long standing problem.

From reasons described in the opening paragraphs as well as from consideration of the strong orientational correlations

here reported on, one would expect to witness within both liquid and RPC states strong deviations from the noninteracting (Debye) limit that leads to exponential relaxation in the dielectric function. The observation of nearly exponential relaxation for both liquids as well as for one of the OD crystals evidences the need of renewed efforts focused onto the understanding of these phenomena.

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