# Evolution of the Local Order in 1,3,5-Trifluorobenzene from the Liquid State up to Supercritical Conditions

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*Received: July 23, 2000*

The local order in 1,3,5-trifluorobenzene has been investigated under isothermal (573 K) and isobaric (16 MPa) conditions from the liquid to the supercritical domain (critical point: $T_c = 530$ K and $p_c = 4$ MPa) using neutron diffraction and molecular dynamics simulation. A progressive evolution of the local ordering is observed when the density decreases from liquid (300 K, 0.1 MPa) to gas values (573 K, 16 MPa) in the supercritical domain. The translational ordering, which is characterized by two well-defined shells of neighboring molecules at ambient conditions, is gradually weakened and extend only to the first shell as the density decreases in the supercritical domain. In contrast, although there is also a loss of the long-range orientational ordering (at about 7 Å) and a tendency to reach a more random distribution, the very short orientational ordering extending on a spatial range of about 4 Å is still present. Therefore, the signature of stacked pairs of molecules existing in the liquid state at ambient conditions is still observed in the entire range of the supercritical domain.

## I. Introduction

Structural investigations using neutron diffraction combined with molecular dynamics (MD) simulations have allowed a discussion of the nature of the intermolecular interactions in liquid benzene and its fluorinated derivatives (hexafluorobenzene and 1,3,5-trifluorobenzene).[1−3] The major insight concerns the role played by the electrostatic forces on the local ordering for these systems in liquid state. Indeed, if it has been known for a long time that the short-range repulsive forces primarily condition the structure of liquids; nevertheless, the dispersive and long-range electrostatic interactions should be taken into account. Actually, the competition between the different interaction mechanisms plays a paramount role in determining the local ordering in these fluids composed of aromatic molecules These structural studies have allowed critical discussion of the validity of considering only a single pair of interacting molecules. In this context, for neat liquids composed of quadrupolar molecules, such as benzene and hexafluorobenzene ($|Q| \approx 3.0\ 10^{-39}$ C m$^2$), it can be argued that perpendicular configurations of neighboring molecules should be favored by the quadrupole−quadrupole interactions. Actually, for these two liquids, both parallel and perpendicular configurations of neighboring molecules were found in the first shell from room temperature to the boiling point.[1−3] For liquid 1,3,5-trifluorobenzene, which is composed of molecules having a very weak quadrupole moment ($Q \approx 0.32 \times 10^{-39}$ C m$^2$), the local ordering can be expected to be quite different. Structural studies have supported this viewpoint and have revealed the existence in the liquid phase of homodimers in which the two moieties have a parallel stacked configuration (with an average intermolecular distance of about 3.8 Å). These dimers are found to exist in the temperature domain extending from the melting point (267 K) to the boiling point (349 K). They have also been put in evidence in diluted carbon tetrachloride solutions.[4] Theoretical calculations for a pair of isolated molecules have shown that the stacked homodimers are stabilized by both electrostatic and dispersion interactions and that the interaction energy is significant with a value of about 16.5 kJ mol$^{-1}$.[5] However, as far as we know, there is no experimental evidence about the existence of such dimers in the gas phase.[6]

The aim of the present study is to assess the stability of the 1,3,5-trifluorobenzene dimers in the supercritical domain using the combination of neutron diffraction measurements and MD simulations. Indeed, under these thermodynamics conditions, the density can be continuously varied from liquid to gas such as values by moderate variations of both pressure $P$ and temperature $T$.[7,8] We take advantage of this property to appreciate the influence of the surrounding molecules on the stability of the dimer when the density of the fluid is varied along the liquid−vapor (LV) coexistence curve and in particular in the SC domain.

## II. Theoretical Background

We briefly summarize here the basic formalism needed to extract structural information from neutron diffraction experiments.[2,3]

For a molecular liquid, the total differential cross section per molecule $(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\text{total}}$ is a sum of four contributions, namely

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\text{total}} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\text{incoh}} + \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\text{self coh}} + \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\text{dist}}_{\text{intra}} + \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\text{inter}} \quad (1)$$

The sum of the first and second terms in the eq 1 is the self-differential cross section given by

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10.1021/jp002612b CCC: $19.00

$$\left(\frac{d\sigma}{d\Omega}\right)^{\mathrm{self}} = \sum_{i=1}^{N}\left[\left(b_i^{\mathrm{incoh}}\right)^2 + b_i^2\right] \tag{2}$$

where $b_i^{\mathrm{incoh}}$ and $b_i$ are respectively the incoherent and the coherent scattering lengths of the nucleus $i$ in the molecule composed of $N$ atoms. The distinct coherent cross section $(d\sigma/d\Omega)^{\mathrm{dist\ coh}}$ is obtained from the sum of the last two terms in eq 1. The intramolecular contribution can be calculated as

$$\left(\frac{d\sigma}{d\Omega}\right)^{\mathrm{dist}}_{\mathrm{intra}} = \sum_{i\neq j} b_i b_j j_0\left(Qr_{ij}\right)\exp\left(-l_{ij}^2 Q^2/2\right) \tag{3}$$

where $j_0(Qr_{ij})$ is the spherical Bessel function of zero order, $r_{ij}$ is the distance between the $i$ and $j$ nuclei of the molecule, $l_{ij}$ is the corresponding rms fluctuation, and $Q$ is the momentum transfer ($Q = 4\pi \sin\theta/\lambda$).

At very large $Q$ values, the intermolecular contribution $(d\sigma/d\Omega)_{\mathrm{inter}}$ approaches zero, and the relevant contribution for the distinct coherent cross section comes almost exclusively from the intramolecular contribution. So the asymptotic value (when $Q \rightarrow \infty$) of the $(d\sigma/d\Omega)^{\mathrm{coh}}$ contribution is the self-coherent cross section. On the other hand, when $Q$ approaches zero, we have

$$\lim_{Q\to 0}\left(\frac{d\sigma}{d\Omega}\right)^{\mathrm{coh}} = \left(\sum_i b_i\right)^2 k_B T \rho \chi_T \tag{4}$$

where $\rho$ and $\chi_T$ are the number density and the isothermal compressibility of the liquid at the temperature $T$.

The intermolecular pair correlation function $g_{\mathrm{inter}}(r)$ can be obtained by Fourier transformation of the intermolecular cross section

$$d_{\mathrm{inter}}(r) = 4\pi\rho r\left(g_{\mathrm{inter}}(r) - 1\right) = \frac{2}{\pi}\int_0^{\infty}\frac{Q}{\left(\sum_i b_i\right)^2}\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{inter}}\sin(Qr)\, dQ \tag{5}$$

where, the $g_{\mathrm{inter}}(r)$ is deduced from the partial pair correlation functions $g_{ij}(r)$

$$g_{\mathrm{inter}}(r) = \frac{\sum_{i,j} b_i b_j g_{ij}(r)}{\left(\sum_i b_i\right)^2} \tag{6}$$

Hence, $g_{\mathrm{inter}}(r)$ is a weighted sum of the partial correlation functions

$$g(r)_{C_6D_3F_3} = 0.27g_{\mathrm{CC}}(r) + 0.07g_{\mathrm{DD}}(r) + 0.05g_{\mathrm{FF}}(r) + 0.27g_{\mathrm{CD}}(r) + 0.23g_{\mathrm{CF}}(r) + 0.11g_{\mathrm{DF}}(r) \tag{7}$$

## III. Experimental Procedure and Data Reduction

**III.1. Experimental Details.** The experiments were performed on the two-axes spectrometer 7C2,[9] situated on the hot source of the Orphée reactor at the Laboratoire Léon Brillouin (Laboratoire Commun CEA-CNRS, Saclay, France). The use of an incident neutron wavelength, $\lambda = 0.7$ Å, combined with the multidetector allowed us to perform measurements in the Q range of 0.4−16 Å$^{-1}$.

The deuterated 1,3,5-trifluorobenzene was synthesized and has an isotopic purity of 97.8%. The sample was contained in a vanadium cylindrical cell with an inner diameter of 4 mm and a thickness of 0.7 mm and was placed in the 50 mm high neutron beam. The cell adapted to high-pressure and high-temperature measurements was mounted in a vanadium furnace. The temperature of the sample was varied from the room temperature to 573 K, and it was kept constant to within $\Delta T = 0.2$ K during the runs. The cell was connected via a stainless steel capillary to a pressurizing system which permits control over the pressure up to 50 MPa with an absolute uncertainty of ± 0.1 MPa and a relative error of ±0.03%. A pressure separator was disposed between the cell and manual pump to separate the pressurizing fluid (water) and the sample. The cell was evacuated under vacuum prior to being filled with deuterated 1,3,5-trifluorobenzene. Independent measurements were performed on the empty cell, the background, a cadmium rod with the same dimensions as that of the cell, and a vanadium rod with the same dimensions as those of the sample. Several runs were accumulated (ranging between 12 and 24 for the sample, 12 for the container, and 6 for the cadmium, vanadium rods, and background) with $10^6$ monitor counts. A typical diffraction pattern for 1,3,5-trifluorobenzene and the empty cell is reported in Figure 1. The background and cadmium runs are also displayed for comparison.

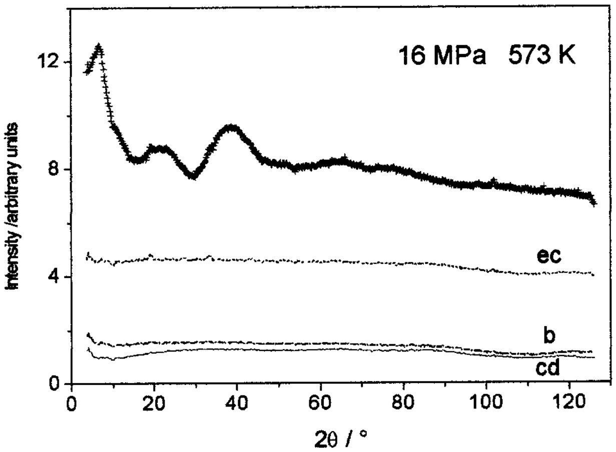

**Figure 1.** Experimental scattered intensities of 1,3,5-trifluorobenzene at 16 MPa and 573 K. The background (b), the empty cell (ec) and the cadmium (cd) runs are also reported.

**III.2. Data Reduction.** Standard corrections of neutron scattering need the density of 1,3,5-trifluorobenzene as a function of temperature and pressure. However, as far as we know, there are no available PVT data for this system. Moreover, the critical point of this fluid has not been reported so far. First of all, we have, in the course of our spectroscopic investigations, determined the critical temperature and pressure by simple visualization of the critical transition in a Raman cell. The critical $P_C$, $T_C$, and $V_C$ have been evaluated using the Ambrose method.[10] The calculated values of $P_C$ and $T_C$ were found to be in good agreement with the experimental ones, as shown in Table 1. Therefore, we can trust the calculated critical density. The density of the fluid has been evaluated as follows for all the thermodynamic states investigated here. The experimental scattered intensity $I_S$ of the sample, after correction for the empty cell contribution, is essentially governed in the $Q$ range of 5−15 Å$^{-1}$ by the intramolecular contribution and is proportional to the density of the medium. We have checked this statement using the experimental neutron data reported for benzene as a function of temperature and pressure[7,] for which the corresponding PVT data are known.[11] Indeed, we have calculated the mean value of the ratio $I_s(T)/I_s(300\ \mathrm{K})$ in the $Q$ range of 5−15 Å$^{-1}$ and plotted it against the ratio of the densities $\rho(T)/\rho(300\ \mathrm{K})$ (Figure 2). The standard deviation calculated for

**TABLE 1: Thermodynamics States of 1,3,5-Trifluorobenzene Investigated in This Study**[a]

| states | $\rho$ ($10^3$ kg m$^{-3}$) | $\rho_r$ | $T$/K | $T_r$ | $P$ (MPa) | $P_r$ |
|---|---|---|---|---|---|---|
| A | 1.27 | 3.38 | 300 | 0.56 | 0.1 | 0.02 |
| B | 1.16 | 3.10 | 373 | 0.70 | 16 | 3.9 |
| C | 1.01 | 2.69 | 473 | 0.89 | 16 | 3.9 |
| D | 0.91 | 2.44 | 523 | 0.98 | 16 | 3.9 |
| E | 0.81 | 2.16 | 573 | 1.08 | 16 | 3.9 |
| F | 0.65 | 1.74 | 573 | 1.08 | 8.8 | 2.2 |
| G | 0.47 | 1.25 | 573 | 1.08 | 6.5 | 1.6 |
| H | 0.29 | 0.78 | 573 | 1.08 | 5.5 | 1.4 |
| I | 0.15 | 0.41 | 573 | 1.08 | 4.0 | 0.99 |
| critical point | 0.375[b] | 1 | 531[c],<br>529.3[b] | 1 | 4.06[c],<br>4.02[b] | 1 |

[a] Values are reported for hydrogenated liquid. [b] Calculated (Ambrose method[10]). [c] Experimental (see text).

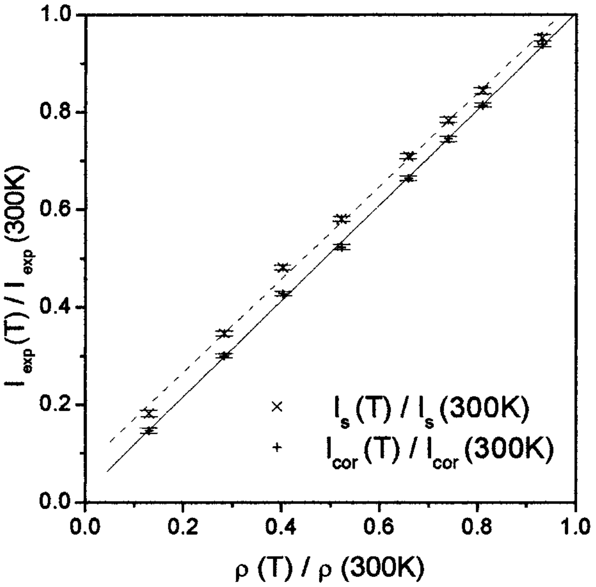

**Figure 2.** Dependence upon the density of the experimental scattered intensities for liquid and supercritical benzene: (×) the sample after correction for the empty cell $I_s(T)/I_s$ (300 K); (+) the corrected (absorption and multiple scattering) intensities $I_{cor}(T)/I_{cor}$(300 K) (see text).

the ratio $I_s(T)/I_s$(300 K) is less than 2%, as represented by the error bars on Figure 2. We observe an almost perfect linear trend with a slope equal to 0.95. The small departure of this value from unity is expected to be related to the influence of small contributions in the scattered-intensity-like absorption, multiple scattering, and inelasticity corrections, which have not been taken into account by simply correcting for the cell contribution. If we use the properly corrected scattered intensity (excluding the inelasticity corrections) now, we find a slope of 0.98 for the mean value of the ratio $I_{cor}(T)/I_{cor}$(300 K) in the same $Q$ range, which is closer to unity than before. Then we used the slope of the linear correlation for this system (0.95) to estimate the density of 1,3,5-trifluorobenzene as a function of temperature and pressure using the corresponding ratios $I_s(T)/I_s$(300 K) and the density of this fluid at ambient conditions. These values have then allowed pretreatment of the row data to correct for absorption and multiple scattering contribution. Finally, we have recalculated the densities of 1,3,5-trifluorobenzene using a linear slope of 0.98 and the new ratios $I_{cor}$(T)/$I_{cor}$(300 K) corrected for the absorption and multiple scattering contributions. The values of the densities obtained in the second treatment (Table 1) are slightly greater but not more than 2% from the previous ones.

**TABLE 2: Simulated Properties of Liquid 1,3,5-Trifluorobenzene for Different Reduced Densities $\rho_r$**

| $\rho_r$ | $T_r$ | $U_p$ (kJ mole$^{-1}$) | $\langle T\rangle$ (K) | $P$ (MPa) |
|---|---|---|---|---|
| 3.58 | 0.53 | −30.6 | 306 ± 7 | 98.8 |
| 3.38 | 0.61 | −28.2 | 344 ± 8 | 71.0 |
| 1.48 | 0.97 | −13.2 | 542 ± 11 | 3.2 |
| 2.94 | 1.02 | −25.2 | 557 ± 11 | 90.9 |
| 2.32 | 1.02 | −19.3 | 586 ± 11 | 24.2 |
| 2.13 | 1.02 | −17.8 | 575 ± 11 | 14.2 |
| 1.89 | 1.02 | −15.9 | 569 ± 11 | 7.7 |
| 1.29 | 1.02 | −11.9 | 565 ± 13 | 5.15 |
| 0.89 | 1.02 | −8.75 | 573 ± 13 | 5.1 |

Corrections for background, container scattering, and self-absorption were carried out using conventional methods[12] based upon Paalman and Pings' formalism,[13] and corrections for multiple scattering were performed using the isotropic approximation of Blech and Averbach.[14] The corrected data have been scaled to absolute units using the vanadium intensities as a standard. The density values of 1,3,5-$C_6D_3F_3$ at the different thermodynamics states used in the calculations have been estimated under the assumption that the molar volumes of the hydrogenated and deuterated 1,3,5-trifluorobenzene are the same (Table 1).

A reliable extrapolation of the corrected intensities when $Q$ approaches zero needs of the values for the isothermal compressibilities, which are not available in the literature for 1,3,5-$C_6H_3F_3$. Therefore, we have estimated these values by supposing that the evolution of the isothermal compressibilities relative to a reference state upon the reduced density was the same for benzene and 1,3,5-trifluorobenzene. As the Fourier transformation of the intermolecular structure factor obtained with these approximate values appears very similar for the very short intermolecular distances at about $r \approx 2$ Å for the different thermodynamics states, the approximate extrapolation procedure seems to be fairly correct.

The inelasticity corrections have been performed using the method previously described.[2,15] The total differential cross section may be written as

$$\left(\frac{d\sigma}{d\Omega}\right)^{\rm exp}_{\rm total} = \left(\frac{d\sigma}{d\Omega}\right)^{\rm dist}_{\rm intra} + \left(\frac{d\sigma}{d\Omega}\right)_{\rm inter} + \left(\frac{d\sigma}{d\Omega}\right)^{\rm self}[1 + P(Q)] \quad (8)$$

where inelasticity contributions to the distinct terms have been neglected. In this equation, the intermolecular contribution $(d\sigma/d\Omega)_{\rm inter}$ becomes negligible for $Q$ values greater than about 5 Å$^{-1}$. The intramolecular contribution $(d\sigma/d\Omega)^{\rm dist}_{\rm intra}$ was calculated from the eq 3 using the molecular parameters reported in Table 2 of ref 2, which have been adjusted for liquid 1,3,5-trifluorobenzene between the melting and boiling points by fitting a calculated intramolecular cross section to the $Q$-weighted distinct cross section in the domain $4 \leq Q \leq 15.8$ Å$^{-1}$ region (see detailed description in refs 2 and 15). Finally, $P(Q)$ in the eq 8 was taken as $P(Q) = A + BQ^2 + CQ^4$.

In the Fourier transform of the intermolecular structure factor (eq 5), a modification function, $M(Q) = j_0(\pi Q/Q_{\max})$, was used to reduce the truncation effects, as $Q_{\max}$ is limited to 15.8 Å$^{-1}$.

## IV. Experimental Observations

The distinct coherent cross sections recorded as a function of pressure and temperature are displayed in Figure 3. At $Q$ values greater than 4 Å$^{-1}$, the predominant contribution comes from the intramolecular structure, which is almost unaffected by the temperature and pressure variations. This is clearly seen from the superposition of the patterns in the referred $Q$ domain. If we consider now the $Q$ domain below 4 Å$^{-1}$, two main observations can be made. The first one concerns the decreasing of the main peak, centered at around 1.2 Å$^{-1}$, which shifts

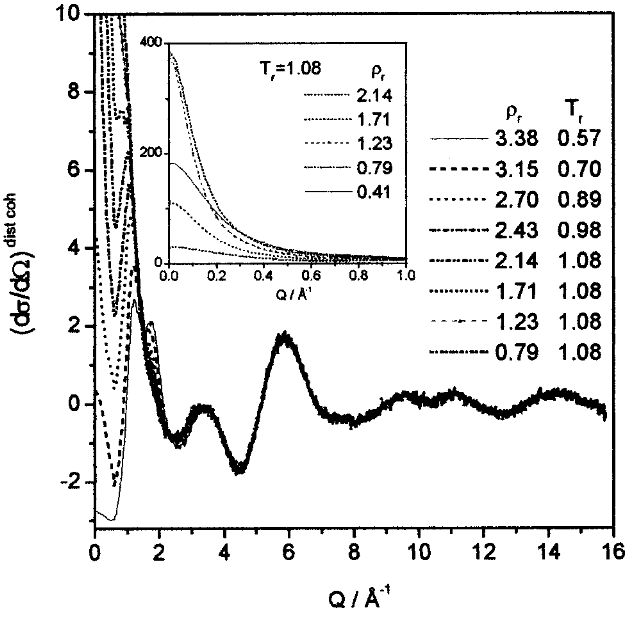

**Figure 3.** Coherent (distinct) cross section of liquid and supercritical 1,3,5-trifluorobenzene. The extrapolated intensities in the $Q$ domain approaching zero are presented in the inset for thermodynamics states on the isothermal $T_r = 1.08$.

toward lower $Q$ values from the liquid to the supercritical state. We observe also that the amplitude of the second, less intense peak at around 1.75 Å$^{-1}$ gradually decreases under the same conditions and almost vanishes at the lowest densities. The second main observation is related to the strong increase at low $Q$ values when the density is close to the critical one. Indeed, the isothermal compressibility $\chi_T$ diverges at the critical point, and therefore, from eq 4 the distinct coherent cross section greatly increases in agreement with our experimental observations (see inset of Figure 3).

The evolution of the intermolecular structure with the density can be better appreciated from the intermolecular cross section, which is obtained from the distinct coherent cross section after subtracting the intramolecular contribution (Figure 4a). The intermolecular cross section $(d\sigma/d\Omega)_{inter}$ of liquid 1,3,5-trifluorobenzene exhibits a well-defined peak centered at about 1.8 Å$^{-1}$ at ambient temperature ($T_r = 0.56$). As the density decreases under isobaric conditions, the intensity of this peak decreases, and a shoulder appears at about 1.4 Å$^{-1}$ and becomes very well defined at $T_r = 0.98$ as the density approaches $\rho_r = \rho/\rho_C = 2.4$. As the density goes down to about $\rho_r = 0.41$ at constant temperature ($T_r = 1.08$), it appears that only a broad profile with a plateaulike structure subsists. If we compare the intermolecular structure factor of benzene under similar thermodynamics conditions, we observe two well-defined peaks centered at about 1.4 and 2 Å$^{-1}$. Upon the decrease of density, a monotonic evolution of the intermolecular structure factor is observed where the intensities of both peaks are reduced and the peak positions shift toward lower $Q$ values. This doublet structure has been shown in previous studies concerning the benzene molecule to be characteristic of an almost isotropic orientational order in which parallel and perpendicular configurations of molecules exist in the fluid.[2] On the contrary, the lone peak observed in the intermolecular structure factor of 1,3,5-trifluorobenzene is characteristic of a short-range local order involving dimers. We may infer here, therefore, that the evolution observed for this compound when the density decreases is the signature of a weakening of the short-range local ordering toward a more random distribution. We notice that the well-defined doublet structure obtained in benzene is not observed in the 1,3,5-trifluorobenzene for the corresponding thermodynamics states. This observation suggests that the dimers still exist in the entire range of the supercritical domain investigated at $T_r = 1.08$ for reduced densities ranging from 2.0 to 0.41.

The intermolecular pair correlation functions $d_{inter}(r)$ calculated from the Fourier transform of the intermolecular cross sections are displayed in Figure 5 for the saturated liquid and the supercritical fluid at different thermodynamics states.

The two shells of neighboring molecules observed at ambient conditions (with the second one significantly damped) are still present at $T_r = 0.7$. For all the other thermodynamics states closer to and higher than critical conditions, only a single shell subsists. These observations indicate that the long-range translational ordering is lost in the supercritical domain. This trend is expected and consistent with the results that we have reported before.[1,7,15] The prepeak centered at about 4.4 Å, which is associated with the existence of the dimers structure, smears out progressively from the liquid phase toward the supercritical regime, where it is barely visible at $T_r = 1.08$ and $\rho_r = 1.7$ (Figure 5b). As the density goes down to about $\rho_r = 0.41$ along the isotherm ($T_r = 1.08$), it is found that this peak reappears, hence suggesting that the specific short-range local ordering involving stacked dimers is still present at the lowest densities investigated here. This modification is accompanied by an overall enhancement of the mean background of $d_{inter}(r)$, and we notice that beyond the first maximum, the ordinate values are always positive and decrease exponentially. This trend is consistent with the appearance of large density fluctuations near the critical point.[7,15-17]

## V. Molecular Dynamics Simulations

To assess the local ordering evolution of the liquid 1,3,5-trifluorobenzene along the liquid−vapor (LV) coexistence curve (from ambient to critical temperatures) and in the SC region of the fluid (under isothermal conditions), we have performed molecular dynamics simulations in the microcanonical ensemble (N,V,E) using 256 non flexible molecules confined in a cubic cell and subjected to periodic boundary conditions. The molecular trajectories were solved by a leapfrog/quaternions algorithm with a time step of 5 fs and were followed over a production run of 150 ps after an equilibration period of 75 ps for all fluid state points investigated (cf. Table 2).

The atom−atom intermolecular potential model used here has already been described in previous studies (model II in the reference)[2] and has shown its ability to reproduce with good agreement the structural properties of liquid 1,3,5-trifluorobenzene from the melting point to the boiling point.[1,2] It should be remembered that this intermolecular potential is given by a sum of atom−atom contributions

$$U_{\alpha\beta}(r_{\alpha\beta}) = B_{\alpha\beta}\exp(C_{\alpha\beta}r_{\alpha\beta}) - \frac{A_{\alpha\beta}}{r_{\alpha\beta}^{\ 6}} + \frac{q_\alpha q_\beta}{r_{\alpha\beta}} \tag{9}$$

where α and $\beta$ refer to the C, H, and F atoms and $r_{\alpha\beta}$ is the distance between the atoms α and $\beta$ belonging to two interacting molecules.

The atom−atom parameter values (A, B, C) and the point charge values $q$ are listed in Table 3. The cross potential parameters are obtained according to the usual Lorentz−Berthelot mixing rules, namely, $A_{\alpha\beta} = (A_{\alpha\alpha}A_{\beta\beta})^{1/2}$, $B_{\alpha\beta} = (B_{\alpha\alpha}B_{\beta\beta})^{1/2}$ and $C_{\alpha\beta} = {}^1/_2(C_{\alpha\alpha} + C_{\beta\beta})$.

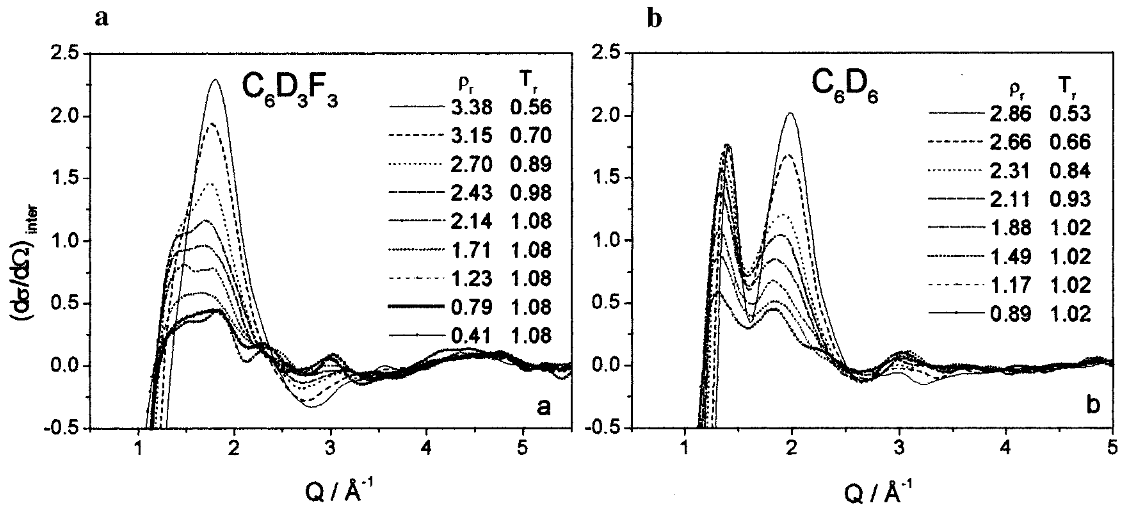

**Figure 4.** Intermolecular cross sections of liquid and supercritical (a) 1,3,5-trifluorobenzene and (b) benzene.[5]

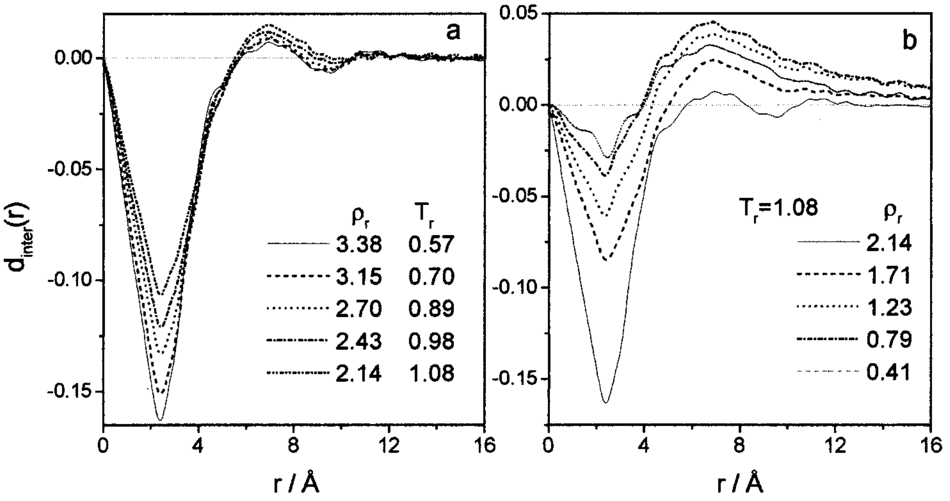

**Figure 5.** Intermolecular pair correlation function $d_{\mathrm{inter}}(r)$ of liquid and supercritical 1,3,5-trifluorobenzene: (a) the isobaric evolution at $P = 16$ MPa from liquid to supercritical state and (b) the isothermal evolution in the supercritical states at $T_r = 1.08$. For comparison, (a) the liquid state at ambient conditions and (b) the gaseous state at $\rho_r = 0.41$ are reported.

**TABLE 3: Intermolecular Potential Parameters and Partial Charges Used in the Molecular Dynamics Simulation**

| potential parameters | $C$ (Å$^{-1}$) | $B$ (kJ mol$^{-1}$) | $A$ (kJ Å$^6$ mol$^{-1}$) |
|---|---|---|---|
| C−C | 3.60 | 369 743 | 2440 |
| F−F | 4.35 | 400 000 | 500 |
| H−H | 3.74 | 11 971 | 136 |
| partial charges (au) | $q_C = +0.12$,<br>$q_F = -0.12$ | | $q_{C'} = -0.153$,<br>$q_H = +0.153$ |

In the present study, we have preliminarily determined the LV coexistence curve and defined the critical point of our model fluid to compare the simulated results with the experimental ones according to the corresponding states law.

For this purpose, we have evaluated by simulations 80 ($P$, $V$, $T$) state points of the simulated fluid 1,3,5-trifluorobenzene in the thermodynamic region 470 K $< T <$ 650 K and 1000 kg m$^{-3}$ $< \rho <$ 10 kg m$^{-3}$. Then these data were interpolated using the analytical Song and Mason equation of state (EOS), expressed as

$$\frac{P}{\rho k_{\mathrm{B}} T} = 1 + B_2\rho + \alpha\rho\left(\frac{8(8 - b\rho)}{(4 - b\rho)^3} - 1\right) \tag{10}$$

where, $\rho$ is the number density of the fluid and $B_2$, $\alpha$, and $b$ are parameters with volume dimensions and depend only upon the temperature. The two latter parameters are related by the equation

$$b = \alpha + T\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{11}$$

In addition, the temperature dependence of the parameters $B_2$ and $\alpha$ for computational purposes can be conveniently expressed as follows:

$$B_2 = X_1 + \frac{X_2}{T} + \frac{X_3}{T^2} \tag{12}$$

and

$$\alpha = \frac{X_4}{T} + \frac{X_5}{T^2} + \frac{X_6}{T^3} \tag{13}$$

where $\{X\}$ defines adjustable parameters.

The fitted values of the parameters involved in the EOS are reported in Table 4. The standard deviation between the fit and the simulated points is about 10%, an accuracy which is on the same order than that expected from MD simulations. Finally, the liquid−vapor coexistence curve has been calculated by applying the Maxwell double tangent construction (not shown).

**TABLE 4: Parameters for the Song−Mason Equation of State Valid for Isotherms at 470 K < T < 650 K[a]**

| | |
|---|---|
| $X_1$ | $+0.1526193 \times 10^{4}$ |
| $X_2$ | $-0.1733361 \times 10^{7}$ |
| $X_3$ | $+0.4057070 \times 10^{9}$ |
| $X_4$ | $+0.2559086 \times 10^{6}$ |
| $X_5$ | $-0.1286392 \times 10^{9}$ |
| $X_6$ | $+0.2414216 \times 10^{11}$ |

[a] Dimensions of $X$ values are such that $B_2$ and $b$ are expressed in cm$^3$ mol$^{-1}$ (see eqs 10−13).

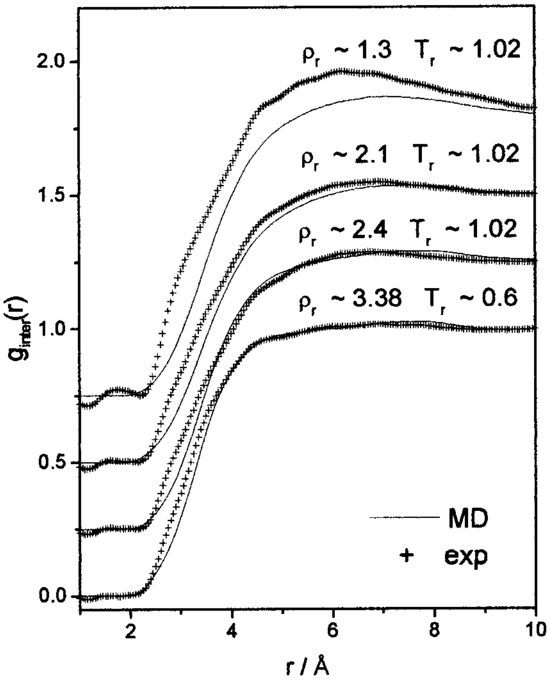

**Figure 6.** Comparison of the calculated (−) and experimental (+) intermolecular pair correlation function $g_{\mathrm{inter}}(r)$ for liquid and supercritical 1,3,5-trifluorobenzene.

The critical parameters obtained for the simulated fluid are

$$T_c \approx 562 \text{ K}, \rho_C \sim 354 \text{ kg cm}^{-3} \qquad P_c \approx 4.5 \text{ MPa}$$

These critical point values can be compared with those experimentally obtained, which are (cf. Table 1)

$$T_c \approx 531 \text{ K}, \rho_C \sim 375 \text{ kg m}^{-3} \qquad P_c \approx 4.1 \text{ MPa}.$$

The thermodynamics points simulated for the 1,3,5-trifluorobenzene fluid and the main calculated thermodynamics quantities are presented in Table 2.

The calculated pair correlation functions $g_{\mathrm{inter}}(r)$ for the 1,3,5-trifluorobenzene are displayed on Figure 6. A good agreement between experiments and MD simulations has been found for the liquid and the dense supercritical fluid, although with less goodness in the vicinity of the critical point. Indeed, the high compressibility of the real fluid in this thermodynamics domain cannot be reproduced by the MD simulations due to the finite size of the cubic cell. This overall agreement allows us to discuss the evolution of the local ordering from the detailed analysis of the simulated pair correlation functions presented in the following section.

## VI. Structural Analysis

The first insights concerning the translational ordering can be provided by the radial distribution function (rdf) of the center of mass $g_{\mathrm{CM}}(r)$, displayed in Figure 7 for different state points. For the liquid on the LV coexistence curve at $\rho_r \approx 3.58$ and $T_r \approx 0.53$, the rdf $g_{\mathrm{CM}}(r)$ exhibits a characteristic prepeak situated at distances of about 4−4.5 Å, previously assigned to the existence of stacked dimers in the liquid phase.[1,2] This prepeak is followed by a broad intense peak at about 6.5 Å and a weaker, broader peak at about 8−12 Å, corresponding to the second shell of neighbors. Upon heating along the LV coexist-

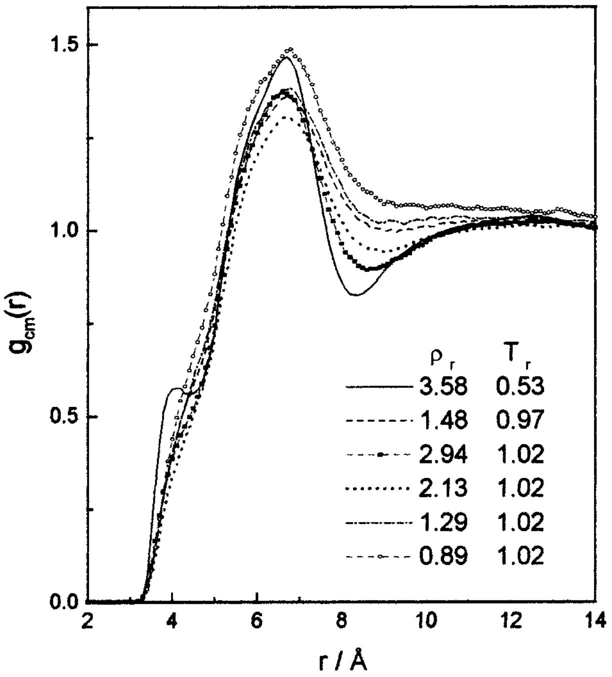

**Figure 7.** Calculated radial distribution function of $g_{\mathrm{cm}}(r)$ for liquid and supercritical 1,3,5-trifluorobenzene.

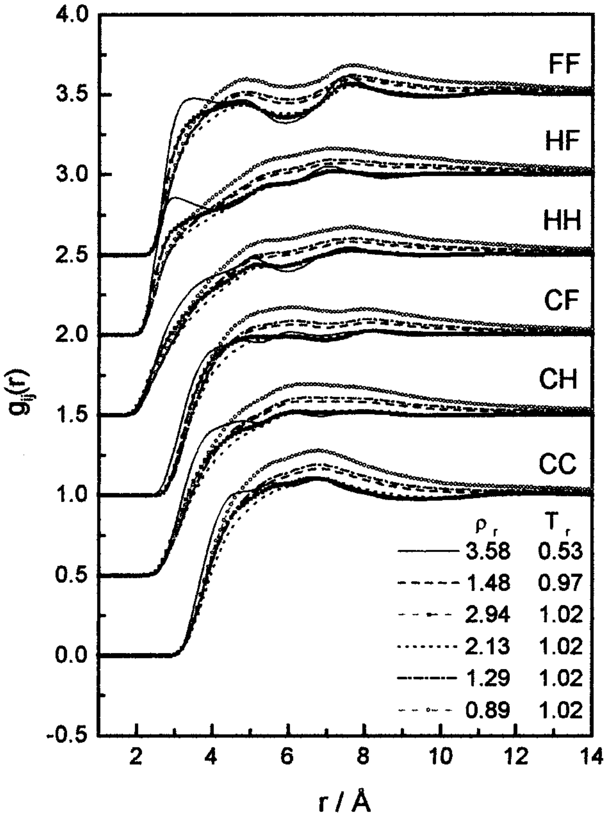

**Figure 8.** Calculated atom−atom radial distribution functions $g_{\mathrm{CC}}(r)$, $g_{\mathrm{CH}}(r)$, $g_{\mathrm{CF}}(r)$, $g_{\mathrm{HH}}(r)$, $g_{\mathrm{HF}}(r)$, and $g_{\mathrm{FF}}(r)$ for liquid and supercritical 1,3,5-trifluorobenzene.

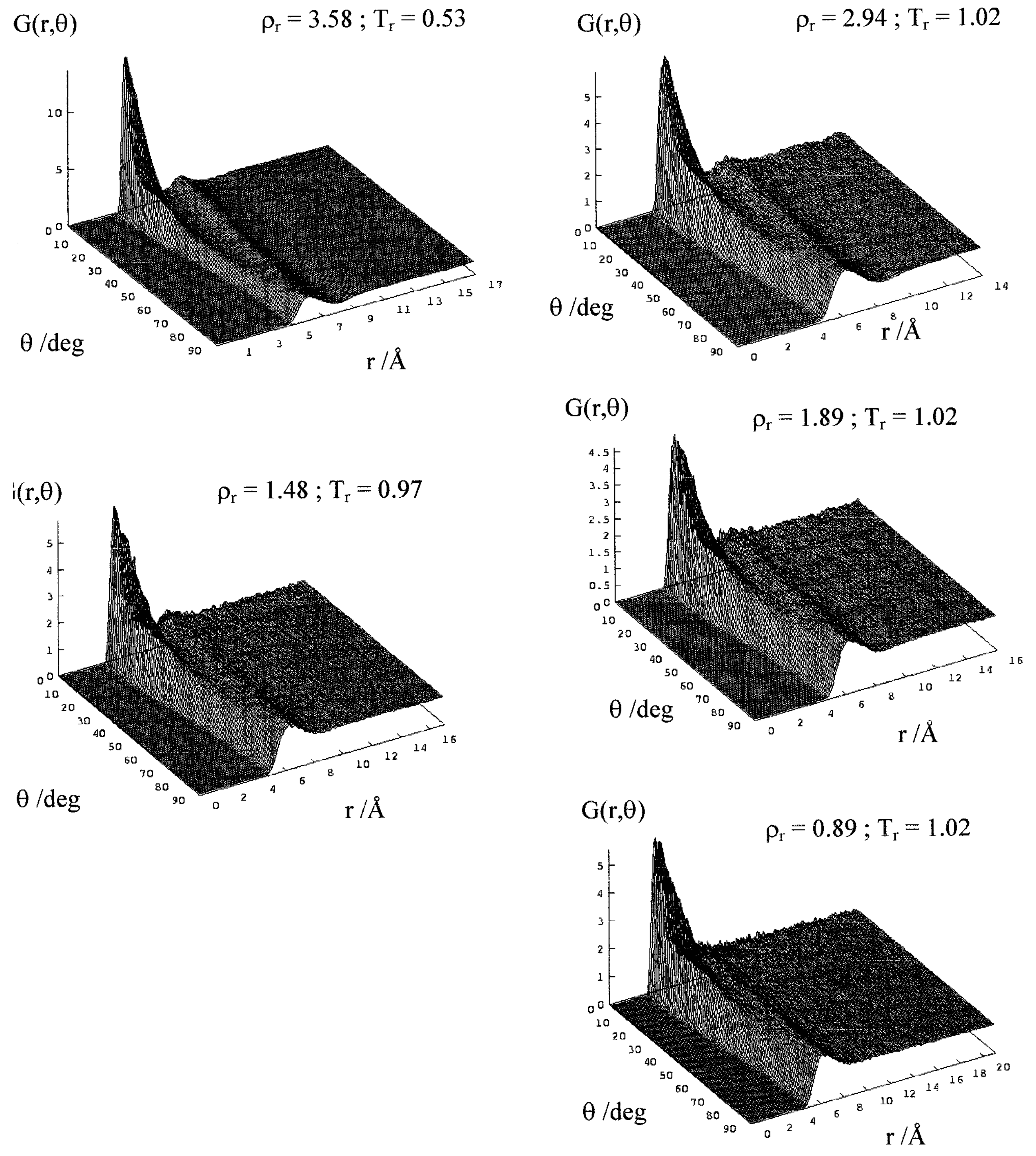

**Figure 9.** Simulated angular pair correlation function $G(r,\theta)$ of 1,3,5-trifluorobenzene along the LV coexistence curve ($T_r$ = 0.53 and 0.97) and in the supercritical domain ($T_r$ = 1.02).

ence curve, the pronounced prepeak is progressively reduced to a single shoulder at distances of about 4−5 Å ($\rho_r \approx 1.48$ and $T_r \approx 0.97$). Moreover, the main peak broadens and slightly shifts at about 6.7 Å. We have also estimated the average number $N_C$ of nearest neighbors around a central molecule situated within a spherical shell of radius $R$, chosen here at a value of 5 Å. For the first state point investigated, the calculated number of nearest neighbors $N_C$ is found to be close to 1.2, and the coordination number $Z$ (average number of molecules contained in the first shell) is equal to 13.7. Therefore, the fraction of molecules engaged in dimers $\Lambda = N_C/Z$ in the first shell is equal to 0.09 in the saturated liquid. Upon heating, the values of $N_C$ and $Z$ decrease and are found respectively to be about 0.45 and 7.50 at $\rho_r \approx 1.48$ and $T_r \approx 0.97$, leading to a proportion of dimers in the first shell close to 0.06.

In the SC domain (along the isotherm $T_r \approx 1.02$ and for reduced densities $\rho_r \approx 2.94$, 2.13, 1.29, and 0.89), the evolution of the translational order is modified comparatively with the structural behavior observed previously along the LV coexistence curve (Figure 7). As the density decreases, the main peak on the rdf $g_{CM}(r)$ significantly broadens, whereas the second shell of neighboring molecules is gradually weakened and finally merges with the first shell at $\rho_r \approx 0.89$ (Figure 7). Therefore, the long-range translational ordering is lost as gaseous-like densities are reached. However, the low-$r$ shoulder on $g_{CM}(r)$, although more tenuous, seems to persist even at the lowest density. For the reduced densities $\rho_r \approx 2.94$, 2.13, 1.29, and 0.89, the calculated values of $Z$ are respectively of about 12.4, 10.5, 6.5, and 6, whereas the corresponding values of $N_C$ are close to 0.97, 0.65, 0.46, and 0.35. However, we notice that the value of the ratio $\Lambda = N_C/Z$ remains nearly constant and close to 0.07 (within a relative uncertainty of 20%) in all the SC domain investigated.

To discuss more deeply the evolution of the local ordering as a function of the temperature and the pressure, we have also reported in Figure 8 the atom−atom rdf of liquid and SC 1,3,5-trifluorobenzene. We observe that the short-range local ordering appears only well-marked under ambient thermodynamics conditions ($\rho_r \approx 3.58$ and $T_r \approx 0.53$). This is clearly apparent from the short-range features exhibited on all the calculated rdf and which have been previously assigned to the stacked dimers in the liquid at room temperature. Nevertheless, this local ordering is strongly affected upon heating, as indicated by the gradual evolution and progressive smoothing leading to the featureless rdf at the lowest densities investigated. This finding indicates in particular that the orientational ordering is drastically affected toward the SC domain. But the discussion of the short-range structure due to the presence of dimers is rather difficult using the rdf, and we have preferred to address this issue from the analysis of the angular pair correlation functions $G(r,\theta)$, defined as

$$\rho G(r,\theta) = (1/N)\left\langle \sum_{i\neq j}^{N} \delta(r - r_{ij})\, \delta(\theta - \theta_{ij}) \right\rangle \qquad (14)$$

Indeed, this function characterizes the orientational ordering between a pair of molecules $i$ and $j$ having their center of mass separated by a distance $r_{ij}$ and where $\theta_{ij}$ is the relative angle formed with their main symmetry axis. These functions are reported in Figure 9 for the liquid and supercritical 1,3,5-trifluorobenzene. The angular pair correlation function $G(r,\theta)$ of liquid under ambient conditions ($\rho_r = 3.58$ and $T_r = 0.53$) exhibits clearly the signature of the stacked dimers structure ($\theta \approx 0$), characterized by the strong peak centered at about 3.5 Å. We note also the presence of a secondary peak at about 7 Å, due to the long-range order induced by the existence of the dimers in parallel configuration, a typical structural property of the liquid 1,3,5-trifluorobenzene as discussed in previous papers.[2,3] After the compound is heated along the LV curve (i.e., at decreasing density), the strong peak at 3.5 Å is still present, whereas the second one is progressively weakened (cf. Figure 9 at the state point $\rho_r = 1.48$ and $T_r = 0.97$). In contrast in the SC domain (along the isotherm $T_r \approx 1.02$), although the first peak at 3.5 Å is still present, the second one is progressively weakened as the density decreases, tending to disappear as the lowest densities are reached ($\rho_r \approx 0.89$ and $T_r \approx 1.02$). Clearly, these findings also evidence the existence of stacked dimers in the SC region despite the continuous loss of-long range ordering.

## VI. Conclusion

In this paper, we have studied the evolution of the local ordering in the 1,3,5-trifluorobenzene from the liquid state to the supercritical domain combining neutron diffraction and MD simulations. Two salient conclusions are worth pointing out. The first one concerns the loss of the long-range translational ordering, which is found to be limited to the first shell of neighboring molecules in the SC domain. This result was expected on the grounds of our former studies on molecular systems. In contrast, the second and unexpected finding concerns the orientational ordering. Although there is also a loss of the long-range local ordering (at about 7 Å) and a tendency to reach a more random distribution, the very short orientational ordering extending on a spatial range of about 4 Å is still present. Clearly, this feature is the signature of stacked pairs of molecules, which appear in the entire range of the SC domain investigated.

**Acknowledgment.** The authors thank Mrs. Ratovelomanana and M.F. Lautié (L.A.S.I.R., UPR 2631, Thiais, France) for their synthesis of the deuterated 1,3,5-trifluorobenzene.The neutron scattering experiments have been performed under the auspices of the Long Term Project (n° 5393) of the Laboratoire Léon Brillouin (C.E.A.-C.N.R.S., Saclay, France) and the authors thank Dr. M.-C. Bellissent-Funel and Mr. J.-P. Ambroise for their valuable help during the experiments. The authors acknowledge the University of Bordeaux I for providing support through a Programme pluri-formation n° 971022 between the "L.P.C.M. UMR 5803, Talence, France" and the "I.C.M.C.B., UPR 9048, Pessac, France", entitled "Etudes Spectroscopiques de Fluides dans le domaine supercritique". M.B. and M.I.C. acknowledge the Programme de Coopération Scientifique et Technique Franco-Portugais and the Reitoria da Universidade Técnica de Lisboa for exchange visit grants. Finally, the authors acknowledge the MASTER of the ENSPCB (Université de Bordeaux I) and the IDRIS (CNRS, Orsay) for allocation of computer time.

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