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Structural study of the 1-3-5 trifluorobenzene dimer stability: from liquid to gas densities using supercritical conditions

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Abstract

The local ordering in 1,3,5-trifluorobenzene has been investigated under isothermal and isobaric conditions from the liquid to the supercritical domain using neutron diffraction and molecular dynamics simulation. The short-range local ordering existing at ambient conditions involving dimers in which the molecules are in a parallel stacked configuration, is progressively weakened at the isobaric condition ($P = 16$ MPa) upon increasing the temperature up to 573 K. Under isothermal conditions (573 K) and as the density goes down to about $\rho_r = \rho/\rho_c = 0.43$ (reduced density), although the orientational ordering reaches in the fluid a more random distribution, dimers are still present (two thirds of the proportion estimated at ambient conditions). © 2000 Published by Elsevier Science B.V.

1. Introduction

Recently, a structural study of neat liquid benzene and its fluorinated derivatives (namely, hexafluorobenzene and 1,3,5-trifluorobenzene) has shown that the local ordering in the liquid state results from a subtle competition between the repulsive, dispersive and electrostatic intermolecular interactions [1–3]. For benzene and hexafluorobenzene liquids composed of molecules having similar molecular shapes and with quadrupole moments of about the same absolute magnitude ($\sim 3.0 \times 10^{-39}$ cm^2), it might be anticipated by reasoning on an isolated pair of molecules, that perpendicular configurations should

be favoured as the quadrupole–quadrupole interactions are significant. Actually, we have shown that there is no average preferential orientations between neighbouring molecules in these two liquids from ambient temperature up to the boiling point. As a matter of fact, both parallel and perpendicular configurations are encountered in the first shell [2,3]. In contrast, for the neat liquid 1,3,5-trifluorobenzene composed of molecules having a very weak quadrupole moment ($\sim +0.32 \times 10^{-39}$ cm^2), the local ordering is expected to be quite different. The structural analysis has supported this viewpoint and has revealed that the short-range local ordering involves homodimers in which the molecules have a parallel stacked configuration (with an average intermolecular distance of about 3.8 Å). These dimers are rather stable and exist in the temperature domain

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extending from the melting point (267 K) to the boiling point (349 K). Moreover, the dimers have also been in evidence in diluted carbon tetrachloride solutions [1–4]. In this context, previous theoretical calculations performed for a pair of isolated molecules have shown that the stacked homodimers are stabilised by both the electrostatic and dispersion interaction and the dimerisation energy is found to be significant with a value of about 16.5 kJ mol^{-1} [6]. As far as we know, there is no experimental evidence reported so far the existence of such dimers in the gas phase. (In this paper according to a private communication (reference 32) gas phase dimers exist with parallel plate alignment; see Ref. [5].)

The aim of the present investigation is to study the stability of the 1,3,5-trifluorobenzene dimers in the supercritical domain using a combination of neutron diffraction measurements and molecular dynamics simulation. Working under these thermodynamic conditions allows the continuous adjustment of the density from liquid to gas like values by appropriate variation of both pressure and temperature [7,8]. Therefore, we will take advantage of this property to appreciate the influence of the surrounding molecules on the stability of the dimer. In other words, is the existence of the dimer due to its confinement in the liquid phase or is the strength of the complex enough to allow it to exist in the gas phase? To answer this issue, we have used the following methodology. We have investigated two different thermodynamics domains; the former explores the 1,3,5-trifluorobenzene liquid near the liquid–vapour coexistence curve under isobaric conditions (16 MPa) from ambient conditions up to $T = 573$ K and the latter, in the supercritical domain under isothermal conditions (573 K) at various pressures ranging between 16 and 4 MPa.

2. Experimental

2.1. Experimental details

The experiments were performed on the two-axes spectrometer 7C2, 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 0.4–16 Å^{-1}.

The deuterated 1,3,5-trifluorobenzene was synthesised and has an isotopic purity of 97.8%. The sample was contained in a vanadium cylindrical cell of 4 mm inner diameter and 0.7 mm thick 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 room temperature up to 573 K and was kept constant, within $\Delta T = 0.2$ K, during the runs. The cell was connected via a stainless steel capillary to a pressurising system which permits the control of 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 the manual pump in order to separate the pressurising fluid (water) and the sample. The cell was evacuated under vacuum prior to filling with deuterated 1,3,5-trifluorobenzene.

Independent measurements of the empty cell, the background and a cadmium rod having the same dimensions as the cell and of a vanadium rod with the same dimensions of the sample were performed. Several runs were accumulated (ranging between 12 and 24 for the sample, 12 for the container, 6 for the background and for the cadmium and vanadium rods) of 10^6 monitor counts. The corrected data have been obtained by using a standard treatment as described

Table 1

Thermodynamic states of 1,3,5-trifluorobenzene investigated in this study. The values are reported for hydrogenated liquid. Critical values: $T_c = 531$ K [10], $P_c = 4.06$ MPa [10], $\rho_c = 375$ kg m^{-3} (calculated from the Ambrose method [9])

T (K)	T_r	P (MPa)	P_r	ρ (10^3 kg m^{-3})	ρ_r
300	0.56	0.1	0.02	1.27	3.38
373	0.70	16	3.9	1.18	3.15
473	0.89	16	3.9	1.01	2.70
523	0.98	16	3.9	0.91	2.43
573	1.08	16	3.9	0.80	2.14
573	1.08	8.8	2.2	0.64	1.71
573	1.08	6.5	1.6	0.46	1.23
573	1.08	5.5	1.4	0.30	0.79
573	1.08	4.0	0.99	0.16	0.43

in a previous paper [2]. The thermodynamic states investigated in this study are reported in Table 1.

2.2. Experimental observations

The intermolecular cross-section $(d\sigma/d\Omega)_{inter}$ obtained from the corrected differential cross-section after removal of the intramolecular contribution is displayed on Fig. 1a for some of the different thermodynamic states investigated. For comparison we have also reported the intermolecular cross-section that we have obtained recently for deuterated benzene in the liquid and the supercritical domain (Fig. 1b) [7]. The intermolecular cross-section $(d\sigma/d\Omega)_{inter}$ of liquid 1,3,5-trifluorobenzene exhibits a well-defined peak centred at about 1.8 Å^{-1} at ambient temperature ($T_r = 0.56$) (Fig. 1a). 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 continues to decrease down to about $\rho_r = 0.43$ at constant temperature ($T_r = 1.08$), it appears that only a broad profile with a plateau-like structure subsists. If we compare the intermolecular cross-section with those of benzene under similar thermodynamic conditions, we observe two well-defined peaks centred at about 1.4 and 2 Å^{-1} (Fig. 1b). Upon the decrease of the density, a monotonic evolution of the intermolecular cross-section is observed for which the intensities of both peaks reduce and the peak positions shift towards lower Q values. In previous studies, this doublet structure observed for benzene at ordinary conditions, has been shown to be

characteristic of an isotropic orientational order in which parallel and perpendicular configurations of a pair of molecules exist. In contrast, the lone peak observed in the intermolecular cross-section of 1,3,5-trifluorobenzene was found to be characteristic of a short-range local order involving dimers. Therefore, we may infer here that the evolution observed for this compound when the density decreases is the signature of a weakening of the short-range local ordering towards a more random distribution. Let us emphasise that the well-defined doublet structure obtained in benzene is not observed in the 1,3,5-trifluorobenzene for the corresponding thermodynamic states. This finding suggests that the dimers still exist over the entire range of the supercritical domain investigated at $T_r = 1.08$ for reduced densities ranging from 2.0 to 0.43.

3. Molecular dynamics simulations

In order to assess the local ordering evolution of the liquid 1,3,5-trifluorobenzene along the liquid–vapour (LV) coexistence curve (on going from ambient to critical temperatures) and in the SC region of the fluid (under isothermal conditions), we have performed molecular dynamics simulations in the micro-canonical 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 leap-frog/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
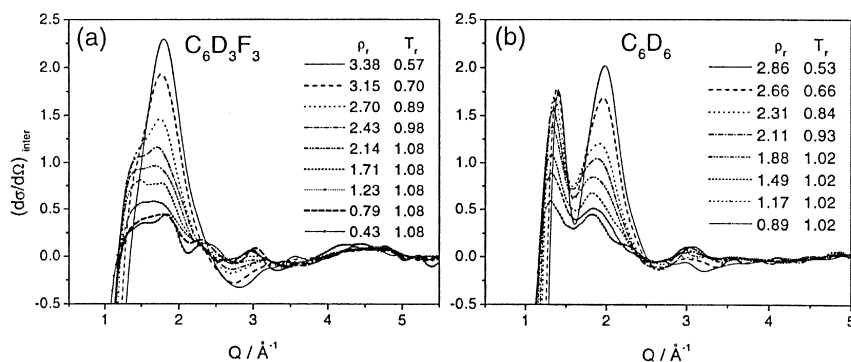

Fig. 1. Experimental intermolecular cross-section obtained from neutron diffraction for liquid and supercritical 1,3,5-trifluorobenzene (a) and benzene (b).

Table 2
Simulated properties of the fluid 1,3,5-$C_6H_3F_3$ for different reduced densities ρ_r

ρ_r	T_r	U_p (kJ mol^{-1})	$\langle T \rangle$ (K)	P (MPa)
3.58	0.534	−30.6	306 ± 7	988.1
3.38	0.614	−28.2	344 ± 8	71.0
2.40	0.745	−21.9	422 ± 10	−14.4
1.89	1.02	−15.9	569 ± 11	7.70
1.29	1.02	−11.9	565 ± 13	5.15
0.89	1.02	−8.75	573 ± 13	5.03

state points investigated (cf. Table 2). The atom–atom intermolecular potential model used here has already been described in previous studies (model II in Ref. [2]) and has shown its ability to reproduce with good agreement the structural properties of liquid 1,3,5-trifluorobenzene under ordinary thermodynamic conditions (from the melting point up to the boiling point) [1,2]. In the present study, we have preliminarily determined the LV coexistence curve of our model fluid in order to compare the simulated results with the experimental ones according to the corresponding state laws. But, we refer the reader to a companion paper to get more details concerning the determination of the LV coexistence curve applying the Maxwell construction and the parameterisation of the results using the Song and Mason equation of state [10]. Finally, the critical parameters obtained for the simulated fluid are respectively $T_c \sim 562$ K, $\rho_c \sim 354$ kg cm^{-3} and $P_c \sim 4.5$ MPa. These critical point values can be compared with those experimentally obtained [10] and are, respectively, $T_c \sim 531$ K, $\rho_c \sim 375$ kg m^{-3} and $P_c \sim 4.1$ MPa.

In the present study, we have calculated the pair correlation functions $g_{inter}(r)$ of the simulated 1,3,5-trifluorobenzene fluid for the different state points mentioned above. Good agreement between experiments and MD simulations has been found for the liquid and the dense supercritical fluid, although with less good agreement in the vicinity of the critical point. These last observations were expected as, indeed, the high compressibility of the fluid in this thermodynamics domain cannot be well reproduced by the molecular dynamics simulations due to

the finite box size [10]. 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.

4. Results and discussion

The intermolecular pair correlation function defined as $d_{inter}(r) = 4\pi \rho r [g_{inter}(r) - 1]$, where ρ is the number density and $g_{inter}(r)$, the weighted sum of the partial atom–atom correlation functions of liquid 1,3,5-trifluorobenzene calculated from the Fourier transform of the intermolecular cross-sections, is displayed in Fig. 2 for liquid and supercritical 1,3,5-trifluorobenzene at different thermodynamic states. The two shells of neighbouring molecules observed at ambient conditions (with the second one significantly damped) are still present at $T_r = 0.7$. In contrast, for the other thermodynamic states (closer and higher than critical conditions) 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 [1,7,11]. If we consider now the pre-peak centred at about 4.4 Å, which is associated with the existence of the dimer structure, we find that it
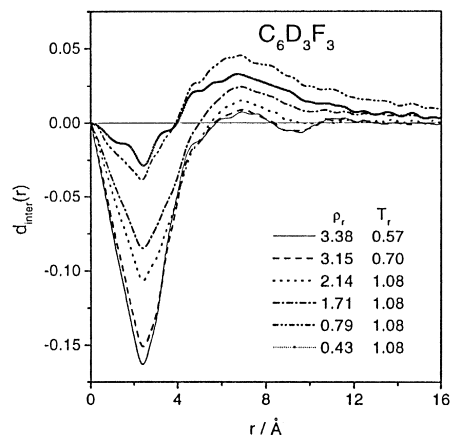

Fig. 2. Intermolecular pair correlation function $d_{inter}(r)$ calculated from a neutron diffraction experiment for liquid and supercritical 1,3,5-trifluorobenzene.

smears out progressively on going from the liquid phase towards the supercritical regime up to $T_r = 1.08$ and $\rho_r = 1.7$, where it is barely visible (Fig. 2). As the density still decreases to about $\rho_r = 0.43$ at constant temperature ($T_r = 1.08$), it is found that this peak reappears hence suggesting that the specific short-range local ordering involving stacked dimers is yet 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 [7,11,12].

Additional insights concerning the translational ordering can be provided by the molecular dynamics simulations by using the radial distribution function (r.d.f.) of the centre of mass $g_{CM}(r)$, displayed on Fig. 3 for different state points. At the reduced density $\rho_r \sim 3.38$ and the reduced temperature $T_r \sim 0.61$ (liquid along the LV coexistence curve), the r.d.f. $g_{CM}(r)$ exhibits a characteristic pre-peak situated at distances about 4-=4.5 Å which has been previously assigned to the existence of stacked dimers in the liquid phase [1,2]. This pre-peak is followed

by a broad intense peak at about 6.5 Å and by a weaker and broader one at higher distances (about 8–12 Å) corresponding to the second shell of neighbours. Upon heating along the LV coexistence curve, the pronounced pre-peak is progressively reduced to a single shoulder at distances about of 4–5 Å ($\rho_r \sim$ 2.40 and $T_r \sim 0.745$). Correlatively, the main peak broadens and slightly shifts towards higher distances (at about 6.7 Å). In order to obtain quantitative information, we have estimated the average number N_c of nearest neighbours around a central molecule situated within a spherical shell of radius R chosen here to be a value of 5 Å. For the first state point investigated, the calculated number of nearest neighbours N_c is found close to 1.1 and the coordination number Z (average number of molecules in the first shell) is equal to 13.4. Therefore, the proportion of dimers $\Lambda = Nc/Z$ in the first shell is equal to 0.08 in the saturated liquid (at $\rho_r \sim 3.38$ and $T_r \sim 0.61$). Upon heating ($\rho_r \sim 2.40$ and $T_r \sim 0.745$), the values of N_c and Z are, respectively, about 0.75 and 10.8. This result suggests that the proportion of dimers in the first shell is now $\Lambda \sim 0.07$.

In the SC domain (along the isotherm $T_r \sim 1.02$ and for reduced densities $\rho_r \sim 2.13$, 1.29 and 0.89, respectively), the evolution of the translational order is modified comparatively with the structural behaviour observed previously along the LV coexistence curve. As the density decreases, the main peak on the r.d.f. $g_{CM}(r)$ significantly broadens whereas the second shell of neighbouring molecules is gradually weakened and finally merges with the first shell at $\rho_r \sim 0.89$ (Fig. 3). 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 $\rho_r \sim 2.13$, 1.29 and 0.89, the calculated values of Z are respectively about 10.5, 6.5 and 5.4 whereas the corresponding values of N_c are respectively found close to 0.5, 0.6 and 0.6 and lead to a value of the ratio $\Lambda = Nc/Z$ close to 0.06 nearly constant in all the SC domains investigated ($\rho_r < 2.5$). Nevertheless, it is rather difficult to assign the short-range structure to the presence of dimers in the SC fluid domain only from the analysis of $g_{CM}(r)$. For this purpose, we address this important issue from a further analysis of the angular pair correlation functions $G(r,\theta)$.

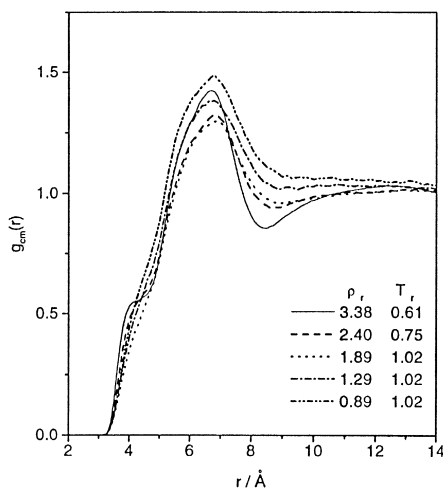Fig. 3. Simulated pair correlation function $g_{CM}(r)$ of the centre of mass of liquid and supercritical 1,3,5-trifluorobenzene.
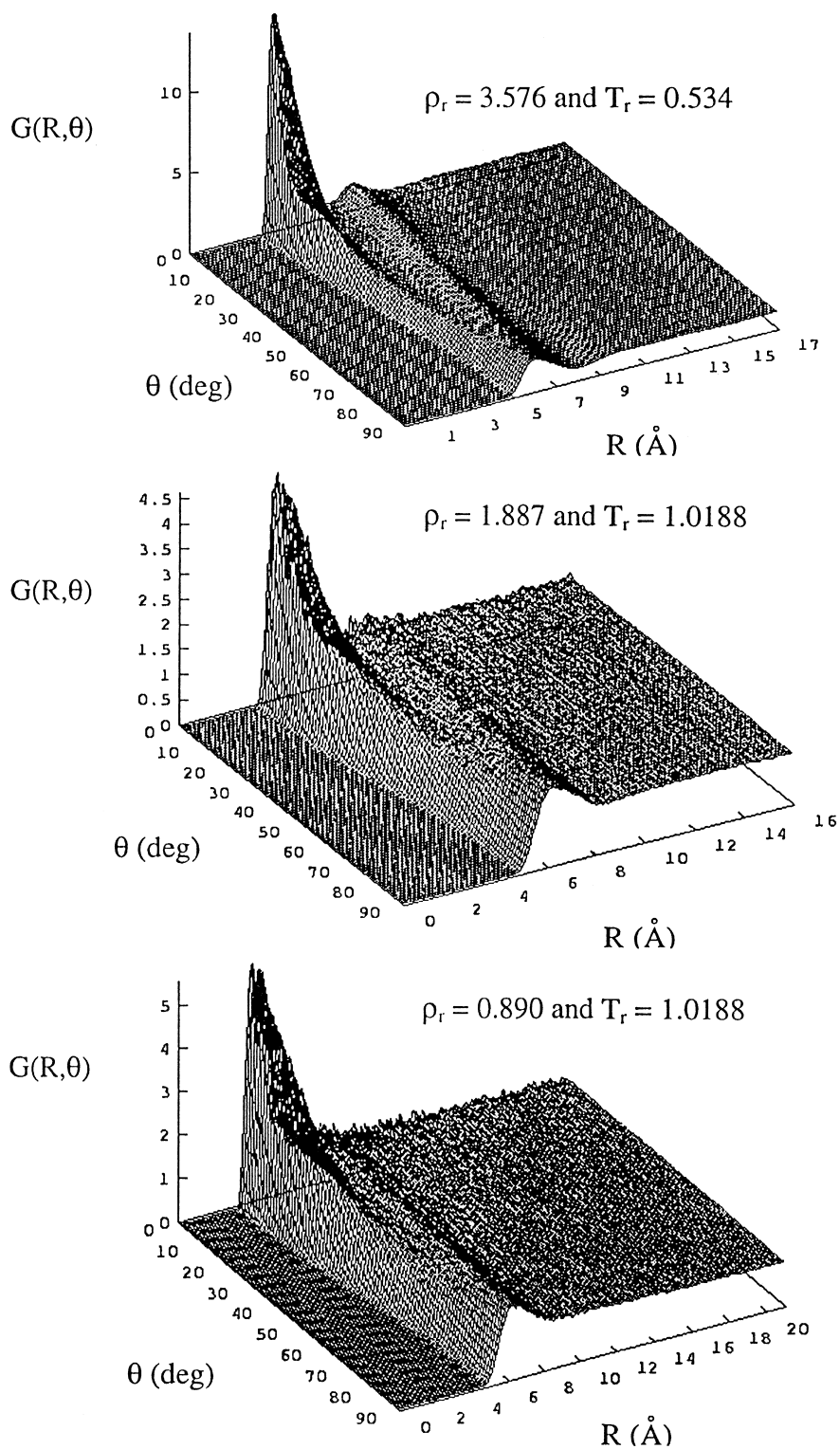
Fig. 4. Simulated angular pair correlation function $G(r, \theta)$ of liquid and supercritical 1,3,5-trifluorobenzene.

In order to obtain deep insights into the behaviour of the orientational order, we have calculated the angular pair correlation function $G(r, \theta)$ defined as

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

These angular pair correlation functions are reported in Fig. 4 for liquid and supercritical 1,3,5-tri-fluorobenzene. Let us remember that this function is the best one adapted to characterise the orientational ordering between a pair of molecules i and j having their centres of mass separated by a distance r_{ij} and where the angle between their main symmetry axis is θ_{ij}. The angular pair correlation functions at ambient conditions ($\rho_r = 3.575$ and $T_r = 0.534$) exhibit clearly the signature of the stacked dimer structure characterised by the strong peak centred at about 3.5 Å. We note also the presence of a secondary peak at about 7 Å, due, as discussed in previous papers [2,3], to the long-range order induced by the existence of the dimer in a parallel configuration, a typical structural characteristic of the 1,3,5-trifluoro-benzene fluid. As the density decreases, the strong peak at 3.5 Å remains present, but we observe that the second one is progressively weakened and almost disappears at the lowest density. Clearly, these findings give evidence of the existence of short-range stacked dimers although the long-range ordering is continuously lost as the lowest densities are approached

5. Conclusion

The combination of neutron diffraction and MD simulation has allowed the study of the local ordering in the 1,3,5-trifluorobenzene as the density of the fluid decreases from liquid-like values to the gas-like ones reached in the supercritical domain. Two main findings may be pointed out. The first one concerns the loss of the long-range translational ordering which is limited to the first shell of neighbouring molecules in the supercritical domain. This trend was expected on the grounds of our former studies on molecular liquids. The second and unexpected result concerns the orientational ordering. Although there is also a loss of the long-range orientational ordering (at about 7 Å) and a tendency to reach a more random distri-

bution, the very short orientational ordering extending to a spatial range of about 4 Å is still present. Clearly, this is the signature of the stacked pairs of molecules observed at ambient conditions and which appear in the entire range of the supercritical domain investigated at $T_r = 1.08$ for reduced densities ranging from 2.0 to 0.43.

Acknowledgements

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