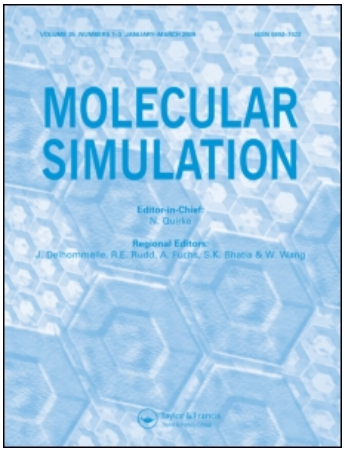

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Thermodynamic and Structural Properties of Fragile Glass-Forming Toluene and Meta-Xylene: Experiments and Monte-Carlo Simulations

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THERMODYNAMIC AND STRUCTURAL PROPERTIES OF FRAGILE GLASS-FORMING TOLUENE AND META-XYLENE: EXPERIMENTS AND MONTE-CARLO SIMULATIONS

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We report a characterization of isobaric and isothermal glass transition of two fragile liquids, toluene and meta-xylene, by elastic neutron scattering, calorimetry, and Monte-Carlo simulations. We studied thermodynamic and structural properties in the supercooled and overcompressed liquid up to the glass transition. The simulated thermodynamic or structural properties are in good agreement with experimental ones. From the Prigogine-Defay ratio, the simulated glass transition seems associated to one order parameter. The structural changes in the metastable regime are attributed to density variations. No structural heterogeneity appears on the experimental or simulated neutron spectra.

Keywords: Fragile liquid; glass; toluene; metaxylene

1. INTRODUCTION

A great variety of liquids can be supercooled below their melting point T_m without crystallizing. If crystallization has been avoided during cooling, the

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supercooled liquid undergoes a glass transition at some lower temperature T_g. As regards the variety of vitrifying systems (atomic, ionic, molecular with various interactions, polymeric, ...) and the different experimental techniques used to study the glass transition, the existence of an universal mechanism driving this transition is still an open question. The continuous progress in experimental spectroscopic techniques and the advent of some new theoretical approaches of the dynamics of supercooled liquids [1] have contributed to the fullness of the information of this aspect of the glass transition. However, few attention has been devoted to a quantitative analysis of the local structure of supercooled liquids. Most of the papers present studies on supercooled liquids and glass transition as function of temperature at atmospheric pressure: the variation of temperature both affects the density and the thermal energy of the samples.

The aim of our work is to separate the effects of density from those of thermal agitation on the local structure in the range of the first neighbouring molecules by a change in pressure at constant temperature, i.e. the density, the kinetic energy remaining constant. These structures are involved in the mesoscopic dynamics near the isobaric glass transition temperature T_g or the isothermal glass transition pressure P_g. We are especially interested in a possible survey of structural heterogeneities in the supercooled liquid when the molecular dynamics slows down.

Among the different features which characterize the glass transition, we have focussed our attention on the following points:

- the structural disorder: the glass keeps the microscopic structure of the supercooled liquid just above T_g
- the freezing-in of the molecular movements associated with the sudden change in the heat capacity C_p at T_g. The value of the drop of C_p at T_g depends on the number of degrees of freedom of the system frozen at the transition.

The central systems are two substituted aromatics liquids, toluene and meta-xylene which present the same thermodynamic signature of the glass transition and are considered as "fragile" according to the Angell classification of liquids [2,3]. Considering the drastic increase of the viscosity η when temperature approaches T_g, the Angell classification is based on its temperature dependence depending on the liquids: the viscosity of a "strong" liquid follows an Arrhenius type law whereas those of fragile liquids have a non-Arrhenius behavior. The fragility increases with the deviation from the Arrhenius behavior (Fig. 1). In molecular glass-forming systems, aromaticity is one of the features which increase the fragility of

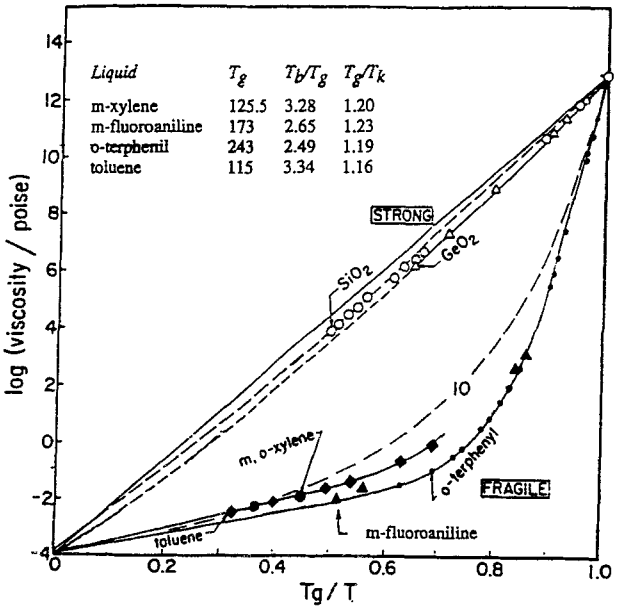

FIGURE 1 T_g/T scaled Arrhenius plot of liquids viscosity showing fragile and strong glass-forming liquids behavior.

liquids regardless the nature of the intermolecular interactions, Van der Waals or hydrogen bond type [4]. Table I presents calorimetric transition points of toluene and meta-xylene at atmostheric pressure.

In the extended pressure-temperature (P, T) phase diagramm opened by supercooling and overcompressing, characteristic lines such as the glass transition line or the melting line are defined and precise knowledges of the macroscopic thermodynamic properties such as the volume V, the isobaric expansivity α, the isothermal compressibility K_T and the heat capacity C_p are required. This was performed by differential scanning calorimetry and isothermal calorimetry. Elastic neutron scattering experiments and Monte Carlo simulations were combined to clarify the temperature and density dependence of the local structure.

TABLE I Calorimetric transition temperatures of meta-xylene and toluene (Ref. 3)

	$T_b(K)$	$T_m(K)$	$T_g(K)$
toluene	383.7	178.2	117.5
meta-xylene	412.1	225.3	125.5 (extrapolated)

I. NEUTRON STUDIES

1. Theoretical Relations

Neutron diffusion experiments lead to a spatial and temporal analysis of the intra and inter-molecular structure of the samples through the static structure factor $S_m(Q)$ and the experimental total pair correlation function $g_1(r)$.

The differential scattering cross section of a liquid is given in the static approximation by:

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\sum_{i,j} b_i b_j \exp(i\vec{Q}.\vec{r}_{i,j})\right) + \sum_i \frac{\sigma}{4\pi}$$

where b_i, b_j are the coherent scattering lengths of atoms i,j and σ_i the incoherent cross section of atom i.

The static structure factor is defined from the coherent total cross section by:

$$S_m(Q) = \frac{1}{\left(\sum_i b_i\right)^2}\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}}$$

For a molecular liquid, the structure factor is split into an intramolecular form factor $f_1(Q)$ and an intermolecular contribution $D_m(Q)$.

$$S_m(Q) = f_1(Q) + D_m(Q)$$

$f_1(Q)$ can be calculated for a known molecular geometry using the following equation:

$$f_1(Q) = \frac{1}{\left(\sum_i b_i\right)^2} \sum_{i,j} b_i b_j \left(\frac{\sin(Q.r_{i,j})}{Q.r_{i,j}}\right) \exp(-\gamma_{i,j}.Q^2)$$

where $r_{i,j}$ is the distance between atoms i and j of the same molecule and $\gamma_{i,j}$ is a Debye-Waller factor proportional to the square of the mean square displacements of atom i and j in the direction $r_{i,j}$.

The Fourier transform of $D_m(Q)$ allows to obtain the intermolecular pair correlation function $g_1(r)$:

$$4\pi\rho_m(g_\ell(r)-1)=\frac{2}{\pi}\int_0^\infty QD_m(Q)\sin(Q.r)dQ$$

where ρ_m is the molar density of the liquid.

2. Experimental Device

The experiments were carried out on the 7C2 spectrometer at the Orphée reactor of the Laboratoire Léon Brilloin (Saclay, France) on deuterated toluene and meta-xylene. Toluene was purchased from Aldrich (France) and meta-xylene from Eurisotop (France). The purity of the two compounds are greater than 99%. Experiments were performed at two incident wavelenghts (0.7 and 1.1 Å).

A thin cyclindric vanadium cell with an internal diameter of 6.0 mm was used for the atmospheric pressure measurement and a high pressure cell made in an incoherent scattering Ti-Zr alloy up to 4 kbar. The data were treated using a standard data correction method described elsewhere [4].

3. Results

The experiments were performed under three different experimental conditions (isobaric, isothermal and isochoric) in order to identify the parameters whose variation gives rise to the structural changes on the neutron spectra in the metastable liquid state.

The fully corrected static structure factor $S_m(Q)$ of liquid meta-xylene at 291 and 231 K at atmospheric pressure is presented on Figure 2-a. In these experimental conditions the thermal energy and the density change with temperature. When temperature decreases the main peak moves to higher Q and its intensity increases. This effect can be attributed to the increase of the density.

Figure 3-a a shows the fully corrected static structure factor $S_m(Q)$ of toluene at 293 K. The experiments were made at atmospheric pressure, 1 kbar and 3 kbar. One can notice the effect of densification on the structure: the maximum of the main peak is displaced to higher Q and the shoulder on the peak disappears progressively as pressure increases. The changes on spectra are correlated to an increase of the compactness of the molecules and the decrease of the isothermal compressibility.

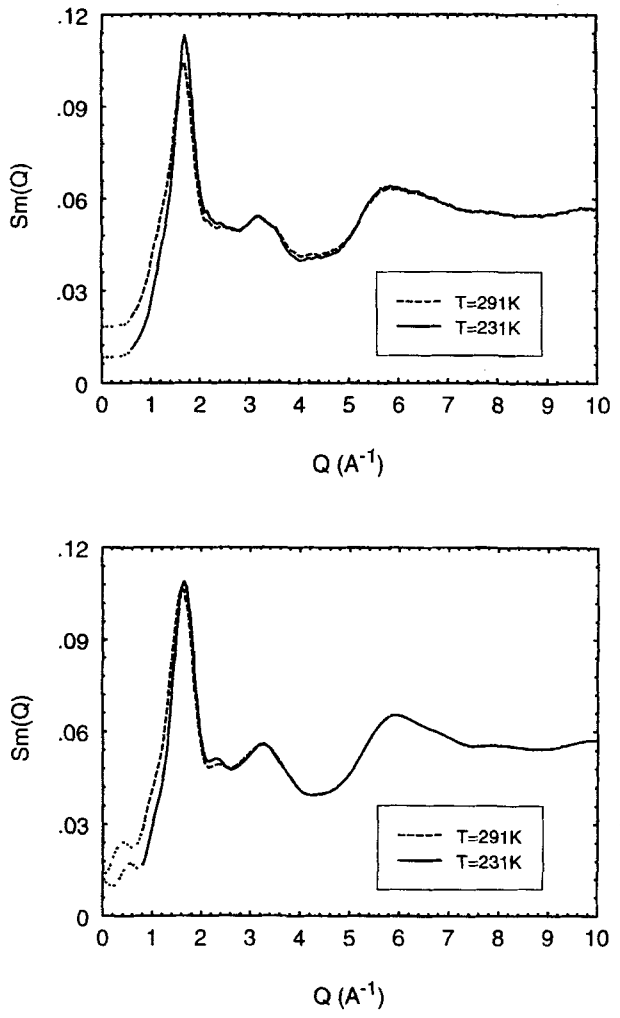

FIGURE 2 Experimental (a) and calculated (b) structure factor of meta-xylene at two temperature at atmospheric pressure.

Isochoric neutron measurements on the toluene sample provide the temperature sensitivity of the structure. The density of the studied samples, which $S_m(Q)$ are shown on Figure 4a, was equal to 1.06 g.cm^{-3} at 293 and 225 K. No significant change appears on the structure factor from 293 to 225 K except at very low Q where $S_m(Q)$ is affected by the change in the isothermal compressibility. An isochoric variation of the temperature does not affect the global structure of the sample in this temperature range.

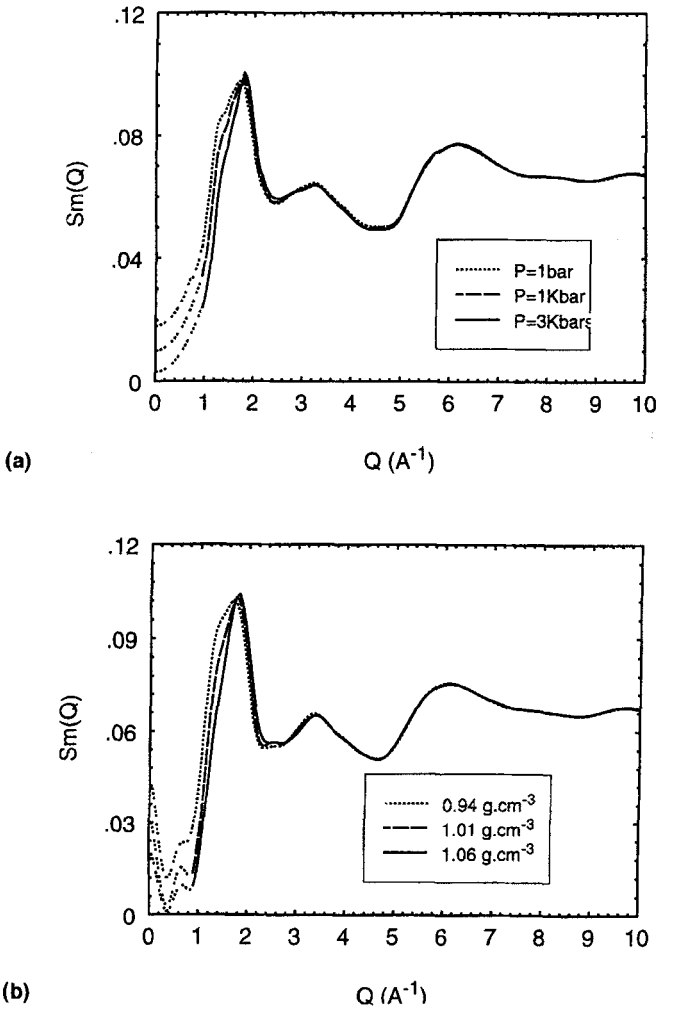

FIGURE 3 (a) Experimental structure factor of toluene at 293 K at 3 pressures (b) simulated structure factor of toluene at densities corresponding to the experimental ones.

The experimental neutron studies showed that the structural changes in liquids are dominated by densities. Change in thermal energy doesnot affect strongly the structural properties.

II. THERMODYNAMIC PROPERTIES

The temperature and pressure dependence of density and thermodynamic coefficients are derived from high precision calorimetric measurement under

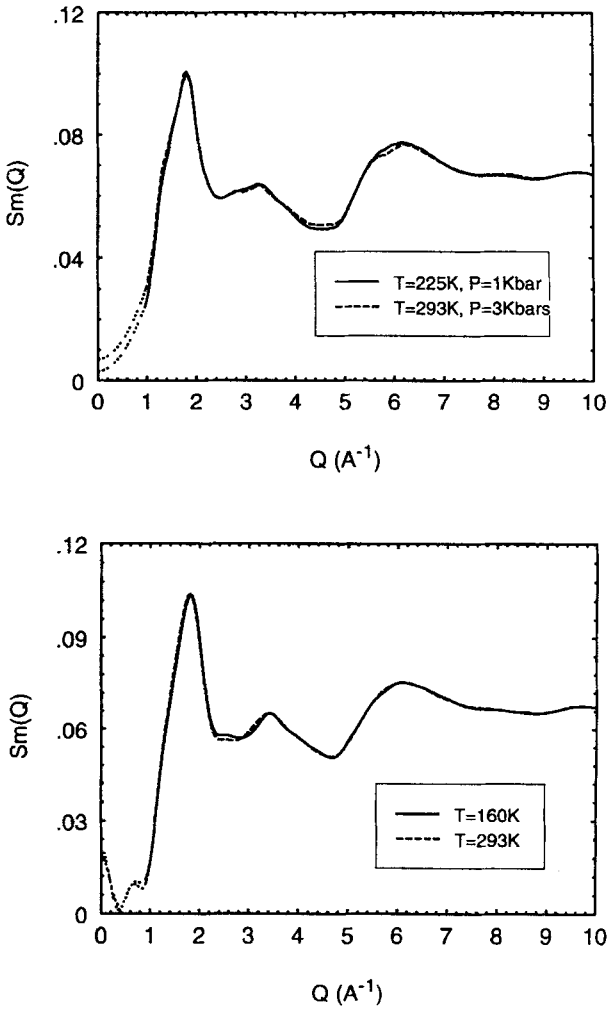

FIGURE 4 Experimental (a) and calculated (b) structure factor of toluene at 2 temperatures along an isochore.

high pressure by the piezothermal method and differential scanning calorimetry. The experimental methods and most of the results were published elsewhere [3, 6].

The calorimetric glass transition temperature T_g of toluene and meta-xylene are respectively 117.5 and 125.5 K. None of the three isomers of xylene is vitrifiable at normal cooling rates but when meta-xylene is mixed with a molar amount of 30 per cent of the ortho-xylene, the glass can be

obtained at normal cooling rates. We assume that the thermodynamic features are identical to those of pure meta-xylene.

Figure 5 shows the heat capacity C_p of meta-xylene as function of temperature from 100 to 250 K. The glass transition signature in the macroscopic time scale is characterized by a jump of C_p of about 77 J K^{-1} mol^{-1} for meta-xylene. The jump is of approximatively 55 J K^{-1} mol^{-1} for toluene. In both cases the glass transition is followed by a small decrease of C_p, stopped by the crystallization.

High pressure thermodynamic studies of pure toluene and other disubstituted benzene were previously performed [6] which main results are summarized as it follows. In the supercooled domain, the thermal expansivity α increases when the temperature decreases, whatever the pressure is; its consequence is seen in the pressure dependence of C_p at constant temperature according to the following equation:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -VT\left(\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right)$$

Thus, C_p presents a more or less pronounced decrease, reaches a minimum value and increases again with pressure. The pressure at which the minimum of C_p occurs decreases with temperature from 1 kbar in the stable liquid down to 1 bar at T_g. The isothermal compressibility K_T slightly decreases with temperature in the supercooled liquid whatever the pressure is.

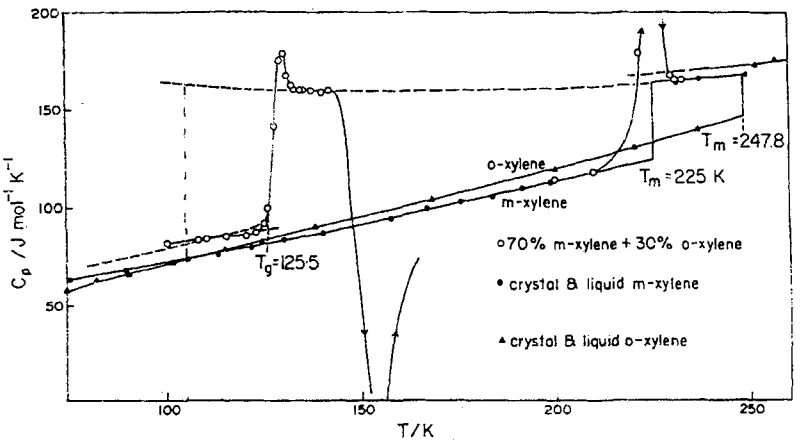

FIGURE 5 Heat capacity of glassforming mixture of 70% meta-xylene + 30% ortho-xylene as function of temperature in the liquid and in the glassy state, and crystal heat capacities of pure meta-xylene and ortho-xylene.

III. MONTE-CARLO SIMULATION TECHNICS

The Monte-Carlo numerical simulation of the glass transition of toluene and meta-xylene are presented in the isothermal-isobaric (NPT) and canonical (NVT) ensembles using an intermolecular Lennard-Jones potential.

1. Potential Models

The molecules are supposed to be rigid and the intermolecular interactions are described by pair atom-atom potentials. The interaction potential between the molecule α and the molecule β is the sum of a Coulomb term and a Lennard-Jones one according to:

$$U_{\alpha\beta} = \sum_i \sum_j \left[\frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \right].$$

The subscripts i and j are used for each atoms of the molecules α and β respectively. Parameters σ_{ij} and ε_{ij} are calculated by combinaison of atomic Lennard-Jones parameters $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$.

The charges of atoms and the Lennard-Jones parameters used have been calculated and optimized for pure liquid benzene and organic functional groups at 25 °C by Jorgensen *et al.* [7]. In this model, the methyl group is considered as a sphere with an electrical charge equal to those of hydrogene. The molecular characteristics and the Lennard-Jones parameters and the charges are summarized in Table II et III. The simulation box is a cubic cell of about 25 Å on a side with periodic boundary conditions. The translations,

TABLE II Geometric properties of meta-xylene (Ref. 7)

	$C_{ar}-C_{ar}$	$C_{ar}-H_{ar}$	$C_{ar}-CH_3$
d/Å	1,400	1,080	1,510
	(CCC)	(CCH)	
angles in degree	120.0	120.0	

TABLE III Potential parameters for metma-xylene and toluene (Ref. 7)

	q_i	$\sigma_i(\text{Å})$	$\varepsilon_i(kcal.mol^{-1})$
$C_{aromatic}$	−0.115e	2.42	0.03
$H_{aromatic}$	0.115e	3.55	0.07
CH_3	0.115e	3.80	0.17

rotations and volume changes were made within bounds of respectively about ± 0.3, Å ± 0.3 rad and 0.2%. No long range interaction correction such as Ewald sum or reaction field methods was used.

2. Simulation Details

Average internal energies U or enthalpies H were computed in the two statistical ensembles on 4.10^6 Monte Carlo steps after a stabilisation period of 4.10^6 steps. Fluctuation formulas were used to determine thermodynamical properties such as constant pressure heat capacity C_p, thermal expansivity α and isothermal compressibility K_T [8]:

$$\bar{\alpha} = \frac{\langle \delta V \delta H \rangle}{kT^2 \bar{V}}, \bar{\kappa}_T = \frac{\langle \delta V^2 \rangle}{kT\bar{V}} \text{ and } \bar{C}_P = \frac{\langle \delta H^2 \rangle}{kT^2}$$

k is the Boltzmann constant.

Total and partial pair correlation functions were averaged over 200 configurations, picked every 10^4 configuration.

The thermodynamic properties are calculated and compared to the experimental data down to the simulated ergodicity breaking. Then, the total and partial pair correlation functions (not available from the experiments) are studied and a correlation between macroscopic and microscopic features of the glass transition established.

IV. RESULTS AND DISCUSSION

1. Macroscopic Properties

Along the Atmospheric Pressure Isobare

We have investigated the properties of meta-xylene from 291 to 91 K at atmospheric pressure.

Figure 6-a shows a good agreement between the experimental densities of meta-xylene [9] and those calculated by Monte-Carlo simulation above the melting point. We estimated that the statistical uncertainty on the calculated densities is about 2%.

The averaged enthalpy H and density ρ have linear variations when the temperature changes in the stable and metastable supercooled liquid. A change in the slope of the curve of H or ρ indicates the glass transition. A

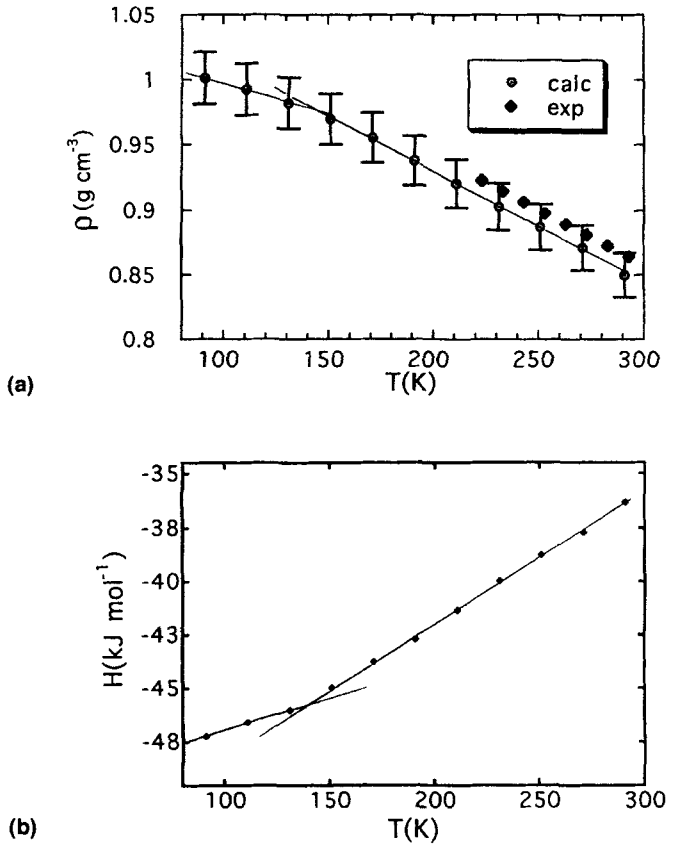

FIGURE 6 (a) Experimental and calculated density of meta-xylene vs temperature in the liquid, metastable supercooled liquid and in the glassy state. (b) Simulated averaged enthalpy of meta-xylene between 291 and 91 K in the liquid, supercooled liquid and glassy state.

temperature T_{gs} of 146 K is related to the simulated glass transition (Fig. 6-a, 6-b). Consequently, a discontinuity appears at this temperature in the thermodynamic properties. The simulated glass transition temperature T_{gs} corresponds to a loss of thermodynamical equilibrium in the time scale of the simulation. This temperature is greater than the experimental calorimetric glass transition temperature, as usually in simulations.

The heat capacity C_p calculated by simulation includes only intermolecular contributions (Fig. 7). The behavior of the simulated heat capacities as function of temperature is also in good agreement with the experimental one: a small increase of C_p is observed when the temperature decreases in the supercooled regime, followed by a drop of about 40 $J.K^{-1}.mol^{-1}$ at the

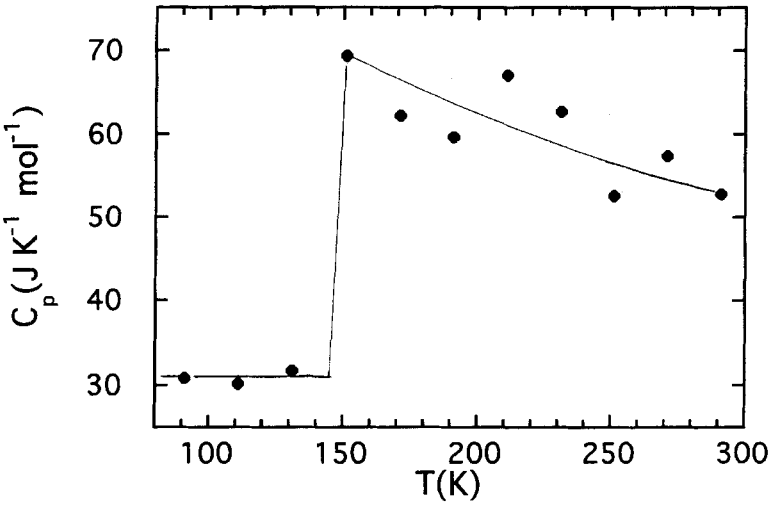

FIGURE 7 Isobaric heat capacity of meta-xylene vs temperture. Lines are guide for eyes.

simulation glass transition point. The change of C_p at the calorimetric T_g, extrapolated from simulation results, was of about 50 J.K^{-1}.mol^{-1}, consistent with the experimental value of 77 J.K^{-1} mol^{-1}.

The expansivity α has a comparable behavior in the supercooled and the glassy regime (Fig. 8) and the drop $\Delta\alpha$ at the transition point T_{gs} is approximatively of 5.6 10^{-4} K^{-1} in agreement with general observations in liquids [6].

The isothermal compressibility K_T decreases linearly with the temperature in the liquid or supercooled liquid domain with a sudden variation ΔK_T of about 1.5 10^{-5} bar^{-1} at T_{gs} (Fig. 9).

C_p, α and K_T remain roughly constant in the glassy state. However, the validity of their values calculated in the non ergodic glassy state is an opened question, since the methods of calculation are based on equilibrium hypothesis. Nevertheless, we can use some classical thermodynamic analysis according to quasi-thermodynamic relations derived from Ehrenfest [10]. When transition occurs in simulations, the relaxation times of the system are in a first approximation equal to 10^{-10} to 10^{-9} s according to the T_g/T scaled plot of Figure 1. No decoupling in V, H and S relaxation times are observed. According to the quasi-thermodynamic relations, we calculated a Prigogine-Defay ratio $\pi = \Delta K_T \Delta C_p / TV(\Delta\alpha)^2 =$ 1.17 close to the value of about 1 usually observed in the Lennard-Jones models.

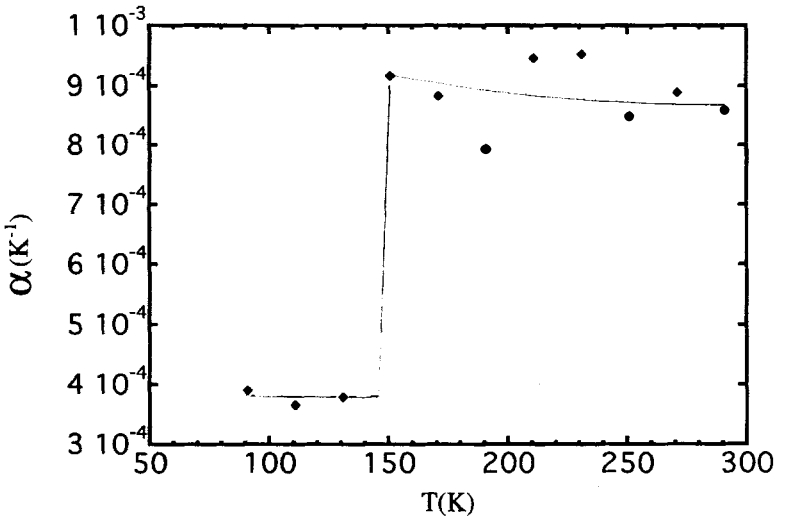

FIGURE 8 Simulated averaged expansivity α of meta-xylene between 291 and 91 K in the liquid, supercooled liquid and glassy state. Lines are guide for eyes.

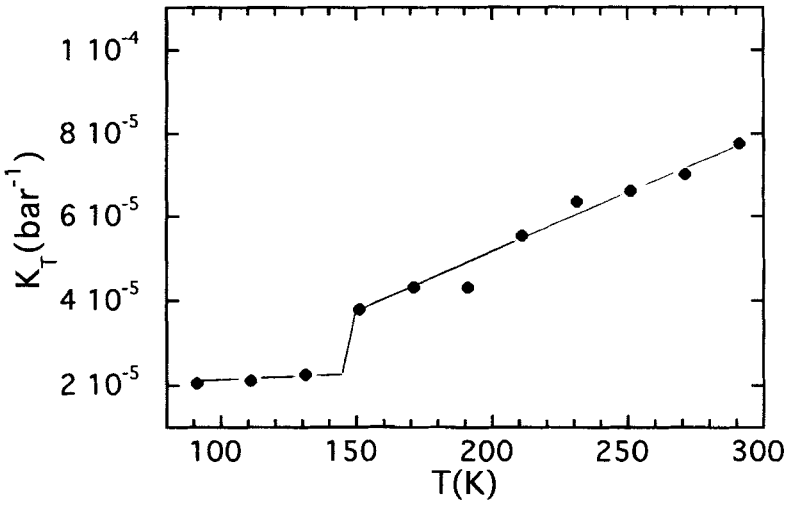

FIGURE 9 Simulated averaged compresibility K_T of meta-xylene between 291 and 91 K in the liquid, supercooled liquid and glassy state. Lines are guide for eyes.

The isobaric thermodynamic properties calculated by Monte-Carlo reproduce with good agreements the experimental results. This demonstrates the validity of the Lennard-Jones parameters and the charges used in the simulations.

Along an Isotherm

We have investigated the isothermal glass transition of meta-xylene at 171 K. The macroscopic properties were calculated as function of the pressure from atmospheric pressure up to 8 kbar. The averaged enthalpy is linear in the whole pressure investigated interval and no curvature or change occurs from atmospheric pressure up to 8 kbar whereas a transition at about 1.15 kbar would be expected if the quasi-thermodynamic Ehrenfest equations are available. The density ρ has a non linear variation in the liquid or overcompressed liquid domain. At high pressure, ρ becomes linear as function of pressure.

The pressure dependence of α is plotted in Figure 10. The curve decreases monotonously in the liquid, overcompressed liquid and glassy state, but no thermodynamic signature of P_g is enhanced according to isothermal glass transition studies in molecular compounds [6]. However, a mean value of 2 $10^{-4}K^{-1}$ in the glassy state is consistent with the experimental values at high pressure. K_T decreases when the pressure increases and no change appears as well in this curve in the studied pressure interval. C_p decreases when pressure increases, reaches a minimum value at 2 kbar and remains roughly constant up to 8 kbar (Fig. 11); no re-increase is observed, mainly because the system is already in the glassy state with a lower C_p than the overcompressed liquid in the simulation time scale.

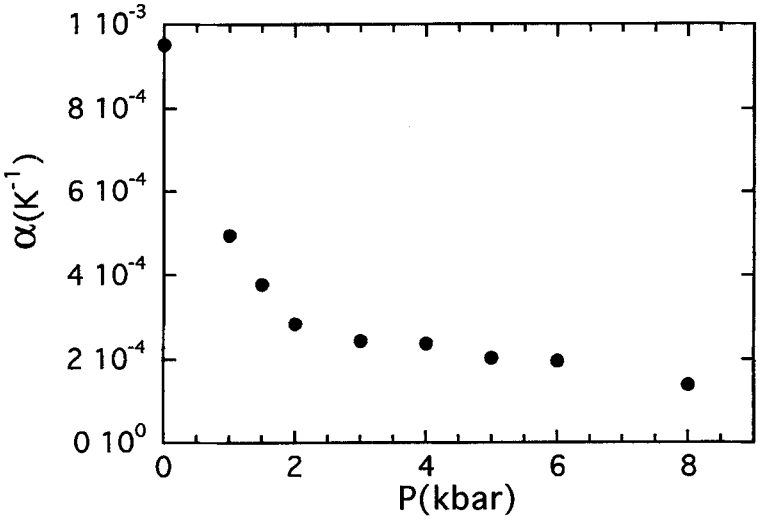

FIGURE 10 Computed averaged expansivity α of meta-xylene as function of pressure along the 171 K isotherm.

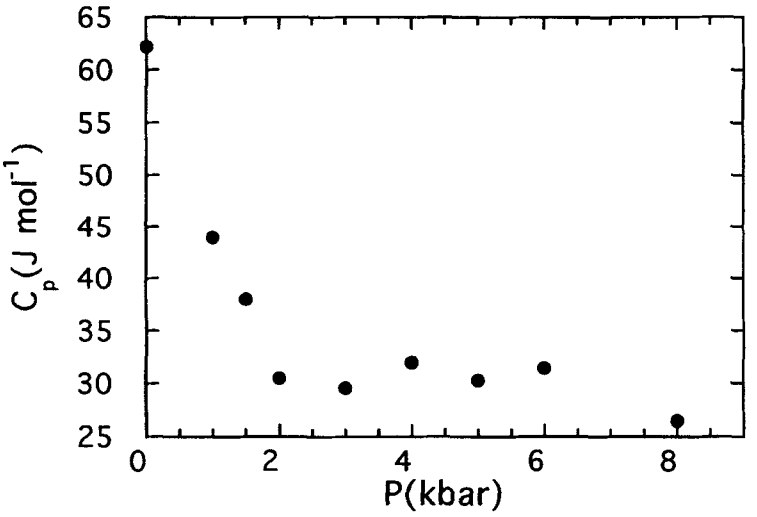

FIGURE 11 Calculated heat capacity of meta-xylene as function of pressure along the 171 K isotherm.

The isothermal glass transition point P_g cannot be clearly defined because no significant change appears in most of the curves of the thermodynamic properties. This is consistent with some experimental observations of high pressure adiabatic and isothermal calorimetry involving respectively purely thermal or mechanical perturbations [6, 11]. However, no dependence of the π ratio can be deduced from these calculations. At this point, dynamical parameters like the diffusion coefficient are required to characterize the isothermal glass transition.

2. Microscopic Features

The simulated and experimental static structure factor are in good agreement with an identical temperature dependence as compared for both liquids in Fig 2-b, 3-b and 4-b.

The isobaric studies as well as isothermal ones for toluene and metaxylene present a shift to higher Q according to an increase of density. The disappearance of the shoulder at 1.4 Å^{-1} corresponds to the shift of center to center calculated partial structure factor and is a-priori not related to some special intermolecular local or intermediate range order. The observed difference in $S(Q)$ between toluene and meta-xylene is attributed to the different chemical constitution and to cancellation effects in the linear combinaison of partial structure factors.

Accordingly, in the isochoric study of toluene computed for a density equivalent to that used in the isochoric experiments no effect is detected even at low temperature. Because any feature in a continuous scattering arises from the overlap of many Fourier harmonics, some special local arrangement can be detected only from specific partial pair correlation functions provided by simulations.

The partial pair correlation function of aromatic carbons allows the distinction of the temperature effects along an isochore (Fig. 12-a): preferred

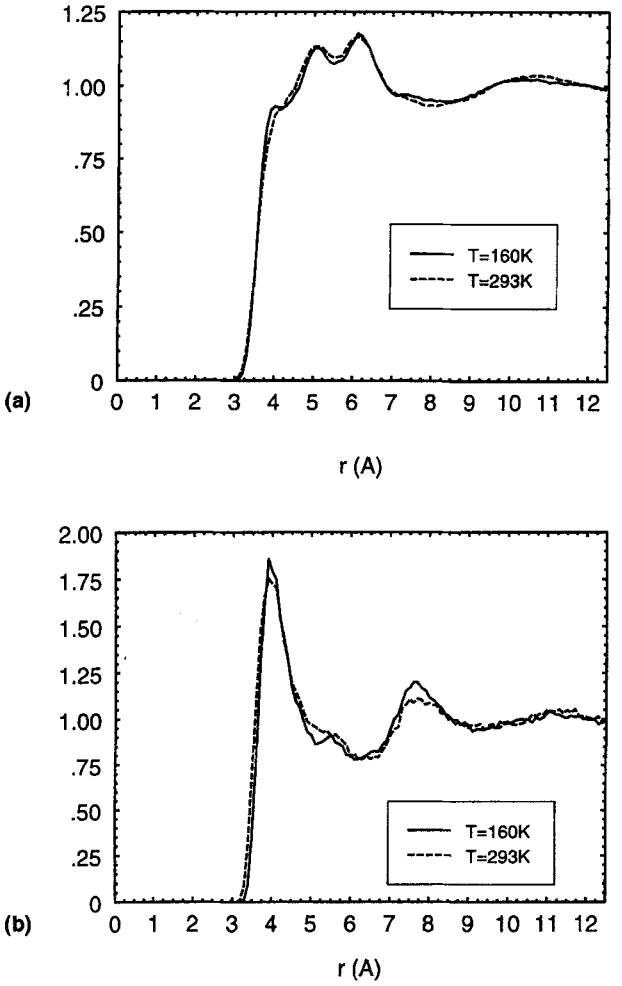

FIGURE 12 (a) Partial pair correlation functions of aromatic carbons along an isochore at 160 and 293 K. (b) Partial pair correlation functions of methyls along an isochore at 160 and 293 K.

orientations between the aromatic rings occur mainly at 4 Å and electrostatic effects will dominate the structure when the temperature decreases. At variance, no significant difference as shown in the methyl-methyl pair correlation functions (Fig. 12-b).

CONCLUSION

Experiments and simulations are in particularly good agreement for the thermodynamic and structural properties in the liquid, supercooled liquid and overcompressed liquid in the time scale of the simulation.

No distinction between entropy and free volume phenomenological approaches is observed and only one order parameter is defined from the Prigogine-Defay ratio π. Further high pressure isobaric simulations are required to establish a density dependence of π at the glass transition and to follow an isochronic line of 10^{-9} sec in the P-T diagramm.

From the microscopic point of view, density and packing effect are dominant in the liquid state. No evidence for structural heterogeneities, which can be associated to the dramatic increase of the relaxation time approaching the glass transition, is found on molecular scales. However, simulations performed at constant density and different temperatures show slight changes in partial pair correlation functions at short distance. This may be attributed to specific first neighbour aromatic rings orientations.

A more detailed study of the partial pair correlation functions and of the molecular dynamics near the transition point will be undertaken.

References

[1] Goetze, W. (1990). "Aspects of structural glass transition" in *Liquids, freezing and the glass transition*, ed by Hansen, J. P., Levesque, D. and Zinn-Justin, J. (North Holland), Amsterdam, p. 287.

[2] Angell, C. A. (1988). "Structural instability and relaxation in liquid and glassy phases near the fragile liquid limit", *J. Non-Crystalline Solids*, **102**(1–2), 205. Angell, C. A. (1988). "Perspectives on the glass transition" *J. Phys. Chem. Solids*, **49**(8), 863.

[3] Alba, C., Busse, L. E., List, D. J. and Angell, C. A. (1990). "Thermodynamic aspects of the vitrification of toluene and xylene isomers and the fragility of liquid hydrocarbons", *J. Chem. Phys.*, **92**(1), 617.

[4] Alba-Simionesco, C., Fan, J., Gonthier-Vassal, A. and Angell, C. A. "Thermodynamic aspects of the glass transition phenomenon II: Molecular liquids with variable interactions", Submitted for publication.

[5] Bellissent-Funel, M. C., Bosio, L. and Teixeira, J. (1991). "The inelastic correction for liquid water in neutron scattering", *J. Phys.: Cond. Matter*, **3**, 4065.

[6] Ter-Minassian, L., Bouzard, K. and Alba-Simionesco, C. (1988). "Thermodynamic properties of liquid toluene", *J. Phys. Chem.*, **92**, 487. Alba-Simionesco, C. (1991).

"Thermodynamic properties of some hydrogen bonded liquids in the undercooled and overcompressed states" in "Hydrogen bonded liquids", eds Dore, J. C. and Teixiera, J. Kluwer Academic Publishers p. 81–88. Alba-Simionesco, C. (1994). "Isothermal glass transition in supercooled and overcompressed liquids" *J. Chem. Phys*, **100**, 2250.

[7] Jorgensen, W. L., Laird, E. R., Nguyen, T. B. and Tirado-Rivers, J. (1993). "Monte Carlo Simulations of Pure Liquid Substituted Benzenes with OPLS Potential Functions" *J. Comp. Chem.*, **14**(2), 206.

[8] Timmermans, J. (1950). "Physico-chemical constants of pure organic compounds" Elsevier Publishing company, Inc.

[9] Allen, M. P. and Tildesley, D. J. (1986). "Computer simulation of liquids", Oxford Science Publications p. 51.

[10] Berg, J. I. and Cooper, Jr, A. R. (1978). "Linear non equilibrium thermodynamic theory of glass transition kinetics", *J. Chem. Phys.*, **68**(10), 4481.

[11] Takahara, S., Yamamuro, O., Suga, H. (1994). "Heat capacities and glass transitions of 1-propanol and 3-methylpentane under pressure. New evidence for the entropy theory", *J. Non Cryst. Solids*, **171**, 259.