Glycerol condensed phases
Part I. A molecular dynamics study

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Using a model potential function we have performed a molecular dynamics simulation of several static and dynamical properties of glycerol in the crystal, glass and liquid phases. Comparison with available experimental data shows an excellent agreement and proves the validity of the potential model used. For the calculation of the molar specific heat of the liquid and of the glass we have developed a theoretical approach which takes into account the contributions of the conformational structure energy and of the vibrational energy computed using the Bose–Einstein statistics.

1 Introduction

Glycerol (1,2,3-propanetriol) is one of the most extensively studied hydrogen-bonded systems. The presence of three hydroxy groups in the molecule gives rise to particularly rich and complex conformational and structural behaviour in condensed phases. As a consequence glycerol is an excellent glass former and the nature of its glass transition has been the object of several experimental investigations.1,2

Past theoretical studies on the structural and dynamical properties of the liquid and glassy states have made extensive use of computer simulation techniques.3–5 Early molecular dynamics (MD) simulations have focused on the structure of the liquid and amorphous solid6 and on glycerol as solvent, highlighting its role in the energy exchanges in non-photochemical hole-burning of resorufin.7 More recently, Benjamin et al.8 used MD simulations to investigate the scattering of Ne atoms from the liquid/vapor interface of glycerol surfaces, while Root and Berne9 carried out a MD simulation on liquid glycerol to characterize the effect of pressure on hydrogen bond formation at room temperature.

All these theoretical investigations rely on a common potential model10 fitted to reproduce the crystal structure10 and a few thermodynamic properties of the solid. In this model, the molecule contains nine atomic interaction sites, the carbon atoms and their directly attached hydrogens being treated as united atoms. This approach, while yielding reasonable results for some bulk properties of the condensed phases, may not be suited for conformational dynamics and hydrogen bonding formation. The absence of the non-acidic hydrogens can have a significant impact on the potential of mean force in the conformational space. In highly flexible systems, there are several examples, ranging from simple hydrocarbons11,12 to Langmuir Blodgett films13 or solvated biomolecules14 where the details of intra-molecular dynamics and the presence of non-acidic hydrogens are important for the conformational structure.

Glycerol can give rise to six backbone conformers classified according to the dihedral angles involving carbon and oxygen atoms. In the crystal only the 12 conformer in the notation of Bastiansen15 exists. In the liquid two conformers, the 12 and 12, were identified10,15–17 although the presence of other conformers was not ruled out completely. Evidence of other conformations, possibly stabilized by inter-molecular hydrogen bonds, was in fact claimed in ref. 18. However, in none of the aforementioned theoretical studies has the interplay of the conformational structure of glycerol with hydrogen bond formation been truly investigated.

In this paper we propose and test a realistic semi-empirical model for glycerol to be used for a study of the liquid and glassy state. A detailed analysis of the conformational dynamics of glycerol is the object of the accompanying paper.19 We have adopted the general purpose AMBER force field proposed in 1995 by Cornell et al.14 for complex molecular systems. In this model non-acidic hydrogens are explicitly included; all covalent bonds, except those involving hydrogen atoms, are assumed to be flexible. The use of efficient multiple time step r-RESPA20–25 (reversible reference system propagator algorithm) integrators makes the computational cost of the extra flexibility comparable to that required by the standard SHAKE procedure26 for implementing bond constraints.

The model is adopted for a thorough analysis of the structural and dynamical properties in the crystal, glassy and liquid states. The simulation results, whenever possible, are compared to available experimental data.

The paper is organized as follows. In section 2 we describe the potential model and provide some technique details about the simulation method. In section 3 we describe the preparation of the samples and the thermalization process for the different phases of glycerol. In Section 4 we compare the properties obtained by the MD simulations on the crystal, glass and liquid states with the experimental counterparts. For the crystal we have computed the equilibrium lattice parameters and a few thermodynamic data obtained in the isobaric-isothermal (NPT) ensemble. Some insight about the hydrogen bonding connectivity in the crystal is also given. A much more exhaustive study is made of the liquid and glass phases, where we have carried out a larger set of simulations as a function of temperature, cooling rate and box dimensions. The glass transition has also been investigated and characterized by computing thermodynamic properties, radial distribution functions and vibrational density of the states (DOS).


2 Methods

2.1 The potential model for glycerol

Glycerol is characterized by a large degree of internal flexibility. A reliable potential model for the condensed phase must hence reproduce as accurately as possible this property. Recently several force fields for biological and organic molecules were proposed.\textsuperscript{14,27–29} These models differ in the analytical form of intra- or inter-molecular interactions, but assume full flexibility (all-atoms models), being constructed to reproduce\textsuperscript{14} the structural and dynamical behaviour of complex molecules in the condensed phases. We have chosen to adopt the AMBER force field\textsuperscript{14} because of its simple analytical form.

Glycerol is considered to be completely flexible except for the covalent bond lengths involving hydrogen atoms which are kept rigid to the AMBER reference value. Constraining the CH and OH bond lengths will not reduce the realism of the model since in any case the CH and OH stretching modes occur at very high frequency and are thus of no importance for the dynamics of the condensed phases. On the other hand it is advantageous to impose constraints on X–H bonds, since it enhances the stability and the efficiency of the multiple time step integrators.\textsuperscript{30}

The intra-molecular potential is described in terms of harmonic stretching, bending and torsion force constants. For atoms separated by more than three covalent bonds, Lennard-Jones and Coulombic interactions are used. The functional forms of the intra-molecular potentials and the corresponding parameters are reported in Table 1. The inter-molecular interaction potential includes only Coulombic and Lennard-Jones atom–atom interactions. Point charges on the atomic nuclei are derived from quantum mechanical calculations\textsuperscript{31} at the B3LYP/6-31G* level, by performing an electrostatic potential (ESP) fit as prescribed by the AMBER protocol.\textsuperscript{14} Charges on equivalent atoms are equalized. The resulting atomic charges are shown in Fig. 1 and the potential parameters are given in Table 1.

2.2 General technical details

All simulations have been performed by the ORAC program\textsuperscript{32} on an IBM SP2 computer.

The first problem to face in a numerical simulation is the influence of the sample size on computed quantities. In order to verify the relevance of the size effects on bulk and microscopic properties of the liquid and glass phases, we have carried out two sets of simulations, one with 10\textsuperscript{8} and the other 32

![Fig. 1 Atomic charges on the glycerol molecule. Charges (in electronic units) have been calculated using the ESP \textsuperscript{14} procedure on B3LYP/6-31G\* ab initio data.](image)

Table 1 AMBER force field\textsuperscript{14} parameters for glycerol\textsuperscript{a}

<table>
<thead>
<tr>
<th>Type</th>
<th>k_J/kcal mol\textsuperscript{-1} Å\textsuperscript{-1}</th>
<th>( r_0/Å )</th>
</tr>
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<tr>
<td>Stretching</td>
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<td></td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>HCHCH</td>
<td>0.1556</td>
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</table>

\( V_{\text{int}} = K_f(r - r_0)^2 \)

\( V_{\text{bend}} = K_d(\theta - \theta_0)^2 \)

\( V_{\text{tors}} = 4\pi\alpha_k\left(\frac{\sigma_i}{R_p} \right)^{12} - 2\left(\frac{\sigma_i}{R_p} \right)^6 \)

\( \alpha_k(\text{Å}) \quad \epsilon(\text{kcal mol}^{-1}) \)

C       3.816       0.1094
O       3.442       0.2100
Hydroxy H 0.000       0.0000
Non-hydroxy H 2.774       0.0157

\( a \) Standard mixing rules, \( e_i = (\sigma_i + \epsilon_i)^{1/2} \) and \( \alpha_k = \frac{1}{2}(\sigma_i + \epsilon_i) \) are adopted for heteroatom Lennard-Jones interactions. Lennard-Jones and Coulombic interactions between atoms separated by exactly three bonds are diminished by the specific factors of 0.5 and 0.8333, respectively.

For the crystal a sample of 240 molecules was used.

All simulations are carried out imposing standard periodic boundary conditions. Coulombic interactions are computed by the smooth particle mesh Ewald (SPME) method.\textsuperscript{33–35} The Ewald convergence parameter \( \alpha \) is set to 0.43 Å\(^{-1}\). For all samples, the grid spacing for the B-spline interpolation of the charges onto the SPME grid is maintained around 1 Å in all simulations. A sixth order cardinal B-spline interpolation is used. Multiple time step integration technique r-RESPA\textsuperscript{24,32} was adopted to integrate the equations of motion.

3 Thermalization procedure

3.1 Crystal

The sample of crystalline glycerol has been prepared by replication of the orthorhombic unit cell\textsuperscript{10} (space group P2_1 2_1 2_1, \( Z = 4 \)) using the experimental crystal structure\textsuperscript{10} at 198 K (\( a = 7.00 \text{ Å}, b = 9.96 \text{ Å}, c = 6.29 \text{ Å} \)). The simulation box sides are 4\( a \), 3\( b \) and 5\( c \), respectively (240 molecules). Since the experimental positions of the hydrogen atoms are not available, their starting values were determined by a steepest descent minimization. The system was allowed to reach equilibrium for \( \sim 50 \) ps at 198 K (melting point at about 291 K, ref. 36) and room pressure in the NPT ensemble. The Parrinello–Rahman periodic boundary conditions\textsuperscript{33} combined with a Nose–Hoover thermostat\textsuperscript{38,35} were used. The averages were computed by a simulation run of 72 ps.
3.2 Liquid and glass

Liquid samples with 108 molecules were obtained by cooling from an equilibrated structure at a temperature of about 400 K and room pressure. The starting configuration was obtained by distributing the molecular centers of mass at the nodes of an ordered face centered cubic box of 25 Å side with random molecular orientations. The final equilibrium distribution of the backbone conformational states in the liquid is found to be independent of the starting distribution: an initial configuration made up of either αα or γγ conformers reaches, after 400 ps, an identical stationary conformational distribution corresponding to mainly αα and γγ conformers. Equilibration was carried out for 400 ps in the NPT ensemble using the Anderson isotropic stress constant pressure method. Two different types of cooling runs were made. A faster one in steps of 10 K (from 400 to 40 K) every 50 ps and a slower one in steps of 10 K every 110 ps. In principle very slow cooling rates (of the order of one degree per minute) should be used to correctly reproduce the glass transition. This is clearly out of the possibility of a MD simulation and thus only a tendency to approach the experimental temperature can be shown as the cooling rate is reduced. We performed microcanonical ensemble (NVE) simulations (each of 126 ps) from 400 to 40 K in steps of 40 K. For a better comparison with the experimental data, an additional run at 300 K was carried out. Before coordinate storage in the NVE ensemble, new equilibrations of 45 ps at each temperature were carried out using the cell parameters obtained from the NPT runs. In the NVE runs, with respect to NPT ones, temperature variations of less than 5 K were found.

The sample containing 500 molecules was prepared as follows: the equilibrated structure of 108 molecules at 400 K was replicated three times in the x, y, z directions; a cubic cell with side-length adjusted to include exactly 500 molecules was then carved out of the replicated system. The system was then equilibrated at 400 K for about 10 ps in the NPT ensemble and frozen down to 40 K using the slower cooling rate as for the 108 molecule sample. Data acquisition in the NVE ensemble was done for 126 ps.

4 Results and discussion

4.1 Crystal properties

The cell parameters obtained in the NPT simulation of the crystal are in excellent agreement with experimental data. The average NPT cell angles are all of 90.0 ± 0.2 degrees and the average side-lengths are, in Å, a = 7.03 ± 0.03, b = 9.87 ± 0.03, c = 6.32 ± 0.03, to be compared to the experimental values a ≈ 7.00 ± 0.04, b = 9.96 ± 0.05, c = 6.29 ± 0.04. The error is below 1% for all lattice constants and for two of them, a and c, the differences are within experimental error. The positions of oxygen and carbon atoms are close to those obtained from X-ray experiments. In the crystal, each molecule (A in Fig. 2) is found to be hydrogen bonded to another four neighboring molecules (B, C, D and E in Fig. 2) by six hydrogen bonds: three as hydrogen donor and three as acceptor. The central molecule A donates a hydrogen atom to the B molecule (one H-bond) and two to the E (two H-bonds) molecule and accepts hydrogen atoms from C (two H-bonds) and D (one H-bond). Each hydrogen donor and oxygen acceptor is involved in only one hydrogen bond.

The inter-molecular oxygen–hydroxy hydrogen and oxygen–oxygen radial distribution functions are shown in Fig. 3. The large intensity of the peaks at ~1.5 Å for the O–H and at 2.8 Å for the O–O function are evidence of strong hydrogen bonding. The separation of about 1 Å of these characteristic peaks shows that the hydrogen bonds in the crystal are practically linear. The secondary peak at 3.25 Å in the O–O function corresponds to the distance between two end oxygen atoms of different molecules.

The experimental enthalpy of melting of glycerol at 18.2 °C is 18.74 kJ mol⁻¹⁻¹. The enthalpy of vaporization, determined at room temperature, is reported to be 76.1 kJ mol⁻¹⁻¹. Their sum represents a reasonable estimate of the cohesive energy of the crystal at the melting point: $E_{coh} \approx 94.8$ kJ mol⁻¹⁻¹. The cohesive energy from MD data is readily obtained as the energy difference between the solid and the gas phase. The potential energy per molecule in the gas was obtained by a NVE run of 32 molecules uniformly distributed into a cubic box of side 1500 Å. The sample was equilibrated at 198 K (the same temperature as the crystal) for about 100 ps and thermodynamic averages were computed on a run of 150 ps. The calculated cohesive energy is 98.3 ± 1.3 kJ mol⁻¹⁻¹, in excellent agreement with the value estimated above.

4.2 Liquid and glass properties

4.2.1 Bulk properties. The enthalpy of vaporization of the liquid at room temperature was computed in the same way as for the cohesive energy of the crystal. The gas sample used for the cohesive energy calculation was further equilibrated at 298 K for 100 ps and the mean potential energy calculated by a run of 150 ps. The calculated enthalpies for the gas and the liquid are 104.1 ± 1.7 kJ mol⁻¹⁻¹ and 31.08 ± 0.74 kJ mol⁻¹⁻¹, respectively. From these values the resulting vaporization enthalpy is $\Delta H_{vap} = 73.0 ± 2.5$ kJ mol⁻¹⁻¹, in good agreement with the experimental value of 76.1 kJ mol⁻¹⁻¹. Computed and experimental molar volumes as a function of the temperature are shown in Fig. 4. The molar volumes predicted by the samples of 108 and 500 molecules are practically the same.
MD data agree very well with experiment\(^{41}\) in the room temperature region. At higher temperatures the agreement is less satisfactory. Nonetheless the error at 400 K is still found to be less than 3%. The clear change in slope occurring at about 210 K is indicative of the liquid–glass transition as confirmed by the molar specific heat calculations reported in the next section. The glass transition temperature is consistent with the experimental value of 185 K\(^{42,43}\) if one takes into account that our slower cooling rate is still too fast to reproduce quantitatively the glass transition. A more detailed discussion of this point is given in the next section.

### 4.2.2 The glass transition: constant volume molar specific heat

The liquid–glass transition has been thoroughly and extensively characterized by calorimetric measurement of molar specific heat\(^{42,44–46}\). In NVE simulations, the molar specific heat, \(C_v\), is usually computed from the kinetic energy fluctuations. For a system of \(N\) molecules and \(n\) degrees of freedom per molecule, \(C_v\) is given by

\[
C_v = R \frac{n}{2} \left[ 1 - 2 \frac{\langle E_{\text{kin}} \rangle - \langle E_{\text{kin}} \rangle^2}{n N k_B T^2} \right]^{-1}
\]

where \(R\) is the gas constant, \(k_B\) the Boltzmann constant, \(T\) the mean temperature, \(E_{\text{kin}}\) the kinetic energy and angular brackets indicate an ensemble average. For systems in the condensed phases, the constant volume \(C_v\) and constant pressure \(C_p\) are virtually identical in a MD simulation since their difference (a few J mol\(^{-1}\) K\(^{-1}\)) at room temperature) is smaller than the statistical uncertainty. MD computed \(C_v\) are hence compared directly to the experimental \(C_v\).

In glycerol there are several high frequency stretching and bending motions involving hydrogens which have a marked quantum behaviour at room temperature with characteristic temperature \(\theta_{\text{vib}} = h \nu/k_B\) exceeding 1000 K. The population of these vibrational states is then virtually unchanged from 0 K to room temperature. In a classical molecular dynamics simulation, each degree of freedom, irrespective of the characteristic frequency, has a kinetic energy of and the square of the amplitude, is in a non-equilibrium state and the cooling rate becomes important: a lower cooling rate decreases the temperature \(T_g\) and the range in which the glass transition occurs. No sample size effects are observed instead.

In the liquid and glassy phases, outside the glass transition range, \(E_{\text{pot}} - E_{\text{kin}}\) is characterized by a nearly linear behav-

**Fig. 4** Glass and liquid molar volume. Experimental data from ref. 41.

corrected for the quantum effects. To this end, the concept of inherent structure\(^{47,48}\) that is the structure at the local minimum of the many particle potential energy surface reached by steepest descent minimization, supplies a strategy which uniquely separates the description of the system into a purely configurational part and a part due to vibrations around the minimum. Any thermodynamic properties, molar specific heat included, may be viewed as a sum of a configurational contribution, due to the inherent structure, and of a vibrational contribution due to the oscillation of the many particle system around the inherent structure minimum. The total energy of the system is then given by

\[
E_{\text{total}} = E_{\text{conf}} + E_{\text{vib}}
\]

In the solid phase, where only one configuration exists, only the vibrational term \(E_{\text{vib}}\) is important, while both the configurational and the vibrational terms are relevant in the liquid phase. This is the reason why the molar specific heat of the liquid is larger than that of the solid.

We start by evaluating from the MD data the configurational contribution to \(C_v\). The potential energy may be written as

\[
E_{\text{pot}} = E_{\text{conf}} + E_{\text{pot}}
\]

where \(E_{\text{conf}}\) is the inherent structure energy and \(E_{\text{pot}}\) is the term due to the oscillation of the system with respect to the inherent structure. If these oscillations are assumed to be harmonic and if the system is at equilibrium, the last right hand term of eqn. (3) is exactly equal to the vibrational kinetic energy \(E_{\text{kin}}\) of the system. The configurational part of the potential energy is therefore given by

\[
E_{\text{conf}} = E_{\text{pot}} - E_{\text{kin}}
\]

Actually, due to the anharmonicity of the real oscillators, eqn. (4) holds only approximately.

The configurational contribution, \(E_{\text{pot}} - E_{\text{kin}}\), is shown as a function of the temperature in Fig. 5 for the samples with 500 and 108 molecules and for two different cooling rates. The glass transition is located at the change of slope. In the liquid phase the configurational energy is virtually independent of the cooling rate, because all samples are in a state of thermodynamic equilibrium. Near the glass transition the system is in a non-equilibrium state and the cooling rate becomes important: a lower cooling rate decreases the temperature \(T_g\) and the range in which the glass transition occurs. No sample size effects are observed instead.

In the liquid and glassy phases, outside the glass transition range, \(E_{\text{pot}} - E_{\text{kin}}\) is characterized by a nearly linear behav-

**Fig. 5** Configurational contribution to the total energy. The configurational energy has been evaluated using eqn. (4) from simulations in the NPT ensemble. Slow and fast cooling corresponds to 0.091 K ps\(^{-1}\) and 0.2 K ps\(^{-1}\), respectively (see section 3). Simulations with 108 molecules have been carried out with the slow cooling rate up to 330 K.
The configurational contribution to the heat capacity,

\[ C^\text{conf}_c = \left( \frac{\partial E^\text{conf}}{\partial T} \right)_v \]  

(5)
is hence approximately constant in both the liquid and the glassy phase.

Under the assumption of harmonic oscillations around the minimum of the inherent structure, the quantum vibrational contribution \( E_{\text{vib}} \) in eqn. (2) may be easily estimated from the knowledge of the vibrational density of states (DOS),

\[ E_{\text{vib}} = n_i N_A \int_0^{\infty} g(T, v) v^2 \left[ \frac{\partial g(T, v)}{\partial T} \right] dv \]  

(6)

where \( N_A \) and \( h \) are Avogadro’s and Planck’s constants, respectively, \( g(T, v) = (e^{hv/k_BT} - 1)^{-1} \) is the Bose–Einstein occupation number, \( g(T, v) \) is the normalized (to one) DOS, and \( n_i \) is the number of degrees of freedom per molecule (for our model \( n_i = 34 \)). By differentiating eqn. (6) with respect to \( T \), we obtain:

\[ C^\text{vib}_v = n_i R \int_0^{\infty} g(T, v) e^{\frac{v^2}{2k_BT}} \left( \frac{\partial g(T, v)}{\partial T} \right) dv + n_i N_A \int_0^{\infty} \left[ \frac{\partial g(T, v)}{\partial T} \right] dv \]  

(7)

where \( u = hv/k_BT \). In the actual calculation we have neglected the last term of eqn. (7) since for glassy and liquid glycerol the DOS is weakly temperature dependent. The vibrational contribution, therefore, plays a small role in the liquid-glass transition and it does not affect substantially the transition temperature and it does not affect substantially the conformational part. The total \( C_v \) is then given by the sum of the configurational [eqn. (5)] and of the vibrational part [eqn. (7)]. In Fig. 6 we compare the calculated \( C_v = C^\text{conf}_v + C^\text{vib}_v \) with the available experimental data. The figure shows that the \( C_v \) calculated with the present theory agrees perfectly with experiments in the regions in which the liquid and the glass exist as well defined phases. In the intermediate region, where the transition occurs, the figure shows very clearly the importance of the cooling rate. For the faster cooling the transition occurs at higher temperature and extends over a broader range. For slower cooling the transition starts at lower temperature and covers a narrower range, approaching the experimental curve. This makes us confident of the fact that if one could perform a very long and expensive cooling at a much slower rate, the calculated curve would agree much better with the experimental one in the transition range. As discussed in the case of the configurational contribution to the total energy, no size effect was detected: in fact the data (not shown) obtained with the sample of 108 molecules and slower cooling agree perfectly with those of the larger sample.

4.2.3 Inter-molecular radial distribution functions and structure factor. The partial radial distribution functions \( g_n(r) \) for different atom types \( n, n' \) are computed in the standard way.\(^4\) The \( g_n(r) \) functions are related to the inter-molecular distribution function \( d(r) \) by the relation

\[ d(r) = 4\pi \rho [\bar{g}(r) - 1] \]  

(8)

where \( \rho \) is the particle density and \( \bar{g}(r) \) is a weighted sum of the partial inter-molecular distribution functions:

\[ \bar{g}(r) = \sum_n c_n b_n^{-2} \sum_{n'} c_{n'} b_{n'} g_{nn'}(r) \]  

(9)

In this equation \( b_n \) is the coherent scattering length for nucleus of type \( n \), \( c_n \) is its relative concentration and the \( g_{nn'}(r) \) are the six distinct partial pair distribution functions for the system. The \( d(r) \) function has been experimentally determined by neutron diffraction\(^8^b\) at 293 K in the liquid state. The \( d(r) \) function for the liquid sample of 500 molecules at room temperature is shown in Fig. 7, where it is compared with the experimental data at about the same temperature.\(^6\)

The experimental \( d(r) \) at 293 K \(^6\) presents well defined modulations beyond 6 Å which are a signature of long range order. Evidence of long range order, in agreement with experiment, is obtained also in our calculations. Site–site correlation functions are found to be very similar to the site–site correlation functions reported by Root and Berne.\(^9\) In Fig. 8a and 8b we show the \( g_{CC}(r) \) and \( g_{OH}(r) \) site–site correlation functions, respectively. In agreement with the data of Root and Berne,\(^9\) we find that only the carbon–carbon pair correlation functions show long range periodicity while the others show virtually no structure beyond 8 Å. Due to the vicinity of the carbon atoms to the molecular center of mass, the \( g_{CD}(r) \) site–site correlation function has the same modulations of the molecular center of mass \( g(r) \) function. The periodic behaviour in the experimental \( d(r) \) is hence due to generic molecular coordination and not to site–site specific interactions.

The \( S(Q) \) static structure factor probes both inter- and intra-molecular structures. The calculated \( S(Q) \)’s are shown in Fig. 9 for the liquid at 300 K and for the glass at 160 K, along with respect neutron scattering measurements at 180 K.\(^8^a\) For the glassy sample the calculated structure factors are noisy, since the glassy structure corresponds to a single frozen liquid configuration. Nonetheless the structure for \( Q > 4 \) Å\(^{-1} \) is sufficiently smooth and essentially identical to that of the liquid. The first peak at \( Q \approx 1.4 \) Å\(^{-1} \) corresponds to the inter-molecular peak in the \( d(r) \) at 5.2 Å (see Fig. 7). The large and broad peak around \( Q = 3 \) Å\(^{-1} \) (≈ 2 Å in direct space) is due
Fig. 8  Carbon–carbon (a) and oxygen–hydroxy hydrogen (b) radial distribution functions. The dashed curves refer to glassy samples. The dotted curves at 400 K were calculated using the sample of 500 molecules. They show the absence of significant size effects. For clarity different curves are upshifted.

to the intra- and inter-molecular hydrogen bonds. The structure beyond \( Q \approx 3 \text{ Å}^{-1} \) is due to short intra-molecular distances and to damped oscillations of the hydrogen bond peak. The damping constant in the \( Q \) space equals half the line-

Fig. 9  Static structure factor. (i): \( T = 300 \text{ K} \); sample of 108 molecules. (ii): \( T = 160 \text{ K} \); sample of 500 molecules. (iii): experimental data\(^{18}\) for the glass. For comparison the experimental curve was upshifted.

Fig. 10  Mean square displacements as a function of temperature. Experimental data: (\( \Delta \)) ref 43; (\( \bigcirc \)) ref. 51. MD results: (\( \cdots \cdots \)).

width in real space. Thus the narrow inter-molecular hydrogen bond peak in \( \theta_{\text{int}}(r) \) gives rise in the \( Q \) space to weakly damped oscillations. In ref. 18, the observed features in the \( S(Q) \) beyond 7 \( \text{ Å}^{-1} \) have been interpreted, on the basis of fitted molecular form factors, as a fingerprint of the \( \beta\gamma \) conformation. According to our calculation, which, indeed, agrees well with the experimental \( S(Q) \), we do not observe a significant presence of such conformer either in the liquid or in the glassy phase. The conformational distribution is dominated by the presence of the \( \alpha\alpha, \alpha\gamma \) and to a much lower extent by the \( \gamma\gamma \) conformers. The stability of such conformational structures is confirmed by \textit{ab initio} data.\(^{49-51}\) In the light of these considerations, the presence of a significant amount of the \( \beta\gamma \) conformation in the glassy or liquid phase is unlikely.

4.2.4 Density of states. The density of states is computed as the power spectrum of the velocity auto-correlation function.\(^4,53\) Recently Cuello et al.\(^{54}\) have measured by incoherent neutron scattering experiments the DOS spectrum at several temperatures from 15 to 280 K. We have calculated the DOS spectra at five temperatures from 80 to 400 K. The calculated curves are displayed in Fig. 11 from 0 to 740 cm\(^{-1}\). In the same figure we show, for comparison, two of the experimental curves of ref. 54, one for the glass at 170 K and one for the liquid at 250 K. The excellent agreement between experiments and simulations confirms the ability of the potential model to reproduce the dynamics of a complex system like glycerol. At low temperatures, our curves reproduce correctly the typical Debye behaviour observed experimentally. As the temperature increases the Debye behaviour gradually decreases, disappearing at 400 K. A further test is offered by the comparison with Raman spectra.\(^{44}\) At higher frequencies, the calculated DOS spectra show four well defined peaks at about 330, 430, 490 and 550 cm\(^{-1}\) which correspond to the four observed Raman bands\(^{44}\) at 339, 412, 471 and 567 cm\(^{-1}\). In addition the Raman spectrum of the liquid and of the glass shows a broad band at about 660 cm\(^{-1}\). In the calculated DOS spectra we observe a very broad band which shifts from about 600 cm\(^{-1}\) at 400 K to about 660 cm\(^{-1}\) at 80 K. This strong temperature shift towards high frequency is characteristic of COH bending motions of H-bonded OH groups and allows us to unambiguously assign this band.

5 Conclusions

We have performed extensive classical MD simulations of the condensed phases of glycerol (liquid, glass and crystal) in a
wide temperature range. Several structural and dynamical properties have been computed. The liquid and glass structures have been investigated by evaluating radial distribution functions and the structure factor. Simulation results are in good agreement with the available neutron scattering experiments. The calculated density of states agrees with recent neutron scattering experiments at low frequencies and shows clear evidence of the presence of an extended H-bonding association. We have developed a theoretical approach to the calculation of the molar specific heat for systems with several internal degrees of freedom. The method takes into account the Bose–Einstein statistics, for the population of the internal modes of vibration, and the configurational contribution to the energy. Agreement with experimental data is surprisingly good. The predicted liquid–glass transition occurs near the experimental transition temperature. A relevant cooling rate dependence on the thermodynamic properties has been observed.

In general, comparison with experimental data shows the validity of the adopted potential model for all the condensed phases of glycerol. Whether or not this will be true for other systems is out of the scope of the present paper and requires further studies. In the following paper,15 we will analyze the molecular conformational properties and hydrogen bonding in the condensed phases. The presence of an extended hydrogen bond network in the liquid will be proved and its dynamical properties will be studied.

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