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Thermal activation of ethylene glycol embedded in carbon nanotubes – Computer simulation study

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ABSTRACT

We performed all atoms molecular dynamics simulations of ethylene glycol embedded inside single walled (17,0) and (10,10) carbon nanotubes, as well as bulk ethylene glycol, to study the influence of the spatial constraints and interaction between the embedded molecules and internal surface of the nanotubes on thermal activation of the system and deviation from purely Debye relaxation characteristic observed in bulk ethylene glycol liquid.

1. Introduction

Molecular systems confined in nanoscale confinement exhibit interesting structural and dynamical properties, which are intensively studied experimentally [1–4], theoretically [5] and by means of computer simulation methods [6–11]. Molecules embedded in carbon nanotubes are studied because they are interesting from scientific point of view as well as because of their interesting potential applications in energy storage, nanoelectronic devices, chemical biosensors, field emission displays and many others [12–14]. Properties of polar molecules embedded in carbon nanotubes have been intensively studied experimentally [15–17] and using computer simulation methods [18–23].

Dipolar relaxation spectra are sensitive to intermolecular interactions and provide information on cooperative processes, revealing features mutual to different types of condensed matter systems [24–26]. Broadband dielectric relaxation spectroscopy provides the link between the methods which probe the properties of the individual molecules and techniques characterizing the bulk properties of the sample [27]. Ethylene glycol (ethane- 1,2 -diol) belongs to a group of diols and is widely used as antifreeze and precursor for polymerization. It also finds application in heating/cooling system as heat transfer agent due to its high boiling point (470 K). Under normal conditions ethylene glycol is a colorless, clear liquid. The presence of two hydroxyl groups in ethylene glycol molecules guarantees the affinity to water and solubility in polar solvents. Due to this properties it is sometimes used as desiccant, to prohibit formation of gas clathrates in long pipelines.

Computer simulations have been applied to study interaction of water–ethylene glycol with carbon nanotubes [28] and thermal conductivity [29]. In both studies special attention has been paid to intermolecular/intramolecular hydrogen bonding and trans – gauche conformation of ethylene glycol. Dynamics of ethylene glycol and other small glass-forming molecules has been intensively studied experimentally, especially using neutron scattering technique [30–36]. Reorientational dynamics of ethylene glycol in sol–gel porous glasses nanopores (approx. 25 A of diameter) was examined by means of light scattering, incoherent inelastic neutron scattering (IINS) and incoherent quasi-elastic neutron scattering (IQENS) [30–34]. Ethylene glycol and poly-ethylene oxide properties were also studied in 2D nanoconfinement [36]. Ethylene glycol molecules were trapped between graphite oxide layers in cavity of approximately 3 A thick. It was shown that in such system crystallization and glass transition are blocked, structure and dynamics of confined ethylene glycol is substantially different from those observed for crystalline and amorphous bulk counterparts.

Molecules embedded in nanoscale porous media exhibit interesting features, which considerably differ from those exposed by bulk fluids and cannot be rationalized in terms of

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classical hydrodynamic theories [37]. The dynamical properties of these systems strongly depend on the spatial confinement and interactions on atomic level and interfacial structures, which can be studied using molecular dynamics simulation method. Relaxation of molecular systems in confinement is often discussed in terms of the cooperatively rearranging regions and characteristic cooperativity length scale [38]. It is generally agreed that limiting the cooperativity length scale by the confinement leads to accelerated dynamics compared to the bulk, however opposite view of the length scale effects has also been proposed [39], suggesting that the cooperativity length represents the amount of material that must be available to enable cooperative reorientation and that nanoscale confinement may lead to decreased mobility. On the other hand, the dynamics of the molecules in nanoporous materials is also affected by the interaction with the surface of the pores, which slows down the mobility. Dynamic and thermodynamic measurements reported for the glass transition in confined geometries, for small molecules confined in porous materials as well as for ultrathin polymer films, indicate that T_g decreases, increases or remains the same compared to bulk materials, and that different behaviors have been observed for the same material depending on the experimental method [40]. For confined fragile glass-forming liquids the non-monotonic variation of T_g with decreasing diameter of the pores has also been reported [41]. In dynamic measurements, the properties of interest are the material relaxation time and deviation from exponential relaxation. The latter is treated as an outcome of the distribution of the relaxation times or a measure of the cooperativity of the process. The deviation from the exponential relaxation usually follows the stretched exponential or Kohlrausch–Williams–Watts (KWW) [42] characteristic, however significant deviation from the stretched exponential is sometimes observed experimentally [43] as well as using computer simulation methods [18].

2. Simulation details

Carbon nanotubes and ethylene glycol molecules have been modeled with flexible model based on the CHARMM 27 force field [44], which includes intramolecular harmonic stretching, harmonic bending, torsional, van der Waals and Coulombic terms (Table 1)

$$V_{\text{total}} = V_{\text{stretch}} + V_{\text{bend}} + V_{\text{torsional}} + V_{\text{vdW}} + V_{\text{Coulomb}}. \tag{1}$$

The model of the ethylene glycol molecule used in calculations is shown in Fig. 1. Charge distribution on the ethylene glycol molecule has been determined using *ab initio* method with 6-31G** basis set and is given in Table 2. Interactions between carbon nanotubes and ethylene glycol molecules have been described with Lennard-Jones 12-6 potential with Lorentz–Berthelot mixing rules and cutoff 2.0 nm. The results have been compared to the results obtained from simulation of bulk ethylene glycol modeled as 1546 molecules in simulation cell. Long range interactions were calculated using Particle Mesh Ewald (PME) [45] summation technique with grid size 50 A. Equations of motion were integrated using Brunger–Brooks–Karplus (BBK) scheme [46], implemented in NAMD 2.7 [47], with the time step of integration 0.5 fs. The simulation was performed in NVT ensemble, for temperatures 250, 300, 350, 400 and 450 K. Temperature was controlled using Langevin thermostat with damping coefficient $\gamma = 5.0\ \text{ps}^{-1}$. The simulated system was thermalized for 1 ns before each trajectory production. The trajectories were produced over 8,000,000 time steps (4 ns).

Table 1
CHARMM based force field parameters for ethylene glycol and single-walled carbon nanotube.

$V_{\text{stretch}} = K_r(r - r_0)^2$ Stretching type	K_r/kcal mol^{-1} A^{-2}	r_0/A	
CC	222.500	1.538	
CH	309.00	1.111	
CO	428.0	1.420	
OH	545.0	0.960	
CC (SWNT)	305.000	1.3750	
$V_{\text{bend}} = K_\Theta(\Theta - \Theta_0)^2$ Bending type	K_Θ/kcal mol^{-1} rad^{-2}	Θ_0/degrees	
CCO	75.700	110.10	
CCH	26.500	110.10	
COH	57.500	106.00	
HCH	35.500	109.00	
OCH	45.900	108.89	
CCC (SWNT)	40.00	120.00	
$V_{\text{torsional}} = \begin{cases} K_\phi(1 + \cos(n\phi - \gamma)) & n \neq 0 \\ K_\phi(\phi - \gamma)^2 & n = 0 \end{cases}$ Torsion type	K_Φ/kcal mol^{-1}	n	γ/degrees
OCCO	0.190	3	0.00
OCCH	0.190	3	0.00
HOCC	0.14	3	0.00
HOCH	0.14	3	0.00
HCCH	0.190	3	0.00
CCCC (SWNT)	3.1000	2	180.00
$V_{\text{vdW}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$ with Lorentz–Berthelot mixing rules Atom type	ε/kcal mol^{-1}	σ/A	
C	-0.0560	3.58	
H5, H6, H7, H9	-0.0280	2.39	
H3, H10	-0.0460	0.40	
O	-0.1521	3.15	
C (SWNT)	-0.0700	3.55	

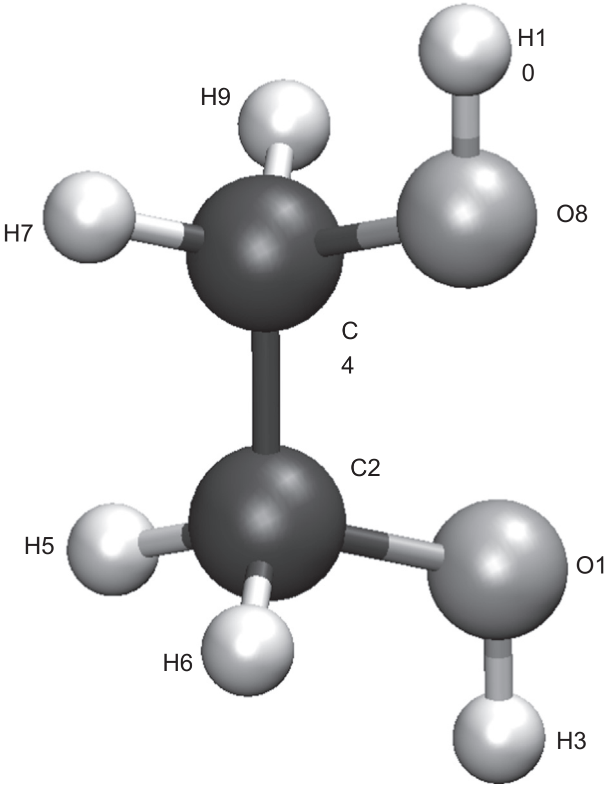

Fig. 1. Model of ethylene glycol molecule.