

CONFINEMENT SIZE EFFECT IN DIPOLAR RELAXATION OF GLYCEROL MOLECULES CLUSTER ENCAPSULATED INSIDE CARBON NANOTUBES – COMPUTER SIMULATION STUDY

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Abstract. We have carried out a fully atomistic molecular dynamics simulation to study dipolar relaxation of glycerol molecules encapsulated in a single-walled carbon nanotube and to compare it with the dipolar relaxation of a free (unconfined) cluster of glycerol molecules. We have calculated the dielectric relaxation spectra of these systems and discussed the effect of confinement on the relaxation time and the shape of the relaxation spectra of glycerol molecules.

1. INTRODUCTION

The properties of molecules in a nanoscale confinement are of great interest to biology, geology and material science [1-6]. Molecular systems confined in various kinds of porous media have interesting structural and dynamical properties and are investigated experimentally [4-5], theoretically [6] and by means of computer simulation methods [7-16]. The application of carbon nanotubes as confining media is an important issue not only for fundamental research but also due to their promising practical applications as energy storage, nanoelectronic devices, chemical biosensors, field emission displays, and many others [17-19].

The relaxation of molecular dipoles can be experimentally studied by the dielectric relaxation spectroscopy which has proved itself to be a useful tool to study the dynamics of many molecular systems, such as glass forming liquids [20-21], polymers [22], mesophases [23], colloids [24], ionic conductors [25], over many decades of frequencies.

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Unlike the NMR or vibrational spectroscopy, the dielectric relaxation spectroscopy is sensitive to intermolecular interactions and capable of monitoring cooperative processes, providing a link between the methods which probe the properties of individual molecules and techniques characterizing the bulk properties of a sample (for example viscoelastic and rheological properties) [26]. The dielectric relaxation spectrum provides information about individual relaxation processes, their relative amplitudes and characteristic relaxation times of the underlying molecular motions.

Glycerol is one of the most extensively studied hydrogen-bonded systems. The presence of its three hydroxy groups gives rise to its very interesting dynamical and structural properties in condensed phases. Glycerol can be easily supercooled, reaching a glassy state at about $T_g = 187\text{K}$, and its transport coefficients exhibit non-Arrhenius behavior. Glycerol has been also studied for its capabilities in long-term preservation of proteins and it is known

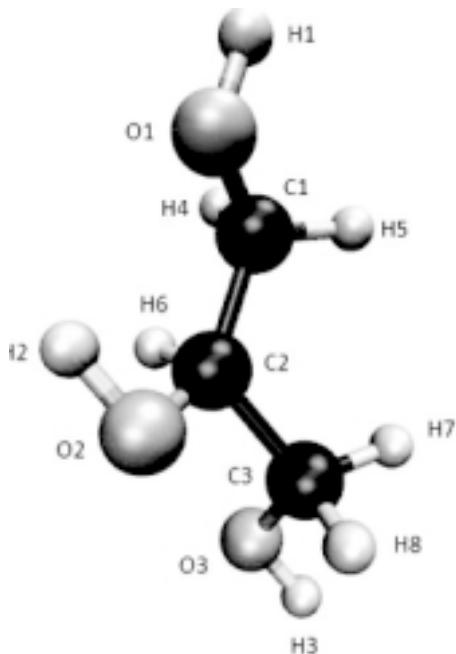


Fig. 1. Glycerol molecule model.

as one of the best cryoprotectant solvents [27-28]. Although, the computer time required to obtain information about the relaxation process from molecular dynamics trajectories is prohibitively large, not only in the case of supercooled liquids, but also in the case of a deep liquid state, a significant progress on glass-forming systems in the high temperature regime has been obtained from molecular dynamics simulations [29-33] which has been related to the development of the mode coupling theory (MCT) [34].

2. SIMULATION DETAILS

The simulated systems consisted of a free (unconfined) cluster of glycerol molecules and a cluster of glycerol molecules confined inside single walled open-ended carbon nanotubes of different diameters. The unconfined cluster and the clusters confined inside the (10,10) and (12,12) nanotubes consisted of 24 glycerol molecules, whereas the cluster confined inside the (15,15) nanotube was composed of 32 glycerol molecules. All the simulations were performed using the NAMD 2.6 simulation code [35]. The simulations were performed in an NVT ensemble, for the temperature $T=300\text{K}$. The system was equilibrated for 0.2 ns before each trajectory production. The classical equations of motion were integrated using the Brunger-Brooks-Karplus (BBK) method

[36] implemented in NAMD 2.6, with the time step of integration of equations of motion at level of 0.2 fs, which ensured sufficient energy conservation. The steady-state distribution generated by the BBK method has an error proportional to Δt^2 [37], although the error in the time correlation function can have an error proportional to Δt [38]. The temperature was controlled using a Langevin thermostat, with the damping coefficient $\gamma = 5.0 \text{ ps}^{-1}$. All the trajectories were produced over 10 000 000 time steps (2 ns). In order to verify to what extent the thermostating method influenced the calculated dipolar relaxation spectra, we continued all runs for the next 10 000 000 time steps in the NVE ensemble, using the velocity Verlet method, and we recalculated the autocorrelation functions. We found that the resulting NVE spectra did not differ significantly comparing to NVT results and did not alter the discussion of the results. The results presented in this work were calculated from NVE trajectories.

Fig. 1 shows the glycerol molecule model which has been described by a flexible model based on the CHARMM 27 force field [39] which includes intramolecular harmonic stretching, harmonic bending, torsional, van der Waals and Coulombic terms

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

The intramolecular interactions between the carbon atoms of the nanotube have also been modeled using a flexible model based on the CHARMM 27 force field while the interaction between the nanotube and the glycerol molecule has been modeled using the LJ 12-6 empirical potential, with a cutoff of 2.0 nm. The parameters of the potential for all the interactions in the system have been collected in Table 1. The charge distribution on the glycerol molecule, calculated on B3LYP/6-31* *ab initio* data, has been taken from [40] and is presented in Table 2.

The information about dipolar relaxation can be obtained from molecular dynamics trajectories in the form of the normalized total dipole moment time correlation function (TCF) defined as [7]

$$\Phi(t) = \frac{\langle \vec{M}(0)\vec{M}(t) \rangle}{\langle \vec{M}(0)\vec{M}(0) \rangle}, \quad (2)$$

$$\vec{M}(t) = \sum_{i=1}^N \vec{\mu}_i(t), \quad (3)$$

where N is the total number of glycerol molecules, and $\vec{\mu}_i$ is the dipole moment of the i -th molecule. The time-domain relaxation spectra are usually ana-

Table 1. CHARMM force field parameters for glycerol and single-walled carbon nanotube.

$V_{stretch} = K_r(r - r_0)^2$	Stretching type	$K_r / \text{kcal mol}^{-1} \text{\AA}^{-2}$	$r_0 / \text{\AA}$
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

$V_{bent} = K_\Theta(\Theta - \Theta_0)^2$	Bending type	$K_\Theta / \text{kcal mol}^{-1} \text{rad}^{-2}$	$\Theta_0 / \text{degrees}$
CCC		58.350	113.50
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

$V_{torsional}$	Torsion type	$K_\Phi / \text{kcal mol}^{-1}$	n	$\gamma / \text{degrees}$
$\begin{cases} K_\Phi(1 + \cos(n\Phi - \gamma)) & n \neq 0 \\ K_\Phi(\Phi - \gamma)^2 & n = 0 \end{cases}$	CCCH	0.200	3	0.00
	CCCO	0.200	3	0.00
	OCCO	0.200	3	0.00
	OCCH	0.200	3	0.00
	HOCC	0.14	3	0.00
	HOCH	0.14	3	0.00
	HCCH	0.200	3	0.00
	CCCC (SWNT)	3.1000	2	180.00

$V_{vdW} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ with Lorentz-Berthelot mixing rules	Atom type	$\epsilon / \text{kcal mol}^{-1}$	$\sigma/2 / \text{\AA}$
C (C1, C2)		-0.0560	2.010
C (C2)		-0.0200	2.275
H (H4, H5, H7, H8)		-0.028	1.3400
H (H6)		-0.022	1.3200
H (H1, H2, H3)		-0.046	0.2245
O		-0.1521	1.77
C (SWNT)		-0.070000	1.992400

lyzed using the Kohlrausch-Williams-Watts (KWW) fit defined as [25]

$$\Phi(t) = \exp\left(-\left(\frac{t}{t_0}\right)^\beta\right), \quad (4)$$

Table 2. Atomic charges on glycerol molecule. Charges (in electronic units) calculated on B3LYP/6-31* *ab initio* data [40].

C1	0.182
C2	0.055
C3	0.182
O1	-0.585
O2	-0.581
O3	-0.585
H1	0.396
H2	0.396
H3	0.396
H4	0.026
H5	0.026
H6	0.040
H7	0.026
H8	0.026

Table 3. KWW fitting parameters for the total dipole moment autocorrelation function of glycerol confined in carbon nanotubes and for an unconfined cluster of glycerol molecules ($T=300\text{K}$).

	τ [ps]	β
cluster confined in (10,10) nanotube	38.71	0.320
cluster confined in (12,12) nanotube	22.18	0.322
cluster confined in (15,15) nanotube	11.93	0.346
free (unconfined) cluster	2.01	0.544

where t_0 is the characteristic relaxation time and $0 < \beta < 1$ is the parameter measuring the broadening of the spectra. The latter is often treated as a measure of the distribution of the relaxation times or a measure of the relaxation process cooperativity [25].

The connection between the frequency domain dielectric permittivity [25]

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega), \quad (5)$$

which can be measured in the frequency domain dielectric spectroscopy experiments, and the total dipole moment time correlation function can be introduced as follows

$$\begin{aligned} \epsilon'(\omega) &= \epsilon_0 - (\epsilon_0 - \epsilon_\infty) \omega \int_0^\infty \Phi(t) \sin \omega t dt \\ \epsilon''(\omega) &= (\epsilon_0 - \epsilon_\infty) \omega \int_0^\infty \Phi(t) \cos \omega t dt \end{aligned} \quad (6)$$

where $\epsilon'(\omega)$ is the real part (permittivity factor) and $\epsilon''(\omega)$ is the imaginary (dielectric loss) part.

In order to verify the usability of our simulation setup to study dipolar relaxation in glycerol, we produced a test trajectory for bulk glycerol (applying periodic boundary conditions and the Ewald summation technique) at the temperature $T=350\text{K}$ and calculated the total dipole moment autocorrelation function and frequency dipole relaxation spectrum in order to compare the resulting spectra with the available broadband dielectric spectroscopy experimental data [21]. The calculated loss peak frequency $f_{\max}=1.41\text{ GHz}$ values and the loss high fre-

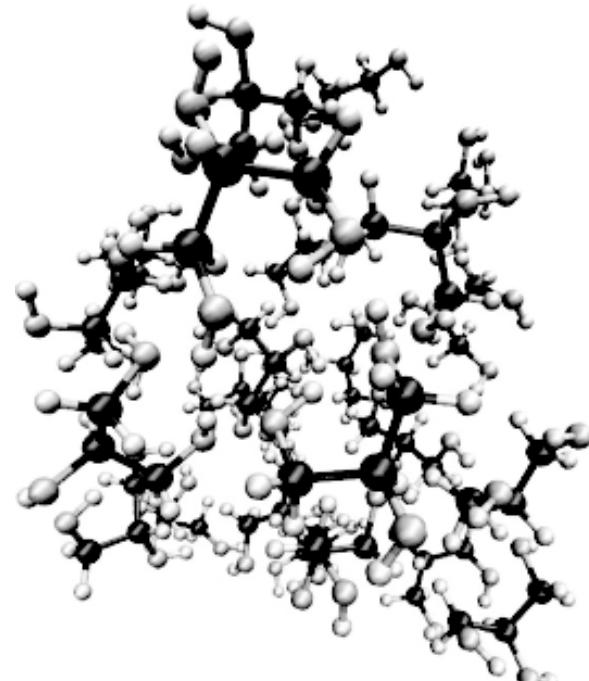


Fig. 2. A snapshot of the simulated system – a free (unconfined) cluster of 24 glycerol molecules.

quency slope $n=0.56$ agree satisfactorily with the experimental values $f_{\max}=1.6\text{ GHz}$ and $n=0.60$ estimated from the dielectric spectroscopy results [21].

3. RESULTS AND DISCUSSION

We have studied the dipolar relaxation of glycerol molecules confined in open-ended single walled carbon nanotubes of different diameters. As a reference system, we have also simulated the relaxation

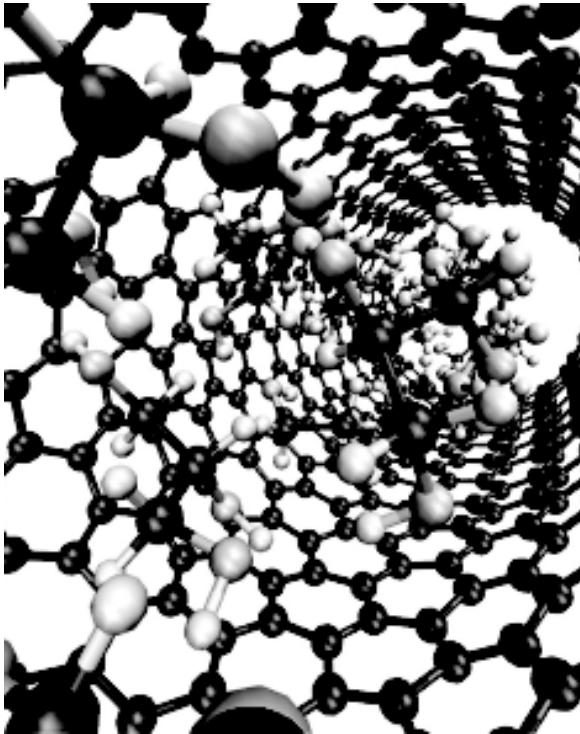


Fig. 3. A snapshot of the simulated system – a cluster of 24 glycerol molecules encapsulated in a (10,10) armchair single walled carbon nanotube.

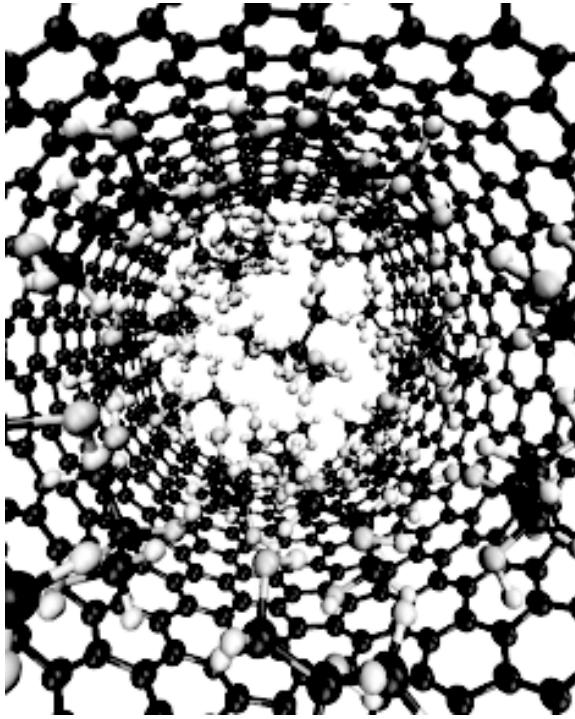


Fig. 4. A snapshot of the simulated system – a cluster of 32 glycerol molecules encapsulated in a (15,15) armchair single walled carbon nanotube

process in a free cluster of glycerol molecules. Snapshots of the simulated systems are presented in Figs. 2-4. Fig. 5 shows the time correlation function of a normalized total dipole moment for all the studied systems. The dashed lines represent the KWW fits to the calculated data. The inset shows the same data in coordinates which make it possible to assess the KWW fits to the data. In the case of the free (unconfined) cluster, the dipole moment autocorrelation function can be represented reasonably well by a single KWW stretched exponential in the whole time regime. In the case of confined clusters, the dipole moment autocorrelation function can be described by a single KWW function approximately up to the time $t = \tau$ and cannot be described for longer times, where the significant deviation from the single stretched exponential behavior occurs. The characteristic relaxation times τ are collected in Table 3 along with the values of the shape parameter β of the KWW fit.

The characteristic features of the dipole moment autocorrelation functions for an unconfined and confined cluster of glycerol molecules are illustrated in Fig. 6. A few regions can be distinguished in the spectra. For the shortest times which correspond

to the far infra-red range of the spectrum, the relaxation clearly does not follow the KWW stretched exponential. Instead, it follows the Gaussian law $\exp(-\alpha t^2)$ terminated by a period of oscillatory behavior. This feature agrees well with the theoretical predictions of Dissado and Hill (DH) [25,41]. For longer times, the relaxation can be well reproduced by the KWW stretched exponential function. Its asymptotic behavior can be related to the shape parameter n . The DH theory provides the meaning of this parameter as a measure of the so called intra-cluster cooperativity of relaxation, where a cluster is defined as a subassembly of molecules relaxing coherently with n being a measure of the degree of this coherence. According to the DH theory, this region ends approximately at a time corresponding to the relaxation time of the system, at which the relaxation of subassemblies is annihilated through an exchange of energy with the phonon bath. The solution of the relaxation equation in this narrow region is the exponential $\exp(-t/\tau)$ known as the Debye relaxation. For longer times, the relaxation evolves into its final stage, which can be identified in the case of a confined cluster (Figs. 5 and 6), and which is characterized by a deviation from the

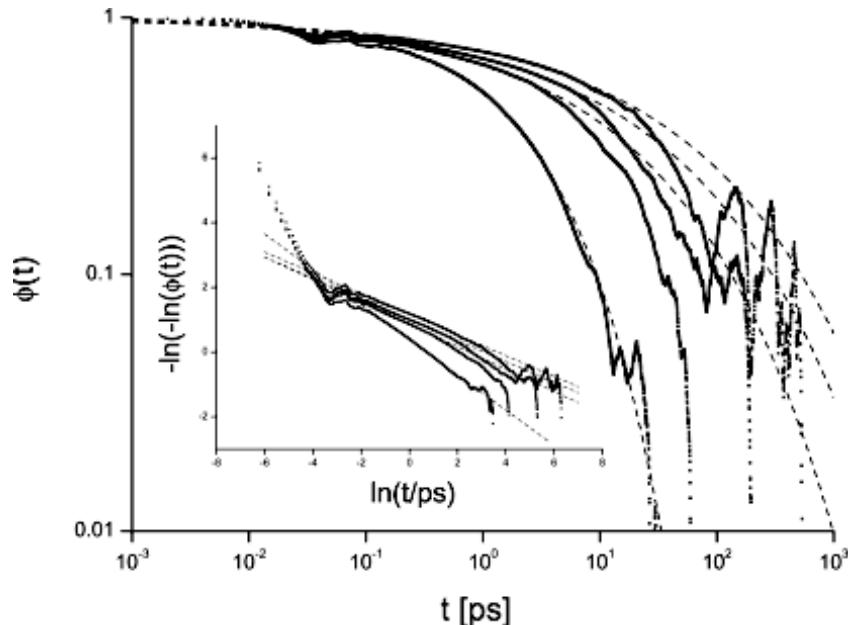


Fig. 5. The calculated total dipole moment autocorrelation function of glycerol molecules confined in (10,10), (12,12) and (15,15) carbon nanotubes, and for an unconfined cluster (from right to left). The dashed lines are KWW fits. The inset shows the same data in the coordinates which permits assessing the KWW fits.

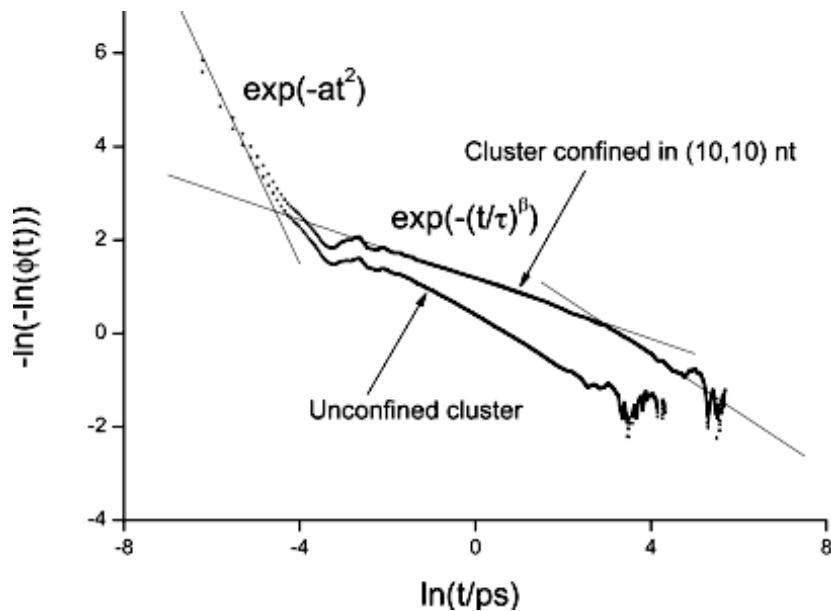


Fig. 6. The calculated total dipole moment autocorrelation function for the cluster of glycerol molecules confined inside a (10,10) carbon nanotube and for an unconfined cluster (the data for the remaining systems have been removed for clarity). The solid lines are guides for the eyes and represent regions that can be distinguished in dipolar relaxation of the simulated systems.

single KWW stretched exponential behavior. Dissado and Hill [25,41] attribute the asymptotic behavior of the relaxation measured by the shape parameter m to the so called inter-cluster relaxation, related to an exchange of the relaxing molecules between more or less coherently relaxed subassem-

bles of molecules. A deviation from the single KWW behavior for the times $t > \tau$ (Figs. 5 and 6) suggests that the presence of the confinement affects the forming of molecular subassemblies and influences the degree of coherence between them. In the case of the cluster confined inside the nanotube, this change

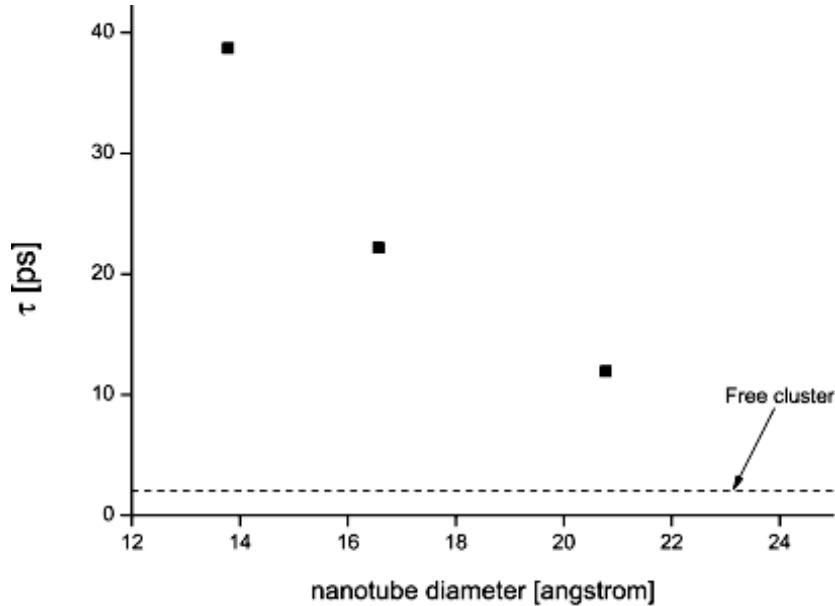


Fig. 7. The dependence of the characteristic relaxation time of the KWW function for glycerol confined in a carbon nanotube on the nanotube diameter. The dashed line represents the value for the free (unconfined) cluster case.

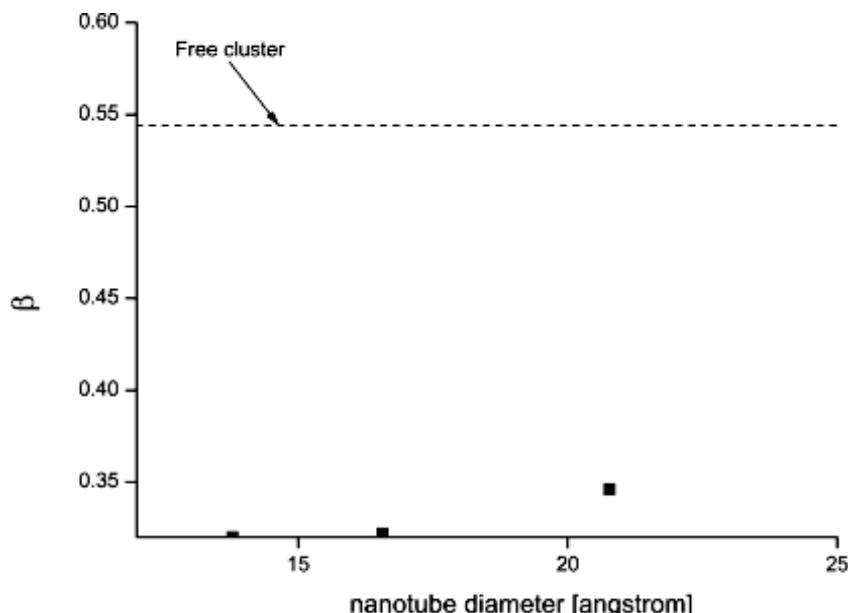


Fig. 8. The dependence of the stretching parameter β of the KWW function for glycerol confined in a carbon nanotube on the nanotube diameter. The dashed line represents the value for the free cluster case.

may be related with the change in the aspect ratio of the cluster, when compared to its unconfined counterpart.

Although, apart from the asymptotic behavior at low- and high-frequency regimes, the exact shape of the DH susceptibility function (Fourier transform of the DH relaxation equation solution) [41] is difficult to verify experimentally, some works have suggested that the DH susceptibility function is more

appropriate to describe the dielectric spectroscopy data than other routinely used fitting functions [42,43]. The DH function has been also applied to rationalize and suggest some modifications in the scaling behavior observed in the dielectric response of many systems [44,45].

The deviation from the single KWW stretched exponential behavior in the case of glycerol molecules confined in nanotubes (Fig. 6) provides the

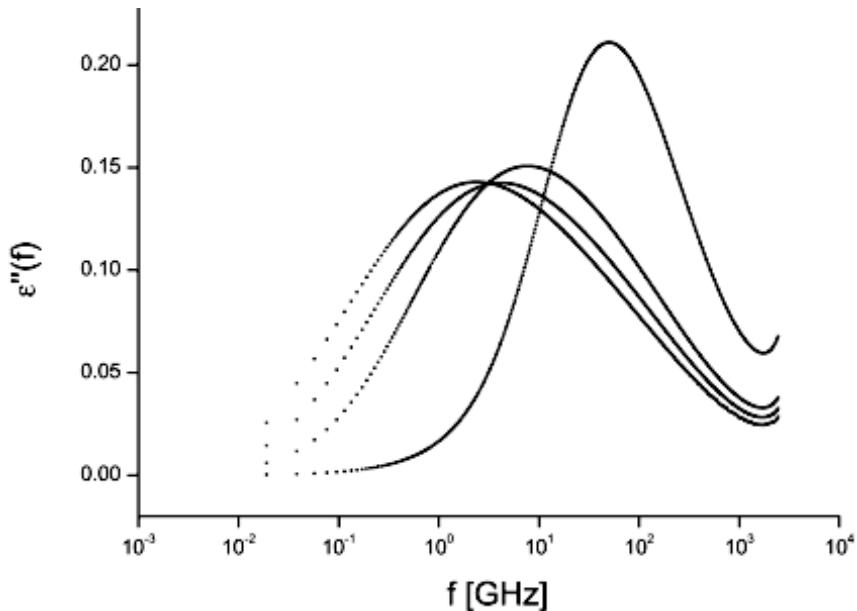


Fig. 9. The frequency dipolar relaxation spectra of glycerol molecules confined in (10,10), (12,12), and (15,15) nanotubes, and for unconfined cluster (from left to right).

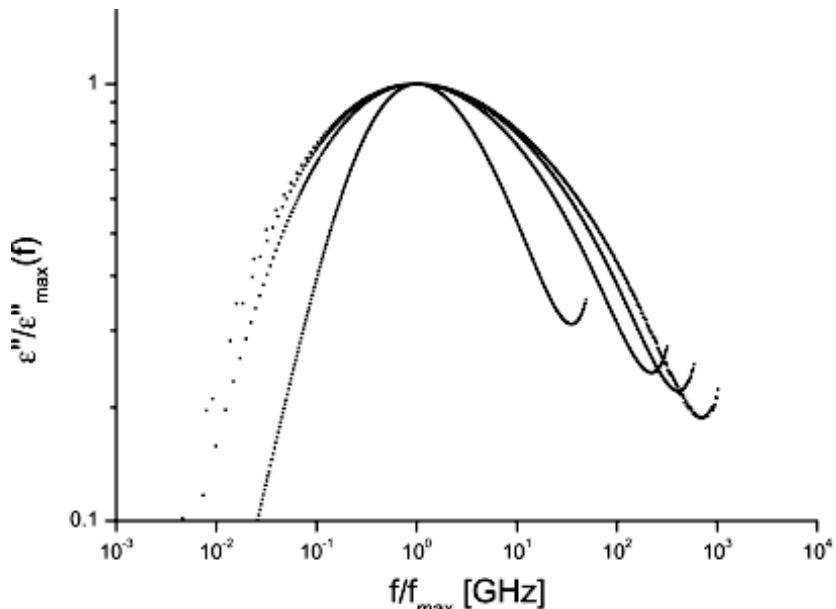


Fig. 10. A change in the shape of the frequency dipolar relaxation spectra of glycerol molecules confined in (10,10), (12,12), and (15,15) nanotubes, and for an unconfined cluster (from outermost to innermost).

rationale for the dielectric spectroscopy results of Pissis et al. [5] who have studied the dielectric relaxation of liquid glycerol, propylene glycol and propylene carbonate confined in Vycor glass (with porosity 0.28, internal surface area 250 m²/g and an average pore diameter of 4 nm) and to compare the results with the results of the bulk measurements. Contrary to the bulk liquids data, the dielectric loss spectra for confined liquids could not be fitted with

the one parameter Cole-Davidson expression [25] and has had to be fitted with the two parameter Havriliak-Negami function [25]. As the Cole-Davidson fitting form imposes the low frequency shape parameter $m = 1$ (analogously as the Fourier transform of the KWW stretched exponential), the results presented in [5] support the conclusion that, the confinement not only shifts the relaxation time and affects the α parameter of the KWW fit, but

imposes more essential change in the relaxation mechanism, as well.

The relaxation time τ and stretching parameter β dependency on the nanotube confinement size is illustrated in Figs. 7 and 8, while Fig. 9 shows the calculated dipolar relaxation loss functions which can be directly compared with frequency domain dielectric spectroscopy measurements. The first conclusion is that the relaxation of the free cluster of glycerol molecules simulated at the temperature $T = 300\text{K}$ is faster by three decades than the relaxation of the bulk glycerol liquid measured experimentally at the temperature $T = 300\text{K}$ [21] and faster by almost two decades than the relaxation simulated in bulk glycerol at $T = 350\text{K}$ (this work). The relaxation time for the free cluster is $\tau = 2.01 \text{ ps}$. The nanotube confinement shifts the relaxation time from $\tau = 11.93 \text{ ps}$ in the case of the (15,15) nanotube to $\tau = 38.71 \text{ ps}$ in the case of the (10,10) nanotube which has been the most narrow nanotube considered in this study. The shape parameter b value for the free cluster is $\beta = 0.544$ and it is slightly smaller than the experimental [21] and simulated (this work) value for bulk glycerol $\beta = 0.45$. Confining the free cluster inside the (15,15) nanotube significantly affects the parameter β value which now has the value $\beta = 0.346$. Confining glycerol molecules inside more narrow nanotubes (12,12) and (15,15) further reduces the parameter β up to the value $\beta = 0.320$ in the case of the cluster confined inside the (10,10) nanotube, but the change is not as pronounced. The change in the shape of the dielectric loss function is illustrated in Fig. 10. The shift of the relaxation time and broadening of the dielectric loss spectra imposed by the nanotube confinement well agrees with the results of the dielectric spectroscopy measurements of glycerol confined inside Vycor glass [5].

4. CONCLUSIONS

Dipolar relaxation of a free cluster of glycerol molecules is much faster than the relaxation in bulk glycerol. Nanotube confinement shifts considerably the relaxation time of a glycerol cluster towards longer times and broadens significantly the shape of its dielectric loss spectrum which suggests more cooperative relaxation. The dipole moment autocorrelation function of the free cluster of glycerol molecules can be well described by the KWW stretched exponential, while in the case of a cluster confined inside a nanotube the significant deviation from the stretched exponential occurs for times longer than τ . The arising deviation from the stretched

exponential behavior suggests a more essential change in the relaxation mechanism and can be rationalized in the framework of the theory proposed by Dissado and Hill. The deviation from the stretched exponential relaxation, a considerable shift of the relaxation time and broadening of the loss spectrum caused by confining the cluster inside a nanotube agrees well with the dielectric spectroscopy measurements of glycerol confined in porous Vycor glass.

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