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The distribution of the relaxation times as seen by bond fluctuation model

J. Molina-Mateo [a], J.M. Meseguer Dueñas [a,b], J.L. Gómez Ribelles [a,b,c], C. Torregrosa Cabanilles [a,*]

[a] Center for Biomaterials and Tissue Engineering, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022, Valencia, Spain
[b] CIBER en Bioingeniería, Biomateriales y Nanomedicina, Valencia, Spain
[c] Regenerative Medicine Unit, Centro de Investigación Príncipe Felipe, Autopista del Saler 16, 46013 Valencia, Spain

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ABSTRACT

The structural relaxation process of an amorphous polymer has been simulated using the Bond Fluctuation Model with a quite simple description of the polymer system. The glass transition, that is apparent when a cooling ramp is simulated, comes as a consequence of chain connectivity and a bond length potential. Annealing of the system at temperatures below the glass transition, in the glassy state, produces a continuous decrease of the total energy of the system at a rate that depends on temperature. The energy evolution is shown to be clearly nonexponential in a certain temperature interval. In this temperature interval, molecular mobility was characterized using different definitions of the relaxation times and calculating a distribution of relaxation times in the system by studying the motions of small regions of the lattice. As annealing temperature decreases the distribution of relaxation times shifts to longer times and slightly broadens. The maxima of the distributions of relaxation times obey the Vogel, Fulcher and Tammann equation.

1. Introduction

Cooperative conformational rearrangements of the chain segments in polymeric materials are responsible for the glass transition and structural relaxation process (the process by which a out of equilibrium glass approach equilibrium at constant temperature and pressure). Cooperativity is responsible for the curvature of the logarithm of the relaxation time versus reciprocal temperature curve, the Arrhenius plot, that represents the temperature dependence of the response rate of the material at temperatures above its glass transition. On the other hand, the relaxation processes due to conformational cooperative motions of the polymer segments are shown to be nonexponential and its kinetics can be described with a formalism of a distribution of relaxation times [1,2]. A certain correlation between nonexponentiallity and cooperativity, i.e., between the width of the distribution of relaxation times and the curvature of the Arrhenius diagram, has been reported in the literature [3].

The glass transition and structural relaxation of a polymer have been simulated using the Bond Fluctuation Model (BFM) [4]. The behaviour of the polymer system in this model is determined by chain connectivity and both intermolecular and intramolecular energy potentials. The role of each of them on conformational mobility was shown in reference [5]. The glass transition is apparent when a cooling ramp is simulated. Annealing of the system at temperatures below the glass transition, in the glassy state, produces a continuous decrease of the total energy of the system at a rate that depends on temperature. Free volume is another key factor in the system dynamics below the glass transition [6,7,8].

In most cases, both experimental and simulation structural relaxation results show only the time dependence of average values of the magnitudes of interest in the system. In particular molecular mobility can be characterized using different definitions of the relaxation times. The information contained in these average values is necessary and sufficient for the study of the system in thermodynamic equilibrium, but may not be enough if the study should be extended to the dynamics of systems out of equilibrium, such as a glass. In this work a simple polymer system consisting of chains of 10 polymer segments and considering only a bond length intramolecular potential is studied. The simulations conducted with the BFM allow us to

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* Corresponding author. Tel.: +34 962849351; fax: +34 962849309.
E-mail address: ctorregr@fis.upv.es (C. Torregrosa Cabanilles).

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obtain directly both the evolution of average magnitudes during structural relaxation and, through the study of the movements of small regions, a distribution of relaxation times can be determined at different temperatures as well, allowing for a more complete characterization of the simulated segmental dynamics.

2. Model hypothesis and simulations

One of the most frequently employed models to simulate the polymeric materials behaviour is the Bond Fluctuation Model [4,9]. Every three carbons of a polymeric chain as, for example, polyethylene can be represented by a monomeric group that occupies the eight vertex of a cube on the lattice [10]. The length of the bonds between monomeric groups can vary between 2 and $\sqrt{10}$ (distance $\sqrt{8}$ is not allowed in order to avoid bond crossing [11]).

The simulation steps consist of choosing randomly a monomeric group and one of the six possible directions of movement. If the resulting distances for the involved bonds are allowed by the model and the volume exclusion is respected then the movement is considered as geometrically viable. In order to include a thermodynamic factor, the movement is finally performed with the probability of the metropolis criterion [11,12],

$$P = \min\left\{1, \exp\left(\frac{-\Delta E}{kT}\right)\right\} \tag{1}$$

In this expression ΔE is the increase of energy caused by the evaluated movement, k is Boltzmann's constant and T is the temperature of the system. The potential employed in this work is the well known bond length potential [10,13]

$$U(l) = U_0(l - l_0)^2$$

where the minimal energy distance is given by $l_0 = 3$ lattice units and $U_0 = 1$.

The simulation parameters consisted of a three dimensional simulation box ($L = 40$) with periodic boundary conditions. This system was occupied by 400 chains formed by 10 monomeric groups, giving a density $\varphi = 0.5$.

The simulations begun with an initial equilibration period of 10^5 Monte Carlo Steps (MCS) at high temperature $kT = 5$, followed by a cooling ramp at a constant rate of -0.1 units of temperature every 1000 MCS. After this cooling ramp, an annealing during 10^7 MCS at different temperatures was performed in order to observe structural relaxation. These parameters have shown in our previous works that are adequate to simulate the glass transition and the structural relaxation process [5,7,8].

Some variables were calculated during simulations. First of all, the energy of the system for different temperatures was averaged in order to observe the evolution of the system. The squared radius of gyration [10] was calculated too as

$$\left\langle R_g^2(N)\right\rangle = \frac{1}{N}\sum_{i=1}^{N}\left\langle(\vec{r}_i - \vec{r}_{cm})^2\right\rangle \tag{3}$$

where N is the number of monomeric groups of the chains, $\vec{r}_{cm}$ is the position of the centre of mass of the chain and $\vec{r}_i$ is the position of every group i of the chain. And the squared end-to-end distance as

$$\left\langle R_{ee}^2\right\rangle = \left\langle(\vec{r}_N - \vec{r}_1)^2\right\rangle \tag{4}$$

In order to analyze the structure of the system, the pair correlation function of the system was calculated [14] as

$$g(r) = \frac{2L^3H(r)}{(\mathrm{NP})^2h(r)} \tag{5}$$

where $H(r)$ represents the histogram that counted the number of times that an allowed distance r occurs, $h(r)$ corresponds to the number of possible r-vectors for a given distance on the lattice, L is the box simulation size and NP is the total number of monomeric groups.

The autocorrelation functions of the polymer's end-to-end distance and of the radius of gyration have been calculated to study their decay, as [10]

$$\Phi_{R_{ee}}(t) = \frac{\left\langle(\vec{r}_N(t) - \vec{r}_1(t))\cdot(\vec{r}_N(0) - \vec{r}_1(0))\right\rangle}{\left\langle(\vec{r}_N(0) - \vec{r}_1(0))^2\right\rangle}, \tag{6}$$

$$\Phi_{R_g}(t) = \frac{\sum_{i=1}^{N}\left\langle(\vec{r}_i(t) - \vec{r}_{cm}(t))\cdot(\vec{r}_i(0) - \vec{r}_{cm}(0))\right\rangle}{\sum_{i=1}^{N}\left\langle(\vec{r}_i(0) - \vec{r}_{cm}(0))^2\right\rangle}. \tag{7}$$

Three time correlation functions were calculated too [10]. A time correlation function in order to study the evolution of the inner molecular groups in the system,

$$g_1(t) = \left\langle\left[\vec{r}_{N/2}(t) - \vec{r}_{N/2}(0)\right]^2\right\rangle \tag{8}$$

a time correlation function in order to study the evolution of the inner groups compared to the centre of mass of the chain,

$$g_2(t) = \left\langle\left[\vec{r}_{N/2}(t) - \vec{r}_{cm}(t) - \vec{r}_{N/2}(0) + \vec{r}_{cm}(0)\right]^2\right\rangle \tag{9}$$

and a time correlation function in order to study the evolution of the centre of mass of the system,

$$g_3(t) = \left\langle[\vec{r}_{cm}(t) - \vec{r}_{cm}(0)]^2\right\rangle \tag{10}$$

Related to these functions, three relaxation times can be defined. A relaxation time τ_1, in order to represent the evolution of the inner molecular groups in the system [10], as

$$g_1(\tau_1) = \left\langle R_g^2\right\rangle \tag{11}$$

A relaxation time τ_2, in order to study the evolution of the inner groups compared to the centre of mass of the chain [10], defined as

$$g_2(\tau_2) = \frac{2}{3}\left\langle R_g^2\right\rangle \tag{12}$$

And a relaxation time τ_5, in order to study the evolution of the centre of mass of the system, as

$$g_3(\tau_5) = \left\langle R_g^2\right\rangle \tag{13}$$

Apart from the average values, all the relaxation times were calculated independently for every molecule taking into account its own evolution. These calculations offered the possibility of building the form of the distribution of the relaxation times, obtaining a more accurate representation of the evolution of the system depending on time. By tracking each single polymer chain during simulations, the distributions of relaxation times $\rho_i(\tau)$ were obtained at different states. These distributions are calculated as the fraction of groups (or chains) that have relaxed individually at the MCS equal to τ_i (defined above). From the first dump of data for each isothermal relaxation (after 10^2 or 10^4 MCS), the relaxed fractions are grouped for logarithmic scale plot into intervals of $2^n \times 10^2$ MCS for $n = 0, 1, 2\ldots$

3. Results and discussion

The system evolution during the isothermal annealing on a wide temperature interval has been obtained by simulation with the BFM. The system energy rapidly decreases with decreasing temperature for $1/kT$ lower than 5 during the cooling scan, and then bends in the glass transition to reach steady values at the lowest temperatures of the simulation. Fig. 1 shows also the energy values attained when the cooling ramp is stopped at a given annealing temperature and then the system relax isothermally for different times up to 10^7 MCS. In that figure, three different regions can be distinguished: for values of $1/kT = 5$ or smaller, the system is or reaches the equilibrium during the first 10^4 MCS of the isothermal stage; between $1/kT = 5$ and 50 there is a continuous energy decrease during annealing between 10^4 and 10^7 MCS, and at $1/kT = 50$ and above (results not shown) the system energy does not change during 10^7 MCS.

The energy decay approaching an equilibrium state is a wide, nonexponential relaxation process as shown in Fig. 2 for the $kT = 0.07$ isotherm, covering more than six time decades. The pair correlation function shows that the system remains in an amorphous state at equilibrium and during annealing at the same temperature $kT = 0.07$ (Fig. 3), without any significant structural change. The peak in $g(r)$ at distance 3, that remains constant during the relaxation at $kT = 0.07$, is higher than at $kT = 5$ because distance 3 corresponds to the minimum energy bond distance, so this bond length is favoured at low temperatures. The $g(r)$ plots calculated at different time instants during the structural relaxation process nearly superimpose.

The time correlation functions g_i and the radius of gyration R_g were calculated during the isothermal relaxations. The squared radius of gyration remains fairly constant around 16 squared units of length, which corresponds to an average end to end distance around 10 units and a Kuhn length around 3 units: the chains are flexible. The displacement of the inner groups relative to the centre of mass (CM), g_2, shows an asymptotic behaviour to the value of the squared radius of gyration.

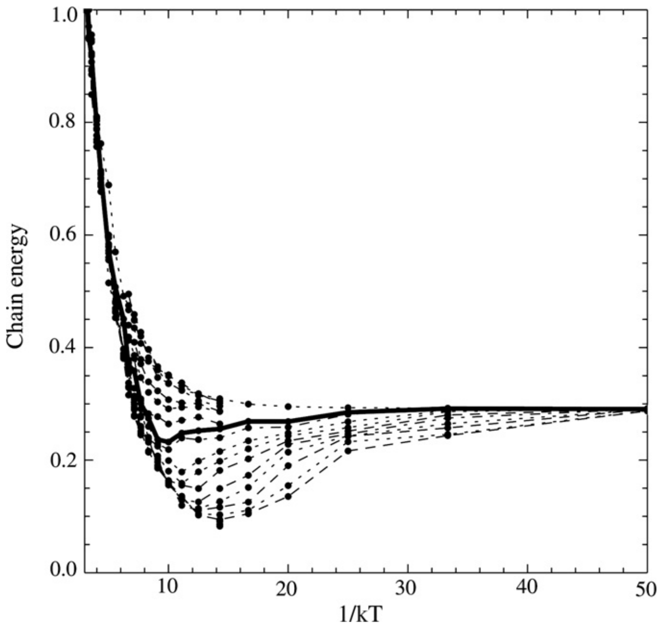

Fig. 1. Energy evolution at different temperatures during the 10^7 MCS isothermal ageing (dots), from the states on a cooling ramp from $kT = 5.0$ to $kT = 0.01$ (upper dots). Lines are joining the isochronal states. Thick line corresponds to 10^4 MCS.

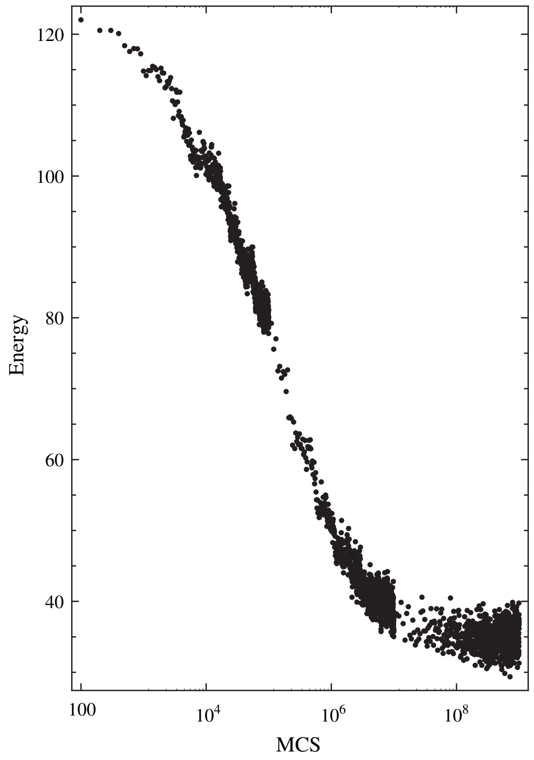

Fig. 2. Nonexponential isothermal relaxation of the system energy at temperature $kT = 0.07$.

The autocorrelation functions of the polymer's end-to-end distance and of the radius of gyration have been calculated (Eqs. (6) and (7)). The scaled autocorrelations overlap quite well, as expected [10], when plotted against $g_3(t)/\langle R_{ee}^2 \rangle$, drawing a stretched exponential with a stretching parameter around 0.7 and following the time–temperature superposition property.

The coordinates of every single group and chain were tracked during the simulations to determine if they fulfil the relaxation conditions. With this method there have been measured the following distributions of relaxation times: $\rho_1(\tau)$, representing the mobility of the inner groups (Eq. (11)), was calculated from the fraction of groups that, at each time interval i between the MCS $T_i = \tau_i$ and $T_{i+1} = 2\tau_i$, moved a distance equal to the radius of

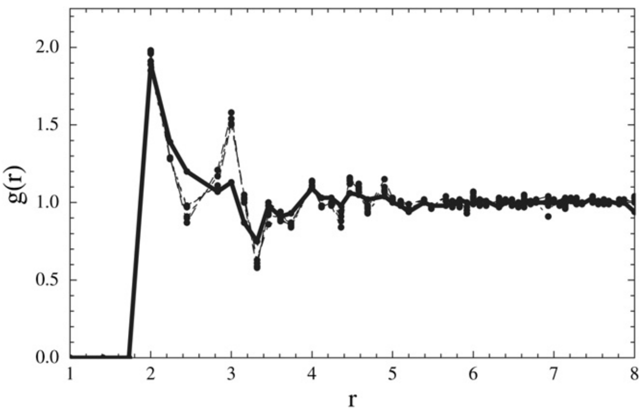

Fig. 3. Pair correlation function in equillibrium at $kT = 5$ (thick line) and during the isothermal relaxation at $kT = 0.07$, at the initial step and after 10^4, 10^5, 10^6 and 10^7 MCS (broken lines).

gyration; $\rho_2(\tau)$, showing the mobility of the inner groups relative to the chain CM (Eq. (12)), and $\rho_5(\tau)$, representing the mobility of the chains in the lattice (Eq. (13)), were calculated by a similar method. This calculations needs to follow the spatial evolution of the polymer chains for a broad time interval (10^6 MCS in this work). In equilibrium states this can be easily performed within the 10^7 MCS of our isothermal stages, and even at the final stages of annealing in the temperature range of the transition. Thus, Fig. 4 shows the results of these distributions of relaxation times for kT ranging between 0.09 and 0.4 ($2.5 \le 1/kT \le 11$). As temperature decreases the distribution of relaxation times shifts to longer times as expected but, interestingly enough, it slightly broadens. Experimental data of relaxation processes due to conformational rearrangements of the polymer chains such as viscoelastic or dielectric relaxations shows a behaviour very close to thermo-rheological simplicity, i.e., a shift of the distribution of relaxation times without shape change when varying temperature above the glass transition [2]. The distribution looks symmetrical and quite narrow for what can be found in experimental viscoelastic or dielectric data. Roughly speaking the width at half height of the peak would correspond to a value of the parameter β of the stretched exponential or Kohlrausch–Williams–Watts equation [15,16] around 0.8–0.9. These values are on the upper part of the typical range between 0.3 and 0.8. This is not strange due to the simplicity of the description of the system, with very short chains and without any intermolecular interaction parameter, but anyway shows the dispersity of the neighbourhood of the polymer chains in the system. The broadening of the distributions as the temperature decreases corresponds to a slight variation of parameter β with temperature. More studies are necessary to correlate the shape of the distribution with the characteristics of the model system. This would help also, by choosing the right parameter values, to map the model to specific polymers.

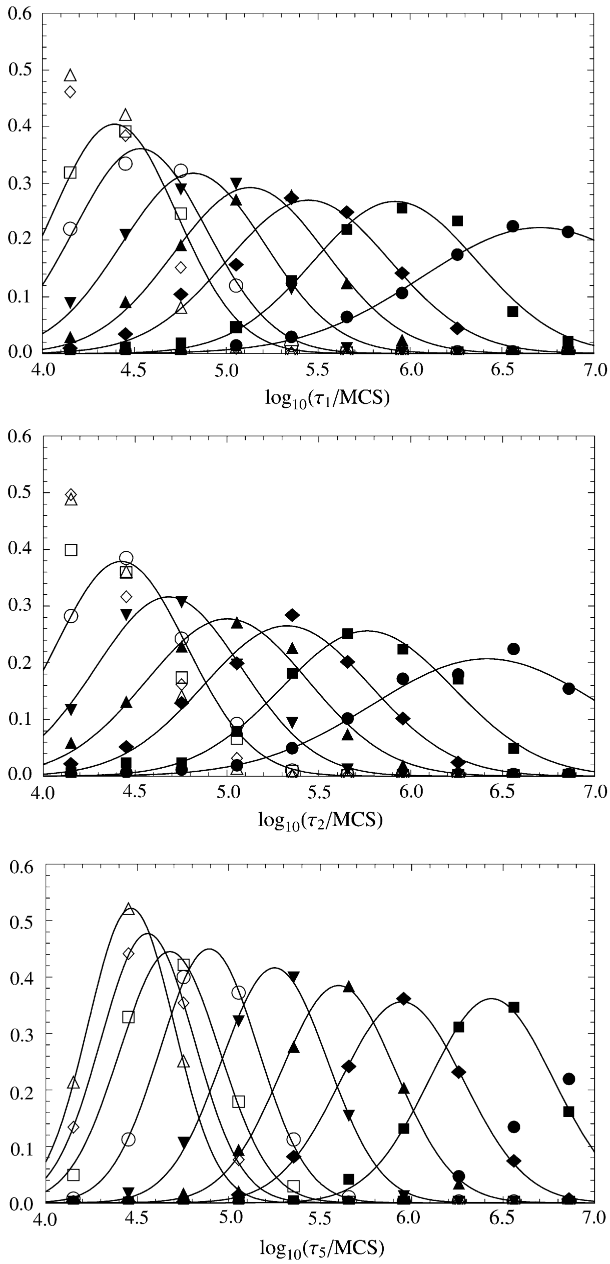

Fig. 4. Distributions of the relaxation times τ_1 (up), τ_2 (centre) and τ_5 (down) (symbols) during isotherms at $kT = 0.09$ (black circles), $kT = 0.11$ (black squares), $kT = 0.13$ (black diamonds), $kT = 0.15$ (black triangles), $kT = 0.18$ (black upside down triangles), $kT = 0.23$ (white circles), $kT = 0.28$ (white squares), $kT = 0.33$ (white diamonds), and $kT = 0.40$ (white triangles) and their fits to gaussian functions (lines).

The maxima of the distributions of relaxation times follow the Vogel, Fulcher and Tammann [17,18] (VFT) equation, with a value of $kT_0 = 0.03$ and values of the relaxation times at infinite temperature between 3000 and 10^4 MCS for all the three relaxation times studied (Fig. 5). The value of $kT_0 = 0.03$ defines the temperature where the relaxation times becomes infinitely large. With good approximation, this temperature agrees with what is found with the simulated isothermal relaxations: at $kT = 0.02$ there is no energy evolution at all during 10^7 MCS. The curvature of the $\log_{10}(\tau/\text{MCS})$ versus $1/kT$ curve calculated from the simulated segmental dynamics is quite apparent and it must be considered a consequence of the cooperativity in the conformational rearrangements.

Unfortunately, many difficulties arose when trying to apply a similar method to determine the distribution of relaxation times in intermediate instants of the isothermal structural relaxation process at lower temperatures. Those distributions have been calculated at three different times for 10^6 MCS each one. The first stage begins with the relaxation, the second starts at 5×10^6 MCS and the third reaches the end from 9×10^6 MCS. The calculation could only be performed at quite high temperatures, $kT = 0.1$ and $kT = 0.15$, and then there is a significant evolution of the state of the system only during the first 10^6 MCS needed for the calculation, thus the results are not very significant. The distributions of relaxation times do not vary significantly as the annealing time increases during isothermal structural relaxation. The shape of the

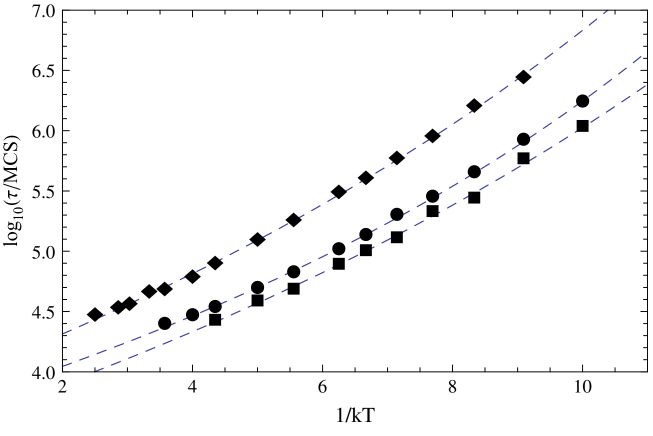

Fig. 5. Maxima of the distributions of relaxation times τ_1 (circles), τ_2 (squares) and τ_5 (diamonds), and their fits to the VFT equation (lines).

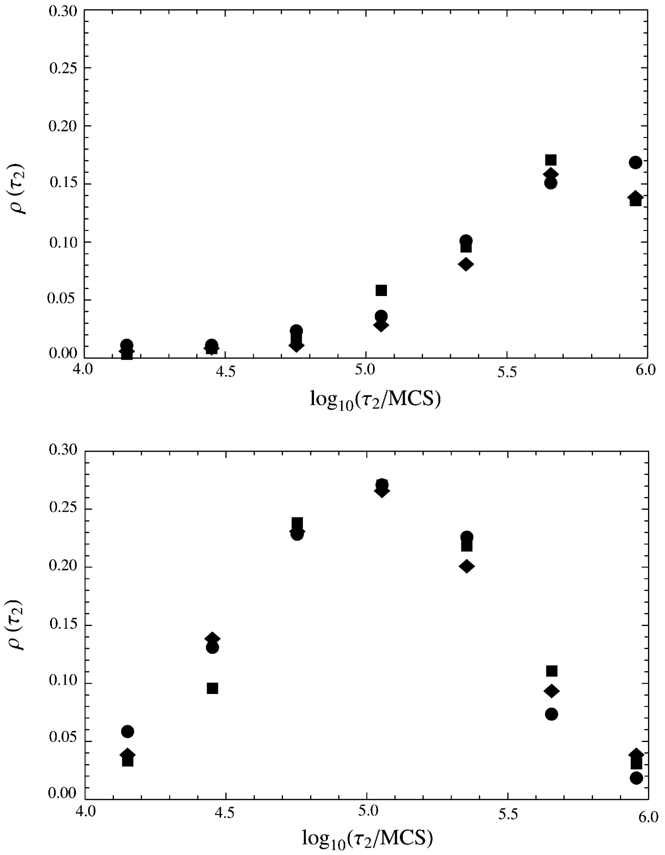

Fig. 6. Distribution of relaxation times τ_2 during three different intervals of 10^6 MCS: at the beginning (circles), after the first half (squares) and at the end (diamonds) of the isothermal relaxations during 10^7 MCS at $kT = 0.10$ (up) and 0.15 (down).

distribution seems to remain unchanged (Fig. 6). It would be interesting to see if the distributions of relaxation times shift to longer times as the system evolves. To study the possible shift we would have to calculate the distributions at lower temperatures, where the relaxation is slower and the three time intervals cited correspond to clearly different states. But at such low temperatures the distribution vanishes for relaxation times below 10^6 MCS. And longer simulations only supply more information on equilibrium states. New definitions of relaxation times may be needed to obtain the distributions from shorter MCS intervals.

Nevertheless, the equilibrium distribution of relaxation times analysis obtained from the simulations can be used as a tool to compare directly the model to the experimental. From the width of the distributions of relaxation times, the stretching parameter β can be calculated as well. And from the dependence of the maxima of the distributions with temperature, the Vogel, Fulcher and Tammann parameters are easily obtained. Compared to the analysis based on the autocorrelation functions, it seems more sensitive to small variations of the width of the distribution of relaxation times with temperature, so also to that of the stretching parameter β.

4. Conclusions

The results of coarse grained simulations such as the BFM used, allow reproducing and studying phenomena similar to that occur in out of equilibrium systems such as amorphous materials in the glass transition region. The results of the simulations have provided information on correlation functions of interest on the individual processes of movement of the chains and their groups.

The monitoring of the movement processes of each molecule provides important information about the system: distributions of relaxation times of the system in equilibrium states have been calculated and even for a quite simple polymer model the simulation reproduces some of the features shown in the relaxation experiments that probes segmental dynamics. As temperature decreases the distribution of relaxation times shifts to longer times and slightly broadens. The maxima of the distributions behave according to the VFT equation. The extension of this analysis to determine the evolution of the distributions of relaxation times during structural relaxation is not easy, in fact it has been possible to determine it in a short temperature interval within the glass transition. In these temperatures the shape of the distribution do not vary significantly as the annealing time increases.

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