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The relationship between diffusion and dynamically accessible volume in polymer chain dynamics simulated with the bond fluctuation model

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Abstract

The dependence of the diffusion coefficient, D, of polymer systems on the Dynamically Accessible Volume (DAV) was calculated in the framework of the Bond Fluctuation Model. The quadratic relationship between dynamically accessible volume and diffusion coefficient, which has been observed for some other models, has been confirmed for high values of DAV, whereas smaller diffusion coefficients than those predicted by the model were shown for DAV values lower than 0.1 independently of the chain length. This critical value is related to the loss of connectivity of the holes of the system and the consequent diminution of the diffusion of the system. The influence of the chain length on this behaviour has been established, showing that there is a linear relationship between the γ parameter (the proportionality constant between D and the squared DAV) and the reciprocal of the chain length.

Keywords: Bond fluctuation model; Dynamically accessible volume; Diffusion

1. Introduction

The relationship between diffusion coefficient and free volume is well known in polymer physics and has been explained by the classical free volume theories [1–4]. According to these theories (and also to the experimental results), the viscosity of the liquid or the diffusion coefficient depends almost exclusively on free volume. The well known Doolitle equation is representative of this dependence

$$\eta = A \exp\left(B\frac{v-v_{\mathrm{f}}}{v_{\mathrm{f}}}\right) \tag{1}$$

where η is the viscosity, v volume, v_{f} is free volume and A and B are constants. This is a key feature in polymer physics, related to the segmental dynamics and its dependence with temperature at temperatures above the glass transition and with thermal history at temperatures in the range or below the glass transition.

Computer simulation is a very attractive tool in the study of segmental mobility and the glass transition process in polymeric materials. Monte Carlo methods are commonly employed to study glass transition and the bond fluctuation model is one of the most employed models [5–8], due to the fact that it offers a good representation of polymeric materials in spite of being a coarse graining model. Bond Fluctuation Model has shown a good performance in representing polymeric materials and their dynamics, so it can be employed to determine the effect of chain length in the behaviour of the system. The influence of the chain length in the glass transition was studied for the bond fluctuation model by Lobe et al. [9] showing that glass transition temperature increases with chain length, as could be expected.

The definition of free volume in a lattice is not a simple task. Recently Dawson has proposed the concept of Dynamically Accessible Volume (DAV) in order to introduce a parameter to characterize the glass transition [10–12]. This concept distinguishes between two kinds of empty cells. The empty cells that can be occupied in one Monte Carlo Step according to the rules of the model are called holes, meanwhile the rest of the empty cells are called vacancies. In order to obtain a normalized value, the number of holes is divided by the total number of cells of the simulation box, so DAV can vary

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between 0 and 1. The mathematical definition of DAV can be expressed in the form

$$\mathrm{DAV} = \frac{1}{L^3}\sum_{j=1}^{L^3}\left(\min\left(1, \sum_{i=1}^{nn}\delta_{ij}\right)\right) \tag{2}$$

where L is the box simulation size, nn is the number of nearest neighbors of a cell and δ_{ij} is a function defined as 1 when a monomeric jump from the cell i to the cell j is allowed and 0 in any other case.

The Dynamically Accessible Volume has been used by our group, in the framework of Bond Fluctuation Model, to study the response of polymeric systems to different thermal histories [13], and the definition of DAV was extended to thermal systems [14].

According to the definition of DAV, only holes are considered to contribute to the diffusion of the system. It has been proved for the Kob–Andersen [15] and Biroli–Mezard [16] models that the relationship between diffusion coefficient and DAV fits to the law [10–12,17]

$$D = \gamma|\nu|^2 \tag{3}$$

where D is the diffusion coefficient, ν is DAV and γ is a non-universal factor that depends on the model. Some models like Kob–Andersen [15] show a deviation from the quadratic behaviour for low values of DAV, but this deviation can be corrected if only connected holes are taken into account [17]. That is, isolated holes are not considered to contribute to the diffusion of the system and then disregarded.

The aim of this work is to study the relationship between diffusion coefficient and the dynamically accessible volume of the system using Bond Fluctuation Model under athermal conditions. The system under consideration consists of polymeric chains of varying length and the results will be compared to some other models that have been tested before for simple beads [10,11]. The introduction of geometric restrictions to polymer segments jumps allows simulating systems with varying mobility and, as a consequence varying dynamic accessibility of the empty sites. This is, to our knowledge, the first time that geometric restrictions to motion are introduced in Bond Fluctuation Model.

2. The dynamically accessible volume and geometric restrictions to movement

In order to control the available volume for a given configuration, some geometric restrictions to movements are included in models like Kob–Andersen [15] and Biroli–Mezard [16]. Geometric restriction in Kob–Andersen model consists of including a new parameter c in such a way that a movement can only be performed if c or less neighbouring cells are occupied at the original position and the destination site of the movement. In a cubic lattice six neighbours are possible, so c can vary between 0 and 6. Biroli–Mezard method includes a geometrical restriction c_i allowing only configurations where all particles of type i have only c_i or less neighbours. So, DAV depends on the configuration of the particles, their density, and the chosen value for the geometric restriction.

These kinds of geometric restrictions have been employed before by Jäckle in order to represent the lack of mobility that all systems experience during the glass transition [18]. In these models some influence cells are defined depending on the topology of the lattice and a geometric parameter is defined in order to evaluate if a movement can be performed or not. It is note worthy that all these geometric restrictions have been applied only to simple models where particles are represented by beads, but they have never been applied to polymeric chains.

In order to control the dynamically accessible volume of the system we have included, in this work, geometric restrictions to the bond fluctuation model. We define the influence cells for a movement as the cells that are close to the molecular group, which is moving. The criterion we have chosen is that the sum of the distance of an influence cell to the molecular group at the beginning and at the end of the movement must be equal or less than $(1+\sqrt{2})$ lattice units. In other words, the distance from the influence cell to the original position of the polymer segment or to the destination site must be one lattice unit and must not exceed $\sqrt{2}$ to any of them. This gives six influence cells in the 2D model, which are just around the molecular group in movement (Fig. 1). If we extrapolate this to the 3D model we obtain 24 influence cells. So we define a parameter c in such a way that a movement can only be performed if c or more influence cells of a movement are empty. A value $c=0$ represents the standard model with no geometric restriction, while increasing c contributes to the geometric frustration that leads to the glass transition in a similar way that the models explained above.

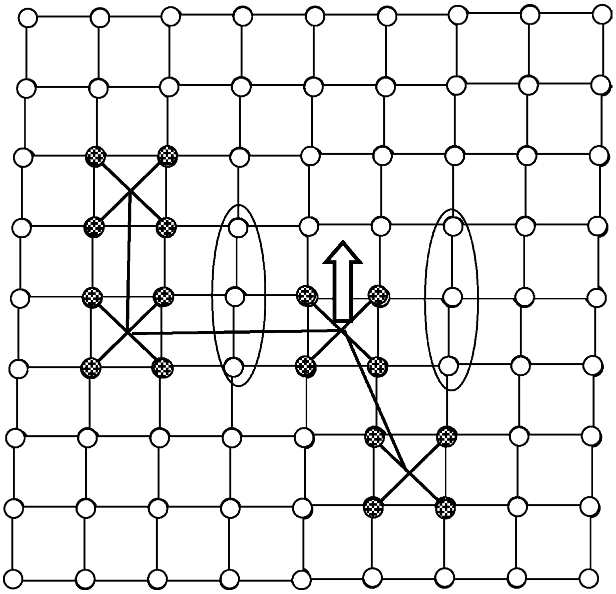

Fig. 1. Schema showing the influence cells for the 2D bond fluctuation model (emphasized) in a typical movement. The distance of influence cells to the molecular group in movement must be one lattice unit at the beginning or at the end of movement and never must exceed $\sqrt{2}$. An extrapolation to the 3D model gives 24 influence cells.

3. Results and discussion

3.1. Method

The characteristics of Bond Fluctuation Model have been described extensively in the literature [5–9,19–37]. All simulations consisted of a 3D box ($L=40$) with continuous boundary conditions [5]. In order to obtain athermal simulations, no Hamiltonian was employed, so movements were governed only by kinetics criteria. That is, when a movement was randomly chosen to be performed, three unique conditions that must be satisfied to accept it are volume exclusion, geometric restriction and bond length maximum. Simulations begun with an initial period of 10^5 Monte Carlo Steps, MCS, in order to equilibrate the sample. After this initial period average values were calculated during 10^4 MCS. All calculations showed in this work were averaged from 20 independent simulations, in order to obtain values not conditioned by initial configurations. Tested size chains were $N=1$ (monomer), 5, 10, 15 and 20.

The Dynamically Accessible Volume was varied by means of density ϕ (fraction of occupied lattice sites) and geometric restriction parameter c. Combination of both parameters led to a concrete value for DAV in every simulation. The maximum density available in the model was limited, in the case of the longest polymer chains, because of the difficulty to find the consecutive empty space necessary to allocate every new chain in the initial configuration.

When chains sized 20 and 15 were simulated, maximal density was $\phi=0.55$ and 0.56, respectively. Lower size chains allowed higher densities. On the other hand, for each density, simulations were conducted with different values of parameter c, between 0 and 18 (maximal possible value was 24), in order to vary the DAV. Greater values for c led to a frozen system in its initial configuration and no diffusion was observed, so this was the reasonable range for the geometric restriction.

The evolution of the system during simulation was observed averaging the DAV, and calculating at the same time the diffusion coefficient [5,6,8,19]

$$D = \lim_{t\to\infty} \frac{g_3(t)}{6t} \tag{4}$$

where $g_3(t)$ is the correlation time function of the centre of mass of the polymer chains [5,6,8,19]:

$$g_3(t) = \left\langle [\vec{r}_{\mathrm{CM}}(t) - \vec{r}_{\mathrm{CM}}(0)]^2 \right\rangle \tag{5}$$

In order to control the dependence of the spatial distribution of polymer segments on DAV, the spatial pair correlation function was calculated too [38]

$$g(r) = \frac{2L^3 H(r)}{(NP)^2 h(r)} \tag{6}$$

where $H(r)$ represents the histogram that counts the incidences for a given distance r in the system, $h(r)$ represents the number of possible r-vectors for this given distance, NP is the number of monomers or molecular groups in the system and L is the size of the simulation box expressed in lattice units.

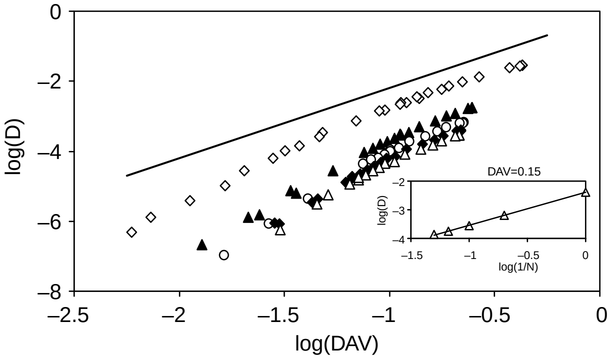

Fig. 2. Dependence of the diffusion coefficient on the DAV for chains sized 1 (ϕ between 0.5 and 0.75) (◇), 5 (ϕ between 0.5 and 0.65) (▲), 10 (ϕ between 0.5 and 0.60) (○), 15 (ϕ between 0.5 and 0.56) (◆) and 20 (ϕ between 0.5 and 0.55) (△). Parameter c is always between 0 and 18. The straight line with slope 2 is also shown (see text). The insert shows a log–log plot that illustrates the dependence of the diffusion coefficient on the inverse chain length for a fixed DAV value (0.15).

3.2. Influence of chain length on the diffusion coefficient

The calculation of the diffusion coefficient depending on DAV for bond fluctuation model (Fig. 2) showed a clear influence of the chain length in the diffusion. Monomers (chain length one) showed a greater diffusion for the same values of DAV. As chain size increased, the expected linear relationship between the diffusion coefficient and $1/N$ was found.

In the double logarithmic plot of Fig. 2, the behaviour described by Eq. (3) corresponds to the straight line with slope 2 that approaches the diffusion coefficient curve for high DAV values for any chain length. Fit of Eq. (3) to the diffusion coefficient corresponding to DAV above around 0.1 allows to determine the N dependence of the parameter γ. Obviously the dependence of γ with the chain length (see Fig. 3) is similar to that of the diffusion coefficient at a fixed value of DAV, shown in the insert of Fig. 2. The molecular weight dependence of the variables related to free volume, such as viscosity, self diffusion coefficient, the glass transition temperature or the internal friction, has been explained in terms of free volume by the additional free volume corresponding to the chain ends of

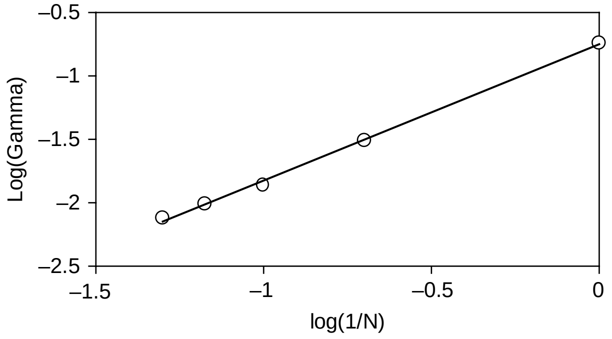

Fig. 3. Value for γ parameter of Eq. (2) depending on inverse chain length. Straight line represents the linear regression.

the polymer chain. This contribution being proportional to the reciprocal molecular weight [4]. As shown in Fig. 3 the model simulation reproduce the expected linear dependence of γ with the reciprocal chain length ($1/N$). The linear dependence on the reciprocal chain length has been observed for the glass transition temperature in the Bond Fluctuation Model [9]. These results illustrate that γ factor is not only characteristic of the simulation model [17], but also this factor depends on chain length, showing the importance of the application of the concept of dynamically accessible volume to polymeric materials. By the other side, this behaviour shows the importance of including a minimal chain length in Bond Fluctuation Model in order to obtain the behaviour of a polymeric material.

These results indicate that chain length diminishes the diffusion coefficient of the chains as could be expected of the previous results that showed the dependence of the glass transition temperature on the size of the chains, but the agreement with the quadratic law was observed in all cases for high DAV values, and the non-quadratic behaviour was observed too, as in Kob–Andersen model [17].

3.3. The loss of the quadratic relationship between DAV and diffusion coefficient

The general trend of the log D vs log DAV plot can be observed in a normalized diagram in which log D/γ is represented against log DAV [12,17], as shown in Fig. 4. The values of γ used in this calculation were those shown in Fig. 3. We can observe that the curves corresponding to the different chain lengths overlap at high DAV values with the slope 2, i.e. with the quadratic dependence of D with DAV.

When DAV is approximately lower than 0.1, all the curves loss the quadratic relationship showing a great decrease in diffusion tendency. This loss is assumed to be caused by the holes, which are isolated in some extent and do not contribute to the diffusion of particles [17]. We can observe that the change of behaviour takes place in the same DAV interval independently of chain length and the critical value of DAV is similar to that observed in literature [17]. Furthermore, previous simulations performed by our group with the bond fluctuation model in thermal systems with the thermal definition of DAV showed that, on cooling from an equilibrium state, the state of the systems separated from the equilibrium line, beginning the glass transition, when DAV was around 0.1 [14].

All these results suggest the existence of a transition in the dynamics of the amorphous material that takes place when the dynamically accessible volume decreases below a certain critical value. Above this value we can observe a liquid in equilibrium where the diffusion coefficient depends on the square of DAV. When the DAV of the system diminishes below the critical value, the diffusion becomes slower due to the lack of enough interconnected holes to allow the diffusion of chain segments. In this work, this behaviour has been observed for the bond fluctuation model in athermal simulations, but a coherent behaviour with this interpretation can be observed with different models [17] and with thermal simulations of bond fluctuation model (employing the thermal definition for DAV) [14]. More work must be tackled in future in order to determine if this critical value, which is around 0.1, appears in some other models.

3.4. Comparison of structures for different configurations

Finally we employed the pair correlation function in order to observe the spatial distribution of the systems. Fig. 5 compares the pair correlation function (Eq. (6)) calculated for the system formed by polymer chains with $N=5$ in situations with different dynamically accessible volume. The graph shows no indication of long-range order in the occupied lattice cells apart from the characteristic peak at $r=2$ induced by the lattice. What is more significant is the fact that the structure is nearly identical for DAV values above and below 0.1. Pair correlation function was calculated for all the other chains size and all of them offered the same amorphous structure independently of the DAV of the system. Even in the case of the system consisting of monomers ($N=1$) (Fig. 6), in which the peaks in $g(r)$ are sharper, no significant differences were found in situations with DAV lower than the critical value with respect to the equilibrium liquid corresponding to high free

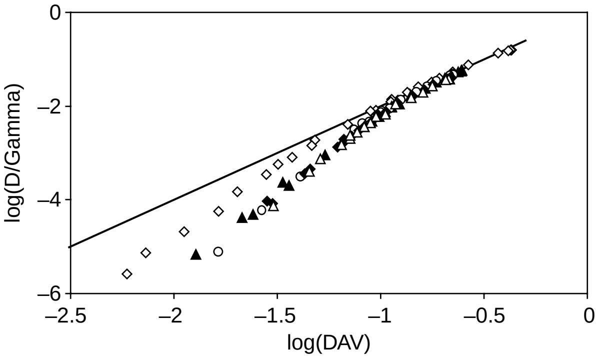

Fig. 4. Values of diffusion coefficient normalized by γ depending on DAV for chains sized 1(◇), 5(▲), 10(○), 15(◆) and 20(△). The γ values were taken from Fig. 3. Straight line represents the quadratic law.

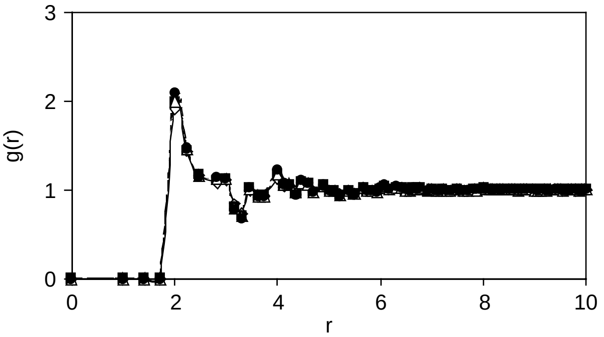

Fig. 5. Pair correlation function of systems formed by chains sized 5 for different values of DAV: 0.21 ($\phi=0.5$; $c=12$)(◇), 0.12 ($\phi=0.52$; $c=15$) (■), 0.09 ($\phi=0.53$; $c=16$) (△) and 0.04 ($\phi=0.55$; $c=18$) (●). Lines are employed only as a guideline for the eye.

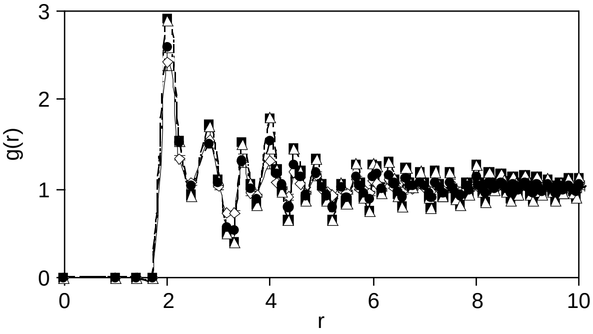

Fig. 6. Pair correlation function for monomeric systems with DAV 0.17 ($\phi=0.5$; $c=17$) (◇), 0.10 ($\phi=0.7$; $c=12$) (■), 0.07 ($\phi=0.7$; $c=13$) (△) and 0.03 ($\phi=0.65$; $c=17$) (●). Lines are employed only as a guideline for the eye.

volume. The conclusion is that the system can be called amorphous in all cases and no additional molecular order is produced by the decrease of dynamically accessible volume even to very small values.

4. Conclusions

In this work, we have verified that the dynamically accessible volume follows in the Bond Fluctuation Model the general behaviour that has been observed for some other models. The quadratic law between DAV and diffusion coefficient has been confirmed for high values of DAV, and the loss of the quadratic relationship for low DAV values has been observed too. Furthermore, the influence of the chain length in this behaviour has been established, showing that there is a linear relationship between γ parameter and the reciprocal of the chain length.

The loss of the quadratic relationship has been associated to a critical value of dynamically accessible volume that is independent of the chain size. This critical value is associated to the loss of connectivity of the holes of the system and the consequent diminution of the diffusion of the system. This fact suggests that more work must be done in order to study the connectivity of the holes and determine the critical value and its possible universality.

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