



Molecular mobility with respect to accessible volume in Monte Carlo lattice model for polymers



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HIGHLIGHTS

- Original dynamic lattice model for amorphous polymers.
- Account for change of temperature by locking lattice sites to the polymer chains.
- Polymer mobility assessed by reptation motions.
- Model shows sharp mobility transition with respect to accessible volume.

ARTICLE INFO

Article history:

Received 7 October 2016

Available online 29 November 2016

Keywords:

Polymer
Glass transition
Lattice model
Dynamic

ABSTRACT

A three-dimensional cubic Monte Carlo lattice model is considered to test the impact of volume on the molecular mobility of amorphous polymers. Assuming classic polymer chain dynamics, the concept of locked volume limiting the accessible volume around the polymer chains is introduced. The polymer mobility is assessed by its ability to explore the entire lattice thanks to reptation motions. When recording the polymer mobility with respect to the lattice accessible volume, a sharp mobility transition is observed as witnessed during glass transition. The model ability to reproduce known actual trends in terms of glass transition with respect to material parameters, is also tested.

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1. Introduction

Amorphous polymers exhibit a glass transition changing from rubbery state at high temperatures to glassy state at low temperatures. At high temperatures, macromolecular chains are mobile, capable of accommodating large strain due to reptation motions. At low temperatures, chains are in a 'frozen' state and show local motions only with restrained cooperative moves [1]. The chain mobility may be linked with the volume surrounding the chains since material volume expands when increasing the temperature. But in the case of polymers, a drastic slowing down of molecular motions is witnessed at the glass transition temperature while the macroscopic volume decreases continuously. Therefore the direct link between volume and molecular mobility is not obvious and proposing a physical theory for the glass transition of polymers remains an open challenge [2–4]. More modestly, the current contribution aims at exploring the change of molecular mobility according to volume surrounding molecular chains running mere lattice Monte Carlo simulations.

On one hand, molecular dynamics simulations may reproduce realistic chain dynamics but are unable to cover the time frame of glass transition of amorphous polymers. On the other hand, Monte Carlo simulations [5] consider schematic

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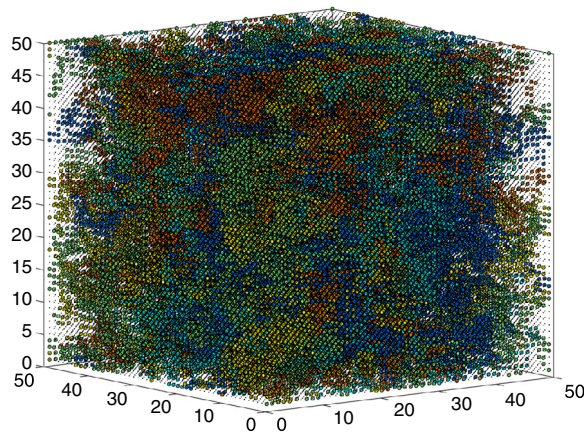


Fig. 1. Periodic cubic lattice of dimension 50^3 containing 5 chains occupying 10,000 sites each.

molecular moves but can produce equilibrated configurations faster [6] and may help understanding issues that are not reachable by molecular dynamics simulations yet [7]. Therefore, three-dimensional lattice Monte Carlo simulations are considered to study the molecular mobility of the macromolecular chains of a generic amorphous polymer defining original rules to assess for the molecular mobility and to account for temperature changes.

2. Lattice dynamic model

2.1. 3D cubic lattice polymer model

A three-dimensional cube lattice with periodic conditions is considered. The cubic box expands infinitely in the three directions of space defined by the cube edges. Polymer chains are built in lattice using self-avoiding walks (SAW). We will be brief on this aspect since the literature is furnished on the topic, see for instance the recent review [8]. A mere SAW inspired by pruned enriched Rosenbluth sampling [9] was used to build the polymer chains in the periodic lattice. The method was validated by estimating the chain end-to-end distance and the chain gyration radius for long chains. Chains were built simultaneously in order to avoid possible bias. Moreover, in order to avoid statistic aberration, up to ten boxes were built and later tested. Actually, very reproducible results were obtained.

Fig. 1 displays an example of periodic lattice of dimension $50 \times 50 \times 50$ containing 5 chains, each occupying 10,000 sites of the lattice. Such a reference box defines three parameters, the box dimension N , the number of polymer chains n_{ch} , and the volume fraction of polymer f_p defined by the number of sites occupied by the polymer over the number of sites in the lattice. In the polymer box exemplifying in **Fig. 1**, one reads $N = 50$, $n_{ch} = 5$ and $f_p = 50\,000/125\,000 = 0.4$.

2.2. Polymer chains dynamics

Once built, the polymer chains may show some mobility. Several motions have been proposed in the literature (**Fig. 2**). The chain-end move on one of its free neighbor sites and the kink jump were both proposed by Verdier and Stockmayer [10] and are used frequently. Later, another motion as the 90° crankshaft has been added [11]. These dynamic motions are local and suit well the glassy state. The pivot move allowing a long end of the chain to rotate around one of its monomer acting as a pivot has been defined to generate fast large chain motions [12]. Finally, snake-like slithering motions or reptation motions were also considered. See [13] for a description of various slithering motions. Only the simplest version of reptation, consisting in the progression of the first end forward while the last end is erased, was retained (**Fig. 2**).

Simulations allowing the chains to move randomly according to the various motions were run, while the polymer mobility was assessed by recording the number of lattice sites visited by the chains within a given duration. First, it was noticed that when the polymer is not highly dilute, the pivot motion is very often denied by the surrounding polymer even when the excluded volume restriction assumption is relaxed. The latter assumption being enforced when non-consecutive monomers cannot be neighbors on the lattice. Second, the chain-end motion, kink jump and crankshaft barely participate to the polymer mobility since they do not allow exploring much of the lattice. As expected, they are representative of local motions that could take place in the glassy state as well as in the rubbery state but do not add to the polymer mobility. To the contrary, the reptation motion enhanced the molecular mobility favoring the visit of the lattice. In order to illustrate the polymer mobility when reptation moves are considered only, simulations were run allowing at each step every chain to increment a reptation move. **Fig. 3** shows the ratio of the visited lattice over simulation duration for the system presented in **Fig. 1**. The ratio of visited lattice is defined by the number of initially unoccupied sites that are visited at least once by the polymer over the number of initially unoccupied sites. Therefore it ranges from zero to one. Adding the other motions

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