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# Hard and soft confinement effects on the glass transition of polymers confined to nanopores

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We present results of molecular dynamics simulations for coarse-grained polymers confined in nanopores in a wide temperature range to investigate the factors that affect the glass transition. We focus on the influences of interaction strength, confinement size and the mobility of boundary on the static and dynamic properties of confined polymers, and further study their influences on the glass transition temperature $T_g$ and the fragility $D_f$, which quantifies how rapidly relaxation times vary with temperature $T$. For the immobile nanopore boundary (i.e. the hard wall confinement model), strong attractive interaction between wall and polymer induces slow polymer dynamics near the wall, while the weak interaction gives rise to a relatively enhanced monomer mobility. The mobile nanopore boundary (i.e. the soft wall confinement model) has a great influence on the shift of $T_g$ and $D_f$: it accelerates the structural relaxation of nearby monomers and leads to a lower $T_g$ and a larger $D_f$. The soft confinement effect is more obvious for nanopores with strong interaction than those with weak interaction. In addition, smaller confinement size leads to lower $T_g$ of confined polymers, except for those confined in hard nanopores with strong attractive interaction. Our analysis demonstrates the change of $T_g$ of confined polymers is mainly controlled by the surface effects originated from the polymer–wall interaction and the mobility of nanopore boundary.

## 1. Introduction

Since Jackson and McKenna [1] first observed a reduced glass transition temperature $T_g$ of organic liquids at the nanoscale confinement, there is a growing interest in investigating the glass transition behavior of geometrically confined glass formers, by using experiments [2–9], simulations [10–16] and theoretical approaches [17–20]. The geometries that have been considered include thin films [3–8,12–15], narrow pores [1,2,10,11] and spherical cavities [9,16].

The motivation to investigate nanoconfinement lies in its significant practical importance related to controlling the properties of materials confined to restricting geometries of nanoscale for various applications in chemistry, medicine and nanotechnology. Moreover, it is also interesting from the theoretical side since it may provide us a better understanding of the mechanism of glass transition in bulk, which is still a very active research subject. For instance, according to Adam and Gibbs theory [21,22], there are cooperatively rearranging regions (CRRs) in glass-forming liquids and the average size of such CRRs can be defined as $\xi_g$, which is also called the “mosaic” length in the random first-order transition theory (RFOT) [23]. In both theories, the length scale $\xi_g$ will grow with decreasing temperature, indicating an increase in relaxation time. Intuitively, the growth of $\xi_g$ should be truncated under the condition of confinement and it will lead to a reduced glass transition temperature $T_g$ [24]. Batistakis et al. have observed the effect of the truncation of the length scale $\xi_g$ in their simulations and found that the increasing segmental dynamics in the middle of the thin polymer films can be strongly enhanced with decreasing film thickness [25]. Unfortunately, the introduction of confinement has more complicated influences rather than only affects the $\xi_g$: the dynamics of the confined glass-formers should be also influenced by surface interaction effects, which have a close relation to the characteristic of the detailed interaction type. The surface effects should increase with the surface-to-volume ratio of confined glass formers since the smaller system has larger proportion of materials close to the confining surface. In general cases, the interfacial effects are often more important [26]. In addition, the confinement also changes the density of the spatially confined glass formers. While the influence of confinement-induced density changes is not

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large for thin films [26,27], this effect on the glass transition of glass formers in pores should be considered [2,26]. These effects have various influences on the dynamics, thus the shift of $T_g$ of confined glass formers depends in a complex way on the properties of surface, glass-forming materials, and confinement size, with $T_g$ decreasing, increasing or remaining unchanged. The attractive interfacial interactions have been generally observed to slow the dynamics of polymers near the interface and then increase $T_g$ [5,28,29]. However, simulations that only employ an attractive potential to study the effect of substrate show that polymer dynamics near the substrate can be enhanced [12,13], demonstrating that roughness of surface is also an important factor that affects the glass transition temperature $T_g$. On the other hand, repulsive interfacial interactions have been consistently found to enhance polymer dynamics and then decrease local $T_g$ [30].

Apart from the studies of free standing polymer film [28,31,32], the hard boundaries are always used to realize the hard confinement, where the position of wall almost cannot change. However, there are a few researches aiming at exploring the influences of soft confinement on the glass transition behavior [33–36]. Under the condition of soft confinement, the environment close to the supercooled glass former is subject to rapidly fluctuation rather than static. Richert et al. have realized the soft confinement in terms of reverse micelles to focus on the microscopic dynamics of glass-forming glycerol confined within microemulsion droplets [35]. Their observation demonstrates the glass former suspended in this fluidic environment exhibits faster glass-transition-related structural relaxation, which is equivalent to a reduction of $T_g$ [35]. In addition, Blochowicz et al. have found the increasingly accelerated dynamics in smaller confinement size and a crossover of the relaxation times from Vogel–Fulcher behavior in the bulk to an Arrhenius law in soft confinement [36]. While the experimental results are generally global and average, the molecular dynamics simulations have the inherent advantage in investigating the local properties, and the various effects that the mobile boundary brings in can be studied in detail to find out their specific influences on the shift of $T_g$. Moreover, the study of polymer dynamics near soft boundaries is also important to understand the self-assembly of diblock copolymers under soft confinement [37,38] and the polymer dynamics under soft confinement in a self-assembled system [39].

Polymer melt is probably one of the most extensively studied system for the topic of glass transition because of its intrinsic difficulty to crystallize [40]. Hence, we choose the polymer as the glass former to study the glass transition behavior under confinement using coarse-grained molecular dynamics simulations, with the aim to obtain both complete time and space resolved information. We study the influences of interaction strength, confinement size and mobility of boundary on the glass transition behavior of confined polymer. In addition, we have simulated a bulk system that can serve as a reference for the comparison. The paper is organized as follows: Section 2 presents details of the model construction and simulation procedure. Section 3 shows the static and dynamic properties of confined polymer and also their glass transition behavior. Finally, the main conclusions are summarized in Section 4.

## 2. Model construction and simulation details

### 2.1. Model construction

Following previous studies of glass transition in polymer melts with molecular dynamics (MD) simulation methods [41,42], polymer chains are represented by the Bennemann (BE) bead-spring model in our work. In this model, one polymer chain contains $M$ identical monomers of mass $m$. Two potentials are used for the interactions between monomers. The first one is a truncated and shifted Lennard–Jones (LJ) potential, which acts between all pairs of monomers including bonded and unbonded ones:

$$U_{\mathrm{LJ}}(r) = 4\varepsilon_{p-p}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + C(r_{\mathrm{cut}}). \qquad (1)$$

The constant shift $C(r_{\mathrm{cut}})$ is applied to the entire potential so that it is zero at the cut-off distance with $r_{\mathrm{cut}} = 2r_{\mathrm{min}}$, where $r_{\mathrm{min}} = 2^{1/6}\sigma$ is the potential minimum. Since it is not our aim to simulate a specific polymer, we use LJ parameters as units. Parameters of $\varepsilon_{p-p}$, $\sigma$, and the mass of the monomer $m$ are set to unity. In the following, all results are reported in reduced units, with length in unit of $\sigma$, temperature in unit of $\varepsilon_{p-p}/k_B$ ($k_B$ is Boltzmann constant), and time in unit of $(m\sigma^2/\varepsilon_{p-p})^{0.5}$. In addition to the LJ potential, bonded monomers along the chain interact through an FENE (finitely extendible nonlinear elastic) potential [43]:

$$U_{\mathrm{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right]. \qquad (2)$$

The parameters of the potential are set to $k = 30$ and $R_0 = 1.5$. This choice can make the bonds have a certain stiffness while avoiding high frequency modes and chain crossing [41]. The choice of chain length $M = 10$ is the result of considering both the computational expedience and polymer-specific effects [26].

To investigate the confinement effect on the properties of polymer, amorphous nanopores with diameter $D$ are generated according to the method described below. We begin by generating an equilibrated configuration of the pure melt comprised of Lennard–Jones particles at $\rho = 1.0$ and $T = 1.0$. The equilibrated configuration has the dimension $40 \times 40 \times 40$, which is also the dimension of the simulation box used in all following studies. We define a function $\eta(x,y,z)$ that equals 1 if $(x,y,z)$ belongs to the wall and 0 if $(x,y,z)$ belongs to the void [11]. The nanopores used in this work can be obtained by removing the void corresponding to $\eta(x,y,z) = 0$ out of the generated equilibrated configuration. For the nanopores, the void is defined as $\eta(x,y,z) = 0$ if $(x^2 + y^2)^{1/2} < D/2$ with a diameter $D$. We have prepared five systems with $D = 7.12$, 10.60, 13.68, 17.31, 19.36, consisting of $N_c = 100$, 300, 500, 800, 1000 chains in the nanopores (i.e., the average monomer density $\rho_m = 0.85$), respectively.

We have frozen the wall particles at their original positions to realize the hard confinement (HC). The wall particles interact with monomers in polymer chains through Eq. (1). Two different polymer–wall interaction strengths ($\varepsilon_{p-w} = 0.8$ and 0.1) have been considered, representing strong interaction and weak interaction, respectively. To simulate the soft confinement (SC), we have restricted the wall particles to their original sites with harmonic springs:

$$U_{\mathrm{harmonic}}(r) = \frac{1}{2}k(r - r_0)^2. \qquad (3)$$

Here, $r_0$ denotes the original position of a wall particle and $k$ the spring constant. In addition, the wall particles are Lennard–Jones particles that interact with each other also through Eq. (1). In our study, we have chosen the spring constant $k = 2$ and $\varepsilon_{w-w} = 0.2$ to make the wall particles mobile enough to realize soft confinement in the full temperature range and guarantee the impenetrability of the wall at the same time. In the soft confinement, the wall particles also interact with monomers through Eq. (1) with two different polymer–wall interaction strengths ($\varepsilon_{p-w} = 0.8$, 0.1) as in the case of hard confinement.

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