Tracer diffusion in a polymer network: influence of network flexibility

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Abstracrt We present a Brownian dynamics simulation study on the diffusion of a neutral tracer particle confined in a regularly crosslinked polymer network, especially, when the tracer size is comparable to the mesh size of the network. Polymer networks with different mesh sizes are prepared and compressed to the extent that the total polymer densities become the same. Irrespective of the network mesh size, the tracer diffusion in the networks is slowed down, showing the subdiffusion on intermediate time scales followed by the normal diffusion at long times. However, the confinement effect on the tracer diffusion becomes more significant when network strands are tightly stretched with smaller mesh size. The time scales of dynamic transitions are analyzed in terms of the probability distribution of time-correlated particle displacements.

Introduction

Molecular transport in crowded, entangled environments plays an important role in many scientific and engineering areas. Biological molecules diffuse through crowded cellular environments to perform their functions responsible for life processes. Pharmaceutical molecules are delivered using hydrogels within which molecular transport can be regulated in more controlled fashion. In this work, we investigate molecular transport in crowded, entangled environment using the Brownian dynamics (BD) simulations[1]. A simple, but highly relevant model system can be a tracer confined in a lattice-like polymeric network and, thus, we study the diffusion of a tracer particle within a regularly crosslinked polymer network[2].

A Brownian particle in bulk moves by diffusion with its mean squared displacement at sufficiently long times proportional to time t, that is, $\langle(\vec{r}(t)-\vec{r}(0))^2\rangle \sim t$, where $\vec{r}(t)$ and $\vec{r}(0)$ are positional vectors of the particle at times t and 0, respectively, and $\langle\cdots\rangle$ is the average. However, on shorter time scales, it was shown that the mean squared displacement increases a bit more slowly with time, that is, $\langle(\vec{r}(t)-\vec{r}(0))^2\rangle \sim t^{\alpha}$, where $\alpha < 1$, and it is called the subdiffusion or anomalous diffusion. The tracer diffusion in entangled polymers or gels is often described by the tracer diffusion in a random media with static obstacles. The effect of confinement or

subdiffusive dynamic behavior is most clearly observed due to the trapping of a tracer in void spaces confined by the static obstacles[3,4].

However, since the entangled polymers or gels are dynamic rather than static obstacles on the time scale of tracer diffusion, the effect of confinement on tracer diffusion is expected to be influenced by the dynamic fluctuation of network strands between crosslinking junctions[5-7]. Therefore, we investigate the diffusive properties of a tracer particle confined in polymer networks with varying strand flexibility[8]. While changing the network flexibility, we measure the mean square displacement and the probability distribution of time-correlated particle displacements to show the effect of dynamic fluctuation of the polymer networks on the tracer diffusion confined in polymer networks.

Simulation model and method

As a model for a polymer network, we consider a crosslink of linear chains, as shown in Figure 1 (a). Linear chains are modeled as a bead-spring chain in which spherical monomers are bonded together linearly by a combination of the finitely extensible nonlinear elastic (FENE) potential

$$U_b(r) = -\frac{1}{2}k_b R_b^2 \ln[1-(r/R_b)^2] \qquad (1)$$

and the repulsive part of the LJ potential

$$U_r(r) = \begin{cases} 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \varepsilon & 0 < r < r_c \\ 0 & elsewhere \end{cases}, (2)$$

where σ is a unit of length in this work, $k_b = 30k_BT/\sigma^2$, $R_b = 1.5\sigma, \varepsilon = 1k_BT$ and the cut-off distance r_c is set to $2^{1/6}\sigma$. Here, k_B is the Boltzmann constant and T is the temperature. To form a polymer network, linear chains are crosslinked regularly at every n monomer along each chain. We made different polymer networks in diverse sizes with controlling the number of monomers between the nearest crosslinking sites ($N_{CC} = n - 1$). We consider the range of network sizes represented by N_{CC} from 3 to 10. To model a polymer network on a large scale, we use the periodic boundary condition with a simulation box size of nearly $30\sigma \times 30\sigma \times 30\sigma$ depending on the network size. The initial box is compressed until the total polymer density represented as a volume fraction (ϕ_P) becomes 0.1 as shown in Figure 1. For the same way, a polymer network with

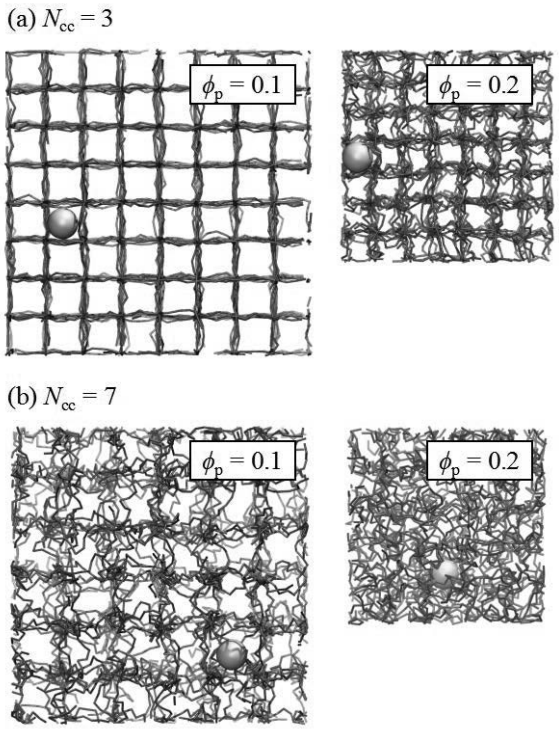

Figure 1. Snapshots of a tracer particle confined in a polymer network. The N_{CC} is defined as the number of monomers between two crosslinking sites. The volume fraction of the polymer network is adjusted to 0.10 and 0.20 by compression.

volume fraction $\phi_P = 0.2$ is made from a initial simulation box (Figure 1).

The excluded-volume interaction between the tracer particle (with diameter of 3σ)and monomers of a polymer network (with diameter of σ) is modeled by the repulsive LJ potential that is described below.

$$U_r(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r-\sigma}\right)^{12} - \left(\frac{\sigma}{r-\sigma}\right)^{6}\right] + \varepsilon & 0 < r < r_c \\ 0 & elsewhere \end{cases}, (3)$$

Since the repulsive barrier starts when the center-to-center distance between a tracer and a monomer becomes less than 2σ, this potential represents the repulsive interaction between two particles with their radii of 1.5σ and 0.5σ, respectively. Although various types of interactions may influence the particle dynamics, we only consider the excluded-volume interaction in order to focus on how the collective effect of a polymer network influences the tracer diffusion.

BD simulations are run to mimic the solvent-induced stochastic dynamics of a tracer and polymer segments. The system is evolved using conventional BD without hydrodynamic interactions. At each time step Δt, the position $r_i(t)$ of a particle *i* is updated via

$$r_i(t + \Delta t) = r_i(t) + \frac{D_0 F_i(t)}{k_B T}\Delta t + R_i(\Delta t) \quad (4)$$

where $F_i(t)$ is the total force acting on the particle *i*, and $R_i(\Delta t)$ is a random displacement with a Gaussian distribution function with zero mean and variance-covariance $\langle R_i(\Delta t) R_j(\Delta t)\rangle = 2D_0\Delta t\delta_{ij}$. D_0 is the diffusion coefficient of each monomer in a polymer chain in pure solvent and sets the time scale by a definition of the unit of time $\tau_{BD} = \sigma^2/D_0$. A time step $\Delta t = 10^{-4}\tau_{BD}$ is used for all the simulations. The total force $F_i(t)$ is given by the gradient of U_{total}, which is the sum of the bonded and non-bonded interactions described above. BD simulations are run using GROMACS v. 5.4.5.

Five sets of simulations with 1×10^9 time steps $(1 \times 10^5 \tau_{BD})$ are run over which the statistical properties are calculated by averaging over.

Results and Discussions

We perform BD simulations of a tracer particle (with diameter of 3σ) confined in a set of polymer networks with different mesh sizes $\boldsymbol{N_{cc}}$ ranging between 3σ and 9σ. From the simulation trajectories, we calculate the mean squared displacement (MSD) of a tracer particle defined as $\langle(\vec{r}(t) - \vec{r}(0))^2\rangle$. It is well known that the MSD in diffusive regime is proportional to time t and the slope of the MSD corresponds to *6D*. Mathematically, $\langle(\vec{r}(t) - \vec{r}(0))^2\rangle = 6Dt$, where *D* is the diffusion coefficient. However, on shorter time scales, the MSD increases more slowly than time t and $\langle(\vec{r}(t) - \vec{r}(0))^2\rangle \sim t^{\alpha}$, where $\alpha < 1$. If the MSD is divided by $6t$ as $\langle(\vec{r}(t) - \vec{r}(0))^2\rangle/6t$, the value is expected to be constant in the diffusive regime attained at long times, but it decreases on shorter time scales as $t^{\alpha-1}$. Therefore, we calculated the MSD from our simulation trajectories and divided it by $6t$ to distinguish the dynamic regimes of subdiffusion and normal diffusion, as shown in Figure 2. We call the MSD/$6t$ as the instantaneous diffusion coefficient, hereafter.

The data for the instantaneous diffusion coefficient are presented for two different volume fractions of polymer networks, $\phi_P =$ 0.1 and 0.20 in Figure 2 (a) and (b),

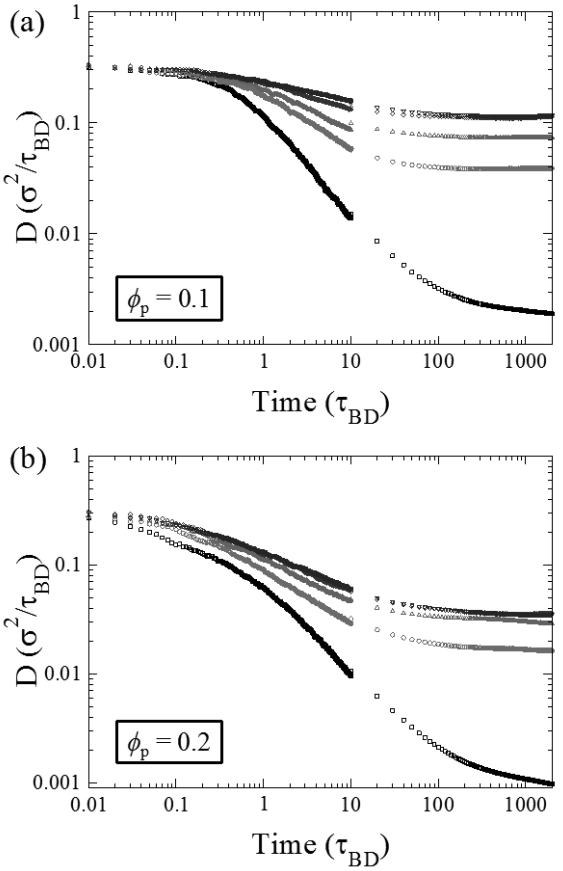

Figure 2. Time-dependent diffusion coefficient defined as the mean square displacement divided by *6t*. (a) At volume fraction 0.1. (b) At volume fraction 0.2. Data are obtained for the $\boldsymbol{N_{CC}(\sigma)}$ of 3, 4, 5, 7, and 9 from bottom to top. respectively. In each figure, the data for different $\boldsymbol{N_{CC}}$ are presented ranging between 3σ and 9σ in different colors. Small values of $\boldsymbol{N_{CC}}$ correspond to the polymer networks with tightly stretched network strands between crosslinking junctions and with smaller mesh sizes. For instance, a tracer of diameter 3σ is likely to be tightly held in a network with mesh size of $\boldsymbol{N_{CC}} = 3\sigma$ whereas the tracer is rather free in a network with mesh size of $\boldsymbol{N_{CC}} = 9\sigma$. Due to the large accumulation of data points required to provide accurate average values, the simulations are performed separately on short and long time scales (separated at $10\tau_{BD}$) and both sets of data from short and long time simulations are presented together in the same color in Figure 2.

A tracer of 3σ diameter has an instantaneous diffusion coefficient of $\sim 0.3\sigma^2/\tau_{BD}$ at the very beginning. This is because we set the diffusion coefficient of a network monomer with size 1σ in bulk as $D_0 = 1\sigma^2/\tau_{BD}$ and the size of the tracer is three times bigger. At the intermediate scales from $1\tau_{BD}$ to $10\tau_{BD}$, neighboring network monomers interacts with the tracer causing it to lose movement speed, so the falling curves are observed in the middle. The plots show that the tracer exhibits anomalous diffusive behavior: the tracer MSD is proportional to t^{α} where the α is smaller than 1. It slowly diffuses because of the confinement effect of a dynamic jam-packed polymer network. The greater the effect of a network, the steeper the slope of the declining line. The slope of a $\boldsymbol{N_{CC}} = 3\sigma$ network falls the most, so it's clear that the network has the largest confinement effect, though the volume fractions of all sets are same.

After a long time of $1000\tau_{BD}$, the tracer recovers its standard diffusive motion. As expected, because the polymer network becomes denser when $\boldsymbol{N_{CC}}$ decreases from top to bottom, the final diffusion coefficient of the confined tracer decreases. A tracer in a $\boldsymbol{N_{CC}} = 3\sigma$ network has an especially low value and it seems to still decline gradually. As volume fraction of the polymer network

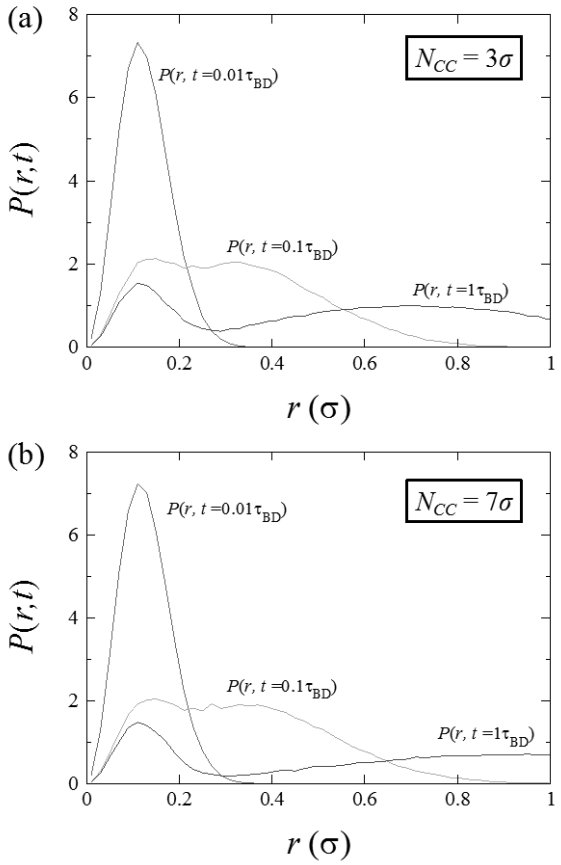

Figure 3. $\boldsymbol{P(r,t)}$ of $\boldsymbol{N_{CC} = 3\sigma}$ and $\boldsymbol{7\sigma}$ on short time scales.

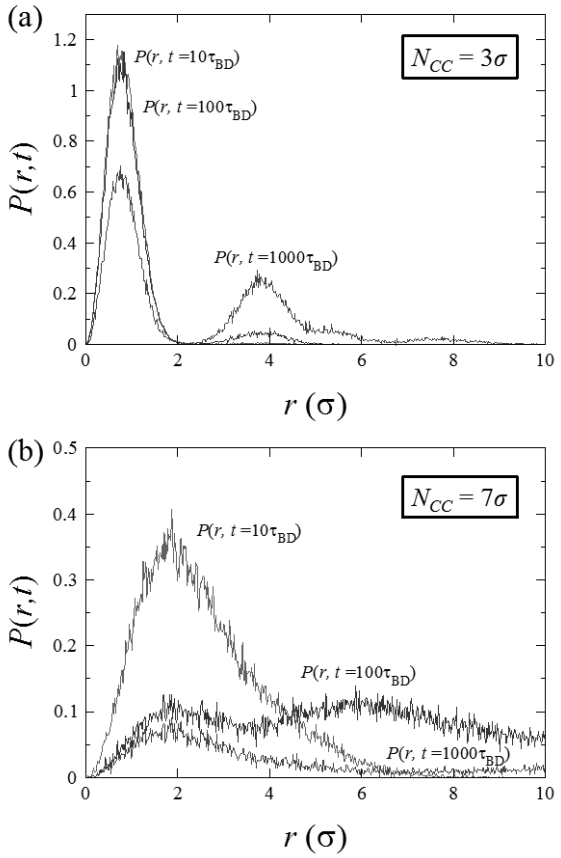

Figure 4. $\boldsymbol{P(r,t)}$ of $\boldsymbol{N_{CC} = 3\sigma}$ and $\boldsymbol{7\sigma}$ on long time scales.

increases from 0.1 to 0.2, the confinement effect of tracer promotes. The tracer gets a lower diffusion coefficient and needs more time to reach standard diffusion in a long-time simulation. We find out why it does not become constant with following figures.

We calculate $P(r,t)$ from short-time simulations, the probability to find a Brownian tracer at some point at a certain time, for every set, then compare $\boldsymbol{N_{CC} = 3\sigma}$ with $\boldsymbol{N_{CC} = 7\sigma}$ in Figure 3. $P(r,t)$ data at $t = 1\tau_{BD}$ are divided into several peaks, which means that the tracer movement is blocked by interactions between the tracer and network monomers. Hence, the subdiffusion occurs and the MSD increases more slowly with time.

Figure 4 is the results of $P(r,t)$ on longer time scales. The spot separating the first and second peaks is the distance where the tracer crashes against the polymer network strands. It doesn't go far until $10\tau_{BD}$ later, just walking around at the same place. At $t = 100\tau_{BD}$, a tracer in a $\boldsymbol{N_{CC} = 7\sigma}$ network is possible to move to the next room and even spreads far away. The other in a $\boldsymbol{N_{CC} = 3\sigma}$ network is still confined. It can diffuse through the network after $t = 1000\tau_{BD}$ passes, but over the half of total probability remains in the initial room. The tracer needs much longer time to diffuse to a distance with a constant diffusion

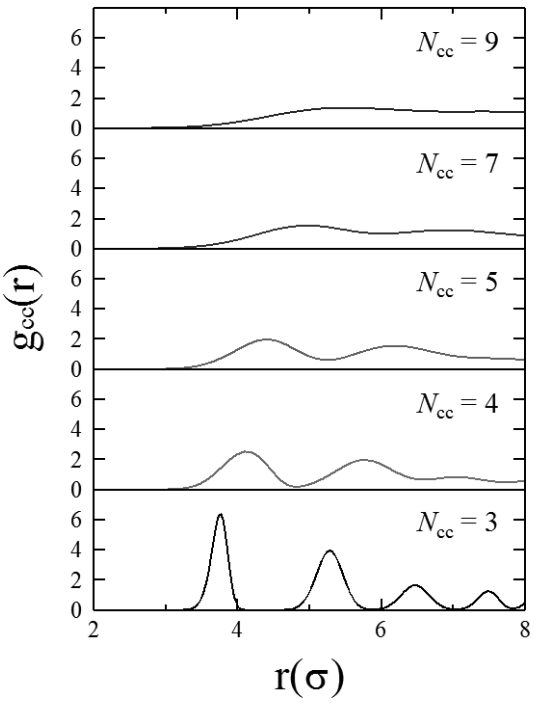

Figure 5. Radial distribution functions between crosslinks.

coefficient. Thus, the tracer in a $\boldsymbol{N_{CC}} = 3\sigma$ network has not reached diffusive motion in Figure 2 (a).

There are radial distribution functions (RDF) of crosslinking junctions on Figure 4. The size of $\boldsymbol{N_{CC}}$, the number of monomers between neighboring two crosslinks, is associated with the shape of RDF, and how sharp or broad it is decides the polymer network flexibility. RDF of a $\boldsymbol{N_{CC}} = 3\sigma$ network is separated into distinct sharp peaks. The crosslinks are fixed in their initial position and try to keep the distance between two neighbors. The immovable rigid network makes a tracer have a difficulty in diffusion. RDF of a $\boldsymbol{N_{CC}} = 7\sigma$ network, however, shows a broad shape. These dynamic crosslinks have relatively free movement, so the soft network monomers can fluctuate making way for the diffusive tracer. Flexibility of polymer network strands reduce the confinement effect on the tracer.

Conclusions

In this work, BD simulations are performed to study a tracer particle diffusion confined in a crosslinked polymer network. The time-dependent mean square displacement of the tracer is proportional to time t at the initial state. On the intermediate scales, the tracer anomalously diffuses due to the confinement effect of the network strands, so the MSD increases with time t^{α}, where $\alpha < 1$. It is called the subdiffusion, and the tracer loses its speed as the $\boldsymbol{N_{CC}}$ becomes small. The tracer recovers standard diffusive motion after a sufficiently long time with a constant diffusion coefficient. When the volume fraction increases from 0.1 to 0.2, the compact network promotes the confinement effect.

$\boldsymbol{P(r,t)}$, the probability to find a Brownian tracer at some point at a certain time, shows that the tracer movement is blocked by interactions between the tracer and network monomers. The 3σ tracer in a relatively rigid polymer network with $\boldsymbol{N_{CC}} = 3\sigma$ needs very long time to diffuse to a distance with a constant diffusion coefficient. Shape of RDF decides the polymer network flexibility. The immovable rigid network of $\boldsymbol{N_{CC}} = 3\sigma$ makes a tracer have a difficulty in diffusion, while dynamic crosslinks of $\boldsymbol{N_{CC}} = 7\sigma$ can freely fluctuate for the tracer diffusion. Flexibility of polymer network strands reduce the effect of confinement on the Brownian tracer.

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