Three-dimensional Brownian diffusion of rod-like macromolecules in the presence of randomly distributed spherical obstacles: Molecular dynamics simulation

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Brownian diffusion of rod-like polymers in the presence of randomly distributed spherical obstacles is studied using molecular dynamics (MD) simulations. It is observed that dependence of the reduced diffusion coefficient of these macromolecules on the available volume fraction can be described reasonably by a power law function. Despite the case of obstructed diffusion of flexible polymers in which reduced diffusion coefficient has a weak dependence on the polymer length, this dependence is noticeably strong in the case of rod-like polymers. Diffusion of these macromolecules in the presence of obstacles is observed that is anomalous at short time scales and normal at long times. Duration time of the anomalous diffusion regime is found that increases very rapidly with increasing both the polymer length and the obstructed volume fraction. Dynamics of diffusion of these polymers is observed that crosses over from Rouse to reptation type with increasing the density of obstacles.

I. INTRODUCTION

The phenomenon of Brownian diffusion of particles in the presence of fixed obstacles – obstructed diffusion – is very ubiquitous in biology, chemistry, and physics. This phenomenon, as a combination of several concepts such as obstructed random walk, hydrodynamic interactions and topological hindrances, introduces a challenging theoretical problem. Two simple models of this problem namely three dimensional random walk in a regular lattice with a fraction of its sites obstructed and diffusion of a pointlike tracer in an ordered medium of spherical obstacles have been studied theoretically and using lattice Monte Carlo method, respectively [1, 2]. Also, existence of anomalous diffusion regime in Brownian diffusion of particles due to the presence of fixed and mobile obstacles has been reported [3, 4].

In the context of obstructed diffusion, the other subject is the diffusion of solute molecules in hydrogels for which there are numerous suggestions (analytical, simulation, and empirical) for diffusion coefficient as a function of obstacles density. In a review of studies of this phenomenon it has been shown that diffusion of solute molecules in hydrogels composed of rigid (flexible) polymers can be described reasonably by obstruction (hydrodynamic) models [5]. Also, the effect of the structure of obstacles medium on diffusion of fluid molecules has been studied recently [6].

The other issue in this category is the Brownian diffusion of polymeric macromolecules in a medium of obstacles which has different branches depending on the polymer chains properties and the strength of induced confinement. In diffusion of polymer chains in a random media, such as exclusion chromatography, the polymers enter in cavities of typical size comparable to or larger than their size. In transition between these cavities the chains have to overcome entropic barriers which are set up due to reduction of their possible configurations [6–11]. In a semidilute solution of polymer chains or when a polymer chain diffuses in a dense medium of fixed obstacles, typical size of cavities is smaller than the polymer size and both topological hindrances and entropic effects are of important role [12–14]. Ratio of the strength of these two effects depends on the flexibility of the chains. The extreme case of a stiff polymer chain is a rod-like polymer for which internal entropy is negligible and topological interactions are dominant in its diffusion in a crowded environment.

Despite pure translational Brownian motion of small isotropic particles, Brownian motion of anisotropic macromolecules such as rod-like polymers contains both translational and rotational parts. Coupling of translational and rotational motions of such macromolecules makes understanding and visualization of their Brownian motion noticeably difficult [15]. Anisotropy affects Brownian motion of a macromolecule more dramatically in the presence of other macromolecules or fixed obstacles. In this case, both hydrodynamic friction coefficient and confinement effects due to the presence of other macromolecules or obstacles are anisotropic. A rod-like macromolecule experiences the least (the most) collisions with other macromolecules or obstacles when it moves along
Numerous interesting phenomena are known to arise from special shape of rod-like macromolecules. Nematic ordering in dense solution of these macromolecules due to only excluded volume interaction \[16, 17\], a variety of their orientational orderings resulted from the competition of entropic effects with long- and short-range interactions \[18, 19\], and their rich dynamic behavior in crowded environments \[20–23\] are examples of these phenomena.

In this paper we study Brownian diffusion of a spherical particle and rod-like macromolecules in the presence of randomly distributed spherical obstacles using molecular dynamics simulations. We find that dependence of the reduced diffusion coefficient of the spherical particle and rod-like macromolecules on the available volume fraction can be described by a simple power law function. In the case of rod-like macromolecules, the exponent of mentioned power law dependence is an increasing and saturating function of the macromolecule length. Despite the case of flexible polymers in which reduced diffusion coefficient has a weak dependence on the length of polymer \[13\], noticeably strong dependence is observed here which originates from stiffness of rod-like macromolecules. In obstructed diffusion of these polymers, an anomalous diffusion regime is observed which its duration time is a rapidly increasing function of both the polymer length and the obstacles density. With increasing the density of obstacles, long time diffusion of these rod-like polymers crosses over from Rouse to reptation dynamics.

The rest of the paper is organized as follows. The model and the simulation method are described in Sec. II. The results are presented in Sec. III. Conclusions and a short discussion are presented in Sec. IV.

II. THE MODEL AND THE SIMULATION METHOD

In our simulations which are performed with the MD simulation package ESPResSo \[24\], a polymer is modeled as a bead-spring chain of length \(N\) (\(N\) spherical monomers of diameter \(\sigma\)). Successive monomers of the polymer chain are bonded to each other by a FENE (finite extensible nonlinear elastic) potential \[22\],

\[
 u_{\text{bond}}(r) = \begin{cases} 
\frac{-1}{2}k_{\text{bond}}R_0^2 \ln(1-(r/R_0)^2) & \text{if } r < R_0, \\
\infty & \text{if } r \geq R_0, 
\end{cases}
\]

with bond strength \(k_{\text{bond}} = 30\epsilon/\sigma^2\) and maximum bond length \(R_0 = 1.5\sigma\). Bending elasticity of the chain is modeled by a bond angle potential,

\[
 u_{\text{bend}}(r) = k_{\text{bend}}(1 - \cos \theta),
\]

in which \(\theta\) is the angle between two successive bond vectors and \(k_{\text{bend}}\) is the bending energy of the chains. The value of the chain persistence length relative to its contour length, \(\frac{L_p}{L_c}\), which is a measure of the flexibility of the chain depends on the value of \(k_{\text{bend}}\) as \(l_p = \frac{3k_{\text{bend}}}{k_{\text{angle}}\sigma}\).

To model a rod-like polymer we consider \(l_p \approx 100L_c\) in our simulations. We also model the spherical obstacles by fixed spheres of diameter \(\sigma\) which are randomly distributed inside the simulation box with their overlapping permitted. Excluded volume interaction between monomers and the obstacles is modeled by a shifted Lennard-Jones potential,

\[
 u_{\text{LJ}}(r) = \begin{cases} 
4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{2} \right\} & \text{if } r < r_c, \\
0 & \text{if } r \geq r_c,
\end{cases}
\]

in which \(\epsilon\) and \(\sigma\) are the usual Lennard-Jones parameters and the cutoff radius is \(r_c = 2^{1/6}\sigma\). Average distance between neighboring monomers which results from combination of FENE and Lennard-Jones interactions is \(b \approx 0.97\sigma\). Simulation box is cubic with periodic boundary conditions and the temperature is kept fixed at \(k_BT = 1.0\epsilon\) using a Langevin thermostat. Simulation box length is \(L = 20\sigma\) and \(L = 25\sigma\) in simulations of polymers with \(N \leq 17\) and the polymer with \(N = 21\), respectively. MD time step in our simulations is \(\tau = 0.01\tau_0\) in which \(\tau_0 = \sqrt{m/\epsilon}\) is the MD time scale and \(m\) is the mass of the monomers. Dynamics of the monomers is assumed to be overdamped by using the friction coefficient \(\Gamma = \frac{m\tau}{\epsilon}\) for each monomer in the Langevin thermostat. In fact, we model the solvent implicitly by the stochastic and dissipation terms in Langevin equation instead of adding solvent molecules explicitly to the system. Accordingly, hydrodynamic interactions are not considered here and dynamics of polymer chains in the absence of obstacles is of Rouse type. In each simulation we first randomly distribute the obstacles inside the simulation box in a way that their overlapping is permitted. Then we put the rod-like polymer in a random position with a random orientation inside the box and start the simulation. After equilibration of the system which is needed because of used potentials and fixed temperature, we probe center of mass position, orientation, and velocity of the polymer for a long time \((N_t\) time steps) to calculate correlation functions. From recorded position of a diffusing particle (position of the center of mass in the case of rod-like polymers), mean square displacement (MSD) at time \(t = n_t\tau\) is calculated as

\[
\text{MSD} = \frac{1}{N_t-n_t} \sum_{n_s=0}^{N_t-n_t} [\vec{r}(n_s+n_t)\tau - \vec{r}(n_s\tau)]^2,
\]

in which \(\vec{r}(t)\) is the position vector of the particle at time \(t\). Diffusion coefficient for each realization of obstacles is obtained from time dependence of MSD. For fixed values of the polymer length and obstacles density we repeat our simulations with 10 different realizations of obstacles to average quantities and obtain error bars.
III. RESULTS

To study obstructed diffusion of a particle or a macromolecule, we first obtain its diffusion coefficient in the absence of obstacles \(D_0\) at given temperature, \(T\), and friction coefficient, \(\Gamma\), which is in consistence with Einstein relation, \(D_0 = \frac{\Gamma k_B T}{6 \pi N_0 a}\). Then we calculate diffusion coefficient, \(D\), in the presence of fixed spherical obstacles of given density. Obstructed volume fraction, \(\phi\), is calculated using ESPResSo package (a mesh based cluster algorithm [24]). This calculation is checked and justified with examples for which obstructed volume fraction can be calculated exactly. Reduced diffusion coefficient for each value of \(\phi\) is defined as \(\tilde{D} = \frac{D}{D_0}\).

A. Obstructed diffusion of a spherical particle

From MD simulations of the Brownian diffusion of a spherical particle in the presence of fixed spherical obstacles, we calculate diffusion coefficient at different values of obstacles density. Diffusion coefficient is calculated from the plot of the particle MSD versus time when its dynamics becomes of diffusion type at long enough times (see the inset of Fig. 1). Reduced diffusion coefficient of the spherical particle versus obstructed volume fraction, averaged over 10 realizations of the system for each value of \(\phi\) is shown in Fig. 1. Examples of functions suggested for \(\phi\) dependence of \(D\) such as \(\tilde{D} = (1 - \phi)^{1/2}\) form Ref. [20], \(\tilde{D} = 1/(1 + \phi/2)\) from Ref. [2] and \(\tilde{D} = (1 - \phi)^{2/3}\) form Ref. [27] are also shown in this figure. As it can be seen, the best fitted function is a power law function of available volume, \(1 - \phi\), with an exponent \(b = 0.86\). The next closer function is the prediction of available volume theory [27]. Our data points are considerably far from that of Ref. [2] at high values of \(\phi\). As we checked by running the simulation with the same configuration of the obstacles as of Ref. [2], this difference doesn’t originate from obstacles configuration. This difference may be because of the fact that studying the diffusion phenomena in the presence of obstacles by lattice and continuous-space methods gives different results [7]. Note that the difference between our results and those of Ref. [27] originates from the fact that we have not used explicit fluid particles in our simulations. \(D_0\) in our work is constant and does not depend on fluid density or free volume fraction. In the case of Ref. [27] however, \(D_0\) depends on the fluid density (Eq. 6 of Ref. [27]).

B. Brownian diffusion of rod-like macromolecule in the presence of spherical obstacles

In simulations of the Brownian motion of rod-like polymers in the presence of spherical obstacles we use Rouse dynamics. Accordingly, hydrodynamic interactions are not considered and in the absence of obstacles friction coefficient is not direction dependent. Anisotropy in dynamics of these macromolecules originate solely from obstruction effects of the obstacles. After equilibration of the system for each value of obstructed volume fraction, \(\phi\), we record the position of the polymer center of mass and its orientation (a unit vector parallel to the polymer axis) at all simulation time steps. From trajectory
of the center of mass and time dependence of polymer orientation we calculate diffusion coefficient and probe orientational relaxation of the polymer. Reduced diffusion coefficient of the center of mass versus \( \phi \) for four polymers of different length are shown in Fig. 2. These diffusion coefficients are obtained from time dependent MSD of the polymers center of mass, two samples of which are shown in Fig. 3. Considering that functionality of dependence of the diffusion coefficient on the obstructed volume fraction is an important question in the subject of obstructed diffusion, we search this functionality here. Our results show that this dependence in the case of rod-like polymers as well as spherical particle can be reasonably described by a power law function of available volume fraction, \((1 - \phi)^b\), in which the value of the exponent \(b\) depends on the length of the polymer. It has already been suggested that obstructed diffusion coefficient can be written as a function of a single parameter, namely the available volume fraction [27]. As it is shown in the inset of Fig. 2 \(b\) grows linearly with increasing the polymer length, \(N\), and becomes saturated. The function for \(\phi\) dependence of \(\tilde{D}\) suggested by Mackie and Mearres [1],

\[
\tilde{D} = \frac{(1 - \phi)^2}{(1 + \phi)^2},
\]

is also plotted as solid line in Fig. 2. This function is quite far from spherical particle and short polymers data. It is close to the data of long polymers of lengths \(N = 17\) and \(N = 21\). Noticeable dependence of \(\tilde{D}_{\text{av}}\) on polymer length which can be seen in this figure is quite different from the case of flexible polymers which is reported in ref. [13]. In a crowded environment that diffusion dynamics of individual monomers is slow relative to the case with no obstacles, diffusion coefficient of a flexible polymer is also diminished by the same factor as monomers diffusion coefficient. In this case, the polymer reduced diffusion coefficient becomes independent of its length. In the case of rod-like polymers however, the monomers have to obey whole polymer dynamics because of its rigidity. In this case longer polymers experience stronger obstruction because of stronger spatial hindrance and the polymer diffusion coefficient considerably depends on the polymer length. Dependence of flexible polymers diffusion coefficient in disordered porous material on matrix volume fraction when numerous polymers diffuse simultaneously has been already reported [14].

In the plot of center of mass MSD versus time in logarithmic scales, Fig. 3 at \(\phi = 0\) in addition to ballistic and diffusion regimes which correspond to linear parts of slopes 2 and 1, respectively, a third semi linear region can be seen. In this region velocity autocorrelation function is not yet vanished and the diffusion regime is not yet started. As it is shown in Fig. 3 another linear regime in addition to ballistic and diffusion regimes can be seen in which velocity autocorrelation function is vanished but the slope of fitted line differs from unity. This region corresponds to anomalous diffusion of the polymer over a time interval during its dynamics. Our results show that duration of anomalous diffusion of the rod-like polymer increases rapidly with increasing its length and the value of the obstructed volume fraction, \(\phi\). In the inset of Fig. 3 time length of anomalous diffusion regime of the polymer, \(\tau_a\), versus its length at three different values of \(\phi\) are shown. These times are roughly obtained from our MSD data as the time interval in which data points are clearly out of two lines of slopes 2 and 1 and the semi linear part in which velocity autocorrelation function is not yet vanished (see main part of Fig. 3). As it can be seen, the value of \(\tau_a\) changes its order of magnitude with increasing the strength of obstruction, namely the value of \(\phi\) and the length of the polymer, \(N\). Increasing of the duration of anomalous diffusion regime with increasing the obstructed volume fraction has also been reported already in the context of particle diffusion in quenched media (see for example refs. [3, 4]).

To investigate anisotropy in diffusion dynamics of rod-like polymers in strongly obstructed conditions, a sample of which is shown in Fig. 4 we calculate diffusion coefficients \(D_{\parallel}\) and \(D_{\perp}\) in directions parallel and perpendicular to the polymer axis, respectively. It is done by decomposing displacement of the polymer center of mass in each time step into two parts, parallel and perpendicular to its axis. For a rod-like diffusing object it is
known that

$$D_{cm} = \frac{D_{||} + 2D_{\perp}}{3} \tag{6}$$

and in the reptation regime where $D_{\perp} \approx 0$, this relation becomes $D_{cm} \approx \frac{1}{3}D_{||}$. For a rod-like polymer consisting of $N = 17$ monomers, $D_{||}$ and $D_{\perp}$ are shown as functions of $\phi$ in Fig. 5. With increasing the value of $\phi$, it can be seen that $D_{\perp}$ vanishes meaning that the polymer dynamics becomes of reptation type. It is known in polymer physics [28] that despite the Rouse dynamics in polymer physics, the polymer dynamics becomes of reptation type. It is known in polymer physics [28] that despite the Rouse dynamics in the case of flexible polymers for which a weak increasing and decreasing function of $\phi$ showing that the polymer dynamics crosses over to the reptation type.

In conclusion, MD simulation study of the Brownian diffusion of a particle and rod-like polymers in the presence of randomly distributed spherical obstacles showed that: 1- Obstructed volume fraction dependence of the reduced diffusion coefficient of a spherical particle, obtained from our off lattice MD simulations differs from that of lattice based study of obstructed random walk. 2- Reduced diffusion coefficient of both rod-like polymers and spherical particle have a power law dependence on the available volume fraction. The exponent of the power law function in the case of rod-like polymers is an increasing and saturating function of the polymer length. 3- Despite the case of flexible polymers for which a weak
dependence of the reduced diffusion coefficient on the obstructed volume fraction has been reported, this dependence is noticeably strong in the case of rod-like polymers. 4- Obstructed diffusion of rod-like polymers is observed that is anomalous at short time scales. Time length of the anomalous diffusion regime is of the same order of the polymer orientational relaxation time and is a rapidly increasing function of both the polymer length and the obstructed volume fraction. 5- With increasing the density of obstacles, diffusion dynamics of rod-like polymers is observed that crosses over from Rouse to reptation type.

Although MD simulation of rod-like polymers as presented here is too time consuming because of using numerous potentials, such simulations don’t suffer from dependence of results on the selected lattice and can give better results. Specially, with overdamped dynamics of diffusing particle and working with constant temperature, the obstruction effect of the obstacles is considered very well.

The main difference between dynamics of flexible polymers and that of semiflexible or rod-like polymers comes from anisotropy in the shape of stiff polymers. Clearly the effects of anisotropic shape of a macromolecule on its dynamics becomes more intense in the presence of obstacles. Dynamics of a flexible polymer in the presence of obstacles is dominantly affected by obstruction of monomers dynamics alone. However, in the case of stiff polymers in addition to obstruction effect of the obstacles on the monomers, topological hindrance originated from polymer stiffness also plays an important role. Strong dependence of diffusion coefficient of rod-like polymers on the obstructed volume fraction relative to flexible polymers and existence of anomalous diffusion regime in dynamics of these polymers are consequences of above mentioned difference.

Analytical approach to obstructed diffusion of rod-like polymers seems a challenging problem. Taking into account the size of the obstacles and non zero diameter of the polymer in obtaining dependence of diffusion coefficient on obstructed volume fraction is not straightforward and an easy task.

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[1] J. S. Mackie and P. Meares, Proc. R. Soc. Lond., A 232, 498 (1955).
[2] J-F. Mercier and G.W. Slater, J. Chem. Phys. 113, 9109 (2000).
[3] M. J. Saxton, Biophys. J. 66, 394-401 (1994).
[4] M. J. Saxton, Biophys. J. 66, 1250-1262 (1996).
[5] A. Wedemeier, H. Merlitz, and J. Langovski, Europhys. Lett. 88, 38004 (2009).
[6] B. Amsden, Macromolecules 31, 8382 (1998).
[7] B.J. Sung and A. Yethiraj, J. Chem. Phys. 128, 054702 (2008).
[8] A. Baumgaertner and M. Muthukumar., J. Chem. Phys. 87, 3082 (1987).
[9] M. Muthukumar and A. Baumgaertner., Macromolecules 22, 1937-1941 (1989).
[10] M. Muthukumar and A. Baumgaertner., Macromolecules 22, 1941-1946 (1989).
[11] V. Yamakov and A. Milchev, Phys. Rev. E 56, 7043 (1997).
[12] V. Yamakov and A. Milchev, Phys. Rev. E 55, 1704 (1997).
[13] K. Avramova and A. Milchev, Eur. Phys. J. E 7, 65 (2002).
[14] R. Chang, A. Yethiraj, J. Chem. Phys. 126, 174906 (2007).
[15] Y. Han, A. M. Alsayed, M. Nobili, J. Zhang, T. C. Lubensky, and A. G. Yodh., Science 314, 626 (2006).
[16] L. Onsager, Ann. N.Y. Acad. Sci. 51, 627 (1949).
[17] G. Cinacchi and L. De Gaetani., J. Chem. Phys. 130, 144905 (2009).
[18] H. Fazli, M.R. Kolahchi, and R. Golestanian, Phy. Rev. E 72, 011805 (2005).
[19] S. Mohammadinejad, H. Fazli, and R. Golestanian, Soft Matter 5, 1522 (2009).
[20] A. J. Moreno and W. Kob., J. Chem. Phys. 121, 380-386 (2004).
[21] Y. Tao, W. K. den Otter, J. T. Padding, J. K. G. Dhont, and W. J. Briels., J. Chem. Phys. 122, 244903 (2009).
[22] F. Hofling, T. Munk, E. Frey, and T. Franosch., Phys. Rev. E 77 060904, (2008).
[23] A. Baskaran, and M. C. Marchetti., Phys. Rev. Lett. 101, 268101 (2008).
[24] H.J. Limbach, A. Arnold, B.A. Mann, C. Holm, Comp. Phys. Communications 174, 704 (2006).
[25] G.S. Grest, K. Kremer, Phys. Rev. A 33, 3628 (1986).
[26] G. Ilgenfritz and F. Runge, Physica A 181, 69 (1995).
[27] J. Mittal, J.R. Errington, and T.M. Truskett, Phys. Rev. E 74, 040102 (2006).
[28] M. Rubinstein and R. Colby, Polymer Physics (Oxford University Press Inc., New York, 2003).