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Diffusion Mode Transition between Gaussian and Non-Gaussian of Nanoparticles in Polymer Solutions

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Abstract The dynamic density functional theory is applied to study the diffusion of nanoparticles in polymer solutions, in which different diffusion modes have been identified by exploiting the density and free energy evolutions. Under the condition of low polymer concentration, diffusion is controlled by particle free motion with a normal Gaussian type. As the concentration increases, the non-Gaussian behavior can be observed when the particle size is comparable to the correlation length of polymer chain. Particles need to penetrate through a cage and overcome an entropic barrier, where the hopping and the model-coupling diffusion coexist. Further increase of polymer concentration can result in complete restriction of the particle by surrounding polymer segments. In this case, the non-Gaussian process fades away, and particle diffusion is controlled by Rouse dynamics of polymer chains with the generalized Gaussian characteristics.

Keywords Nanoparticle; Polymer solution; Diffusion modes; Driving force; Dynamic density functional theory

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INTRODUCTION

The diffusion of nanoparticles in polymer solutions is of broad interests in physics, material science, cell biology, and medicine.^[1–4] In simple liquids, nanoparticle diffusion follows the well-known Stokes-Einstein (SE) relation.^[5] In some polymer solutions, however, experiments indicated that the motions of nanoparticles are significantly faster than the predicted limit given by the SE relation,^[6–9] and the radius of gyration, R_g , of polymer chains is the crossover length scale for the nanoparticles experiencing nanoviscosity or macroviscosity.^[10] These results provided global knowledge on how polymer structure and additive properties can influence nanoparticle diffusion. In fact, the situations are more complex. There are several lengths and interaction scales such as the radius of nanoparticle, the segment size and correlation length of polymer chain, as well as the interactions of particle-polymer and polymer-polymer. Moreover, the dynamical behavior is strongly affected by the solvent-induced hydrodynamic interactions.^[11,12] It is rather complicated to understand the diffusion of different nanoparticles in polymer solutions, because the competing mechanism of nanoparticles and polymer chains remains still an open and difficult problem.

Over the past decades, there have been many pioneer investigations devoted to understanding the dynamics of nanoparticles in polymer matrixes to optimize the comprehensive properties and to facilitate their processing.^[13–18] More importantly, a variety of theoretical models have been proposed to correlate these factors with diffusion processes. For instances, de Gennes and co-workers identified three diffusion modes in semidilute solutions depending on solvent viscosity and macroscopic viscosity.^[19,20] If the particles are small enough and can slip smoothly through the polymer mesh, the diffusion is mainly controlled by the solvent viscosity. In the opposite limit, particles are restricted by polymer network, thus the diffusion is governed by the macroscopic viscosity of the solution. In these cases, nanoparticle diffusion can be described by the SE equation. In the transition regime, however, particle diffusion can proceed in a particularly difficult way, and the SE equation is no longer suitable. Phillies and Cukier offered a model of probing diffusion and argued that hydrodynamic interactions dominate over topological constraints and proposed an equation of $D/D_0 \sim \exp(-\beta\phi^p)$.^[21,22] Cai *et al.*^[23] proposed a scaling theory by considering the effects of chain architecture and constraint on the mobility of nanoparticles, where the polymer mesh size was transferred to R_g . If the particle size R_0 is smaller than R_g , the particle motion is implicated by polymer segments rubbing the nanoparticle surface, which yields $D \propto 1/R_0^3$. Otherwise the diffusion is dominated by the hydrodynamic contribution given as $D \propto 1/R_0$. The aforemen-

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tioned endeavors fitted a wide concentration range of polymers with different configurations,^[24–26] but none of these models considered explicitly the microscopic characteristics of nanoparticle dynamics. In recent years, Schweizer *et al.* developed a microscopic statistical mechanical theory for predicting the diffusion coefficients of nanoparticle in unentangled and entangled polymer chains.^[27,28] They found that the hopping diffusivity is generally smaller than the SE prediction. These investigations aimed at testing fundamental idea of nanoparticle diffusion and provided some insights regarding the dynamical modes of free diffusion, hopping diffusion, model-coupling diffusion, and Rouse dynamic diffusion. However, these investigations cannot directly show the non-Gaussian diffusion or the transition from Gaussian to non-Gaussian.

In this work, we try to present a quantitative and comprehensive understanding of particle diffusion in polymer solutions using the dynamic density functional theory (DDFT). We pay more attention to the co-evolution of microscopic structure induced by the driven force from density and free energy gradients. In the theoretical model, the free energy functional is integrated into Smoluchowski equation, which has been successfully applied to study self-assembly,^[29] Brownian dynamics of dilute colloidal suspensions,^[30–34] and polymer diffusion.^[35] It is obvious that this theory can reflect the details of density fluctuation relaxation on intermediate time and length scales to decipher the driving force for particle motion.

We firstly study the pure polymer solutions to obtain the dynamics of polymer chains with special consideration about the shifts of connected segments during time evolution. Sub-

sequently, we derive the time-dependent density and free energy for a test nanoparticle in different polymer solutions to identify the effects of particle size, chain concentration, and interaction strength of particle-polymer on the transport of the test particle. Finally we show the influence of particle volume fraction on diffusion dynamics. To test the reliability of the theoretical approach, some predicted diffusion coefficients are compared with the reported experimental data.^[10]

THEORY AND EQUATIONS

For description of nanoparticle diffusion, we combine the DDFT approach with the Percus' test particle limit.^[36] Accordingly, we treat the system as a ternary mixture containing species *o* (test nanoparticle), *n* (nanoparticle), and *p* (polymer). Density evolution of the test particle can represent the motion behavior of particles, whereas the density evolutions of particles and polymers around the test particle provide the driving force. At initial stage, the density distributions of particles and polymers surrounding the test particle are related to the radial distribution functions. The polymer chain is modeled as the tangent spheres with diameter σ_p , the chain length is set as 1000 to ignore the tail effect of polymer chain, and the overlap concentration is about 4.0^{-3} . The nanoparticles are modeled as spheres with diameter σ_n . The interaction potentials of particle-particle and polymer-polymer are given by the Lennard-Jones potential. For the interaction of particle-polymer, however, the size ratio of particle to polymer segment is exceedingly large. Description of such highly asymmetric interaction can be simplified as^[37–39]

$$v_{np}(r) = \begin{cases} \infty & r - \Delta_{np} < 2^{1/6}\sigma_p \\ 4\varepsilon_{np}[(\sigma_p/(r - \Delta_{np}))^{12} - (\sigma_p/(r - \Delta_{np}))^6] & 2^{1/6}\sigma_p \leq r - \Delta_{np} \leq r_s \\ a_{np}(r - \Delta_{np} - r_c)^2 + b_{np}(r - \Delta_{np} - r_c)^3 & r_s < r - \Delta_{np} < r_c \\ 0 & r_c < r - \Delta_{np} \end{cases} \quad (1)$$

with $\Delta_{np} = (\sigma_n - \sigma_p)/2$, $r_s = (26/7)^{1/6}\sigma_n$, $r_c = (67/48)r_s$, $a_{np} = -(24192/3211)(\varepsilon_{np}/r_s^2)$, and $b_{np} = -(387082/61009)(\varepsilon_{np}/r_s^3)$. Here r and ε are the separation and Lennard-Jones well depth.

We think the motion of the test particle is induced by the collective density fluctuation relaxation, including the local density fluctuation of particle and polymer and Rouse dynamics of polymer chains, $D_{\text{total}} = D_{\text{local}} + D_{\text{Rouse}}$.^[40] In particular, the hydrodynamic contributions arising from the solvent-flow mediated interactions of particle-particle and particle-polymer are integrated into the density and energy evolution. Since Rouse dynamics has been well addressed in our previous work,^[35] here we pay more attention to the local density fluctuation.

In general, the time-dependent full probability density distribution $P(\mathbf{r}^N, t)$ for N interacting spheres at positions $\mathbf{r}^N = \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ and time t can be approximately represented by the Smoluchowski equation

$$\frac{\partial P(\mathbf{r}^N, t)}{\partial t} = \sum_i \sum_j \nabla_i \cdot \mathbf{D}_{ij}(\mathbf{r}^N) \cdot \left[\nabla_j + \frac{\nabla_j U(\mathbf{r}^N)}{k_B T} \right] P(\mathbf{r}^N, t) \quad (2)$$

where $k_B T$ is the thermal energy, $\mathbf{D}_{ij}(\mathbf{r}^N)$ is the configuration-dependent diffusion tensor, $U(\mathbf{r}^N)$ is the summarization of the pair interaction potential $v_{kl}(\mathbf{r}_k, \mathbf{r}_l)$ with $U(\mathbf{r}^N) = \frac{1}{2} \sum_{k=1}^N \sum_{l \neq k}^N v_{kl}(\mathbf{r}_k, \mathbf{r}_l)$. The hydrodynamic interactions mediated

$\mathbf{D}_{ij}(\mathbf{r}^N)$ is given by^[30]

$$\mathbf{D}_{ij}(\mathbf{r}^N) \approx D_{i,0} \mathbf{1}_{ij} + D_{i,0} [\delta_{ij} \sum_{l \neq i}^N \boldsymbol{\omega}_{11}(\mathbf{r}_i - \mathbf{r}_l) + (1 - \delta_{ij}) \boldsymbol{\omega}_{12}(\mathbf{r}_i - \mathbf{r}_j)] \quad (3)$$

where δ_{ij} is the Kronecker's delta, $D_{i,0}$ is the diffusion constant for the i^{th} sphere in good solvent, $\boldsymbol{\omega}_{11}$ and $\boldsymbol{\omega}_{12}$ represent the self and distinct hydrodynamic tensor.^[41]

By integrating Eq. (2) with $N \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_{N_i}$ for a given species i with N_i interactive spheres, the equation for the time-dependent density in the multiple-component system can be written as

$$\frac{\partial \rho_i(\mathbf{r}, t)}{\partial t} = D_{i,0} \nabla \cdot [\mathbf{j}_{i,1} + \mathbf{j}_{i,2} + \mathbf{j}_{i,3}] \quad (4)$$

with the current densities

$$\mathbf{j}_{i,1} = k_B T \nabla \rho_i(\mathbf{r}, t) + \sum_j \int d\mathbf{r}' \rho_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', t) \nabla \sum_{\mathbf{r} \neq \mathbf{r}'} v_{ij}(\mathbf{r}, \mathbf{r}') \quad (5)$$

$$\mathbf{j}_{i,2} = \sum_j \int d\mathbf{r}' \boldsymbol{\omega}_{11}(\mathbf{r} - \mathbf{r}') \cdot \left\{ k_B T \nabla \rho_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', t) + \nabla \sum_{\mathbf{r}' \neq \mathbf{r}} v_{ij}(\mathbf{r}, \mathbf{r}') \rho_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', t) + \sum_k \int d\mathbf{r}'' \rho_{ijk}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', t) \nabla \sum_{\mathbf{r}'' \neq \mathbf{r}'} v_{ij}(\mathbf{r}', \mathbf{r}'') \right\} \quad (6)$$

$$\mathbf{j}_{i,3} = \sum_j \int d\mathbf{r}' \boldsymbol{\omega}_{12}(\mathbf{r} - \mathbf{r}') \cdot \left\{ k_B T \nabla \rho_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', t) + \nabla \sum_{\mathbf{r}' \neq \mathbf{r}} v_{ij}(\mathbf{r}, \mathbf{r}') \rho_{ij}^{(2)}(\mathbf{r}, \mathbf{r}', t) + \sum_k \int d\mathbf{r}'' \rho_{ijk}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', t) \nabla \sum_{\mathbf{r}'' \neq \mathbf{r}'} v_{ij}(\mathbf{r}', \mathbf{r}'') \right\} \quad (7)$$

where $\mathbf{j}_1$ is proportional to the thermodynamic force that is independent of the hydrodynamic interactions. In the opposite, $\mathbf{j}_2$ and $\mathbf{j}_3$ are from the solvent-flow mediated hydrodynamic interactions. The distinct hydrodynamic tensor $\boldsymbol{\omega}_{12}$ is approximated by the Rotne-Prager expression,^[42] and the self-term $\boldsymbol{\omega}_{11}$ is trivial and neglected.^[30] As a consequence, the DDFT equation can be generalized as the following form

$$\frac{\partial \rho_i(\mathbf{r}, t)}{\partial t} = D_{i,0} \nabla \left[\rho_i(\mathbf{r}, t) \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho_i(\mathbf{r}, t)} + \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}', t) \boldsymbol{\omega}_{ij}(\mathbf{r} - \mathbf{r}') \cdot \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho_i(\mathbf{r}', t)} \right], \quad i \in [o, n, p] \quad (8)$$

where the two-body density $\rho^{(2)}(\mathbf{r}, \mathbf{r}', t)$ can be simplified as $\rho^{(2)}(\mathbf{r}, \mathbf{r}', t) = \rho(\mathbf{r}, t) \rho(\mathbf{r}', t) g(|\mathbf{r} - \mathbf{r}'|)$.^[43] $F[\rho(\mathbf{r}, t)]$ accounts for the intrinsic Helmholtz free energy of the system.

For the particles and polymer chains surrounding the test particle, the free energy can be written as

$$\beta F[\rho(\mathbf{r}, t)] = \sum_{i \in [o, n, p]} \int d\mathbf{r} \rho_i(\mathbf{r}, t) [\ln \rho_i(\mathbf{r}, t) - 1] + \beta F_{\text{ex}}[\rho(\mathbf{r}, t)] \quad (9)$$

where the first term on the right-hand side is the free energy for ideal gas while $F_{\text{ex}}[\rho(\mathbf{r}, t)]$ accounts for the excess free energy due to the contribution of hard-sphere repulsion, dispersive attraction, and chain connectivity. According to the fundamental measure theory,^[44] the hard-sphere part is written as

$$\beta F_{\text{hs}}[\rho(\mathbf{r}, t)] = \int d\mathbf{r} \Phi[n_\gamma(\mathbf{r}, t)] \quad (10)$$

and $\Phi[n_\gamma(\mathbf{r})]$ is the free energy density which stems from the modified fundamental theory including both the scalar and vector contributions^[45]

$$\Phi[n_\gamma(\mathbf{r}, t)] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \mathbf{n}_{V1} \cdot \mathbf{n}_{V2}}{1 - n_3} + \frac{1}{36\pi} \left(n_3 \ln(1 - n_3) + \frac{n_3^2}{(1 - n_3)^2} \right) \frac{n_2^3 - 3n_2 \mathbf{n}_{V2} \cdot \mathbf{n}_{V2}}{n_3^3} \quad (11)$$

where $n_\gamma(\mathbf{r}, t)$ with $\gamma = 0, 1, 2, 3$, V_1 , V_2 are the weighted densities, and can be calculated by^[46]

$$n_\gamma(\mathbf{r}) = \sum_{i \in [o, n, p]} \int d\mathbf{r}' \rho_i(\mathbf{r}') w_i^\gamma(\mathbf{r}' - \mathbf{r}) \quad (12)$$

Here the weight functions are given as $w_i^2(\mathbf{r}) = \delta(d_i/2 - |\mathbf{r}|)$, $w_i^3(\mathbf{r}) = \theta(d_i/2 - |\mathbf{r}|)$, $w_i^0(\mathbf{r}) = w_i^2(\mathbf{r})/\pi d_i^2$, $w_i^1(\mathbf{r}) = w_i^2(\mathbf{r})/2\pi d_i$, $w_i^{V2}(\mathbf{r}) = \mathbf{r} \delta(d_i/2 - |\mathbf{r}|)/|\mathbf{r}|$, and $w_i^{V1}(\mathbf{r}) = w_i^{V2}(\mathbf{r})/2\pi d_i$, and $\delta(\mathbf{r})$ and $\theta(\mathbf{r})$ denote the Dirac delta function and Heaviside step function, respectively.

The attractive contribution due to the attractive interactions can be integrated into

$$\beta F_{\text{att}}[\rho(\mathbf{r}, t)] = \sum_{i \in [o, n, p]} \sum_{j \in [o, n, p]} \beta F_{\text{att},ij}[\rho(\mathbf{r}, t)] \quad (13)$$

In the considered systems, the nanoparticle-nanoparticle and polymer-polymer attractive interactions are symmetric, thus $F_{\text{att},ii}[\rho(\mathbf{r})]$ can be expressed as^[47]

$$F_{\text{att},ii}[\rho(\mathbf{r})] = \int d\mathbf{r}' \rho_i(\mathbf{r}) a_{\text{att}}[\bar{\rho}_i(\mathbf{r})] d\mathbf{r}' \quad (14)$$

in which a_{att} is the free energy per particle from attractive contribution, and can be given by a sum of perturbation terms.^[48] The weighted density $\bar{\rho}_i(\mathbf{r})$ is given by^[49,50]

$$\bar{\rho}_i(\mathbf{r}) = \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_{\text{att}}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (15)$$

with

$$\omega_{\text{att}}(r) = \frac{v_{ii}^{\text{att}}(r)}{\int d\mathbf{r} v_{ii}^{\text{att}}(r)} \quad (16)$$

$\omega_{\text{att}}(r)$ is the weight function, and $v_{ii}^{\text{att}}(r)$ is the attractive part of Lennard-Jones interaction.

For the attractive free energy arising from the asymmetric interaction of particle-polymer, the weighted density approximation is no longer suitable. For simplicity, $F_{\text{att},ij}[\rho(\mathbf{r}, t)]$ can be given by

$$\beta F_{\text{att},ij}[\rho(\mathbf{r}, t)] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_i(\mathbf{r}, t) \rho_j(\mathbf{r}', t) v_{\text{np}}^{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \quad (17)$$

$$v_{\text{np}}^{\text{att}}(r) = \begin{cases} -\varepsilon_{\text{np}} & r - \Delta_{\text{np}} < 2^{1/6} \sigma_{\text{p}} \\ v_{\text{np}}(r) & r - \Delta_{\text{np}} \geq 2^{1/6} \sigma_{\text{p}} \end{cases} \quad (18)$$

The free energy contribution from the molecular connectivity is based on the associating theory^[51]

$$\beta F_{\text{chain}}[\rho(\mathbf{r}, t)] = \frac{1}{2} \int d\mathbf{r}' \sum_{\alpha=1} \rho_\alpha(\mathbf{r}', t) \sum_{\alpha'}^{\{\alpha\}} \left(1 - \ln \left[\int d\mathbf{r}'' \frac{\delta(|\mathbf{r}' - \mathbf{r}''| - \sigma_{\alpha\alpha'})}{4\pi\sigma_{\alpha\alpha'}^2} y_{\alpha\alpha'}(\{\xi_\gamma\}) \rho_{\alpha'}(\mathbf{r}'', t) \right] \right) \quad (19)$$

where α' denotes the neighboring associating point which bonds with site α , $y_{\alpha\alpha'}(\{\xi_\gamma\})$ is the reference fluid cavity correlation function between α and α' ,^[52]

$$y_{aa'}(\{\xi_y\}) = \frac{1}{1-\xi_3} + \frac{3\sigma_a\sigma_{a'}}{\sigma_a + \sigma_{a'}} \frac{\xi_2}{(1-\xi_3)^2} + 2\left(\frac{\sigma_a\sigma_{a'}}{\sigma_a + \sigma_{a'}}\right)^2 \frac{\xi_2^2}{(1-\xi_3)^3} \quad (20)$$

$$\xi_y(\mathbf{r}) = \sum_{a \in [n,p]} \int d\mathbf{r}' \frac{\sigma_a^y}{8\sigma_a^3} \theta(\sigma_a - |\mathbf{r} - \mathbf{r}'|) \rho_a(\mathbf{r}') \quad (21)$$

For the test particle, however, the interaction within the test particle no longer exists. In this limit, the excess free-energy given by Eq. (9) can be simplified as

$$\beta F_{\text{ex},o}[\rho(\mathbf{r},t)] = \beta F_{\text{ex}}[\rho(\mathbf{r},t)] - \beta F_{\text{ex}}[\rho_o(\mathbf{r},t)] \quad (22)$$

For the DDFT calculation, the initial density distribution in an equilibrium state for the species o is given by $\rho_o(\mathbf{r},0) = \delta(\mathbf{r}) \approx G(\mathbf{r},\alpha) = (\alpha/\pi)^{3/2} \exp(-\alpha|\mathbf{r}|^2)$. For species of n and p , the initial density distributions are $\rho_i(\mathbf{r},0) = \rho_{i,b} g_i(|\mathbf{r}|)$. Along with the time evolution, we assume the coordinate system to be fixed in the space. To determine the dynamic behavior, we integrate Eq. (8) forward in time using the Euler-forward algorithm with time steps of $dt = 10^{-5}\tau_B$ and $\tau_B = \sigma_p^2/D_{o,0}$ as the unit timescale. The partial derivatives are calculated numerically, and the spatial integrations are performed using the trapezoidal rule with $dr = 0.01\sigma_p$. Since D_0 cannot be obtained by the theory itself, we derive it by simulating one particle in good solvent using the large scale atomic/molecular massively parallel simulator (LAMMPS),^[53] in which the real units are used to ensure the dimensional quantities. For simplicity, we assume polyethylene chain as the model polymer in the whole theoretical calculations with the transferable potentials for phase equilibria united-atom (TraPPE-UA) force field.^[54] Meanwhile, nanoparticles are modeled as LJ spheres with the diameter σ_n and interaction strength ε_n . To generate the initial configurations, a particle is placed in the center of a large periodic box, and then some good solvent molecules are added. The influence of good solvent molecules is neglected in theoretical calculations. In simulation systems, however, the solvent molecules exist. The total packing density of the system is given as 0.8, a general liquid density. The system is equilibrated for at least 10^6 steps for each simulation in the NVT ensemble at given temperature. When the average fractional difference of the radial distribution functions of solvent between the simulation and theoretical yields is less than 0.01, the equilibrium is achieved. The equilibrium structure is used as the initial configuration for further simulation of 10^6 molecular dynamics steps and mean square displacement (MSD) $\langle \Delta R^2 \rangle$ of the nanoparticle per 1000 steps is output. Finally, the diffusion coefficient is determined by the Einstein relation, $D_{o,0} = \lim_{t \rightarrow \infty} \langle \Delta R^2 \rangle / (6t)$. During each molecular dynamics run, a time step of 1.0 fs is used with a multiple time step integrator (RESPA).^[55] In calculation of the dynamic evolution of the free energy function, the dependence of $\rho_i(r,t)$ is only on the distance to the origin $r = |\mathbf{r}|$. The asymptotic behavior of the species o , n , and p in the thermodynamic limit is given by

$$\lim_{r \rightarrow \infty} \rho_o(r,t) = \lim_{t \rightarrow \infty} \rho_o(r,t) = 0 \quad (23)$$

$$\lim_{r \rightarrow \infty} \rho_i(r,t) = \lim_{t \rightarrow \infty} \rho_i(r,t) = \rho_{i,b}, \quad i \in [n,p] \quad (24)$$

The partial derivatives of the density and energy functions need to be considered as the spherical symmetric form. For example, the partial derivative of chemical potential

$$\mu_i(\mathbf{r},t) = \frac{\delta F[\rho(\mathbf{r},t)]}{\delta \rho_i(\mathbf{r},t)} \text{ can be calculated by}$$

$$\nabla \mu(\mathbf{r},t) = \frac{\partial}{\partial r} \mu(r,t) = \frac{\mu(r_2,t) - \mu(r_1,t)}{2dr} \quad (25)$$

with $r_1 = r - dr$, and $r_2 = r + dr$. For the density flowing $\mathbf{J}_i(\mathbf{r},t) = \nabla \rho_i(\mathbf{r},t) \nabla \mu_i(\mathbf{r},t)$, the mass conservation should be applied to give

$$\nabla \rho(\mathbf{r},t) \nabla \mu(\mathbf{r},t) = \frac{\partial}{\partial \mathbf{r}} r^2 \rho(r,t) \nabla \mu(r,t) = \frac{r_2^2 \rho(r_2,t) \nabla \mu(r_2,t) - r_1^2 \rho(r_1,t) \nabla \mu(r_1,t)}{2r^2 dr} \quad (26)$$

Accordingly, the hydrodynamic interaction is also calculated in the same method. During the dynamic evolution, the density distributions at time $t_1 = dt$ and $t_n = t_{n-1} + dt$ can be obtained by

$$\rho_i(r,t_1) = \rho_i(r,0) + J_i(r,0)dt \quad (27)$$

and

$$\rho_i(r,t_n) = \rho_i(r,t_{n-1}) + J_i(r,t_{n-1})dt \quad (28)$$

After the derivation of the time-dependent local density distributions of particle and polymer, we can calculate MSD of the test particle from a simple statistical formula $\langle \Delta R^2 \rangle = \int d\mathbf{r} \rho_o(\mathbf{r},t) |\mathbf{r}|^2$. Finally, the local diffusion coefficient D_{local} is determined by the Einstein relation. In a given polymer concentration (ρ_p) system, the correlation length of polymer chain (L_c), defined as the average mesh size, can be simplified as shown in Fig. 1

$$\rho_p \sigma_p^3 = \frac{3\sigma_p^2(L_c + \sigma_p)}{(L_c + \sigma_p)^3} \quad (29)$$

and

$$L_c = \frac{3\sigma_p}{(\rho_p \sigma_p^3)^{1/2}} - \sigma_p \quad (30)$$

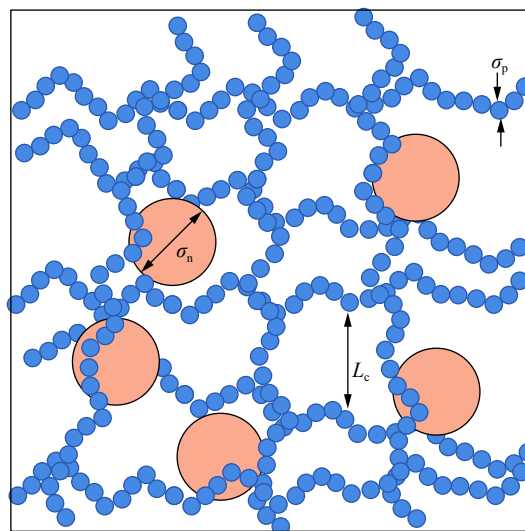


Fig. 1 Schematic visualization of particles in polymer network

RESULTS AND DISCUSSION

Firstly, we consider the test particle with the size of $10\sigma_p$ diffusing in different polymer solutions, which are similar to the experimental systems.^[10] Fig. 2 shows MSDs of the hard-sphere particle related to the local diffusion. At different polymer concentrations, the minimum apparent exponent, $\Delta r^2 \sim t^a$, varies from the free diffusion with $a \sim 1$ to the trapped diffusion with ~ 0.0 . Such phenomenon is associated with the transient trapping and slowing down of particle motion. In addition, no ballistic motion can be seen at short time, because the initial structure is assumed to be in the equilibrium state. Therefore, collisions exist between particle and polymer segments. Under the condition of extremely low overlap concentration ($\rho_p \sigma_p^3 \leq 0.001$), the polymer network has not been formed and particle transport shows a free-style mode. The influence of polymer Rouse dynamics is trivial. As the polymer concentration increases, particle size is comparable to L_c ; the motion slows down since the particle should penetrate the polymer mesh. This is a traditional non-Gaussian process. Finally, the particle is completely restricted by the surrounding polymer chains, and the diffusion behavior is entirely controlled by Rouse dynamics of polymer relaxation.

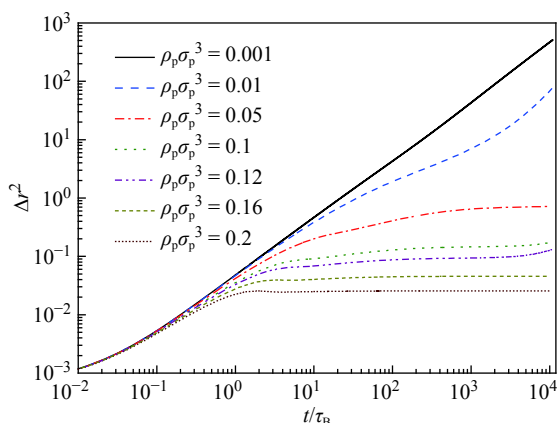


Fig. 2 Mean-squared displacement of nanoparticle ($\sigma_n = 10\sigma_p$) at different polymer concentrations and $T^* = 6.0$

Fig. 3 displays the calculated diffusion coefficients for the local and total density fluctuation relaxations in different polymer solutions. Here a total coefficient includes the local and Rouse diffusions, and the second term is calculated by a simple treatment of Hayakawa and Ichiki,^[56] $D_{\text{Rouse}}(\eta)/D_{\text{dilute}} = (1 - \eta)/[1 + 2\eta + 1.492\eta(1 - \eta)^3]$, where D_{dilute} has been determined in our previous work.^[35] For comparison, the corresponding experimental data are also plotted in the figure. As the polymer solution varies from dilute to semidilute state, the local diffusion coefficient decreases about three orders of magnitude, whereas the total diffusion coefficient decreases about one order. By fitting the values of local diffusion with $D \sim \rho^\nu$, we obtain the exponent $\nu = -2.5$. In contrast, the exponent for the total diffusion coefficient is -1.0 . As the polymer concentration increases, local diffusion declines and finally disappears. When the local diffusion has been strictly constrained,

particle motion is carried by the surrounding polymer segments, showing the Rouse type diffusion. This conclusion is consistent with the previous reports.^[10,23] The exponent ν can be used as a measure to judge the confinement on particle, and lower ν means stronger confinement. The phenomenon is the result of competition between local diffusion and Rouse relaxation. Due to the asymmetrical sizes of large particle and small segment, segments can slip easily through the meshes but particle cannot, which means that the local diffusion is sensitive to polymer concentration. In the regime of $\rho_p \sigma_p^3 \geq 0.004$, the calculated diffusion coefficients are in general agreement with the experimental values,^[10] showing a quantitatively reasonable description of the dynamics of nanoparticle in polymer solutions.

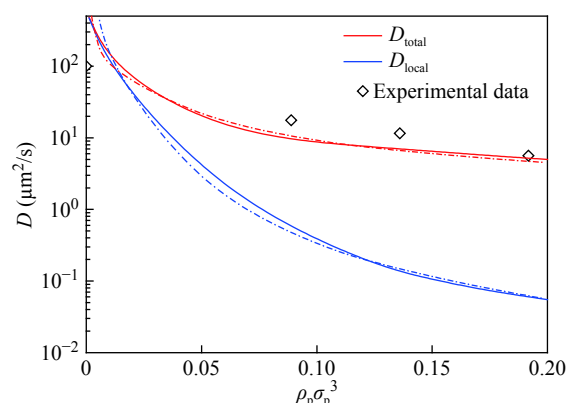


Fig. 3 Local and total diffusion coefficients of the test particle ($\sigma_n = 10\sigma_p$) at different polymer volume fractions with $T^* = 6.0$ as obtained by the theory and reported experiment.^[10] The dash lines are the power law fit with $D \sim \rho^\nu$.

In order to clarify the details of nanoparticle diffusion process, we consider a moderate particle size, since too big or too small particle could not reflect some details. Fig. 4 presents the diffusion of a smaller nanoparticle ($\sigma_n = 5\sigma_p$) in different polymer solutions. The diffusion mode at low polymer concentration is nearly the same as that for larger one, but the diffusion rate increases. In the regime of $0.10 \leq \rho_p \sigma_p^3 \leq 0.15$, one sees an obvious cage effect, first occurring as an inflection point and then as a full-fledged plateau, which is caused by the neighboring cage effect, and has been well addressed in those simple molecule glass systems.^[57,58] Due to the frequent collisions with its neighboring polymer segments, the particle is confined to a small region but then escapes. In the intermediate crossover regime ($0.20 \leq \rho_p \sigma_p^3 \leq 0.30$), the second inflection point and full-fledged plateau emerge, which could arise from the spontaneous elastic fluctuation of polymer chains. This phenomenon has not been discussed by previous experiments or molecular simulations, since the MSD regarding hopping diffusion has not been clearly shown. It means that the test particle has escaped from the surrounding chains, which was reported as an activated hopping process.^[5,6] Once the polymer packing increases up to 0.40, the hopping behavior disappears due to the strong confinement effect. Such effect is also induced by particle size, as shown in Fig. 2.

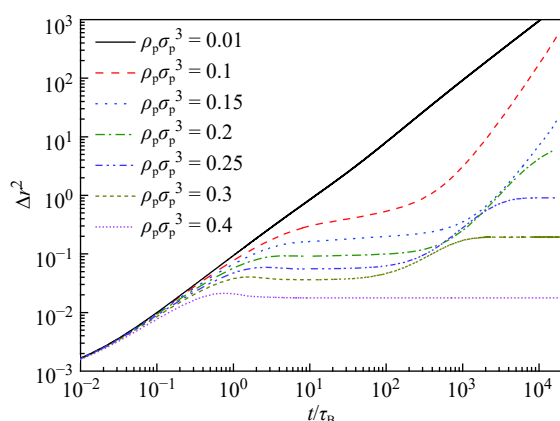


Fig. 4 Mean-squared displacement of particle ($\sigma_n = 5\sigma_p$) with different polymer packing with $T^* = 6.0$

Compared with those macroscopic theoretical models, the current DDFT approach has an obvious advantage of displaying the density evolution during the diffusion process, which offers a visible intuition of diffusion details. As an example, Fig. 5 illustrates the local density relaxation of nanoparticle by means of the time-dependent density distributions. In the “penetrant” regime (Fig. 5a), the particle diffusion displays a pure Gaussian distribution in the initial stage ($t \leq 0.1\tau_B$). In the intermediate stage ($t \approx 5.0\tau_B$), however, the diffusion behavior transfers from Gaussian to non-Gaussian type, where the density distribution can decompose into several Gaussian functions with different peak positions. After a period of time ($t \geq 50.0\tau_B$), the diffusion displays non-Gaussian feature, which is caused by the confinement effects of surrounding polymers. A similar effect observed in gases and liquid crystals has been explained with the mechanism of diffusional hopping.^[59–61] In the intermediate crossover regime ($\rho_p\sigma_p^3 = 0.25$), one can see from Fig. 5(b) that the density distribution can be divided into caged and uncaged parts after $5\tau_B$. In the caged part, the density profiles keep constant, suggesting that the particle is restricted by polymer segments and cannot move. In the uncaged part, the density profiles lose their structure as time evolves, and the particle henceforward diffuses and meets the definition of hopping motion. This phenomenon has not been found in simple molecule systems, where particle shows either caged or uncaged dynamical properties at a long scale time.^[59,60] Fig. 5 offers a direct evidence to explain the two caging-like regimes in Fig. 4.

In order to understand the driving force for particle diffusion in polymer solutions, we present the evolution of total free energy in the system, and correlate the energy with displacement of the test particle. In this way, we can obtain the driving force on the tagged particle by analyzing the spatial derivative. The similar free energy study has been given in Ref. [27] but some approximations have been included. Here we obtain more reasonable results. From Fig. 6, one can identify three regimes based on the free energy evolution. In the free diffusion regime, $F(\Delta r(t))$ decays monotonically with particle displacement. As the polymer concentration increases, an entropic barrier arising from the polymer deple-

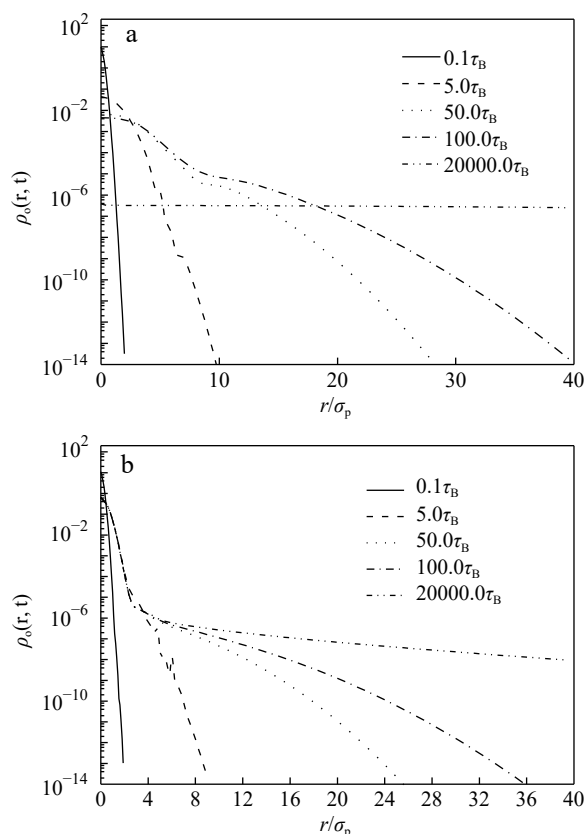


Fig. 5 The density fluctuation relaxation of particle for (a) $\rho_p\sigma_p^3 = 0.10$ and (b) $\rho_p\sigma_p^3 = 0.25$. The ordinate axis in the nanoparticle part shows a logarithmic scale and $T^* = 6.0$.

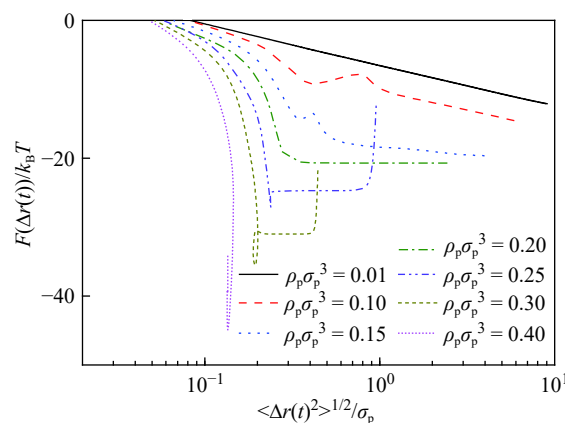


Fig. 6 Dynamic free energy profiles, in units of thermal energy, of the test particle as a function of particle displacement under different polymer concentrations with $T^* = 6.0$

tion can be observed whose location corresponds to the first caging-like regime in Fig. 4. In the regime of $0.10 \leq \rho_p\sigma_p^3 \leq 0.15$, $F(\Delta r(t))$ still decays after hopping over the entropic barrier. The location of the free energy minimum is at $r = \infty$, and the particle can diffuse *via* thermal perturbation. In the intermediate crossover regime ($0.20 \leq \rho_p\sigma_p^3 \leq 0.30$), $F(\Delta r(t))$ cannot over the entropic barrier but shows a plateau in diffusion process. This plateau reveals that the particle motion does not influence the total free energy, showing an inertial motion mode. As for polymer, the plateau implies a

reconstitution process of polymer network, and the resistance of network matches the thermal driving force of particle. By comparing the figure with Fig. 4, one can find that the length of this plateau maps with the second plateau, which means the hopping process is based on the reconstitution of polymer but not the thermal perturbation. Once the polymer packing increases up to 0.40, the plateau disappears and the particle is completely caged. On the other hand, a knot appears at the location of free energy minimum, where the same value of $\langle \Delta r(t)^2 \rangle^{1/2}$ corresponds to two different values of $F(\Delta r(t))$. This knot could be induced by the restrictive effect of surrounding polymer network, where the motion of the test particle has been frozen. Since then, the polymer structure starts to reconstruct due to thermal fluctuation, and hopping diffusion emerges. It is unnecessary to cross over a high free energy barrier given by the initial polymer network. In other words, the hopping diffusion cannot happen once the minimum resistance given by polymer structure reconstruction is larger than the thermal driving force for particle motion.

We note that the non-Gaussian density distribution can be approximately decomposed into two Gaussian functions with $\rho_o(r) = (1 - \phi_{\text{hopping}})G(r, \alpha_0) + \phi_{\text{hopping}}G(r, \alpha_1)$, $\alpha_0 > \alpha_1$. The second item corresponds to the hopping diffusion. Fig. 7 shows the hopping probability, ϕ_{hopping} , as a function of polymer packing. Here ϕ_{hopping} is calculated *via* integrating the density distribution at $100\tau_B$, at which the density distribution has been transferred from Gaussian to non-Gaussian type but has not yet lost the structure characteristics. Under the condition of extremely low polymer concentration, the value of ϕ_{hopping} approaches to zero, which means that the particle can diffuse freely and follow a Gaussian type. As the polymer packing increases up to 0.27, L_c is close to particle size, and the strengthening restrictive effect results in ascending probability of particle hopping. In this regime, the non-Gaussian process gradually strengthens. Further increase of polymer packing, however, leads to the descending probability of hopping diffusion. Once the value of ϕ_{hopping} returns back to zero, the particle can be frozen thoroughly, and the non-Gaussian diffusion no longer occurs. The second

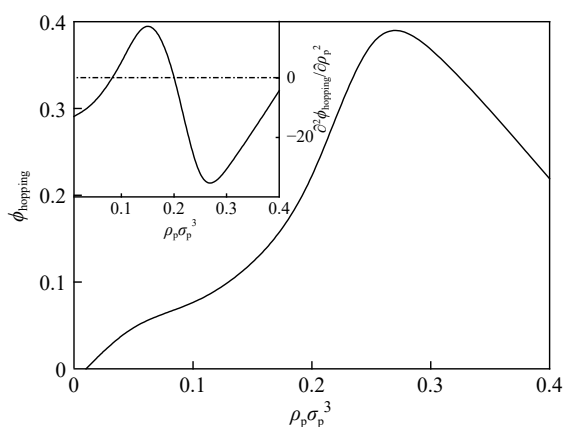


Fig. 7 Hopping probability of particle ($\sigma_n = 5\sigma_p$) as a function of polymer packing at $100\tau_B$. The inset shows the second derivative of ϕ_{hopping} versus polymer packing ($T^* = 6.0$).

derivative of ϕ_{hopping} versus polymer packing is additionally shown in the inset of Fig. 7. One sees two inflection points located at $\rho_p \sigma_p^3 = 0.08$ and $\rho_p \sigma_p^3 = 0.20$. These two inflection points correspond to the prerequisites to producing the first and second cages, as shown in Fig. 4.

Fig. 8 shows the calculated local and total diffusion coefficients of a smaller nanoparticle. The results are no longer in line with the power law fitting. It seems that particle mobility exhibits concentration-dependent behavior controlled by (i) local diffusion *via* thermal perturbation, and (ii) Rouse dynamics *via* polymer flow. The different trends indicate that the local diffusion is inadequate to describe the particle dynamics in semidilute solution ($\rho_p \sigma_p^3 \geq 0.25$), where the contribution of Rouse diffusion to the total diffusion becomes important. For a relatively small particle, the polymer concentration region has been enlarged for the local diffusion.

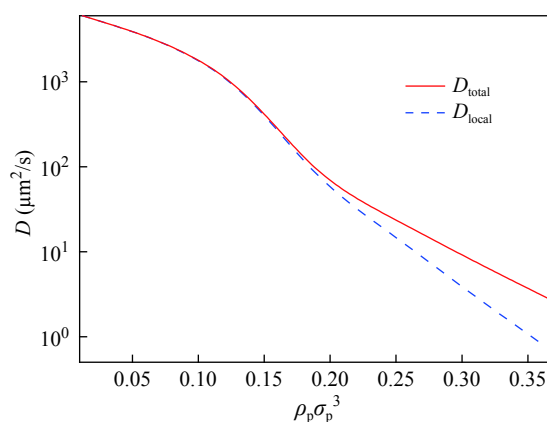


Fig. 8 Diffusion coefficients of nanoparticle ($\sigma_n = 5\sigma_p$) as a function of polymer concentration with $T^* = 6.0$

Hereafter, we analyze the influence of the geometrical and chemical properties of particles on diffusion dynamics. For simplicity, the polymer concentration is set to 0.1, at which L_c is $8\sigma_p$. Fig. 9 summarizes the time-dependent MSDs for different nanoparticles and the corresponding dynamic free energy evolutions. In the moderately asymmetric systems ($3\sigma_p < \sigma_n < 8\sigma_p$), one sees that an intermediate caging regime emerges and an entropic barrier appears at the corresponding location. In these situations, the particles can hop over the entropic barrier, which means they can escape and henceforward diffuse as normal motion. In a highly asymmetric system ($\sigma_n = 10\sigma_p$) the particle cannot cross the entropic barrier and is finally constrained by the surrounding polymer segments. On the other hand, the plateau or the knot in Fig. 6 is not observed in Fig. 9(b). This phenomenon results from the weak confinement effect of the dilute polymer solution, where the reconstitution process of system and the diffusion of particle coexist. By combining Figs. 2, 6, and 9, we can draw a conclusion: polymer concentration and particle size play a similar role in particle motion, and the influence of polymer concentration is more remarkable.

Fig. 10 summarizes the diffusion coefficients of nanoparticles with different sizes. Clearly, the size-dependent diffusion exhibits staircase characteristics, similar to the con-

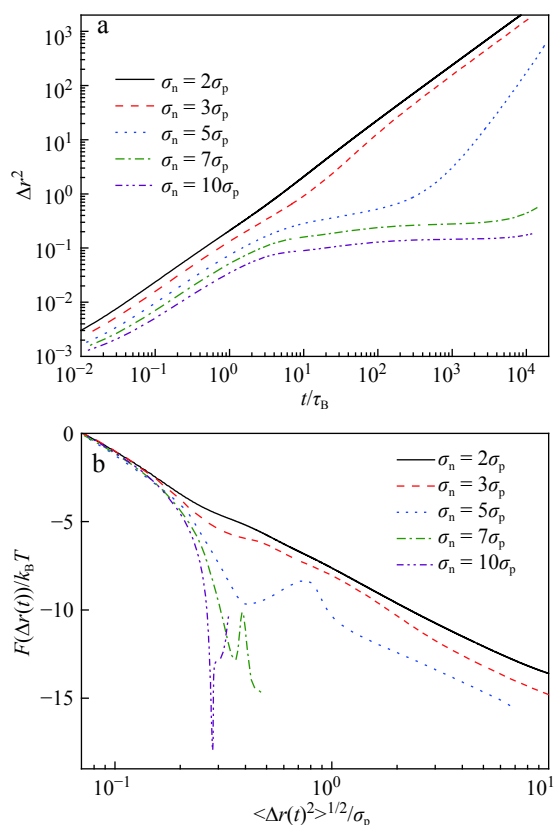


Fig. 9 (a) Mean-squared displacements and (b) dynamic free energy of particles with different sizes. The polymer concentration is 0.1 and $T^* = 6.0$.

centration-dependent behavior shown in Fig. 8. The two stages are connected by a sharp but continuous crossover. More interestingly, small particles (smaller than L_c) are found to diffuse about 200 times faster than the predictions given by Rouse dynamics,^[5,6] whereas the diffusion rate of large particles (close to or larger than L_c) is in the same order of magnitude as Rouse dynamics. Therefore, the ratio of particle size to L_c is a critical parameter to control the diffusion process. This remarkable behavior is due to the reduced frictional drag acting on small particle, and has been confirmed by previous experiment.^[5]

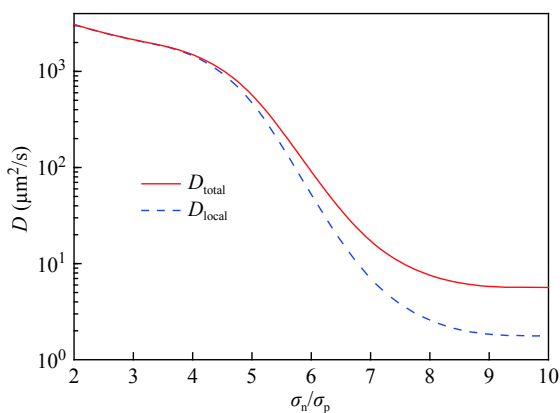


Fig. 10 Power-law dependence of diffusion coefficients for nanoparticles with different sizes. The polymer concentration is 0.1 and $T^* = 6.0$.

Fig. 11 gives the diffusion coefficients as a function of the particle-polymer interaction to clarify the effect of chemical attribute on dynamics of nanoparticle. The value decreases monotonically with the interaction strength, and the variation of coefficient is limited in one order of magnitude. As the interaction strength increases, the absorbed layer of polymer around the particle grows so that particle moves slowly and is easier to be trapped. However, such effect is unobvious, since this absorbed layer has not bonded with the particle and can easily slide from its surface. Therefore, particle motion is not sensitive to the particle-polymer interaction when the particle size is large enough.^[27] In other words, it is not an effective method to promote nanoparticle dispersion *via* changing the interaction between particle and polymer segments in semidilute polymer solution.

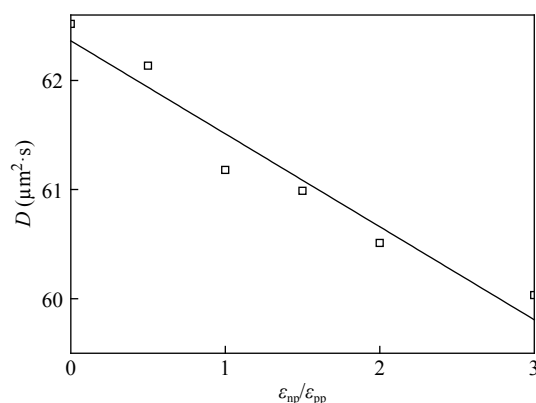


Fig. 11 Diffusion coefficient as a function of the nanoparticle-polymer interaction at $T^* = 6.0$. The squares represent the calculated results. The solid line is the linear fit. The polymer concentration is 0.1, and particle size is $5\sigma_p$.

In polymer nanocomposites, the volume fraction of particle, $\phi_n = \rho_n \sigma_n^3 / \rho_p \sigma_p^3$, also influences particle diffusion. Fig. 12 depicts the diffusion coefficient variation as a function of the particle volume fraction. If the particle size is much smaller than L_c , the diffusion coefficient is independent of the particle volume fraction. Otherwise the coefficient increases monotonically with the particle volume fraction, and the slope also increases with particle size. Once the

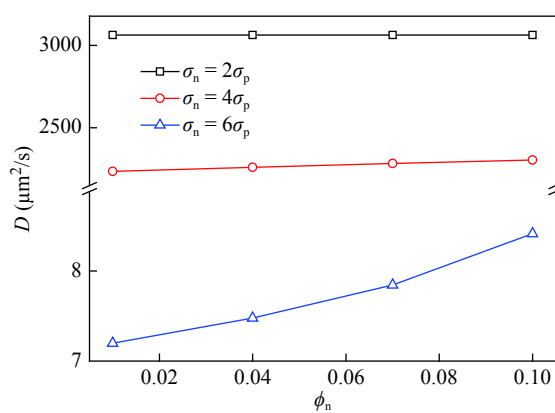


Fig. 12 Diffusion coefficients as a function of nanoparticle volume fraction ($\phi_n = \rho_n \sigma_n^3 / \rho_p \sigma_p^3$) and size. The polymer concentration is 0.1 and $T^* = 6.0$.

particle size is close to or larger than L_c , the surrounding meshes will be shoved and form a channel for particle diffusing with the particle volume fraction growing. In principle, the effect of particle volume fraction is similar to the one of particle size or polymer density.

CONCLUSIONS

In summary, the evolutions of density and free energy of nanoparticles in polymer solutions have been studied using the dynamic density functional theory, in which the microscopic hydrodynamic and non-hydrodynamic interactions have been integrated into the time-dependent free energy function. The effects of nanoparticle size, polymer concentration, particle-polymer interaction, and particle volume fraction on particle diffusion have been analyzed to clarify the main factors affecting particle transport. Some results have been tested by experiment data. It has been shown that, in the local diffusion region, both concentration and particle size are important to regulate the dynamics from free diffusion to hopping and model-coupling style, showing the mode transition from Gaussian to Non-Gaussian. By contrast, the influences of interaction strength and particle volume fraction are relatively trivial in semidilute solutions. When a particle has been completely constrained by the surrounding polymer segments, its motion is controlled by Rouse dynamics of polymer chain.

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