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# Diffusion of nanoparticles in semidilute polymer solutions: A mode-coupling theory study

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We have proposed a theoretical formalism to study the long-time diffusion behavior of nanoparticles in polymer solutions by using mode-coupling theory (MCT). The non-hydrodynamic part $D_{\text{micro}}$ of the total diffusion coefficient $D$ is calculated in the MCT framework where the polymer dynamic scattering function $\Gamma_{pp}(k,t)$ in the solution plays an important role. By introducing an approximate summation form for $\Gamma_{pp}(k,t)$, where both limits of short and long length scales are properly accounted for, we can compute $D_{\text{micro}}$ straightforwardly and investigate explicitly how $D$ depends on the volume fraction $\phi$ of the polymer solution, the nanoparticle size $R$, the degree of polymerization $N$, as well as the entanglement effects. For illustration, we adopt our theoretical approach to analyze the diffusion of gold nanoparticles in semidilute poly(ethylene glycol) (PEG)-water solutions which has been studied in detail experimentally. We find that our theoretical results show very good quantitative agreements with the experimental data in many aspects, such as the strong dependence on $\phi$, the large deviation from Stokes-Einstein relation particularly for small particles, as well as the effects of the PEG molecular weight. Such good agreements clearly demonstrate the validity of our MCT framework, which may serve as a good starting point to study many more complex dynamical behaviors associated with polymer solutions. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4926412]

## I. INTRODUCTION

Understanding the transport properties of nanoparticles (NPs) in complex fluids and gel networks is a problem of broad importance in diverse fields ranging from materials science to cellular biophysics and even drug delivery.[1–8] In particular, in biophysics, there is a growing interest to understand how macromolecules such as proteins move through crowded cytoplasmic environments.[9] The diffusive dynamics in such complex environments is crucially important for the modeling of cellular processes, the formation of protein complexes, and the self-assembly of various supramolecular structures like fibrillar aggregates.[10] Experimentally, dynamic light scattering[11,12] and fluctuation correlation spectroscopy (FCS)[13–15] are most popular in this area of research.

For polymer melts and solutions, the mobility of NPs has received a lot of attention.[16–26] Generally, there is a good understanding of the diffusion motion of very large NPs in polymer solutions or melts. When the particle radius ($R$) is much greater than the correlation length ($\xi$) of the polymer, the diffusion coefficient ($D$) follows the well-known Stokes-Einstein (SE) relation,[27] $D = D_{\text{SE}} = k_B T/(f\pi\eta_{\text{macro}}R)$, where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\eta_{\text{macro}}$ is the *macroscopic* viscosity of the solution which is commonly measured by standard rheometers, and $f = 4$ or 6 for slip or stick boundary conditions, respectively. If the particle size is comparable to the characteristic length scale

of the system, such as the correlation length $\xi$ or the entanglement tube diameter $d_T$, large deviations from $D_{\text{SE}}$ have been observed, by recent experiments[7,20–23,26] and molecular dynamics (MD) simulations.[28–30] Interestingly, it was argued that if one replaces the macroscopic viscosity by a so-called microscopic viscosity $\eta_{\text{micro}}$ which may depend on the size of the probe particle, the SE relation might be valid for all length scales.[11,26] Nevertheless, for a ternary mixture containing polymer chains, solvent, and the nanoparticle, multiple length scales are relevant which leads to the understanding of diffusive dynamics of NPs rather complicated or even controversial. Many open problems still remain.

Very recently, an important theoretical framework based on mode-coupling theory (MCT) has been proposed to study the long-time diffusion coefficient of NPs in complex solutions, from a microscopic level explicitly accounting for the solute-solvent interactions. It starts from the calculation of the friction kernel $\zeta(t)$, defined as the time correlation function of the random force exerted on the NP. Generally, the friction may result from the short-time binary collisions between the NP and the surrounding particles, the coupling to the solvent structural relaxation modes, and the coupling to the long-time transverse hydrodynamic currents. With standard mode-coupling approximation, one can express $\zeta(t)$ as a function of the static and dynamic structure factors of the system. This approach is concise and self-consistent and does not require large computational cost such as MD simulations. With the calculated $\zeta(t)$, the diffusion coefficient $D$ can be obtained directly via fluctuation-dissipation theorem. Thanks mainly to the excellent works of Schweizer and coworkers,[31,32] MCT has

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been successfully applied to polymer melts, being both unentangled and entangled, which provides deep physical insights and is really helpful to understand many important experimental observations. Egorov[33] performed a slightly different MCT study on the anomalous diffusion behavior of NPs in polymer melts and solutions, but only unentangled regime was considered and the effect of solvent was implicitly accounted for. To the best of our knowledge, a unified MCT study of NPs diffusion in polymer solutions, with systematic investigation of the dependence on volume fraction, particle size, and polymer molecular weight, is still lacking.

In the present paper, we establish a consistent MCT analysis of the long-time diffusion coefficient of a single spherical NP dissolved in a semidilute polymer solution. A unified polymer-polymer dynamic scattering function valid for semidilute and entangled polymer solutions is proposed so that the dependence of diffusion coefficient $D$ on the volume fraction $\phi$ and particle size $R$ as well as the entanglement effect can be addressed explicitly. The obtained diffusion coefficient $D$ can be separated into a microscopic part $D_{\text{micro}}$, which mainly results from the coupling of the NP dynamics with the density fluctuation of polymer solution, and a macroscopic part $D_{\text{hydro}}$, which is due to the coupling to the hydrodynamic current. This partitioning facilitates us to investigate the deviation of diffusion coefficient $D$ from the traditional SE relation in a simple way. We have applied our theory to study the diffusion of gold NPs in semidilute poly(ethylene glycol) (PEG)-water solutions which has been measured by FCS.[26] Excellent agreements with the experimental data are obtained with only necessary parameters of the PEG molecule as input and no additional parameter fitting is required.

The remainder of the paper is organized as follows. In Sec. II, we elaborate our theoretical formulation. MCT approach employed to compute the long-time diffusion coefficient $D$ in semidilute polymer solutions is elaborated. In Sec. III, we apply our theory to analyze the diffusion of NPs in semidilute PEG-water solutions. The effect of polymer concentration, the effect of NP size, as well as the deviation from SE relation are particularly addressed. To demonstrate the validity of MCT approach for polymer solutions, our theoretical results are compared with the experimental data. Section IV concludes the paper.

## II. THEORETICAL FORMULATION

We consider a single tagged spherical NP dissolved in a semidilute polymer solution under good solvent conditions. As already well-established in the literature,[31] the long-time diffusion coefficient $D$ has microscopic and hydrodynamic contributions,

$$D = D_{\text{micro}} + D_{\text{hydro}}. \tag{1}$$

As mentioned above, the microscopic part $D_{\text{micro}}$ results from the coupling to the density fluctuation mode of polymer solutions, while the hydrodynamic part $D_{\text{hydro}}$ is due to the coupling to the transverse hydrodynamic current mode. For the latter part, one can employ the SE relation,

$$D_{\text{hydro}} \approx \frac{k_B T}{6\pi \eta_{\text{macro}} R}, \tag{2}$$

with $\eta_{\text{macro}}$ being the macroscopic shear viscosity of the polymer solution. The microscopic part can be expressed in terms of a non-hydrodynamic friction constant, which is related to the total time integral of the correlation function of the random force exerted on the NP. The force-force correlation function can be approximately computed using MCT based on several simplifications, including replacement of the projected force by the total force, projection of the force onto bilinear products of the slow solvent density fluctuation mode, and factorization of four-point correlations into products of two-point correlations. These standard procedures finally lead to [34,35]

$$D_{\text{micro}} = \frac{k_B T}{\zeta_{\text{micro}}}, \tag{3}$$

with

$$\zeta_{\text{micro}} = \frac{\rho_P k_B T}{6\pi^2} \int_0^\infty dt \int_0^\infty dk\, k^4 C_{np}^2(k) S_{pp}(k) \Gamma_{pp}(k,t), \tag{4}$$

where $\rho_P = \phi d N_A / M_0$ is the number density of polymer segment, with $M_0$ being the molecular weight of a segment, $d$ the polymer mass density, and $N_A$ the Avogadro's number. $C_{np}(k)$ is the site-site nanoparticle-polymer direct correlation function in the Fourier space. $S_{pp}(k)$ is the static structure factor. $\Gamma_{pp}(k,t)$ is the dynamic scattering function of the polymer solution normalized to $S_{pp}(k)$. Note here, we have applied the simplification that the self-intermediate dynamic structure factor of the NP is nearly unity.

Usually, the equilibrium properties $C_{np}(k)$ and $S_{pp}(k)$ appeared in Eq. (4) can be determined using polymer reference interaction site model integral equation theory which has been discussed in depth elsewhere.[36] In the present work, we mainly address the diffusion of a single spherical nanoparticle dissolved in an unentangled (short chain) or entangled (long chain) semidilute polymer solution under good solvent conditions. The polymer is modeled as a chain composed of $N$ statistical segments with length $\sigma$ which interact intermolecularly via pair-decomposable hard core repulsions of diameter $d_{pp}$. In general, the particle size $R$ is much larger than $d_{pp}$. For simplicity, here, we take an analytic thread model corresponding to take the limit $d_{pp} \to 0$, to calculate the static properties. By using the Percus-Yevick site-site closure and the Lorentzian approximation to the intrachain structure factor, one can easily derive the static structure factor $S_{pp}(k)$ as well as the nanoparticle-polymer total correlation function in Fourier space $h_{np}(k)$ as[37]

$$S_{pp}(k) = \frac{12}{k^2 \sigma^2 + \sigma^2/\xi^2}, \tag{5a}$$

$$h_{np}(k) = \frac{4\pi k\,[R\cos(kR) - \sin(kR)]}{k^3}$$
$$- \frac{4\pi R\xi\,[k\xi \cos(kR) + \sin(kR)]}{k\,(1 + k^2 \xi^2)}. \tag{5b}$$

Herein, $\xi$ denotes the correlation length of the polymer chain in the solution which may depend on the volume fraction $\phi$. The direct correlation function $C_{np}(k)$ can then be calculated

through

$$C_{np}(k) = h_{np}(k)/S_{pp}(k). \tag{6}$$

On the other hand, a full understanding of the dynamic structure factor, the intermediate-scattering function $\Gamma_{pp}(k,t)$ of polymer solutions, valid for both unentangled and entangled chains, is an open and difficult theoretical problem, in particular, for polymers in semidilute regime. For polymer melts, Yamamoto and Schweizer[31] have proposed a useful summation form, where the total scattering function is separated into two parts, one accounting for the time correlation in the small length-scale (large wave vector $k$) limit, and the other for large-scale (small $k$) limit with a further Debye-Waller (DW) factor addressing polymer chain localization and the spatial dependence or constraint porosity of the slowly relaxing density fluctuations. Nevertheless, that formula cannot apply to polymer solutions directly, in particular, when the role of concentration $\phi$ needs to be clarified.

In the present paper, we propose an approximate summation formula for $\Gamma_{pp}(k,t)$ applicable for polymer solutions, by properly taking into account both the small and large limits of the length scale. Importantly, the role of polymer concentration $\phi$ may be appropriately incorporated, and both unentangled and entangled regimes are included. Finally, our formula reads

$$\Gamma_{pp}(k,t) = \exp\left(-\frac{k_B T}{16\eta_0}k^3 t\right) + \exp\left(-\frac{k_B T \rho_P}{3S_0 \eta_s}t\right)$$
$$\times \exp\left(-\frac{k^2 a^2}{3\pi^2 S_{pp}(k)}\right), \tag{7}$$

where $\eta_0$ is the neat solvent viscosity, $S_0 \equiv S_{pp}(k = 0)$, $\eta_s$ is the *microscopic* shear viscosity of polymer solution as will be discussed below, and $a$ is a length scale characterizing the localization of the polymer chain.

The first term in Eq. (7) describes collective density fluctuation relaxation on relatively small length scales $k\xi \gg 1$. In this regime, the dynamics is dominated by the single chain behavior and one can see the internal motion of the chain. Under Gaussian approximation, the dynamic scattering function of semidilute polymer solutions has been argued analytically,[38] following the single exponential form. Particularly, the $k^3$ dependence in this limit has been well confirmed experimentally. Note that for polymer melts, single exponential decay is also expected in this regime; however, a $k^2$ dependence was adopted as a natural consequence of the $k$-dependent viscosity of the melt. The second term in Eq. (7) describes $\Gamma_{pp}(k,t)$ in the limit $k\xi \ll 1$, where the dynamics is determined by the overall translational motion beyond a certain localization length scale $a$. One should note that the explicit form of $\Gamma_{pp}(k,t)$ in this regime is rather complicated and approximations must be made for tractable purpose. Herein, we have adopted a form similar to that proposed by Yamamoto and Schweizer,[31] but with necessary extensions to polymer solutions. The second term shown in Eq. (7) includes two factors: an exponentially time-dependent part $\exp\left(-\frac{k_B T \rho_P}{3S_0 \eta_s}t\right)$ accounting for the long time diffusion of the whole chain over a large length scale and a second spatial-dependent part $\exp\left(-\frac{k^2 a^2}{3\pi^2 S_{pp}(k)}\right)$ called DW factor describing the localization within the "local enough" scale $a$.

To proceed, one needs to pay close attentions to the two important parameters appeared in Eq. (7), namely, the shear viscosity $\eta_s$ of the solution and the localization length $a$. We note here that for a complex fluid like polymer solution where diverse length scales coexist, the viscosity $\eta_s$ may depend upon the length scale at which it is probed. If the probe size is very large compared to the polymer radius of gyration, the detected viscosity reaches the macroscopic value $\eta_{\text{macro}}$, wherein each polymer can be viewed as a small solvent particle. On the other hand, for a probe with size comparable to the characteristic length of the polymer chain, the relevant viscosity should be the so-called microscopic one $\eta_{\text{micro}}$, which is neither the viscosity of the neat solvent $\eta_0$ nor $\eta_{\text{macro}}$. In the present paper, we are interested in the diffusion behavior of a NP with radius $R$. Therefore, it is quite reasonable to consider $\eta_s$ in Eq. (7) as the *microscopic* viscosity experienced by a probe with size $R$, rather than the macroscopic value. According to these considerations, we can adopt the following size-dependent scaling formula for $\eta_s$, which has been widely validated for polymer solutions by FCS and electrophoresis:[5,11,17]

$$\eta_s = \eta_0 \exp\left(\lambda\left(\frac{R}{\xi}\right)^\delta\right) \quad (R < R_g^{(0)}), \tag{8a}$$

$$\eta_s = \eta_0 \exp\left(\lambda\left(\frac{R_g^{(0)}}{\xi}\right)^\delta\right) \quad (R > R_g^{(0)}), \tag{8b}$$

where $R_g^{(0)}$ denotes the polymer radius of gyration under dilute condition, $\lambda$ and $\delta$ are system dependent parameters.[39] Note that for $R > R_g^{(0)}$, $\eta_s$ recovers the macroscopic viscosity $\eta_{\text{macro}}$.

Another parameter is the localization length $a$ involved in the DW factor, which accounts for the kinetically arrested density fluctuations within a certain "local enough" length scale. The DW factor is estimated as the normalized single chain dynamic structure factor at the onset time when a diffusing segment hits the boundary of this localization length.[31] For entangled polymer melts, it was argued that this localization length scale could be just the tube diameter $d_T$. For polymer solutions considered in the present paper, however, this length scale should be concentration dependent. As already well established in polymer physics, there exists a critical volume fraction $\phi_e$ for entanglement in polymer solutions. For volume fraction above $\phi_e$, polymer entanglement becomes relevant and the localization length should be chosen as the tube diameter $d_T$ as expected. For relatively dilute solutions with $\phi < \phi_e$, entanglement is not relevant. However, the diffusing behavior of a polymer segment should still be confined, at least within the end-to-end distance $R_c$ of a single chain. Therefore, it is reasonable for us to choose $a$ to be $R_c$ for $\phi < \phi_e$. As a consequence, we propose that

$$a = \begin{cases} R_c & (\phi^* < \phi < \phi_e), \\ d_T & (\phi_e < \phi < \phi^{**}), \end{cases} \tag{9}$$

where $\phi^*$ denotes an overlap volume fraction marking the onset of semidilute regime and $\phi^{**}$ denotes a crossover concentration from semidilute to concentrated regimes. We note that $R_c$ is actually identical to $d_T$ at $\phi_e$, such that this choice of $a$ facilitates us to investigate the dependence on volume fraction

$\phi$ systematically with continuous crossover from unentangled to entangled regimes.

Based on above discussions, we suggest that Eq. (7) can be an appropriate approximation for dynamic scattering function applicable for polymer solutions with proper considerations of the entanglement effects. Consequently, combining Eqs. (3)-(7), we can calculate the microscopic contribution to the long-time diffusion constant, $D_{\text{micro}}$. Together with the hydrodynamic contribution $D_{\text{hydro}}$ given by Eq. (2), we finally obtain the total diffusion coefficient

$$D = \frac{\eta_0}{\eta_{\text{macro}}} D_0 + D_0 \left\{ \int_0^\infty dk\, k \frac{h_{np}^2(k)}{S_{pp}(k)} \left[ \frac{4\rho_P}{9\pi^3 R} + \frac{S_0 \eta_s}{12\pi^3 R \eta_0} k^3 \exp\left( -\frac{k^2 a^2}{3\pi^2 S_{pp}(k)} \right) \right] \right\}^{-1}, \tag{10}$$

where $D_0 = k_B T/(6\pi\eta_0 R)$ is the diffusion coefficient of the nanoparticle in the neat solvent. The first term in the right side corresponds to $D_{\text{hydro}}$ and the second term refers to $D_{\text{micro}}$.

To calculate the diffusion constant by using Eq. (10), especially to investigate its dependence on the volume fraction $\phi$, we need to introduce several scaling relations regarding the characteristic length scales involved. Note here that the effective segment diameter $\sigma$, correlation length $\xi$, end-to-end distance $R_c$, and tube diameter $d_T$ are all dependent on the volume fraction $\phi$. As already well-established in the literature,[40] one has for $\phi^* < \phi < \phi^{**}$,

$$\sigma = \sigma^{(0)} \left( \frac{\phi}{\phi^*} \right)^{-1/8}, \tag{11a}$$

$$\xi = R_g^{(0)} \left( \frac{\phi}{\phi^*} \right)^{-3/4}, \tag{11b}$$

$$R_c = R_c^{(0)} \left( \frac{\phi}{\phi^*} \right)^{-1/8}, \tag{11c}$$

$$d_T = d_T^{(1)} \phi^{-3/4}. \tag{11d}$$

Herein, $\sigma^{(0)}$, $R_g^{(0)}$, and $R_c^{(0)}$ are, respectively, the segment diameter, polymer radius of gyration, and end-to-end distance under dilute condition, while $d_T^{(1)}$ is the tube diameter in the melt. In addition, these parameters can be determined by the degree of polymerization $N$ and the properties of polymer melts according to

$$d_T^{(1)} = \sqrt{N_e^{(1)}} \sigma^{(1)}, \ \sigma^{(0)} = \sigma^{(1)} N^{0.1}, \ R_g^{(0)} = \sqrt{N/6}\, \sigma^{(0)}$$

and

$$R_c^{(0)} = \sqrt{N} \sigma^{(0)}, \tag{12}$$

where $\sigma^{(1)}$ and $N_e^{(1)}$ denote, respectively, the segment diameter and the number of monomers in an entangled strand in the melt. $\sigma^{(1)}$ is assumed to be independent of $N$ and $\phi$. The overlap volume fractions $\phi^*$ can be calculated easily from

$$\phi^* = \frac{3M_0 N}{4\pi d N_A R_g^{(0)3}}. \tag{13}$$

The critical volume fraction $\phi_e$ for entanglement can be determined by the condition when the tube diameter $d_T$ equals to the end-to-end distance $R_c$, which yields

$$\phi_e = \left( \frac{N}{Ne^{(1)}} \right)^{-5/4} \left( \frac{11M_0}{\pi d N_A \sigma^{(1)3}} \right)^{-1/5}. \tag{14}$$

For a given polymer solution, $M_0$, $d$, $N_e^{(1)}$, $\sigma^{(1)}$ are determined by the polymer molecule itself and are input parameters from which we can obtain the required parameters to calculate the diffusion constant. Our theoretical formulation thus provides a systematic framework to investigate the diffusion of nanoparticles in semidilute polymer solutions, with particular attentions paid on its dependence on the volume fraction $\phi$, the degree of polymerization $N$, and the NP size $R$, without any other fitting parameters.

We would like to point out that the requirement to use $\eta_s$ as an input in Eq. (10) could potentially limit the use of our MCT formulation. It would be very helpful if one can separately get $\eta_s$ as a function of the probe size $R$, which definitely deserves more theoretical work. At the current stage, nevertheless, we only use scaling forms for $\eta_s$ given by Eq. (8).

## III. RESULTS

As mentioned above, experimentally, many works have been devoted to the diffusion dynamics of nanoparticles in various polymer solutions. For example, by using FSC, Kohli and Mukhopadhyay[26] used gold nanoparticles to investigate the length-scale-dependent dynamics in semidilute PEG-water solutions. In Sec. II, we have established a theoretical framework based on MCT. In this section, we will apply it to the PEG systems to check its validity.

For the PEG system, the basic parameters are shown in Table I, where the parameters $\lambda$ and $\delta$ for microscopic viscosity in Eq. (8) are obtained from experimental data.[11] PEG samples of two different molecular weights 5 kg/mol (PEG 5K) and 35 kg/mol (PEG 35K) will be explicitly analyzed. Key parameters for these two polymer systems, including the relevant length scales under dilute conditions $\sigma^{(0)}$, $R_g^{(0)}$, and $R_c^{(0)}$, as well as the critical volume fraction for the onset of semidilute regime $\phi^*$ and that for entanglement $\phi_e$ are listed in Table II, which are obtained according to Eqs. (12)–(14). Besides, we have $\eta_0 = 0.85 \times 10^{-3}$ Pa S for the shear viscosity of the neat solvent (water) at room temperature. With these values, we are ready to calculate the diffusion coefficient $D$ for a nanoparticle in the PEG semidilute solutions by using Eq. (10).

### A. The effect of polymer concentration

First of all, we investigate how the total diffusion coefficient $D$ depends on the polymer concentration, here denoted

TABLE I. Parameters for PEG.

| $M_0$ (kg/mol) | $d$ (kg/m$^3$) | $\sigma^{(1)}$ (nm) | $N_e^{(1)}$ | $d_T^{(1)}$ (nm) | $\lambda$ | $\delta$ |
|---|---|---|---|---|---|---|
| 0.12 | 1126 | 0.7 | 33 | 4 | 1.6 | 0.89 |

by the volume fraction $\phi$. The macroscopic viscosity $\eta_{\text{macro}}$ of PEG-water solutions at various concentrations, required in Eq. (10), is obtained from Eq. (8b) combining the scaling relation of $\xi$ with $\phi$ given by Eq. (11b). We mainly consider a concentration range from $\phi^*$ to 0.4, in accordance with that taken into account by experiments in Ref. 26, as shown in Table II, $\phi^* = 0.08$ and 0.02 for PEG 5K and PEG 35K, respectively. Furthermore, for PEG 5K, the polymer chain is short and entanglement does not matter ($\phi_e = 0.68$), therefore the localization length $a = R_c$ in the considered range of volume fraction. For PEG 35K, however, the chain is long and entanglement occurs for volume fraction larger than $\phi_e = 0.16$. In such a case, $a$ is a piecewise function according to Eq. (9), shifting its value from $\phi$-dependent end-to-end distance $R_c$ for $\phi < 0.16$ to $\phi$-dependent tube diameter $d_T$ for $\phi > 0.16$.

We have calculated the diffusion coefficient for three different radii of nanoparticle, i.e., $R = 2.5, 5$, and $10$ nm which have been investigated by experiments. Fig. 1 shows the plot of $D$ as a function of $\phi$ based on Eq. (10) (lines), for both PEG 5K and 35K systems. The experimental data (symbols) obtained by fluctuation correlation spectroscopy[26] are also presented for comparison. Strikingly, our theoretical results show perfect agreements with the experimental ones. Note that in our framework, one only needs to input the specific system parameters, such as those in Tables I and II for PEG, and then can calculate $D$ at various concentrations in an explicit and straightforward way. We would like to emphasize here that the agreement is not the resultant of a parameter fitting. The perfect coincidence of our calculated results with the experiments justifies our theory to be a good microscopic strategy to understand the diffusivity of nanoparticles in polymer solutions. In particular, it justifies the validity of the summation form of the dynamic scattering function $\Gamma_{pp}(k,t)$ we propose in Eq. (7).

Moreover, as pointed out by Kohli and Mukhopadhyay,[26] the phenomenological Phillies' equation of stretched exponential function $D/D_0 \propto \exp(-\gamma\phi^\nu)$ with adjustable parameters $\gamma$ and $\nu$ fails to fitting the experimental data at high concentrations for PEG 35K and $R = 10$ nm (dashed-dotted line in Fig. 1). In fact, this deviation occurs in entanglement regime, where the simple Phillies' equation cannot account for the entanglement effect which becomes significant. In contrast, our theory is applicable for both unentangled and entangled polymer solutions, within a unified formalism Eq. (10).
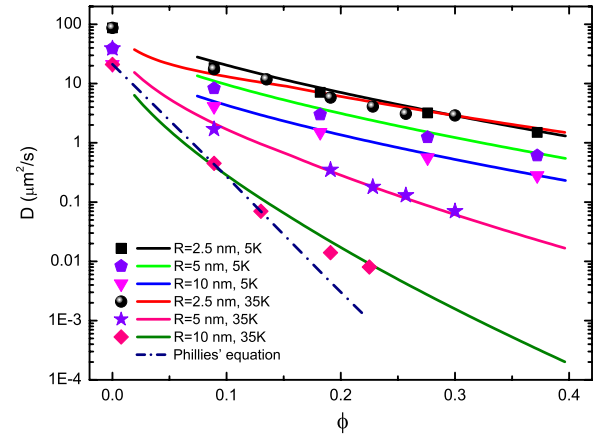


FIG. 1. Theoretical results based on Eq. (10) (lines) for the diffusion coefficient $D$ as a function polymer volume fraction $\phi$, for nanoparticles with radii $R = 2.5, 5$, and $10$ nm in solutions PEG 5K and PEG 35K. The corresponding experimental data (symbols) are also shown for comparison. The dashed-dotted line refers to a fitting of the experimental data for PEG 35K and $R = 10$ nm using Phillies' equation $D \propto \exp(-\gamma\phi^\nu)$.

## B. The effect of nanoparticle size

We go further to study the effect of nanoparticle size on the diffusion coefficient. As an example, we consider a PEG 35K solution with volume fraction $\phi = 0.2$ which is in the entangled regime. Accordingly, the required length scales at this volume fraction are $\xi = 1.5$ nm, $R_g = 6.4$ nm, and $a = d_T = 13.4$ nm. The macroscopic viscosity is $\eta_{\text{macro}} = 1.73$ Pa S which is several orders of magnitude larger than that of neat solvent. The microscopic viscosity $\eta_s$ is dependent on the particle size $R$ according to Eqs. (8a) and (8b). We consider nanoparticles with $R/R_g^{(0)}$ ranging from 0.1 to 2, where $R_g^{(0)} = 8.6$ nm as shown in Table II.

As illustrated in Eq. (10), the total diffusion coefficient is the sum of $D_{\text{hydro}}$ and $D_{\text{micro}}$. In Fig. 2, the total diffusion coefficient and the two parts of contributions, calculated from Eq. (10), are presented. For comparison, experimental data reproduced from Ref. 26 are also shown. Clearly, our theoretical results are in very good agreements with the
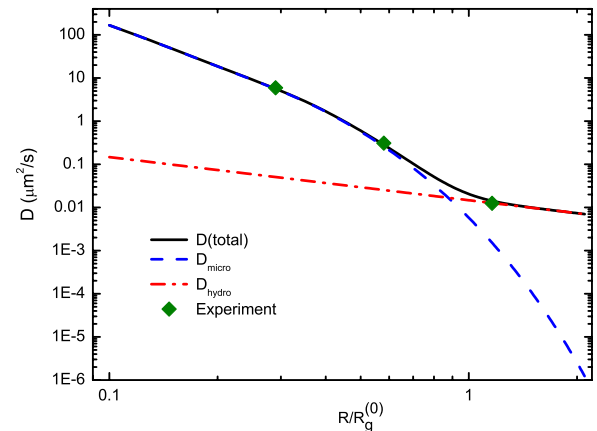


FIG. 2. The total diffusion coefficient $D$ (solid line), the microscopic contribution ($D_{\text{micro}}$) (dashed line), and the hydrodynamic contribution ($D_{\text{hydro}}$) (dashed-dotted line) are plotted as functions of nanoparticle radius scaled by the polymer radius of gyration $R/R_g^{(0)}$ for PEG 35K at $\phi = 0.2$. The experimental data (squares) reproduced from Ref. 26 are also shown.

TABLE II. Parameters for solutions of PEG 5K and PEG 35K.

| Symbol | $N$ | $\sigma^{(0)}$ (nm) | $R_g^{(0)}$ (nm) | $R_c^{(0)}$ (nm) | $\phi^*$ | $\phi_e$ |
|---|---|---|---|---|---|---|
| PEG 5K | 46 | 1.0 | 2.8 | 7.0 | 0.08 | 0.68 |
| PEG 35K | 292 | 1.2 | 8.6 | 21.1 | 0.02 | 0.16 |

experimental results. In addition, we find there are three typical size regimes wherein the microscopic and hydrodynamic contributions exhibit alternative roles. As $R/R_g^{(0)} < 1$, it is obvious that the microscopic contribution $D_{\text{micro}}$ largely dominates the diffusivity of the nanoparticle. It exceeds the hydrodynamic contribution $D_{\text{hydro}}$ up to several orders of magnitude, such that $D_{\text{hydro}}$ is negligible. As $R$ increases, the significance of $D_{\text{micro}}$ decreases, while $D_{\text{hydro}}$ becomes more and more important. As $R$ approaches $R_g^{(0)}$, both microscopic and hydrodynamic terms give comparable contributions to the total diffusion coefficient. Finally, for even larger nanoparticles with $R/R_g^{(0)} > 1$, $D$ is largely determined by the hydrodynamic contribution $D_{\text{hydro}}$, while the contribution from $D_{\text{micro}}$ is negligible. We have also applied our theory to study the PEG 5K system, similar behaviors (not shown here) have been found as in Fig. 2.

In the experimental studies of diffusion behavior of nanoparticles in complex solutions, one of the main concerns is whether the conventional SE relation is violated or not. Actually, many evidences have shown that large deviation from SE may occur especially for small particles. Generally, SE says that the diffusion coefficient $D$ should be inversely proportional to the macroscopic viscosity of the solution, which can be derived from macroscopic hydrodynamics. According to Eq. (10), such a SE should be satisfied if the macroscopic part $D_{\text{hydro}}$ dominates. As already shown in Fig. 2, this should take place for large nanoparticles with $R/R_g^{(0)} \gtrsim 1$. But for small particles, $D_{\text{micro}}$ plays an important role and one expects that large deviation from conventional SE should be observed.

To quantitatively investigate the deviation of the total diffusion coefficient $D$ from the SE relation, we have studied the situations that $R = 2.5$ and $5$ nm for PEG 35K ($R_g^{(0)} = 8.6$ nm) and $R = 2.5$ nm for PEG 5K ($R_g^{(0)} = 2.8$ nm), for which $R/R_g^{(0)} \approx 0.3$, 0.6, and 0.9, respectively. Fig. 3 presents the ratio $D/D_{\text{SE}}$, where $D_{\text{SE}}$ is just obtained via $D_{\text{hydro}}$, as a function of volume fraction $\phi$ for these three typical values of $R/R_g^{(0)}$. The upper two curves describe PEG 35K, and the lowest curve is for PEG 5K. The experimental data obtained by FCS[26] are also shown for comparison. As already

demonstrated in Fig. 1, the total diffusion coefficient $D$ by our analysis coincides with the experimental results excellently. Thus, the good agreement of $D/D_{\text{SE}}$ with the experimental data here is not surprising. We see that as $\phi$ increases, the deviation of $D$ from $D_{SE}$ relation becomes more and more remarkable. Moreover, for nanoparticles much smaller than the polymer gyration radius $R_g^{(0)}$ (squares and circles), the deviation of $D_{\text{SE}}$ from $D$ can exceed up to several orders of magnitude. In such cases, it is just the microscopic contribution $D_{\text{micro}}$ rather than $D_{\text{hydro}}$ which plays dominant role on the diffusivity of nanoparticles in polymer solutions. While for $R/R_g^{(0)} = 0.9$ (triangles), the ratio $D/D_{\text{SE}}$ is approximately unity and changes little with the polymer concentration. We emphasize again that in our analysis, both unentangled and entangled concentrations for PEG 35K are included.

## C. D versus microscopic viscosity

Figs. 2 and 3 have demonstrated as $R > R_g^{(0)}$, SE relation works well. While for small particles $R < R_g^{(0)}$, the deviation of diffusion coefficient from this relation is evident. Recently, several works[11,26] have pointed out that the SE relation is well sustained once we replace the macroscopic viscosity in Eq. (2) by the microscopic viscosity which depends on the nanoparticle size in case of $R < R_g^{(0)}$. Previously, this understanding is mainly based on a phenomenological deduction and lack of theoretical interpretation. It is therefore desirable for us to check the relationship between diffusion coefficient and the microscopic viscosity by using our MCT analysis. As mentioned above, by fluorescence correlation spectroscopy and capillary electrophoresis,[11] the scaling form of microscopic viscosity at all length-scales in PEG system (see Eq. (8)) is proposed. In view of it, we directly investigate how the diffusion coefficient depends on the microscopic viscosity, taking the advantage of our microscopic study based on MCT. Note that in explicit expression (10), the equilibrium structure functions $S_{pp}(k)$ and $h_{np}(k)$, the segment number density $\rho_P$, the localization length $a$, as well as the microviscosity $\eta_s$ are all dependent on the volume fraction $\phi$. Thus, we can choose $\phi$ as a variable parameter and then calculate $D$ versus $\eta_s$. As a result, Fig. 4 presents the scaled diffusion coefficient $D_0/D$ (remind here $D_0$ is the diffusion coefficient in neat solvent) as a function of the scaled viscosity $\eta_s/\eta_0$, which includes two cases: $R > R_g^{(0)}$, which corresponds to $R = 5$ and $10$ nm for PEG 5K and $R = 10$ nm for PEG 35K; and $R < R_g^{(0)}$, corresponding to $R = 2.5$ nm for PEG 5K and $R = 2.5$ and $5$ nm for PEG 35K. The experimental data for these cases are presented also for comparison. If $D_{\text{SE}}$ holds, one should have $D_0/D = \eta_s/\eta$ such that the curves should collapse into a single line with slope one, shown as the dashed-dotted line in Fig. 4.

We can make a couple of remarks from Fig. 4. First, our theoretical results show good agreements with the experimental data. Both theoretical and experimental data although display a clear tendency to degenerate to the SE relation but do not exactly collapse into the dashed line, indicating that there do exist deviations from the exact SE relation. Second, the curves show good linear dependence, except for some obvious deviations for small particles $R/R_g^{(0)} = 0.3$ in the range
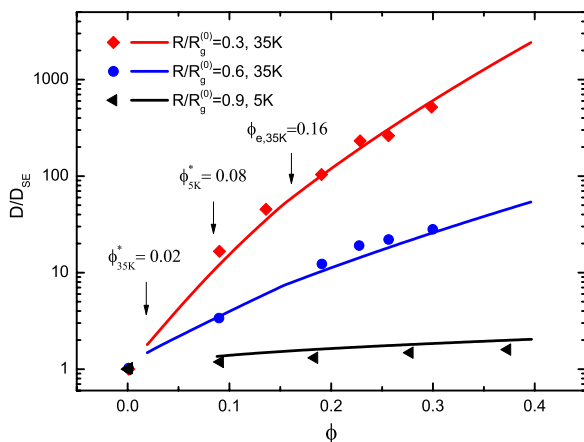


FIG. 3. The ratio $D/D_{\text{SE}}$ calculated by MCT (lines) and obtained by experiments (symbols)[26] is plotted versus polymer volume fraction $\phi$, for three typical size ratios $R/R_g^{(0)} = 0.3$, 0.6, and 0.9. The particular onset volume fractions for semidilute and entangled regimes are denoted.
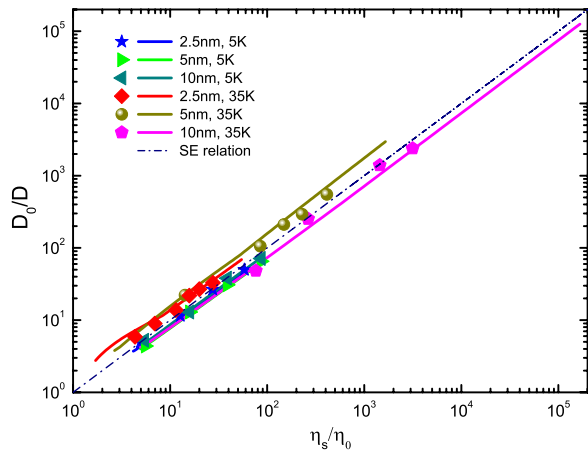
FIG. 4. Theoretical results based on Eq. (10) (lines) for the dependence of the scaled diffusion coefficient $D_0/D$ on the scaled viscosity $\eta_s/\eta_0$, for nanoparticles with radii $R = 2.5, 5,$ and $10$ nm in solutions PEG 5K and PEG 35K. The corresponding experimental data (symbols) are also shown. The dashed-dotted line refers to the SE-relation $D_0/D = \eta_s/\eta_0$.

where $\eta_s/\eta_0$ is small, indicating that $D_0/D = \kappa (\eta_s/\eta_0)$, with $\kappa$ slightly different from one which holds for relatively large particles. Therefore, although our formulation is quite different from the simple SE form, the calculated $D$ does show rather good consistence with SE-prediction using the microviscosity $\eta_s$ given that the particle size is not too small. For small particles, the deviations are expected to be more remarkable. This is because, for small nanoparticles, it might experience a non-homogenous environment composed of polymer chains and solvent molecules. Such a non-homogeneity might induce the decoupling of diffusion coefficient from the viscosity of the solution.[41]

## IV. CONCLUSION

In summary, we have applied a MCT theoretical formalism to study the long time diffusion behavior of nanoparticles in polymer solutions. The total diffusion constant can be separated into the summation of a macroscopic hydrodynamic term $D_{hydro}$ and a microscopic non-hydrodynamic contribution $D_{micro}$. The hydrodynamic term can be obtained via the traditional SE relation, while the microscopic term is calculated using MCT framework where the polymer dynamic scattering function $\Gamma_{pp}(k,t)$ in the solution plays an important role. We propose a particular approximate summation form for this correlation function, wherein one term mainly describes the diffusion behavior of polymer segments in short length and time scale and another term accounts for the diffusion of the polymer as a whole over large length scale. The former is just a single exponential decay function with time but with an interesting $k^3$ dependence for polymer solutions compared to $k^2$ dependence for pure polymer melts. The latter also contains an exponentially time-decaying factor involving the so-called microscopic viscosity $\eta_s$ of the solution, but with a necessary DW factor characterizing the kinetical arrest of the polymer segments within a local enough length scale $a$, which reads the end-to-end distance $R_c$ of the polymer chain in the unentangled regime and crosses over to the tube diameter $d_T$ within the

entangled regime. By properly employing the scaling relations of $\eta_s$ with the volume fraction $\phi$ and the particle size $R$, we can calculate the long-time diffusion constant $D$ in a systematic and straightforward way, with certain parameters specific to the polymer molecule as input. In particular, the formalism facilitates us to investigate how $D$ depends on the volume fraction $\phi$ of the solution, the nanoparticle size $R$, and the degree of polymerization $N$, in both unentangled and entangled situations, which can be compared directly to experimental results. We can also use the theory to study the deviation from traditional SE relation in a quantitative manner. For illustration, we apply our theoretical approach to analyze the nanoparticle diffusion in PEG-water system which has been studied in detail experimentally. We find that our theoretical results show very good quantitative agreements with the experimental data in many aspects, such as the dependence of $D$ on $\phi$ and $R$, and the deviation from SE relation, for different nanoparticle sizes and PEG molecular weights. Such good agreements clearly demonstrate the validity of our MCT framework as well as the particular form of the polymer dynamic scattering function $\Gamma_{pp}(k,t)$. We believe that our present work here provides a sound starting point for future studies about time-dependent diffusion behaviors of nanoparticles in complex polymer solutions.

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