Study of Active Brownian Particle Diffusion in Polymer Solutions

Yunfei Du, Zhonghuai Hou*

Department of Chemical Physics and Hefei National Laboratory for Physical Sciences at Microscales,

iChEM, University of Science and Technology of China, Hefei, Anhui 230026, China

The diffusion behavior of an active Brownian particle (ABP) in polymer solutions is studied using Langevin dynamics simulations. We find that the long time diffusion coefficient D can show a non-monotonic dependence on the particle size R if the active force F_a is large enough, wherein a bigger particle would diffuse faster than a smaller one which is quite counterintuitive. By analyzing the short time dynamics in comparison to the passive one, we find that such non-trivial dependence results from the competition between persistence motion of the ABP and the length-scale dependent effective viscosity that the particle experienced in the polymer solution. We have also introduced an effective viscosity η_{eff} experienced by the ABP phenomenologically. Such an active η_{eff} is found to be larger than a passive one and strongly depends on R and F_a . In addition, we find that the dependence of D on propelling force F_a presents a well scaling form at a fixed R and the scaling factor changes non-monotonically with R. Such results demonstrate that active issue plays rather subtle roles on the diffusion of nano-particle in complex solutions.

I. INTRODUCTION

Transport properties of macromolecule are of great importance in various fields including biophysics[1–4], material [5–8], medicine [9, 10], and so on. One of the research interests in recent years is the diffusion of macromolecule (protein or nano-particle) in complex solution systems. Especially in living cells, a variety of structural and functional proteins are immersed in crowded cytoplasmic environments, involved in diverse biochemical processes such as enzyme reactions [11], signal transmission [1], gene transcription and self-assembly of supramolecular[12]. Experimentally, one would usually focus on nano-particle (NP) in complex environment such as polymer solution. And study of diffusive behavior of NP can provide important information about the local structure, viscoelastic properties and also the crowding effect of polymer liquids[13–15].

In the past decades, diffusion of NPs in polymer solutions has received a lot of attention both experimentally [16–20] and theoretically [21–27]. In experiments, fluctuation correlation spectroscopy (FCS) [28–31], dynamic light scattering (DLS) [29, 32], and capillary viscosimetry are general tools to investigate the diffusion of a NP in complex fluids. It is found that as the particle radius Rdecreases to nanoscale, the diffusion coefficient D would increase exponentially with R and violates the Stokes-Einstein (SE) relation apparently [33–37]. Phillies et al, based on the analysis of a great deal of experimental data, proposed an empirical formula $D = D_0 \exp(-\alpha c^v)$, where D_0 is the diffusion coefficient in a purely background solvent, c is the concentration of polymer solution and α , v are fitting parameters relevant to a specific system [38]. Although this stretched exponential form matches the experimental data very well, the underlying physical meaning of these two parameters are quite blurry[39]. Recently, Holyst et. al proposed a length-scale dependent viscosity theory [40, 41]. They argued that the diffusion of a NP in polymer solution was characterized by at least three length scales: the particle size R, the polymer hydrodynamic radius R_h and the correlation length ξ of the solution. Concretely, the formula reads $D/D_0 \sim$ $\exp[b(R_{\text{eff}}/\xi)^a]$, where $R_{\text{eff}} = \sqrt{R^2 R_h^2/(R^2 + R_h^2)}$ denotes an effective size, a and b are fitting parameters. If R is small with respect to ξ , the particle motion experiences the local viscosity which is smaller than the macro-viscosity by order of magnitude. While if R is much larger than R_h or R_g , the particle motion would no more be affected by the local structures of polymer and touches the macro viscosity finally, and obeys the Stokes-Einstein relation automatically. Also, there are some other interesting models in this field such as the hopping model[42], walking confined diffusion model[43] and depletion model[44]. Liu et al used a MD simulation to study the diffusion of a NP in polymer melt [45]and the core results are similar to Holyst's work, where R_q could be the boundary of NP size to experience the local viscosity to macro viscosity. Note that, it is hard to take a simulation work on this issue especially the polymer solution, which on one side the solvent accounts for a large proportion and costs a huge computational resource, and on other side a reasonable diffusion coefficient needs so much long time to evolve the system. To our best of knowledge, only in the recent two years, Li et al [46, 47] and Pryamitsyn et al [48] had studied this issue in a simulation way, using Multiparticle Collision Dynamic (MPCD) and Dissipative Particle Dynamic (DPD) method respectively.

Most of the present works focus on the diffusion of passive NP. But note that, in real biological system, especially in a living cell, the active proteins widely exist. Typical active proteins include motor molecule[49, 50], microtubule or active filament[51, 52]. By consuming the ATP, they get a propel force that extremely enhance the transport efficiency in various biochemical process. Actually, the dynamics behavior of active matter has gained much attention in recent years. Instead of the living species such as bacteria[53], spermatozoa[54, 55] and the micro protein in cell as mentioned above, there are also much artificial objects capable of self-propulsion such as Janus particles[56], chiral particles[57], and vesicles[58]. And a wealth of new non-equilibrium phenomena have been reported, including phase separation[59], active turbulence[60], and active swarming[61], both experimentally and theoretically.

Recently, much interests arised on the dynamic behaviors of an active particle in complex environment [62–65]. And a number of studies indicated that there exists a twoway coupling between the active matter and the ambient environment, which the motion of active suspensions can alter the local property of its environment, while simultaneously the complex fluid rheology can modify the dynamics of the active matters [65]. For instance, Patteson *et al* reported an experiment on the diffusion of an Escherichia coli in polymeric solution[66]. They found that the translational diffusion of cell is enhanced and the rotational diffusion is sharply declined respected to the diffusion behavior in water-like fluid, due to the complicated interaction with the polymers in solution. It was also found that activity has a fascinating effect on the viscosity of active suspensions, even sometimes leading to a "vanishing" viscosity phenomenon in bacterial suspensions[67]. Even for a single swimmer, there is no universal answer to whether mobility is enhanced or hindered by fluid elasticity [65]. Despite lot of interesting progresses made so far, there still remains many open questions to be answered, even some fundamental ones. For instance, how would the long time diffusion coefficient of an active particle depends on its size in a complex fluid, although being a quite straightforward question, has not been systematically studied yet.

In the present work, we have addressed such a topic by investigating the diffusion dynamics of an active Brownian particle (ABP) in polymer solutions, as depicted schematically in Fig.1. The ABP is modeled by a spherical particle subjected to an active force along the direction denoted by **n**, which changes randomly with time. Three-dimensional Langevin simulations are performed to calculate the long time diffusion coefficient D of the ABP as a function of the particle size R, for a variety of different active force F_a as well as polymer concentration ϕ . Very interestingly, we find that D shows a non-monotonic dependence on R if the active force F_a is large enough: D first increases with the particle size R, reaches a maximum value at an optimal particle size $R_{\rm opt}$, after which it decreases monotonically. The optimal value R_{opt} moves to a larger value with the increment of active force F_a and to a smaller value with increasing polymer concentration. Further analysis of the time dynamics of the mean-square displacement (MSD) indicates that it is the competition between the persistence motion of the particle, which is the reason for superdiffusion, and the cage effect of the polymer solution, which leads to the subdiffusion behavior, that causes the optimal size effect for long time diffusion. We have also introduced an effective viscosity experienced by the ABP by introducing a phenomenological model describing the ABP moving in a fluid with effective viscosity η^a_{eff} . Such an effective

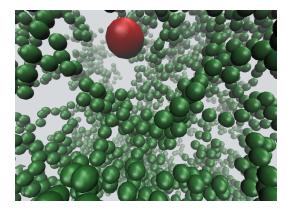


Figure 1. The illustration of a ABP immerses in polymer solution, which the big red particle represents ABP and the green particle around represents polymer bead.

viscosity is found to be larger than that experienced by a passive particle, and it shows strong dependency on the particle size R as well as the active force amplitude F_a . In addition, we have found that D shows a power law dependence on the active force F_a , i.e., $D \sim F_a^{\alpha}$, for a fixed particle size. More interestingly, the exponent α also shows a non-monotonic dependence on the particle size R: $\alpha < 2.0$ for small R, then it increases with R to a maximum value $\alpha \sim 2.5$ for an intermediate particle size, and finally approaches 2.0 in the large size limit. Our findings demonstrate that interplay between particle activity and local structure in complex solution may lead to interesting dynamics of the ABP.

The paper is organized as follows. In section II , we describe the model and simulation method. Results and discussion are presented in section III followed by conclusion in section IV .

II. SIMULATION METHOD

As shown in Fig.1, we consider a three dimensional system containing a single ABP of radius R in polymer solution. The polymers are modeled as bead-spring chains, each consisting of N beads with diameter σ . All non-bonded (excluded volume) interactions between the beads are modeled by purely repulsive Weeks-Chandler-Andersen (WCA) potentials[68]:

$$U_{\rm BB}(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6 + \frac{1}{4} \right] & r_{ij} < \sqrt[6]{2}\sigma \\ 0 & r_{ij} \ge \sqrt[6]{2}\sigma \end{cases}$$
(1)

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the two beads *i* and *j* (with position vectors given by \mathbf{r}_i and \mathbf{r}_j , respectively), ϵ represents strength of the WCA potential. The bond interaction between two nearby beads

is modeled by the FENE (finite extensible nonlinear elastic) potential[69]:

$$U_{\text{FENE}}(r_{ij}) = -\frac{1}{2}\epsilon_F r_F^2 \ln\left[1 - (\frac{r_{ij}}{r_F})^2\right]$$
(2)

where ϵ_F is the interaction strength and $r_F = 2.0\sigma$ denotes the upper bound of r_{ij} .

The interactions between the NP and polymer beads are also described by the truncated WCA potential which is offset by the interaction range $R_{ev} = R - \sigma/2$:

$$U_{BN}(r_{jn}) = 4\epsilon \left[\left(\frac{\sigma}{r_{jn} - R_{ev}} \right)^{12} - \left(\frac{\sigma}{r_{jn} - R_{ev}} \right)^6 + \frac{1}{4} \right]$$
(3)

for $R_{ev} < r_{jn} < R_{ev} + 2^{1/6}\sigma$, where r_{jn} denotes the distance between bead j and the nano-particle with position given by \mathbf{r}_n . While for $r_{jn} \leq R_{ev}$, $U_{BN}(r_{jn}) = \infty$ and for $r_{jn} \geq R_{ev} + 2^{1/6}\sigma$, $U_{BN}(r_{jn}) = 0$.

The dynamics of the polymer beads are described by the following Langevin equations(ignoring hydrodynamic interactions):

$$m_{\rm B} \frac{d^2 \mathbf{r}_j}{dt^2} = -\gamma_{\rm B} \frac{d\mathbf{r}_j}{dt} - \nabla_{\mathbf{r}_j} U' + \sqrt{2k_{\rm B}T\gamma_{\rm B}} \boldsymbol{\xi}_j(t) \qquad (4)$$

where $U' = \sum_{i \neq j} U_{\text{BB}}(r_{ij}) + U_{\text{BN}}(r_{jn})$, m_B is the bead mass and γ_B is the friction coefficient of the bead in the background pure solvent, $\boldsymbol{\xi}_j(t)$ denotes independent Gaussian white noises with zero means and unit variances, i.e., $\langle \boldsymbol{\xi}_j(t) \rangle = 0$, $\langle \boldsymbol{\xi}_i(t) \boldsymbol{\xi}_j(t') = 2\delta_{ij} \mathbf{I} \delta(t-t') \rangle$ where \mathbf{I} is the unit tensor.

The dynamics of the ABP is given by

$$m_{\rm N} \frac{d^2 \mathbf{r}_n}{dt^2} = -\gamma_{\rm N} \frac{d\mathbf{r}_n}{dt} + F_a \mathbf{n} - \nabla_{\mathbf{r}_n} \left[\sum_j U_{\rm BN} \left(r_{jn} \right) \right] + \boldsymbol{\xi}_n(t)$$
(5)

$$\frac{d\mathbf{n}}{dt} = \boldsymbol{\eta}\left(t\right) \times \mathbf{n} \tag{6}$$

where m_N is the mass of the ABP and γ_N is the friction coefficient of the ABP in the pure solvent. \mathbf{r}_n is the position vector of the ABP, $r_{jn} = |\mathbf{r}_j - \mathbf{r}_n|$ is the distance between polymer bead j and the ABP. F_a represents the amplitude of active force with orientation specified by the unit vector \mathbf{n} . $\boldsymbol{\xi}_n(t)$ is also a Gaussian white noise vector with $\langle \boldsymbol{\xi}_n(t) = 0 \rangle$ and $\langle \boldsymbol{\xi}_n(t) \boldsymbol{\xi}_n(t') \rangle = 2D_t \mathbf{I} \delta(t - t')$, where $D_t = k_B T / \gamma_N$ is the (short time) translational diffusion coefficient. The stochastic vector $\boldsymbol{\eta}(t)$ is also Gaussian distributed with zero mean and has time correlations given by $\langle \boldsymbol{\eta}(t) \boldsymbol{\eta}(t') \rangle = 2D_r \mathbf{I} \delta(t - t')$, where D_r denotes the rotational diffusion coefficient. Since we consider a spherical particle here, D_t is related to D_r via $D_r = 3D_t / (2R)^2$.

All simulations were performed in a cubic box with a 25σ edge length with periodic boundary conditions in all directions. A value $\epsilon = k_B T$ was used for all particle interactions, where $k_{\rm B}$ is Boltzmann's constant and Ttemperature. The polymers were modeled using N = 64beads and the parameters for bond-interactions are $k_{\rm F} =$ $10k_{\rm B}T\sigma^{-2}$ and $r_{\rm F} = 2.0\sigma$. If not otherwise specified, we considered a system containing 72 polymer chains, corresponding to a bead-number concentration $\phi \simeq 0.3$. For other polymer concentrations, we simply varied the number of polymer chains. We assumed equal densities of the ABP and polymer bead, thus $m_{\rm N} = 8R^3/\sigma^3 m_{\rm B}$. Since the friction coefficient γ is proportional to $6\pi\eta_0 R$ for a spherical particle of radius R in the pure solvent, where η_0 is the zero-shear viscosity of the pure solvent, we have $\gamma_{\rm N} = (2R/\sigma) \gamma_{\rm B}$. We set $m_{\rm B} = 1$, $k_{\rm B}T = 1$, $\sigma = 1$ for dimensionless units and then fixed $\gamma_{\rm B} = 1$. The remained variable parameters are the active force amplitude F_a and the particle radius R. Velocity-Verlet algorithm was used to simulate the dynamic equations with a time step $\Delta t = 0.01$. All the reported data below were obtained after averaging over 20 independent runs with long enough time.

III. RESULTS AND DISCUSSION

A. Optimal Size for Active Particle Diffusion

In the present paper, we are mainly interested in how the activity would influence the NP diffusion behavior in the polymer solution. For comparison, we first investigate the diffusion behavior of a passive particle in the system set above. The long time diffusion coefficient Dis calculated via

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle \Delta r_n^2(t) \rangle$$

where $\langle \Delta r_n^2(t) \rangle = \langle |\mathbf{r}_n(t) - \mathbf{r}_n(0)|^2 \rangle$ is the mean square displacement (MSD) of the NP with $\mathbf{r}_n(t)$ being the particle position at time t. As already mentioned in the introduction section, passive particle diffusion in polymer solutions may strongly deviates the SE relation. In particular, the diffusion coefficient D can be described by scaling relations involving the correlation length of the polymer solution and an effective size. Note that the system parameters used in our present work may not fit well the experimental conditions. In Fig.2(a), the diffusion coefficients D of a passive NP as functions of the radius R for several fixed values of polymer concentration $\phi = 0.1, 0.2$ and 0.3 are presented. Clearly, D decreases monotonically with increasing of R as well as the polymer concentration ϕ as expected. We can introduce an effective (so-called) nano-viscosity η_{eff} experienced by the NP via the standard SE relation $D = k_B T / 6 \pi \eta_{\text{eff}} R$. In the large particle size limit, η_{eff} would be the macroscopic zero-shear viscosity η_{macro} of the polymer solution. For small particle size, however, η_{eff} is much smaller than

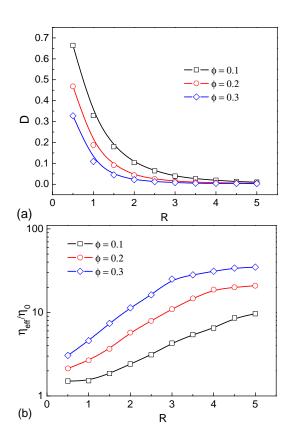


Figure 2. The diffusion coefficient D (a) and the effective viscosity η_{eff} (b) of a passive NP with respect to different size R, under the concentration of polymer $\phi = 0.1, 0.2$ and 0.3, respectively. Note that η_{eff} is reduced by the viscosity of pure solution η_0 . The solid lines are drawn to guide the eyes.

 η_{macro} leading to large deviations from the SE relation. In Fig.2(b), the nano-viscosity as a function of the NP size R is shown for different concentration ϕ . η_{eff} firstly increases fiercely with R until it finally reaches the macroscopic value η_{macro} for large particle sizes. It suffices to reach η_{macro} for a NP with size to be just a few times of that of a polymer bead and NP in a more concentrated polymer solution can reach η_{macro} at a smaller R.

We now turn to the ABP. In Fig.3(a), D as a function of R at a fixed concentration $\phi = 0.3$ is presented, for a few different values of propelling force F_a . For a relatively small active force, e.g., $F_a = 20$ as shown in black line in Fig.3(a), D decreases monotonically with the particle size R, which is similar to the case of a passive particle as shown in Fig.2. For larger active forces, however, D shows an interesting non-monotonic dependence on the particle size R, i.e., D first increases with Runtil it reaches a maximum value D_{max} at an optimal size R_{opt} and then decreases again, as demonstrated clearly in Fig.3(a) for $F_a = 40, 60, \text{ and } 80$, respectively. With increasing F_a , the overall values of D become larger and the optimal size slightly R_{opt} shifts to larger values. In Fig.3(b), dependence of the optimal particle size R_{opt} on the active force F_a for a few different polymer concentrations ϕ are depicted. For a fixed ϕ , R_{opt} increases with F_a

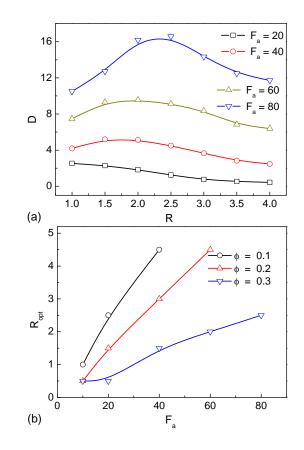


Figure 3. (a) The diffusion coefficient D of ABP as a function of the particle radius R, for difference active forces $F_a = 20$, 40, 60 and 80 and fixed $\phi = 0.3$. (b) Dependence of $R_{\rm opt}$ on active force F_a for different number concentrations $\phi = 0.1$, 0.2 and 0.3. The solid lines are drawn to guide the eyes.

as already shown in Fig.3(a), while R_{opt} decreases with ϕ if F_a is fixed.

The above findings about the non-monotonic dependence of D on R is quite counterintuitive at the first glance, particularly in terms of the increasing of D with R. Generally, one would expect that a larger particle would diffuse more slowly as the conventional SE relation would tell. For a passive nano-particle in a polymer solution, although large deviations from the SE relation were observed and a length-scale viscosity should be used in replace of the macroscopic viscosity η_{macro} , D is always a decreasing function of R as already shown in Fig.2. Therefore, the increase of D with R as shown in Fig.3(a) must be related to the active feature of the ABP. Indeed, if the active force is not large enough, as shown for $F_a = 20$ in Fig.3(a), D will still be a decreasing function of R, being same to the case of a passive NP. For large active force, the non-monotonic dependence of D on R suggests the existence of two competitive factors that influence the ABP diffusion.

B. Subdiffusion and Superdiffusion

In order to understand in more detail about such nontrivial dependence of D on R, we further analyze the short time dynamics of the ABP by investigating the MSD as a function of time t, and compare it to that of a passive one.

Fig.4(a) presents the MSDs for passive NPs with radius R = 1, 2 and 4 for $\phi = 0.3$. The curves share some common features, namely, ballistic diffusion at very short time while normal diffusion at very long time, correspond to MSD $\sim t^2$ and MSD $\sim t$ respectively. For a small NP, such as R = 1.0, the dynamics transformers from ballistic motion to normal diffusion gradually. With increasing particle size, the NP may experience a "cage effect" resulting from the surrounding polymer beads and the MSD shows a sub-diffusion regime at the middle time scale, wherein MSD ~ t^{α} with $\alpha < 1$. This is shown more clearly in Fig.5(a), where the instantaneous exponent α is depicted as a function of time corresponding to Fig.4(a). Obviously, with increasing the NP size, the cage effect is more remarkable and α decreases to a smaller value in the intermediate time scale, corresponding to a stronger and longer subdiffusion behavior. Also note that the curve for a larger particle always lies below that for a smaller one in the whole time range.

For an ABP, however, the behavior is quite different, as shown in Fig.4(b) and Fig.5(b) for $F_a = 60$. For this large active force, the diffusion coefficient D shows nonmonotonic dependence on R as demonstrated in last subsection. For a small particle with R = 1.0, the behavior shows no distinct difference from that of a passive one in terms of both the MSD curve as well as the exponent α . For a larger particle with R = 2.0, however, we find that the particle undergoes a much longer superdiffusion time regime with $1 < \alpha < 2$ before it finally reaches the long time normal diffusion regime. Interestingly, the exponent α shows an apparent plateau at $\alpha \sim 1.7$ as shown in Fig.5(b) which spans two orders of magnitude of time. Such a superdiffusion behavior with α slightly smaller than 2 implicates that the particle moves more persistently along a direction than randomly along different directions. Note that this persistence of motion along a direction reflects the very feature of an active Brownian particle. For an even larger particle R = 4.0, one can see that the exponent α first decreases sharply to a value at 0.9 in the short time range, namely indicated a sub-diffusion behavior, and then increases again to a high value close to 2 in the intermediate range before it finally decreases to the normal diffusion value $\alpha = 1$. The sharp decrease of α in the short time range should result from the cage effect of the surrounding polymers. Due to the large activity of the particle, however, such a cage effect can not last for a long time and finally the particle jumps out of this cage leading to the increase of α in the intermediate time range. In the short time range, ABP with a smaller size moves faster than a larger one as shown in Fig.4(b). However, in the long time limit, the

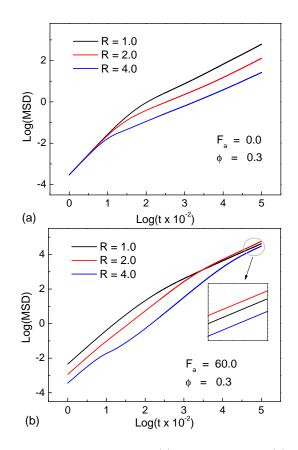


Figure 4. MSD of an active NP (a) and a passive NP (b) with size R = 1.0, 2.0, 4.0. The short line indicates the time scaling at different time scale. For an active NP, the magnitude of propelling force is fixed at $F_a = 20.0$.

curve for a middle particle size R = 2 lies above those of R = 1 and 4, corresponding to a maximum value of long time diffusion coefficient D for R = 2 compared to those others two in accordance with Fig.3.

The above analysis suggests that the occurrence of an optimal particle size for ABP diffusion in polymer solution is the consequence of two competitive effects. One is that the cage effect of the surrounding polymers which would become stronger as the particle size becomes larger. Without activity, this cage effect would lead to subdiffusion behavior of a particle and decrease of the long time diffusion coefficient D. Such a cage effect results in a length-scale dependent viscosity experienced by the particle as described in Fig.2(b) which increases with R. The other is the persistence motion due to the particle activity which would become longer as the particle size increases. As well known for an ABP and described in the model section, the persistence time τ_p for an isolated ABP is given by $(2D_r)^{-1}$, where D_r scales as R^{-2} for the ABP as shown in section II. Therefore, the ABP would move along the propelled direction longer as the particle size gets larger, leading to superdiffusive behavior and thus accelerating the long time diffusion. When the particle size is small, e.g. R = 1, both cage and persistence effects are not significant and the particle trans-

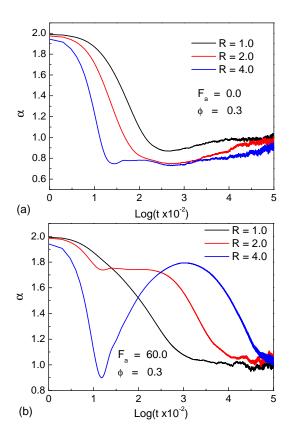


Figure 5. The differential of MSD of of a passive NP (a) and an ABP (b) with size R = 1.0, 2.0 and 4.0 in the polymer solution with concentration $\phi = 0.3$. α is just the slope of curve in Fig.4 or the scaling exponent at different time scale. For an ABP depicted in (b), the magnitude of propelling force is fixed at $F_a = 60.0$.

fers gradually from ballistic to diffusion motion for both passive and active particles. For a relatively larger particle, the persistence effect would dominate, thus leading to increase of D. If the particle size is too large, however, the cage effect would dominate and the diffusion coefficient would decrease again. Besides, increasing the magnitude of F_a , the persistence motion would be enhanced. Clearly, this enhancement will be more apparent for a bigger ABP with longer τ_p . Therefore, the stronger F_a promotes R_{opt} to a bigger value as shown in Fig.3(b).

C. Effective Viscosity η_{eff}

As discussed in Section 3.1, a passive particle would experience an effective viscosity η_{eff} that is dependent on its size R, which could be much smaller than the macroscopic zero-shear viscosity η_{macro} . For a passive particle, this effective viscosity is determined according to the SE relation, $D = k_{\text{B}}T/(6\pi\eta_{\text{eff}}R)$. It is thus also interesting for us to ask the question what is the effective viscosity the ABP experiences in the polymer solution.

At first thought, one may also just use the SE relation to obtain this effective viscosity η_{eff} , i.e., η_{eff} = $k_{\rm B}T/(6\pi DR)$ where D is the long time translational diffusion coefficient obtained by simulation above. Nevertheless, this may not be appropriate for an active particle, since we must take into account the particle activity which would lead to an active contribution to D. As already discussed in the model section, for an isolated ABP of radius R in a simple fluid with friction coefficient γ , the dynamics can be described by the following overdamped Langevin equation (LE),

$$\frac{d\mathbf{r}}{dt} = \gamma^{-1} F_a \mathbf{n} + \sqrt{2D_t} \boldsymbol{\xi}(t)$$
(7)
$$\frac{d\mathbf{n}}{dt} = \boldsymbol{\zeta}(t) \times \mathbf{n}$$

where $\boldsymbol{\xi}(t)$ and $\boldsymbol{\zeta}(t)$ are both Gaussian white noise vectors with zero mean and unit(tensor) variance, $D_t = k_B T/\gamma$ and $D_r = 3D_t/4R^2$. In a coarse-grained time scale, it was shown that the self-propulsion force for ABP can be mapped into a colored noise[70], i.e.,

$$\langle \mathbf{n}(t) \mathbf{n}(t') \rangle \simeq \frac{1}{3} e^{-\left|t-t'\right|/\tau_p} \mathbf{1}$$

where **1** denotes the unit tensor and $\tau_p = (2D_r)^{-1}$ denotes the persistence time of the self-propulsion force. With this approximation, one can obtain the mean-square displacement (MSD) of the ABP as follows,

$$\left\langle \delta r^{2}\left(t\right)\right\rangle =\frac{2F_{a}^{2}\tau_{p}}{\gamma^{2}}\left[t+\tau_{p}\left(e^{-t/\tau_{p}}-1\right)\right]+6D_{t}t$$

In the long time limit, this gives the diffusion coefficient

$$D = \lim_{t \to \infty} \frac{1}{6} \frac{\left\langle \delta r^2\left(t\right) \right\rangle}{t} = D_t + \frac{F_a^2 \tau_p}{3\gamma^2}$$

If we use the fact that $\tau_p = (2D_r)^{-1}$ and $D_r = 3D_t/4R^2$, then we have

$$D = \frac{k_B T}{\gamma} + \frac{2F_a^2 R^2}{9k_B T \gamma} = \frac{1}{6\pi\eta_0 R} \left(k_B T + \frac{2F_a^2 R^2}{9k_B T} \right) \quad (8)$$

where we have used the Stokes relation $\gamma = 6\pi\eta_0 R$ in the simple fluid with η_0 the zero-shear viscosity. This analysis shows how the long time diffusion coefficient Ddepends on the viscosity η_0 of a simple fluid. The first term is surely the SE relation, while the second term denotes the contribution from particle activity. For small T or large F_a , the second active term would dominate and the relation between D and η_0 is totally different from the SE relation.

Actually, eqn (8) provides us a scheme to introduce an effective viscosity experienced by the ABP in the surrounding solution. We consider now that the ABP is moving in a pure fluid with effective viscosity η_{eff} , whose dynamics is also described by eqn (7), but with γ replaced by an effective $\gamma_{\text{eff}}^a = 6\pi \eta_{\text{eff}}^a R$ (the superscript 'a' stands for 'active'). The (short time) translational diffusion constant D_t is determined then by γ_{eff}^a through fluctuation-dissipation theorem $D_t = k_{\rm B}T/\gamma_{\rm eff}^a$, which in turn gives D_r . Clearly, the long time diffusion coefficient D would also be given by eqn (8) with η_0 replaced by $\eta_{\rm eff}^a$, i.e.,

$$D = \frac{1}{6\pi \eta_{\text{eff}}^a R} \left(k_{\text{B}} T + \frac{2F_a^2 R^2}{9k_{\text{B}} T} \right) \tag{9}$$

Therefore, the effective viscosity of the polymer solution experienced by the ABP could be defined as

$$\eta_{\rm eff}^a = \frac{1}{6\pi DR} \left(k_{\rm B}T + \frac{2F_a^2 R^2}{9k_{\rm B}T} \right) \tag{10}$$

In Fig.6(a), we show the effective viscosity η_{eff}^a calculated by eqn (10) as functions of the particle size Rfor different concentrations $\phi = 0.1, 0.2$ and 0.3, where the values of D are obtained by simulations as shown in Fig.3. The amplitude of the active force is $F_a = 20$. Also shown are the values for a passive particle, which were already presented in Fig.2(b). As can be seen, η_{eff}^a increases with R as expected, similar to the case of η_{eff} for a passive particle. Interestingly, η^a_{eff} is much larger than η_{eff} as shown in Fig.6(a), indicating that the active particle seems to move in a "more viscous" fluid than the passive one. Nevertheless, one should be careful to draw the conclusion that particle activity induces thickening of the polymer solution, since η_{eff}^a here is defined via eqn (6). As discussed above, this equation is obtained by modeling the motion of ABP in polymer solution as if it were in an viscous fluid with η^a_{eff} , while keeping fluctuationdissipation theorem and all other features of ABP unchanged. Indeed, the effective viscosity experienced by an ABP characterize more the local environment surrounding the particle, and it is not identical to the zeroshear macro-viscosity of the solution. Our arguments here indicate that the ABP does feel a much more viscoelastic local environment than a passive one, otherwise it would diffuse much faster. In Fig.6(b), the effective viscosity η_{eff}^a as a function of active force amplitude F_a for different particle size R are presented. If the particle size is relatively small, say R = 1.0, η_{eff}^a is a monotonic increasing function of F_a , implying that a more active particle feels a more viscoelastic local fluid. For large particle sizes, however, more interesting features can be observed: η_{eff}^a shows a non-monotonic dependence on F_a . For R = 3.0, for instance, η_{eff}^{a} first increases sharply to a very large value with increment of F_a and then decreases relatively slowly to a moderate value when F_a is large. Since η^a_{eff} is calculated via definition in our present work, the mechanism behind these interesting observations is still open to us and may deserve more detailed study in future works.

D. Scaling of D with active force F_a

Another feature shown in Fig.6(b) is that η^a_{eff} becomes not sensitive to F_a if F_a is large enough. Now considering

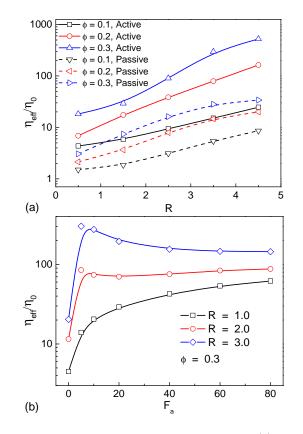


Figure 6. Effective viscosity η_{eff} as a function of (a) particle size R for different values of concentration $\phi = 0.1, 0.2$ and 0.3 with fixed active force $F_a = 20$, and (b) active force F_a for different particle size R = 1.0, 2.0 and 3.0 with fixed concentration $\phi = 0.3$. Note that η_{eff} is reduced by the viscosity of pure solution η_0

eqn (9) for the long time diffusion constant D, one can see that the second term would dominate if F_a is large. Therefore, D would scale approximately as F_a^2 in the range of large F_a . Motivated by this observation, we have also investigated quantitatively how D depends on F_a in the whole range.

Surprisingly, we find that D shows a rather good power-law scaling with F_a , i.e., $D \sim F_a^{\alpha}$, as shown in Fig.7(a) for different particle sizes and fixed concentration. For R = 1.0, 2.0 and 3.0, the scaling exponent α reads approximately 1.40, 1.99 and 2.31, respectively. In Fig.7(b), the dependence of α exponent on particle size R is depicted, where one observes a rather interesting nonmonotonic variation: α increases from 1.4 at R = 1.0 to a maximum value $\alpha \simeq 2.4$ at R = 5.0 and then decreases again to about 2.2 at R = 7.0 which is the largest particle size considered in the present work (to get a reliable data at R > 5.0 that avoiding the finite-size effects, we have to extend the system to $l = 30.0\sigma_0$ consisting of totally 126 polymers). In the limit of very large particle size, one would imagine that the polymer solution can be viewed as a simple fluid, and the exponent would become 2.0 again.

In the current stage, we are yet not able to understand

the power-law scaling between D and the active force F_a . eqn (9) would simply give $D \sim F_a^2 R/\eta_{\text{eff}}^a$ when the active term dominates, which seems to suggest an exponent to be 2.0 if η_{eff}^a is not dependent on F_a . Nevertheless, eqn (9) is just a definition of η_{eff}^a which is obtained from the simulated value of D, and the calculated values of η_{eff}^a do depend on F_a as already shown in Fig. 6. Therefore, to understand the power-law dependence of D on F_a , one has to derive a separate theory for the diffusion of ABP in polymer solutions, which is important but beyond the scope of current study.

Here in the present paper, we would like to take a qualitative description to highlight the active effects. According to the MCT framework to study the diffusion of a passive NP in polymer solution, the long time diffusion coefficient can be decomposed into two different parts, i.e., $D = D_{\text{micro}} + D_{\text{hydro}}$, where D_{hydro} is the conventional SE term, while D_{micro} is due to the microscopic level interactions between the particle and polymer molecules. The friction related to D_{micro} results from direct *binary collisions* between the NP and the polymer beads and *density fluctuation* of the solution. For large particles in entangled solutions with strong topological constraints, however, one should take into account another possible mechanism for diffusion, namely, the hopping process[42], wherein the particle can diffuse by overcoming barrier between neighboring confinement cells. Now we take the particle activity into account. Clearly, enhancement of particle activity would lead to more frequent direct collisions between the particle and polymer beads, thus leading to a larger effective viscosity compare to that experienced by a passive particle. Since we only consider a single particle here, the density fluctuation contribution to the friction would not change much with the variation of the particle activity. Nevertheless, particle activity would facilitate the hopping process if the particle is large enough, which would result in a relatively smaller effective viscosity. Therefore, for a small particle such as R = 1.0, the effective viscosity experienced by an ABP would increase with the amplitude F_a , since hopping diffusion is not relevant for small particles. In this case, the scaling exponent α would be less than 2.0 since η_{eff} scale as F_a^{λ} with $\lambda > 0$. For a large particle such as R = 3.0, both binary collisions and hopping processes will be enhanced by the particle activity. These two effects competes with each other, leading to the nonmonotonic dependence of η^a_{eff} with F_a as demonstrated in Fig.6(b). In the small F_a range, enhanced binary collision dominates leading to an sharp increase of η^a_{eff} , while for large F_a , enhanced hopping dominates which results in decrease of η^a_{eff} . In this case, the exponent α should be larger than 2.0 in the large F_a range. For a particle of proper size, the positive and negative effects of particle activity may cancel, which leading to weak dependence of η^a_{eff} on F_a and the exponent α would be approximately 2.0. For a very large particle size, however, the effect that activity enhances hopping may become weaker than that for a relatively smaller particle, such that α would

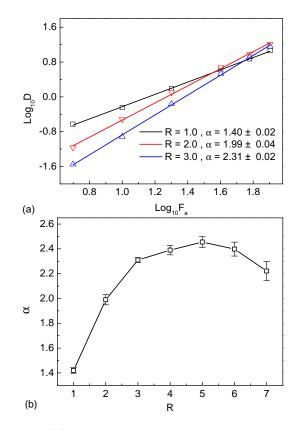


Figure 7. (a)dependence of diffusion coefficient D on propelling force F_a in a scaling form. The radius of NP are fixed at R = 1.0, 2.0 and 3.0, represented by black, red and blue dots, respectively. The solid lines are scaling fits to the data(b)The scaling factor of the function between D and F_a in a fixed size of NP. The solid line is drawn to guide eyes.

decrease with R. All these features are consistent with the observations in Fig.7(b).

IV. CONCLUSION

In conclusion, we have used Langevin Dynamic simulation method to investigate the diffusion behavior of an ABP in semidilute polymer solution. Extensive simulations indicate that the activity can markedly enhance the diffusion of NP in this complex environment, respected to a passive NP. Interestingly, we have found that the dependence of long time diffusion coefficient D on the particle radius R is non-monotonic and D reaches a maximum value at a certain optimal value R_{opt} , if exerted a propelling force F_a strong enough. Consequently, the NP with a bigger size would get a higher D than a relatively smaller one, which is greatly against the common sense that a larger particle usually diffuse slower for a passive NP.

The subsequent analysis from the short time dynamics reveals that this abnormal phenomenon is due to the two fold impacts of ABP on diffusion. In detail, the increasing size of ABP gains more obstruction from the polymer beads that leads to more apparent cage effects, which finally slows down the diffusion. However, on the other side, a bigger size could usually make the rotation tougher and result in the longer rotational relaxation time τ_p . This would lead to longer persistence motion along a direction and cause superdiffusion behavior which would cover the subdiffusion from the cage effect, and finally facilitates the diffusion. It is the competition between the persistence motion and the cage effect that leads to the non-monotonic dependence of the long time diffusion D on the particle size R.

We have also introduced a phenomenological model to describe the ABP dynamics, assuming that the ABP is moving in a simple viscous fluid with effective viscosity η_{eff}^a . We find that this effective viscosity shows strongly dependency on the particle size R as well as active force F_a . Interestingly, this effective viscosity experienced by the ABP is larger than that experience by a passive nanoparticle of the same size, which means that the ABP feels a much more viscoelastic local environment, otherwise it would diffuse much faster. For an ABP of small size, η_{eff}^a increases monotonically with F_a , while for a large ABP, η_{eff}^a can even show a non-monotonic dependence on F_a bypassing a maximum.

A more striking finding is that D shows a power-scaling with the active force F_a in an excellent manner. The exponent α is not equal to the value 2.0 that observed in a simple liquid, but non-monotonically depends on R. It increases from a value quite smaller than 2.0 to a maximum value at about 2.5, and then decreases again to 2.0 if R is large enough. Although a rigorous theory for the diffusion behavior of ABP in polymer solutions is not available at the current stage, we have tried to understand the effect of activity on particle diffusion through its influence on the binary collisions between the particle and polymer beads and on the hopping process of a large particle out of confinement cells.

Our results indicate that activity combined with the inner structure of the polymer solution indeed largely affects the diffusion dynamics of an active particle, both short time and long time, which is greatly different to a passive one. We believe that our work can open more perspectives on the study of active matter in complex solutions and may shed some new lights on understanding such an important process in real biological systems.

ACKNOWLEDGMENTS

This work is supported by the Ministry of Science and Technology of China(Grant Nos. 2013CB834606, 2016YFA0400904), by National Science Foundation of China (Grant Nos. 21673212, 21521001, 21473165, 21403204), and by the Fundamental Research Funds for the Central Universities (Grant Nos. WK2030020028, 2340000074).

- Y. Wang, L. A. Benton, V. Singh, and G. J. Pielak, The journal of physical chemistry letters 3, 2703 (2012).
- [2] A. B. Sigalov, Molecular bioSystems 6, 451 (2010).
- [3] T. Pederson, Nature Cell Biology 2, E73 (2000).
- [4] P. Cluzel, M. Surette, and S. Leibler, Science 287, 1652 (2000).
- [5] P. Struntz and M. Weiss, Journal of Physics D: Applied Physics 49, 044002 (2015).
- [6] D. Gersappe, Physical review letters 89, 058301 (2002).
- [7] T. H. Zhou, W. H. Ruan, M. Z. Rong, M. Q. Zhang, and Y. L. Mai, Advanced Materials **19**, 2667 (2007).
- [8] D. Shah, P. Maiti, D. D. Jiang, C. A. Batt, and E. P. Giannelis, Advanced Materials 17, 525 (2005).
- [9] R. Rohilla, T. Garg, A. K. Goyal, and G. Rath, Drug delivery 23, 1645 (2016).
- [10] M. Huo, J. Yuan, L. Tao, and Y. Wei, Polymer Chemistry 5, 1519 (2014).
- [11] H. Berry, Biophysical journal 83, 1891 (2002).
- [12] R. M. Macnab, Science **290**, 2086 (2000).
- [13] Q. Lu and M. J. Solomon, Physical Review E 66, 061504 (2002).
- [14] T. A. Waigh, Reports on Progress in Physics 68, 685 (2005).
- [15] P. Cicuta and A. M. Donald, Soft Matter 3, 1449 (2007).
- [16] I. Kohli and A. Mukhopadhyay, Macromolecules 45, 6143 (2012).
- [17] T. Chen, H.-J. Qian, and Z.-Y. Lu, The Journal of Chemical Physics 145, 106101 (2016).
- [18] V. Pryamitsyn and V. Ganesan, Journal of Polymer Sci-

ence Part B: Polymer Physics 54, 2145 (2016).

- [19] J. Lee, A. Grein-Iankovski, S. Narayanan, and R. L. Leheny, Macromolecules 50, 406 (2017).
- [20] R. Poling-Skutvik, R. Krishnamoorti, and J. C. Conrad, ACS Macro Letters 4, 1169 (2015).
- [21] R. Tuinier and T.-H. Fan, Soft Matter 4, 254 (2008).
- [22] V. Ganesan, V. Pryamitsyn, M. Surve, and B. Narayanan, The Journal of Chemical Physics 124, 221102 (2006).
- [23] U. Yamamoto and K. S. Schweizer, Macromolecules 48, 152 (2014).
- [24] Y. Dong, X. Feng, N. Zhao, and Z. Hou, The Journal of Chemical Physics 143, 024903 (2015).
- [25] X. Feng, A. Chen, J. Wang, N. Zhao, and Z. Hou, The Journal of Physical Chemistry B 120, 10114 (2016).
- [26] S. Egorov, The Journal of Chemical Physics 134, 084903 (2011).
- [27] U. Yamamoto and K. S. Schweizer, The Journal of Chemical Physics 135, 224902 (2011).
- [28] R. A. Omari, A. M. Aneese, C. A. Grabowski, and A. Mukhopadhyay, The Journal of Physical Chemistry B 113, 8449 (2009).
- [29] R. Holyst, A. Bielejewska, J. Szymaski, A. Wilk, A. Patkowski, J. Gapiski, A. ywociski, T. Kalwarczyk, E. Kalwarczyk, M. Tabaka, *et al.*, Physical Chemistry Chemical Physics **11**, 9025 (2009).
- [30] A. Michelman-Ribeiro, F. Horkay, R. Nossal, and H. Boukari, Biomacromolecules 8, 1595 (2007).
- [31] C. A. Grabowski, B. Adhikary, and A. Mukhopadhyay,

Applied Physics Letters 94, 021903 (2009).

- [32] G. H. Koenderink, S. Sacanna, D. G. A. L. Aarts, and A. P. Philipse, Phys. Rev. E 69, 021804 (2004).
- [33] X. Ye, P. Tong, and L. Fetters, Macromolecules **31**, 5785 (1998).
- [34] H. K. Schachman and W. F. Harrington, Journal of the American Chemical Society 74, 3965 (1952).
- [35] A. Tuteja, M. E. Mackay, S. Narayanan, S. Asokan, and M. S. Wong, Nano letters 7, 1276 (2007).
- [36] I. Kohli and A. Mukhopadhyay, Macromolecules 45, 6143 (2012).
- [37] Y. Wang, C. Li, and G. J. Pielak, Journal of the American Chemical Society 132, 9392 (2010).
- [38] G. D. Phillies, Macromolecules **19**, 2367 (1986).
- [39] T. Kalwarczyk, K. Sozanski, A. Ochab-Marcinek, J. Szymanski, M. Tabaka, S. Hou, and R. Holyst, Advances in colloid and interface science **223**, 55 (2015).
- [40] R. Holyst, A. Bielejewska, J. Szymański, A. Wilk, A. Patkowski, J. Gapiński, A. Żywociński, T. Kalwarczyk, E. Kalwarczyk, M. Tabaka, *et al.*, Physical Chemistry Chemical Physics **11**, 9025 (2009).
- [41] T. Kalwarczyk, N. Ziebacz, A. Bielejewska, E. Zaboklicka, K. Koynov, J. Szymanski, A. Wilk, A. Patkowski, J. Gapinski, H.-J. Butt, *et al.*, Nano letters **11**, 2157 (2011).
- [42] L.-H. Cai, S. Panyukov, and M. Rubinstein, Macromolecules 48, 847 (2015).
- [43] A. Ochab-Marcinek and R. Hołyst, Soft Matter 7, 7366 (2011).
- [44] R. Tuinier and T.-H. Fan, Soft Matter 4, 254 (2008).
- [45] J. Liu, D. Cao, and L. Zhang, The Journal of Physical Chemistry C 112, 6653 (2008).
- [46] S. Li, H. Jiang, and Z. Hou, Chinese Journal of Chemical Physics 29, 549 (2016).
- [47] A. Chen, N. Zhao, and Z. Hou, Soft matter 13, 8625 (2017).
- [48] V. Pryamitsyn and V. Ganesan, Journal of Polymer Science Part B: Polymer Physics 54, 2145 (2016).
- [49] J. Zheng, W. Shen, D. Z. He, K. B. Long, L. D. Madison, and P. Dallos, Nature 405, 149 (2000).
- [50] Y. Duan, D. Huo, J. Gao, H. Wu, Z. Ye, Z. Liu, K. Zhang, L. Shan, X. Zhou, Y. Wang, *et al.*, Nature communications 7 (2016).
- [51] Y. Sumino, K. H. Nagai, Y. Shitaka, D. Tanaka,

K. Yoshikawa, H. Chaté, and K. Oiwa, Nature **483**, 448 (2012).

- [52] M. Loose and T. J. Mitchison, Nature cell biology 16, 38 (2014).
- [53] A. Sokolov, I. S. Aranson, J. O. Kessler, and R. E. Goldstein, Physical Review Letters 98, 158102 (2007).
- [54] D. Woolley, Reproduction **126**, 259 (2003).
- [55] I. H. Riedel, K. Kruse, and J. Howard, Science **309**, 300 (2005).
- [56] J. R. Howse, R. A. Jones, A. J. Ryan, T. Gough, R. Vafabakhsh, and R. Golestanian, Physical review letters 99, 048102 (2007).
- [57] A. Ghosh and P. Fischer, Nano letters 9, 2243 (2009).
- [58] A. Joseph, C. Contini, D. Cecchin, S. Nyberg, L. Ruiz-Perez, J. Gaitzsch, G. Fullstone, J. Azizi, J. Preston, G. Volpe, *et al.*, bioRxiv, 061325 (2016).
- [59] Y. Fily and M. C. Marchetti, Physical review letters 108, 235702 (2012).
- [60] J. Dunkel, S. Heidenreich, K. Drescher, H. H. Wensink, M. Bär, and R. E. Goldstein, Physical review letters 110, 228102 (2013).
- [61] J. A. Cohen and R. Golestanian, Physical review letters 112, 068302 (2014).
- [62] X. Shen and P. E. Arratia, Physical review letters 106, 208101 (2011).
- [63] D. A. Gagnon, N. C. Keim, and P. E. Arratia, Journal of Fluid Mechanics 758, R3 (2014).
- [64] B. Thomases and R. D. Guy, Physical review letters 113, 098102 (2014).
- [65] A. E. Patteson, A. Gopinath, and P. E. Arratia, Current Opinion in Colloid & Interface Science 21, 86 (2016).
- [66] A. Patteson, A. Gopinath, M. Goulian, and P. Arratia, Scientific reports 5 (2015).
- [67] H. M. López, J. Gachelin, C. Douarche, H. Auradou, and E. Clément, Physical review letters 115, 028301 (2015).
- [68] J. D. Weeks, D. Chandler, and H. C. Andersen, The Journal of chemical physics 54, 5237 (1971).
- [69] K. Kremer and G. S. Grest, The Journal of Chemical Physics 92, 5057 (1990).
- [70] C. Bechinger, R. Di Leonardo, H. Löwen, C. Reichhardt, G. Volpe, and G. Volpe, Reviews of Modern Physics 88, 045006 (2016).