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Dissipative Dynamics of a Single Polymer in Solution: A Lowe-Andersen Approach

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Abstract. We study the equilibrium dynamics of a single polymer chain under good solvent condition. Special emphasis is laid on varying the drag force experienced by the chain while it moves. To this end we model the solvent in a mesoscopic manner by employing the Lowe-Andersen approach of dissipative particle dynamics which is known to reproduce hydrodynamic effects. Our approach captures the correct static behavior in equilibrium. Regarding the dynamics, we investigate the scaling of the self-diffusion coefficient D with respect to the length of the polymer N, yielding results that are compatible with the Zimm scaling $D \sim N^{-3/5}$.

1. Introduction

Dynamics of a polymer chain in a dilute solution, although being extensively studied, is still a topic of utmost importance [1, 2]. In particular, this topic serves as a benchmark for establishing a coarse-grained or mesoscopic approach to understand more realistic problems on larger time and length scales. The dynamics of a single chain, generally, is characterized by the self-diffusion coefficient D which scales with chain length N as

$$D \sim N^{-x}. \tag{1}$$

In the free-draining limit where hydrodynamic effects are absent or screened, one has $x = 1$, whereas in the non-draining limit where hydrodynamic interactions are important, one expects $x = 3/5$. The former is referred to as Rouse scaling [3] and the latter as Zimm scaling [4].

Over the years these results have been verified both experimentally [5] as well in computer simulations [6]. Before the advent of present-day sophisticated experimental setups, when it was difficult to keep track of a single polymer movement, numerical simulations were considered to be the only way to verify the available theoretical understanding. Monte Carlo simulations cannot capture the real dynamics due to the absence of hydrodynamic effects. Even when doing Molecular Dynamics (MD) simulations, one has to be careful about the choice of the thermostat. The effect of hydrodynamics is achieved via the preservation of local linear and angular momentum during the entire simulation.

In the context of polymer dynamics another major issue is the consideration of explicit solvents. The introduction of dissipative particle dynamics (DPD) has eased this task [7]. There one has the luxury of considering the solvent explicitly via a mesoscopic approach which allows

to access larger time and length scales [8, 9]. In addition, DPD also allows to tune the Schmidt number, i.e., the ratio of the kinematic viscosity and the self-diffusion coefficient. This makes consideration of solvents having viscosities comparable to real fluids quite plausible. However, from a technical point of view, one has to be cautious when integrating the equations of motion using a Verlet-type algorithm in the DPD formalism as it often disturbs the detailed balance and thereby does not produce the correct equilibrium properties unless sufficiently small time steps are used [10, 11]. There have been few attempts to use more advanced integration schemes that can overcome this difficulty. In this context, Lowe instead of aiming at improving the integration scheme, modified the DPD approach in the spirit of the Andersen thermostat, of course, with the effect of hydrodynamic interactions being intact [12]. With Lowe's approach, which also goes by the name Lowe-Andersen (LA) thermostat, one is not only allowed to use relatively larger time steps [13] but also has the option to tune the dissipation of velocities of particles, thereby gaining access to fluids with Schmidt numbers as high as observed in real fluids [12]. Motivated by these advantages, here, we construct a model polymer with explicit solvent particles and perform MD simulations for a wide range of effective solvent viscosities, i.e., frictional-drag experienced by the particles. Our results show that the dynamics in good solvent produces the theoretically expected Zimm scaling valid in the presence of hydrodynamics.

The paper is organized as follows. In the next section we present the details of our model and the method of simulation. Following that, we present results concerning static and dynamic properties of our model. In the final section we present a summary of our results and an outlook to future work.

2. Model and Method

We consider a bead-spring model of a flexible homopolymer in three spatial dimensions. The bonds between successive monomers are maintained via the standard finitely extensible non-linear elastic (FENE) potential

$$E_{\mathrm{FENE}}(r_{ii+1}) = -\frac{K}{2}R^2 \ln \left[1 - \left(\frac{r_{ii+1} - r_0}{R} \right)^2 \right],$$ (2)

with $K = 40$, $r_0 = 0.7$ and $R = 0.3$. The monomers and the solvent molecules both are considered to be spherical beads of mass $m = 1$ and diameter σ. All nonbonded interactions, i.e., solvent-solvent, solvent-monomer, and monomer-monomer interactions are modeled by

$$E_{\mathrm{nb}}(r_{ij}) = E_{\mathrm{LJ}}\left[\min(r_{ij}, r_c) \right] - E_{\mathrm{LJ}}(r_c),$$ (3)

where $E_{\mathrm{LJ}}(r)$ is the standard Lennard-Jones (LJ) potential given as

$$E_{\mathrm{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$ (4)

with $\sigma = r_0/2^{1/6}$ as the diameter of the beads, $\epsilon(= 1)$ as the interaction strength and $r_c = 2^{1/6}\sigma$ as cut-off radius that ensures a purely repulsive interaction.

As already mentioned, we simulate our system via MD simulations at constant temperature using the LA thermostat. In this approach, one updates the position $\vec{r}_i$ and velocity $\vec{v}_i$ of the i-th bead using Newton's equations as follows,

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i, \frac{d\vec{v}_i}{dt} = \vec{f}_i,$$ (5)

where $\vec{f}_i$ is the conservative force (originating from the bonded and nonbonded interactions) acting on the particle. This part of the simulation is the usual microcanonical MD. For

controlling the temperature with the LA thermostat, one considers a pair of particles within a certain distance R_T. Then, with a probability $\Delta t \Gamma$, a bath collision is executed following which the pair gets a new relative velocity from the Maxwellian distribution. Here, Δt is the width of the time step chosen for the updates in Eq. (5) and Γ determines the collision frequency. The exchange of relative velocities with the bath is only done on its component parallel to the line joining the centers of the pair of particles, thus conserving the angular momentum. Additionally, the new velocities are distributed to the chosen pair in such a way that the linear momentum is also conserved. In summary, the work flow for our LA approach has the following form:

(i) Update $\vec{v}_i \leftarrow \vec{v}_i + \frac{1}{2m}\vec{f}_i \Delta t$ and $\vec{r}_i \leftarrow \vec{r}_i + \vec{v}_i \Delta t$.

(ii) Calculate $\vec{f}_i$ and then $\vec{v}_i \leftarrow \vec{v}_i + \frac{1}{2m}\vec{f}_i \Delta t$.

(iii) Choose all pairs of particles with $r_{ij} < R_T$ and with probability $\Delta t \Gamma$ do the following:

    (a) Draw $\vec{v}\prime_{ij} \cdot \vec{n}_{ij}$ from the distribution $\xi_{ij}\sqrt{2k_B T/m}$ where $\vec{v}\prime_{ij}$ is the new relative velocity of particles i and j, $\vec{n}_{ij}$ is a unit vector, ξ_{ij} is a Gaussian white noise, and T is the desired temperature.

    (b) Calculate the change $2\vec{\Delta}_{ij} = \vec{n}_{ij}(\vec{v}\prime_{ij} - \vec{v}_{ij}) \cdot \vec{n}_{ij}$.

    (c) Distribute the change as $\vec{v}_i \leftarrow \vec{v}_i + \vec{\Delta}_{ij}$ and $\vec{v}_j \leftarrow \vec{v}_j - \vec{\Delta}_{ij}$.

(iv) Calculate physical quantities and go to (i).

It is to be noted that the LA approach is an alternative approach to DPD, however, with the liberty to use large Δt. The other advantage of the method is that by varying R_T and Γ one can tune the bath collision frequency, i.e., effectively controlling the frictional drag or in other word the solvent viscosity. In this work, we restrict ourselves to the case where $R_T = r_c$ and vary Γ within the range $[0.1, 250]$ with the goal to cover solvents with diverse viscosity. We do our simulations using LAMMPS [14] which we modified to implement the LA thermostat.

We first generate a random walk of length N on a simple-cubic lattice and then put this walk or chain in a box of size $L = 1.25N^{3/5}$. Subsequently, we insert solvent particles keeping the density fixed to $\rho = 0.7$ and make sure that the solvent particles do not overlap with the monomers of the polymer chain. Then we run our MD simulation with LA thermostat at temperature $T = 1.0$ for 10^7 MD steps with $\Delta t = 0.005$ and allow the system to equilibrate. In our simulations, the unit of temperature is ϵ/k_B (where we chose $k_B = 1$) and the unit of time is the standard LJ time unit $\tau = (m\sigma^2/\epsilon)^{1/2}$. Once the system is equilibrated, we let it run for another period of $10^4\tau$ and simultaneously start measuring various physical quantities that will be presented subsequently. We have used polymers of chain length $N \in [16, 512]$. All results presented are averaged over 100 different independent runs for $N < 512$ and 50 runs for $N = 512$.

3. Results
As a first step to benchmark our proposed framework we calculate the radius of gyration as

$$R_g = \sqrt{\sum_{i,j} \frac{(\vec{r}_i - \vec{r}_j)^2}{2N^2}}, \qquad (6)$$

which is a measure for the size of the polymer. Under good solvent condition, this scales with the chain length N as $R_g \sim N^\nu$ where the critical exponent $\nu \approx 3/5$. In Fig. 1(a) we show the plots of R_g as function of N for three different Γ values of the solvent. A fitting of the data using the form $R_g = R_0 N^\nu$ provides $\nu \in [0.58, 0.61]$. Fixing $\nu = 3/5$ in the fitting, also works quite well as shown by the continuous lines in Fig. 1(a). This implies that our framework reproduces the correct equilibrium static behavior of a polymer in good solvent, irrespective of the value of Γ.
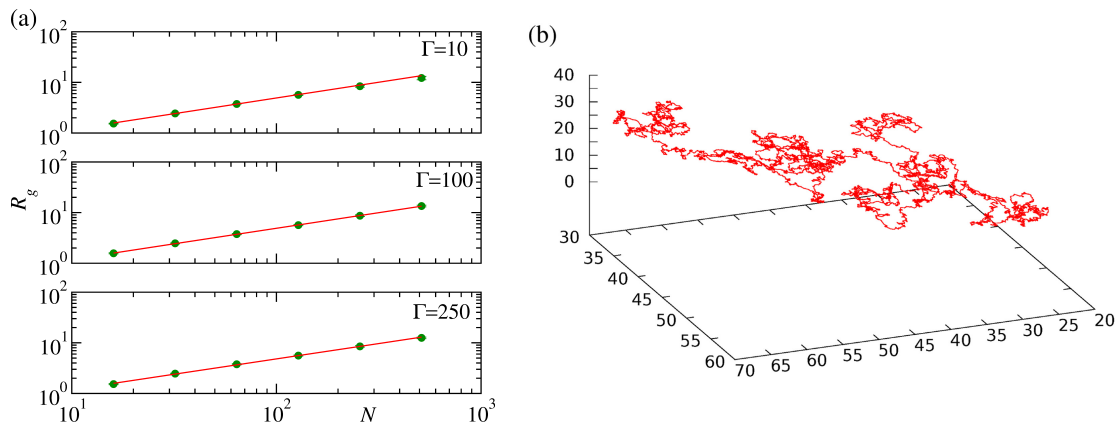
Figure 1. (a) Radius of gyration R_g as function of the chain length N in good solvents for three different Γ. The solid line in each case is a fit using the form $R_g = R_0 N^{3/5}$, the expected scaling behavior. (b) The trajectory of the center of mass of a polymer of length $N = 512$, over a time period of 200τ in equilibrium at $T = 1.0$.

Next we move to the dynamic properties. In Fig. 1(b), we show the equilibrium trajectory of the center of mass (cm) of a polymer of length $N = 512$ over a time interval of 200τ. Tracking the motion of the cm of a polymer is crucial when one wants to measure its diffusion in the solvent. The trajectory seems to be stochastic in nature and hence is indicative of a Brownian motion. To check the nature of the motion we calculate the mean squared displacement of the cm of a polymer given as

$$MSD = \langle [\vec{R}_{\rm cm}(t) - \vec{R}_{\rm cm}(t_0)]^2 \rangle, \tag{7}$$

where $\vec{R}_{\rm cm}(t)$ is the position vector of the cm of the polymer at time t, and t_0 is the time when the measurement starts. From Einstein's equation it is known that for Brownian motion in the long-time limit [1, 2]

$$MSD = A + 6Dt, \tag{8}$$

where D is the self-diffusion coefficient of the polymer and A is a constant. In Fig. 2(a) we show the plots of MSD as function of time t for different chain lengths N in a solvent with $\Gamma = 10$. In the large t limit, for all N the data is consistent with $\sim t$ behavior, whereas at early times for a brief period it is expectedly ballistic in nature, i.e., $\sim t^2$. A similar behavior is observed in Fig. 2(b) where we show plots of MSD for polymers having fixed chain length $N = 128$ in solvents having different Γ.

To have a more comprehensive understanding of the effect of variation of the solvent, i.e., Γ, we aim to calculate the self-diffusion coefficient D of the polymer. In this regard, one can calculate the velocity (of the cm of the polymer) autocorrelation function $C(t) = \langle \vec{v}(t_0) \cdot \vec{v}(t) \rangle$ which is related to D via the Green-Kubo relation as

$$D = \frac{1}{d} \int_{t_0}^{t} C(t)dt, \tag{9}$$

where d is the spatial dimension. However, here, we calculate D using the Einstein relation (8) as follows. We pick two times t_1 and t_2 in the long-time limit. From Fig. 2, one can easily observe that for $t > 100\tau$ for all N and Γ, the mean squared displacement MSD is consistent with the linear behavior. Thus, we chose t_1 and t_2 to be such that $t_2 > t_1$ and $t_1 \geq 100\tau$. Then
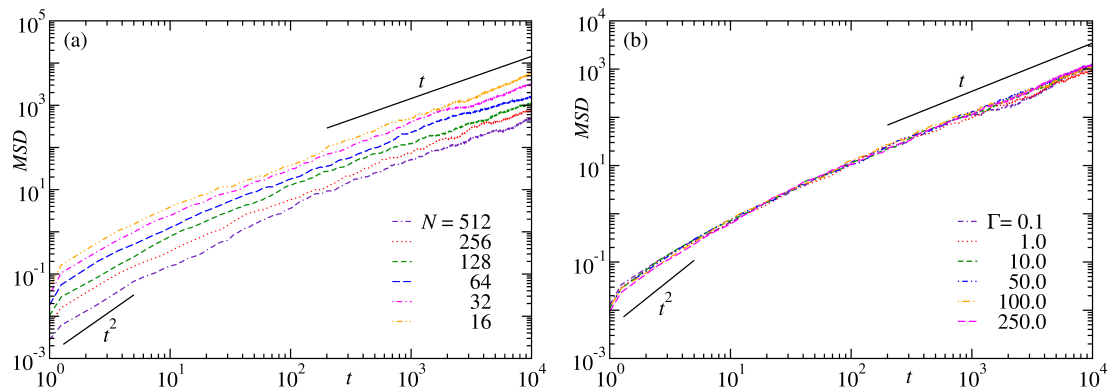
Figure 2. (a) Time dependence of mean squared displacement MSD of the center of mass of a polymer for different chain lengths N in a solvent having $\Gamma = 10$ at $T = 1.0$. The solid line at small t corresponds to ballistic motion $\sim t^2$ and the one at large t corresponds to Brownian motion $\sim t$. (b) Same as (a) but for a polymer of fixed length $N = 128$ in solvents having different Γ. The solid lines there have the same meaning as in (a).

using (8) one can write down

$$D = \frac{1}{6}\left[\frac{MSD(t_2) - MSD(t_1)}{t_2 - t_1}\right]. \tag{10}$$

Equation (10) provides a set of values of D for different choices of the pair (t_1, t_2). This allows one to have appropriate error bars, independent of the usual fitting exercise using the form (8).

Figure 3(a) demonstrates the scaling of the self-diffusion coefficient D with chain length N for different solvents as indicated by the Γ values therein. The dashed line there corresponds to the Rouse scaling with the exponent $x = 1$ in the form (1) whereas the solid line represents the Zimm scaling with $x = 3/5$. Consistency of our data with the solid line indicates the validity of the Zimm scaling, expected in the presence of hydrodynamic effects. Fits using the form $D = D_0 N^{-x}$ yield x within $[0.6, 0.68]$, slightly higher than $x = 3/5$ expected for the Zimm scaling. However, a fit using the same form by fixing $x = 3/5$ also yields reasonably acceptable $\chi_r^2 (< 2.5)$ values, where χ_r^2 is the goodness of fit parameter χ^2 divided by the degrees of freedom.

Finally, in Fig. 3(b) we show the dependence of the self-diffusion coefficient D on the collision frequency Γ that controls the effective viscosity of the solvent. The data show no signature of strong dependence, rather in a broader sense D seems to be pretty constant for different Γ. This behavior is similar to the conclusion drawn in Ref. [13] where, for an ideal gas, they did not observe any strong dependence of D on Γ. Nevertheless, the data presented here are for a relatively high temperature $T = 1.0$, hence, the influence of viscosity is not severely pronounced. At low temperatures, the diffusion might get suppressed due to high effective viscosity [15].

4. Conclusion

Motivated by dissipative particle dynamics, here, we have constructed an explicit solvent model for a polymer. Instead of using the standard approach of doing it, we rely on the Lowe-Andersen approach of the bath collision. This allows us to control the drag force applied by the solvent on the polymer, i.e., the effective viscosity. Via the scaling of the radius of gyration R_g with the chain length N as $R_g \sim N^{3/5}$ we confirm that our approach yields the known static critical exponent. The method conserves both the linear and angular momenta locally, thereby preserving the hydrodynamics. The scaling of the self-diffusion coefficient D with chain length N indicates a much faster dynamics than the Rouse dynamics, and in fact is pretty consistent
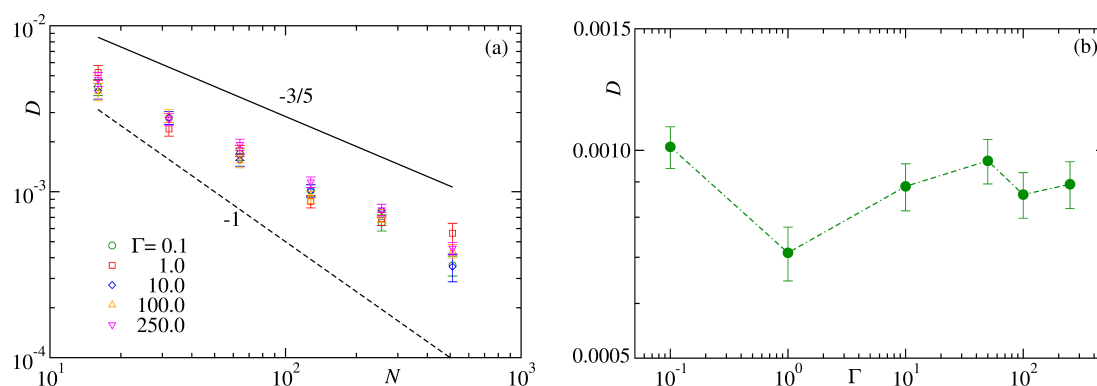
Figure 3. (a) Plots showing the dependence of the self-diffusion coefficient D on the chain length N of a polymer for different solvents with Γ as indicated. The solid line and dashed lines represent respectively the Zimm and Rouse scaling. (b) Variation of D as function of Γ for a polymer of length $N = 128$ at $T = 1.0$.

with Zimm scaling $D \sim N^{-3/5}$ valid in the presence of hydrodynamic effects. The successful application of this method opens up opportunities to explore other aspects of polymer dynamics including nonequilbrium scenarios, e.g., during collapse of a polymer [16, 17, 18, 19]. There, the effect of varying the collision frequency Γ has a stronger influence on the structure formation, and in principle such phenomena could well be tuned by the degree of dissipation [20].

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