Microscopic Verification of Dynamic Scaling in Dilute Polymer Solutions: A Molecular-Dynamics Simulation

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The dynamics of a single polymer chain immersed in a large number of solvent particles is studied by molecular dynamics. This is the first simulation where chain length (30, 40, and 60 monomers) and statistical accuracy are sufficient to test the predictions of the Zimm model as a result of the particle-particle interactions: The short-time diffusion constant is in good agreement with the Kirkwood prediction, and the monomer motions exhibit the expected dynamic scaling. The long-range hydrodynamic interaction requires a data analysis that explicitly includes the periodic images via Ewald sums.

Since the pioneering work of Kirkwood and co-workers[1] it is well known that the Brownian motion of long flexible macromolecules in dilute solution is dominated by hydrodynamic interactions, i.e., correlations in the displacements of the monomers mediated by fast momentum transport through the solvent. The standard theory[1-3] describes this via a Smoluchowski equation for the probability distribution function Ψ in the space of the coordinates $\mathbf{r}_i$ of all N monomers:

$$\frac{\partial}{\partial t}\Psi(\{\mathbf{r}_i\}) = \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial}{\partial \mathbf{r}_i}\mathbf{D}_{ij}(\{\mathbf{r}_i\})$$
$$\times\left[\frac{\partial}{\partial \mathbf{r}_j}-\frac{\mathbf{F}_j}{k_B T}\right]\Psi(\{\mathbf{r}_i\}), \quad (1)$$

where $\mathbf{D}_{ij}$ is the diffusion tensor, $\mathbf{F}_j$ the effective force acting on the jth monomer, k_B Boltzmann's constant, and T the temperature. The hydrodynamic interaction is described by the off-diagonal elements of the diffusion tensor, which is usually taken as the Oseen tensor,

$$\mathbf{D}_{ij} = D_0\delta_{ij}\mathbf{1} + (1-\delta_{ij})\frac{k_B T}{8\pi\eta r_{ij}}\left[1+\frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2}\right]. \quad (2)$$

This form results from the physical picture of point forces causing incompressible, low-Reynolds-number hydrodynamic flow of the continuous solvent with shear viscosity η. D_0 is the monomer diffusion constant, and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. Although Eq. (2) is only a rough approximation which can be improved in various aspects,[4-6] it is expected to take the leading long-wavelength, low-frequency contributions properly into account.

A result of this theory is the Kirkwood formula for the short-time chain diffusion constant:

$$D^{(K)} = \frac{D_0}{N}+\frac{k_B T}{6\pi\eta}\left\langle\frac{1}{R_H}\right\rangle. \quad (3)$$

Here

$$\left\langle\frac{1}{R_H}\right\rangle = \frac{1}{N^2}\sum_{i\neq j}\left\langle\frac{1}{r_{ij}}\right\rangle \quad (4)$$

defines the hydrodynamic radius. R_H is almost inaccessible by *direct* experiments. In most cases, the short-time decay in dynamic light scattering[7,8] is used to determine R_H by Eq. (3), neglecting D_0/N.

In contrast to experiment, in a molecular-dynamics (MD) computer simulation it is possible to determine all discussed quantities separately in order to test the validity of the concept as well as the dynamic scaling.[9] With $\langle R_G^2\rangle = \frac{1}{2}N^{-2}\sum_{ij}\langle(\mathbf{r}_i-\mathbf{r}_j)^2\rangle$, the radius of gyration, one expects for the diffusion constant $D\propto R_G^{-1}$, $R_G\propto N^\nu$, where $\nu=0.59$ in the good-solvent regime. The longest relaxation time τ_Z (Zimm time) should be proportional to $R_G^2/D\propto N^{3\nu}$, and the mean-square displacement of a single monomer should have a time dependence $\langle(\Delta\mathbf{r})^2\rangle\propto t^{2/3}$ for intermediate times. For the same time and length scales the dynamic structure factor

$$S(k,t) = \frac{1}{N}\sum_{ij}\left\langle\frac{\sin[k|\mathbf{r}_i(t)-\mathbf{r}_j(0)|]}{k|\mathbf{r}_i(t)-\mathbf{r}_j(0)|}\right\rangle \quad (5)$$

is predicted to exhibit the scaling behavior

$$S(k,t) = k^{-1/\nu}f(k^3 t), \quad (6)$$

while a chain without hydrodynamic interactions would obey the scaling of the Rouse model:[2,9,10] $\tau_R\propto N^{1+2\nu}$, $\langle(\Delta\mathbf{r})^2\rangle\propto t^{1/(1+1/2\nu)}=t^{0.54}$,

$$S(k,t) = k^{-1/\nu}f(k^{2+1/\nu}t) = k^{-1/\nu}f(k^{3.7}t).$$

Calculations of $S(k,t)$ beyond the simple scaling picture have been done using phenomenological[11] as well as renormalization-group[12] approaches.

We performed an MD simulation of a single polymer

chain and a large number of solvent particles in a cubic box with periodic boundary conditions. Similar attempts have been made previously,[13-19] but were restricted to too short chains or poor statistics—a reasonable configurational sampling for long chains requires long runs. Moreover, simulating momentum transport properly needs a microcanonical MD, where simply Newton's equations of motion are integrated (we used a fifth-order predictor-corrector scheme[20])—but such an algorithm is intrinsically unstable. To avoid this problem, we generated many configurations using an MD with noise.[10] This provides us with a statistical sample of well-equilibrated states for the whole system and reliable estimates of static configurational averages. Then from these states microcanonical runs were started, which were used to analyze the dynamics.[21]

All particles interacted via a purely repulsive Lennard-Jones potential

$$U_{LJ}(r) = \begin{cases} 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6 + \frac{1}{4}], & r \le 2^{1/6}\sigma, \\ 0, & r \ge 2^{1/6}\sigma, \end{cases} \quad (7)$$

at density $\rho = 0.864\sigma^{-3}$ and temperature $k_B T = 1.2\varepsilon$. Time is measured in units of $\tau_{LJ} = (m\sigma^2/\varepsilon)^{1/2}$, where m is the particle mass. Without noise and with a time step $h = 0.004\tau_{LJ}$, our program[20] performed roughly 3×10^5 particle movements per second on one CRAY-YMP processor. The solvent viscosity η was estimated by Green-Kubo integration[22] with $h = 0.001\tau_{LJ}$ for systems of up to 8000 particles, giving $\eta = (2.4 \pm 0.1)(m\varepsilon)^{1/2}\sigma^{-2}$.

A polymer chain was introduced into the system by an additional attractive potential U_{ch} which acts between the monomers i and $i+1$, $i = 1, \ldots, N-1$, along the chain. We chose

$$U_{ch}(r) = -\frac{1}{2} k R_0^2 \ln(1 - r^2/R_0^2), \quad (8)$$

with $k = 7\varepsilon\sigma^{-2}$, $R_0 = 2\sigma$. The chain monomers were assigned the mass $2m$. In particular, we studied a chain of $N = 30$ monomers in 4066 solvent particles, as well as $N = 40$ in 4056 and $N = 60$ in 7940 solvent particles.

From the MD runs with noise ($h = 0.006\tau_{LJ}$) we find that the static structure factor $S(k, t = 0)$ agrees very well with a $k^{-1/\nu}$ decay with $\nu = 0.58 \pm 0.01$, indicating the expected good-solvent behavior.[23] R_G is 3.28σ, 3.78σ, and 4.78σ for $N = 30$, 40, and 60. The corresponding box sizes are $L = 16.8\sigma$, 16.8σ, and 21σ and hence self-overlap effects are rather small. We saved all coordinates every $300\tau_{LJ}$ to generate about 700 starting states for each system. Each of these configurations ran microcanonically for $100\tau_{LJ}$, using the interval $[20\tau_{LJ}, 100\tau_{LJ}]$ for the analysis of the dynamics.

For the chain diffusion constant D we found $6.82 \times 10^{-3}\sigma^2\tau_{LJ}^{-1}$, $5.45 \times 10^{-3}\sigma^2\tau_{LJ}^{-1}$, and $4.25 \times 10^{-3}\sigma^2\tau_{LJ}^{-1}$, for $N = 30$, 40, and 60, while $\langle R_H^{-1} \rangle$ according to Eq. (4) gave $\langle R_H^{-1} \rangle = 0.34\sigma^{-1}$, $0.30\sigma^{-1}$, and $0.25\sigma^{-1}$ for $N = 30$, 40, and 60. Using the Kirkwood formula, the results are not consistent. However, this is
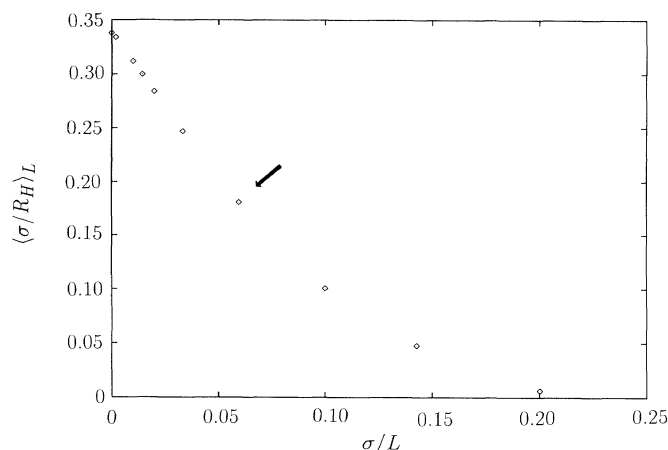

FIG. 1. The effective inverse hydrodynamic radius $\langle R_H^{-1} \rangle_L$ in units of σ^{-1}, evaluated for the configurations of the $N = 30$ chain and for various inverse box sizes L^{-1} (same units). The data point where the simulation was actually performed ($L = 16.8\sigma$) is indicated by an arrow.

not surprising, since Eq. (3) assumes infinite dilution. In the case of a finite box, the long-range nature of the hydrodynamic interaction has to be taken into account. The chain interacts with its own periodic images. This can be incorporated in the Kirkwood theory by replacing the Oseen tensor, Eq. (2), by the corresponding Ewald sum.[24] This defines an effective hydrodynamic radius, which depends on both the chain configurations and the box size L, as illustrated in Fig. 1. In our case, $\langle R_H^{-1} \rangle_L$ is roughly a factor of 2 smaller than $\langle R_H^{-1} \rangle_{L=\infty}$ ($\langle R_H^{-1} \rangle_L = 0.18\sigma^{-1}$, $0.15\sigma^{-1}$, and $0.13\sigma^{-1}$ for $N = 30$,
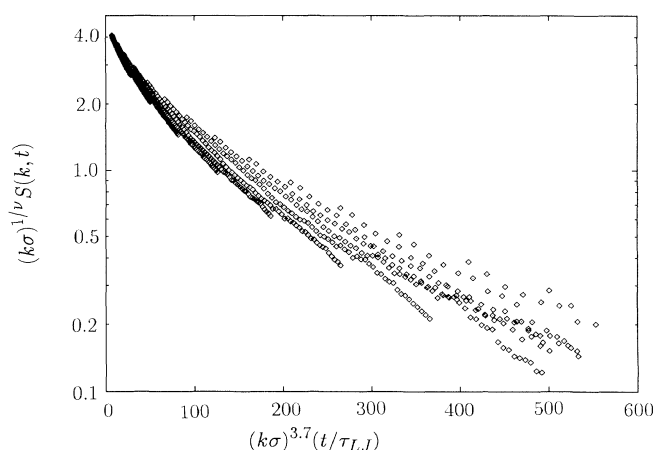

FIG. 2. Data-collapsing plot of the decay of the dynamic structure factor $S(k, t)$ for $N = 60$ in Rouse scaling form, $(k\sigma)^{1/\nu}S(k, t)$ vs $(k\sigma)^{3.7}(t/\tau_{LJ})$. We used $\nu = 0.59$ and restricted the data to the scaling regimes $0.7\sigma^{-1} \le k \le 3\sigma^{-1}$ and $20\tau_{LJ} \le t \le 80\tau_{LJ}$. Moreover, data with $S \le 0.05$ were eliminated for reasons of statistical accuracy.

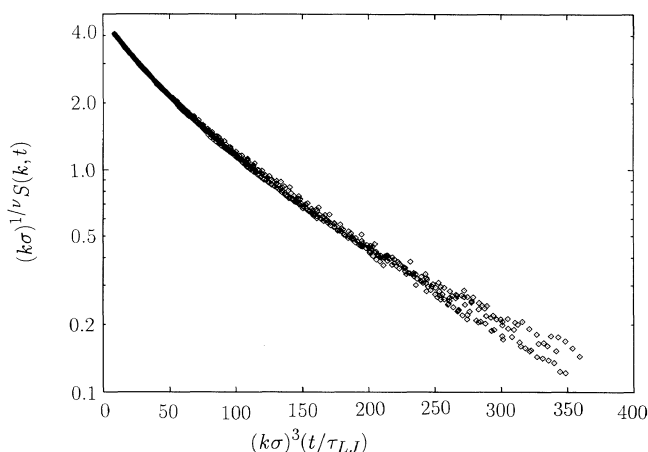FIG. 3. Same as Fig. 2 for Zimm scaling: $(k\sigma)^{1/\nu}S(k,t)$ vs $(k\sigma)^3(t/\tau_{LJ})$.

behavior of the mean-square displacement, averaged over the four inner monomers, we found a $t^{0.7\pm0.05}$ law for all three chains,[23] in good agreement with the expected $\frac{2}{3}$ power.

In summary, the present study shows that today MD simulations are able to successfully treat the problem of Brownian motion with hydrodynamic interactions from a *first-principles* point of view—if the large finite-size effects associated with long-range hydrodynamic correlations are properly taken into account. Similar simulations of suspensions and of semidilute polymer solutions (which are less well understood) should be feasible.

40, and 60). From Fig. 1 one sees that a suppression of this finite-size effect by a sufficiently large system is practically impossible with today's computer power. The modified R_H is consistent with D, and Eq. (3) can be used to determine the monomer diffusion constant D_0 $\approx 0.06\sigma^2\tau_{LJ}^{-1}$ for all three systems, which is somewhat smaller than the asymptotic value of the solvent particle $(0.076\sigma^2\tau_{LJ}^{-1})$. The determination of D_0 is only meaningful for sufficiently accurate data (we estimate the error of D, R_H, and R_G as a few percent). Because of our limited observation time $(80\tau_{LJ})$ the Zimm time was roughly estimated as $\tau_Z \approx \langle R_G^2\rangle/6D = 260\tau_{LJ}$, $440\tau_{LJ}$, and $900\tau_{LJ}$ for $N=30$, 40, and 60, in amazingly good agreement with the predicted $N^{3\nu}$ behavior.

We now reconsider the dynamic scaling of the Zimm model. The relevance of the system size requires a generalization of the scaling theory analogous to finite-size scaling in critical phenomena. From the Ewald-sum representation of $D^{(k)}$ (Ref. 24) it is easy to see[23] that the natural generalization of the relation $D \propto R_G^{-1}$ is $D = R_G^{-1}g(R_G/L)$, where g is some scaling function. Hence, $\tau_Z \propto R_G^3/g(R_G/L)$. Writing the dynamic structure factor as

$$S(N,L,k,t) = N\hat{f}(kR_G,t/\tau_Z)$$
$$= N\tilde{f}(kR_G,tR_G^{-3}g(R_G/L)), \qquad (9)$$

we assume invariance of S with respect to the scaling transformation $N \to \lambda N$, $R_G \to \lambda^\nu R_G$, $L \to \lambda^\nu L$, yielding

$$S(N,L,k,t) = k^{-1/\nu}f(k^3tg(R_G/L)). \qquad (10)$$

This means that only the decay rates, but not the exponents, are affected by the finite-size effect. All chains exhibit a decay of $S(k,t)$, observed in the time interval $[20\tau_{LJ},80\tau_{LJ}]$, which is in much better agreement with the Zimm model than with Rouse behavior, as demonstrated for $N=60$ in Figs. 2 and 3. For the subdiffusive

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