Molecular dynamics simulation for polymers in the presence of a heat bath

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We describe an efficient and general algorithm for simulating polymers, which can be used for single, large chains as well as many-chain systems. It allows us to distinguish solvent effects from interchain effects on the dynamics of the chains. The method is tested for linear and cyclic chains of 50 to 200 monomers. We have confirmed two theoretical results which have not been observed numerically or experimentally, namely, the anomalous behavior of $S(q)$ for rings and the $t^{0.54}$ power law for the motion of a monomer in a self-avoiding chain undergoing Rouse relaxation.

The physics of polymeric materials is of great interest both from a fundamental viewpoint and for their various technical applications.[1] As our basic understanding of these systems increases, the questions we try to address become more complex. In addition to theoretical and experimental approaches, computer simulations have played an important role in our understanding of polymers.[2] For static properties Monte Carlo methods have been widely used and give excellent results for static critical exponents. To investigate dynamic properties three different methods—Monte Carlo (MC),[3-6] molecular-dynamics (MD),[7,8] and Brownian dynamics[9] methods—have been used. Detailed microscopic dynamics of a specific polymer model has also been studied.[10] Here we describe a continuum approach which can be effectively used in a wide variety of systems, such as linear, ring, or star polymers. We describe the new method and show that for the Rouse model it gives correct results for linear and cyclic polymers. New results include the confirmation of the predicted anomalous behavior in $S(q)$ for ring polymers and the $t^{0.54}$ power law for the motion of a single monomer of a self-avoiding chain undergoing Rouse relaxation.

The Rouse model for the dynamics of a single polymer describes the motion of an ideal chain immersed in a viscous solvent.[1,11] This model neglects the self-repelling of the chain monomers as well as any hydrodynamic effects.[12] Although this so-called "free-draining" limit is somewhat artificial, it has been very useful for understanding polymer dynamics. The Rouse model describes the motion of a single monomer by a Langevin equation:[13]

$$\frac{\partial \mathbf{r}_i}{\partial t} = \mu \left(\mathbf{F}_i + \frac{3k_B T}{\sigma^2} \frac{\partial^2 \mathbf{r}_i}{\partial n^2} + \boldsymbol{\phi}_i \right) . \tag{1}$$

$\mathbf{r}_i$ is the position of the ith monomer, μ the mobility, and $\mathbf{F}_i$ the force from the surroundings other than the chain itself. The last two terms describe the elastic force along the chain ($\propto \partial^2 \mathbf{r}/\partial n^2$) and the inner-chain interactions $\boldsymbol{\phi}_i$. Because the inner-chain forces have to sum to zero, one finds a diffusion coefficient[1] $D = \mu k_B T / N$ for a chain of N monomers using an Einstein relation. For an ideal chain (random walk) one finds a longest relaxation time (Rouse time) $\tau_N \propto N^2$. For the motion of a single monomer this leads to the following relations (τ_0 is a microscopic time):

$$g_1(t) = \langle [\mathbf{r}_i(t_0) - \mathbf{r}_i(t_0 + t)]^2 \rangle \propto \begin{cases} t^{1/2}, & \tau_0 \ll t \ll \tau_N , \\ t, & t \gg \tau_N , \end{cases} \tag{2}$$

$$g_2(t) = \langle \{ [\mathbf{r}_i(t_0) - \mathbf{R}_{\text{c.m.}}(t_0)] - [\mathbf{r}_i(t_0 + t) - \mathbf{R}_{\text{c.m.}}(t_0 + t)] \}^2 \rangle \propto \begin{cases} t^{1/2}, & \tau_0 \ll t \ll \tau_N , \\ t^0, & t \gg \tau_N , \end{cases} \tag{3}$$

where

$$\mathbf{R}_{\text{c.m.}} = 1/N \sum_{i=1}^{N} \mathbf{r}_i$$

is the center of gravity, and for the center-of-mass motion

$$g_3(t) = \langle [\mathbf{R}_{\text{c.m.}}(t_0) - \mathbf{R}_{\text{c.m.}}(t_0 + t)]^2 \rangle \propto t, \quad t \gg \tau_0 . \tag{4}$$

At the Rouse time

$$g_1(\tau_N) \approx g_2(\tau_N) \approx g_3(\tau_N) \approx \langle R_G^2(N) \rangle .$$

$\langle R_G^2 \rangle$ is the mean-square radius of gyration. Qualitatively, Eqs. (2)–(4) mean that monomer motion is governed by the fluctuation around the center of gravity until the average distance reaches approximately R_G; then the diffusion of the chain as a single object dominates. For self-avoiding chains[1] one finds $\langle R_G^2 \rangle \propto N^{2\nu}$, with $\nu = 0.59$ ($d = 3$) instead

of $\nu = \frac{1}{2}$. A scaling analysis leads to a relaxation time[13] $\tau_N \propto N^{2\nu+1} \propto N^{2.18}$. Ceperly, Kalos, and Lebowitz[9] confirmed this result by simulations, while another consequence,[5]

$$g_1(t) \propto g_2(t) \propto t^{2\nu/(1+2\nu)} \propto t^{0.54}, \quad t \ll \tau_N , \tag{5}$$

has not been seen numerically.[14] D is not affected by these arguments.

In a MC simulation the chain moves stochastically through random moves of a small number of monomers at a time. The number of bonds involved typically varies from two for chains in free space to four for lattice chains (diamond lattice). This technique reproduces the Rouse behavior and is especially suitable for scalar computers. Unfortunately, the method suffers from two disadvantages. First, it is very difficult to write an efficient parallel MC algorithm for polymers.[2] The second problem is that for

dense systems, the motion is almost reduced to cooperative fluctuations. Partially, this problem is compensated for by using very large systems at moderate densities.[3,15] This method has been the most successful and will remain very important at low and moderate densities. In a quasi-Brownian dynamics method[9] the Smoluchowski equation is solved for the position of the monomers by a MC algorithm. Due to the mainly stochastic nature of the motion, only moderate densities ($\rho \leq 0.5$) have been used. In both methods the Rouse dynamics is built in due to the stochastic nature of the chain motions. One cannot make a clear distinction between the influence of the small solvent particles or other long chains on the local dynamics of a polymer. This is important at the moderate densities where these methods work. The third alternative is to use a standard MD method.[7,8] Here Newton's equations of motion are solved directly for each monomer. Since both momentum and energy are conserved, one simulates a microcanonical ensemble. However, in order to sample the entire phase space for a chain and to get the Rouse dynamics there must be an exchange of energy and momentum with the surroundings. This can be done by taking the solvent molecules (monomers or very small chains) explicitly into account. Typically, one needs as many as 20 times (or more) solvent particles than monomers of the chain. This makes the algorithm so inefficient that it has only been used for small systems.[7,8]

It would be very useful to find a simulation method, which combines the positive aspects of these algorithms and avoids most of their negative aspects. To be precise we want to have a method which is (1) almost as effective as the MC methods for a single chain and reproduces the Rouse model and (2) should be effective at high densities and allow us to clearly distinguish the solvent from the interchain interactions. In addition, the algorithm should be general enough that one can incorporate constant-pressure methods[16] to calculate moduli for an entangled melt or a polymer glass. To achieve this aim, we propose a MD algorithm where each particle is coupled weakly to a heat bath. Schneider and Stoll[17] used a similar method to simulate a system with a distortive phase transition. They made the coupling so weak, that they could neglect the influence of the heat bath on the dynamics of the system. We want just the opposite. Since the coupling of the polymer to its surroundings is not weak, the influence of the heat bath on the dynamics of the chain must be investigated. Thus, we solve the equations of motion:

$$\ddot{\mathbf{r}}_i = -\nabla U_i - \Gamma \dot{\mathbf{r}}_i + \mathbf{W}_i(t) \quad , \tag{6}$$

where Γ is the bead friction and $\mathbf{W}_i(t)$ describes the random force of the heat bath acting on each monomer. $\mathbf{W}_i(t)$ is a Gaussian white noise with

$$\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = \delta_{ij} \delta(t - t') 6 k_B T \Gamma \quad . \tag{7}$$

Using the Einstein relation this leads to a diffusion coefficient $D_0 = k_B T / \Gamma N$. The potential[8,9,18] U_i has two parts $U^0 + U^{ch}$. U^0 is a shifted, purely repulsive Lennard-Jones potential,

$$U_{ij}^0 = \begin{cases} 4\epsilon \left[\left(\dfrac{\sigma}{r_{ij}} \right)^{12} - \left(\dfrac{\sigma}{r_{ij}} \right)^6 + \dfrac{1}{4} \right], & r_{ij} \leq \sigma 2^{1/6} \quad , \\ 0, & r_{ij} > \sigma 2^{1/6} \quad , \end{cases} \tag{8}$$

between any two monomers. The potential

$$U_{ij}^{ch} = \begin{cases} -0.5 k R_0^2 \ln[1 - (r_{ij}/R_0)^2], & r_{ij} \leq R_0 \quad , \\ 0, & r_{ij} > R_0 \quad , \end{cases} \tag{9}$$

gives the additional interaction between nearest neighbors along the chain. The parameters we used are $R_0 = 1.5\sigma$, $k = 30.0\epsilon/\sigma^2$, and temperature $k_B T = 1.2\epsilon$. These parameters are different from those used previously[8,9] in order to prevent the chains from crossings. We used a time step[19] $\Delta t = 0.004\tau$ or 0.008τ. Here $\tau = \sigma(m/\epsilon)^{1/2}$. The equations were solved using a fifth-order predictor corrector loop.[20] Note that Δt cannot be mapped directly onto a microscopic time scale, because a single monomer corresponds to a number of real bonds, which depends on the actual chemistry. The relevant parameters for this are the persistence length and the longest relaxation times. The range of Γ we tested is $0.5 \leq \Gamma \leq 1.5$, which confines the ballistic motion of a monomer between one and four bond lengths. The chain lengths studied are $N = 50$, 100, and 200 for linear chains and rings. We also analyze a random-walk (RW), ideal chain of $N = 200$, where the potentials only act between consecutive monomers along the chain. Typically, we run 8–15 times as long as shown in the plots. For the dynamic quantities we then average over at least 1000 initial configurations.

For the ratio of $\langle R_G^2(N) \rangle$ and the mean-square end-to-end distance $\langle R^2 \rangle$ we find the expected value $\frac{1}{6}$, as well as consistency with $\langle R_G^2 \rangle_{\text{ring}} / \langle R_G^2 \rangle_{\text{linear}} \simeq 0.56$.[21] Because we only studied a few chain lengths, it is very difficult to extract a convincing result for ν from the N dependence of our data. Therefore, we calculated the static structure function $S(q)$.[22,23] For

$$2\pi/\langle R^2 \rangle^{1/2} << q << \frac{2\pi}{\sigma}, \quad S(q) \propto q^{-1/\nu} \quad .$$

Figure 1 gives the result for $S(q)$ with $\nu = 0.59$ for $N = 50$. We find excellent agreement with the expected behavior. We also show results for a ring of $N = 50$. The ring is not self-entangled. The behavior of the ring is different from
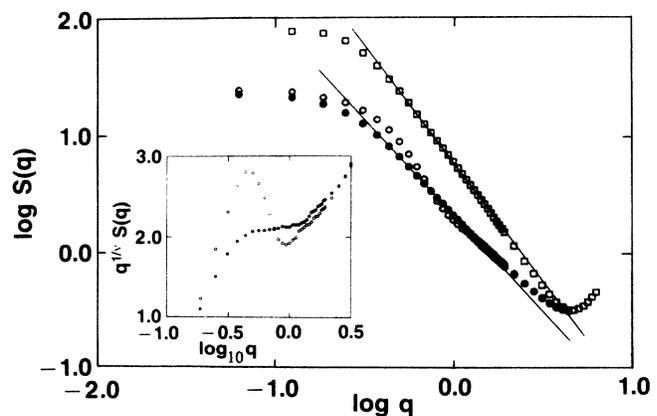

FIG. 1. $S(q)$ vs q for linear (●) and ring (○) polymers of chain length $N = 50$ and random-walk chain (□) for $N = 200$. In the inset, the data for the linear and ring polymer are replotted as $q^{-1/\nu} S(q)$ vs $\log_{10} q$ with $\nu = 0.59$. This plot is much more sensitive and shows that the actual value of ν differs slightly from the expected behavior.

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that for linear chains, as expected from the results for RW rings.[24,25] For self-avoiding rings $S(q)$ is only calculated as a series expansion in moments of R_G^2. For $q \ll 2\pi/\langle R_G^2 \rangle^{1/2}$ expanding $S(q)$ gives

$$S(q) = N(1 - \tfrac{1}{3}q^2\langle R_G^2 \rangle + \cdots)$$

for both the ring and linear chain. Because

$$\langle R_G^2(N) \rangle \approx 2\langle R_G^2(N) \rangle_{\text{ring}}$$

we find $S(q)_{\text{ring}} > S(q)$. For $q \gg 2\pi/\langle R^2 \rangle^{1/2}$ one only measures the local fractal structure of the ring and therefore,

$$S(q)_{\text{ring}} = S(q) \propto q^{-1/\nu} \ .$$

In order to fulfill these requirements, there must be a region where $S(q)_{\text{ring}}$ is steeper than for the linear chain. This is the region where the sphere of radius q^{-1} typically covers more than one strand of the ring, while it would cover only one strand for a linear chain. This is true up to $q \approx 2\pi/\langle R_G^2 \rangle^{1/2}$, the mean extension of the chain. This implies that the q range for the overshooting decreases with increasing chain length, in agreement with a study of longer rings,[26] in which no overshooting was observed. Figure 1 also shows the result for a RW linear chain with $N = 200$, for which $\nu = 0.50 \pm 0.02$.

For a given Γ, we expect, for times $t \ll \Gamma^{-1}$, the undamped motion of a monomer within the chain constraints, while for $t \gg \Gamma^{-1}$ we expect to find the typical Rouse behavior, Eqs. (2) and (3). Figure 2 shows the result for an inner monomer of a random walk of $N = 200$. Inner means that the average is taken over the ten middle monomers. With $\Gamma = 0.5$, Eq. (2) gives a diffusion constant $D_0 = k_B T / N\Gamma = 0.012$, in good agreement with that measured from Fig. 2. We find that the outer monomers are much more mobile than the inner ones, but display qualitatively the same behavior.

For a more systematic approach consider a self-avoiding chain. The RW results show that for $\Gamma^{-1} \ll \tau_N$, the standard Rouse behavior is observed. Within this limit we are free to vary Γ, which means we can change the prefactor α of $\tau_N = \alpha N^{2.18}$. Figure 3(a) gives a schematic plot of what is expected. To be precise, this algorithm gives us the oppor-
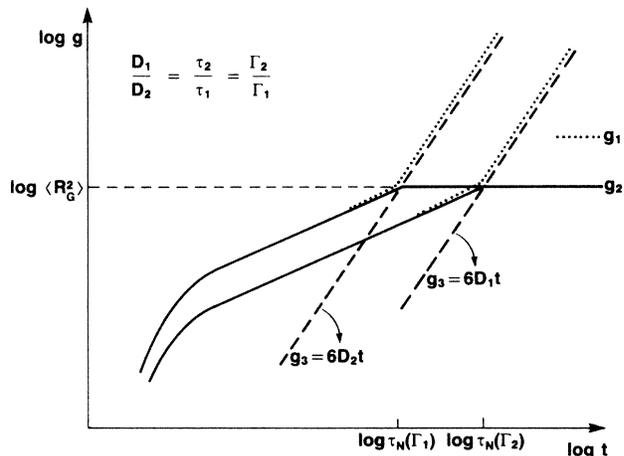
(a)
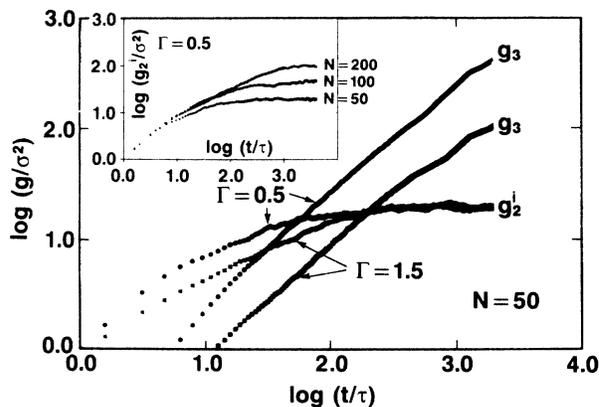
(b)

FIG. 3. (a) Schematic plot of g_1, g_2, and g_3 for fixed N and different Γ. The ratios of $\tau_N(\Gamma)$ and $D_N(\Gamma)$ are indicated. (b) Same as (a), but now for inner monomers of a linear chain of $N = 50$ for $\Gamma_1 = 0.5$ and $\Gamma_2 = 1.5$. The ratios of $g_3(\Gamma_1)/g_3(\Gamma_2) = \tau(\Gamma_2)/\tau(\Gamma_1) = 3.0$ are in good agreement with (a). The inset shows g_2 for $\Gamma = 0.5$ for $N = 50$, 100, and 200 (inner monomers) to show that $g_{1,2}$ for $t \ll \tau_N$ is independent of the chain length.
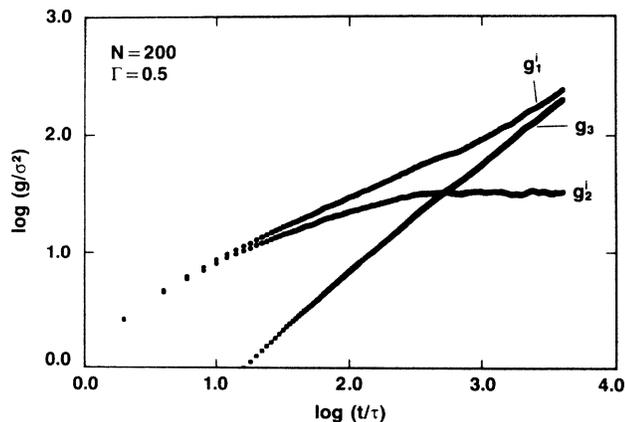

FIG. 2. $g_1 g_2$ for an inner monomer and g_3 for a random-walk linear chain of $N = 200$. Total run $(7.2\times10^4)\tau$.
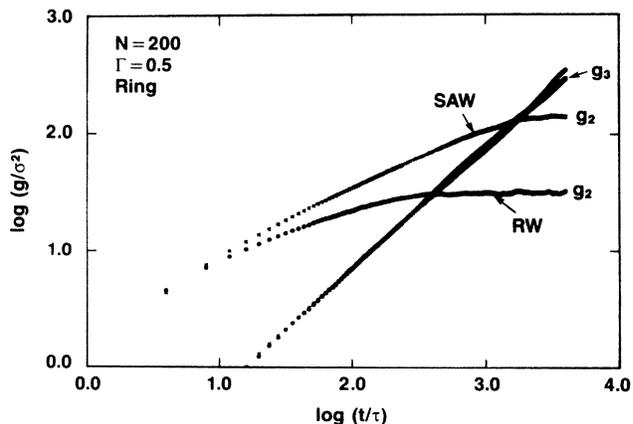

FIG. 4. g_2 and g_3 for a random-walk (RW) and a self-avoiding (saw) ring for $N = 200$ and $\Gamma = 0.5$. Total run $(3.2\times10^4\tau)$.

tunity to decrease Γ when we increase N, improving its effectiveness considerably. For higher densities, the dynamics of our system will be governed by the chain-chain interaction, and we simulate a constant T, canonical ensemble. In Fig. 3(b) the results for $\Gamma = 0.5$ and 1.5 are shown for $N = 50$. It shows the expected behavior, $D_1/D_2 \simeq 3.0$. The inset shows g_2 for fixed Γ but different N. For $t < \tau_N$, g_2 is independent of N. The deviations for $N = 50$ are due to the fact that ten inner momomers already represent 20% of the chain. Now let us consider the somewhat delicate difference of g_1/g_2 between the random walk and the self-avoiding chains due to Eq. (6). This can show how accurate our method is, even for a relatively low friction, $\Gamma = 0.5$. In Fig. 4, $g_2(t)$ for an $N = 200$ ring is shown since it displays the cleanest power law behavior. For comparison we include the data for the RW ring. We find a different power for $g_2(t) \propto t^x$, $x = 0.53 \pm 0.02$, instead of the $t^{1/2}$ for the RW.

To conclude, we have developed a rather general and highly effective method for the simulation of polymers. By changing Γ, local configurational fluctuations are governed by a ballistic dynamics up to a time $t(\Gamma)$. This is faster than purely Brownian relaxation. Within this framework it is straightforward to generalize it to a constant-pressure algorithm,[17] which allows us to study dense systems under stress. During the test of the method, we showed the difference in $S(q)$ for a ring compared to a linear chain, which was expected, but not seen for self-avoiding rings. In addition, for the first time the difference between the power laws in the Rouse behavior of g_2/g_1, between the ideal chain and the real chain, was demonstrated.

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