Force-extension curves for a single polymer chain under varying solvent conditions

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We show that Langevin dynamics can be used to obtain force-extension curves for a single polymer chain under varying solvent conditions. We find that the chains obey Hooke-type and Pincus regime behavior for Θ and good solvents. However, in poor solvents a coil-strand coexistence is observed in the equilibrium state and this leads to a quite different type of deformation behavior. [S1063-651X(99)10309-X]

I. INTRODUCTION

The mechanical properties, deformation behavior, and relaxation of macromolecules or single polymer chains have been a subject of some interest in recent years because of its importance in understanding the structure and function of cells and muscles. Much useful information about the mechanical response of polymers and macromolecules can be obtained from an investigation of the effect of different stretching forces on a simple polymer chain. Thus, for example, Perkins *et al.* [1] have studied the behavior of the DNA molecule under flows and its subsequent relaxation. Smith *et al.* [2] have been able to take measurements of the elasticity of single DNA molecules by using magnetic beads. Computer simulations afford a relatively simple approach to determining the microscopic mechanisms responsible for the observed mechanical response. Many of the observed properties of polymer chains may be attributed to topological constraints due to noncrossing of chains and can be modeled by the excluded volume interaction. Other properties may be a consequence of the stiffness and torsional constraints associated with the polymer.

De Gennes [3] and Pincus [4] were among the first to investigate the static properties of polymers subject to an external force using scaling analyses. Pincus showed that under good solvent conditions the extension of a chain can be described by a Hooke-like behavior only for weak forces. In the strong force limit, he showed that the extension was related to the force through a $\frac{2}{3}$ power law. The latter force-extension relation, termed the Pincus regime, can be explained in terms of a "blob" model of the polymer chain, in which the chain is said to break up into an ideal string of noninteracting blobs, each of which is made up of a number of monomers. The nonlinear dynamic behavior of a deformed, isolated polymer chain was studied by Sheng *et al.* [5] using Monte Carlo (MC) computer simulations. They were able to demonstrate the different relaxation dynamics in the different elastic regimes. Wittkop *et al.* [6] considered the deformation behavior of a single three-dimensional polymer chain, above and below the Θ temperature. Using the bond-fluctuation model, they found that for poor solvent regimes, the deformation was inhomogeneous and could be represented by a coil-strand coexistence, which became unstable for large strains. Force-extension relations of polymer chains have also been derived by Kroy and Frey [7], who studied a wormlike chain of arbitrary stiffness.

In this paper, we have focused on a single polymer chain

and performed molecular-dynamics (MD) simulations of the stretching of the chain when it is subject to an external tensile force. MD simulations have the advantage over techniques such as the MC method in being able to observe real time dynamic behavior, including relaxation times, and they also offer greater flexiblity in estimating the effects of stiffness, torsion, etc. In addition, the force-extension curves are also determined dynamically by the direct application of a force to the ends of a chain. This is in contrast with static methods, which extend the chain and then allow it to equilibrate. It is important to know if both approaches give similar results. In the next section, we outline the computational method used in the simulations and then go on to describe the results.

II. COMPUTATIONAL METHOD

The numerical simulations were performed by modeling a single polymer chain by N spherical beads interconnected by $(N-1)$ springs in a three-dimensional space. The monomer-monomer interactions between all monomers (bonded or not) were described by a composite potential

$$V = V_M + V_{\text{bond}}. \tag{1}$$

The Morse potential between two monomers labeled i and j is given by

$$V_M(r_{ij})/\epsilon = \exp[-2\alpha(r_{ij}-a)] - 2\exp[-\alpha(r_{ij}-a)];$$

$$r_{ij} < r_c,$$

$$V_M(r_{ij})/\epsilon = 0; \quad r_{ij} > r_c \tag{2}$$

and evaluates the effect of the excluded volume interaction and monomer attractions through the solvent. a defines the minimum of the potential and is, consequently, the initial bond length associated with the polymer. The bead radius, σ, is defined through $V_M(\sigma) = 0$, and the cutoff radius, r_c, is taken to be 1.5σ. The parameter α was chosen to be $10/\sigma$. ϵ was taken in units of the thermal energy, $k_B T$, and the distances are in units of the bead radius.

The attractive part of the Morse potential is not enough to describe the strong bonding forces between adjoining beads along the backbone of the polymer chain. Consequently, additional attractive forces are required to form the bead-bead interaction in the chains. This is done through the bonding potential V_{bond} given by

$$V_{\text{bond}}(r_{ij}) = -0.5\gamma R_{\text{max}}^2 \ln[1 - (r_{ij}/R_{\text{max}})^2]; \quad r_{ij} < R_{\text{max}},$$

$$V_{\text{bond}}(r_{ij}) = \infty; \quad r_{ij} > R_{\text{max}}. \quad (3)$$

The maximum bond length over which this interaction is nonzero was taken to be $R_{\text{max}} = 1.5\sigma$ and the potential strength is given by $\gamma = 30\epsilon/\sigma^2$.

The initial chain configurations were constructed by means of a random walk along the three-dimensional lattice and the system was allowed to relax according to the classical equations of motions for each bead. One of the difficulties in performing simulations of realistic polymer chains is in representing the influence of the solvent. Although this is partially taken into account in the model potential, there is no way of varying the solute-monomer interaction without affecting the monomer-monomer interactions. The inclusion of explicit solute effects would make the simulation more realistic and meaningful. However, explicit inclusion of solvent species atoms would overcomplicate the simulation. Grest and Kremer [8] proposed a simple method based on Langevin dynamics (LD), which actively took account of the presence of solvent. Furthermore, it was shown to be as computationally effective as MC methods for single chains. In this approach, each particle is weakly coupled to a heat bath so that the equations of motion for each bead/monomer become

$$\ddot{\mathbf{r}}_i = -\nabla U_i - \Gamma\dot{\mathbf{r}}_i + \mathbf{w}_i(t), \quad (4)$$

where Γ represents the viscosity of the solvent and $w_i(t)$ describes the random force of the heat bath acting on each monomer. The presence of the heat bath allows for work to be done on the system (e.g., extension) without a corresponding increase in the temperature. $w_i(t)$ and Γ are connected through the fluctuation-dissipation theorem,

$$\langle\mathbf{w}_i(t)\cdot\mathbf{w}_i(t')\rangle = \delta_{ij}\delta(t-t')6k_BT\Gamma, \quad (5)$$

and ensures that the temperature is kept constant. Note that if Γ were included without the w term, the system would simply dissipate and no temperature effects could be addressed. Thus LD allows us to explicitly introduce solvent effects and
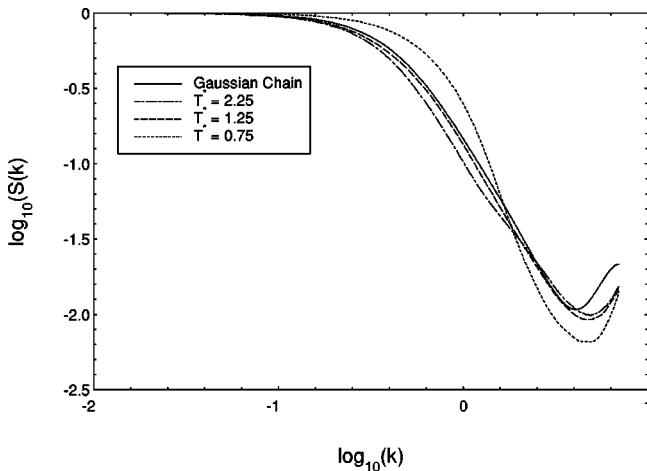
FIG. 1. Structure factor $S(k)$, curves for $N = 60$ chain at different reduced temperatures. Also shown, for comparision, is the $S(k)$ for a Gaussian chain, which is found to closely follow the calculated $S(k)$ in the Θ solvent case.
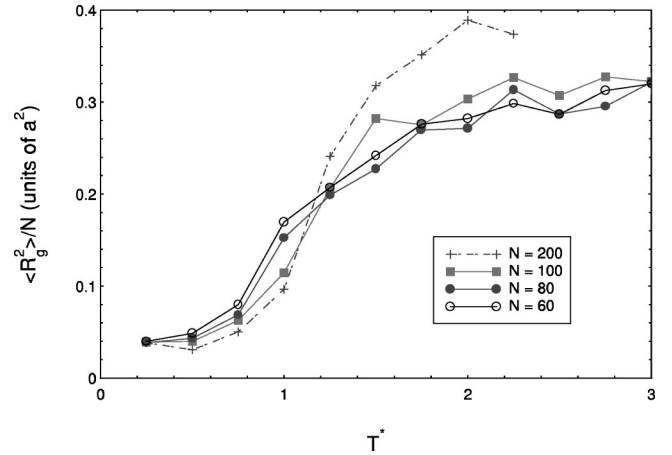
FIG. 2. Mean square radius of gyration for different chain lengths as a function of the scaled temperature.

also enables us to perform dynamic simulations of the force-extension curves. It would not be possible to use standard MD to do this, as the introduction of a force would raise the temperature of the system and these effects would have to be considered in a nontrivial way. However, by introducing the heat bath, a force may be applied directly and the dynamic simulations performed in the standard manner. The equations of motion were integrated using the Verlet algorithm with a time step of $\delta t = (\epsilon/m\sigma^2)^{-1/2}$ and the system was allowed to relax to find its equilibrium configuration. The relaxed chain was then used as the starting point in determining the force-extension relations. This was done by applying tensile forces to both ends of the chain and allowing the chain to respond to the force. The force was then increased in a stepwise manner and the process repeated until it was greater than the thermal force kT/σ. For each force step, the system was allowed to equilibrate for 500 000 steps and then sampled for one million steps to extract the chain configuration, the radius of gyration, R_g, and the end-to-end distance, R_N.

III. RESULTS AND DISCUSSION

As a preliminary to determining the force-extension curves, we performed the simulations on linear and random
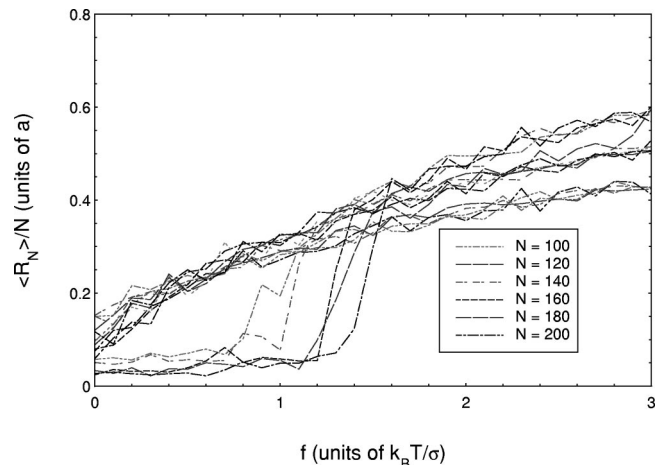
FIG. 3. Scaled extensions for varying polymer lengths in poor, Θ, and good solvents as a function of the applied force (in reduced units).
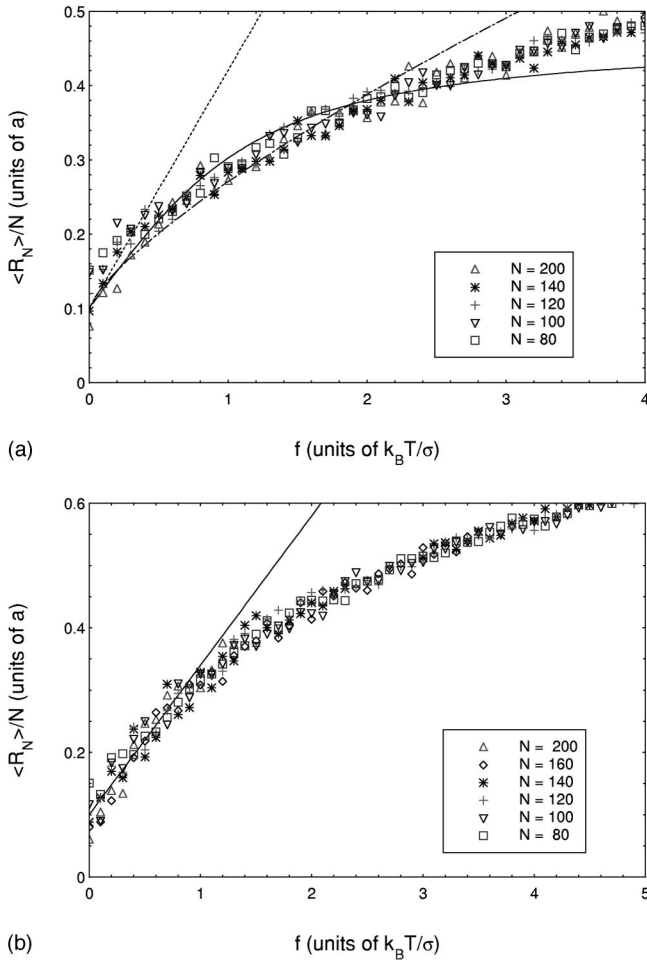
(a)

(b)

FIG. 4. Scaled extensions for varying polymer lengths as a function of the applied force (in reduced units). (a) In good solvents with, for comparision, Hooke's law (dotted line), the Pincus relation (dash-dot line), and the FJC model (full line) results. (b) In Θ solvents with, for comparision, the Hooke's law result (full line).

walk generated free-standing chains for a range of temperatures to identify the temperatures associated with the poor, Θ, and good solvent regimes. The structure factor should satisfy the relation

$$S(k) \sim k^{-1/\nu}; \quad \frac{\langle R_N \rangle}{2\pi} \leq \frac{1}{k} \leq \frac{\sigma}{2\pi} \qquad (6)$$

such that ν should be 0.59 for good solvents and less than 0.5 in poor solvents. At the Θ temperature, the attractive interaction compensates for the repulsion in such a way as to give near ideal chain behavior with $\nu = 0.5$. As shown in Fig. 1, we found that for reduced temperatures $T^* = k_B T / \epsilon$ equal to 2.25, 1.25, and 0.75, ν took the values 0.61, 0.5, and 0.33, respectively, which correspond to the three different solvent conditions. This demonstrates the applicability of this simulation method for modeling polymer behavior in varying solvent conditions simply by varying the reduced temperatures. We have also calculated the dependence of the mean square radius of gyration, R_g^2, for chains of different lengths over a range of temperatures, and this is plotted in Fig. 2. The crossing point of all the curves identifies the Θ temperature. It may be noted that for longer chains, the crossover from
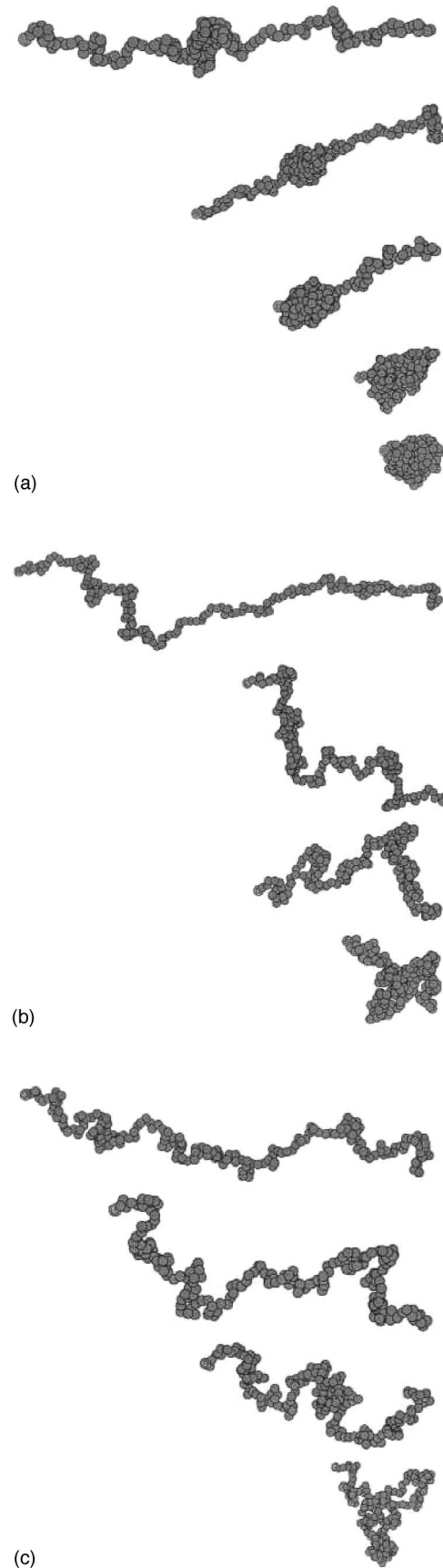

FIG. 5. Change in conformation of $N = 200$ polymer chain in (a) poor solvent for $f = 0, 0.6, 0.9, 1.1, 1.3$; (b) Θ solvent for $f = 0, 0.1, 0.5, 1$; and (c) good solvent for $f = 0, 0.1, 0.5, 1$. f is in units of $k_B T / \sigma$.
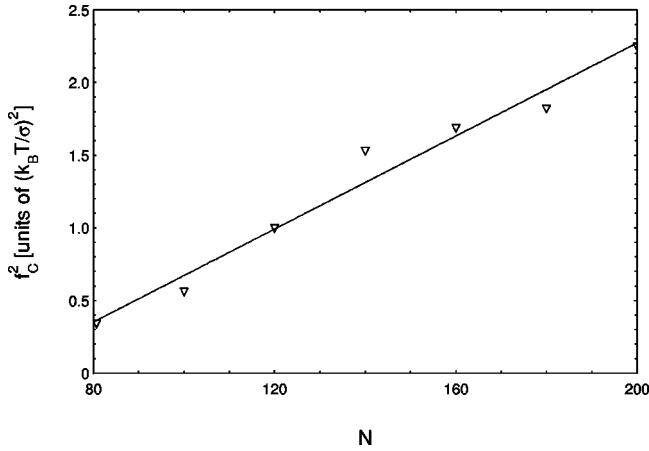
FIG. 6. Plot of the square of the critical force, f_c^2, vs the number of monomers, N.

poor to good solvent conditions is faster. This is consistent with $R_g \approx N^\nu$, which we found to hold for all the chain lengths shown in Fig. 2. The equilibrated chains were then subject to an extension force with a view to determining the force-extension relation. This was done for chain lengths $N = 80$, 100, 120, 140, 160, and 200 in all three solvent conditions. The nature of the solvent on the force-extension curve may be seen by examining the results for the scaled lengths, $\langle R_N \rangle / N$, displayed in Fig. 3.

In the poor solvent case, there is minimal extension until the applied force reaches some critical value, whereupon there is a sudden power-law increase in the extension. By contrast, in both Θ and good solvents, the curves display very similar behavior, which for small applied forces appears to be Hooke's law type linear behavior. This is consistent with the results of de Gennes and Pincus, who showed that the force extension relation was linear for Θ solvent conditions, but which displayed a nonlinear $\frac{2}{3}$ power law for intermediate extensions in good solvents. For much larger extensions ($f > 2k_BT/\sigma$), the relationship tends to be model specific.

To examine the force-extension curves in more detail, we have compared them with the analytical results, viz., the Hooke's law for small extensions, ΔR_N,

$$\langle \Delta R_N \rangle = \left(\frac{Na^2}{k_BT}\right) f,$$

and the Pincus type nonlinear behavior for intermediate extensions,

$$\langle \Delta R_N \rangle = Na\left(\frac{af}{k_BT}\right)^{(1-\nu)/\nu},$$

and these are shown in Fig. 4. In good solvents, the extension deviates from the Hooke's law linear behavior for even the smallest applied forces, but follows the Pincus relation for up to $2k_BT/\sigma$. It may be noted that the freely jointed chain (FJC) model [9] could also be used to describe this region. For forces greater than this, the calculated extensions lie between the Pincus and FJC models. By contrast, the extension in the Θ solvent follows Hooke's law up to $f \sim k_BT/\sigma$.

To get a better understanding of the behavior of chains in poor solvent conditions, we have charted the change in the equilibrium chain conformations as the applied force is increased. For purposes of clarity, it is best to observe one of the larger chains considered, and these are shown in Fig. 5. From these pictures, it is clear that the difference in the observed behavior in poor solvents may be attributed to the initial closed form of the polymer. For each polymer chain, a minimum force is required before this closed configuration can open. At this critical force, there is a sudden near-spontaneous uncoiling of the polymer, after which the extension appears to take the same form as for the other solvent conditions. This is in the model-dependent regime. The persistence of the coil-like region of the chain even for quite large forces suggests that whereas the increased temperature in good solvents is sufficient to overcome the strong bonding forces, it is not the case in poor solvents. In good solvents, the extensions propagate through the whole chain, whereas in poor solvents there is a tendency for the coil to unravel only slowly. This unraveling process can only come about once the applied force is large enough to break the bonds formed between parts of the chain in the coiled state. This critical force will of course depend on the number of such bonds that need to be broken. If the coil were a two-dimensional structure, the number of bonds (nearest neighbor) will vary linearly with the size of the chain. However, in the coiled state it might be expected to form fewer bonds, with the number varying as the gyration radius of the polymer leading to $f_c \sim N^{0.5}$. From the plot of f_c^2 versus N in Fig. 6, it may be seen that this relationship is fairly well satisfied by the simulation results. However, this agreement is not fully conclusive and the results could also point to a linear relationship. This ambiguity in determining the true relationship is due to the sparsity of points and to the error in determining f_c. Once the chain has unraveled, the force, which by now is very strong, simply extends it, as in the good solvent case. We have also examined the change in the lateral size of the chains and found that there is a nonlinear reduction with force for intermediate to large stresses.

IV. CONCLUSION

We have demonstrated that molecular dynamics gives a very flexible method of modelling polymers in different solvent conditions. We have also shown that the application of a Langevin dynamics approach is a very powerful method that takes solvent effects into account and can be used effectively to determine the response of polymers to an external applied force in a dynamical fashion. The calculated force extension curves are found to be in very good agreement with the results of analytical models. We have found that the polymer conformations under the different solvent conditions match those obtained by Wittkop *et al.* [6] using Monte Carlo techniques. We can thus confirm the so-called coil-strand coexistence of polymer chains at low temperatures.

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