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An Explanation for the High-Frequency Elastic Response of Dilute Polymer Solutions

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ABSTRACT: The behavior of polymer molecules in dilute solutions under high-frequency oscillations is revisited, with consideration given to the barriers to bond rotation that we argue can make the chain dynamically rigid at high frequency. Thus, the dynamical Kuhn length of the chain exceeds the static one, and the chain at high frequencies acts like a freely jointed chain of "bent rigid wires" in which each bent rigid wire is a "dynamical Kuhn length" containing many static Kuhn lengths connected together in a rigid random walk. We show that this model is consistent with anomalous high-frequency behavior of polystyrene solutions under shear observed by Schrag and co-workers[1−3] and Amelar et al.[4] and predicts that there is a minimum "spring" size corresponding roughly to $\exp[\Delta E_a/(3\nu + 1)k_BT]$ Kuhn steps that will behave elastically at high frequencies, where ΔE_a is the barrier to bond rotation, and $\nu = 0.5-0.6$ is the Flory exponent.

The bead−spring model is commonly, and successfully, used to describe the linear viscoelastic properties of dilute solutions of high-molecular-weight polymers.[4,5] The justification for this model rests on a coarse-graining approximation in which the atomistic structure and dynamics of the real chain are represented at long time and distance scales by those of the fictitious bead−spring chain. This representation should be successful when the bonds in a submolecule of the real chain corresponding to a single spring of the bead−spring chain relax quickly enough on the time scale of the flow to sample their equilibrium configuration distribution.

Accurate predictions can therefore be made from the bead−spring model for flows slow enough that individual springs remain nearly unstretched, so that the submolecule represented by a single spring is nearly at equilibrium. If the flow becomes too fast for this to hold, then more springs can be used to represent the whole molecule, so that each spring represents a smaller submolecule, one in which equilibrium is still achieved at the faster rate. If the flow is made continually faster, for a finite molecular weight polymer it will eventually no longer be possible to make the submolecule small enough to remain equilibrated and yet be well represented as an entropic spring. In general, we expect that, since the size of a submolecule that is represented by a "spring" is to some extent arbitrary, the bead−spring model should only be applied when its predictions are insensitive to the exact number of springs chosen, as long as enough are chosen that each individual spring remains almost unstretched at the flow frequency considered.

While all of this is well understood, what is not well understood is the manner in which the bead−spring model breaks down in high-frequency flows for which the smallest possible submolecule that can accurately be represented as a "spring" is deformed too fast to stay near equilibrium. Surprisingly, oscillatory birefringence data on polystyrene and polyisopene solutions dissolved in Aroclor, and other small-molecule solvents and oligomers by Lodge, Miller and Schrag,[1] Peterson et al.,[3] Amelar and co-workers,[4] and others show good agreement with the bead−spring model predictions over the entire frequency range of the experiments, all the way up to high frequencies where one might expect the bead−spring model to fail, because of inability of an individual "spring" to correctly approximate the forces produced by individual bond motions. This good agreement is attained under certain conditions. One condition is that hydrodynamic interaction (HI) and excluded-volume (EV) effects are incorporated into the model. HI is typically incorporated by using the Zimm analysis, and EV can be incorporated in a variety of ways, the simplest being an adjustment of the parameters of the bead−spring model to account for the reduced hydrodynamic interactions present when the chain's dimensions are swollen by excluded-volume effects. The approximations involved are discussed elsewhere at length[6] and are not the focus of this paper.

What is of interest here is the unusual way in which the bead−spring model can be made to match the experimental data at high frequencies. For polystyrene in Aroclor, agreement is achieved over the entire frequency regime of the experiments, which includes frequencies that deform single springs, if the number of springs is chosen to equal the molecular weight of the polystyrene divided by around 5000. This is surprising because of the seeming arbitrariness of the rule for the choice of a "spring", and because this choice is successful even if applied to molecules of molecular weight 5000, that are therefore represented by only a single spring! In view of the above discussion, we would have expected the bead−spring chain to fail at frequencies so high that individual springs become deformed.

What is especially remarkable is that fast enough oscillatory deformation causes the individual springs to deform elastically, and this elastic spring deformation accurately describes the in-phase and out-of-phase contributions to the dynamic birefringence at high frequencies (i.e., reduced frequencies of 10^5-10^6 s^{-1} or even higher). This would seem to imply that the chain "runs out of modes" once a submolecule is reduced to a size corresponding to a molecular weight of roughly 5000 Da. This is surprising since a molecular weight of 5000

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for polystyrene corresponds to 100 backbone bonds, about 10 times larger than the number contained in a "Kuhn" length or effective link of a freely jointed chain representation of polystyrene. Thus, while 100 backbone bonds might possibly be the smallest length of chain that can act like an entropic spring, there are shorter portions of the chain (i.e., the Kuhn lengths) that can take on orientations that are statistically independent of each other, and the exploration of these microstates should therefore dissipate energy. In fact, in melts of the same polymer, viscoelastic response corresponding to modes that involve much smaller portions of the chain, corresponding to a molecular weight of only 500 for polystyrene, can be detected.[3] Why the modes corresponding to these small-scale motions do not seem to show up in dilute solutions is what we wish to explain here.

Let us consider a polystyrene chain containing n backbone bonds, each of length l. A freely jointed chain model of the flexible polymer molecule, whose coarse-grained conformation in a Θ solvent or the melt is a random walk, will have the same equilibrium mean-square end-to-end length $\langle R^2\rangle_0 = C_\infty n l^2$ and fully extended length L as the real polymer if the freely jointed step length b_K and the number of steps N_K of the freely jointed chain are chosen appropriately, i.e., so that $b_K{}^2 N_K = \langle R^2\rangle_0$ and $b_K N_K = L$. The fully extended length of a chain whose n backbone bonds, each of length l, are tetrahedrally bonded (as is the case for carbon−carbon bonds) is given by

$$L = 0.82nl \tag{1}$$

where the factor 0.82 enters because the backbone has a zigzag configuration in the most extended state that still preserves the tetrahedral backbone bond angle restrictions. (For molecules that do not have simple tetrahedral bonds in the backbone, the prefactor in eq 1 will be changed somewhat, but this will have little effect on what is presented here.) From this, and the definition of the "characteristic ratio" C_∞,[7] we obtain the following formulas for the equivalent freely jointed step length b_K and the number of steps N_K:

$$b_K = \frac{C_\infty}{0.82} l; \quad N_K = \frac{(0.82)^2}{C_\infty} n \equiv \alpha n; \quad \text{with } \alpha \equiv \frac{(0.82)^2}{C_\infty} \tag{2}$$

For polystyrene molecules, for example, with $C_\infty = 9.6$,[8] $l = 1.54$ Å, and $n = M/52$, these formulas yield a Kuhn step length $b_K = 1.8$ nm, and number of Kuhn steps $N_K = M/742$, where M is the molecular weight in daltons.

Since the real chain backbone is not freely jointed, but consists of short ($l = 1.54$ Å) backbone bonds with energetically preferred bond angles, the real molecule's configurations only match those of a freely jointed chain when the former is coarse-grained over enough real bonds to recover freely jointed chain statistics. One might therefore expect the bead−rod model to be accurate as long as the chain is not deformed at a level approaching that of a single Kuhn step, represented by a single rod in the bead−rod chain. However, in addition to having preferred bond orientations, real chains have activation barriers that limit the rates at which transitions can occur from one preferred orientation to another.

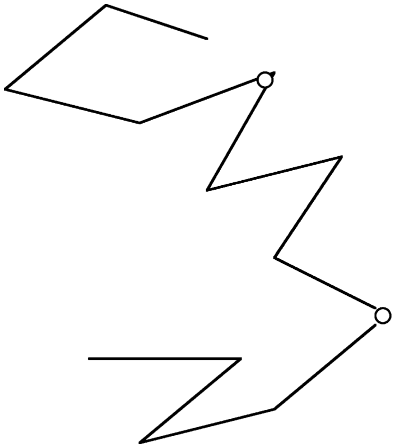

Figure 1. A stiff, bent wire model of a polymer molecule with internal barriers to bond rotations.

For example, suppose that τ^0 is the time constant for a purely diffusive transition of a bond orientation between trans and gauche states in a viscous medium, governed by friction coefficient of a monomer in the solvent. If ΔE_a is the activation barrier between the trans and gauche states, then $\tau_b \sim \tau^0 \exp(\Delta E_a/k_B T)$ is the typical time required for this transition to occur. A more precise formula for the barrier-crossing time from Kramers' reaction rate theory can be found in Skolnick and Helfand;[9] in it, τ^0 is proportional to $\zeta l^2/k_B T$, where ζ is a drag coefficient and the constant of proportionality depends on the shape of the barrier while its height (ΔE_a) appears in the exponential. If τ_b exceeds the reorientation time of a single rod of the bead−rod chain used to model the polymer, then the assumption of freely jointed bead−rod hinges fails, not because it does not represent the equilibrium distribution of chain configurations on length scales longer than a rod but because the real chain cannot locally reconfigure itself as fast as the corresponding bead−rod chain can, since the latter has no activation barrier for rotation of the rods.

Note that the activation time for bond reorientation, $\tau_b = \tau^0 \exp(\Delta E_a/k_B T)$, does not simply rescale the relaxation of the entire chain so that all motions are slowed by the same factor $\exp(\Delta E_a/k_B T)$ relative to the diffusive time set by the drag coefficient ζ. For long time scales, it is the diffusive motion of subchains containing many bonds that controls the relaxation of the chain, and this motion is not influenced by the activation barrier ΔE_a. To see this, consider the diffusion of the molecule as a whole. This diffusive motion is only influenced by the chain's equilibrium distribution of configurations, and the viscosity of the solvent, not the rates of internal transitions between one configuration and another. Similarly, relaxation times of the polymer that are much longer than τ_b are governed by the rate of monomer diffusion, which is represented by a bead or monomer drag coefficient ζ, and are not influenced by the bond rotational activation barrier ΔE_a. Thus, there must be a crossover from behavior at high frequencies of small numbers of Kuhn steps, whose relaxation is dominated by the activated rotation of bonds, to the behavior at low frequencies of large numbers of Kuhn steps, whose relaxation is controlled by diffusive motion through the medium. Since the chain acts freely jointed at long length scales, but stiff at shorter ones that are nevertheless longer than the static Kuhn length, a simple model of the chain is a freely jointed chain of stiff, bent wires (see Figure 1).

In this model, beads permitting free rotation connect the bent rods, and each bent rod is a random (but stiff) walk containing $N_{K,0}$ Kuhn steps. The bent wire is therefore a dynamical Kuhn length, which consists of a random walk of many static Kuhn lengths. Of course, this model is not intended to imply that the chain can only change configuration by pivoting about a small, fixed, set of locations along the chain, but only that at fast time scales, rather large portions of the chain move more or less rigidly.

One can also infer the existence of a crossover from diffusive relaxation at low frequencies to relaxation controlled by activated bond rotation at high frequencies from the bead–rod Brownian dynamics simulations of Helfand and co-workers,[9,10] which included rotational barriers to trans–gauche transitions through Ryckaert–Bellemans bond rotational potential. In these simulations, the parameters for the rotational potentials were chosen to mimic polyethylene, with a barrier height of 3 kcal/mol, about the same as that of polystyrene. The simulations give a time constant for bond rotation of around 0.25 ns (a rotation rate of 4.19 ns). However, the bead friction constant ζ (obtained from the first two entries in Table 1 of Skolnick and Helfand) is 2.3×10^{-9} g/s, which we find corresponds to a bead of radius 1 Å (corresponding to a carbon atom) in a solvent of viscosity 1 cP. From this drag coefficient and the Stokes–Einstein law for the diffusivity $D = k_BT/\zeta$, one can readily compute that the time it takes a bead to diffuse a distance of about one bond length (1.54 Å) is 0.6×10^{-11} s, almost 2 orders of magnitude less than the bond rotational time. This implies that the short-range motions of the chain are controlled by the barriers to bond rotation, not simple diffusion, which governs larger scale, slower relaxations. These simulations also show that the barrier to bond rotation is roughly the height of a single trans–gauche transition, despite the fact that rotation about a bond must be accompanied by counter-rotation of one or more neighboring bonds to avoid the necessity of swinging one or both ends of the molecule through the solvent in a large arc. We also note that if we scale up the bead drag coefficient from the simulations of Helfand and co-workers to that for Aroclor, which at 25 °C has a viscosity of around 2 P, we expect that the barrier crossing time in Aroclor will be around 10^{-7} s, not too far from what is observed[3] for the inverse of the shortest relaxation time exhibited by polystyrene in Aroclor in oscillatory shearing. Thus, it appears that the time for rotational barrier crossing is setting the frequency at which the polymer molecular "runs out of modes".

Now let us estimate the crossover condition between relaxation dominated by diffusive motion and that controlled by activated bond rotation. Suppose we gradually increase the frequency of oscillation ω, starting from a low value where viscous diffusion dominates. The time available for chain relaxation to occur is given by $\tau = 1/\omega$. At low frequency or large τ, there is ample time for large portions of the chain to relax to equilibrium, the largest submolecule able to do so being given roughly by the diffusion time required for that submolecule to diffuse its own end-to-end distance. Let us say that this submolecule contains $N_{K,0}$ Kuhn steps. Then, if the mean-square end-to-end distance for the submolecule is denoted by $\langle R^2\rangle_0$, it follows that the time τ for it to relax diffusively is given approximately by

$$\tau \approx 0.4\,\frac{{\langle R^2\rangle_0}^{3/2}\eta_s}{k_BT} = 0.4\,\frac{{N_{K,0}}^{3\nu}{b_K}^3\eta_s}{k_BT} \qquad (3)$$

where ν is the Flory exponent in the scaling relationship between coil size $\langle R^2\rangle_0^{1/2}$ and chain length $N_{K,0}$, which is 0.5 for Θ conditions and roughly 0.6 for good-solvent conditions, and η_s is the solvent viscosity. The above result can be obtained by estimating the relaxation time of a polymer molecule with root-mean end-to-end distance $\langle R^2\rangle_0^{1/2}$ from Zimm theory.[11] This calculation assumes dominant hydrodynamic interactions. If the piece of chain is small enough to be free draining, a Rouse time would result, which would change the power of 3ν to 2 in eq 3, but will not make much difference in the results obtained here.

As the frequency increases, the time τ available for diffusive motion eventually drops below $\tau_b = \tau^0 \exp(\Delta E_a/k_BT)$, the time required for bond rotation. At a time $\tau < \tau_b$, only a fraction τ/τ_b of the bonds are able to rotate in the time available, and the chain will start to become dynamically rigid. We expect the subchain will retain enough flexibility to relax at times somewhat less than τ_b since not all bonds in the subchain need to be able to rotate for the submolecule to relax its configuration. Thus, the crossover time should be lower than τ_b by a factor as great as $N_{K,0}$ or so. Thus, we take the crossover condition to be

$$\frac{\tau_b}{\tau} \sim N_{K,0} \qquad (4)$$

We can now use eq 3 and the expression $\tau_b = \tau^0 \exp(\Delta E_a/k_BT)$ to estimate $N_{K,0}$ for the crossover size of the submolecule. As noted earlier, τ^0 is a diffusive time for a single bond rotation through the solvent, given by $\beta\zeta l^2/k_BT \approx 6\pi\beta\eta_s l^3/k_BT$, where β is a dimensionless prefactor that can be estimated from the shape of a typical rotational potential and $\zeta \approx 6\pi\eta_s l$. Using the simulation results reported by Skolnick and Helfand, which gives a transition rate of 4.19 ns^{-1} for a potential mimicking polyethylene with $\Delta E_a/k_BT = 4$, $\zeta = 2.3 \times 10^{-9}$ g/s, and $l = 1.53$ Å, one can deduce that $\beta \approx 25$. Combining these results quickly gives

$$N_{K,0} \sim ((15\pi\beta)^{1/3}(l/b_K))^{3/(3\nu+1)} \exp\left(\frac{\Delta E_a}{(3\nu+1)k_BT}\right) = \left(10.6\,\frac{l}{b_K}\right)^{3/(3\nu+1)} \exp\left(\frac{\Delta E_a}{(3\nu+1)k_BT}\right) \qquad (5)$$

The factor $3\nu + 1$ ranges from 2.5 for Θ conditions to 2.8 for good solvents.

Since b_K/l is close to 10, the prefactor to the exponential is close to unity. For typical $\Delta E_a/k_BT$, around 1.5–7 at room temperatures for most flexible polymers,[11] the number of Kuhn steps in the bent wire can range from slightly above unity to perhaps 100 or so, depending on the dynamic flexibility of the chain. For polystyrene, in units of moles rather than molecules, the barrier to bond rotation is around 3 kcal/mol[12,13] so that in a Θ solvent $\exp(\Delta E_a/3\nu k_BT)$ is around 8 or so, which is close to the observed value corresponding to the number of Kuhn steps in a polystyrene "spring", namely $5000/742 = 6.7$. We note that if the crossover condition corresponds to $\tau \approx \tau_b$, rather than $\tau \approx \tau_b/N_{K,0}$, eq 5 is only changed by everywhere replacing $3\nu + 1$ with 3ν. This leads to an estimate that $N_{K,0} \approx 30$, somewhat too large. However, the value of the time constant at the crossover seems to be closer to τ_b than to $\tau_b/N_{K,0}$, which is more consistent with the assumption that $\tau \approx \tau_b$.

To make more accurate predictions, we would need to either do simulations of model polystyrene chains with bond rotational barriers (such as the model studied by Helfand and co-workers or, better, fully atomistic simulations with molecularly resolved solvent) under high-frequency oscillatory flows or gather data on different polymers under high-frequency oscillatory flows, to see whether a correlation can be developed between a "minimal" spring size and the activation barrier ΔE_a. At this point, we can only say that our estimate of the minimal spring size based on the "bent wire" argument is roughly consistent with the experimental data for dilute solutions of polystyrene. As we discuss shortly, we can also say that we expect elastic, rather than dissipative, behavior at frequencies higher than those needed to excite a single "minimal" spring, and this is also in agreement with experiments.

Note from the range of activation energies for typical polymers that the bead−rod chain will only represent the dynamics of polymers at time scales longer than $\exp(\Delta E_a/k_BT) = 10-10^3$ times the diffusive rotational time τ^0 of a single bond. At the larger end of this scale, the freely jointed bead−rod model is no improvement over the bead−spring model, since at time scales long enough for the bead−rod chain to be accurate, the bead−spring chain will be valid as well.

We remark that the above estimates assume that the prefactor for local rotational motion, τ^0, is proportional to η_s, the solvent viscosity. This should be true if the only way solvent can permit local polymer bond rotations is by hydrodynamic flow, governed by the solvent viscosity. If the solvent has a flow activation energy $\Delta E_{a,s}$, then $\eta_s \propto \exp(\Delta E_{a,s}/k_BT)$, and bond rotation therefore has a net activation energy of $\Delta E_{a,s} + \Delta E_a$, which exceeds by ΔE_a that for large-scale polymer relaxation. However, local rotation of polymer bonds might be accommodated in some cases by local solvent motion that involves a lower activation barrier than for hydrodynamic flow.[13] This is especially likely to be the case for bulky solvent molecules, or solvent near its glass transition temperature, where solvent flow requires more extensive movement of solvent molecules than is required merely to permit a polymer chain to reorient several bonds. This possibility is especially pertinent when the solvent is itself a melt of the same polymer, which is what prevents us from applying our "bent wire" argument directly to the melt state. To the extent that the local polymer motion is impeded by solvent to a degree less than that for viscous flow, the above estimate of the number of Kuhn steps in each "bent wire" will be too high.

Setting aside this caveat for the time being, we can inquire: what will happen if the chain is deformed at a frequency higher than the inverse of $\tau^0 \exp(\Delta E_a/k_BT)$, the fastest time scale for bond reorientation? This frequency is high enough that chain of bent wires deforms affinely. Since the Kuhn steps within the bent wire are too sluggish to relax at this frequency, the only movement left to the chain is to distort the bond angles within the bent wire against their potential barriers. Thus, the bent wire will act like a spring! But the elasticity of the bent wire will not be entropic, but energetic, arising from the rotational energy barriers. We can estimate the spring constant H_E for the bent-wire "spring" by approximating the rotational potential as harmonic and matching the energy $H_EL_{max}^2/2$ to straighten out the wire to its maximum length, L_{max}, to the energy $n_0\Delta E_a$ needed to bring all n_0 bond angles over their potential barriers. This implies that

$$\frac{1}{2}H_EL_{\max}{}^2 \approx n_0\Delta E_a \tag{6}$$

But $L_{\max} = 0.82n_0l$, so we quickly obtain

$$H_E \approx \frac{2\Delta E_a}{(0.82)^2n_0l^2} \approx \frac{2C_\infty}{(0.82)^2}\frac{\Delta E_a}{N_{K,0}b_K{}^2} \tag{7}$$

Comparing this to the ordinary entropic spring constant for the same piece of chain

$$H = \frac{3k_BT}{N_{K,0}b_K{}^2} \tag{8}$$

we find that H_E exceeds H by a factor of $[2C_\infty/3(0.82)^2]\Delta E_a/k_BT$, that is, by a factor of 10−100. Note that this "stiffness" H_E is for dynamics only; the equilibrium root-mean-square end-to-end distance of the submolecule corresponding to a single bent wire is controlled by the static stiffness, which is the entropic spring constant H.

It should also be noted that while at high frequencies we expect an elastic response from the polymer, the solvent will contribute a substantial viscous response to any mechanical measurements, and this must be subtracted from the data to obtain the pure polymer contribution. The subtraction is often not trivial, for the presence of the polymer can modify the solvent's viscous properties.[14] Such a modification was at one time mistaken for evidence of "internal viscosity", a hypothetical polymer contribution to the viscous response of the solution due to dissipation during bond rotations.[15] Careful spectroscopic studies revealed instead that the additional dissipation thought to be due to polymer "internal viscosity" really had arisen from the solvent.[16] (Internal viscosity is sometimes represented as a "dashpot" in parallel with the usual spring−dashpot model of ordinary entropic polymer viscoelasticity.) Our new analysis, if correct, shows that there is indeed a contribution from bond rotational energy that supplements entropic elasticity but that this contribution, when it is important, is actually elastic, rather than viscous, and so is quite different from "internal viscosity". This conclusion should not be too surprising, since a contribution that is purely dissipative at even high frequencies would need to have a very fast relaxation time, which would only be the case if the barriers to rotation are very weak, and in this case the chain would be very limp and unaffected by these barriers.

Finally, we note again that our argument cannot be applied in a simple way to melts, since in melts the friction that one chain experiences is controlled by the motions of neighboring chains. Hence, the activation barrier for bond rotation of chains in the medium influences the frictional properties experienced by each chain. Since the time scale for polymer−solvent friction is governed by the relaxation times of the solvent, in melts, a separation of polymer bond rotational time scales from frictional ones is not possible, since the polymer and "solvent" are one and the same. In dilute solutions, however, the solvent relaxation time is typically much faster than the polymer bond rotation time, at least for small-molecule solvents away from their glass transition temperature.[3] Thus, there can be a large separation of frictional time scales from polymer bond rotational time scales, and this, in essence, is the reason for the loss of polymer modes. The "lost" high-frequency local modes in solutions are allowed by the low friction with the solvent but prevented by sluggishness of the polymer to cross the rotational barriers. In melts, there is also evidence that fast chain relaxations are much more heavily influenced by rotational barriers than are slow ones.[17] Indeed, in some melts, different time–temperature superposition scalings apply to slow (rubbery) motions and to fast (glassy) relaxations.[18] However, in polystyrene at least, the rubbery motions in melts contain modes corresponding to motions involving subchains as small or smaller than the Kuhn length,[18] while we have seen that in dilute solutions modes with relaxation time near that corresponding to motion of the Kuhn length are absent. While fast modes are present in melts, their behavior can be complex and not easily be interpreted in terms of motions of Kuhn segments.[19]

To recap, for dilute polymer solutions, consideration of the energetic barriers to bond rotation leads us to expect a transition with increasing frequency from a regime where the bead–spring model can be refined or coarsened simply by changing the number of springs to a regime where there is a "smallest possible spring", which represents a piece of chain whose size is exponential in the bond rotational barrier, and that this smallest possible spring behaves elastically when deformed. These expectations seem to be in agreement with high-frequency oscillatory data for polystyrene solutions and lead to a formula for the "smallest possible spring" that should be valid for other polymers as well. It would be very interesting to check these predictions. Our findings, if valid, further imply that many polymers, namely those whose bond rotational barrier is several multiples of k_BT or more, will have no regime in which the freely jointed bead–rod model is superior to the bead–spring model. Of course, a bead–rod model containing energetic barriers to rotation would in principle be more accurate than the bead–spring model at high frequencies but would be computationally very demanding, since the stiffness of these barriers would require very small time steps to resolve. Nevertheless, exploration of bead–rod models containing such barriers would be quite interesting. Rigorous testing of the ideas presented here, using atomistic simulations of polymers in continuum or even atomistic solvents, might soon be possible using high-speed computers.

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