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Dynamics of Charged Polymers. 1

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ABSTRACT: We use full classical dynamics to study the properties of isolated multiply charged polymeric ions. The polymer is taken to be a chain of 1000 "atoms" with bonding and nonbonding potential terms; in these initial studies, no polarization or dielectric terms are included. We treat polymers with 1, 5, 10, 15, and 20 charges equally spaced along the 1000 atom chain and conduct a 600-ps simulation of the charged species. Each simulation required approximately 7 h on a Cray YMP. Because the simulation is limited in time and the potential adopted is relatively simple, the results are interpreted qualitatively as a function of charge density. At high charge densities the ions force the polymeric ion to adopt a stretched out, essentially planar conformation, in marked contrast to the highly folded conformation adopted by an uncharged polymer. This conformation minimizes the ionic interactions within the constraints imposed by chemical bonding. These descriptions are supported by the statistical data obtained during the simulation.

I. Introduction

Multiply charged polymeric ions have been observed in the gas phase in mass spectrometric measurements of biological substances;[1] the existence of highly charged species is important in the mass spectrometric analysis. The review cited in ref 1 identifies the occurrence of proteins with molecular mass of 40 000 having as many as 45 charges. One appropriate question is to ask about the conformation of these gas-phase ions; we consider this question here for a model homologous polymer.

The nature of the structure of multiply charged polymers (ionic polymers) and of ionomers has been under investigation for some time, but the details have not been pinned down as yet. Here we bring a new tool to the investigation, by using a full molecular dynamics method to ascertain the structure. The use of molecular dynamics to study polymer properties has proven fruitful in a number of other situations, where the approach has been used to simulate crystal melting,[2] mesophase transitions such as the Condis transition,[3] defect motion,[4] laser interactions,[5] collisional interactions,[6] spectral properties,[7] and related areas.[8]

In this work we apply the methods of molecular dynamics to the study of the structure of multiply charged polymers. The molecular dynamics approach has the advantage that the complete physics of the problem can be incorporated and that time-dependent properties can be directly computed. The method is not restricted to comparing possible equilibrium structures which depend only on an energy criterion. Other approaches to mapping out the structure of ionomers have focused on using Monte Carlo methods. Although this technique is very powerful and can handle larger systems than can molecular dynamics, the latter can now treat polymers and provide the same kinds of information with a more realistic model. Among the disadvantages to the molecular dynamics approach are that the results can depend upon the selection of initial conditions, that only a limited portion of the phase space can be investigated, and that the time period during which the evolution of a polymer can be studied is limited by the available computer time and by the accuracy of the numerical integration routines. First, we attend to these issues by focusing our attention on determining the trends in the properties as a function of charge density, rather than attempting to predict the properties of a particular charged species itself. Second, this goal permits us to use a simple potential to model the polymer. Finally, we employ a consistent set of initial conditions for each of the polymeric ions, to facilitate the comparisons and reduce the problems associated with computational limits for such systems.

In the next section we discuss the model of the charged polymer employed and in section III present the results of the simulations.

II. Method

A. Multiply Charged Polymeric Ion. The goal in establishing the parameters for the model system is to relate to the behavior of polymers found in mass spectrometers, that is, large, isolated polymer systems with multiple charges. The number of monomer units in the chain, N_M, is taken to be 1000; each monomer is assigned a mass of 14 amu, representing a CH_2 group. The number of charges is denoted by N, and we treat cases with N = 1, 5, 10, 15, and 20. (Since there are no Coulombic interactions present when $N = 1$, it serves in place of an uncharged reference case, permitting the use of the same computer code for the reference.) The ions are distributed along the polymer chain symmetrically about the center at equally spaced intervals of $1000/N$; this is a low-energy distribution of charges along a rigid chain. The symmetric distribution places the first charge at the monomer located at position $1000/2N$ from one end; as a result, any edge effects due to charges located at or near the chain termini are minimized. These assumptions concerning the structure of the multiply charged ion then represents an uncomplicated model of the distribution of the charges in the isolated homologous polymeric ion, as it might occur in a mass spectrometric experiment.

B. Specification of the Potential. In this section the potential energy which serves to define the model of the charged polymer employed is specified; as an isolated system is studied, only intramolecular forces need to be included. The non-Coulombic portion of the potential employed has been fully described elsewhere, so only a brief description is given here. The potential[9] V is given

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by a sum:

$$V = V_{2b} + V_{3b} + V_{4b} + V_{nb} + V_c \qquad (1)$$

The chemical bonds between the monomers on the backbone chain are expressed as Morse functions in the term designated V_{2b}, with an equilibrium bond length of 1.53 Å and Morse parameters D = 80 kcal/mol and α = 1.99 Å^{-1}; the sum extends over adjacent pairs. The three-body bending term, V_{3b}, is evaluated as a quadratic in the cosine of the angle with a force constant of 31.1 kcal/mol and an equilibrium bond angle of 113°; the four-body torsion term, V_{4b}, is represented by linear and cubic powers of the cosine of the torsion angle. The nonbonded interactions between nonadjacent monomers, represented by V_{nb}, are taken to be Lennard-Jones 6–12 potentials with ϵ = 0.114 kcal/mol and σ = 3.98 Å. The nonbonded terms occur over long ranges and are attractive in nature; they are therefore important in determining the conformation of *uncharged* polymers. Nonetheless, at very long range their influence on the conformation is small, while the number of such tiny interactions increases rapidly with distance. Consequently, the large number of terms requires a large amount of computation time. We have therefore chosen to cut off the nonbonded interactions if the atoms are separated by more than some critical distance R_M, which was set at 10 Å. At this distance the nonbonded forces and energies are quite small compared to the terms included in the summation. Even with this cutoff, the number of such terms in the polymer may be quite large, and their cumulative contribution to the total energy can be substantial.

The Coulombic interaction between the charges is designated V_c and is taken in these initial studies to involve singly charged ions with a dielectric constant of unity and no polarization of nearby atoms; then it is given in atomic units by

$$V_c = +\sum_{i>j} \frac{1}{r_{ij}} \qquad (2)$$

where i and j range over all ion pairs. As a result of the neglect of polarization effects, the range of influence of the charges is surely overestimated. These conditions, somewhat unrealistic, tend to emphasize the influence of the charges on the structure of the polymer.

The potential should thus be regarded as a model potential for the evaluation of the influence of the charges, rather than as a detailed description of the forces in a real polymer. It is sufficiently representative that we do expect comparisons of results between ions of different charges to provide realistic estimates of the trends, providing the structure/property relationships sought.

The full Hamiltonian is the sum of the potential energy given in eq 1 and the kinetic energy T, as given in eq 3.

$$T = \sum_{i=1}^{1000} \left(\frac{1}{2m_i}\right)(p_{x_i}^{\,2} + p_{y_i}^{\,2} + p_{z_i}^{\,2}); \quad H = T + V \qquad (3)$$

C. Classical Dynamics and Initial Conditions. Classical dynamics involves the integration of the Hamiltonian equations of motion for the particles comprising the system

$$\frac{\mathrm{d}q_i}{\mathrm{d}t} = \frac{\partial H}{\partial p_i}; \quad \frac{\mathrm{d}p_i}{\mathrm{d}t} = -\frac{\partial H}{\partial q_i} \qquad (4)$$

where the range of i extends over the three Cartesian directions for each of the 1000 monomers. Thus, the number of equations to be integrated, 6000 for a chain of 1000 monomers, is quite large, and long-time simulations severely tax available computing power; a number of programming techniques introduced elsewhere, in particular the use of geometrical statement functions,[10] are employed here to reduce this computing effort.

The classical equations of motion for all the 3000 coordinates of the 1000 monomers are integrated using a standard code.[11] The initial conditions specify a chain in a zigzag conformation in the x–z plane, with the momenta chosen randomly to correspond to a high temperature and with the center-of-mass motion set to zero. Several other sets of initial conditions were considered, but the simple choice given above produces results as representative and consistent as other, more complicated initial conditions.

D. Dynamics. The differential equations of motion were integrated for a total time period τ, typically taken to be 600 ps.[12] Larger values for τ would require both longer computer runs and tighter control on the numerical accuracy per step, in order to preserve the global accuracy of the integration. The value of τ was selected to be small enough for accuracy, while demonstrating the behavior of the ionic polymer at long times. Each such simulation involves a long computer run, averaging about 7 h on a Cray YMP. Various properties and the conformation of the polymer ion are stored periodically during the integration.

A number of factors affect the ability of the present calculations to provide direct comparisons with experiment. The first and most important of these factors is the simple model potential. A second such factor is the variation in the energy and temperature of the different polymeric ions, due to the introduction of additional potential energy with each additional charge pair interaction. Another contribution to the energy variation stems from the cutoff in the long-range terms in the potential: as discussed below, folding of the polymers may drastically change the number of long-range potential terms included. On this basis, we do not attempt to conserve the total energy of the polymer to high accuracy in the simulation. This also means that a relatively simple integration code, a fourth-order Runge–Kutta method, can be employed in order to obtain as short a computer time as possible. In practice, the *temperature* behavior during and at the end of each of the runs turns out to be similar for each of the ionic polymers studied, and on that basis we believe that the results are comparable polymer to polymer.

III. Results

In this section we report the results of the simulations, considering the values of a number of properties. Several of the properties of the polymer chain are measured at 1-ps intervals during the course of the simulation and provide a fine-grained set of data for the properties of the polymeric ions. Other properties are sampled less frequently, at 50-ps intervals, providing a more coarse-grained set of data.

We consider first the kinetic temperature of the polymer, as defined by

$$T = \frac{2}{3N_M k_B} \sum_{i=1}^{N_M} [\{p_{x_i}^{\,2} + p_{y_i}^{\,2} + p_{z_i}^{\,2}\}/(2m_i)] \qquad (5)$$

where k_B is Boltzmann's constant. The temperature, which behaves in an essentially identical fashion for each of the polymer ions, is subject to fairly rapid but small oscillations of 5–10 K while undergoing a slow secular decrease from its initial value of about 290 K to a final value of about 220 K. The small, rapid fluctuations are determined by

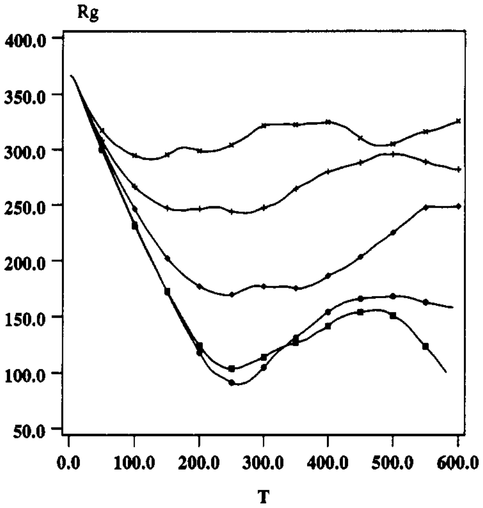

Figure 1. Radius of gyration R_g plotted versus time (ps) for each of the polymeric ions: (●) $N = 1$; (■) $N = 5$; (◆) $N = 10$; (+) $N = 15$; (×) $N = 20$.

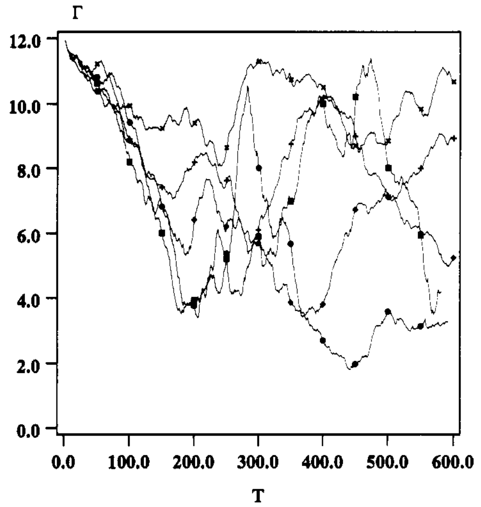

Figure 2. Ratio Γ plotted versus time (ps) for each of the polymer ions: (●) $N = 1$; (■) $N = 5$; (◆) $N = 10$; (+) $N = 15$; (×) $N = 20$.

local and transient dynamic conditions and have little influence on global properties. The secular rate of decrease of the temperature is essentially linear at about 2 K per 15 ps. The decrease in the temperature corresponds directly to a decrease in the kinetic energy of the entire polymer and therefore must represent an energy transfer to the potential energy of the polymer. As the rate of temperature change does not seem to correlate with the conformation of the polymer, the energy transfer does not appear to be closely coupled to the changing number of van der Waals nonbonded interactions. The consistency of the rate of decrease regardless of the number of charges indicates that the number and strength of the Coulombic interactions do not dominate the effect, either. We ascribe this slow temperature decrease to certain technical aspects of the simulation, as discussed in the appendix. The conclusion of that interpretation is that the secular change in the temperature during the simulation does not play a significant role in the dynamic conformation of the polymers and that the temperature may then be regarded as effectively constant.

We note that there is a minor increase in the temperature range with the number of charges introduced in the polymer. This would imply that there is a small amount of kinetic energy transfer mediated by the Coulombic potential terms, when these terms begin to play a significant role.

The radius of gyration of the polymer, R_g, provides one measure of the conformation of the polymer. The radius of gyration is defined by

$$R_g = [\sum_{i=1}^{N}(r_i - r_{CM})^2]^{1/2} \tag{6}$$

where r_i is the distance to the ith unit of the chain, and r_{CM} is the distance to the center of mass of the polymer, as measured from an arbitrary origin. For convenience, we simultaneously consider the quantity Γ, defined as the ratio of the square of the end-to-end distance to the radius of gyration.

$$\Gamma = R_e^{\,2}/R_g^{\,2} \tag{7}$$

In this equation the end-to-end distance is defined as the separation of the first member of the chain from the last. The data obtained for these properties are shown in Figures 1 and 2.

The selection of the extended chain as the initial condition leads to an initial value of R_g which is quite large, and consequently it undergoes a rapid decrease with time. This rapid relaxation toward a more coiled conformation duplicates the behavior found previously for uncharged polymers.[13] Eventually, the coiling must encounter a limit. Here this occurs when R_g reaches a minimum at about $t = 250$ ps for each of the ionic species, although the time required to reach the minimum decreases slightly for the more highly charged ions. The polymer subsequently rebounds from that tightly coiled structure. The momentum which the polymer acquires during the relaxation cannot be dissipated instantaneously, so the polymer does not simply relax directly to the final conformation and one or more oscillations occur, as measured by the radius of gyration.

In Figure 2, the ratio Γ is shown as a function of time. As can be seen, Γ has achieved a value of slightly under 5 at the conformation discussed above.

Following the minimum, all the polymers undergo a qualitatively similar behavior, rebounding from the relaxation minimum encountered dynamically and then undergoing at least one oscillation in the value of the radius of gyration. However, a comparison of the ionic polymers show quantitative differences in behavior. The $N = 1$ and $N = 5$ cases are virtually identical, indicating that for $N = 5$ the density of the charges along the chain is not sufficiently high to affect the dynamical behavior in any significant way. The forces introduced by the charges of course decrease with the square of the separation distances, and apparently for the $N = 5$ case the charges remain sufficiently well separated that the Coulombic forces are negligible. The restrictions of the relative locations of the charges are few, and any two charges on the chain could undergo a close encounter due to a folding of the polymer; however, this apparently occurs infrequently at low charge densities, and to little observable effect.

As the charge density increases, the radius of gyration is influenced more strongly by the ions. For $N = 10$ the radius of gyration does not fall to quite such a small value as at the lower charge densities, the minimum being approximately twice the value of the minimum in the $N = 1$ case. For higher charge densities the effect is even stronger, with the value of the minimum steadily increasing with charge density. At the higher charge densities, the value of the radius of gyration remains large thoughout the entire dynamical simulation. The ratio Γ displays

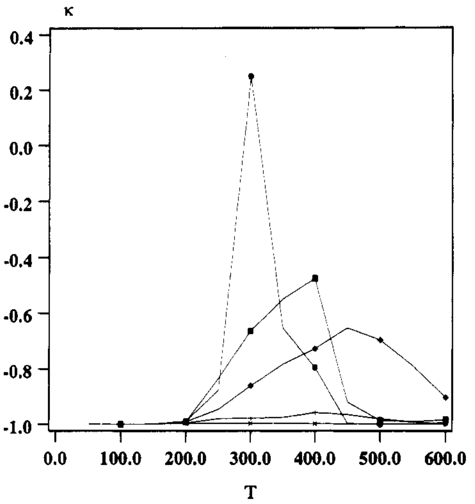

Figure 3. Asymmetry parameter κ plotted versus time for each of the polymeric ions. Here, the time scale is coarse grained, and each point is separated by 50 ps: (●) $N = 1$; (■) $N = 5$; (◆) $N = 10$; (+) $N = 15$; (×) $N = 20$.

more complex behavior, reflecting the fact that it is a ratio of two quantities; the significant point in Figure 2 is that for the high charge densities the value of Γ again becomes large at long times.

This result, and the results discussed below, indicates that the dynamics supports an important low-frequency component. In terms of a vibrational language, this would be related to the lowest frequency acoustic modes of the polymer chain. This mode is driven primarily by the initial conditions chosen for the systems; the results show that coupling to the modes is low enough that the energy in these modes is not rapidly equilibrated to the other modes, in the vacuum environment assumed. A number of the effects discussed about the behavior of R_g are attributable to this motion, and the Coulombic forces strongly influence its behavior at high charge density.

Another classic measure of molecular shape is provided by the moments of inertia. The inertia tensor and the principal moments of inertia for the polymers are determined at 50-ps intervals during the simulation, providing coarse-grained information. The inertia tensor[14] $\mathbf{I}_{xyz}$ is the symmetric matrix with elements

$$I_{qq} = \sum m_i[(q_i')^2 + (q_i'')^2]; \quad \mathbf{I}_{qq'} = -\sum m_i q_i q_i' \qquad (8)$$

The principal moments of inertia, the eigenvalues of this matrix, specify the overall shape of the molecule. Since all the monomers have the same mass, the inverse square roots of the principal moments of inertia are proportional to the lengths of the corresponding principal axes of the polymer. However, the essential information for present purposes can be obtained from a single parameter, the asymmetry parameter κ

$$\kappa = [2B - (A + C)]/[A - C] \qquad (9)$$

where A, B, and C are inversely proportional to the corresponding moments of inertia. κ ranges from −1, for a prolate symmetric top, to +1, for an oblate symmetric top. The coarse-grained time plot of this parameter is given as Figure 3. All the ions start as highly prolate (nearly) symmetric tops and become less highly prolate during the simulation. For the reference case the value of the maximum actually exceeds 0, shifting over to the oblate side. The maximum value of κ decreases steadily with increasing charge density. This behavior shows that as the charge density increases the breathing of the ion toward a more oblate shape is greatly inhibited. At the highest charge density considered, the multiply charged ion is unable to change its conformation significantly from the highly prolate initial conformation at any time during the simulation.

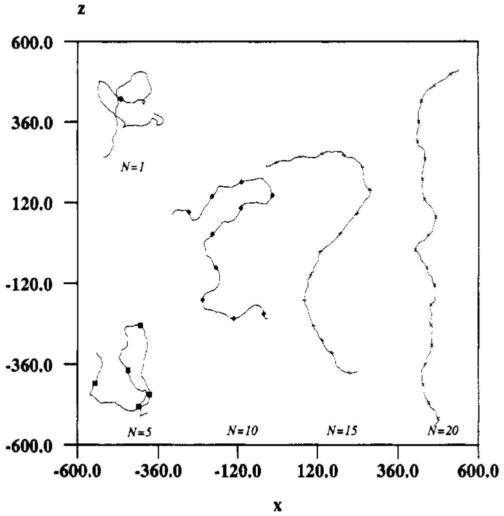

Figure 4. Two-dimensional representation of the polymers at $t = 250$ ps in the principal axis coordinate system. Symbols indicate the position of each charge.

The singly charged ion shows a maximum in κ at around 250 ps, in agreement with the radius of gyration data; the other ions show a maximum at somewhat longer times, often corresponding to the time of the second minimum in the radius of gyration data. The conformation in each case then moves steadily back toward the highly prolate limit. This behavior appears to be correlated most directly with the low-frequency modes discussed above.

It is informative to consider plots of the conformation of the polymers at a time of 250 ps, to contrast the shapes as a function of charge density. This time selected corresponds approximately to a highly folded conformation. While this is not representative of the conformations, it does provide the extreme conformation attained by the ions. This is shown in Figure 4 after transformation of the coordinates to the principal axis representation and projection into the plane in which the polymer has the least extension (is most nearly flat). In the case of the $N = 1$ ion and to nearly the same extent the $N = 5$ ion, this is not a faithful representation, because the ion is not in fact particularly flat. However, the regular modification of the shape of the ion with the increase in the charge density is readily apparent, and the lack of a faithful representation is in fact not deleterious. The plots support the other evidence in indicating that the low charge density ions find significantly more folded conformations than those at high charge density.

Another measure of the conformation of the polymer is provided by the persistence length, defined here similarly to that[15] used in the study of random coils. Here the persistence length is defined as the average distance between monomers separated by M monomer units. For convenience, we actually employ a fractional persistence length, defined as the ratio of the persistence length to the length of the fully extended polymer of M monomer units:

$$L_M = \frac{1}{N_M - M}\sum_{i=1}^{N_M-M}[[r_{i+M} - r_i]^2]^{1/2}/[MR^\circ]$$

A persistence length of 1 means that the (average)

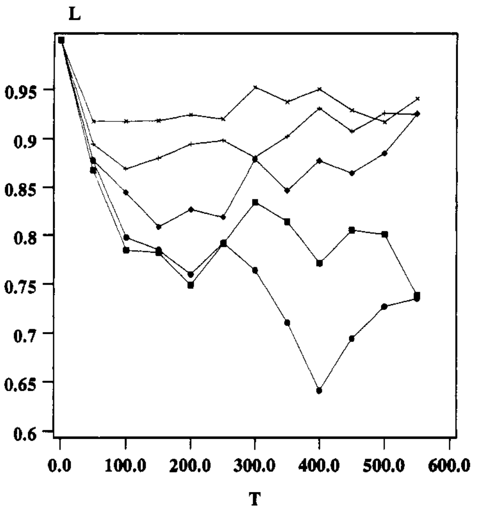

Figure 5. Plot of the fractional persistence length L_{100} for each of the polymeric ions as a function of time: (●) N = 1; (■) N = 5; (◆) N = 10; (+) N = 15; (×) N = 20.

conformation is stretched compared to the bond length; this is of course the value at the initial conformation. Smaller values of the persistence length indicate that the conformation is folded.

A coarse-grained time plot of L_M is presented in Figure 5 for M = 100, a value large enough that substantial folding could occur. The spacing interval of M is more-or-less arbitrary; similar results were obtained for a number of values with M in the range of 10–100. The plot shows that, for the two lowest charge densities, a considerable amount of folding occurs and that the degree of folding decreases as the charge density increases. At higher charge densities the fractional persistence length is notably larger and for the highest charge densities never drops below 0.85. In such cases the polymer chain is unable to display much flexibility. These plots also show the change in the conformation from the initial state and, at the lower charge densities, the low-frequency oscillations seen previously.

Each of these measures of the behavior of the polymeric ions leads to the same qualitative conclusions about the conformation.

(1) The conformations of the multiply charged polymer ions are strongly influenced by the Coulombic forces above a critical charge density; that critical charge density found here is in the vicinity of 1 ion per 100 chain units (N = 10). There is a critical charge density because the Coulombic forces, though relatively long-ranged do fall below the short-range molecular forces as the separation between adjacent charges increases. Because we have ignored polarization and dielectric effects, we cannot claim to have identified the precise value of the critical charge density; rather, these data indicate the trend which will occur in real systems.

(2) As the charge density increases above the critical value, the role of the Coulombic forces becomes increasingly dominant; at the highest charge densities considered, the ions force the molecular ion to adopt a nearly flat conformation. Again, as the number of charge–charge interactions increases, the polymer adjusts its conformation to keep the charges either (i) as far apart as possible or (ii) far enough apart to exceed the critical distance past which the Coulombic forces do not dominate the remainder of the forces.

(3) The simulation here has not proceeded for a long enough time that an "equilibrium" conformation has been *clearly* attained. The data also do not support the conclusion that 600 ps is not long enough to reach equilibrium, as the initial conditions for the simulation employed here are both highly artificial and far removed from what might be expected for normal situations. In addition, to consider equilibrium properties, one should employ multiple dynamic simulations and suitably average the results. We do not consider this to be a significant drawback to the present results, as the strength of a molecular dynamics computation is the determination of time-dependent properties, not equilibrium positions.

(4) The polymer supports an low-frequency longitudinal mode, in particular one which corresponds to the breathing mode (large-amplitude acoustic mode) shown by the R_g data. This mode does not lead to rapid energy randomization, due in part to the selection of the initial conditions. This randomness cannot occur unless the motion is chaotic, and the computations show that only a small amount of randomization has occurred.

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Appendix

In this appendix we discuss the "technical" reasons which lead us to conclude that the secular temperature change is not particularly significant with respect to overall polymer conformation. The "technical" reasons refer to details of the implementation of the coding, in particular with regard to the inclusion of the nonbonded terms. The nonbonded Lennard-Jones potential terms fall off rapidly with distance. However, as the distance increases, the number of these terms can increase very rapidly. To reduce computing time, we establish a neighbor list for each monomer on the chain; the neighbor list includes all other monomers within a certain cutoff distance R_c, taken to be 10 Å for the simulations reported here. The nonbonded interactions are considered for all monomers in the neighbor list and ignored for all not in the list. The static effect of this exclusion is minimal, because R_c is taken to be a large value, so that the interactions ignored are very small. As the simulation proceeds, the conformation changes and some interacting monomers separate past the limit and others move inside. To account for this, the neighbor list is updated every 1 ps throughout the run. However, the net effect is to introduce suddenly, at 1-ps intervals, those pairs which have moved within the cutoff radius and to remove suddenly those pairs which have moved outside the cutoff radius. This permits small incremental changes in the total energy of the system, which shows up here a slow change in the kinetic temperature.

A short trial run with a larger cutoff radius does show a reduction in the rate of change of the temperature, which supports the analysis given here.

References and Notes

(1) See the monograph: *Mass Spectrometry of Biological Materials*; McEwen, C. N., Larsen, B. S., Eds.; Marcel Dekker, Inc.: New York, 1990. See the review: Smith, R. D.; Loo, J. A.; Edmonds, C. G.; Barinaga, C. J.; Udseth, H. R. *Anal. Chem.* **1990**, *62*, 882.

(2) (a) Noid, D. W.; Pfeffer, G. A.; Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1988**, *21*, 3482. (b) Sumpter, B. G.; Noid, D. W.; Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1990**, *23*, 4671.

(3) (a) Noid, D. W.; Sumpter, B. G.; Wunderlich, B. *Macromolecules* **1990**, *23*, 664. (b) Noid, D. W.; Sumpter, B. G.; Varma-Nair, M.; Wunderlich, B. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 377. (c) Sumpter, B. G.; Noid, D. W.; Wunderlich, B. *J. Chem. Phys.* **1990**, *93*, 6875.

(4) Xenopoulos, A.; Noid, D. W.; Sumpter, B. G.; Wunderlich, B. *Makromol. Chem.* **1990**, *191*, 2261.

(5) (a) Noid, D. W.; Gray, S. K. *AIP Conf. Proc.* **1988**, *172*, 756. (b) Sumpter, B. G.; Voth, G. A.; Noid, D. W.; Wunderlich, B. *J. Chem. Phys.* **1990**, *93*, 6081.

(6) (a) Gelb, A.; Sumpter, B. G.; Noid, D. W. *J. Phys. Chem.* **1990**, *93*, 809. (b) Gelb, A.; Sumpter, B. G.; Noid, D. W. *Chem. Phys. Lett.* **1990**, *169*, 103. (c) Sumpter, B. G.; Noid, D. W.; Gelb, A.; Wunderlich, B. *Chim. Oggi*, in press.

(7) (a) Noid, D. W.; Broocks, B.; Gray, S. K.; Marple, S. L. *J. Phys. Chem.* **1988**, *92*, 3386. (b) Noid, D. W.; Pfeffer, G. A. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2321. (c) Sumpter, B. G.; Noid, D. W.; Wunderlich, B. *Polymer* **1990**, *31*, 1254. (d) Noid, D. W.; Sumpter, B. G.; Wunderlich, B. *Anal. Chim. Acta* **1990**, *235*, 143.

(8) Klein, M. L.; Lewes, L. J. *Chem. Rev.* **1990**, *90*, 459. Landman, U. *Computer Simulation Studies in Condensed Matter Physics*; Springer-Verlag: Berlin, 1988.

(9) (a) Boyd, R. H. *J. Polym. Sci.* **1986**, *24b*, 1039. (b) Boyd, R. H. *Macromolecules* **1974**, *7*, 855. (c) Brown, D.; Clarke, J. H. R. *J. Chem. Phys.* **1986**, *84*, 2858. (d) Neusy, E.; Nose, S.; Klein, M. J. *Mol. Phys.* **1984**, *52*, 269.

(10) Noid, D. W.; Sumpter, B. G.; Wunderlich, B.; Pfeffer, G. A. *J. Comput. Chem.* **1990**, *11*, 236.

(11) We used a computer code adapted from: Shampine, L. F.; Gordon, M. K. *Computer Solution of Ordinary Differential Equations: The Initial Value Problem*; Freeman: San Francisco, CA, 1975.

(12) The accuracy of the integration invariably degrades as the time period increases.

(13) Noid, D. W.; Sumpter, B. G.; Wunderlich, B. *Macromolecules* **1990**, *23*, 664.

(14) Levine, I. N. *Molecular Spectroscopy*; John Wiley and Sons: New York, 1975.

(15) Peterlin, A. In *Polymer Science and Materials*; Tobolsky, A. V., Mark, H. F., Eds.; Wiley-Interscience: New York, 1971; Chapter 3.