cation in *Polymer*.
(28) Williams, G. Private communication, 1989.
(29) Cochrane, J.; Harrison, G.; Lamb, J.; Phillips, D. W. *Polymer* 1980, *21*, 837.
(30) Allen, G.; Gee, G.; Mangaraj, D.; Sims, D.; Wilson, G. J. *Polymer* 1960, *1*, 467.

Stress-Induced Infrared Frequency Shifts in Polyethylene

G. A. Pfeffer*

Department of Chemistry, University of Nebraska at Omaha, Omaha, Nebraska 68182-0109

D. W. Noid[†]

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6182.

Received October 11, 1989

ABSTRACT: The molecular dynamics technique is used to study the spectral response of a polyethylene chain in a crystal environment under a mechanical deformation. The MUSIC method, which was previously shown to accurately compute dispersion curves from the time-dependent structure factor, is used. A complete characterization of frequency shifts is presented for various lamellar thickness, temperatures, stress (or pressure), and mass defects.

I. Introduction

The study of the mechanical deformation of highly oriented polymeric materials is motivated by the possible use of these materials in structural reinforcement or other applications requiring maximum strength and minimum weight. Previous work has ranged from measuring the stress required to tear a film or break a fiber to more sophisticated methods designed to probe the molecular details of the deformation. One example of the latter category is the stress-IR or Raman experiments carried out in the 1970s and 1980s[1-3] in which the IR (or Raman) spectrum was monitored as the material was pulled along the polymer chain orientation axis. The materials varied, but we restrict our current study to ultraoriented polyethylene (PE) films. In the case of –C–C– backbone stretches, the frequencies shifted to lower values as the stress increased. These carbon skeleton modes exhibited the largest shifts and will exclusively occupy our attention in the present work. The shifts ($\Delta\nu$, in reciprocal centimeters) could be related to the stress (σ, in gigapascal) for small stresses via

$$\Delta\nu = \alpha\sigma \qquad (1)$$

where α has units of reciprocal centimeters per gigapascal and is usually negative (indicating a shift of peaks to smaller frequencies under stress). Although some conclusions regarding the microenvironment of the stressed films were drawn indirectly from these experiments, more direct conclusions about the atomic response to the externally applied stress were drawn from theoretical investigations.[3,4] The earlier studies, using static methods[3-5] and incomplete models of the films,[3,4,6] showed that the polymer atoms had to be coupled anharmonically to induce the negative shifts observed experimentally. The magnitudes of the shifts were found to be approximately correct, and several other details concerning the relative contributions of bend and torsion to the relaxation of the induced stresses were presented.

More recently, the time-dependent theoretical technique of molecular dynamics (MD) has been used to follow the atomic motion during the stress event.[7,8] Among other results, workers noted that the frequency shift has a wavevector dependence[7] and that the nonbonded forces become more important when the polymer chain is under tension.[8] Both studies used multichain models with more than one type of interaction. Noid and Pfeffer[7] have calculated the IR spectrum of the PE (stressed and unstressed) via the extremely fast MUSIC[9] method and found $\Delta\nu$ directly; therefore, we concentrate upon their work. The present work extends the previous work by investigating the dependence of $\Delta\nu$ upon the wavevector, k, as certain model parameters are changed and for different temperatures, stresses, and chain lengths.

In section II, we discuss the theoretical methods. The results follow in section III, and a discussion of the work is given in section IV, the final section.

II. Theoretical Methods

Molecular Dynamics. Since this technique is well-known and recently reviewed,[10] only a minimum of detail is presented. Basically, one needs to solve Hamilton's equations or any other formulation of the classical equations of motion starting with some initial positions and momenta of all of the atoms in the polymer involved and propagate the solution at a series of (usually) equally spaced time steps. The solution method we used was ODE.[11] Our initial positions were those occupied by PE chains in an orthorhombic crystal structure[12] or some set of positions related to that structure. Our initial momenta were always chosen to give zero total momentum and depended upon the temperature we wished to obtain. For example, picking *all* initial momenta equal to zero gave a temperature of about 1 K or less. The temperature used here is based upon the calculated average kinetic energy through $^3/_2\,kT$. The potential energy is required in the

---

[†] Research sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

0024-9297/90/2223-2573$02.50/0

Table I
Parameters for the Potential Energy[a]

$D = 0.1324\ h$
$\alpha = 1.018\ a_0^{-1}$
$\bar{r} = 2.89\ a_0$

$\epsilon = 1.90 \times 10^{-4}\ h$
$\sigma = 7.559\ a_0$
$\gamma_\theta = 4.951 \times 10^{-2}\ h$
$\theta_0 = 113.3°$

[a] Values taken from ref 13. $1\ h = 4.36 \times 10^{-18}$ J; $1\ a_0 = 5.29 \times 10^{-11}$ m.

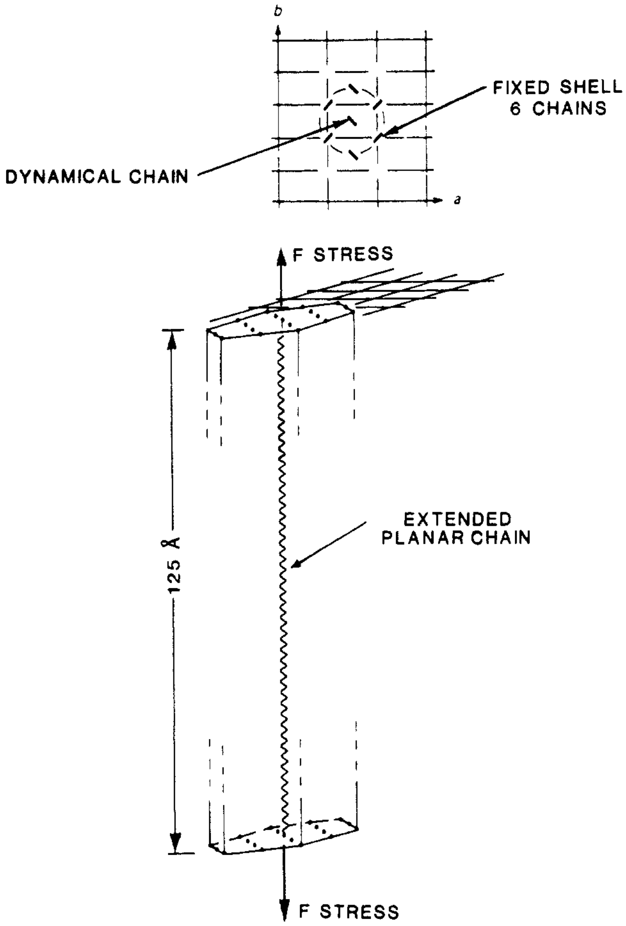

Figure 1. Model of polyethylene crystal showing the central, moving chain and the surrounding stationary chains.

classical equations, and we have used the multiterm form previously described[7,13] and briefly listed here as

$$V_{\mathrm{bonded}}(r_{ij}) = D[1 - \exp(-\alpha(r_{ij} - \bar{r}))]^2 \qquad (2)$$

for the adjacent, bonded atoms

$$V_{\mathrm{nonbonded}}(r_{ij}) = 2\epsilon[(\sigma/r_{ij})^9 - 3/2(\sigma/r_{ij})^6] \qquad (3)$$

for the interaction between any two atoms *not* directly bonded together, and

$$V_{\mathrm{bend}}(\theta_{ijk}) = {}^1/_2\gamma_\theta(\cos\theta_{ijk} - \cos\theta_0)^2 \qquad (4)$$

for the bending of a three-atom sequence. D, α, and $\bar{r}$ represent the usual Morse oscillator parameters, and ϵ and σ represent the usual Lennard-Jones parameters. γ_θ is the bending force constant and θ_0 is the equilibrium value of the angle formed by the three atoms of interest in a particular bond.[13] The values are listed in Table I. The model of PE consisted of seven chains of various numbers of atoms each. Five chains made up a unit cell in crystalline PE, while the other two chains were from the next two closest (to the central chain) unit cells as shown in Figure 1. The unit cell lengths along the a and b axes were 7.4 and 4.9 Å, respectively, and were varied somewhat, as discussed below. The central chain was the only chain allowed to move and to be stressed in this preliminary model, but nonbonded interactions between the central chain and all stationary chains were taken into account. The intrachain nonbonded interactions in the central chain were also included. Since the experimentally observed peak shifts were largest for the C–C backbone model, we considered all chains to be solely carbon "atoms" with masses of 14.5 amu (average mass of a CH_2 and CH_3 group). The external stress was applied via an extra force on the first two atoms and last two atoms of the central chain or the first and last atoms only.

Spectrum Generation. The usual method of generating a spectrum from the positions of atoms at a series of time steps is to take the fast Fourier transform (FFT) of the appropriate function of the positions.[9,14] The resolution of the FFT is $\sim 1/t_m$ where t_m is the maximum time of the MD run that generated the position/time information. Since experimental $\Delta\nu$'s were $\sim$2–10 cm^{-1}, the resolution should be at least the same and requires MD runs of several thousands of time steps, an intractably large number for these complicated systems. Fortunately, there exist other methods designed to generate the spectrum from smaller series of data; in particular, we have used the *mu*ltiple *si*gnal *c*lassification (MUSIC) method[9] or related variants, which has proven useful in many recent studies[7,15,16] by drastically reducing the number of time steps (and hence the execution time of the MD program) needed to give good spectra. In some instances, run time reductions which exceeded a factor of 1000[15,16] could be obtained with only 64 time steps, which would have given a resolution via the FFT of only 520 cm^{-1}. Details of the application of the MUSIC method to MD calculations exist in the literature[7,9,15,16] and are not presented here. It is important to note that the MUSIC method does require reasonable choices of certain parameters describing, for example, the expected number of signals in the data. Comments about these choices exist in the earlier work;[9,15] consequently, we also do not discuss these details here.

A CRAY X/MP (single processor) was used in all calculations and the program was highly vectorized.[17] Up to 400 atoms in each of seven chains were considered as well as stresses of 0.67–6.4 GPa and temperatures of <1–50 K. Due to the spectrum generation method, the MD run times were only a few tenths of a picosecond and required at most a few seconds of CRAY execution time.

III. Results

As mentioned in a previous paper,[7] the potential energy and PE model used here do not reproduce the PE spectrum exactly but do give peaks in the range 800–1200 cm^{-1} where the absorptions due to the carbon skeleton longitudinal optic mode occur in the true PE spectrum. The qualitative nature of the generated spectra is sufficient, since we are interested in differences of peak frequencies, i.e., peak shifts, as a function of stress rather than the actual peak positions. We have monitored the same peak (about 800 cm^{-1} for a wavevector of 0 a_0^{-1}) for the material that follows.

The MUSIC method required only 64 time steps ($\sim$0.004 166 ps/step) to form an acceptable spectrum; consequently, the longer time behavior of the central moving chain was not originally monitored. Subsequent checking of this longer time motion showed that the chain was collapsing when no stress was applied. A simple way to stop the collapse would be to change the strength of the nonbonded interactions, but as the nonbonded potential

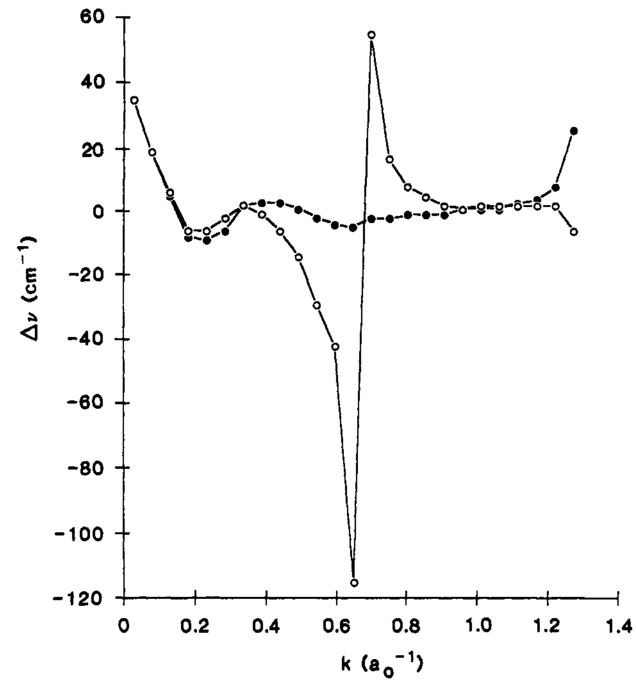

Figure 2. Frequency shift vs wavevector for a force applied to the first and last atoms (●) and the first two and last two atoms (○) of the central chain.

was specifically developed for the C–C bonds used here,[13] the function was not changed. Instead, we reduced the unit cell dimensions of our crystal to effectively increase the nonbonded interactions by moving the chains closer together. Because our PE model ignores the hydrogens, is based upon an interaction potential developed for small alkane liquids, and neglects the torsional interaction, there is an inherent error which could easily account for forces being too weak or too strong to anchor the atoms in exactly the known crystal structure. Reducing the unit cell lengths by 0.9 produced a stable system (only a 0.4% change in the end-to-end distance of the unstressed moving central chain). Incidentally, the resulting approximate distance between the central chain and the "bulk crystal" carbons of the four stationary chains in the same unit cell is about 7.6 Å, the minimum of $V_{\text{nonbonded}}$, the only relevant interaction between these moving and stationary carbons. All results reported here have a cell reduction of 0.9; earlier conclusions[7] are not affected by this change.

Previous theoretical work on the stressed IR spectrum of PE[3,7,8] applied the external force to at least two atoms on each end of the chain(s) of interest. Similar previous theoretical work on polypropylene[4] applied the external force to only the first and last atoms of the chain. Having already applied the stress on the first two atoms and last two atoms of the moving chain,[7] we applied a force upon only the first and last atoms and observed the curious behavior of $\Delta\nu$ vs k shown in Figure 2. Clearly, $\Delta\nu$ is unaffected by the pulling mechanism for small k values, which are the k values probed in the IR spectrum (k = 0); therefore, previous work is unaffected, but at intermediate k values, there is an enormous difference. Since there has been no experimental indication that such a response exists and since we have only just begun to determine how dependent this observation is upon the interaction potential used, we have based the remainder of this work upon pulling only the first and last atoms (i.e., the continuous curve). A possible explanation of this behavior is based upon concepts from nonlinear dynamics and chaotic jumps of the trajectory from one resonance region of phase space to another, but to fully develop the argument requires a separate report.

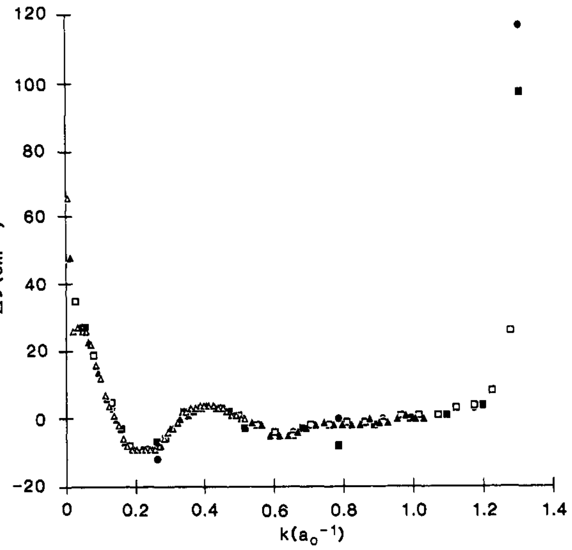

Figure 3. Dependency of the frequency shift vs wavevector behavior upon the number of atoms in a chain (all chains having the same number): 11 (●), 21 (○), 51 (■), 101 (□), 201 (▲), and 401 (△).

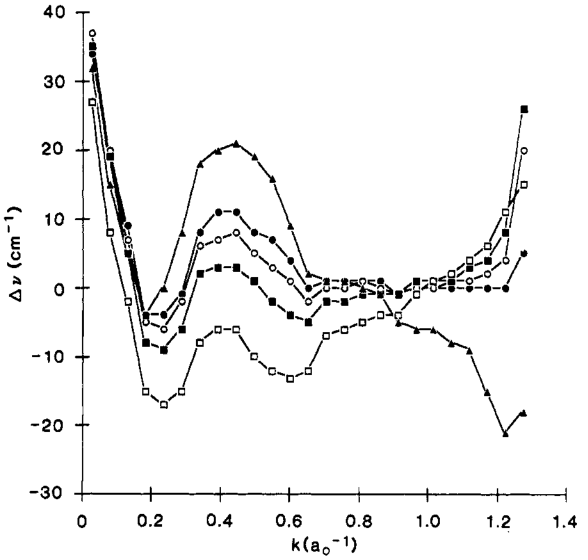

Figure 4. Frequency shift vs wavevector behavior as a function of applied stress (GPa): 0.67 (●), 1.7 (○), 3.3 (■), 6.4 (□), and −3.3 (▲), a compression rather than an elongation.

The sensitivity of our results to the length of the chains is shown in Figure 3. Two major observations are made. First, chains of 101 atoms or more give nearly identical results. Second, at high ($k \sim k_{\max}$) and low ($k \sim 0$) k values, all chain lengths studied give similar results. On the basis of these curves, a chain length of 101 atoms has been used for the rest of the work herein reported.

Figure 4 summarizes the stressed chain results for stresses in the range of 0–6.4 GPa. One negative stress (a push on the end atoms rather than a pull) is also included to see the effect of compression with our model. The consistency of the simulations is encouraging. The curves tend to have the same shape with maxima and minima at the same k, but displaced from each other by 5–10 cm^{-1} up to $k \sim 0.7$ where the oscillations in the curves dampen and the curves coalesce. At that k, the compression curve actually diverges from the stretching curves.

When the compression curve is disregarded, the values of α in eq 1 range from positive to negative. The

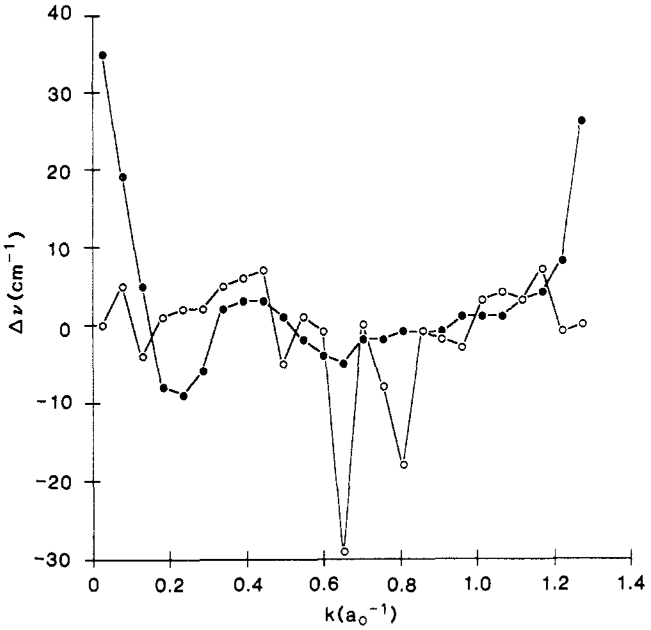

Figure 5. Temperature dependence of the frequency shift vs wavevector behavior: ~1 K (●) and ~50 K (○).

positive values, indicating shifts of the IR peaks to higher frequencies, are found at $k \lesssim 0.1\ a_0^{-1}$, $0.2\ a_0^{-1} \lesssim k \lesssim 0.6\ a_0^{-1}$, and $k \gtrsim 1.1\ a_0^{-1}$. Unfortunately, at $k \sim 0$, the calculated shifts, even with an anharmonic potential, are positive, whereas the experimental shifts are negative. Negative values are seen for the remaining k values and fall in the range of ca. $\simeq 1$ to ca. $\simeq 6$ cm^{-1}/GPa, which is in qualitative agreement with the experimental α values (though the present results are for $k \neq 0$) for the carbon backbone modes of -6 to -11 cm^{-1}/GPa. We attribute the disagreement to the crude model used in this initial study.

Finally, the dependence of the $\Delta\nu$ vs k curves upon temperature was studied and is summarized in Figure 5. The temperatures involved here are ~1 K ($p_{\mathrm{initial}} = 0$) and ~55 K ($p_{\mathrm{initial}} = 0.1$). Increasing the temperature decreases the magnitudes of $\Delta\nu$ at low and high k values but increases the magnitude of $\Delta\nu$ and the number of oscillations at intermediate k. If the larger shifts reflect larger strains/stresses, then increasing the temperature seems to have increased the strain upon medium-sized segments of the mobile chain, while decreasing the strain/stress for small-and large-sized segments. The experimental work was performed at room temperature, and one can see that $\Delta\nu$ becomes more negative for small k as the temperature increases. Our model does give a $\Delta\nu$ dependence upon temperature in agreement with experiment. Wool et al.[2] found experimentally that the frequency shifts did indeed become more negative (but these shifts started out negative) as the temperature was increased in the range 20–80 °C for polypropylene.

IV. Discussion and Conclusions

In this second part of a preliminary study of stressed PE, we have established that $\Delta\nu$ vs k is relatively independent of chain length for chains of 100–400 atoms and has predictable behavior with stress. The $\Delta\nu$ vs k curves depend upon temperature and follow experimental trends for $k \approx 0$. It is worth noting that the large number of vibrational modes involved in these polymeric systems can lead to chaotic, uninterpretable spectra as the temperature increases[15] when the usual FFT spectral generation method is used, whereas the MUSIC method generates clean spectra at all temperatures. This is to be contrasted with all previous theoretical calculations of stress-induced frequency shifts where normal-coordinate analysis would also lead to quasi-periodic behavior and no uninterpretable spectra upon increasing the temperature.

The discontinuous behavior observed when the end *two* atoms were pulled deserves further investigation, which is underway. Similar discontinuities were seen with masses other than 14.5 amu, and this behavior may be tied to chaotic dynamics and nonlinear resonances.

In future work we plan to study the spectral shifts with several dynamical chains and a more realistic potential with torsions included.

Acknowledgment. We have benefited from helpful discussions with Professors Boyd, Wool, and Wunderlich in the course of this work. G.A.P. thanks Oak Ridge Associated Universities for a Research Travel Contract which aided his collaboration.

References and Notes

(1) Prasad, K.; Grubb, D. T. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 381. Lee, Y.-L.; Bretzlaff, R. S.; Wool, R. P. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 681. Wool, R. P. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1795. Wool, R. P.; Stratton, W. O. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1575. Roylance, D. K.; DeVries, K. L. *Polym. Lett.* **1971**, *9*, 443. Zhukov, S. N.; Vettegrén, V. I.; Korsukov, V. E.; Novak, I. I. *Sov. Phys.-Solid State (Engl. Transl.)* **1969**, *11*, 233.
(2) Bretzlaff, R. S.; Wool, R. P. *Macromolecules* **1983**, *16*, 1907. Wool, R. P. *Polym. Eng. Sci.* **1980**, *20*, 805. Wool, R. P.; Statton, W. O. In *Applications of Polymer Spectroscopy*; Brame, E. G., Jr., Ed.; Academic Press: New York, 1978; Chapter 12.
(3) Wool, R. P.; Bretzlaff, R. S.; Li, B. Y.; Wang, C. H.; Boyd, R. H. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1039.
(4) Wool, R. P.; Boyd, R. H. *J. Appl. Phys.* **1980**, *51*, 5116.
(5) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574. Boyd, R. H.; Breitling, S. M.; Mansfield, M. *Am. Inst. Chem. Eng. J.* **1973**, *19*, 1016.
(6) Chang, S. J.; McNally, D.; Shary-Tehrany, F.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.
(7) Noid, D. W.; Pfeffer, G. A. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1989**, *27*, 2321.
(8) Brown, D.; Clarke, J. H. R. *J. Chem. Phys.* **1986**, *84*, 2858.
(9) Marple, S. L. *Digital Spectral Analysis with Applications*; Prentice-Hall: Englewood Cliffs, NJ, 1987; Chapter 13.
(10) Fincham, D.; Heyes, D. M. *Adv. Chem. Phys.* **1986**, *63*, 493. Hoover, W. G. *Molecular Dynamics*; Springer-Verlag: Berlin, 1986.
(11) Shampine, L. F.; Gordon, M. K. *Computer Solutions of Ordinary Differential Equations: The Initial Value Problem*; Freeman, San Francisco, CA, 1975.
(12) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973; Vol. I.
(13) Weber, T. A. *J. Chem. Phys.* **1979**, *70*, 4277; **1978**, *69*, 2347. The Morse function parameters in the present work were determined from the harmonic oscillator functions in these references.
(14) Champeney, D. C. *Fourier Transforms and Their Physical Applications*; Academic Press: London, 1973.
(15) Noid, D. W.; Broocks, B.; Gray, S. K.; Marple, S. L. *J. Phys. Chem.* **1988**, *92*, 3386.
(16) Noid, D. W.; Gray, S. K. *Chem. Phys. Lett.* **1988**, *145*, 9. Noid, D. W.; Bloor, J. E.; Koszykowski, M. L. *Chem. Phys. Lett.* **1989**, *154*, 391.
(17) Noid, D. W.; Sumpter, B. G.; Wunderlich, B.; Pfeffer, G. A. *J. Comput. Chem.* **1990**, *11*, 236.