Theoretical studies of the effects of anharmonicity on polymer dynamics: temperature dependence of heat capacity

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The molecular dynamics method is used to study the effects of anharmonicity on the dynamics of various polymer chains. The results show that there is a transition from a regime where the harmonic approximation to the molecular vibrations is adequate to a regime where the motion can no longer be accurately described with a harmonic approximation. The group vibrations which make up the optical branch of a dispersion curve become chaotic in this regime.

INTRODUCTION

Heat capacity is one of the most basic thermal characteristics of matter. The information obtained from the heat capacity is fundamental to the overall thermodynamic description of matter[1]. From heat capacity, one can derive the other thermodynamic functions such as entropy, and thus obtain information on the flexibility and conformational ordering of polymers[2]. Although there are a larger number of polymers for which some heat capacities have been measured[3-5], the measurements are usually only for limited temperature ranges.

The ability to reliably predict heat capacities plays an important role in thermal analysis[2]. A basic part of the existing methods for calculating heat capacities for solids is the harmonic oscillator. There has also been considerable recent interest in the temperature dependence of heat capacity below 1 K and its deviation for amorphous polymers from the Debye model. The heat capacity of solids should always obey the $C_V \sim T^3$ law for sufficiently low temperatures.

The heat capacity of crystalline polyethylene, as well as other crystalline polymers, can be computed from an approximate normal mode frequency distribution with excellent agreement with experiment up to the premelting transition[2]. This has been accomplished using the Tarasov model[6,7], where a three-dimensional Debye term is used for the lower frequencies and a one-dimensional term is used for the higher frequencies of the skeletal vibrations. The procedure used to obtain a two-parameter experimental fit for the Tarasov approximation is to use a normal mode, isolated chain calculation to assign the group vibrations[6,7]. From the group vibration spectrum, the contribution to the heat capacity is calculated. The group vibration contribution to the heat capacity at constant volume C_V is then subtracted from the experimental heat capacity to yield the 'experimental heat capacity of the skeletal modes' to be fitted to the Tarasov

equation. The model appears to work well for crystalline and amorphous solids from a few kelvins to the glass transition and often for crystals, even up to the melting temperature. As the temperature is increased, the contributions of the high frequency group vibrations to the heat capacity increase to become the dominant factor[6,7]. It is just in this regime of high temperature (energy) that anharmonicity should become important. Recent results in non-linear dynamics demonstrate that energetic vibrational motion is actually chaotic motion (see, for example, ref. 8).

In this paper we are interested in investigating the effect of anharmonicity on the behaviour of the molecular vibrations (skeletal and group) in polymers using molecular dynamics. The underlying dynamics will be used to obtain information on the effect of anharmonicity on the calculation of heat capacity. We have previously studied both the condis[9] and melting phase transitions[10,11], pyrolysis[12], mechanical properties of polymers[13], laser ablation[14], and also, in a preliminary study, the temperature dependence of spectra[15]. In the present paper, we consider three different polymer chains and will discuss the existence of collective modes.

Method

The molecular dynamics[16-18] method is used to simulate the motion of the atoms in a polymer chain. The application of the molecular dynamics method to polymers presents some unique difficulties. We have given a detailed account of this in a previous paper[19]. In brief, the molecular dynamics method treats atoms as classical objects. The position and momenta can be determined at any given time by evaluating Hamilton's equations of motion,

$$\frac{\partial H}{\partial p_i} = \frac{\partial q_i}{\partial t} = \dot{q}_i, \qquad -\frac{\partial H}{\partial q_i} = \frac{\partial p_i}{\partial t} = \dot{p}_i \qquad (1)$$

The propagation of the coordinates (q_i) and momenta (p_i) in time (classical trajectory) yields information which

can be used to study many important properties of polymers. In the present paper, we study the dynamics of a monatomic $(Se)_N$, diatomic $(CO)_N$, and a triatomic $(CCO)_N$ chain, where N was varied from 100–5000. Our models are restricted to be linear; that is, only bond–bond stretching is allowed at a constant angle of 180°. The Hamiltonian is

$$H = 1/2 \sum_{i=1}^{N} p_i^2/m_i + V(q-q_0) + V[L-(q_N-q_1)-q_0] \quad (2a)$$

where

$$V(q-q_0) = D_e[1-\exp\{-\alpha_e(q-q_0)\}]^2 \quad (2b)$$

or

$$V(q-q_0) = D_e\alpha_e^2(q-q_0)^2 \quad (2c)$$

The quantity L represents the fixed length of the chain, and periodic boundary conditions are used to connect the first and last atoms in the chain as given in equation (2). These constraints keep the polymer chain from breaking bonds. The parameters for the Hamiltonians are given in *Table 1*. Because we are interested in studying the effects of anharmonicity, we want to examine the behaviour at temperatures which are sufficiently high to allow large amplitude motion and chaos. Our simulations provide evidence that the molecular vibrations then occur as local type motion rather than a collective motion.

Initially, a particular temperature is generated by placing a random distribution (Monte Carlo) of kinetic energy in the chain. The system is then allowed to equilibrate this energy by running a trajectory for several picoseconds. It has been shown in a previous study that the time required to reach a statistical distribution of the energy is on a sub-picosecond time scale[12]. The average temperature is

$$Nk\langle T\rangle = \left\langle \sum_{i=1}^{N} p_i^2/2m_i \right\rangle \quad (3)$$

where N is the number of atoms in the chain and k is the Boltzmann constant. The average in equation (3) is computed from simulations of 100 ps using a step size

Table 1 Parameters for the Hamiltonian of equation (2)

$(Se)^a$	$M = 79.942$ amu
	$D = 212.26$ kJ/mol
	$\alpha = 23.9$ nm^{-1}
	$K_0 = 242\,595.43$ kJ mol nm^2
	$q_0 = 0.273$ nm
$(CO)^b$	$M_C = 12$ amu
	$M_O = 16$ amu
	$D = 288.78$ kJ/mol
	$\alpha = 17.7$ nm^{-1}
	$K_r = 181\,878.48$ kJ/mol nm^2
	$q_0 = 0.143$ nm
(CCO)	$M_C = 12$ amu
	$M_O = 16$ amu
	$D_{CC} = 334.72$ kJ/mol
	$\alpha_{CC} = 19.2$ nm^{-1}
	$K_{r_{CC}} = 257\,274 \cdot 29$ kJ/mol nm^2
	$D_{CO} = 288.78$ kJ/mol
	$\alpha_{CO} = 17.7$ nm^{-1}
	$K_{r_{CO}} = 181\,878.48$ kJ/mol nm^2
	$o_{CC} = 0.153$ nm
	$q_{0_{CO}} = 0.143$ nm

^{a} References 30 and 31
^{b} Reference 29

Table 2 Heat capacities as a function of temperature: $N = 1000$; 100 ps simulations. The units for the heat capacities are reported as per mole of chain atoms

	T (K)	(J/mol K)
$(Se)_N$	1.0	8.32
	18.5	8.32
	112	8.32
	443	8.16
	698	6.82
$(CO)_N$	9	8.28
	30	8.28
	110	8.28
	650	8.24
	1490	8.20
	2700	8.16
	4200	7.99
	6070	7.91
	8400	7.49
	10500	7.40
$(CCO)_N$	35	8.32
	288	8.32
	1037	8.28
	2046	8.28
	2926	7.61

for sampling of eight samples per vibration of the highest frequency mode. The constant volume heat capacity is determined from the change in the average temperature (equation 3) resulting from a given change in energy,

$$C_V = \frac{(E_1-E_2)}{\langle T_1\rangle - \langle T_2\rangle} \quad (4a)$$

A second method was also employed. In this method, the constant volume heat capacity is calculated from the fluctuations of the temperature about its mean[20],

$$C_V = \frac{3kN}{[1-2N/3\{(\langle T^2\rangle - \langle T\rangle^2)/\langle T\rangle^2\}]} \quad (4b)$$

Dispersion curves and time dependent frequencies of the optical and acoustical modes are calculated by frequency analysing $\rho(K, t)$, the particle density correlation function

$$\rho(K, t) = \sum_{j=1}^{N} e^{iKq_j(t)} \quad (5)$$

For a one-dimensional chain, there will be two peaks in the dispersion curve for a two-atom repeating unit $(CO)_N$, one peak for a monatomic $(Se)_N$, and three peaks for a triatomic $(CCO)_N$. The frequency analysis of $\rho(K, t)$ was accomplished using the MUSIC method[21]. We have not described this remarkable method in this paper, as we have described it in our previous studies[13,22–24] and it is also well documented in a recent book by Marple[21]. Fundamentally, this method generates very accurate frequencies from very short trajectories.

RESULTS AND DISCUSSION

The constant volume heat capacities for the linear chains $(Se)_N$, $(CO)_N$, $(CCO)_N$ are given in *Table 2*. The values in this table are for the anharmonic model (equation (2b)) and are calculated using equation (4a). The heat capacity as a function of temperature for the harmonic

model (equation (2c)) always yields a value of $C_V = R$, independent of temperature. The harmonic results are not shown in *Table 2*. We mention briefly that our simulations were able to obtain the correct limit for the heat capacity of a set of N harmonic oscillators (MR, where M is the number of dimensions of space; here, $M = 1$).

The heat capacity of the anharmonic models reveals that for low temperatures the values are the same as for the harmonic calculations C_V/R, but at higher temperatures, C_V/R begins to decrease. This deviation of the heat capacity is due to anharmonicity. The question is, why does the heat capacity change at all since we are using classical mechanics, which assumes that there are a continuum of states available at all times? The answer lies in the assumptions used in the equation for the heat capacity, equation (4a). The average energy of a molecule in a system of independent molecules is[25]

$$\bar{E} = \frac{\iint H\, e^{-\beta H}\, dP_1 \cdots dq_s}{\iint e^{-\beta H}\, dP_1 \cdots dq_s} \qquad (6)$$

Given that the Hamiltonian is a harmonic oscillator,

$$H = p^2/2m + (K/2)X^2 \qquad (7)$$

evaluation of the integrals in equation (6) gives $\bar{E} = \frac{1}{2}KT + \frac{1}{2}KT$. Each quadratic term in equation (7) contributes $\frac{1}{2}$ of the total energy, i.e., $\bar{E} = \frac{1}{2}KE + \frac{1}{2}PE$. If, however, we ask what is the distribution of an energy $\bar{E}$ between the kinetic and potential energy for an anharmonic oscillator, it is not clear that one should expect to find the same equi-partition. In fact, we find that in the simulations there is a critical value of temperature at which the equi-partition (thus, the harmonic approximation) is no longer valid. This temperature is dependent on the particular chain. For $\{CO\}_N$ the anharmonicity begins to become important at approximately 1490 K; for $\{Se\}_N$, 443 K; and for $\{CCO\}_N$, 2926 K.

In each of the polymer chains, we see a decrease in the heat capacity above this critical temperature. This indicates that the deviation from an equi-partition of energy is toward a decrease in potential energy. This can be seen by examining equation (4a). For C_V to decrease,
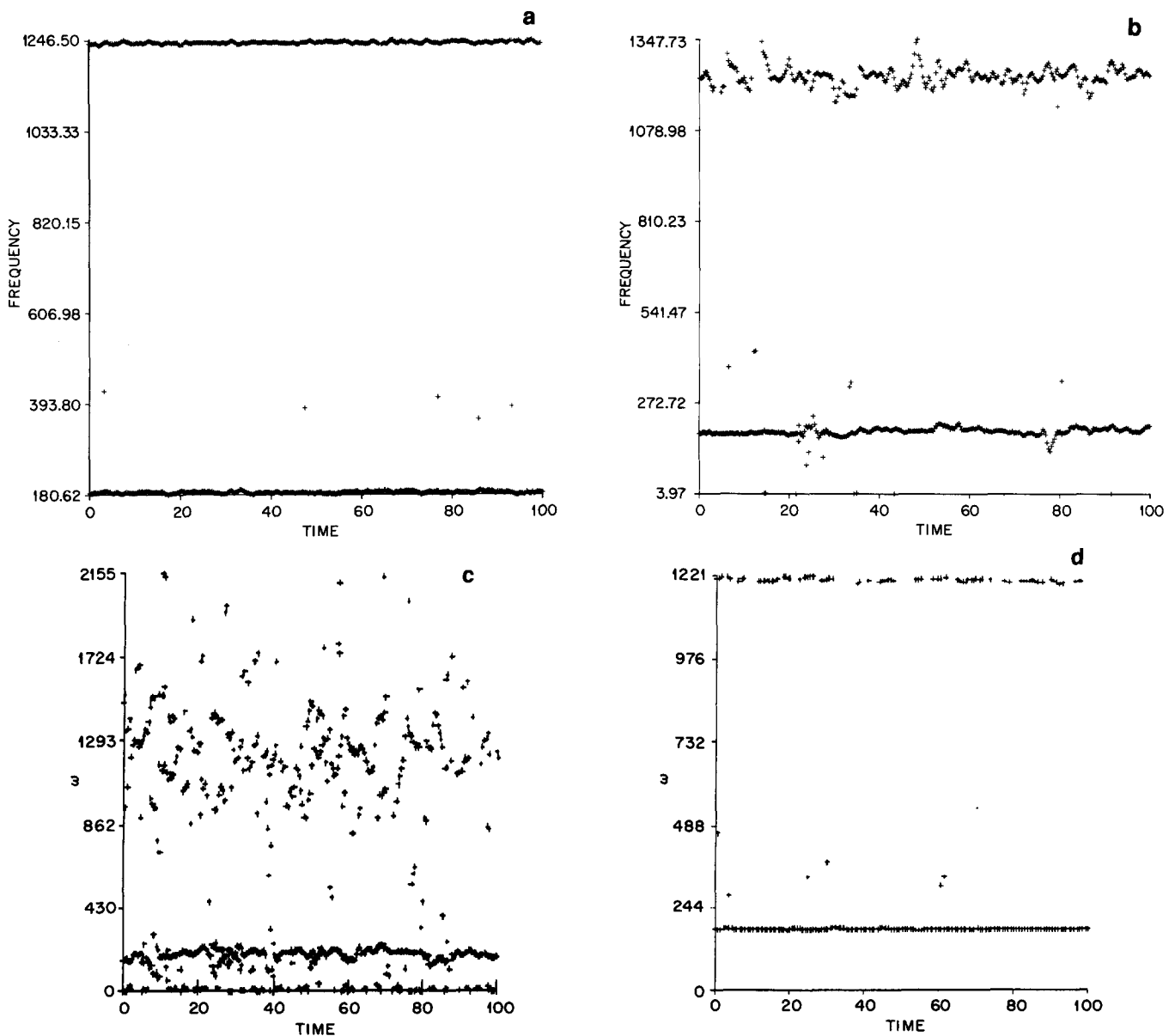

Figure 1 (a) Time dependent frequencies of $S(k, \omega)$ for $k = 2\pi n/L = 0.116756a_0^{-1}$ at 10 K for the $\{CO\}$ chain; (b) same as (a) except for 300 K; (c) same as (a) except for 4000 K; (d) same as (c) except for the harmonic model of $\{CO\}$

the change in temperature must increase. For a set of M coupled anharmonic oscillators, the energy in the system must become localized such as to cause the bond–bond displacement of one or more bonds to become large. In the limit, each of the M bonds will be broken and there will be $M + 1$ atoms with translational motion. The heat capacity C_V should thus go from R to $R/2$.

It should be pointed out that we are only treating bond–bond motion. The effect of adding bending and hindered rotations will be discussed in a future paper[15].

From *Table 2*, we have found several important features. First, the heat capacity is the same as that calculated from a harmonic model at low temperatures. Second, there is some critical temperature at which the anharmonicity begins to cause the heat capacity to decrease. Third, the decrease is due to a decrease of potential energy as compared to the equi-partition theory. In a limit of complete decomposition, one should expect that the heat capacity decreases to $\frac{1}{2}R$. This decrease is due to a change from vibrations to translations. There are no modes that are frozen out. In contrast to this observation, it has recently been suggested that for N atom chains the optical (high frequency) modes

become frozen out, and thus, besides a decrease in heat capacity, one would not observe the ultraviolet catastrophe, even from a classical viewpoint[24]. In the present case, we observe a decrease in heat capacity, but for a different reason.

Examination of the time-dependent frequencies of the optical and acoustical modes of $\{CO\}_N$ [anharmonic model] gives some interesting insight into the behaviour of the optical mode. *Figure 1* is a plot of the optical (high frequency) and acoustical (low frequency) modes as a function of time at different temperatures. Comparison of *Figures 1a, b,* and *c* shows the effect of temperature. As the temperature is increased from 10 (*Figure 1a*) to 300 (*Figure 1b*) to 4000 K (*Figure 1c*), the behaviour of the optical mode becomes increasingly chaotic. There is a broad range of frequencies shown in *Figure 1c* as compared to *Figure 1a*. It should also be pointed out that the optical frequency decreases very rapidly with temperature, while the acoustical mode is relatively stable. It is interesting to note that the temperature which causes the optical mode to behave chaotically in frequency space is the same temperature at which we observe the beginning of the decrease in heat capacity. The reason
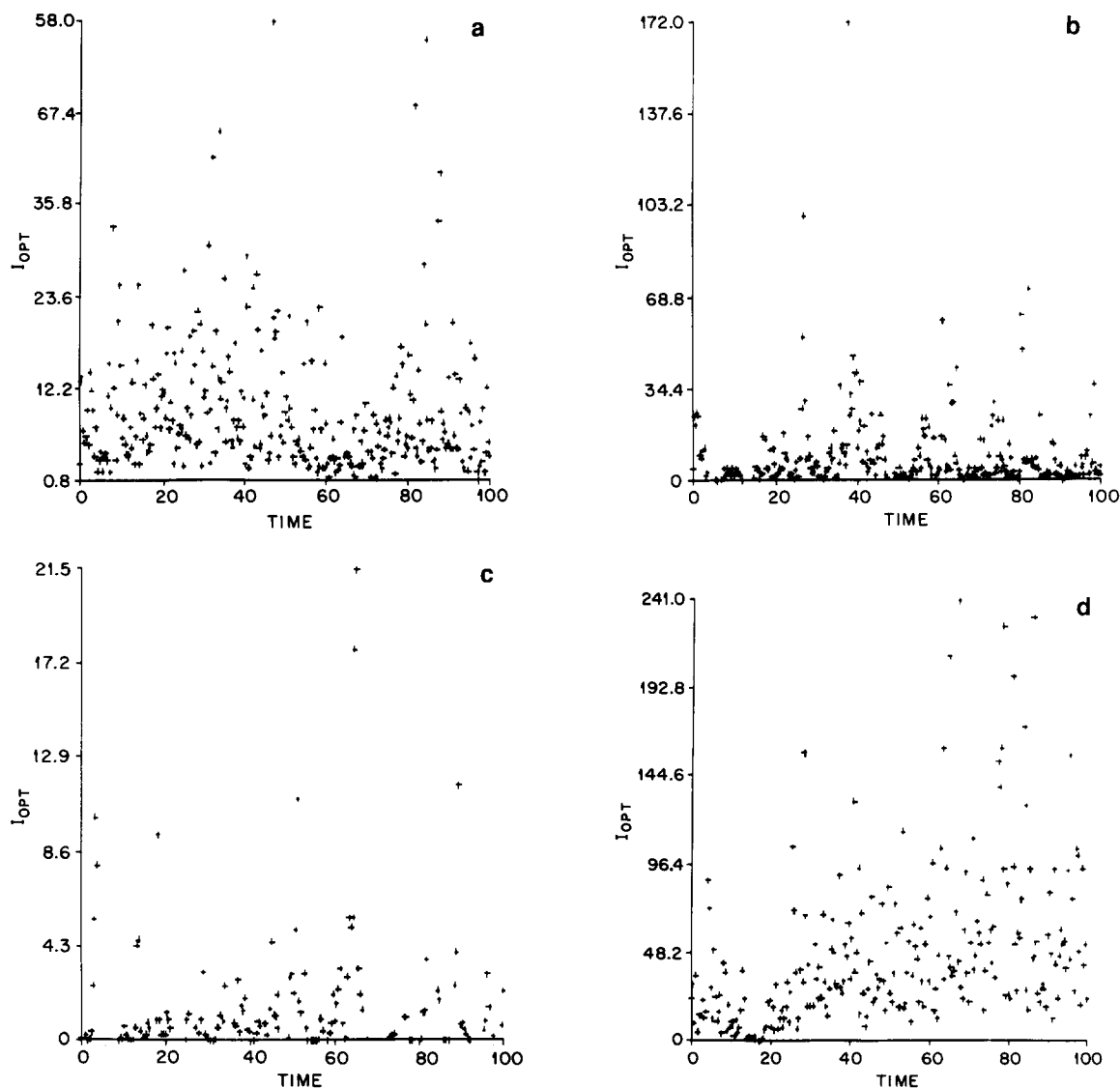
Figure 2 (a) Plot of the intensities of the optical modes for $\{CO\}$ as a function of time for the same conditions as *Figure 1a*; (b) same as (a) except for 300 K; (c) same as (a) except for 4000 K; (d) same as (c) except for the harmonic model of $\{CO\}$
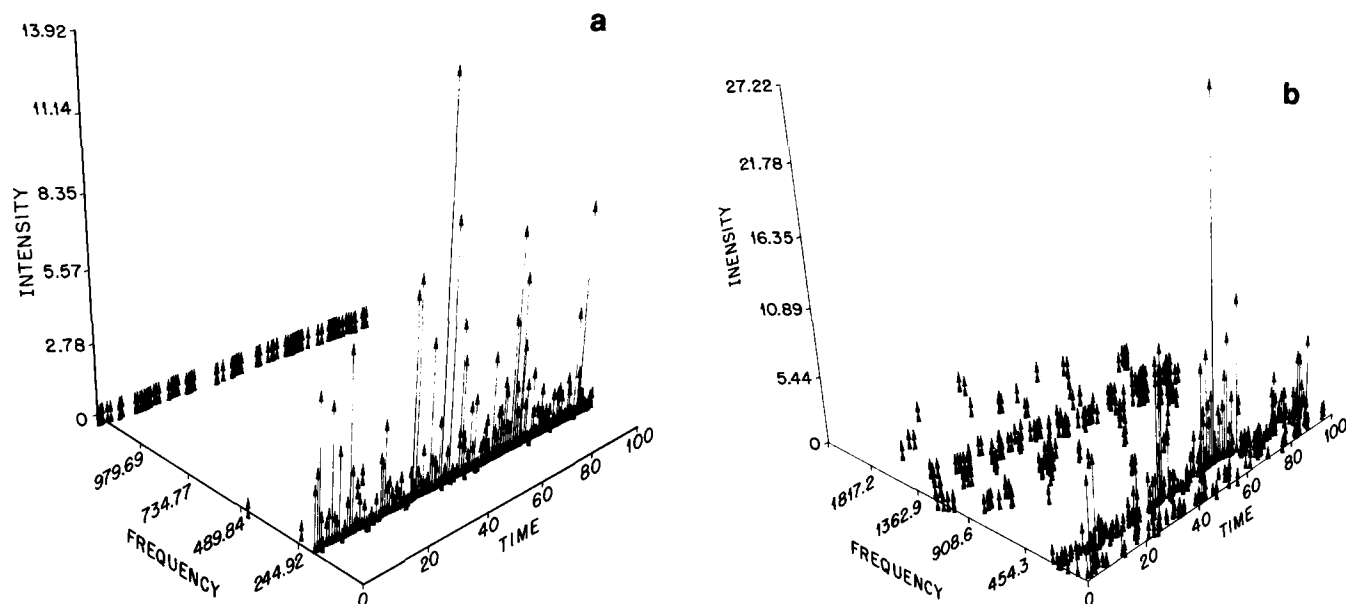
Figure 3 (a) Three dimensional plot of the time-dependent frequencies *versus* the intensities for a temperature of 5 K; (b) same as (a) except for 2617 K

for this decrease is thus that the group vibrations which make up the optical mode no longer exist. This is because the energy in the molecule is distributed such that some bonds have very large displacements (deficit of potential energy). These irregularities are of local nature, and thus any group motion consisting of a combination of these modes will become chaotic. What has happened is that the description of the motion of the atoms has changed. There are still the same number of vibrational modes, but the group vibrations which describe the optical mode at low temperature no longer exist. In the harmonic model, the group vibrations always exist and there can never be chaotic motion. For anharmonic non-separable Hamiltonians, chaotic motion destroys the coherence of the collective modes. *Figure 1d* shows the time-dependent frequencies of the optical and acoustical modes of the harmonic model for a temperature of 4000 K. This figure should be compared to *Figures 1c* and *1a*. As can be seen, there is little difference between *Figures 1a* and *1d*, but there is a large difference between *Figures 1c* and *1d*. Again, this shows that the effect of anharmonicity at large temperatures (*Figure 1c*) is significant, while there are no effects at low temperatures (*Figure 1a*).

Figure 2 shows the intensity of the optical mode as a function of time. This figure corresponds to *Figure 1*. The principle feature of *Figure 2* is that, for lower temperatures (*Figures 2a, b*) and the harmonic model (*Figure 2d*), the distribution of intensity is very broad and the values are much larger than those found for the high temperature (*Figure 2c*). The intensity of the optical mode for the low temperatures and harmonic cases is larger because there are a group of regular vibrations which are sufficiently populated, while at higher temperatures the group of vibrations are chaotic and they cannot be populated. *Figure 3* shows a comparison of the intensities of the acoustical and optical modes at a low temperature. Even for temperatures where the group vibrations are a good approximation (*Figure 3a*), the population is predominantly in the acoustical modes. If the temperature is increased in order to attempt to populate the optical modes, chaotic motion occurs,

(*Figure 3b*). This is in agreement with a previous study where FFT methods could not locate optical modes at all over a 4 ps trajectory (see *Figure 4* of ref. 22). In that study, we did not fully explain the significance of this result because the purpose of that work was to demonstrate the new capability of the MUSIC analysis for polymer dynamics.

CONCLUSIONS

We have shown that the description of the vibrations in a polymer chain using collective modes is not valid for high temperatures. The optical modes are the most sensitive to anharmonicity and thus to temperature. There is a critical temperature at which the optical vibrations begin to behave more as a set of N local modes. The acoustic modes appear to remain stable over a large range of T. It is fortunate that the temperature required to cause sufficiently large amplitude vibrations is greater than that of the melting transition. However, we expect that when the lower force-constant bending and torsional degrees of freedom are added, this critical temperature will be reduced, and as the temperature approaches the critical temperature for chaos, the accuracy of the harmonic approximation decreases. Finally, we mention that while the optical modes do tend to disappear in the sense that they become chaotic, the total number of vibrations does not change until there is a phase change. Work is in progress to study the ramification of this behaviour for other dynamical processes.

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