Thermal conductivity of a single polymer chain

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Numerical experiments have been performed with use of a fairly realistic model for polyethylene which has enabled the effects of anharmonicity, temperature, and positional disorder on the thermal conductivity to be investigated. It has been shown that the classical conductivity may be substantially increased by both increasing the strength of the anharmonic forces and by decreasing the chain temperature. Although the conductivity of individual chains is found to be high, realistic values for the conductivity of a bulk material may be understood provided that due account is taken of the polymer conformation and interchain coupling.

I. INTRODUCTION

The thermal conductivity, κ , of amorphous and partially crystalline polymers at room temperature may be considerably enhanced by drawing or stretching.^{1,2} In addition there is evidence that the conductivity is dependent on the molecular weight or chain length.^{3,4}

Measurements on highly drawn polyethylene (PE) reveal a considerable increase in κ in the draw direction. The mechanism by which this happens is not yet clear. The increase could be entirely due to the orientation and modification of the crystalline fraction within the amorphous matrix, but may also be due to the stretching and alignment of the amorphous material.^{2,5} The conductivity of amorphous rubber (parallel to the axis of orientation) shows enhancement as the rubber is stretched,⁶ so at first sight it may be considerably modified by drawing. However, this conclusion is complicated by the tendency of some rubbers to crystallize on extension.⁷

For undrawn amorphous polymers, κ is usually of the same order of magnitude as other electrically insulating amorphous materials and indeed the vibrational component of κ in amorphous metals. It does not follow, however, that the mechanisms of conduction are the same. The spectrum and nature of the vibrational states is completely different in a material with only short-range order, as opposed to a polymeric material containing many thousands of molecular units. The observation that for molten polymers, κ increases as the square root of the molecular weight M_w (in the low-molecular-weight regime and saturating for higher molecular weights) also points to a conduction mechanism which is different than that in other amorphous materials.

There have been a number of interpretations of the enhancement with drawing and the molecular-weight dependence (summarized in Refs. 1–3). In addition it has been suggested⁸ that vibrations, essentially confined to a polymer chain, can travel long distances along the chain without being attenuated. This was postulated as a mechanism for explaining the $(M_w)^{1/2}$ behavior, on the grounds that the effective mean free path would be the rms end-to-end distance of a polymer molecule. This would be

come independent of the molecular weight, if the mean free path were much less than the chain length. Similarly, extension of a polymer molecule in the direction of draw would enhance the effective mean free path for conduction in the draw direction. The fact that ordinary glassy materials have conductivities comparable with amorphous polymers was explained on the basis that only a relatively small fraction of the vibrational modes have long mean free paths.

There are two difficulties with this idea.

(a) It is well known that the mean free path resulting from anharmonic scattering in crystals at room temperature is typically ~ 100 Å. If this was the case in a polymer chain, the mean free path would be limited to much less than the chain length. This point was considered by use of an extremely simple model of the anharmonic processes in a linear chain.⁸ It was found that there was a "window" in the scattering as a function of frequency so that vibrations in the middle of the frequency range could have long mean free paths. In a real structure, however, the selection rules for scattering become very complex and it is difficult to come to a general conclusion.

(b) Polymer chains are not isolated and vibrational wave packets initiated on a particular chain will "leak" away onto other chains. In an amorphous material this will not happen in a singular and coherent way as it would in a crystal. The rate will depend in quite a complicated way on the coupling between chains and the masses of atoms coupled together.

Another interesting possible explanation for the $(M_w)^{1/2}$ dependence of the conductivity is in terms of soliton conduction. Solitons have been suggested as the origin of the enhanced conduction observed in computer experiments on disordered anharmonic lattices.^{9,10} In this work we consider the simulation of heat conduction in an isolated extended chain of PE, using molecular dynamics. We show that for classical heat conduction, anharmonicity also enhances the conductivity indicating the possibility of soliton conduction. However, at the present time it is not known how to "count" the number of solitons at high (classical) temperatures or to what extent they may be regarded as independent entities.

In the next section we describe the fairly realistic model

of PE based on the Kirkwood model¹¹ in which the hydrogen atoms in the CH_2 chemical repeat unit are treated as rigid masses attached to the carbon atoms. In Sec. III we consider the simulation of a heat-diffusion equation and we present the results for the conductivity in a variety of polymer conformations. Finally in Sec. IV we consider the nature of heat transfer between coupled chains and the effect of the polymer conformation on the conductivity.

II. A MODEL FOR POLYETHYLENE

A simplified model for PE which has been used by other authors,¹² involves ignoring the motion of the hydrogen atoms by attaching them rigidly to the carbon atoms on the backbone. The potential energy is chosen to be in the form,

$$\phi = (\gamma_r/2) [\Delta r_j(t)]^2 - (\mu_r/3) [\Delta r_j(t)]^3 + (\nu_r/4) [\Delta r_j(t)]^4 + (\gamma_{\Theta}/2) [\Delta \Theta_j(t)]^2 - (\mu_{\Theta}/3) [\Delta \Theta_j(t)]^3 + (\nu_{\Theta}/4) [\Delta \Theta_j(t)]^4,$$

$$j = 1, \dots, N \quad (1)$$

where

$$\Delta \boldsymbol{r}_{j}(t) = | \boldsymbol{r}_{j}(t) - \boldsymbol{r}_{j-1}(t) | - \boldsymbol{r}_{0}$$
⁽²⁾

and

POTENTIAL ENERGY (MODEL UNITS)

-300

-200

$$\Delta \Theta_{j}(t) = \frac{[\mathbf{r}_{j}(t) - \mathbf{r}_{j-1}(t)][\mathbf{r}_{j+1}(t) - \mathbf{r}_{j}(t)]}{|\mathbf{r}_{j}(t) - \mathbf{r}_{j-1}(t)| |\mathbf{r}_{j+1}(t) - \mathbf{r}_{j}(t)|} + \cos \Theta_{0}$$
(3)

which is a generalization of the Kirkwood model¹¹ and includes anharmonic terms up to the fourth order. A particular feature of this form is that the potential energy is not expressed as a function of displacements from equilibrium sites. In the above equation $\mathbf{r}_j(t)$ denotes the position of the *j*th chemical repeat unit at time *t*. γ_r and γ_{Θ} denote the harmonic force constants for stretching and bending the carbon-carbon bond, respectively. The potential energy as a function of angle between two adjacent

0. IC

0.08

0:04

0.03

-100

.02 .01

BOND ANGLE (deg)

FIG. 1. Rotational potential energy function. Solid line, harmonic model; dashed line, anharmonic model; and dot-dashed line, spring model.

0

300

200

100

carbon-carbon bonds is shown in Fig. 1, with and without "anharmonic" terms. Some clarification must be made of the term "anharmonic" since ϕ is still anharmonic if the force constants μ_r , v_r , μ_{Θ} , and v_{Θ} are put equal to zero. The reason for this can be seen by considering the usual "spring model" of a linear chain which has potential energy terms $[U(j) - U(j')]^2$ where U(j) denotes the displacement of atom *i* from equilibrium (also shown in Fig. 1). In this form the potential energy increases as two "atoms" pass through each other. This is unimportant for small displacements, but for this model a potential energy form is required which behaves correctly as one bond is rotated about the axis defined by an adjacent bond. The degree of anharmonicity-that is, the percentage deviation from the perfectly harmonic potential, for energy forms with and without "anharmonic" terms-is shown in Fig. 2. The form of the potential for bond stretching and the resultant anharmonicity due to the addition of "anharmonic" terms are shown in Figs. 3 and 4, respectively. The equilibrium C—C distance is denoted by r_0 and Θ_0 (which is roughly equal to the tetrahedral angle where $\cos\Theta_0 = -\frac{1}{3}$) corresponds to the "equilibrium" angle between carbon-carbon



FIG. 2. Degree of anharmonicity in the rotational potential energy. Solid line, harmonic model; dashed line, anharmonic model.



FIG. 3. Radial potential energy function. Solid line, harmonic model; dashed line, anharmonic model.

bonds in the "zigzag" configuration shown in Fig. 5. The form of the potential is such that defects can be formed in the chain by rotation of the bonds, even if the chain is set up initially in the form shown with the end repeat units fixed [i.e., the zeroth and (N + 1)st repeat units are assumed to have infinite mass]. Alternatively, the chain can be set up in a positionally disordered configuration by choosing the sign of the equilibrium angle between adjacent bonds at random. Moreover, an amorphous polymer will contain defects quenched in from the molten state and will have vibrational modes associated with them.¹³

The thermal conduction properties of the chain will



FIG. 4. Degree of anharmonicity in the radial potential energy.



FIG. 5. Planar zigzag skeleton of a polyethylene chain showing the definition of the natural displacement coordinates.

clearly depend on the configuration, but for most of the simulations the chain is taken to be initially in the zigzag form and at rest. The equations of motion take the form,

$$\frac{M d^2 \mathbf{r}_j(t)}{dt^2} = -\frac{\partial}{\partial \mathbf{r}_j} \phi, \quad j = 1, \dots, N , \qquad (4)$$

where M is the mass of the CH₂ monomer unit.

The numerical method for solving the equations of motion is as follows.

(a) The initial positions of the atoms are chosen as described above. In this configuration the potential energy of the system is taken to be zero. The chain is not constrained to the plane of the zigzag, but is allowed to move in three dimensions. Only nearest-neighbor interactions are considered.

(b) A random set of velocities (in three dimensions) is chosen to mirror those found at room (or chosen) temperature in a real polymer. This step is carried out with the aid of a random-number generator. Velocities are selected from a Boltzmann distribution characterized by a temperature T_{local} given by

$$\Gamma_{\text{local}} = M v^2 / k_B \ . \tag{5}$$

Initially, T_{local} is taken to be equal to twice the desired temperature, since at this point all of the energy in the system is kinetic.

(c) The equations of motion are used to advance the time t by an increment Δt . A fourth-order Runge-Kutta procedure was used throughout. The increment Δt is preassigned and is small compared to the minimum vibration period of the system. This step is repeated until the system reaches a steady state and the potential and kinetic energies share the total energy of the system. For a random initialization this takes ~ 10^5 steps.

The parameters and units used in the numerical experiments were chosen to be as close as possible to those found in PE. The force constants $used^{14}$ were

$$\gamma_r = 420 \text{ N m}^{-1}$$

and

$$\gamma_{\Theta} = 37 \text{ Nm}^{-1}$$
,

with the anharmonic force constants taken to be

$$\mu_r = 0.35\gamma_r, \ \mu_\Theta = 0.35\gamma_\Theta$$

and

$$v_r = 0.069 \gamma_r, v_\Theta = 0.069 \gamma_\Theta$$

which are appropriate for the noble-gas solids. The unit

Designation	<i>T</i> (K)	Dimension	Details	Diffusivity (mm²/s)
300a	300	3	Zigzag model at 300 K	~7
300h	300	3	300a with no anharmonic terms	~2
2Da	300	2	300a in two dimensions	~20
300Da	300	3	300a in a random configuration (see text)	~7
300Dh	300	3	300Da with no anharmonic	~7
3a	3	3	terms Zigzag model at 3 K	~45

TABLE I. Details of configurations used in the computer experiments.

of length was chosen to be the length of the C—C bond found in PE (1.54 Å). The unit of mass was the mass of the CH₂ repeat unit (14 a.u.). The unit of time (after Ref. 9) is the "second"= $2/\omega_m = 7.44 \times 10^{-15}$ s, or $1/\pi$ times the minimum period of harmonic oscillation on the chain. With this choice of units the force constant γ_r becomes unity. [ω_m is given by

$$\omega_m = (4\gamma_r / M)^{1/2} \tag{6}$$

which is equal to 2 for a monatomic harmonic chain of unit masses.]

The size of the time step used in the integration was reduced until the total energy of the system was conserved to better than 1% over 2×10^5 steps. The size of this step was found to be 1/4000th of a "second."

Experiments were performed using chains set up in a total of six different conformations. The parameters of temperature, anharmonicity, and positional disorder, together with the simulation designations are given in Table I.

III. THE NUMERICAL EXPERIMENTS

The pioneering work of Payton, Rich, and Visscher⁹ involved the simulation of heat conduction in lattices containing isotropic impurities. The method corresponded to setting up a temperature gradient by means of two heat reservoirs and computing the heat current. This basic method has also been used by other authors.¹⁵ An alternative procedure is to use linear-response theory and evaluate the current-current correlation function.

The method used in this work is one of direct simulation which involves raising the system of ~500 CH₂ repeat units to the required temperature and then carrying out a classical heat-diffusion experiment. This is performed by raising the temperature in one region and measuring the temperature decay with time. The change in temperature as a function of time is then compared with the solution¹⁶ of the diffusion equation, which, for a distance x from the position of the pulse is given by

$$T(x,t) = T_0 + (\Delta T/2) \left[\operatorname{erf} \left[\frac{d+x}{2\sqrt{\alpha t}} \right] + \operatorname{erf} \left[\frac{d-x}{2\sqrt{\alpha t}} \right] \right],$$
(7)

where for three dimensions in the classical limit, and for a harmonic system, the thermal diffusivity α is given by

$$\alpha \simeq \kappa/3R$$
, (8)

where R is the gas constant. All other symbols are as indicated in Fig. 6. From the above equation the values for the diffusivity and conductivity are extracted. We consider times sufficiently short such that the temperature pulse has not spread out too far so that (7), the result for an in-



FIG. 6. Temperature profile of 300-K chain immediately after the application of a 300-K pulse to repeat units 290 through 300.

finite system, is valid.

In order to smooth out any local temperature inhomogeneity, the pulse width was chosen to be ten chemical repeat units and the pulse height summed over the total number of steps of the experiment. The pulse was added in such a way that both the potential and kinetic energies were increased in the same proportion and that the total increase in energy was equal to one-half of the total energy of the system. This rather large input is necessary to distinguish the pulse from temperature fluctuations. However, this should not be a problem since κ is a slowly varying function of T.

A. Progress towards initial thermal equilibrium

The progression towards initial thermal equilibrium for the six conformations used were similar. An example is shown in Fig. 7. In all cases the kinetic and potential energies share the total energy of the system. The intrinsic fluctuations in the temperature in a model containing Nparticles is

$$\delta T \sim T / \sqrt{N} \tag{9}$$

so that for a collection of 500 particles (as in the present work) at 300 K, $\delta T \sim 14$ K. After $\sim 10^5$ time steps the oscillations fall within $3\delta T$, and the system can be said to have established equilibrium. It should be mentioned that with peak-peak fluctuations of $3\delta T$, the system will be stable to within δT for 90% of the time. The sinusoidal oscillations seen in Fig. 7 appear to be intrinsic to the system. Clearly, many modes contribute to the thermal equilibration leading to a complicated decay pattern. The observed oscillations can be understood in terms of the distribution of phases present at the start of the simulation. In the Appendix to this paper, the effect of the initial-phase distribution on the progress towards thermal equilibrium is considered using a simpler one-dimensional harmonic chain.

Although the total energy of the system is always conserved (see Fig. 7), for the three-dimensional models, the kinetic energy is always greater than the potential energy. For the two-dimensional model however, (and indeed for one-dimensional models tested), the kinetic and potential energies share the total energy almost equally.

B. Thermal diffusivity and conductivity

The result of the first 50 "seconds" of the simulations described in Sec. III A are displayed in Fig. 8. The period of 50 "seconds" is chosen since by this time the process of diffusion is well established, but the simulation is short enough to ensure that even for the fastest diffusing models, the pulse applied has not completely diffused away. Complete diffusion would be indicated by a positive change in slope so that the data points would run parallel to the zero diffusivity line. Consistent results were obtained when the position of the pulse was altered by up to 20 repeat units towards either end of the chain. The total height of the initial pulse was necessarily large due to the great variation in temperature found along the chain (a typical temperature profile is shown in Fig. 6).

It should first be noted that all of the diffusivities calculated are significantly greater than the experimental value of 0.23 mm²/s found for high-density polyethylene.⁸ This result will be discussed in Sec. IV. The diffusivity of the extended chain is found to be highly sensitive to both the temperature and the degree of anharmonicity. Note particularly that the chain linked by



FIG. 7. Progress of three-dimensional polyethylene model towards thermal equilibrium at 300 K.



FIG. 8. Integral of pulse height with respect to time. Pulse of width 10 repeat units and height $\Delta T_0 = T_0$. Numbered lines represent thermal diffusivities calculated, using the diffusion equation (in mm²/s). ∇ , 300h; \triangle , 300a; \bigcirc , 300Da; +, 300Dh; \Box , 2Da; and \diamondsuit , 3a.

bonds possessing only "harmonic" terms in the potential energy has a thermal diffusivity approximately one-third of that which has anharmonic modulating terms included. The anharmonic chain with a classical temperature of 3 K, however, has a diffusivity which is of the order of a factor 6 higher than that which has a temperature of 300 K. Both of the above results are entirely consistent with previous computer experiments.⁹

Constraining the chain to two dimensions increases the 300-K value of the diffusivity by a factor of nearly 3. This would correspond to an increase in conductivity by a factor of over 4, since the specific heat of the system will be a factor of three-halves lower. It is speculated that coupling between modes in the three-dimensional chain may lead to a thermal resistance not experienced by the two-dimensional model, and of course the two-dimensional model is not able to form defects.

Allowing the chain to become positionally disordered (i.e., the sign of the angle Θ_0 between adjacent bonds is chosen at random, allowing the chain to become coiled rather than extended-the chain in fact performs a random walk) appears to have little effect on the diffusivity of the anharmonic chain, but is found to increase the diffusivity of the "harmonic" chain to a value close to that found for the chain with anharmonic terms included in the potential energy. This result seems reasonable in view of the fact that the random nature of the chain is likely to introduce extra anharmonicity into the system. This would have the effect of increasing the thermal diffusivity as shown above. However, Payton, Rich, and Visscher found that the increase in thermal conductivity due to increasing the anharmonic strength remained constant for values of μ above 0.35, the value used in this work. This would explain why the diffusivity of the anharmonic chain remained unaltered.

It must be emphasized that the results mentioned above, as well as those of Payton, Rich, and Visscher⁹ are totally different to those expected for crystalline materials,¹⁷ for which the addition of anharmonic terms into the potential would be expected to increase instead of decrease the thermal resistivity.

IV. THE EFFECT OF THE POLYMER CONFORMATION AND THE TRANSFER OF ENERGY BETWEEN CHAINS

The diffusivities found from the numerical experiments on a single chain are considerably greater than measured values for high-density polyethylene. This is not surprising since we have considered noninteracting chains and it is clear that the chain conformation and the interactions between the chains have very important effects. Suppose we consider a solid formed from noninteracting chains performing random walks. It would seem that there is no true length-independent resistivity in this case. In Fig. 9 we show schematically a slab of material with the temperature constrained to be T_1 and T_2 on the surfaces of the slab. Some chains will start on one surface and return to the same surface. One-half of the chains will have this behavior and will not contribute to the thermal resistance.



FIG. 9. Slab of material formed from noninteracting polymer chains.

The remaining chains performing a random walk from one surface to the other will have an average length of the order of L^2/d , where L is the thickness of the slab, and d is the length of the monomer unit. The resistance of these chains in parallel will then be proportional to L^2 rather than L, so that the resistivity will be length dependent. This of course is an extreme example, and in reality the coupling between the chains will give rise to a macroscopic uniform temperature gradient across the slab. If we denote by L_s the length scale over which the temperature gradient can be regarded as uniform, we see that the computed thermal conductivities or diffusivities should be divided by a factor of (L_s/d) . Hence, for the zigzag model at 300 K corresponding to a random configuration, we require L_s/d to be ~30 to obtain the measured value of the diffusivity. Assuming that the random configuration is



FIG. 10. Model of two interacting polymer chains.

roughly an unrestricted random walk this implies that we can only treat the polymer molecules as noninteracting over a distance of approximately 900 monomer units. It would seem significant that the conductivity of molten polythylene as a function of molecular weight shows signs of saturation for about 10³ monomer units.⁸ This does not seem unreasonable, but clearly, such results will depend strongly on the cross-linking and coupling between the chains. The transfer of energy between chains will be very complex in general, but the simple model shown in Fig. 10 is quite revealing. We consider two linear chains A and B coupled together by a shear-force constant (γ_2) via an atom with mass m_2 . The masses of the two chains are denoted by m_1 and they are coupled by springs with force constant γ_1 . The motion is constrained to be in the direction of the chains. We now give expressions for the reflection coefficient of a wave traveling along chain A (R), the transmission coefficient along chain $A(T_A)$, and the transmission coefficient to chain $B(T_B)$. The transmission coefficient onto chain B is the same for waves traveling in both directions away from the coupling point so that $R + T_A + 2T_B = 1$. We find

$$R = \frac{\gamma^2 [\omega_1^2 m^2 \gamma^2 + (1 - \omega_1^2)(\gamma - 4m\omega_1^2)^2]}{[\gamma^2 + 16\omega_1^2(1 - \omega_1^2)][\gamma^2 m^2 \omega_1^2 + (1 - \omega_1^2)(2\gamma - 4m\omega_1^2)^2]},$$
(10)

$$T_{A} = \frac{(1-\omega_{1}^{2})[\gamma^{4}+4m\omega_{1}^{2}\gamma^{2}(4m\omega_{1}^{2}-2\gamma)+16\omega_{1}^{2}(1-\omega_{1}^{2})(2\gamma-4m\omega_{1}^{2})^{2}]}{[\gamma^{2}+16\omega_{1}^{2}(1-\omega_{1}^{2})][\gamma^{2}m^{2}\omega_{1}^{2}+(1-\omega_{1}^{2})(2\gamma-4m\omega_{1}^{2})^{2}]},$$
(11)

and

$$T_{B} = \frac{(1-\omega_{1}^{2})\gamma^{4}}{[\gamma^{2}+16\omega_{1}^{2}(1-\omega_{1}^{2})][\gamma^{2}m^{2}\omega_{1}^{2}+(1-\omega_{1}^{2})(2\gamma-4m\omega_{1}^{2})^{2}]},$$
(12)

where in reduced units $m = m_2/m_1$, $\gamma = \gamma_2/\gamma_1$, and $\omega_1 = \omega/\omega_{\text{max}}$ and $\omega_{\text{max}} = 2\sqrt{\gamma_1/m_1}$. In Figs. 11–13 we show some examples of the behavior of R, T_A , and T_B for various choices of m and γ . In Fig. 11 it can be seen that the transmission coefficient along chain A can be large over a range of frequencies, when the chains are cou-

pled via a light mass, and with $\gamma_1 = \gamma_2$. For a heavy mass (Fig. 12) there is a pronounced resonance structure in the reflection coefficient. The most important case is in Fig. 13 where for a light mass and weak coupling, the transmission coefficient along chain A is very close to



FIG. 11. Reflection and transmission coefficients for the case where $\gamma = 1$ and $m = \frac{1}{12}$, as a function of reduced frequency ω_1 .



FIG. 12. Reflection and transmission coefficients for the case where $\gamma = 1$ and m = 12, as a function of reduced frequency ω_1 .



FIG. 13. Reflection and transmission coefficients for the case where $\gamma = \frac{1}{10}$ and $m = \frac{1}{12}$, as a function of reduced frequency ω_1 .

unity. It is difficult to translate this simple model to realistic models of polymer interaction but the message is clear, weak coupling via a light mass such as a H atom can result in very weak interchain coupling. It would be very interesting in the future to investigate more realistic situations by computer simulations.

These remarks are necessarily qualitative, but it is clear that the notion of heat conduction along polymer chains is a viable one. Experimental work involving the systematic cross-linking of polymers in different ways may well help in verifying this physical picture. The recent paper by deGennes¹⁸ on the electrical conductivity of polymers with interchain and intrachain conductance should prove valuable in this context.

V. SUMMARY

Numerical experiments have been performed with use of a fairly realistic model for PE which have enabled the effects of anharmonicity, temperature, and disorder on the thermal conductivity of polymers to be investigated. It has been shown that the classical conductivity may be substantially increased by both increasing the strength of the anharmonic forces and by decreasing the chain temperature. It has been found that although the conductivity of individual chains may be high, realistic values of the conductivity of the bulk material may be understood, provided that due account is made of the polymer conformation and the effects of interchain coupling in establishing a macroscopically uniform temperature gradient.

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APPENDIX: PERIODIC OSCILLATIONS IN THE KINETIC ENERGY OF HARMONIC OSCILLATORS

The periodic oscillations observed in the kinetic energy in Fig. 7 when approaching thermal equilibrium, can be understood in terms of the distribution of phases, $\phi(k)$, of the phonon modes, k, present at the start of the simulation. For a one-dimensional chain consisting of N particles separated by a distance "a," the displacement of the *n*th particle $U_k(n,t)$ due to a mode k acting at time t is given by (assuming periodic boundary conditions)

$$U_k(n,t) = (1/N_k) \sin(kx_n) \sin[\omega(k)t + \phi(k)], \quad (A1)$$

where

$$\sin(kNa) = 0 \tag{A2}$$

for

$$k = n\pi/(L = Na) \tag{A3}$$

and

$$N_k^2 = \sum_{n=0}^N \sin^2(kx_n) = N/4 , \qquad (A4)$$

so that

$$U_k(n,t) = (2/\sqrt{N}) \sum_k A_k \sin[k(na)] \times \sin[\omega(k)t + \phi(k)], \quad (A5)$$



FIG. 14. Progress of uncoupled one-dimensional chain towards thermal equilibrium. Solid line, initial conditions input at step zero; dashed line, initial conditions input over first 600 time steps.

of phases.

where A_k is some amplitude. The average kinetic energy of the system is given by

$$\bar{T} = (1/2m) \sum_{k} |A_{k}|^{2} \sin^{2}[\omega(k)t + \phi(k)] .$$
 (A6)

Taking an average over all phases, $\phi(k)$, present; that is

$$(1/2\pi) \int_0^{2\pi} \sin^2(\omega t + \phi) d\phi = \frac{1}{2} .$$
 (A7)

So choosing $\phi(k)$ randomly should produce a timeindependent kinetic energy, or at least there will not be oscillations which are the same regardless of the original set

- ois 706 (1967).
 - ¹⁰M. Toda, Phys. Scr. 20, 424 (1979).

duced (dashed curve in Fig. 14).

- ¹¹J. G. Kirkwood, J. Chem. Phys. 7, 506 (1939).
- ¹²C. Schmid and K. Holzl. J. Phys. C 6, 2401 (1973).
- ¹³K. Holzl, C. Schmid, and P. C. Hagele, J. Phys. C 11, 9 (1978).

Clearly then, the procedure adopted for the simulations shown in Fig. 7 does not correspond to initializing the system with a set of random phases. To test the validity of this argument, numerical experiments were performed using a simple one-dimensional harmonic chain. It was

found that when the kinetic energy was introduced instantaneously at the start of the simulation, large oscillations were observed (solid curve in Fig. 14). However, if the ki-

netic energy was introduced progressively over a period of

some 600 time steps the oscillations were considerably re-

- ¹⁴R. Zbinden, Infrared Spectroscopy of High Polymers (Academic, New York, 1964).
- ¹⁵R. D. Mountain and R. A. MacDonald, Phys. Rev. B 28, 3022 (1983).
- ¹⁶P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 862.
- ¹⁷N. W. Aschroft and N. D. Mermin, *Solid State Physics* (Holt-Sanders, New York, 1976), p. 495 ff.
- ¹⁸P. G. deGennes, Physica 138A, 206 (1986).

- illations which are the same regardless of the original set
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- 61801. ¹C. L. Choy, Polymer 18, 984 (1977).
- ²D. Greig, in *Developments in Oriented Polymers-I*, edited by I.
- M. Ward (Applied Sciences, London, 1982).
- ³D. Hanson and C. C. Ho, J. Polym. Sci., Part A 3, 659 (1965).
- ⁴P. Lohe, Kolloid Z. **204**, 7 (1965).
- ⁵C. L. Choy, W. H. Luk, and F. C. Chen, Polymer **19**, 155 (1978).
- ⁶H. Tautz, Exp. Tech. Phys. 7, 1 (1959).
- ⁷M. Morton, in *Rubber Technology*, 2nd ed., edited by M. Morton (Van Nostrand-Reinhold, New York, 1973), p. 12.
- ⁸G. J. Morgan and P. D. Scovell, J. Polym. Sci., Polym. Lett. Ed. 15, 193 (1977).
- ⁹D. N. Payton, M. Rich, and W. M. Visscher, Phys. Rev. 160,