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Thermomechanical Behavior of Interacting Tie Molecules in Semicrystalline Polymers

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ABSTRACT: An atomistic model of two interacting tie molecules connecting a pair of parallel crystalline lamellae is studied by computer simulation. The tie molecules are found to be in tension at large interlamellar spacing, to be under compression at small spacing, and to have a zero-force intermediate equilibrium configuration. Interaction between the atoms of the two tie molecules, represented here by a Lennard-Jones potential, is found to have little effect on the force–spacing relation.

I. Introduction

An important structural feature of semicrystalline polymers is the existence of crystalline lamellae that are interconnected by a large number of long-chain molecules as shown schematically in Figure 1. It is believed that these molecules, referred to as tie molecules, along with cilia and loops, form an amorphous zone between the lamellae and, if the temperature is not too low, they are free to execute thermal motion as envisioned in the theory of rubber elasticity. Recent work[1] points to the importance of these amorphous regions and their tie molecules in the understanding of crack propagation in semicrystalline polymers.

In attempting to understand the thermomechanical behavior of these amorphous interlamellar layers, a natural question that arises is the effect of the constraints that the lamellae impose upon the motion of the atoms of the tie molecules. This problem has been treated theoretically by a number of authors.[2-8] Recently, the behavior of a model that can be interpreted as representing a single tie molecule has been studied by computer simulation using the method of Brownian dynamics.[9] In this model, two types of atomic interaction were distinguished: (i) the covalent interactions between neighboring atoms along the tie molecule and (ii) the noncovalent interactions between nonneighboring atoms and between the tie-molecule atoms and the bounding lamellae. It was found that the covalent interactions resulted in a tensile force tending to pull the lamellae together. This is the usual entropic spring effect. On the other hand, the noncovalent interactions between the tie-molecule atoms and the bounding lamellae exerted a pressure upon them, tending to push them apart. The tensile force increases with increasing interlamellar spacing while the pressure decreases; an equilibrium spacing is found at which the two forces just balance.

The work just described[9] treated the behavior of a single tie molecule. The purpose of the present paper is to study the effect of interaction between tie molecules. The model we use is described in section II. Computer simulation results are presented in section III, and section IV contains conclusions and directions for future work.

II. Model System

The model represents two tie molecules that connect the same pair of crystalline lamellae, Figure 2. Each molecule corresponds to a freely jointed chain with N bonds. The positions of the atoms of chain 1 are denoted by $\mathbf{x}_j$, while the positions of those of chain 2 are denoted by $\mathbf{y}_j$, $j = 0, 1, ..., N$. The end atoms of each chain are fixed in the lamellae, which are parallel and at a distance r, and the fixed atoms of the chains are at a distance c from each other. That is, in terms of the coordinate system shown, the (ξ, η, ζ) coordinates of the end atoms are as follows:

$$\mathbf{x}_0\text{:}\ \ (0, 0, 0), \qquad \mathbf{y}_0\text{:}\ \ (c, 0, 0) \tag{1a}$$

$$\mathbf{x}_N\text{:}\ \ (0, r, 0), \qquad \mathbf{y}_N\text{:}\ \ (c, r, 0) \tag{1b}$$

The covalent interactions between neighboring atoms along each chain are modeled by the potentials

$$V_c(\mathbf{x}_0, ..., \mathbf{x}_N) = \frac{1}{2}\kappa_c \sum_{j=1}^{N} (|\mathbf{x}_j - \mathbf{x}_{j-1}| - a)^2 \tag{2}$$

for chain 1, and an analogous potential for chain 2, where a is the unstretched bond length and κ_c is a large spring constant that represents the covalent bonds.

In addition to these covalent interactions, noncovalent interactions between all of the noncovalently bonded atoms of the system are modeled by a Lennard-Jones potential

$$V_{\text{L-J}}(\rho) = 4\epsilon\left[\left(\frac{\sigma}{\rho}\right)^{12} - \left(\frac{\sigma}{\rho}\right)^{6}\right] \tag{3}$$

where ρ is the distance between any pair of atoms, and σ and ϵ are parameters characterizing the potential, with σ denoting the effective hard-core radius and ϵ the well depth.

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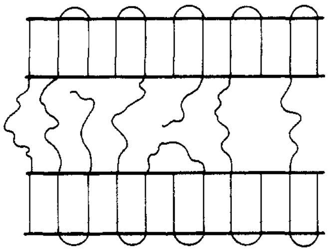

Figure 1. Schematic representation of two parallel crystalline lamellae separated by an amorphous zone. Shown in the latter are tie molecules (one end connected to each lamella), loops (both ends connected to same lamella), and cilia (one free end).

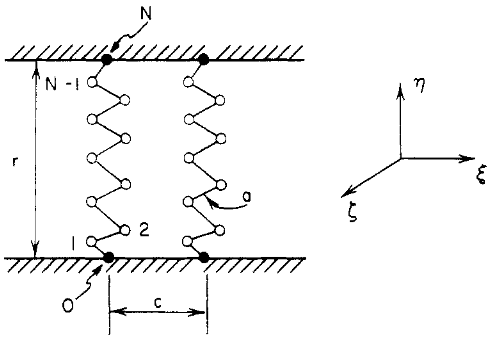

Figure 2. Model of two tie molecules connecting the same pair of parallel crystalline lamellae.

Finally, to model the interaction between the atoms of the tie molecules and the lamellae, we introduce for chain 1 the potential

$$V_L(\mathbf{x}_1, ..., \mathbf{x}_{N-1}) = \sum_{j=1}^{N-1} [g_-(\eta_j) + g_+(\eta_j)] \tag{4}$$

where η_j is the η-coordinate of $\mathbf{x}_j$ and

$$\begin{aligned} g_-(\eta_j) &= \tfrac{1}{2}\kappa_n \eta_j^2 \quad \text{for } \eta_j < 0 \\ &= 0 \quad \text{for } \eta_j > 0 \end{aligned} \tag{5a}$$

$$\begin{aligned} g_+(\eta_j) &= \tfrac{1}{2}\kappa_n (\eta_j - r)^2 \quad \text{for } \eta_j > r \\ &= 0 \quad \text{for } \eta_j < r \end{aligned} \tag{5b}$$

A similar potential applies for chain 2.

III. Computer Simulation of Model

Computation Procedure. The behavior of the model under conditions of thermal equilibrium at temperature T is simulated by the following procedure: The classical equations of motion of the model are solved numerically subject to initial atomic velocities that are chosen from a Gaussian distribution corresponding to the temperature T. Periodically, a new set of random initial velocities is chosen from the same distribution and the computation is repeated. Apart from these periodic choices of random initial velocities, no heat bath interactions are included in the numerical calculations. Time averages of relevant quantities over this periodically perturbed trajectory are then taken as representative of the phase averages of these quantities over a canonical ensemble. The accuracy of the procedure was checked by performing the computer simulation of a single chain with no constraining walls or Lennard-Jones potential and comparing the numerical results with the known analytical solution; excellent agreement was found.

Various forces are computed by this procedure. The force $\mathbf{f}_c^-$ exerted by the lower crystal on tie molecule 1 through the covalent bond between atoms $j = 0$ and $j = 1$ (Figure 2) is

$$\mathbf{f}_c^- = -\nabla_1 V_c \tag{6}$$

where ∇_1 is the gradient with respect to $\mathbf{x}_1$. The force $\mathbf{f}_L^-$ exerted by the lower crystal on tie molecule 1 through the potential V_L (eq 4 and 5) is

$$\mathbf{f}_L^- = -\sum_{j=1}^{N-1} g_-'(\eta_j) \tag{7}$$

where the prime denotes derivative. The corresponding forces exerted by the upper crystal on tie molecule 1 are

$$\mathbf{f}_c^+ = -\nabla_{N-1} V_c \tag{8a}$$

$$\mathbf{f}_L^+ = -\sum_{j=1}^{N-1} g_+'(\eta_j) \tag{8b}$$

It may be seen from the definition of V_L, eq 4 and 5, that $\mathbf{f}_L^-$ acts in the direction $+\eta$ and $\mathbf{f}_L^+$ acts in the direction $-\eta$; that is, they are compressive forces. We set

$$f_p = \tfrac{1}{2}\langle \mathbf{f}_L^+ - \mathbf{f}_L^- \rangle \cdot \mathbf{e}_\eta \tag{9}$$

where the angular brackets denote a long-time average and $\mathbf{e}_\eta$ is a unit vector in the η-coordinate direction. It is seen that $f_p \leq 0$ and $-f_p$ is the magnitude of the pressure force exerted by the atoms of tie molecule 1 on the bounding lamellae.

The instantaneous values of $\mathbf{f}_c^+$ and $\mathbf{f}_c^-$ do not, in general, act in the η-direction. However, this will be the case for their long-time averages, and we write

$$f_c = \tfrac{1}{2}\langle \mathbf{f}_c^+ - \mathbf{f}_c^- \rangle \cdot \mathbf{e}_\eta \tag{10}$$

It will be seen that, in general, $f_c \geq 0$ and f_c is the tensile force exerted by the lamellae on tie molecule 1.

Analogous force definitions apply to tie molecule 2 and henceforth we use the notation f_p and f_c to denote the average of the values computed for both tie molecules. Finally, we set

$$f = f_p + f_c \tag{11}$$

f is therefore half of the resultant time-averaged force, acting in the η-coordinate direction, which is exerted by the upper crystal on the two tie molecules (or the negative of that force exerted by the lower crystal). A positive value of f corresponds to the tie molecules in tension while a negative value of f indicates they are in compression.

As a measure of the degree of interaction between the atoms of the two tie molecules through the Lennard-Jones potential of eq 3, a time-averaged effective force of interaction F was computed, where

$$F = \left\langle \left[\frac{1}{N-1} \sum_{j=1}^{N-1} f_j^2 \right]^{1/2} \right\rangle \tag{12}$$

where f_j^2 is the square of the magnitude of the Lennard-Jones force exerted by the moving atoms of tie molecule 2 on the jth atom of tie molecule 1.

Model Parameters. The model parameters were taken to be representative of a carbon backbone chain. The value of κ_c was chosen so that $\omega_0 = (\kappa_c/m)^{1/2} = 1.3 \times 10^{14}$ s^{-1}. Previous test calculations showed that the results were insensitive to the ratio κ_c/κ_n, as long as κ_c and κ_n were of the same order of magnitude, and the calculations reported used $\kappa_n = \kappa_c$. The temperature $T = 300$ K and $N = 10$. The effective hard-core radius σ of the Lennard-Jones potential, eq 3, was taken as $\sigma/a = 0.5$ and the well depth $\epsilon/kT = 2.47 \times 10^{-5}$ for $T = 300$ K. The small value of the latter ratio indicates that only the repulsive portion of the potential is significant in the present simulations. The time

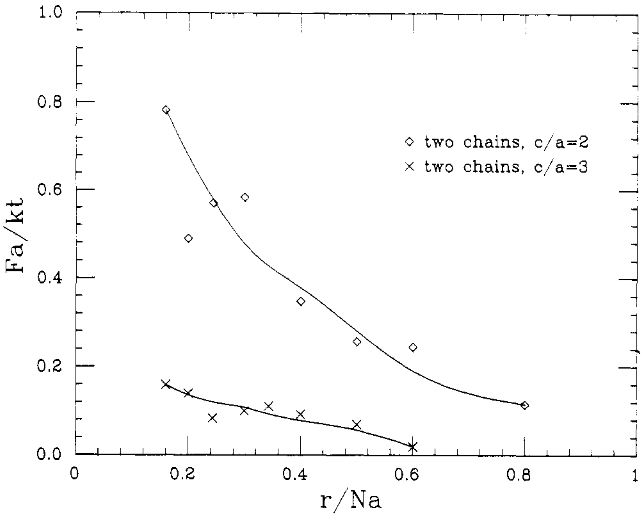

Figure 3. Force F, eq 12, which measures the degree of interaction between two tie molecules, and its dependence on their separation c and extension r. Curves here, and in analogous figures, are drawn by computer smoothing routine.

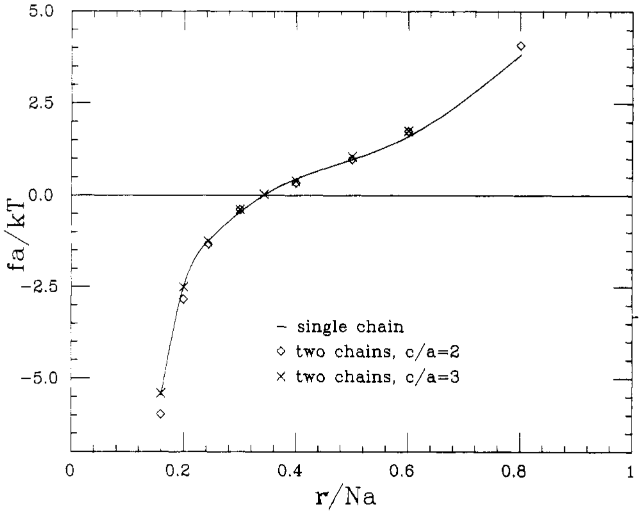

Figure 4. Net force f, eq 11, acting on each tie molecule and its dependence on interlamellar distance r. Positive f denotes tension, and negative f denotes compression.

step $\Delta t = 3 \times 10^{-16}$ s was used in the numerical integration.

Numerical Results. We begin by considering the degree of interaction between the two tie molecules as measured by F, eq 12. Results are shown in Figure 3 for various values of r, the interlamellar spacing, and c, the interchain spacing. As expected, F decreases with the increase of either of these parameters.

The substantial interaction between chains evidenced in Figure 3 has surprisingly little effect on the relation between the resultant force f exerted by the crystals on the tie molecules, eq 11, and the interlamellar spacing r. This is shown in Figure 4, which shows the force f per tie molecule for the case of a single molecule and for a pair of interacting molecules at spacings $c/a = 2$ and 3. Note that F, the measure of the force due to chain interaction shown in Figure 3, is of comparable magnitude to the per-chain force f shown in Figure 4.

Another method[10-13] of representing the confining effect of adjacent tie molecules on the motion of a given tie molecule is to enclose the latter in a square tube with side c with the axis of the tube in the η-direction. Computations were performed for this configuration, with the tube wall interaction modeled in the same way as that of the crystal lamellae (see eq 4 and 5). The results are shown in Figure 5; as for the case of chain–chain interaction, it is again seen that the presence of the confining tube has

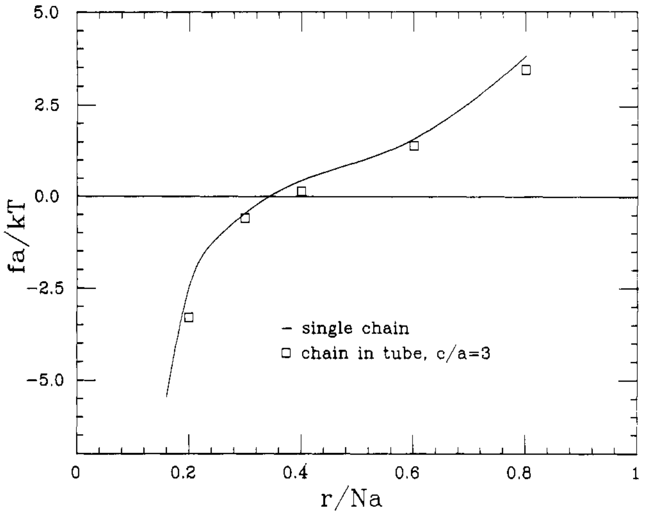

Figure 5. Net force f acting on single, unconfined, tie molecule and on the same molecule when confined in a square tube.

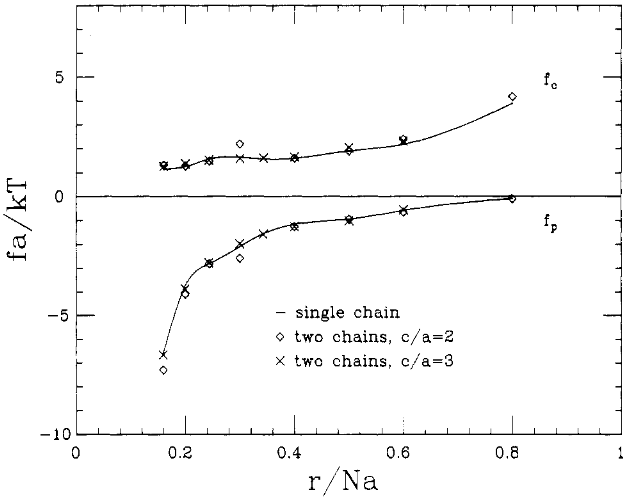

Figure 6. Components of net force f acting on a tie molecule: f_c is exerted through covalent bonds to lamellae, and f_p is pressure force exerted by lamellae on atoms of the tie molecule. Forces shown are per tie molecule for a single isolated chain and for two interacting chains.

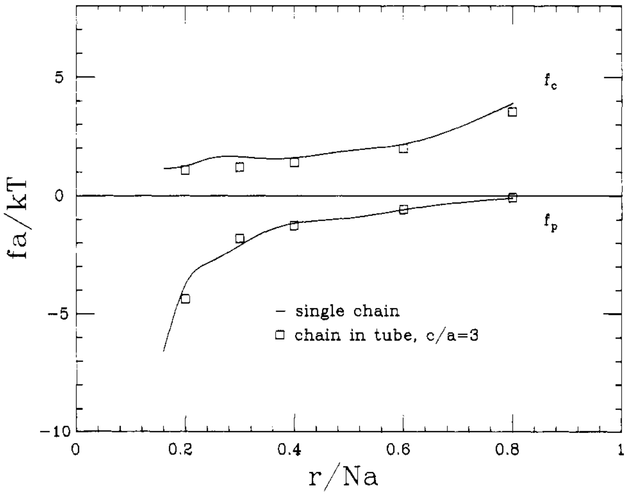

Figure 7. Same as Figure 6, but comparing an isolated chain and a chain confined to a square tube.

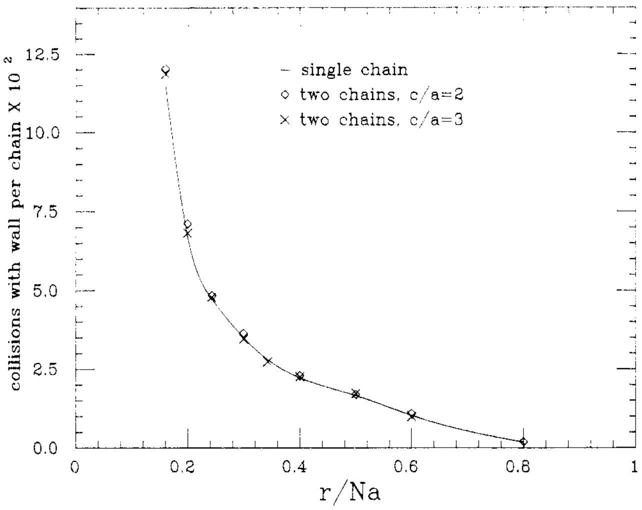

Figure 8. Total number of collisions in time period of calculation per tie molecule of the tie molecule atoms with the bounding lamellae. With model parameters representative of a carbon backbone chain, the total period of calculation corresponds to 150 ps.

little effect on the f–r relation.

The insensitivity of the f–r relation to the interaction between tie molecules extends to other aspects of the process. This is seen in Figure 6, which shows the components f_p and f_c, whose sum is f, eq 11, in Figure 7, which shows the same quantities for a single chain in a tube, and in Figure 8, which shows the number of collisions per tie molecule of the tie molecule atoms with the bounding lamellae. Note that the number of collisions decreases with increasing extension because of the constraints imposed by the covalent bonds.

IV. Conclusions

The computer simulation results presented here demonstrate, for the cases treated, that the interaction between a pair of tie molecules has little effect on the force–length relation as found for a single tie molecule. A similar result is found when chain–chain interaction is modeled by enclosing a single tie molecule in a tube which restricts the lateral motions of its atoms.[14]

It is difficult, of course, to generalize with assurance from the results of a limited number of computer simulations. Nevertheless, it appears plausible to conjecture that similar behavior will be found for larger numbers of interacting molecules and for similar types of models. In particular, we expect that the observed features of tensile forces at large separation and compressive forces at small separation with a zero-force intermediate equilibrium configuration[15] will apply as well for further generalizations of models of the amorphous layer.

Numerous questions remain for further study. Among these are the effect of chain length, the behavior of cilia and loops, and the effects of entanglements among tie molecules. We hope to return to these in future work.

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Temperature-Dependent Studies of the Elastic Constants of Oriented Semicrystalline Polypropylene Films

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ABSTRACT: Longitudinal and transverse hypersonic velocities are determined by Brillouin scattering for isotactic polypropylene films (PP) as a function of stretch ratio at various temperatures ranging from 150 to 330 K. Particular emphasis is placed upon the analysis of the elastic constants C_{33}, C_{11}, C_{13}, and C_{44} for the stretched and unstretched films. The study shows that the effect of temperature is most pronounced on C_{33}. Comparison of the Brillouin scattering data with the ultrasonic results shows significant disagreement between the two methods. Theoretical calculations using the reorientation model show good agreement with the Brillouin data. The Voigt affine deformation model of Ward gives a result slightly lower than the Brillouin values for both C_{11} and C_{33}.

Introduction

The study of orientation on polymers by Brillouin scattering leads to information about how the propagation of sound occurs in deformed polymeric solids. For example, it has been shown that when semicrystalline polymers are uniaxially stretched or extruded, the sound velocity propagating along the stretch direction is significantly increased. This anisotropy has been revealed by the in-

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