

A Polymer Crystal-Transition Theory

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Macromolecules undergo a variety of physicochemical changes of state in both solution and the solid state. A considerable amount of effort has gone into the theoretical description of monomacromolecular transitions, e.g., dilute-solution changes of state. The linear macromolecule has been considered equivalent to a one-dimensional crystal.

In turn, a one-dimensional, two-state Ising model¹ has been used to describe transitions in the crystal. B. H. Zimm² and S. Lifson³ have laid much of the groundwork for deriving equations based upon the Ising model which are applicable to isolated macromolecules. Transitions within this framework are cooperative processes. That is, a very small change in an external variable such as temperature, pressure, or solvent composition can lead to a large change in the physicochemical state of the macromolecule. Applequist⁴ has given an excellent description of cooperative macromolecular processes, while Poland and Scheraga⁵ have collected many of the important papers, both theoretical and experimental, dealing with macromolecular transitions.

Relatively little theoretical work has been done to treat macromolecular transitions in the solid state. Yenni and McCullough have modeled the orthorhombic-to-monoclinic phase transition of polyethylene using molecular energy calculations.⁶ Statistical-mechanical treatments of the glass transition,⁷⁻⁹ i.e., the onset of liquid-like rubbery state, have been reported for amorphous polymers. Some computer-based simulation studies of chain-molecular assemblies¹⁰ have also been performed, but these almost complete the catalog of serious solid-state theoretical efforts.

Crystalline polymers exhibit both crystal-crystal and crystal-melt transitions. For example, polytetrafluoroethylene undergoes, upon heating, two crystalline rearrangements before melting,¹¹ and hence three transitions are observed. The crystal-melt transition for highly crystalline and structurally simple polymers, like highly linear polyethylene, appears to be a true first-order phase transition.

The purpose of this Account is to report some progress we have made in developing an equilibrium formalism to describe crystal-melt polymer transitions. More recently we have begun to study crystal-crystal transitions in polymeric materials and report some preliminary findings. We have focused upon developing a theory which has the capacity to yield first-order phase transitions.

The philosophy adopted is a generalization of the ideas of mean-field theory and involves the replacement

of the complicated and unknown interaction between neighboring chains by an averaged interaction dependent only on the properties of a single chain. The free energy, expressed as a function of some average property of a chain, is then minimized to yield a first-order phase transition in a natural way. The theory as presented contains no adjustable parameters.

Model and Formalism

Basic Theory. The model¹² we chose to represent a crystal composed of linear macromolecules is shown in a schematic two-dimensional representation in Figure 1. The chains are assumed to be infinite in length. For the moment let us concentrate on the Hamiltonian for the "soft" variables of the crystal, by which we mean those variables such as torsional rotations about single bonds that are capable of large excursions from their equilibrium values. The Hamiltonian is taken to be the sum of the kinetic energy of translation, τ , of the individual monomeric units and the potential energy of interaction, V . The potential energy V can be divided into an intramolecular component, V_1 , dependent only upon the torsional angles θ of rotation about the backbone of the monomers and an intermolecular component, V_2 , which depends upon the translational coordinates of the monomer units as well as the angles θ . The intrachain energy per monomer unit can be expressed as

$$V_1 = \int \int U(\theta, \theta') n(\theta, \theta') d\theta d\theta' \quad (1)$$

where $U(\theta, \theta')$ is the intrachain potential energy of nearest-neighbor pairs of torsional angles. The quantity $n(\theta, \theta') d\theta d\theta'$ is the fraction of the total number of consecutive segments of the chain in which a torsional angle lying between θ and $\theta + d\theta$ is immediately preceded by one lying between θ' and $\theta' + d\theta'$, as shown in Figure 2A. We also define the angular density

$$n(\theta) = \int n(\theta, \theta') d\theta' \quad (2)$$

and note that

$$\int n(\theta) d\theta = 1 \quad (3)$$

- (1) E. Ising, *Z. Phys.*, **31**, 253 (1925).
- (2) B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, **31**, 526 (1959).
- (3) S. Lifson and A. Roig, *J. Chem. Phys.*, **34**, 1963 (1961).
- (4) J. Applequist in "Conformation of Biopolymers", Vol. 1, G. N. Ramachandran, Ed., Academic Press, New York, 1967, p. 403.
- (5) See D. Poland and H. A. Scheraga, "Theory of Helix-Coil Transitions in Biopolymers", Academic Press, New York, 1970.
- (6) T. Yenni and R. L. McCullough, *J. Polym. Sci., Phys. Ed.*, **11**, 1385 (1973).
- (7) J. H. Biggs, *J. Chem. Phys.*, **25**, 185 (1956).
- (8) J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
- (9) E. A. DiMarzio and J. H. Gibbs: (a) *J. Chem. Phys.*, **28**, 807 (1958); (b) *J. Polym. Sci.*, **40**, 121 (1959).
- (10) J. G. Curro, *J. Chem. Phys.*: (a) **61**, 1203 (1974); (b) **64**, 2496 (1976).
- (11) C. A. Sperati and H. W. Starkweather, *Fortschr. Hochpolym. Forsch.*, **2**, S465 (1961).
- (12) F. P. Boyle, P. L. Taylor, and A. J. Hopfinger, *J. Chem. Phys.*, **67**, 353 (1977).

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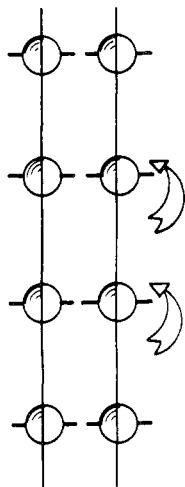


Figure 1. A two-dimensional representation of adjacent polymer chains. The spheres represent monomer units and the lines connecting spheres correspond to the covalent bonds between monomers in the same chain. Reprinted with permission from ref 12. Copyright 1977, American Institute of Physics.

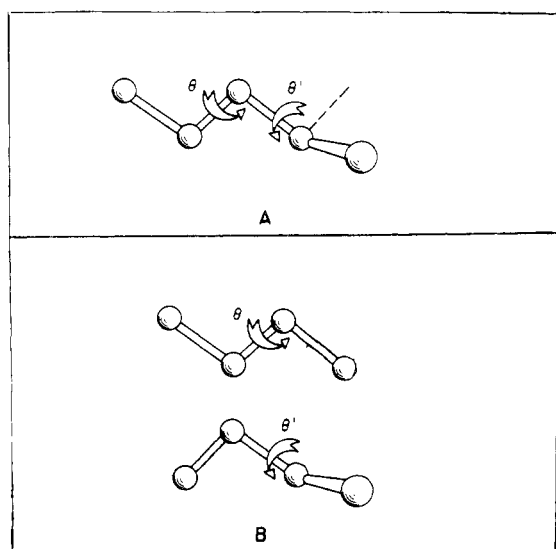


Figure 2. (A) Pentameric segment of a polymer chain used to calculate the intrachain potential $V(\theta, \theta')$. Both θ and θ' vary between 0 and 2π so that both nearest and second-nearest neighbor interactions are considered. The spheres correspond to monomer units. Reprinted with permission from ref 12. Copyright 1977, American Institute of Physics. (B) Tetrameric chain segments of two adjacent polymer chains used to compute interchain potential energy as a function of θ and θ' as well as the relative translational and rotational degrees of freedom of one segment with respect to the other.

The interchain potential is much more difficult to specify. In addition to depending upon θ from multiple chains, V_2 depends also upon the interchain translational coordinates. We have circumvented these dimensional complexities by choosing a generalized mean-field model for V_2 by writing

$$V_2 = W[n(\theta)] \quad (4)$$

where the functional W is of the form

$$W[n(\theta)] = W_0 + \int W_1(\theta)n(\theta)d\theta + \int \int W_2(\theta, \theta')n(\theta)n(\theta')d\theta d\theta' + \int \int \int \dots \quad (5)$$

Because W_0 is a constant and W_1 merely acts to modify the intrachain potential, the first term capable of

leading to a phase transition in the expansion is the second-order term $W_2(\theta, \theta')$. Enhanced attenuation of interchain correlations may be expected to occur as a consequence of chain misalignments at elevated temperatures; this has been modeled in terms of third-, fourth-, and sixth-order expansions formed by successive convolution of $W_2(\theta, \theta')$ with $n(\theta)$ and $n(\theta')$. These rapidly varying terms containing products of three, four, or six n 's yield sharper phase transitions.

A principal omission of the present model is the kinetic energy of rotation of the monomeric units. A partial justification of this approach is that the requisite motions are inhibited by the strong mutual steric repulsions of the constituent atoms. The validity of this approach has been supported by Go and Scheraga.¹³ In total, the Hamiltonian per monomer unit for our model is

$$H = \int \int U(\theta, \theta')n(\theta, \theta')d\theta d\theta' + W[n(\theta)] \quad (6)$$

The Helmholtz energy F' of this model is found to be given by the relation

$$F' = \beta^{-1} \ln \lambda_m + \int h(\theta)n(\theta)d\theta + W[n(\theta)] \quad (7)$$

where $\beta^{-1} = k_B T$, the temperature expressed in energy units, and λ_m is the largest eigenvalue of the integral eigenvalue equation

$$\lambda \psi(\theta) = \frac{1}{2\pi} \int \exp\left(-\beta\left\{U(\theta, \theta') - \frac{1}{2}[h(\theta) + h(\theta')]\right\}\right) \psi(\theta')d\theta' \quad (8)$$

The function $h(\theta)$ is a fictitious "applied field" introduced as a computational device and given by

$$\delta\lambda/\delta h = \beta n\lambda$$

Minimization of F' with respect to $n(\theta)$ yields the relation

$$h(\theta) = -\delta W[n(\theta)]/\delta n(\theta) \quad (9)$$

The addition relation

$$n(\theta) = \psi_m^2(\theta) / \int \psi_m^2(\theta')d\theta' \quad (10)$$

allows an iterative approach to be taken. An initial guess at $n(\theta)$ leads to a better approximation through application of eq 9, 8, and 10 in turn.

Calculation of Molecular Energetics. A fixed-valence-geometry molecular-mechanics method has been used to calculate both intra- and interchain potential energies.^{14,15} In this approximation the energy is assumed to be the sum of pairwise atomic interactions involving dispersion attraction, steric repulsion, and electrostatic terms. An "intrinsic" torsional potential for bond rotations is also included in intrachain calculations.

Usage of the calculated potential energies in the statistical mechanical formalism involves a critical step. One must assume that the effective potential energies

(13) N. Go and H. A. Scheraga, *Macromolecules*, **9**, 535 (1976).

(14) A. J. Hopfinger, "Conformational Properties of Macromolecules", Academic Press, New York, 1973.

(15) R. Potenzzone, Jr., E. Cavicchi, H. J. R. Weintraub, and A. J. Hopfinger, *Comput. Chem.*, **1**, 187 (1977).

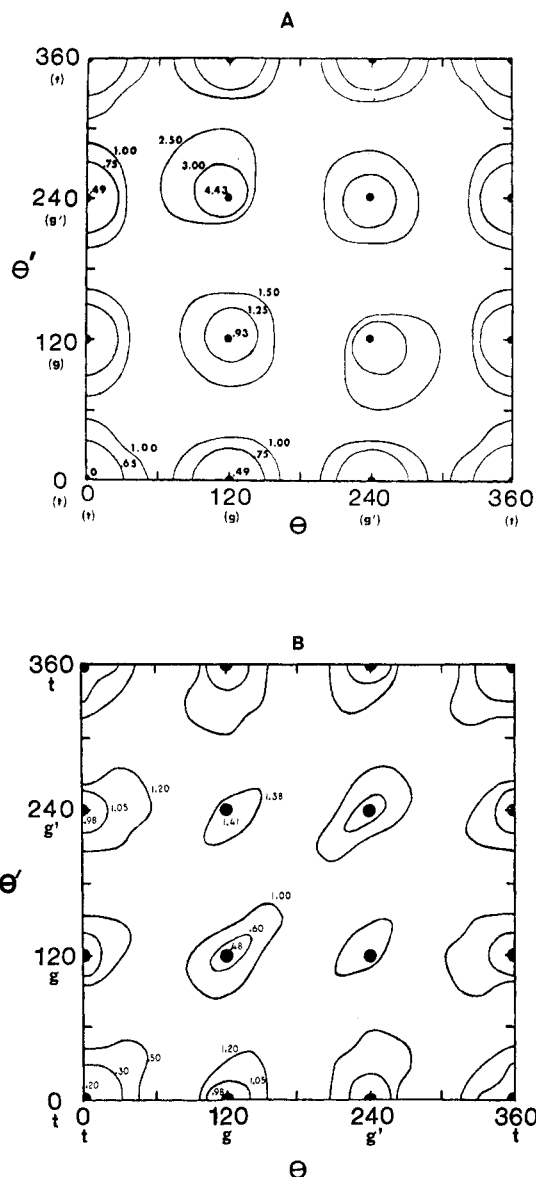


Figure 3. (A) Isoenergy contour map of the intrachain potential energy for PM based upon the structure shown in Figure 2A. Energies are in kcal/mol with the global energy minimum of the all-trans conformer state defined as zero. Reprinted with permission from ref 17. Copyright 1975, American Institute of Physics. (B) Isoenergy contour map of the interchain potential energy of two adjacent PM chain segments based upon the structures shown in Figure 2B. Energies are based upon the scale of (A).

calculated from molecular mechanics are independent of temperature. The applicability of our theory for modeling thermal phase transitions depends upon the reasonableness of this assumption. We are not the first to use calculated conformational potential energies to estimate macromolecular features. Flory has successfully used this approach to predict chain statistical properties at constant temperature.¹⁶ We are, however, first to set aside a constant temperature constraint.

Application to Polymethylene, $(\text{CH}_2)_n$. The theory has been used to model the crystal-melt transition of single crystals of polymethylene (PM). PM exists as a planar zig-zag of methylene units (an all-trans structure) in the crystalline conformation. The linear

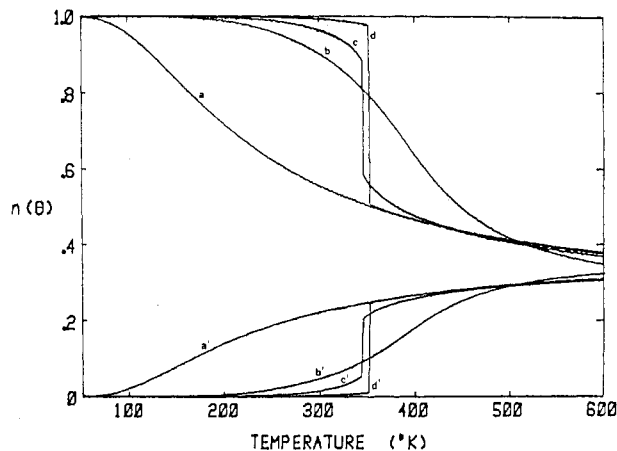


Figure 4. Fraction of PM trans conformers, $n(\theta)$, vs. temperature for (a) single chain; (b) single chain + second-order term; (c) single chain + third-order term; (d) single chain + fourth-order term. The prime (') letter curves correspond to the gauche plus gauche' populations, $(n(120^\circ) + n(240^\circ))$. $T_m(\text{exp}) \approx 415$ K. Only models c and d yield a true first-order phase transition. Reprinted with permission from ref 19. Copyright 1973, American Institute of Physics.

chains normally pack into an orthorhombic lattice.

The intrachain potential energies have been calculated using a pentameric chain segment (see Figure 2A) of PM which includes second-nearest-neighbor interactions.¹⁷ The resultant isoenergy contour map is shown in Figure 3A. The interchain energies, and corresponding chain separation distances, can be estimated using two tetrameric chain segments (see Figure 2B) of PM. Each segment is fixed in a conformational state. The potential energy for each pair of intermolecular conformer states, i.e., trans-trans, trans-gauche, etc., is computed under the constraint that the vectors defining the chain axes of the all-trans conformers in each tetrameric unit are held parallel for all packing states. One tetrameric unit is fixed in space. The other tetramer rotates about the fixed one. The mobile tetrameric unit is also allowed to translate and rotate with respect to its all-trans chain axis in the search for the minimum interchain potential energy. The interchain packing potential energy map is shown in Figure 3B; the angles θ and θ' belong to different chains as defined in Figure 2B. A set of chain separation distances and corresponding potential energies was recorded for each pair of θ and θ' for use in the volume expansion and phonon calculations discussed below.

In the numerical computation, integrals over angle θ are replaced by discrete sums, and the coarseness of the grid used in this approximation has a marked effect on the accuracy of the results. The most drastic approach considers only three values of the torsional angle, trans, gauche, and gauche', and may be considered as a variant of the Ising model. After addition of some corrections¹⁸ to allow for the shape of the potential wells this approach yields the results shown in Figure 4. In curve a the interchain mean field is absent, while in curve b it is approximated by a second-order term, bilinear in the distributions $n(\theta)$. In curves c and d

(17) F. P. Boyle, P. L. Taylor, A. J. Hopfinger, and R. Simha, *J. Appl. Phys.*, **46**, 4218 (1975).

(18) F. P. Boyle, P. L. Taylor, A. J. Hopfinger, and R. Simha, *Macromolecules*, **9**, 599 (1976).

(16) See P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley-Interscience, New York, 1969.

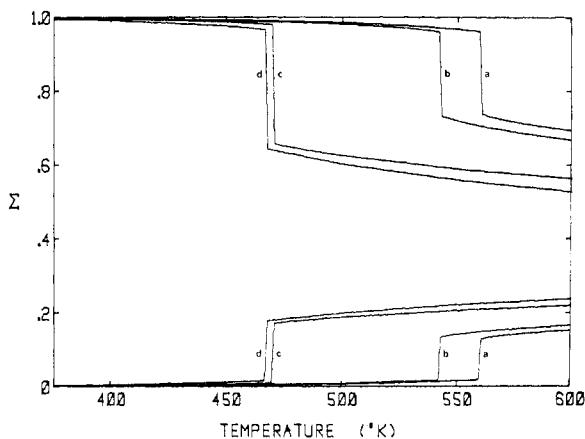


Figure 5. The fraction of torsional rotational angles lying within 60° of the trans conformation (upper curves) and within 60° of the gauche conformation (lower curves) is plotted as a function of temperature for PM. The curves a, b, c, and d refer to approximations in which integrations over torsional angles were replaced by discrete sums over 3, 6, 12, and 24 values, respectively. Reprinted with permission from ref 12. Copyright 1977, American Institute of Physics.

Table I
Interchain Lattice Breakdown and
Corresponding T_m and ΔS

$$W[n(\theta)] = \alpha_1 \int \int \int \int W(\theta_1 + \theta_2, \theta_3 + \theta_4) n(\theta_1) n(\theta_2) n(\theta_3) \times n(\theta_4) d\theta_1 d\theta_2 d\theta_3 d\theta_4 + \alpha_2 \int \int \int \int W(\theta_1 + \theta_2 + \theta_3, \theta_4 + \theta_5 + \theta_6) n(\theta_1) n(\theta_2) n(\theta_3) n(\theta_4) n(\theta_5) n(\theta_6) d\theta_1 d\theta_2 d\theta_3 d\theta_4 d\theta_5 d\theta_6$$

$\alpha_1 + \alpha_2 = 1$		
α_1	T_m, K	$\Delta S, \text{ cal}/(\text{mol}\cdot K)$
0.00	470.5	2.25
0.10	470.8	2.08
0.25	471.4	1.80
0.50	473.3	1.22
1.00	a	a

^a No transition.

third-order and fourth-order interchain potentials are used, respectively. These higher order terms provide an ad hoc inclusion of the effects of chain misalignment. In this case only the third- and fourth-order terms yield phase transitions.

From the calculated free energies one may also obtain the heat capacity and, when a transition occurs, the entropy of melting, ΔS . The value of ΔS predicted by the fourth-order model is in the vicinity of 2 cal/(mol·K); this quantity and the heat capacity at neighboring temperatures are in qualitative agreement with experiment.^{19,20}

These initial calculations, in which the drastic approximation was made of replacing the continuous range of torsional angles by only the three values 0, $2\pi/3$, and $4\pi/3$, served to show that a first-order phase transition at a realistic temperature could be obtained from the formalism. This modest success justified a more careful calculation in which the integration over the range of 2π of the torsional angle was replaced by a sum over m uniformly spaced values, with m equal to 6, 12, and 24 as well as the original value, 3. These approximations are referred to as m -state models.¹² The results of these calculations for various m are shown in Figure 5 for PM. In this case the interchain interaction was represented by a sixth-order mean field in the sense

(19) V. Bares and B. Wunderlich, *J. Polym. Sci., A-2*, 11, 397 (1973).

(20) B. Wunderlich, *J. Phys. Chem.*, 69, 2078 (1965).

Table II
Calculated Crystal-Melt Transition Properties for PM

a. Variation in T_m (K) and ΔS (cal mol⁻¹ K⁻¹) as a Function of m

m	3	6	12	24	exptl ¹⁹
T_m	561	542	470	466	415
ΔS	1.07	1.36	2.22	2.00	2.32

b. C_∞ for an Isolated Chain of Infinite Length

m	3	6	12	24	exptl ¹⁶
C_∞	8.13	8.05	5.30	5.46	6.6-6.8

c. C_∞ for a Chain in the Crystal as a Function of Temperature Using the $m = 12$ Approximation

temp, K	C_∞	temp, K	C_∞
0	∞	470	75.1
100	1.49×10^4
200	802	471	6.40
300	312	500	5.63
400	153	600	4.39

d. T_m (K) and ΔS (cal mol⁻¹ K⁻¹) for Phonon Models Based upon the $m = 12$ Approximation

	without phonons		with phonons		exptl ¹⁹
		$K = 90.6^a$	$K = 181$		
T_m	470	425	437	415	
ΔS	2.22	2.72	2.52	2.32	

e. Zero-Temperature Orthorhombic Unit Cell a and b Dimensions Predicted and Extrapolated from Experimental Data²³

	lattice dimension, Å		
	$k = 90.6$	$k = 181$	exptl
a	7.69	7.69	7.12
b	4.48	4.47	4.88

^a K given in kcal Å⁻² mol⁻¹.

of eq 5; that is, the interchain potential was taken to be a convolution of a function containing the product of six factors of the distribution $n(\theta)$ of torsional angles. Interestingly, as can be seen in Table I, the form of the thermal dispersion of the interchain potential for an $m = 12$ model has a pronounced effect on heat capacity, but only a minimal contribution to the location of T_m .

Transition temperatures and entropies of melting are listed in Table IIa for the various m -state models. The $m = 3$ and $m = 6$ approximations do a relatively poor job in the estimation of T_m . However, both $m = 12$ and 24 yield reasonably accurate melt transition temperatures which, in turn, differ only slightly from one another. The complexity of the computational procedure limits the usage to the twelve-state model. The comparison of ΔS in Table IIa for the different approximations indicates that none are quite adequate. On the other hand, both $m = 12$ and $m = 24$ yield relatively consistent results, and so disagreement with the experimental ΔS value may be a consequence of degrees of freedom omitted from our original Hamiltonian rather than any lack of precision in its solution.

We have tested how sensitive the model is to inclusion of the actual lowest energy state and corresponding distinct energy grid set. Instead of using energy values centered on the trans state, energy values were used which correspond to a uniform displacement from this reference state. A 5% change in θ and θ' for the lowest energy values yielded less than a 5% change for both T_m and ΔS .

The nearest-neighbor distribution is also found when solving for the angular distribution of torsional angles

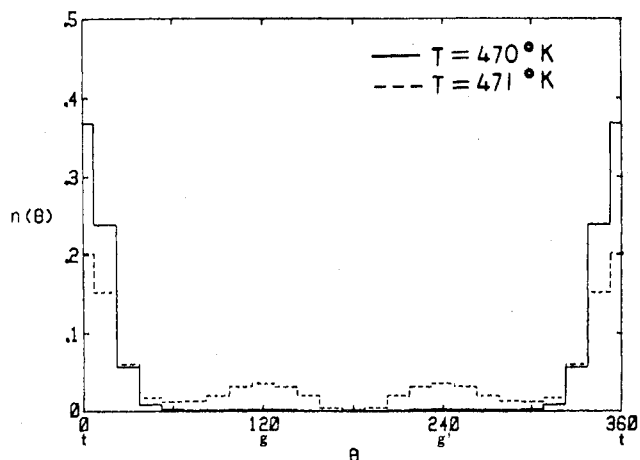


Figure 6. Histograms of the angular distribution $n(\theta)$ vs. θ for PM using the $m = 12$ approximation. The solid line is for just below the T_m while the dotted line is for just above T_m . Note the loss of trans population and increase in number of gauche and gauche' states immediately upon passing T_m . Reprinted with permission from ref 12. Copyright 1977, American Institute of Physics.

of the system. This information can be used to determine the characteristic ratio,¹⁶ C_∞ , of the individual chains. This quantity is defined by the relation

$$C_\infty = 1 + 2a/l$$

where l is the bond length and where a , the persistence length, is given by the sum over bonds in a single chain

$$a = \sum_{i=2}^{\infty} (\mathbf{l}_i \cdot \mathbf{l}_1) / |\mathbf{l}_i|$$

The quantity C_∞ is a measure of how the change in the population of rotamer states, in this case as a function of temperature, modifies the statistical spatial features of a chain molecule. Table IIb contains the C_∞ for an infinite, isolated, PM chain as a function of m and T as well as an experimental value of C_∞ under θ conditions (distant-neighbor intrachain excluded volume effects are canceled by polymer-solvent interactions).¹⁶ The reasonably good agreement between theory, for $m = 12$ and 24, and experiment is added evidence in support of the general model.

Table IIc contains values of C_∞ for a series of temperatures below and above T_m using the $m = 12$ approximation for a crystalline PM chain. Significant changes occur in C_∞ for the crystalline phase prior to melting. The magnitude of the drop in C_∞ near T_m is not in the observed range. This suggests that the predicted trans population falls off too rapidly immediately prior to melting. Variation in C_∞ with temperature above T_m is not as large as is the case below T_m . The magnitudes of C_∞ above T_m suggest that the individual polymer chains behave, in the melt, like an isolated chain under θ conditions. The large change in C_∞ between 470 and 471 K corresponds to passage through T_m . Figure 6 depicts the major redistribution of conformer states that occurs at melting and which leads to the dramatic change in C_∞ for the $m = 12$ approximation.

Contribution from Phonon Anharmonicity

Formalism. The formalism embodied in eq 2 through 10 reasonably estimates some physicochemical features of PM. However, the prediction of the percent

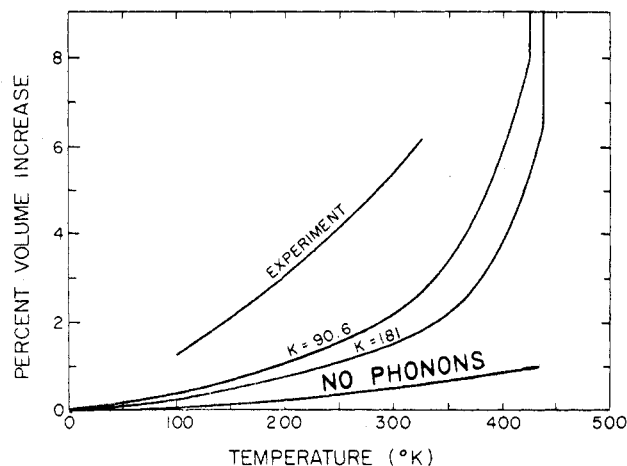


Figure 7. The thermal expansion of crystalline PM according to (a) theory neglecting phonons, (b) phonons included with $K = 181$, (c) phonons included with $K = 90.6$, (d) experiment. Taken in part from ref 21.

of volume increase as a function of temperature for PM, as shown in Figure 7, is poor. We felt that the neglect of vibrational contributions to lattice breakdown might explain why our calculated volume expansions are so much less than those observed experimentally. Hence we attempted to include the effects of phonon anharmonicity in a self-consistent fashion within the existing formalism²¹ That is to say, we considered the effects of the non-Hookean nature of the forces in modifying the normal modes of vibration of the system.

In the quasiharmonic approximation the phonon free energy is of the form²²

$$F_p = \beta^{-1} \sum_{qs} \{ \ln [1 - \exp(-\beta \hbar \omega_{qs})] + \frac{1}{2} \hbar \omega_{qs} \} \quad (11)$$

with ω_{qs} being the frequency of the phonon with wavenumber q and polarization s . The sum over the wavenumbers is determined by the number and spacing of the individual monomer units. There are three polarizations of the waves since the polymers are in a three-dimensional space. The frequencies ω_{qs} are themselves functionals of $n(\theta)$ since the restoring forces acting on a displaced monomer depend on the distribution of torsional angles. The total free energy of the crystal or melt now reads

$$F = \beta^{-1} \ln \lambda_m + \int h(\theta) n(\theta) d\theta + W[n(\theta)] + F_p[n(\theta)] \quad (12)$$

Minimization of F with respect to $n(\theta)$ now yields

$$h(\theta) = \frac{-\delta \{ W[n(\theta)] + F_p[n(\theta)] \}}{\delta [n(\theta)]} \quad (13)$$

since the phonon contribution appears as an extra term in the mean-field energy. An iterative solution of eq 13, 8, and 10 is the appropriate procedure to obtain a self-consistent solution.

The approach followed in this calculation is first to determine the pair potential between a monomer and its nearest neighbor. The potential is then expanded to second order in small displacements in real space and subsequently transformed to wavenumber space from

(21) F. P. Boyle, P. L. Taylor, and A. J. Hopfinger, *J. Chem. Phys.*, **68**, 4730 (1978).

(22) C. Kittel, "Thermal Physics", Wiley-Interscience, New York, 1969.

which the normal modes of the system are then determined. The frequencies and polarizations are thus found.

The pair potentials are found by considering each of the monomer units as a separate symmetric entity in a three dimensional space. Each entity lies along straight lines representing chains as shown in Figure 1. A monomer unit interacts with its nearest neighbor along the chain via a harmonic force. This potential representation is consistent with the treatment of hard variables in normal coordinate analysis. The inverse-power law is assumed to hold for interchain interactions, and hence the potential-energy function for the remaining two dimensions perpendicular to the chain axis can be written in the general form

$$V(r, \theta, \theta') = V_0 + [\alpha / (r - R_0)^P] - [\beta / (r - R_0)^Q] \quad (14)$$

where α , β , V_0 , R_0 , P , and Q are all functions of θ and θ' of adjacent interchain segments. Numerical values of the requisite parameters of eq 14 for θ and θ' are empirically determined by curve fitting against the interchain potential energies found in the molecular mechanics calculations.

Results for PM. Table II d lists the computed T_m and ΔS for PM using the $m = 12$, sixth-order mean-field expansion model. Column one contains the results when phonons are neglected. Column four includes experimental findings. Columns two and three contain the results when phonons are included using two different intrachain force constants, K . The reason for considering two different values of K is the uncertainty in the weighting of in- and out-of-plane (of the trans conformation) force constants to obtain K as well as an innate uncertainty in assigning these individual force constants. The choices of K represent opposite extremes in possible values. It is clear that inclusion of phonons in the calculation, irrespective of the choice of K , improves the agreement of predicted and observed T_m . The entropy change becomes larger when phonons are included in the model. However, as indicated in Table II a, this increase could be counteracted as more than 12 states are included.

Table II e compares the $T = 0$ K lattice dimensions for the two values of K with experimental values²³ extrapolated to $T = 0$ K. The theory finds an a dimension that is too large and a b dimension that is too small. This error is believed to be a consequence of the combined inability of an adjacent-chain-segment molecular mechanics calculation and mean-field interchain representation to describe the necessary packing anisotropy of a chain perpendicular to its axis.

The thermal expansion predicted by theory is compared in Figure 7 to the empirical curve of Davis, Eby, and Coulson²³ for the case where fold length of the single crystal is set equal to infinity. The theoretical curves are the increase of the product of the a and b dimensions. The c dimension is fixed by the assumed harmonic nature of the potential in that direction. Inclusion of phonons brings the predicted volume increases closer to the experimental extrapolation.

(23) G. T. Davis, R. K. Eby, and J. P. Coulson, *J. Appl. Phys.*, **41**, 4316 (1970).

However, the phonon-dependent theory predicts a thermal expansion that is only 30–40% of that observed experimentally. The theoretical expansion is isotropic, while the actual expansion is not. The discrepancy could possibly be attributed to poor extrapolation of what might already be a large error in the potential-well shapes and/or innate anisotropy of the chains and their packing.

Concluding Remarks

The simple models adopted in the formalism to describe polymer melt transition behavior have definite limitations. These limitations are made more stringent when the quantitative application of the formalism depends upon the geometric and energetic terms determined from molecular mechanics calculations. It is difficult to estimate the range of error in molecular mechanics calculations. Geometric parameters can probably be determined more accurately than energetic parameters as a consequence of the manner in which the method is parameterized. Overall, a 10% error limit is probably inherent to molecular mechanics calculations.

Nevertheless, the partitioned manner in which contributing transition mechanisms are included in the formalism, coupled with the capability of making at least semiquantitative assignments to requisite transition terms, lends a meaningful utility to our model. For a given polymeric system we are able to evaluate the relative importance of the various contributions (intrachain, interchain, phonons, etc.) to transition behavior. In such a way it is possible to gain insight into the structure–thermodynamic interrelationship responsible for the properties of a polymer crystal. In this regard we have also applied the formalism presented here to describe the crystal–melt transition¹² of polytetrafluoroethylene [(CF₂CF₂)_n]. The accuracy of the predicted results to observed findings is about as good as achieved for PM.

Currently, the theory is being applied to describe both crystal–crystal (phase I–phase II) and crystal–melt transitions of poly(vinylidene fluoride), (CF₂CH₂)_n. In order to model the stress-induced phase II to phase I transition, the formalism has been modified by adding to the free energy a stress-length term acting in the chain-axis direction. Several metastable phases emerge from this calculation. Four of these can be identified with the melt and the three known crystalline phases, but an additional phase, not yet observed, has also been found in a preliminary search.

Lastly, we have had some initial success in combining the transition formalism with a model of solitary-wave propagation²⁴ to describe the poling process in phase-I PVF₂ which is necessary for inducing piezoelectric properties in this material.

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(24) A. J. Hopfinger, A. J. Lewanski, T. J. Sluckin, and P. L. Taylor, "Proceedings of the Oxford Conference on Solutions in Condensed Matter", Springer, New York, 1978.