References and Notes

(1) Meier, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1974**, *15*, 71.
(2) Helfand, E.; Wasserman, Z. *Macromolecules* **1978**, *11*, 960.
(3) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(4) Leibler, L.; Pincus, P. A. *Macromolecules* **1984**, *17*, 2922.
(5) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(6) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443; **1982**, *15*, 482.
(7) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.
(8) Bates, F. S.; Cohen, R. E.; Berney, C. V. *Macromolecules* **1982**, *15*, 589.
(9) Bates, F. S.; Berney, C. V.; Cohen, R. E. *Macromolecules* **1983**, *16*, 1101.
(10) Bates, F. S.; Berney, C. V.; Cohen, R. E.; Wignall, G. D. *Polymer* **1983**, *24*, 519. Berney, C. V.; Kofinas, P.; Cohen, R. E. *Polymer* **1986**, *27*, 330.
(11) Berney, C. V.; Cohen, R. E.; Bates, F. S. *Polymer* **1982**, *23*, 1222.
(12) Molecular weight values quoted were determined chromatographically.
(13) Bates, F. S.; Cohen, R. E.; Argon, A. S. *Macromolecules* **1983**, *16*, 1108.
(14) Kato, K. *Polym. Lett.* **1966**, *4*, 35.
(15) Phillips, W. C.; Rayment, I. *J. Appl. Crystallogr.* **1982**, *15*, 577.
(16) Guinier, A.; Fournet, G. *Small-Angle Scattering of X-Rays*; Wiley: New York, 1955.
(17) Kinning, D. J.; Thomas, E. L. *Macromolecules* **1984**, *17*, 1712.
(18) Percus, J. K.; Yevick, G. J. *Phys. Rev.* **1958**, *110*, 1.
(19) Wertheim, M. S. *Phys. Rev. Lett.* **1963**, *10*, 321.
(20) Thiel, E. *J. Chem. Phys.* **1963**, *39*, 474.
(21) Bacon, G. E. *Neutron Diffraction*; Oxford University Press: London, 1962.
(22) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(23) Ballard, D.; Wignall, G. D.; Schelten, J. *Eur. Polym. J.* **1973**, *9*, 965.
(24) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.

Theory of the Phase Transition under Stress in Poly(butylene terephthalate)

Radi Al-Jishi*

Department of Physics and Astronomy, California State University, Los Angeles, Los Angeles, California 90032

P. L. Taylor

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106.

Received September 14, 1987; Revised Manuscript Received January 4, 1988

ABSTRACT: Poly(butylene terephthalate) undergoes a reversible phase transition when subjected to a longitudinal stress. The temperature dependence of the critical stress is examined in terms of a model of nucleation and growth and is related to the temperature dependence of the width in stress of the hysteresis loop.

Introduction

In a previous paper[1] two models were proposed for the reversible phase transition that occurs when poly(butylene terephthalate), PBT, is subjected to a longitudinal stress.[2-4] Both these models treated the equilibrium equation of state of PBT and were analyzed in a mean-field approximation. The principal conclusion of this work was that the width of the hysteresis in stress as the sample was cycled between α and β phases was predicted to vary as $(T_c - T)^{3/2}$, with T_c the critical temperature for the phase transition. This conclusion applied to both of the models examined. In the first of these, the benzene rings of the terephthalate group on one chain were bound to those on an adjacent chain by harmonic forces. In the alternative model the rings were permitted to slide past each other in a sinusoidal force field. A comparison with the work of Brereton et al.[2] showed that the hysteresis did behave in the predicted way for temperatures below T_c and that the model of linked benzene rings produced a better prediction of the absolute magnitude of the hysteresis than did the other model. While it was gratifying to observe such good agreement between theory and experiment, there was some weaknesses in this treatment. One difficulty lay in the fact that the critical stress for the onset of transition was observed[3] to vary with temperature in a way not predicted in either model studied. A second inadequacy was the fact that all hysteresis was calculated to vanish sharply at T_c in both models, whereas measurements found only a steady narrowing of the loop as the temperature was raised.

These discrepancies between experiment and the admittedly greatly simplified model used in ref 1 suggest a number of improvements that might be made to obtain a theory with wider predictive power. For example, the inclusion of internal degrees of freedom of the tetramethylene segment or of the terephthalate segment would add an additional temperature-dependent term to the free energy of PBT. Another likely possibility is that the boundary between the crystalline and amorphous regions of the material must be expected to contain stresses that would act to broaden the transition.

A more fundamental point, however, lies in the essentially time-dependent character of the hysteretic phenomenon. A hystersis measurement must always be performed at a frequency greater than the reciprocal of the relaxation time for the process under investigation. This raises the question of the microscopic mechanism whereby the $\alpha \rightarrow \beta$ transition takes place and necessitates a discussion of the nucleation and growth of the β phase in a sample of α-phase PBT.

In this paper we comment briefly on the effects of phonon frequencies and internal stresses and then describe a model for nucleation and growth in PBT.

Phonon Frequencies

The entropy of an assembly of classical harmonic oscillators of frequencies ω_i contains the term

$$S_f = -k_B \sum_i \ln \omega_i \qquad (1)$$

In the transition from α to β phase these frequencies will

0024-9297/88/2221-2240$01.50/0

be variously raised and lowered as the tetramethylene segments take on their planar zigzag form. In particular the low-frequency characteristic of the out-of-plane motion and the high-frequency characteristic of in-plane motion will appear. Because the total magnitudes of the forces acting on the carbon atoms will to some extent be unchanged, while only their directions are radically altered in the transition, we may expect the trace of the dynamical matrix to remain approximately constant. This trace is equal to the quantity

$$\Omega^2 = \sum_i \omega_i^2 \qquad (2)$$

The curvature of the logarithmic function then leads to the conclusion that the entropy component defined in eq 1 is likely to increase as the spread of frequencies increases and hence as the $\alpha \rightarrow \beta$ transition proceeds. This adds to the free energy an additional term linear in the length L of the chain. The effect is thus identical with that of an additional applied stress proportional to the temperature T. The critical stress for the $\alpha \rightarrow \beta$ transition is now predicted to decrease linearly with T in the range in which this argument is valid. A comparison of this prediction with the observations of ref 3 indicates that while there is sufficient agreement to give some credibility to our hypothesis, the clear deviations from linearity of the experimental results shows that other effects must be present.

Stresses at the Crystal Surface

An implicit assumption of the mean-field theory is that the tension is equal in all the chain segments of a crystallite. One must expect this to be a source of error in the theory. In the crystallization process the boundary of a lamella will be determined by a balance between two opposing forces. On one hand, the crystalline arrangement has a lower free energy than the amorphous conformation, and this will tend to make the crystal grow at the expense of the amorphous regions. On the other hand, the physical restrictions of chain length and entanglement limit the extent to which this can occur. One must consequently expect to find that even in equilibrium each chain segment that traverses a lamella will be subject to a stress. While the detailed consequences of these stresses cannot be calculated in a mean-field model, one may nevertheless make some qualitative statements about their effect on the stress–strain curve. Although the critical temperature of different regions of a crystallite will remain approximately unchanged, the critical stress will now be a function of position. That is to say, the actual stress $S(r)$ acting on a chain will differ from the average stress S by some function $s(\mathbf{r})$ representing the stress introduced in that particular chain during the process of crystallization. The observed strain will then no longer be the value $\Delta L(S)$ predicted for the ideal model, but will be given by

$$\Delta L = \frac{\int \Delta L[S + s(\mathbf{r})]\, \mathrm{d}^2\mathbf{r}}{\int \mathrm{d}^2\mathbf{r}}$$

with the integral proceeding over the two-dimensional surface of the lamella normal to the chains. The observed stress–strain curve is thus a convolution in the stress direction of the predicted curve for an ideal crystal with the distribution of local stresses.

Surface stresses are thus capable of accounting for the observed finite slope of the stress–strain curve for transitions occuring below T_c. They cannot, however, simply account for the temperature dependence of the critical stress.

Nucleation and Growth

The preceding discussion shows that neither inclusion of internal degrees of freedom of the tetramethylene units nor the distribution of stresses at the crystalline–amorphous interface could successfully account for the temperature dependence of the center and width of the hysteresis in stress. We are thus led to consider the kinetics of the crystal–crystal phase transition in PBT. We have carried out such an analysis within the context of a model of nucleation and growth as discussed below.

We assume that a nucleus of the β phase is formed once the stress applied to the α phase reaches a certain value. The high degree of anisotropy in polymer crystals precludes a spherical shape for such a nucleus. A cylindrical or rectangular shape may be assumed since we require that whole chain segments traversing the crystallite thickness be included in the nucleus. It makes little difference for our subsequent analysis whether the formed nucleus of the β phase is cylindrical or rectangular. Consequently we take the nucleus shape to be a rectangular parallelpiped whose height equals the lamellar width L. In the a and b directions, the nucleus width is x and y, respectively. The number of chain segments in the nucleus is then given by xy/A, where A is the cross-sectional area per chain in the β phase.

Both the α and β phases are taken as prefectly ordered. The change in free energy due to the formation of the β phase nucleus is then assumed to be given by

$$\Delta F = (-SA\Delta L + \Delta V)xy/A + 2\sigma(x + y)L \qquad (3)$$

where S is the applied stress, ΔL is the increase in chain length due to formation of the β phase, $\Delta V = V_\beta - V_\alpha$, with V_α and V_β being the average free energy of a chain in the α and β phases, respectively, and σ is the surface energy density of the wall separating the two phases. If this nucleus succeeds in reaching a critical size it will grow freely afterwards. In this model $-SA\Delta L + \Delta V < 0$, while $\sigma > 0$. The critical size is determined by maximizing ΔF, yielding critical x and y given by

$$x_c = y_c = \frac{2\sigma L}{S\Delta L - \Delta V/A} \qquad (4)$$

and the maximum free-energy change, ΔF^*, is given by

$$\Delta F^* = \frac{4\sigma^2 L^2}{S\Delta L - \Delta V/A} \qquad (5)$$

Because the transition probability is proportional to $\exp(-\Delta F^*/k_B T)$, with k_B being the Boltzmann constant and T the temperature, it follows that for this transition to be observable, ΔF^* cannot be too much larger than $k_B T$. If a transition rate of the form $\nu_0 \exp(-\Delta F^*/k_B T)$ is assumed, with ν_0 being an attempt frequency of the order of a phonon frequency, $\nu_0 \sim 10^{13}$ Hz, then for the transition to be observable, we must have $\Delta F^* = pk_B T$, where $p \lesssim 30$. Then it follows from eq 5 that

$$S^*_{\alpha\beta} = \frac{\Delta V}{A\Delta L} + \frac{4\sigma^2 L^2}{pk_B T\Delta L} \qquad (6)$$

where $S^*_{\alpha\beta}$ is the critical stress for the α to β transition. After the nucleus succeeds in growing to the critical size, it is then most probable that the whole lamellar crystallite makes the transition to the β phase.

It is necessary to reduce the stress to induce a transition back to the α phase. In a similar manner we find a critical stress $S^*_{\beta\alpha}$ for transition from β to α given by

$$S^*_{\beta\alpha} = \frac{\Delta V}{A'\Delta L} - \frac{4\sigma^2 L^2}{pk_B T\Delta L} \qquad (7)$$

where A' is the average cross-sectional area of a chain in the α phase; in PBT it is the case that $A' > A$. The hysteresis width, $\Delta S = S^*_{\alpha\beta} - S^*_{\beta\alpha}$ is therefore given by

$$\Delta S = \frac{\Delta V}{\Delta L}\left[\frac{1}{A} - \frac{1}{A'}\right] + \frac{8\sigma^2 L^2}{pk_B T \Delta L} \tag{8}$$

In practice, however, experimental measurements usually involve determination of the force exerted on a sample of known initial cross section, and so the first term of the right-hand side of eq (8) must be omitted. Even if this were not the case, the contribution from this term would not be significant because the difference between A and A' in PBT is very small.[5-7]

The temperature dependence of ΔS is thus readily obtained once that of σ is known. Although it is generally accepted that σ decreases with increasing temperature T, there is no well-developed method by which the variation of σ with T is determined. In the nucleation and growth model for polarization reversal in ferroelectrics, it is believed[8] that $\sigma \propto P^2$, where P is the polarization and σ is the interfacial energy density between the nucleus of reversed polarization and the rest of the crystal. It is tempting to propose a similar quadratic dependence of σ on the order parameter difference for the $\alpha \rightarrow \beta$ transition in PBT; this would be inappropriate, however, because the interchain interaction in PBT is of short range and lacks the long-range dipole component of a ferroelectric material. One would expect the surface energy density σ to be proportional to the interchain coupling energy, since it is this coupling energy that is radically reduced at the interface between the α and β phases. The temperature dependence of σ is thus determined by the temperature dependence of the interatomic interaction energy between atoms on adjacent chains in a single PBT phase. If the equilibrium positions of two such atoms are denoted by $\mathbf{R}_{i0}$ and $\mathbf{R}_{j0}$, and the deviation from these positions by $\mathbf{u}_i$ and $\mathbf{u}_j$, respectively ($\mathbf{R}_i = \mathbf{R}_{i0} + \mathbf{u}_i$, $\mathbf{R}_j = \mathbf{R}_{j0} + \mathbf{u}_j$), then

$$\langle \mathbf{u}_i^2 \rangle = \frac{1}{NM}\sum_{\mathbf{q}\lambda}\frac{\langle E_{\mathbf{q}\lambda}\rangle}{\omega_{\mathbf{q}\lambda}^2} \tag{9}$$

where $3N$ is the number of normal modes in the system, M the atomic mass, $\mathbf{q}$ and λ refer to the phonon wave vector and branch, respectively, $\omega_{\mathbf{q}\lambda}$ is the phonon frequency, and

$$\langle E_{\mathbf{q}\lambda}\rangle = \hbar\omega_{\mathbf{q}\lambda}[\langle n_{\mathbf{q}\lambda}\rangle + 1/2]$$

Here $n_{\mathbf{q}\lambda}$ is the phonon occupation number, and the broken brackets denote thermal averaging. For $T_D < T < T_M$, with T_D and T_M denoting the Debye and melting temperatures respectively, $\langle E_{\mathbf{q}\lambda}\rangle = k_B T$, and

$$\langle \mathbf{u}_i^2 \rangle = \frac{k_B T}{NM}\sum_{\mathbf{q}\lambda} 1/\omega_{\mathbf{q}\lambda}^2 \tag{10}$$

The interatomic interaction energy between atoms i and j may be written

$$V(\mathbf{R}_i - \mathbf{R}_j) = V(\mathbf{R}_{i0} - \mathbf{R}_{j0}) + \tfrac{1}{2}k\langle(\mathbf{u}_i - \mathbf{u}_j)^2\rangle + \cdots \tag{11}$$

where $V(\mathbf{R}_{i0} - \mathbf{R}_{j0}) < 0$, since the interaction is attractive, and k is a constant. Straightforward evaluation of $\langle(\mathbf{u}_i - \mathbf{u}_j)^2\rangle$ gives

$$\langle(\mathbf{u}_i - \mathbf{u}_j)^2\rangle = \frac{2k_B T}{NM}\sum_{\mathbf{q}\lambda}\frac{1}{\omega_{\mathbf{q}\lambda}^2}(1 - \exp[i\mathbf{q}\cdot(\mathbf{R}_{i0} - \mathbf{R}_{j0})]) \tag{12}$$

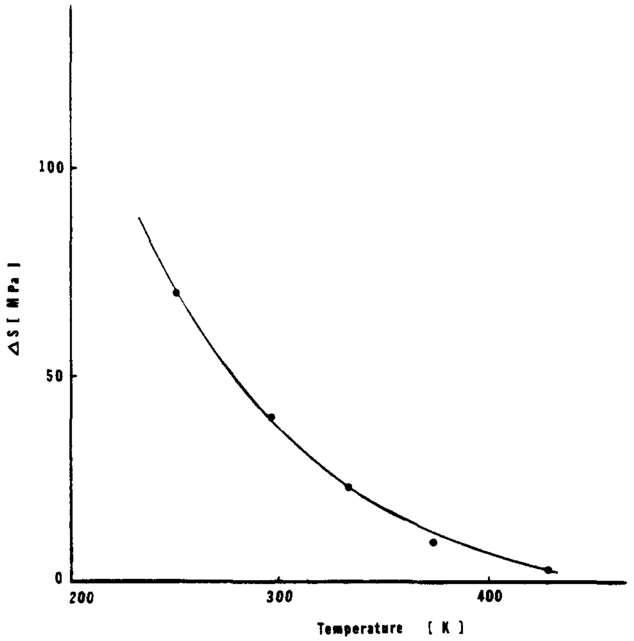

Figure 1. Hysteresis in stress for the $\alpha \rightarrow \beta$ transition in PBT plotted as a function of temperature. The solid dots are experimental results taken from ref 2, while the solid curve represents the results of our calculations.

We can assume that upon the formation of a β nucleus, the coupling between nearest-neighboring atoms on opposite sides of the wall separating the α and β phases changes from $V(\mathbf{R}_i - \mathbf{R}_j)$ to an average value of zero. Consequently, we take σ, multiplied by some characteristic area, to be given by $-V(\mathbf{R}_i - \mathbf{R}_j)$ as given by eq 11. Then, it follows from eq 11 and 12 that

$$\sigma(T) = c_1 - c_2 T$$

where c_1 and c_2 are adjustable positive constants such that $c_1 > c_2 T_M$. From eq 8, the temperature dependence of the hysteresis width in PBT is given by

$$\Delta S = (a - bT)^2/T \tag{13}$$

where a and b are constants satisfying $a > bT_M$ and related to c_1 and c_2 by

$$a = 2c_1\left(\frac{2L^2}{pk_B\Delta L}\right)^{1/2}, \quad b = 2c_2\left(\frac{2L^2}{Pk_B\Delta L}\right)^{1/2}$$

The requirement that $a > bT_M$ is due to the fact that $|V(\mathbf{R}_i - \mathbf{R}_j)|$ decreases linearly with increasing temperature far below the melting point but drops rapidly in the vicinity of the melting temperature.

The variation of ΔS with T as predicted by eq 13 for the choice

$$a^2 = 73 \text{ GPa K} \qquad b^2 = 0.30 \text{ MPa K}^{-1}$$

agrees very well with experimental measurements of Brereton et al.[2] as shown in Figure 1. The above choice of a and b satisfies the condition that $a > bT_M$ and corresponds to a value of σ of 2×10^{-3} J m^{-2} at room temperature for $p \sim 30$, giving a critical-size nucleus of about 18 chains.

The temperature dependence of the difference in energy, ΔV, between the two phases is expected to be a slowly decreasing function of T, which we could then represent as $\Delta V_0 - cT$ with $c \ll \Delta V_0/T_M$. Because of thermal expansion, the area per chain is a slowly increasing linear function of T. Thus we expect $\Delta V/A$ to decrease slowly and linearly with increasing T. Equation 6 for the critical stress can thus be written as

$$S^*_{\alpha\beta} = (a' - b'T) + \Delta S/2 \tag{14}$$

where the expression for ΔS in eq 8 has been used, and a' and b' are treated as adjustable positive constants. Using eq 13 for ΔS, we then find that $S^*_{\alpha\beta}$ can be expressed as

$$S^*_{\alpha\beta} = D_1 - D_2 T + a^2/2T \tag{15}$$

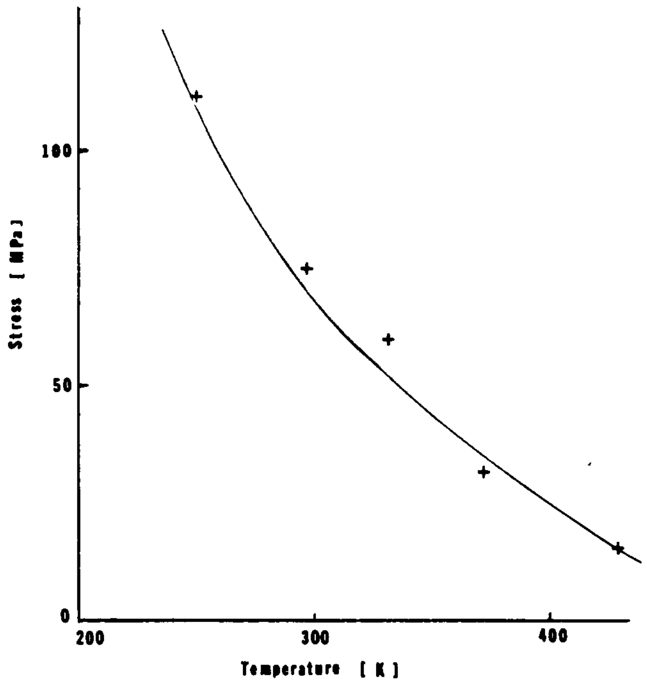

Figure 2. Temperature dependence of the critical stress shown for the onset of the $\alpha \rightarrow \beta$ transition in PBT. The plus signs are taken from the experimental results of ref 2, while the solid curve is a prediction based on the observed hysteresis width reported in the same paper.

with D_1 and D_2 constants.

The fact that the only term in eq 15 that is not linear in T arises directly from the contribution of the hysteresis width ΔS to eq 14 allows us to make a concrete prediction: the curvature of a plot of ΔS with temperature should be exactly twice that of a temperature plot of the critical stress $S^*_{\alpha\beta}$. This prediction is tested in Figure 2, in which the experimental values of Brereton et al.[2] for the critical stress are shown. The solid line represents half the hysteresis width found experimentally in the same study but with a term linear in temperature added to fit the line to the data at the two end points. The agreement is close enough to suggest that the nucleation and growth hypothesis may have some validity.

The values of D_1 and D_2 used to fit Figure 2 yield a value of 1.2 kJ/mol per monomer unit for ΔV. This number is consistent with the requirement that $-SA\Delta L + \Delta V$ be negative for nucleation to occur. Such a requirement places an upper bound on ΔV. The observation that the transition proceeds at room temperature at 75 MPa indicates that $\Delta V < 1.6$ kJ/mol per monomer. This number, incidentally, is considerably less then the value of 25 kJ/mol per monomer suggested by the molecular energy calculation of Yokouchi et al.[7]

We have examined a number of mechanisms that might affect the critical stress and hysteresis width for the $\alpha \rightarrow \beta$ transition in PBT. While contributions to the entropy from changes in phonon frequencies at the transition and internal stresses caused by morphological effects may play some role, they do not appear capable of accounting for the observed temperature dependence of the critical stress. A model of nucleation and growth, on the other hand, appears consistent with the observed data in that a predicted relation between the critical stress and the width of the hysteresis loop is obeyed.

Acknowledgment. We gratefully acknowledge support from the Materials Research Group program of the National Science Foundation through Grant DMR 84-17875.

Registry No. PBT (copolymer), 26062-94-2; PBT (SRU), 24968-12-5.

References and Notes

(1) Datye, V. K.; Taylor, P. L. *Macromolecules* **1985**, *18*, 671.
(2) Brereton, M. G.; Davies, G. R.; Jakeways, R.; Smith, T.; Ward, I. M. *Polymer* **1978**, *19*, 17.
(3) Tashiro, K.; Nakai, Y.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1980**, *13*, 137.
(4) Stambaugh, B.; Lando, J. B.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1063.
(5) Menzik, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2173.
(6) Stambaugh, B.; Koenig, J. L.; Lando, J. B. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1053.
(7) Yokouchi, M.; Sakakibara, K.; Chatani, Y.; Tadokoro, M.; Tanaka, T.; Yoda, Y. *Macromolecules* **1976**, *9*, 266.
(8) Merz, W. J. *Phys. Rev.* **1954**, *95*, 690.

Comparing the Flory Approach with the DiMarzio Theory of the Statistical Mechanics of Rodlike Particles

Walter R. Romanko* and Stephen H. Carr

Departments of Chemical Engineering and Materials Science and Engineering and the Materials Research Center, Northwestern University, Evanston, Illinois 60208.

Received August 24, 1987; Revised Manuscript Received November 6, 1987

ABSTRACT: Three descriptions of the rod orientation in the Flory lattice model for rods (generalized to a continuum) are compared in an athermal system with the more accurate DiMarzio model for rodlike particles in a continuum. The Flory-type rod orientation distribution functions yield distributions quite similar to the DiMarzio distribution. The Flory-type distribution function obtained from the rod orientation expression $(y - 1) = (x - 1) \sin \theta$ can be used in the DiMarzio entropy equation at a calculational advantage to yield entropies which are virtually indistinguishable from the original. Flory-type nematic and isotropic entropies differ from the DiMarzio entropies, giving slightly different phase equilibria. A solution to the "entropy catastrophe" for rods is explained in terms of the improper use of a one-dimensional boundary condition in the third dimension.

Introduction

The study of liquid crystals has become quite an important area of research in the past two decades. It is because of certain molecular anisotropies that a fluid displays liquid crystalline properties.[1] One of the simplest shape anisotropies resulting in liquid crystalline order is that of the rigid rodlike molecule or macromolecule. Various approaches of determining the implications of the impenetrability of these particles have been employed to model the thermodynamics of these rigid rodlike particles.