$$^0F \simeq \tfrac{1}{2}(2\pi)^{d/2} \tag{26a}$$

$$g^* \simeq (\pi^2/4)\epsilon \tag{26b}$$

and for $d = 3$, we obtain the crude result

$$^0F \simeq 2.46$$

Thus for large x, we find

$$F_{\text{theor}}(x) = 2.46x^{1.309\pm0.006} \tag{27}$$

and, using the conversion formula (12) we obtain in this way

$$G_{\text{theor}}(x) \simeq 1.51x^{1.309\pm0.06} \qquad x \gg 1 \tag{28}$$

Again, we see that there is a good agreement between this expression and the experimental result (14). The experimental value of ν obtained by writing $1/(3\nu - 1) = 1.32_5$, namely

$$\nu_{\text{exptl}} = 0.585 \tag{29}$$

is slightly smaller than expected, but crossover effects or polydispersity effects may well explain this fact.

IV. Conclusion

The predictions of renormalization theory concerning the behavior of the osmotic pressure of long chains in good solvents seem to agree with the experimental results, with one exception concerning the ratio ρ of the third virial coefficient to the square of the second virial coefficient. Polydispersity effects or the fact that the polymer is not infinitely long may explain this discrepancy. Anyway, more work is needed to obtain a really precise description of the universal function that describes the asymptotic behavior of the osmotic pressure.

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$$R_G^2/R^2 = 0.157 \pm 0.002 = \tfrac{1}{6}(1 - 0.06 \pm 0.01)$$

(Wall and Erpenbeck[17])

$$R_G^2/R^2 = 0.155 \pm 0.001 = \tfrac{1}{6}(1 - 0.07 \pm 0.01) \quad \text{(Domb[18])}$$

More recently, similar results have been found by McCrackin, Mazur, and Guttman.[19] These values are smaller than the theoretical values (see eq 8 and 11). However, these "experimental values" are not completely reliable. Weill and des Cloizeaux[20] have shown that R_G approaches the asymptotic limit more slowly than R. This effect appears clearly in the results of McCrackin, Mazur, and Guttman,[19] who have found different (effective) indices for R and R_G. Owing to this fact, the ratio R_G^2/R^2 is probably, in many cases, underestimated.

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Thermodynamics of Crystallization in a Model Polymer Network

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ABSTRACT: A new thermodynamic theory of crystallization in polymer networks subjected to a constant deformation was formulated. Many drastic model assumptions used by other authors were abandoned, and the effect of junction displacement caused by crystallization was taken into account. A variety of crystallite types with respect to morphology size and orientation were allowed to coexist in a partially crystalline network. The free energy of such a network was calculated on the basis of the rubber elasticity theory, and the equilibrium state of the network was found by minimization of the free energy with respect to crystallinity variables. The average equilibrium degree of crystallinity and a change in stress due to equilibrium crystallization were determined. Example computations were performed for a uniaxial deformation and a tetrafunctional regular network composed of Gaussian chains of equal contour lengths.

Introduction

Polymer crystallization seems to be one of the most important problems in polymer physics. It has been established that in the case of un-cross-linked polymers, kinetic factors play a dominant role in crystallization.[1] On the contrary, it is usually presumed that crystallization of polymer networks is mostly controlled by thermodynamics. We have made an attempt to formulate a new thermodynamic theory of crystallization in polymer networks subjected to a constant deformation. Several theories on this subject have been published. The most fundamental paper was presented by Flory in 1947.[2]

A few drastic assumptions were involved in the original Flory theory. All crystallites were assumed to have the

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same morphology (fully extended chains), size, and orientation. The process of crystallization was not allowed to affect the end-to-end vectors of the network chains. These assumptions are not quite justified and efforts have been made to abandon them. Smith[3] modified Flory's theory to account for different crystallite orientations. Wu[4] developed the theory for chain-folded crystallization. None of these theories included the effect of junction displacements caused by crystallization. This effect was not taken into account in many other theories (Roe, Smith, and Krigbaum,[5] Baranov and Elyashevich,[6] and Gaylord[7]). The importance of junction mobility in the crystallization process was noticed in the paper of Jarecki and Ziabicki.[8] However, their model network, based on the Flory–Rehner tetrahedron, seems to be oversimplified. The second assumption used in almost all theories was to imply equal sizes and morphologies of crystallites. The exceptional treatment has been recently presented by Allegra.[9] The author considered the coexistence of extended-chain crystallites of different size.

In our paper we shall abandon the important, but not quite justified assumptions mentioned above. A broad class of crystallite types will be allowed to appear simultaneously in a partially crystallized network. The choice of crystallite sizes and morphologies will be based on a thermodynamic criterion. Furthermore, we shall assume a more realistic model of the network. In this model positions of internal junctions of the network will be affected by the crystallization process. Our discussion will be confined to the most fundamental properties of crystallizing network: free energy, stress, and degree of crystallinity.

Model Assumptions

In some polymer systems crystallization may be assumed as having an intrachain nature. This assumption is justified for helix–coil transitions in polypeptides or cross-linked polymers mixed with linear chains. In the latter case the assumption of intrachain crystallization of network chains seems to be correct because the chains do not interact with one another. If the foregoing assumption is valid, the effects of crystallization correspond to partial stiffening of chains. The state of each crystallizing chain can be described by the end-to-end vector of the chain ($\mathbf{h}$), the end-to-end vector of the crystallite ($\mathbf{r}$), the contour length of the chain (l), and the degree of crystallinity (s), defined as the ratio of the contour length of the crystalline part to the total contour length of the chain ($s = l_{\text{cryst}}/l$).

Let us now discuss assumptions involved in the method of calculation of free energy changes accompanying the process of intrachain crystallization. For the sake of simplicity we shall consider a single-chain system. The free energy change is due to transition from a fully amorphous chain, with end-to-end vector $\mathbf{h}$, to a partially crystalline chain, with end-to-end vector $\mathbf{h}'$. Although it is easy to calculate the free energy of a crystal or that of a fully amorphous chain, it is not obvious that the free energy change for a mixed system can be obtained. The important point is that one cannot compare free energies of *different systems* unless the method of free energy calculation for both systems is defined uniquely and consistently. At first glance, it seems improper to treat the free energy change due to the amorphous part as a different between the free energy of the amorphous subchain of a partially crystallized chain and the free energy of the initial totally amorphous chain (these are different systems).

The problem discussed may be easily solved when the crystallization process is formally divided into three steps, as shown in Figure 1. Two intermediate states are involved in this treatment, i.e., states involving unconstrained amorphous and partially crystalline chain. The free energy of crystallization may be written in the form

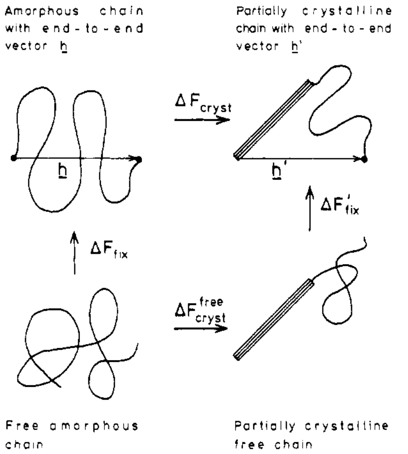

Figure 1. Various states of a single polymer chain. ΔF_{cryst}, $\Delta F_{\text{cryst}}^{\text{free}}$, ΔF_{fix}, and $\Delta F_{\text{fix}}'$ are free energy changes accompanying transitions indicated by arrows.

$$\Delta F_{\text{cryst}} = \Delta F_{\text{fix}} + \Delta F_{\text{cryst}}^{\text{free}} + \Delta F_{\text{fix}}' \qquad (1)$$

where ΔF_{fix} and $\Delta F_{\text{fix}}'$ are free energy changes caused by imposing constraints (fixed end-to-end vectors $\mathbf{h}$ or $\mathbf{h}'$) on a free-end chain. Both of them refer to the same system (fully amorphous chain or amorphous subchain) and can be easily calculated. $\Delta F_{\text{cryst}}^{\text{free}}$ is the free energy of crystallization for a free chain. It has a proper physical meaning and is independent of deformation.

In this paper we define entropy as the logarithm of configurational probability multiplied by the Boltzmann constant. This assumption allows us to put the free energy of a freely jointed, unconstrained chain equal to zero. Equation 1 can be rewritten as follows:

$$\Delta F_{\text{cryst}} = \Delta F_{\text{cryst}}^{\text{free}} + F^{\text{am}}(\mathbf{h}') - F^{\text{am}}(\mathbf{h}) \qquad (2a)$$

or

$$\Delta F_{\text{cryst}} = \Delta F_{\text{cryst}}^{\text{free}} + \Delta F^{\text{am}} \qquad (2b)$$

where $F^{\text{am}}(\mathbf{h})$ and $F^{\text{am}}(\mathbf{h}')$ are the free energies of the amorphous part in the two terminal states $\mathbf{h}$ and $\mathbf{h}'$, respectively. It is important to note that ΔF^{am} does not express the free energy change in any single system. It describes systematically derived difference of the free energies of two *different* systems, viz., that of the initial amorphous chain and that of its amorphous part after crystallization. The uniqueness of ΔF^{am} results from the cancellation of the two equal terms related to the free energy of a freely jointed, unconstrained chain. If these terms were not equal, eq 2a,b would not be correct.

It may be proved that eq 2b holds true also in the case of polymer networks. Thus we arrive at the conclusion that the free energy of crystallization consists of two terms—one, $\Delta F_{\text{cryst}}^{\text{free}}$, depending on the state of crystallinity and physical properties of the polymer chains, and the other, ΔF^{am}, controlled by the deformation of the amorphous part of the sample.

We shall focus our attention on the deformation-dependent term ΔF^{am}. Its importance is obvious in the case of deformation-induced crystallization. Furthermore, ΔF^{am} is the only term influenced by the network structure (topology, contour lengths).

If crystallite orientations and lengths are assumed constant, it can be easily understood that the amorphous part of the crystallizing network behaves like another network. The problem is how to describe this newly formed network.

The most general description in the "one crystallite per chain" case would require three scalar and three vector variables, i.e., three contour lengths, l_{am}', l_{am}'', and l_{cryst}, and three end-to-end vectors, $\mathbf{h}_{\mathrm{am}}'$, $\mathbf{h}_{\mathrm{am}}''$, and $\mathbf{r}$, because crystallization divides the chain into two amorphous parts and one crystalline part. For fixed positions of the chain ends ($\mathbf{h}$ = constant), constant crystallite orientation and length ($\mathbf{r}$ = constant, l_{cryst} = constant), only two of these variables are independent. We can choose them to be contour length and end-to-end vector of the one amorphous part of the chain—l_{am}' and $\mathbf{h}_{\mathrm{am}}'$. It is worth noticing that these variables are an internal property of the chain configuration. Therefore we can simplify the calculations to be performed in the next section for the whole network by first integrating the configurational statistics of the chains over their internal degrees of freedom (l_{am}' and $\mathbf{h}_{\mathrm{am}}'$) which are independent of the positions of network junctions. If the two amorphous parts of the chain obey Gaussian statistics, this task can be easily achieved. It is well-known that the statistics of a partially crystalline chain resulting from the integration over all possible configurations of one amorphous part of the chain is identical with that of a single chain with contour length $l = l_{\mathrm{am}}' + l_{\mathrm{am}}''$ and end-to-end vector $\mathbf{h} = \mathbf{h}_{\mathrm{am}}' + \mathbf{h}_{\mathrm{am}}'' = \mathbf{h} - \mathbf{r}$. Further on, we may formally treat partially crystalline chains as if the crystallites were located near one of their ends. The results would be the same as if the crystallites were randomly located along the chains and the amorphous parts of the chains were free to take any of their configurations. These statements hold true provided that Gaussian statistics of amorphous subchains is valid, which is an approximation, becoming better for longer subchains.

On the basis of foregoing considerations we are allowed to treat the amorphous part of the crystallizing network as a new amorphous network. The previously defined parameters $\mathbf{h}$, $\mathbf{r}$, s, and l must be given for all network chains if a complete description of the network is required. There is no need to specify locations of the crystallites within the chains however. We shall adopt results of the amorphous network theory and proceed to the calculation of the free energy for a partially crystallized network. Then equilibrium properties will be derived from the free energy change occurring due to crystallization.

Free Energy of Crystallization: Amorphous Part Contribution

At this point what we need is an appropriate expression for the free energy of the amorphous network. Let us follow the main ideas introduced by James and Guth[10] in their theory of rubber elasticity. The fundamental concept is to treat a network as having mobile internal junctions and fixed junctions on a surface subjected to deformation. Each network configuration is well defined by end-to-end vectors ($\mathbf{h}_{ij}$) of all chains. We may choose one of these configurations ($\mathbf{h}_{ij}^0$) as a reference configuration. In any other configuration end-to-end vectors are given by the following formula:

$$\mathbf{h}_{ij} = \mathbf{h}_{ij}^0 + \mathbf{u}_j - \mathbf{u}_i \tag{3}$$

where vectors $\mathbf{u}_i$ ($i = 1, ..., N$) are displacements of network junctions from their positions in the reference configuration. Obviously, $\mathbf{u}_i$ are different from zero for internal junctions only.

We shall introduce some simplifying assumptions. The first is that chain segments do not interact with one another (within the whole system). The second is that all chains obey Gaussian configurational statistics. In the system with internal energy equal to zero, the Helmholtz free energy is solely determined by the entropy term. This leads to the following expression for free energy:

$$F = -kT \times \ln \left\{ \int ... \int \prod_{i,j} \frac{\exp\left[-\frac{3}{2} \frac{(\mathbf{h}_{ij}^0 + \mathbf{u}_j - \mathbf{u}_i)^2}{l_{ij}a_s} \right]}{(l_{ij}a_s)^{3/2}} \, \mathrm{d}\mathbf{u}_1 ... \mathrm{d}\mathbf{u}_N \right\} + \text{constant} \tag{4}$$

The value of the constant appearing in eq 4 is dependent on the infinitesimal fluctuations of surface junctions (we shall assume that these fluctuations are independent of deformation and crystallinity of the network). The contour length of the chain attached to the junctions i,j and the length of the statistical segment are denoted, respectively, by l_{ij} and a_s.

It can be easily seen that the integral in eq 4 is the partition function of the Gaussian network with $3N$ degrees of freedom, viz., $\mathbf{u}_1, \mathbf{u}_2, ..., \mathbf{u}_N$. To simplify calculation of the partition function, it is convenient to introduce the so-called connectivity matrix. Its elements are defined as follows:

$$\epsilon_{ik} = \sum_j a_s/l_{jk} \qquad \text{for } i = k \tag{5a}$$

$$\epsilon_{ik} = -a_s/l_{ik} \qquad \text{for } i \neq k \tag{5b}$$

$$\epsilon_{ik} = \epsilon_{ki} \tag{5c}$$

Integration in eq 4 can be easily performed. The result is

$$F = -kT \ln \left[\left(\frac{\pi}{3/2} \right)^{3N/2} \frac{\exp(-F^*/kT)}{\det \epsilon} \right] \tag{6}$$

where F^* is the minimum of the exponent appearing in the integrand in eq 4 multiplied by $-kT$ with respect to vectors $\mathbf{u}_i$, $i = 1, ..., N$. The foregoing result can be obtained by diagonalization of the quadratic form appearing in the exponent in eq 4 before integration. However, it is necessary to assume that integration limits over $\mathbf{u}_i$ ($i = 1, ..., N$) are extended to the entire space. This approximation is justified because the integrand has a sharp maximum and quickly vanishes when approaching physical boundaries of the integration space.

Minimization of the exponent in eq 4 is equivalent to finding the most probable configuration of the network. The necessary condition for a minimum reads

$$\bigwedge_j \frac{\partial}{\partial \mathbf{u}_j} \left[\sum_{i,k} \epsilon_{ik} \frac{\mathbf{u}_i \mathbf{u}_k}{a_s^2} - 2 \sum_i \mathbf{b}_i \frac{\mathbf{u}_i}{a_s} + \sum_{\substack{i,k \\ i<k}} \left\{ \frac{(\mathbf{h}_{ik}^0)^2}{l_{ik}a_s} + \ln \frac{l_{ik}}{a_s} \right\} \right] = 0 \tag{7}$$

where $\mathbf{b}_i = \sum_{j \neq i} \mathbf{h}_{ij}^0 / l_{ij}$. Equation 7 yields values of the most probable displacements of the network junctions

$$\mathbf{u}_k^* = \sum_i (\epsilon^{-1})_{ki} \mathbf{b}_i a_s \tag{8}$$

and the minimum exponent

$$\frac{F^*}{{}^3\!/_2 kT} = \sum_{\substack{i,k \\ i<k}} \left[\frac{(\mathbf{h}_{ik}^0)^2}{l_{ik}a_s} + \ln \frac{l_{ik}}{a_s} \right] - \sum_{i,k} (\epsilon^{-1})_{ki} \mathbf{b}_i \mathbf{b}_k \tag{9}$$

Using symmetry properties of ϵ, $\mathbf{h}_{ij}$, and l_{ij} ($i, j = 1, ..., N$), one can replace the summation over junctions in formula 9 by the summation over chains or, what is equivalent, by the summation over pairs of junctions. We rewrite eq 9 as follows:

$$\frac{F^*}{{}^3\!/_2kT} = -\sum_{(i,l)}\sum_{(k,m)}[(\epsilon^{-1})_{ik} + (\epsilon^{-1})_{lm} - (\epsilon^{-1})_{im} - (\epsilon^{-1})_{kl}]\frac{\mathbf{h}_{il}{}^0\mathbf{h}_{km}{}^0}{l_{il}l_{km}} + \sum_{(i,k)}\left[\frac{(\mathbf{h}_{ik}{}^0)^2}{l_{ik}a_s} + \ln\frac{l_{ik}}{a_s}\right] + \text{constant} \quad (10)$$

The free energy defined in eq 4 is related to minimum exponent F^* by eq 6, i.e.

$$F = F^* + kT\ln(\det\epsilon) + \text{constant} \quad (11)$$

The foregoing treatment allows description of the behavior of an amorphous network during deformation. In most of physical experiments the deformation of the sample is applied through a surface. In the theoretical approach of James and Guth this is equivalent to the displacement of surface junctions. This effect enters the present formalism via the reference configuration: deformation induces changes into the reference configuration. If the sample is subjected to a homogeneous deformation, it is sufficient to replace $\mathbf{h}_{ij}{}^0$ by $\Lambda\mathbf{h}_{ij}{}^0$ (where Λ is the deformation gradient tensor) to satisfy the constraints imposed on the fixed surface junctions.

At this point we are able to return to the problem of the free energy of crystallization. As already discussed, the amorphous part of the crystallizing network can be formally treated as a new amorphous network. The following changes take place in the amorphous part of the network during its crystallization: chain contour lengths are shortened, $l_{ik} \rightarrow (1 - s_{ik})l_{ik}$; end-to-end vectors in the reference configuration are modified, $\mathbf{h}_{ij}{}^0 \rightarrow \mathbf{h}_{ij}{}^0 - \mathbf{r}_{ij}$. The change in contour lengths affects also the connectivity matrix ($\epsilon \rightarrow \tilde{\epsilon}$).

The reference configuration may be arbitrarily chosen from the whole set of configurations which satisfy constraints imposed on surface junctions. For the sake of simplicity we shall choose the reference configuration such that

$$\Lambda\sum_j\sum_j \mathbf{h}_{ij}{}^0/l_{ij} = 0 \quad (12)$$

From eq 8 it comes that this choice coincides with the most probable configuration (i.e., one leading to F^*).

It is convenient to introduce a new notation. Let us number the chains by subscripts $i = 1, ..., M$ and denote by i_1 and i_2 terminal junctions of the ith chain. From now on we shall use the new variables $\mathbf{H}_i$, $\mathbf{R}_i$, and s_i defined as

$$\mathbf{H}_i = \mathbf{h}_{i_1i_2}{}^0/(l_{i_1i_2}a_s)^{1/2} \quad (13a)$$

$$\mathbf{R}_i = \mathbf{r}_{i_1i_2}/(l_{i_1i_2}a_s)^{1/2} \quad (13b)$$

$$s_i = s_{i_1i_2} \quad (13c)$$

From eq 10 and 13 we obtain the free energy of the amorphous part of the network in the form

$$\frac{F^{\text{am}}}{{}^3\!/_2kT} = -\sum_{i,k}^{M} a_{ik}\frac{s_i\mathbf{H}_i - \mathbf{R}_i}{1 - s_i}\,\frac{s_k\mathbf{H}_k - \mathbf{R}_k}{1 - s_k} + \sum_i^M\left[\frac{(\mathbf{H}_i - \mathbf{R}_i)^2}{1 - s_i} + \ln(1 - s_i)\right] + \ln(\det\tilde{\epsilon}) + \text{constant} \quad (14a)$$

where

$$a_{ik} = \frac{(\tilde{\epsilon}^{-1})_{i_1k_1} + (\tilde{\epsilon}^{-1})_{i_2k_2} - (\tilde{\epsilon}^{-1})_{i_1k_2} - (\tilde{\epsilon}^{-1})_{i_2k_1}}{(l_{i_1i_2}l_{k_1k_2})^{1/2}} \quad (14b)$$

After some rearrangements, the free energy change in the amorphous part of the network caused by crystallization results as

$$\frac{\Delta F_{\text{cryst}}{}^{\text{am}}}{{}^3\!/_2kT} = -\sum_i a_{ii}\frac{(s_i\mathbf{H}_i - \mathbf{R}_i)^2}{(1 - s_i)^2} - \sum_{i,k} a_{ik}\frac{s_i\mathbf{H}_i - \mathbf{R}_i}{1 - s_i}\,\frac{s_k\mathbf{H}_k - \mathbf{R}_k}{1 - s_k} + \sum_i\left[\frac{s_i\mathbf{H}_i{}^2 - 2\mathbf{H}_i\mathbf{R}_i + \mathbf{R}_i{}^2}{1 - s_i} + \ln(1 - s_i)\right] + \ln\frac{\det\tilde{\epsilon}}{\det\epsilon} \quad (15)$$

The coefficients a_{ij} (dependent on the network structure and degree of crystallinity s_i, $i = 1, ..., M$) can be formally expressed in a more compact form. The connectivity matrix of the partially crystallized network $\tilde{\epsilon}$ is related to a similar matrix of a pure amorphous network, ϵ, as follows:

$$\tilde{\epsilon}_{ij} = \epsilon_{ij} + \sum_k(x_{ik}a_s/l_{ik}) \qquad \text{for } j = i \quad (16a)$$

$$\tilde{\epsilon}_{ij} = \epsilon_{ij} - x_{ij}a_s/l_{ij} \qquad \text{for } j \neq i \quad (16b)$$

where

$$x_{i_1i_2} = s_{i_1i_2}/(1 - s_{i_1i_2}) \equiv x_i$$

From the simple rules of differentiation of determinants it follows

$$\partial\ln(\det\tilde{\epsilon})/\partial x_{i_1i_2} = [(\tilde{\epsilon}^{-1})_{i_1i_1} + (\tilde{\epsilon}^{-1})_{i_2i_2} - (\tilde{\epsilon}^{-1})_{i_1i_2} - (\tilde{\epsilon}^{-1})_{i_2i_1}]\frac{a_s}{l_{i_1i_2}} = a_{ii} \quad (17a)$$

and

$$\frac{\partial^2\ln(\det\tilde{\epsilon})}{\partial x_{i_1i_2}\,\partial x_{j_1j_2}} = -a_{ij}{}^2 \quad (17b)$$

It is important to note that the connectivity matrix affects the free energy of crystallization only via the determinant. $\det\tilde{\epsilon}$ is a function of the crystallinity variables s_i or x_i, $i = 1, ..., M$.

The determinant of the connectivity matrix may be expressed as an explicit function of the variables x_i. It follows from eq 16 that $\det\tilde{\epsilon}$ is a polynomial function of x_i:

$$\det\tilde{\epsilon} = \det\epsilon\sum_k\frac{1}{k!}\sum_{\alpha_1,...,\alpha_k} A_{\alpha_1,...,\alpha_k}{}^0x_{\alpha_1}x_{\alpha_2}...x_{\alpha_k} \quad (18)$$

In the above formula $A_{\alpha_1,...,\alpha_k}{}^0$ is a minor of the determinant of the matrix $a_{ij}{}^0 \equiv a_{ij}|_{x_1=x_2=...=x_M=0}$, where only k columns and rows, viz., $\alpha_1, ..., \alpha_k$, are left. The summation denoted by the prime extends over different subscripts $\alpha_1, \alpha_2, ..., \alpha_k$; $\alpha_l \neq \alpha_m$. Due to eq 18 we arrive at the conclusion that the determinant of the connectivity matrix, $\det\tilde{\epsilon}$, in the given state of crystallinity depends on the coefficient matrix $[a_{ij}{}^0]$ for the amorphous network. The coefficients $a_{ij}{}^0$ are determined by network topology and contour lengths of the network chains.

At the first stage it seems to be much too complicated a task to discuss the problem of crystallization in its most general form, i.e., including all coefficients $a_{ij}{}^0$. We shall introduce a simplifying assumption and we shall neglect the nondiagonal elements of the matrix $[a_{ij}{}^0]$. This approximation may be justified by the following argument. From eq 8 it can be easily seen that the effect of crystallization on the change in the most probable end-to-end vector of the ith chain is given by

$$\Delta\mathbf{H}_i{}^* \equiv \frac{\mathbf{u}_{i_1}{}^* - \mathbf{u}_{i_2}{}^*}{l_ia_s} = \sum_j a_{ij}\frac{s_j\mathbf{H}_j - \mathbf{R}_j}{1 - s_j} \quad (19)$$

In the general case, the position of each junction is affected by crystallization of all chains in the system. It is intuitively understood that when crystallites are small and widely separated from one another (in the sense of network topology), $\Delta\mathbf{H}_i^*$ is mostly controlled by the state of crystallinity of the ith chain. Therefore

$$\Delta\mathbf{H}_i^* = \sum_j a_{ij} \frac{s_j\mathbf{H}_j - \mathbf{R}_j}{1 - s_j} \simeq a_{ii} \frac{s_i\mathbf{H}_i - \mathbf{R}_i}{1 - s_i} \tag{20}$$

for $s_1, s_2, ..., s_M \rightarrow 0$ and widely separated crystallites. This assumption is equivalent to the assumption of vanishing nondiagonal elements a_{ij}^0 for crystallizing chains. It is important to emphasize that we do not assume here that *all* coupling constants a_{ij}^0 are equal to zero for $i \neq j$, but only those *which refer to partially crystallized chains* (crystallites are assumed to be located far apart from one another). Of course, it would not be correct to neglect *other* coupling coefficients a_{ij}^0. Although they do not appear in eq 8 in explicit form, their values are determined by the network topology. A drastic assumption that all coefficients a_{ij}^0 vanish would affect the connectivity matrix ϵ and would result in complete chain decoupling. In our approach we assume that only some of coupling coefficients (those referring to partially crystallized chains) may be neglected without significant changes of the connectivity matrix determinant. This assumption is strictly correct when there is only one crystallite in the whole network, but it seems to be a reasonable approximation for many crystallites, provided that they are widely separated.

Having made the crucial assumption that $a_{ij}^0 = 0$ ($i \neq j$), we are now able to develop the theory a little bit further and to discuss the obtained results. From eq 17 and 18 we get the expression for the coefficients a_{ij} in the form

$$a_{ij} = 0 \qquad \text{for } i \neq j \tag{21a}$$

$$a_{ij} = \frac{a_{ii}^0}{1 + a_{ii}^0 x} = \frac{a_{ii}^0(1 - s_i)}{1 + s_i(a_{ii}^0 - 1)} \qquad \text{for } i = j \tag{21b}$$

Substituting $1 - a_{ii}^0$ by Γ_i^0 and making use of eq 15 and 21, we obtain the change in the free energy of the amorphous part of the network:

$$\frac{\Delta F_{\text{cryst}}^{\text{am}}}{{}^3\!/_2 kT} = \sum_i \left[\frac{s_i\mathbf{H}_i^2 - 2\mathbf{H}_i\mathbf{R}_i + \Gamma_i^0\mathbf{R}_i^2}{1 - s_i\Gamma_i^0} + \ln\,(1 - s_i\Gamma_i^0) \right] \tag{22}$$

We thus arrive at the point where the expression for $\Delta F_{\text{cryst}}^{\text{am}}$ contains a reduced set of parameters Γ_i^0 or a_{ii}^0, $i = 1, 2, ..., M$, dependent on the network topology only. It appears that in infinitely large networks, a_{ii}^0 is the contraction coefficient of ith chain. This interpretation implies that

$$0 < a_{ii}^0 \leq 1; \qquad 0 < \Gamma_i^0 \leq 1 \tag{23}$$

For infinitely large and regular networks consisting of chains of equal contour lengths, it follows from symmetry requirements that

$$\bigwedge_i \Gamma_i^0 = \Gamma = \text{constant} \tag{24}$$

Let us remind in this point that eq 22 does not involve the assumption of vanishing nondiagonal coupling coefficients a_{ij}^0 (for $i \neq j$) when there is only one crystallite in the whole network. In this case it is easy to trace how mobility of internal junctions of the network manifests itself. If the internal junctions had fixed positions, crystallization of a single chain would affect the free energy of this particular chain only, and the free energy change in the amorphous part would be equal to eq 22 with $\Gamma = 1$ (which can be easily proved). On the other hand, when the internal junctions are free to move, crystallization of a single chain affects the free energy of all other chains. The total free energy change of the amorphous part of the network is again given by eq 22, but with a smaller value of the parameter Γ ($\Gamma < 1$), dependent on the contraction coefficient of the crystallizing chain.

Mobility of internal junctions proves to be of special importance when the fully crystallized chain is considered. For fixed positions of the internal junctions of the network ($\Gamma = 1$) eq 22 diverges at $s = 1$, unless the crystallite morphology is such that the end-to-end vector of the entirely crystallized chain is identical with the end-to-end vector of the amorphous chain. This is understood because at $s \rightarrow 1$, the infinitely small amorphous part of the chain would be extremely deformed to match the fixed end-to-end vector. This effect does not appear when the junctions are mobile since they can always adjust their positions to reduce deformation of the short amorphous subchain. This must be accompanied by deformation of other chains, however. Equation 22 has a physical meaning even for a fully crystallized chain ($s = 1$), including the free energy change due to the deformation of all network chains. Moreover, it holds true independently of the configurational statistics assumed for amorphous subchain because the contribution to the free energy change from this subchain vanishes as $s \rightarrow 1$.

Total Free Energy of Crystallization

To complete considerations concerning the free energy of crystallization in a polymer network, we should specify the term $\Delta F_{\text{cryst}}^{\text{free}}$ in eq 2. Obviously, this free energy contribution does not depend on deformation and is solely determined by the state of crystallinity and physical properties of the chains. In general, $\Delta F_{\text{cryst}}^{\text{free}}$ consists of two terms—the bulk and the surface free energies. We shall adopt the simplest approach and assume that in the case of extended-chain morphology, there are no surface effects and the free energy change $\Delta F_{\text{cryst}}^{\text{free}}$ for a single chain is proportional to the degree of crystallinity of the chain. In the case of chain-folded crystallites we shall include a free energy of folding the chain. In the first approximation the number of folds can be assumed to be proportional to the end-to-end distance of the crystallite. Thus we obtain for a single-chain crystallization

$$\Delta F_{\text{cryst}}^{\text{free}} = -s\mu \qquad \text{for extended-chain morphology} \tag{25a}$$

$$\Delta F_{\text{cryst}}^{\text{free}} = -s\mu + q|\mathbf{R}| \qquad \text{for chain-folded morphology} \tag{25b}$$

The parameters μ and q may be calculated for specified values of the enthalpy of crystallization per unit volume (Δh), the melting temperature of an ideal, infinitely large crystal (T_{m}^0), the free energy of a single fold (q'), the fold width (b), and the volume of the fully crystallized chain (v). The appropriate formulas for μ and q are

$$\mu = \frac{v\Delta h}{{}^3\!/_2 kT_{\text{m}}^0} \frac{T_{\text{m}}^0 - T}{T} \tag{26a}$$

$$q = q'(la_s)^{1/2}/b \tag{26b}$$

In further analysis we shall confine ourselves to the case of crystallization at temperatures lower than T_{m}^0. It is equivalent to the condition $\mu > 0$.

Finally, we may conclude that the change in free energy when the network is transformed from the amorphous state to the partially crystalline state (parameters s_i) at the same macroscopic deformation takes the following form:

$$\frac{\Delta F_{\mathrm{cryst}}}{{}^3\!/_2 kT} = \sum_i \left[\frac{\Gamma_i^0 \mathbf{R}_i^2 - 2\mathbf{H}_i\mathbf{R}_i + s_i\mathbf{H}_i^2}{1 - s_i\Gamma_i^0} + \ln(1 - s_i\Gamma_i^0) + q_i|\mathbf{R}_i| - \mu s_i \right] \qquad (27)$$

The term $q|\mathbf{R}_i|$ in eq 27 must be omitted for extended-chain crystallites.

Equilibrium Crystallization under Constant Deformation

In the foregoing treatment the crystallinity variables s_i and $\mathbf{R}_i$, $i = 1, ..., M$, were assumed to be known a priori. There are very few experiments where all these variables could be controlled independently. From the experimental point of view, it seems to be useful to consider the state of equilibrium.

The equilibrium state of a partially crystallized network is the state of minimum free energy. Minimization of the free energy change given by eq 27 should be performed with respect to all crystallinity variables s_i and $\mathbf{R}_i$, $i = 1, ..., M$, keeping $\mathbf{H}_i$ constant. As can be easily seen, the crystallinity variables for different chains in eq 27 are not coupled. This is a consequence of the adopted approximation: $a_{ij}^0 = 0$ for $i \neq j$. This allows us to express the minimum free energy change as the sum of the contributions from crystallizing single chains. Thus the function to be minimized assumes the form

$$\frac{\Delta F_{\mathrm{cryst}}^1}{{}^3\!/_2 kT} = \frac{\Gamma\mathbf{R}^2 - 2\mathbf{H}\mathbf{R} + s\mathbf{H}^2}{1 - s\Gamma} + q|\mathbf{R}| - s\mu + \ln(1 - s\Gamma) \qquad (28)$$

We have omitted subscripts because they are unimportant at this stage of calculation. The instantaneous conclusion coming from the analysis of eq 28 is that minimization with respect to the orientation of the vector $\mathbf{R}$ gives an obvious result: $\mathbf{R}$ is parallel to $\mathbf{H}$. It simplifies the problem and we can replace the vector variables $\mathbf{H}$ and $\mathbf{R}$ by the scalars $H = |\mathbf{H}|$ and $R = |\mathbf{R}|$.

Minimization of the free energy should be performed within the range of physically admissible states. There are several evident constraints imposed on R and s. These are

$$0 \leq s \leq 1 \qquad (29a)$$

and

$$0 \leq R \leq s(l/a_s)^{1/2} \qquad (29b)$$

The equality $R = s(l/a_s)^{1/2}$ holds for crystallites with fully extended chains. It must be also noted that chain-folded crystallites cannot be formed with end-to-end distances less than one fold width b. The area of physically realizable states on the plane (R,s) is presented in Figure 2.

At this point a minimization procedure may be applied to the function defined by eq 28. It comes from an elementary calculation that there is no free energy minimum inside the triangle BDC defined by inequalities 29a,b. Thus the minimum value of the free energy is reached at the boundary. This suggests that three types of crystallites are to be expected in the equilibrium state: crystallites with fully extended chains, crystallites with a single fold, and folded crystallites comprising the whole chain. Let us omit long calculations and go directly to the conclusions (for a full discussion, see Appendix A).

It turns out that the function $\Delta F_{\mathrm{cryst}}^1$ restricted to the points on the line AB has a minimum there, independently of temperature (provided that $T < T_m^0$) and end-to-end distance H. This proves that if we are confined to the extended-chain morphology, there always exists a nonzero equilibrium crystallinity degree for all temperatures less than T_m^0. The minimum free energy calculated in this case need not be a minimum with respect to other crystallite structures. There can appear free energy minima on the lines BC and DC for certain values of T and H. Unfortunately, it is not possible to give a clear analytic criterion establishing which boundary minimum is the deepest one. This question can be answered by comparing numerical results. We may formally write down the minimum free energy change in the form

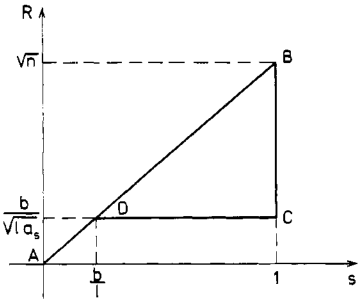

Figure 2. Physically admissible states of a partially crystalline chain on the (s,R) plane. AB, fully extended chain crystallites; BC, folded-chain crystallites comprising a whole chain; DC, folded-chain crystallites with one fold only; interior of the triangle DCB, folded-chain crystallites.

$$\Delta F_{\mathrm{cryst}}^{1*} = \min(\Delta F_{\mathrm{AB}}^*, \Delta F_{\mathrm{BC}}^*, \Delta F_{\mathrm{CD}}^*) \qquad (30)$$

where the function min (x,y,z) takes the value of its smallest argument.

The minimum free energy change for the whole network is given by the sum of minimum free energies $\Delta F_{\mathrm{cryst}}^{1*}$ (see eq 27). We must return to appropriate subscripts of $\Delta F_{\mathrm{cryst}}^1$. This can be easily done when we notice that the dependence of $\Delta F_{\mathrm{cryst}}^1$ on the chain number enters $\Delta F_{\mathrm{cryst}}^{1*}$ via the end-to-end distance H_i. Thus we obtain the free energy change during equilibrium crystallization in the form

$$\Delta F_{\mathrm{cryst}}^* = \sum_i^M \Delta F_{\mathrm{cryst}}^{1*}(H_i) \qquad (31)$$

The summation in eq 31 can be performed in the following way. Let us adopt an assumption that in the reference configuration of the undeformed amorphous network the square end-to-end distances of all chains are proportional to the average square distances in the un-cross-linked system. We shall choose the proportionality constant equal to $^1/_2$, that is, the value of the average contraction factor for infinitely large, regular tetrafunctional networks.[11] Furthermore, we shall assume that in the reference configuration, which is the most probable configuration, the sample is isotropic. This implies a uniform distribution of chain orientations. On the basis of these assumptions we may express the reduced end-to-end distances in the deformed network:

$$H_i = (2^{1/2}/2)|\Lambda \mathbf{e}_i|$$
$$|\mathbf{e}_i| = 1; \qquad i = 1, ..., M \qquad (32)$$

where vectors $\mathbf{e}_i$ are uniformly oriented in space. Since the network consists of a large number of chains, the summation in eq 31 may be well approximated by integration over the initial orientations of the chains. Thus we obtain

$$\Delta F_{\mathrm{cryst}}^* = \sum_i^M \Delta F^{1*}(H_i) \simeq \frac{1}{4\pi}\int \Delta F^{1*}\left(\frac{2^{1/2}}{2}|\Lambda \mathbf{e}|\right) \mathrm{d}\mathbf{e} \qquad (33)$$

The integration in eq 33 cannot be performed analytically.

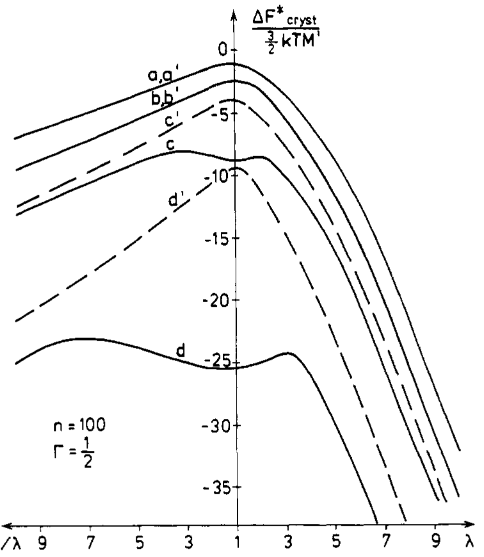

Figure 3. Free energy of an equilibrium crystallization $\Delta F_{\rm cryst}{}^*$ per crystallizing chain vs. deformation (deformation ratio λ for extension; $1/\lambda$ for compression). Dashed and continuous curves present, respectively, results for extended-chain crystallites and crystallites of various morphologies coexisting in the network. The plots were obtained for given values of supercooling $\Delta T = T_{\rm m}{}^0 - T$ (curves a,a′, ΔT = 1 K; curves b,b′, ΔT = 20 K; curves c,c′, ΔT = 40 K; curves d,d′, ΔT = 80 K). Crystallizing network was assumed to be regular, tetrafunctional, infinitely large ($\Gamma = {}^1/_2$), and consisting of chains comprising n = 100 statistical segments each.

Results to be presented in this paper are based on numerical computation.

The free energy change due to equilibrium crystallization is the fundamental quantity describing the crystallization process. There are also other characteristics especially interesting from the experimental point of view. One of them is stress. Normal stress difference is usually used as the measure of stress in incompressible materials. From now on we shall confine our discussion to the problem of crystallization in a network subjected to a homogeneous, uniaxial, isochoric deformation. The deformation gradient is of the form

$$\Lambda = \begin{bmatrix} 1/\lambda^{1/2} & 0 & 0 \\ 0 & 1/\lambda^{1/2} & 0 \\ 0 & 0 & \lambda \end{bmatrix} \tag{34}$$

In this case the proper measure of stress is the difference $p_{33} - p_{11}$, where p_{33} is the normal stress along the deformation axis and p_{11} is oriented in the perpendicular direction.

Let us follow the continuum mechanics approach and adopt a general relation between the stress tensor and the deformation gradient tensor Λ[12] as follows:

$$\mathbf{p} = \frac{1}{V}\Lambda^{\rm T}\frac{\partial F}{\partial \Lambda} \tag{35}$$

where V is the volume of the sample.

We shall focus our attention on stress changes due to crystallization. For the equilibrium crystallization the change in stress is given by the formula

$$\Delta(p_{33}{}^* - p_{11}{}^*) = \frac{1}{V}\Lambda^{\rm T}\frac{\partial\, \Delta F_{\rm cryst}{}^*}{\partial \Lambda}\bigg|_{33-11} = \frac{M'}{4\pi V}\left\{\Lambda^{\rm T}\frac{\partial}{\partial\Lambda}\int \Delta F_{\rm cryst}{}^{1*}\left(\left|\frac{2^{1/2}}{2}\Lambda \mathbf{e}\right|\right) \mathrm{d}\mathbf{e}\right\}_{33-11} \tag{36}$$

where M' is the number of crystallizing chains.

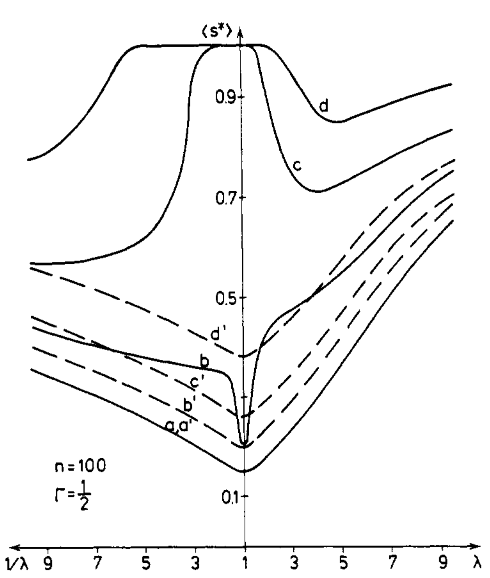

Figure 4. Average equilibrium degree of crystallinity of a crystallizing chain $\langle s^*\rangle$ vs. deformation (deformation ratio λ for extension; $1/\lambda$ for compression). Dashed and continuous curves present, respectively, results for extended-chain crystallites and crystallites of various morphologies coexisting in the network. The plots were obtained for given values of supercooling $\Delta T = T_{\rm m}{}^0 - T$ (curves a,a′, ΔT = 1 K; curves b,b′, ΔT = 20 K; curves c,c′, ΔT = 40 K; curves d,d′, ΔT = 80 K). Crystallizing network was assumed to be regular, tetrafunctional, infinitely large ($\Gamma = {}^1/_2$), and consisting of chains comprising n = 100 statistical segments each.

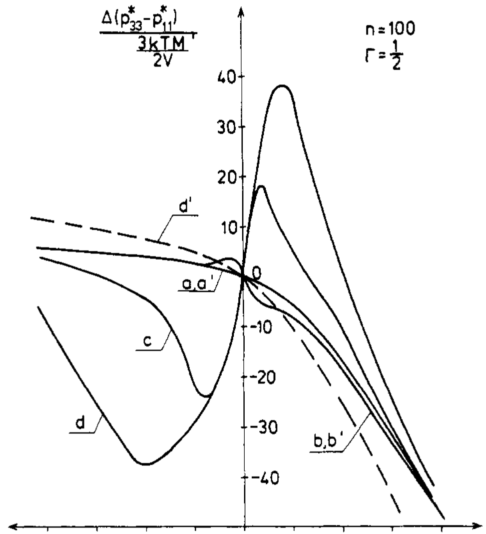

Figure 5. Change in normal stress difference due to equilibrium crystallization $\Delta(p_{33}{}^* - p_{11}{}^*)$ per unit concentration of crystallites in the sample, M'/V, vs. deformation (deformation ratio λ for extension; $1/\lambda$ for compression). Dashed and continuous curves present, respectively, results for extended-chain crystallites and crystallites of various morphologies coexisting in the network. The plots were obtained for given values of supercooling $\Delta T = T_{\rm m}{}^0 - T$ (curves a,a′, ΔT = 1 K; curves b,b′, ΔT = 20 K; curves c,c′, ΔT = 40 K; curves d,d′, ΔT = 80 K). Crystallizing network was assumed to be regular, tetrafunctional, infinitely large ($\Gamma = {}^1/_2$), and consisting of chains comprising n = 100 statistical segments each.

We may reverse the order of integration and differentiation. Then the integrand is easily calculable and we get

$$\Delta(p_{33}{}^* - p_{11}{}^*) = \frac{M'}{4\pi V}\left[\int \frac{\partial}{\partial H} \min\,(\Delta F_{\rm AB}{}^*, \Delta F_{\rm CD}{}^*, \Delta F_{\rm AC}{}^*)\Lambda^{\rm T}\frac{\partial H}{\partial \Lambda}\, \mathrm{d}\mathbf{e}\right]_{33-11} \tag{37}$$

It can be shown that

$$\Lambda^{\mathrm{T}}\frac{\partial H}{\partial \Lambda} = \frac{2^{1/2}}{2}\,\frac{\Lambda \mathbf{e} \otimes \Lambda \mathbf{e}}{|\Lambda \mathbf{e}|} \tag{38}$$

Calculation of the stress change $\Delta(p_{33}^* - p_{11}^*)$ must be performed numerically.

The last physical quantity to be discussed in this paper is the average degree of crystallinity of the crystallizing chain. The minimization procedure presented in the foregoing treatment gives as an intermediate result the equilibrium degree of crystallinity of each chain s_i^*. The value s_i^* of the variable s_i minimizes the free energy with respect to the ith chain crystallization. It is not of great importance to discuss the behavior of all s_i, $i = 1, ..., M'$, independently. Therefore we introduce the quantity $\langle s^* \rangle$, which is the arithmetic mean of s_i, $i = 1, ..., M'$. It may be presumed that $\langle s^* \rangle$ is directly related to the macroscopic degree of crystallinity.

Numerical Results

Formulas 33 and 36 and the definition of $\langle s^* \rangle$ make a basis for numerical computation. They cannot be performed before the values of the required parameters are specified. We shall present results for the polyethylene network. The following parameters have been taken from the literature: enthalpy of crystallization per unit volume $\Delta h = 3 \times 10^9$ erg/cm^3,[1] melting temperature of an ideal crystal $T_m{}^0 = 414.8$ K,[7] free energy of a single fold formation $q' = 4.5 \times 10^{-13}$ erg,[1] fold width $b = 5 \times 10^{-8}$ cm,[1] and length of the statistical chain segment 1.5×10^{-8} cm.[7] It has been assumed that the network considered is regular, infinitely large, and tetrafunctional and consists of chains of equal contour lengths. The contour length parameter is closely related to the number of statistical segments in a chain n. Results to be presented have been obtained for $n = 100$.

The assumptions concerning the network structure affect the parameters $\Gamma_i{}^0$. In the case of a regular network all $\Gamma_i{}^0$ have the same value. Tetrafunctionality implies $\Gamma = {}^1/_2$.

We shall not discuss the details of the numerical procedures. However, we must make clear one essential point. The free energy of crystallization in the equilibrium state has been defined as the minimum of energies ΔF_{AB}^*, ΔF_{CD}^*, and ΔF_{BC}^* (see eq 30). The choice depends on the deformation and temperature and is not restricted with respect to morphology. It is possible to perform the calculations with only one type of morphology allowed. We may assume that minimum free energy state is realized for extended-chain crystallites ($\Delta F_{\mathrm{cryst}}^* = \Delta F_{AB}^*$). The results of this type calculation will be presented by dashed lines. The comparison of the results obtained by the two methods discussed above (unrestricted morphology choice and morphology limited to extended chains) indicates the possibility of morphological transitions.

The results of free energy calculations are presented in Figure 3. The free energy change $\Delta F_{\mathrm{cryst}}^*$ per crystallizing chain divided by thermal energy ${}^3/_2kT$ is plotted vs. deformation. The deformation ratio λ has been chosen as the measure of deformation for extension. In the case of compression, $\Delta F_{\mathrm{cryst}}^*$ is plotted vs. $1/\lambda$. Different curves have been obtained for given values of supercooling ΔT, defined as the difference between the ideal melting temperature $T_m{}^0$ and the temperature of crystallization T.

For small supercoolings ΔT, free energy change $\Delta F_{\mathrm{cryst}}^*$ falls with increasing deformation, both for extension and compression (Figure 3). Dashed and continuous curves overlap fully. This leads to the conclusion that most of the crystallites have the form of extended chains. The thermodynamic stability of these crystallites is enhanced by the deformation because it is easier to form extended-chain crystallites when the chains are stretched. The results obtained for compression are not in contradiction since the average end-to-end distance is increased during isochoric compression of the sample as well.

At sufficiently low temperatures, important changes take place. The free energy change $\Delta F_{\mathrm{cryst}}^*$ increases with increasing deformation at deformation ratios below some critical value. Then $\Delta F_{\mathrm{cryst}}^*$ falls. There is also a large discrepancy between the dashed and continuous curves. It is clear that all these changes are due to the formation of chain-folded crystallites. The thermodynamic stability of folded-chain crystallites is reduced by deformation.

The morphology changes can be easily observed when the average equilibrium crystallinity degree of a crystallizing chain $\langle s^* \rangle$ is plotted vs. deformation (Figure 4). At small supercoolings $\langle s^* \rangle$ increases with an increase of deformation. When the temperature is sufficiently lowered, the crystallinity degree $\langle s^* \rangle$ decreases with increasing deformation, reaches a minimum, and rises again.

Interesting changes occur in the behavior of stress (see Figure 5). When the formation of extended-chain crystallites is preferred (small supercoolings or high supercoolings and large deformations), the change in stress caused by crystallization is negative for extension and positive for compression. Thus the resultant total stress (which is the sum of stress in the deformed amorphous network and stress change due to crystallization) is reduced by crystallization. "Relaxation" of stress occurs. Contrary effects are predicted for high supercoolings and small deformations where the resultant stress is increased by crystallization.

The foregoing results are additionally illustrated in Figures 6 and 7. The same quantities, i.e., the change in stress $\Delta(p_{33}^* - p_{11}^*)$ and the average equilibrium degree of crystallinity $\langle s^* \rangle$, are plotted as functions of supercooling for given values of deformation ratio.

Discussion

The fundamental aim of this paper has been to formulate a new thermodynamic approach to the problem of crystallization in polymer networks subjected to constant deformation. Earlier attempts to solve this problem were confined to single-chain crystallization because no mechanical coupling between chains was allowed. The most common assumption was to keep the positions of internal junctions fixed in space independently of the crystallization process. The problem was greatly simplified by some other approximations as well. It was usually taken for granted that crystallite morphology is the same for all chains. This does not seem to be true unless a specific system is considered. One may expect that both morphology and crystallite size should depend on the molecular deformation of the chain. Thus the sample should include a variety of different crystallites.

We managed to abandon these assumptions. The theory presented in this paper is based on a more realistic model. Its most important feature is that chains are arranged in the network structure—they are coupled with one another due to the existence of mobile internal junctions. The equilibrium state is found by minimization with respect to local crystallinity. Thus the chains may be characterized by different degrees of crystallinity and different crystallite morphologies. Network structure affects the results via the topology parameter Γ. Unfortunately, we were not able to solve the most general problem. The results presented concern the case of intrachain crystallization. There are several physical systems where this requirement is satis-

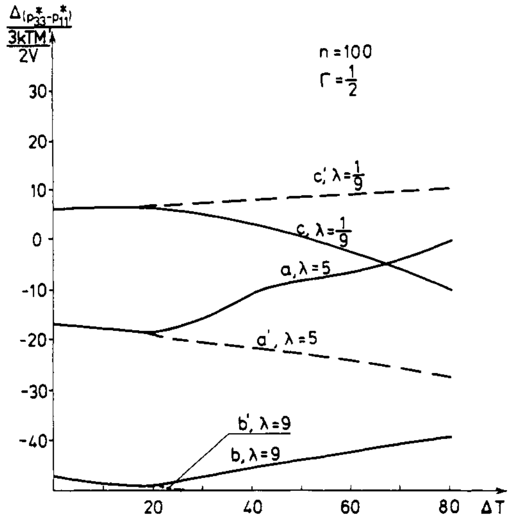

Figure 6. Change in normal stress difference due to equilibrium crystallization $\Delta(p_{33}^* - p_{11}^*)$ per unit concentration of crystallites, M'/V, vs. supercooling $\Delta T = T_m{}^0 - T$. Dashed and continuous curves present, respectively, results for extended-chain crystallites and various types of crystallites coexisting in the crystallizing network. The plots were obtained for given values of deformation ratio (curves a,a′, $\lambda = 9$; curves b,b′, $1/\lambda = 9$; curves c,c′, $\lambda = 5$). Crystallizing network was assumed to be regular, tetrafunctional, infinitely large ($\Gamma = {}^1/_2$), and consisting of chains comprising $n = 100$ statistical segments each.

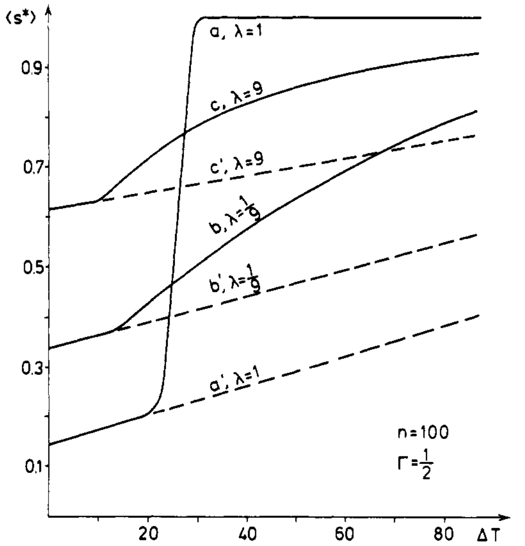

Figure 7. Average equilibrium degree of crystallinity of a crystallizing chain $\langle s^* \rangle$ vs. supercooling $\Delta T = T_m{}^0 - T$. Dashed and continuous curves present, respectively, results for extended-chain crystallites and crystallites of various morphologies coexisting in the crystallizing network. The plots were obtained for given values of deformation ratio (curves a,a′, $\lambda = 1$; curves b,b′, $1/\lambda = 9$; curves c,c′, $\lambda = 9$). Crystallizing network was assumed to be regular, tetrafunctional, infinitely large ($\Gamma = {}^1/_2$), and consisting of chains comprising $n = 100$ statistical segments each.

fied. The helix-coil transition in a polypeptide network is one example. The example chosen in this paper has been the crystallization of the network chains together with chains from an un-cross-linked material. The second approximation we could not abandon was to neglect direct dependence of the crystallinity state of a given chain on the crystallinity of all other chains. This assumption is justified when the crystallites are rare in the network, i.e., when they are widely separated from one another in the sense of network topology.

Although the theoretical model of the crystallization process was simplified, the numerical results are in qualitative agreement with experimental data.[13-16] Some of the theoretical predictions are of special interest.

The results suggest that morphology changes may occur when temperature and/or deformation changes. For temperatures close to $T_m{}^0$ the most stable crystallites are those with fully extended chains. At sufficiently low temperatures and small deformations, folded-chain crystallites may be preferable from the thermodynamic point of view. Fundamental properties of networks crystallized with mostly folded or mostly extended-chain crystallites are entirely different. The formation of extended-chain crystallites is accompanied by the reduction in the normal stress difference $(p_{33}^* - p_{11}^*)$ and the average equilibrium degree of crystallinity is an increasing function of deformation. In the case of folded-chain crystallites the opposite is true. Crystallization causes an increase of the normal stress difference. The average equilibrium degree of crystallinity is reduced by deformation. All these effects have been observed experimentally.[13-16] A part of the predictions confirms the results of previous theories.[4,6,7] The distinctive feature of our approach is that states consisting of different types of crystallites are allowed.

The theoretical formalism presented in this paper may be easily adopted in some problems other than crystallization. The theory may be applied in the case of block copolymer networks, where the chains consist of stiff and flexible components. The stiff part corresponds to the crystalline part in our model. The flexible component is equivalent to the amorphous part.

The problem of copolymer networks seems to be an interesting subject to be studied on the basis of the presented theory.

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Appendix A. Minimization of the Free Energy of Crystallization for a Network with a Single Crystallizing Chain

The change in free energy of a network with a single crystallizing chain was given by eq 28. The minimization prrocedure can be easily performed when new variables $\tilde{s}$ and $\tilde{R}$ are introduced as follows:

$$\tilde{R} = H/\Gamma - R$$
$$\tilde{s} = 1/\Gamma - s \qquad \text{(A.1)}$$

The new variables must satisfy conditions corresponding to inequalities 29a,b, i.e.

$$\tilde{R} = H/\Gamma - (1/\Gamma - \tilde{s})n^{1/2}$$
$$1/\Gamma - 1 \le \tilde{s} \le 1/\Gamma \qquad \text{(A.2a)}$$

for extended-chain crystallization and

$$H/\Gamma - (1/\Gamma - \tilde{s})n^{1/2} \le \tilde{R} \le H/\Gamma - B$$
$$1/\Gamma - 1 \le \tilde{s} \le 1/\Gamma - B/n^{1/2} \qquad \text{(A.2b)}$$

for folded-chain crystallization. B and n denote, respectively, reduced width of a single fold, $b/(la_s)^{1/2}$, and the number of statistical segments in a chain, l/a_s. The free energy change $\Delta F_{\text{cryst}}{}^1$ expressed by the new variables reads

$$\frac{\Delta F_{\text{cryst}}{}^1}{{}^3\!/_2 kT} = \frac{\tilde{R}^2}{\tilde{s}} - q\tilde{R} + \mu\tilde{s} + \ln\tilde{s} + C \qquad \text{(A.3)}$$

where

$$C = -\frac{H^2}{\Gamma} + q\frac{H}{\Gamma} - \mu\frac{1}{\Gamma} + \ln\Gamma$$

Necessary conditions for a minimum are

$$\partial\Delta F_{\mathrm{cryst}}{}^{1}/\partial\tilde{R} = 0$$

$$\partial\Delta F_{\mathrm{cryst}}{}^{1}/\partial\tilde{s} = 0 \tag{A.4}$$

From eq A.3 and A.4 we obtain

$$2\tilde{R}^{*}/\tilde{s} - q = 0$$

$$-\tilde{R}^{*2}/\tilde{s}^{*2} + \mu + 1/s^{*} = 0 \tag{A.5}$$

Thus

$$\tilde{R}^{*} = 2q/(q^{2} - 4\mu)$$

$$\tilde{s}^{*} = 4/(q^{2} - 4\mu) \tag{A.6}$$

The matrix of second derivatives is given by

$$\begin{bmatrix} \dfrac{2}{\tilde{s}} & -\dfrac{2\tilde{R}}{\tilde{s}^{2}} \\ -\dfrac{2\tilde{R}}{\tilde{s}^{2}} & +\dfrac{2\tilde{R}^{2}}{\tilde{s}^{3}} - \dfrac{1}{\tilde{s}^{2}} \end{bmatrix} \tag{A.7}$$

It can be seen from the analysis of matrix A.7 that the point $(\tilde{R},\tilde{s})$ does not correspond to a minimum of the function $\Delta F_{\mathrm{cryst}}{}^{1}$. Thus the minimum value of $\Delta F_{\mathrm{cryst}}{}^{1}$ is reached at the boundary of the region of admissible states. Equality signs hold true in formulas A.2a,b for the boundary points. From elementary calculations we can look for minimum values of $\Delta F_{\mathrm{cryst}}{}^{1}$ in the three boundary regions defined as (cf. Figure 2)

region CD

$$\tilde{R} = H/\Gamma - B, \qquad 1/\Gamma - 1 < \tilde{s} < 1/\Gamma - B/n^{1/2} \tag{A.8a}$$

region CB

$$\tilde{s} = 1/\Gamma - 1, \qquad H/\Gamma - n^{1/2} < \tilde{R} < H/\Gamma - B \tag{A.8b}$$

region AB

$$\tilde{R} = n^{1/2}\tilde{s} - (n^{1/2} - H)/\Gamma, \qquad 1/\Gamma - 1 < \tilde{s} < 1/\Gamma \tag{A.8c}$$

We shall denote the corresponding minima by $\Delta F_{\mathrm{CD}}{}^{*}$, $\Delta F_{\mathrm{CB}}{}^{*}$, and $\Delta F_{\mathrm{AB}}{}^{*}$. A simple minimization procedure yields for $\mu > 0$

$$\frac{\Delta F_{\mathrm{CD}}{}^{*}}{{}^{3}\!/_{2}kT} = [1 + 4\mu(H/\Gamma - B)^{2}]^{1/2} + \ln\frac{[1 + 4\mu(H/\Gamma - B)^{2}]^{1/2} - 1}{2\mu} - q(H/\Gamma - B) + C \tag{A.9a}$$

for $B\Gamma + (1 - \Gamma)[\mu + \Gamma/(1 - \Gamma)]^{1/2} < H < B\Gamma + [1 - (B/n^{1/2})\Gamma]\left[\mu + \dfrac{\Gamma}{1 - (B/n^{1/2})\Gamma}\right]^{1/2}$

$$\frac{\Delta F_{\mathrm{CD}}{}^{*}}{{}^{3}\!/_{2}kT} = \frac{(H - B\Gamma)^{2}}{\Gamma(1 - \Gamma)} - q\left(\frac{H}{\Gamma} - B\right) + \mu\frac{1 - \Gamma}{\Gamma} + \ln\frac{1 - \Gamma}{\Gamma} + C \tag{A.9b}$$

for $H \le B\Gamma + (1 - \Gamma)[\mu + \Gamma/(1 - \Gamma)]^{1/2}$

and

$$\frac{\Delta F_{\mathrm{CB}}{}^{*}}{{}^{3}\!/_{2}kT} = \frac{1 - \Gamma}{\Gamma}\left(\mu - \frac{q^{2}}{4}\right) + \ln\frac{1 - \Gamma}{\Gamma} + C \tag{A.10}$$

for $B + \dfrac{q}{2}(1 - \Gamma) < H < n^{1/2} + \dfrac{q}{2}(1 - \Gamma)$

Furthermore

$$\frac{\Delta F_{\mathrm{AB}}{}^{*}}{{}^{3}\!/_{2}kT} = \left[1 + 4(n + \mu)\left[\frac{n^{1/2} - H}{\Gamma}\right]^{2}\right]^{1/2} + \ln\frac{\left[1 + 4(n + \mu)\left[\dfrac{n^{1/2} - H}{\Gamma}\right]^{2}\right]^{1/2} - 1}{2(n + \mu)} - 2n^{1/2}\frac{n^{1/2} - H}{\Gamma} + C' \tag{A.11a}$$

for $H < n^{1/2} - (1 - \Gamma)[n + \mu + \Gamma/(1 - \Gamma)]^{1/2}$

and

$$\frac{\Delta F_{\mathrm{AB}}{}^{*}}{{}^{3}\!/_{2}kT} = \frac{(H - \Gamma n^{1/2})^{2}}{\Gamma(1 - \Gamma)} + \mu\frac{1 - \Gamma}{\Gamma} + \ln\frac{1 - \Gamma}{\Gamma} + C' \tag{A.11b}$$

for $H \ge n^{1/2} - (1 - \Gamma)[n + \mu + \Gamma/(1 - \Gamma)]^{1/2}$

where

$$C' = -H^{2}/\Gamma - \mu/\Gamma + \ln\Gamma \tag{A.12}$$

The formulas A.9 to A.11 give explicit expressions for the free energy minima occurring in regions CD, CB, and AB defined by (A.8a–c). However, it is not possible to give a general analytic criterion for which of these minima is the deepest one. This question must be answered on the basis of numerical computation.

Appendix B. Change in Stress due to Equilibrium Crystallization

The relation between free energy and stress was given by eq 35. For a particular case of equilibrium crystallization, the change in normal stress difference $\Delta(p_{33}{}^{*} - p_{11}{}^{*})$ is related to that in free energy via eq 36 or, in a more explicit form, via eq 37. As can be seen from the analysis of eq 37 and 38 the crucial point of stress calculation is the differentiation of free energy with respect to the variable H, which is the end-to-end distance of a crystallizing chain. We can perform this differentiation for the minimum free energies found in three boundary regions (see Appendix A) to obtain

$$\frac{\partial}{\partial H}\frac{\Delta F_{\mathrm{AB}}{}^{*}}{{}^{3}\!/_{2}kT} = \frac{1}{\Gamma}\left[2n^{1/2} - \frac{\left[1 + 4(n + \mu)\left[\dfrac{n^{1/2} - H}{\Gamma}\right]^{2}\right]^{1/2} + 1}{\dfrac{n^{1/2} - H}{\Gamma}}\right] + \frac{\partial C'}{\partial H} \tag{B.1a}$$

for $H < n^{1/2} - (1 - \Gamma)[n + \mu + \Gamma/(1 - \Gamma)]^{1/2}$

$$\frac{\partial}{\partial H}\frac{\Delta F_{\mathrm{AB}}{}^{*}}{{}^{3}\!/_{2}kT} = \frac{1}{\Gamma}\left[2n^{1/2} - 2\frac{n^{1/2} - H}{\Gamma}\,\frac{\Gamma}{1 - \Gamma}\right] + \frac{\partial C'}{\partial H} \tag{B.1b}$$

for $H \ge n^{1/2} - (1 - \Gamma)[n + \mu + \Gamma/(1 - \Gamma)]^{1/2}$

and

$$\frac{\partial}{\partial H}\frac{\Delta F_{\mathrm{CD}}{}^{*}}{{}^{3}\!/_{2}kT} = \frac{1}{\Gamma}\left[\frac{[1 + 4\mu(H/\Gamma - B)^{2}]^{1/2} + 1}{H/\Gamma - B} - q\right] + \frac{\partial C}{\partial H} \tag{B.2a}$$

$$\text{for}\quad B\Gamma + (1-\Gamma)\left[\mu + \frac{\Gamma}{1-\Gamma}\right]^{1/2} < H < B\Gamma + (1-\Gamma B/n^{1/2})\left[\mu + \frac{\Gamma}{1-\Gamma B/n^{1/2}}\right]^{1/2}$$

$$\frac{\partial}{\partial H}\,\frac{\Delta F_{\mathrm{CD}}^*}{{}^3\!/_2 kT} = \frac{1}{\Gamma}\left[2\left(\frac{H}{\Gamma} - B\right)\frac{\Gamma}{1-\Gamma} - q\right] + \frac{\partial C}{\partial H} \qquad \text{(B.2b)}$$

$$\text{for}\quad H < B\Gamma + (1-\Gamma)[\mu + \Gamma/(1-\Gamma)]^{1/2}$$

and

$$\frac{\partial}{\partial H}\,\frac{\Delta F_{\mathrm{BC}}^*}{{}^3\!/_2 kT} = \frac{\partial C}{\partial H} \qquad \text{(B.3a)}$$

$$\text{for}\quad \Gamma B + q(1-\Gamma)/2 < H < \Gamma n^{1/2} + q(1-\Gamma)/2$$

$$\frac{\partial}{\partial H}\,\frac{\Delta F_{\mathrm{BC}}^*}{{}^3\!/_2 kT} = \frac{1}{\Gamma}\left[2\left(\frac{H}{\Gamma} - B\right)\frac{\Gamma}{1-\Gamma} - q\right] + \frac{\partial C}{\partial H} \qquad \text{(B.3b)}$$

$$\text{for}\quad H < B\Gamma + q(1-\Gamma)/2$$

where

$$\partial C/\partial H = -2H/\Gamma + q/\Gamma \qquad \text{(B.4a)}$$

$$\partial C'/\partial H = -2H/\Gamma \qquad \text{(B.4b)}$$

The choice of the deepest free energy minimum (ΔF_{AB}^*, ΔF_{BC}^*, ΔF_{CD}^*) is based on the comparison of numerical results. This choice determines also which one of the free energy derivatives $\partial\Delta F_{\mathrm{AB}}^*/\partial H$, $\partial\Delta F_{\mathrm{BC}}^*/\partial H$, or $\partial\Delta F_{\mathrm{CD}}^*/\partial H$ has to be inserted into eq 38 to yield the change in normal stress difference caused by equilibrium crystallization.

References and Notes

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Theory of Density Fluctuations in the Glassy State: High and Low Temperatures

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ABSTRACT: A formal extension of the classical equilibrium theory of thermal density fluctuations to systems with nonvanishing chemical affinity has been given by Wendorff and Fischer. It has been evaluated explicitly by us earlier with the aid of our equation-of-state theory of the glassy state. The same methods are now applied to a polystyrene and a poly(methyl methacrylate) glass. In the range between $T_g - 50$ and T_g good agreement between theoretical prediction and measurements of Ruland and Wiegand ensues. These results once more demonstrate the only *partial* freeze-in of the theoretical free volume function in the glass transition. By means of the low-temperature equation of state, the approach of the thermal density fluctuation to the zero limit at $T = 0$ is derived. Experiment, however, indicates the onset of departures from theory in the region of the β process, which ultimately results in substantial residual contributions at $T = 0$. An analysis in terms of essentially temperature-independent inhomogeneities is given. The results indicate that these cannot be associated with the free volume quantity introduced in connection with the configurational thermodynamics of the glass. Instead, more numerous and smaller inhomogeneities must be invoked.

Introduction

We have recently derived expressions for the mean square thermal density fluctuations,[1] based on equation-of-state theory for the glassy state. The important structure parameter in this theory is a hole or free volume fraction h. In the equilibrium melt it is uniquely determined by the minimization of a configurational free energy. At the glass transition, a partial freeze-in process starts, which so far has been evaluated by a combination of equation-of-state measurements for glasses of specified formation history with theoretical expressions. Two alternative procedures have been employed. One involves the numerical solution of a partial differential equation derived from the free energy expression.[2] The other and approximate procedure requires the numerical solution of an algebraic equation.[3,4] For several polymers, the latter procedure only has been applied. For two poly(vinyl acetate) (PVAc) glasses on the other hand, a comparison of the two solutions shows numerically small differences in absolute values, albeit larger differences in the temperature coefficients of h. The results of the elaborate treatment were employed to compute the density fluctuations of PVAc in the range $T_g - 60 < T < T_g - 10$.[1] The limits are imposed by the range of validity of the numerical solutions of the differential equation. The results are consistent in the neighborhood of T_g with the approximation of Wendorff and Fischer[3] and derived from their general theory,[5] which forms also the basis for our theory. Their approximation involves the compressibility of the melt at T_g and should not be valid at lower temperatures.

For purposes of comparison, total intensity measurements for PVAc have only recently become available.[6] On

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