Thermodynamically controlled crystal orientation in stressed polymers: 1. Effects of strain energy of crystals embedded in an uncrosslinked amorphous matrix and hydrodynamic potential

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Thermodynamics is one of the factors which control the orientation distribution of polymer crystals. The present paper deals with crystal orientation in uncrosslinked polymer systems, in which small, isolated crystals are embedded in a viscous matrix. With transient effects neglected, and in the absence of the production of new crystals, orientation is controlled by the orientation-dependent free energy of an anisotropic crystal, $F(\underset{\sim}{\theta})$, and a hydrodynamic potential of the velocity field, $\Phi(\underset{\sim}{\theta})$. Example distributions for uniaxially stressed polyethylene are discussed. It has been shown that different mechanisms control crystal orientation depending on the stress difference $\Delta p = p_{33} - p_{11}$ applied, and the crystal shape factor, ϕ. At low stresses, Δp and high assymetry factors, ϕ, crystal orientation is practically controlled by the hydrodynamic potential. At high stresses and/or low asymmetry ratios it is the strain energy of anisotropic crystals, $F(\underset{\sim}{\theta})$, which is responsible for orientation distribution. In the intermediate range both mechanisms have to be considered.

INTRODUCTION

It is well known that physical and mechanical properties of crystalline polymers depend not only on the degree of transformation but also on the orientation of crystals developed during the formation and processing of the product. The orientation of crystals embedded in a stressed amorphous matrix can be controlled by four independent mechanisms: hydrodynamic, kinetic, diffusional and thermodynamic[1,2]. One of these possibilities is thermodynamically controlled orientation resulting from the orientation-dependent free energy of crystals embedded in a stressed amorphous matrix.

The stress in the matrix arises from deformation and orientation of polymer macromolecules induced by external forces. The stress leads to deformation of crystals. The deformation and free energy of such a crystal both depend on the orientation of the crystal with respect to the stress field.

In the case of zero nucleation rate (no crystallization) we can consider combined thermodynamic and hydrodynamic effects of orientation. The continuity equation for the angular distribution function of crystallities, $\Psi(\underset{\sim}{\theta})$, reduces to the homogeneous form[1,2]:

$$\partial\Psi/\partial t - \mathrm{div}_\theta\{\Psi \underset{\sim}{D}\,\mathrm{grad}_\theta\,[F(\underset{\sim}{\theta})/kT + \ln\Psi] + \Psi\dot{\underset{\sim}{\theta}}{}^0\} = 0 \qquad (1)$$

where t is time, $\underset{\sim}{\theta}$ is a vector composed of three Euler angles describing orientation of the crystal, $\underset{\sim}{D}$ is a rotational diffusion tensor and $F(\underset{\sim}{\theta})$ is the orientation-dependent free energy. Operators grad_θ and div_θ are defined in the Riemannian space. $\dot{\underset{\sim}{\theta}}{}^0$ is the hydrodynamic (convected) rotation velocity.

Generally, free energy, $F(\underset{\sim}{\theta})$, can be expressed as a sum of the orientation-dependent free energy of the crystal, $F_{cr}(\underset{\sim}{\theta})$ and the free energy of amorphous surroundings, $F_{am}(\underset{\sim}{\theta})$:

$$F(\underset{\sim}{\theta}) = F_{cr}(\underset{\sim}{\theta}) + F_{am}(\underset{\sim}{\theta}) \qquad (2)$$

Absence of the crystal–crystal interaction has been assumed here. If the free energy of amorphous surroundings, F_{am}, does not depend on crystal orientation, as is the case with crystals in an uncrosslinked polymer, then the orientation is controlled by the orientation-dependent free energy of the crystal, $F_{cr}(\underset{\sim}{\theta})$, in the absence of a hydrodynamic field. The steady-state solution $(\partial\Psi/\partial t = 0)$ of the orientation equation (1) can thus be written in the form:

$$\Psi_{st}^{th}(\underset{\sim}{\theta}) = C\exp[-F_{cr}(\underset{\sim}{\theta})/kT] \qquad (3)$$

where C is a normalization constant.

The dependence of crystal free energy, F_{cr} on its orientation $\underset{\sim}{\theta}$ is derived in the present paper. The stress field in the matrix has been determined assuming an affine deformation of polymer chain macromolecules. Example computations have been performed for polyethylene crystals in uniaxially stressed systems and distribution of crystal orientation has been calculated from equation (3).

Another source of an orientation-dependent potential is a hydrodynamic field in the viscous medium under steady-state flow. If the velocity field in the medium is potential, the corresponding potential, $\Phi(\underset{\sim}{\theta})$, which determines the velocity $\dot{\underset{\sim}{\theta}}{}^0$ in the orientation equation (equation 1) contributes to steady-state crystal orientation distribution in the same way as does strain energy of an isolated crystal, $F_{cr}(\underset{\sim}{\theta})$.

MODEL ASSUMPTIONS

A system containing a number of crystallites embedded in an amorphous matrix is considered. The crystallites are much smaller than the macroscopic dimensions of the system, but much larger than kinetic elements of the amorphous phase (statistical chain segments). Consequently, the amorphous matrix can be considered as a continuum surrounding small crystalline inclusions.

On the molecular level the amorphous matrix may exist as a network of chains connected by crosslinks, or it can be a system of free, uncrosslinked chain molecules (polymer solutions, melts). An uncrosslinked amorphous phase (polymer solutions or melts) behaves as a viscous liquid. In such a case deformation of macromolecules may result from friction with solvent molecules (diluted solutions) and/or contact friction with surrounding chains (concentrated solutions, melts) during flow.

As a result of molecular deformation, an elastic force $\underset{\sim}{f}$, directed along the end-to-end vector $\underset{\sim}{h}$, arises between the ends of the macromolecule. This force is responsible for the 'local' stress $\underset{\sim}{p}$ in the vicinity of the chain[3]:

$$\underset{\sim}{p}(\underset{\sim}{h}) = v\underset{\sim}{f}\underset{\sim}{h}^T - p_0\underset{\sim}{I} \tag{4}$$

where v is number of chains in unit volume of the amorphous phase, p_0 is the ambient pressure and $\underset{\sim}{I}$ is the unit tensor. The elastic force $\underset{\sim}{f}$ is defined as:

$$\underset{\sim}{f}(\underset{\sim}{h}) = \frac{\partial \mathscr{F}(\underset{\sim}{h},T)}{\partial h}\frac{\underset{\sim}{h}}{h} \tag{5}$$

where $\mathscr{F}$ is the free energy of the chain macromolecule and T is the absolute temperature.

For a Gaussian chain with neglected intramolecular interactions the elastic force can be expressed as a linear function of the end-to-end vector[4]:

$$\underset{\sim}{f}(\underset{\sim}{h}) = 3\frac{kT}{\langle h_0^2\rangle}\underset{\sim}{h} \tag{6}$$

where the statistical parameter $\langle h_0^2\rangle$ is mean square end-to-end distance of a free chain.

In the case of non-Gaussian chains (Kuhn–Grün distribution) with intramolecular interactions, in the rotational isomeric approximation the expression for elastic force assumes the form[5]:

$$\underset{\sim}{f}(\underset{\sim}{h}) = (kT/\langle h_0^2\rangle)\left[\sum_1^\infty A_i(\epsilon_0 h^2/\langle h_0^2\rangle)^{i-1}\right]\underset{\sim}{h} \tag{7}$$

In the above formula the parameter $\langle h_0^2\rangle$ is a limiting value of the mean square end-to-end distance for a chain consisting of freely jointed segments of length a_0:

$$\langle h_0^2\rangle = la_0, \qquad a_0 = \lim_{\substack{h\to 0\\ l\to\infty}} a(h,l) \tag{8}$$

where a is the length of the statistical segment of a deformed chain ($h \neq 0$) with contour length l.

Coefficients A_i in equation (7) are:

$$A_i = \sum_{j=i}^{\infty} A_{ij}\epsilon_0^{j-i} \tag{9}$$

where the parameter ϵ_0 is a reciprocal number of statistical chain segments N_0

$$\epsilon_0 = N_0^{-1} = a_0/l \tag{10a}$$

The coefficients A_{ij} derived for the case of chains of chains consisting of three types of isomers (*trans*, *gauche*–1, *gauche*–2) read[5]:

$$A_{11} = 3 \tag{10b}$$

$$A_{12} = 3\sin^2(\alpha/2)(1-\cos\beta)(1+2w)^2/[1+(1+\cos\beta)w]^3 \tag{10c}$$

$$A_{22} = 9(1/5 - A_{12}/6)/2 \tag{10d}$$

α denotes the valence angle, and β is the rotation angle for the *gauche* isomer measured from the position of the *trans* isomer. It was assumed, that the rotational potential is symmetric with respect to the *trans* isomer. Then

$$w = \exp(-\Delta E/kT) \tag{10e}$$

where ΔE is the difference in energy between *gauche* (E_g) and *trans* (E_t) isomers

$$\Delta E = E_g - E_t \tag{10f}$$

The stress tensor at any point in the amorphous matrix is the average of the 'local' stress tensor $\underset{\sim}{p}$ with respect to the actual distribution of end-to-end vectors, $W(\underset{\sim}{h})$:

$$\langle \underset{\sim}{p}\rangle = \iiint \underset{\sim}{p}(\underset{\sim}{h})W(\underset{\sim}{h})\mathrm{d}\underset{\sim}{h} \tag{11}$$

Assuming affine deformation of end-to-end vectors **h**, the stress tensor ⟨**p**⟩ can be written in the form:

$$\langle \underset{\sim}{p}\rangle = \frac{vkT}{(\det\underset{\sim}{\Gamma})^{1/2}}\left[\frac{A_1}{3}\frac{\langle h_*^2\rangle}{\langle h^2\rangle}\underset{\sim}{\Gamma} + \frac{A_2}{15}\frac{\langle h_*^4\rangle}{\langle h_0^2\rangle^2}(2\underset{\sim}{\Gamma}^2 + \underset{\sim}{\Gamma}\mathrm{tr}\underset{\sim}{\Gamma})\epsilon_0 + \ldots\right] - p_0\underset{\sim}{I} \tag{12}$$

where $\underset{\sim}{\Gamma}$ is the molecular deformation tensor

$$\underset{\sim}{\Gamma} = \underset{\sim}{\Lambda}\underset{\sim}{\Lambda}^T \tag{13}$$

and $\underset{\sim}{\Lambda}$ is the displacement gradient tensor. $\langle h_*^{2n}\rangle$ ($n = 1, 2, 3$) are average values for an undeformed system of real chains (networks, melts, solutions), i.e. one in which $\underset{\sim}{\Gamma} = \underset{\sim}{I}$.

Stresses in the amorphous matrix induce deformation of crystallites embedded in the matrix. This deformation is much smaller than the deformation of the matrix itself due to crystal moduli which are three or four orders of magnitude higher than those for an amorphous material. Despite their morphology, in the range of stresses discussed, the crystallites can be considered as uniform bodies, exhibiting anisotropic, linear elasticity. This is true even when nonlinear deformations of the amorphous matrix are involved.

To formulate the boundary conditions, it is assumed that on the surface of each inclusion (crystal) acts a uniform stress field, σ, the same as in the amorphous phase without any crystallites.

$$\underset{\sim}{\sigma}(\partial\underset{\sim}{X}) = \langle\underset{\sim}{p}\rangle = \text{constant} \tag{14}$$

where $\partial\underset{\sim}{X}$ denotes the boundary of the crystallite. In fact, the presence of crystals perturbs the uniformity of the stress field in the matrix. These perturbations, however, can be neglected when crystals are not too numerous and small as compared with the macroscopic dimensions of the whole sample.

DEFORMATION ENERGY OF A UNIFORM, ANISOTROPIC BODY

Stress ($\underset{\sim}{\sigma}$) and strain ($\underset{\sim}{e}$) fields within a crystalline body with boundary conditions given by equation (14) can be determined from the equations of the theory of elasticity. Three equations of equilibrium, with neglected inertia read:

$$\sigma_{ij,j} = 0 \text{ (for } i,j = 1,2,3) \qquad (15)$$

and the continuity equations:

$$e_{ij,kl} + e_{kl,ij} - e_{ik,jl} - e_{jl,ik} = 0 \qquad (16)$$

where σ_{ij}, e_{ij} are components of the stress and strain tensors respectively, expressed in an external, Cartesian coordinate system.

We can treat the polymer crystal embedded in a stressed amorphous matrix as a body which obeys Hooke's Law, and assume the linear constitutive equation

$$\underset{\sim}{e} = \mathscr{S} : \underset{\sim}{\sigma} \qquad (17)$$

valid for any point in the body. The fourth-valence compliance tensor $\mathscr{S}$ is given in the same coordinate system as the stress tensor, and is constant in the whole volume of the body.

It can be found that the solution of equations (14)–(17) is a uniform stress field within the body considered, equal to the stress in the amorphous surroundings:

$$\underset{\sim}{\sigma}(\underset{\sim}{X}) = \underset{\sim}{\sigma}(\partial \underset{\sim}{X}) = \langle \underset{\sim}{p} \rangle \qquad (18)$$

Notice, however, that the assumptions of affine molecular deformation in the matrix and uniform deformation of the inclusion are incompatible with the continuity conditions of deformation on the boundary between the body and the amorphous matrix.

In the case of an isothermal and quasistatic deformation, one can calculate the free energy for a linearly elastic body, using the formula:

$$F = V \int \underset{\sim}{\sigma} : \mathrm{d}\underset{\sim}{e} = V \mathrm{tr}(\underset{\sim}{e} . \underset{\sim}{\sigma})/2 \qquad (19)$$

where V is volume of the body.

Based on the solution, equation (15), one can use Hooke's law, equation (17) to obtain

$$\underset{\sim}{e} = \mathscr{S} : \langle \underset{\sim}{p} \rangle \qquad (20)$$

Hence

$$F = V \mathrm{tr}[(\mathscr{S} \langle \underset{\sim}{p} \rangle \langle \underset{\sim}{p} \rangle] \qquad (21)$$

Usually, components of the compliance tensor $\mathscr{S}$ are expressed in the system of crystal main axes, so it is more convenient to write equation (21) in the same system. Each crystallite has different orientation with respect to the external coordinate system in which the stress tensor $\langle \underset{\sim}{p} \rangle$ was defined. Therefore, equation (21) should be applied separately to each body (crystal) by means of appropriate transformations to the system of main axes.

Let the main axes of the crystal form Eulerian angles $\underset{\sim}{\theta} = (\theta, \phi, \Psi)$ with respect to the external coordinate system. The stress tensor $\langle \underset{\sim}{p} \rangle$ under those conditions assumes the form:

$$\langle \underset{\sim}{p} \rangle \to \mathscr{R}(\underset{\sim}{\theta}) \langle \underset{\sim}{p} \rangle \mathscr{R}^{T}(\underset{\sim}{\theta}) \qquad (22)$$

where $\mathscr{R}$ is the appropriate rotation tensor.

With this result, the free energy can be written as:

$$F(\underset{\sim}{\theta}) = (V/2) \mathrm{tr}\{[\mathscr{S} : (\mathscr{R} \langle \underset{\sim}{p} \rangle \mathscr{R}^{T})] \mathscr{R} \langle \underset{\sim}{p} \rangle \mathscr{R}^{T}\} \qquad (23)$$

The free energy dependence on the orientation of the body embedded in the stressed continuum is therefore determined by the dependence of the rotation tensor $\mathscr{R}$ on the Eulerian angles. Knowing components of the tensor $\mathscr{S}$ from experimental studies[6] and the stress tensor $\langle \underset{\sim}{p} \rangle$ in the amorphous matrix, one can calculate the free energy of a crystal oriented at $\underset{\sim}{\theta}$. The stress tensor $\langle \underset{\sim}{p} \rangle$ can be measured or expressed in terms of the (affine) deformation of amorphous chains $\underset{\sim}{\Gamma}$. Applying equation (12) to the calculation of free energy, one obtains:

$$F = F(\underset{\sim}{\theta}, \underset{\sim}{\Gamma}) \qquad (24)$$

DEFORMATION OF A BODY WITH UNIAXIAL SYMMETRY

Orientation of a uniform, linear, uniaxially symmetric body is completely described by two angles θ and ϕ (*Figure 1*). The strain $\underset{\sim}{e}$ for such a body can be written in the form:

$$\underset{\sim}{e} = K_1(\mathrm{tr}\underset{\sim}{\sigma})\underset{\sim}{I} + K_2\underset{\sim}{\sigma} + K_3(\underset{\sim}{r}^T\underset{\sim}{\sigma}\underset{\sim}{r})\underset{\sim}{I} + \tfrac{1}{2}K_4[(\mathrm{tr}\underset{\sim}{\sigma})\underset{\sim}{r}\underset{\sim}{r}^T + (\underset{\sim}{r}^T\underset{\sim}{\sigma}\underset{\sim}{r})\underset{\sim}{I}]$$
$$+ \tfrac{1}{2}K_5[\underset{\sim}{r}(\underset{\sim}{\sigma}\underset{\sim}{r})^T + \underset{\sim}{\sigma}\underset{\sim}{r}\underset{\sim}{r}^T] \qquad (25)$$

where K_i ($i = 1, 2, \ldots 5$) are elasticity constants and **r** is the unit vector of the symmetry axis. In the matrix notation (ref 7) the compliance tensor $\mathscr{S}$ is represented by a 6 x 6 square matrix s_{ij}. For a uniaxially symmetric body the matrix is determined by five independent material constants:

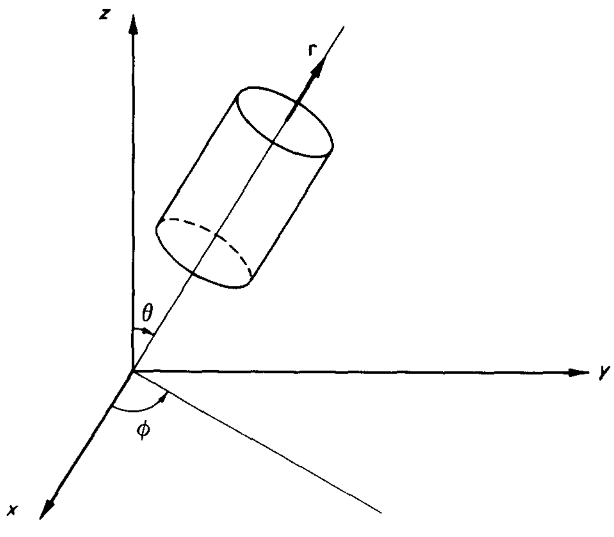

Figure 1 Crystal with rotational symmetry oriented at θ, ϕ in an external coordinate system. $\underset{\sim}{r}$ is a unit vector of the symmetry axis

$$s_{ij} = \begin{bmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ \cdot & s_{11} & s_{13} & 0 & 0 & 0 \\ \cdot & \cdot & s_{33} & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & s_{44} & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & s_{44} & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & 2(s_{11}-s_{13}) \end{bmatrix} \qquad (26)$$

Comparison of the Hooke's law written in matrix and tensor forms leads to the following expressions for the elasticity constants:

$$K_1 = s_{12} \qquad (27a)$$

$$K_2 = s_{11} - s_{12} \qquad (27b)$$

$$K_3 = s_{11} - s_{33} - 2s_{13} - s_{44} \qquad (27c)$$

$$K_4 = 2(s_{13} - s_{12}) \qquad (27d)$$

$$K_5 = 2s_{12} - 2s_{11} + s_{44} \qquad (27e)$$

Substitution of the stress tensor, equation (18), into equation (25) yields the free energy of a uniform, uniaxially symmetric crystallite with symmetry axis oriented at angles θ and ϕ.

$$F(\theta,\phi) = (V/2)\{K_1(\mathrm{tr}\langle \underset{\sim}{p}\rangle)^2 + K_2\,\mathrm{tr}\langle \underset{\sim}{p}\rangle^2 + K_3[\mathrm{tr}(\underset{\sim}{rr}^T\langle \underset{\sim}{p}\rangle)]^2 + K_4(\mathrm{tr}\langle \underset{\sim}{p}\rangle\mathrm{tr}(\underset{\sim}{rr}^T\langle \underset{\sim}{p}\rangle) + K_5\mathrm{tr}(\underset{\sim}{rr}^T\langle \underset{\sim}{p}\rangle^2)\} \qquad (28)$$

In deriving equation (28) it was taken into account that, generally:

$$\mathrm{tr}(\underset{\sim}{rr}^T\langle \underset{\sim}{p}\rangle) = \underset{\sim}{r}^T\langle \underset{\sim}{p}\rangle\underset{\sim}{r}, \qquad \langle \underset{\sim}{p}\rangle^T = \langle \underset{\sim}{p}\rangle,$$

$$\mathrm{tr}(\underset{\sim}{rr}^T\langle \underset{\sim}{p}\rangle^2) = \mathrm{tr}(\langle \underset{\sim}{p}\rangle\underset{\sim}{rr}^T\langle \underset{\sim}{p}\rangle) \qquad (29)$$

Expression (28) for the free energy reduces to simpler form when the stress tensor $\langle \underset{\sim}{p}\rangle$ also has an uniaxial symmetry:

$$\langle \underset{\sim}{p}\rangle = \begin{bmatrix} p_{11} & 0 & 0 \\ 0 & p_{11} & 0 \\ 0 & 0 & p_{33} \end{bmatrix} \qquad (30)$$

In the latter case the free energy of the body depends only on the single angle θ.

$$F(\theta)/V = b_0 + b_1\cos^2\theta + b_2\cos^4\theta \qquad (31)$$

Constants b_i depend on the compliance constants of the body and on the components of the stress tensor $\langle \underset{\sim}{p}\rangle$.

$$2b_0 = (K_1\mathrm{tr}\langle \underset{\sim}{p}\rangle + K_4p_{11})\mathrm{tr}\langle \underset{\sim}{p}\rangle + K_2\mathrm{tr}\langle \underset{\sim}{p}\rangle^2 + (K_3 + K_5)p_{11}^2 \qquad (32a)$$

$$b_1 = (p_{33} - p_{11})[(K_4 + K_5)p_{33}/2 + (K_3 + K_4 + K_5/2)p_{11}] \qquad (32b)$$

$$b_2 = K_3(p_{33} - p_{11})^2/2 \qquad (32c)$$

Consequently, thermodynamically controlled angular distribution of uniaxial crystals in the uniform, uniaxially symmetric stress field can be described as:

$$\Psi_{st}^{th}(\underset{\sim}{\theta}) = C\exp[-A_{th}(\cos^2\theta + B\cos^4\theta)] \qquad (33)$$

where

$$A_{th} = b_1V/kT, \quad B = b_2/b_1 \qquad (34)$$

ORIENTATION OF ELLIPSOIDS IN A POTENTIAL HYDRODYNAMIC FIELD

We will compare the effects of thermodynamic orientation controlled by strain energy of crystals with an orientation of rotational ellipsoids governed by a hydrodynamic mechanism. The classical linear theory of suspensions of ellipsoids in a viscous medium[8–10] leads, for rotational ellipsoids, to the following orientation equation:

$$\partial\Psi/\partial t + \mathrm{div}_r[\Psi R\dot{\underset{\sim}{r}}^0 + D\,\mathrm{grad}\,\Psi] = 0 \qquad (35)$$

where $\dot{\underset{\sim}{r}}^0$ is the hydrodynamic (convected) rotation velocity expressed in the fixed coordinate system, and $\underset{\sim}{r}$ is a unit vector defining orientation of the symmetry axis of the ellipsoid (*Figure 2*). The constant R characterizes the shape of the ellipsoid:

$$R = (\rho^2 - 1)/(\rho^2 + 1) \qquad (36)$$

and $\rho = a/b$ is the axial ratio. D is the diffusion constant of the ellipsoid given by Debye formula:

$$D = kTZ(\rho)/V(\eta) \qquad (37)$$

η is the viscosity of the medium, and $Z(\rho)$ is a shape function:

$$Z(\rho) = \frac{\rho^2}{4(\rho^4 - 1)}\left[\frac{2\rho^2 - 1}{2\rho(\rho^2 - 1)^{1/2}}\ln\frac{\rho + (\rho^2 - 1)^{1/2}}{\rho - (\rho^2 - 1)^{1/2}} - 1\right] \text{ for } \rho > 1$$

$$Z(\rho) = \frac{\rho^2}{4(\rho^4 - 1)}\left[\frac{2\rho^2 - 1}{\rho(\rho^2 - 1)^{1/2}}\,\mathrm{arc\,tan}\left[\frac{(1 - \rho^2)^{1/2}}{\rho}\right] - 1\right] \text{ for } \rho < 1 \qquad (38)$$

If the flow of the medium is characterized by a symmetric velocity gradient ($\underset{\sim}{L} = \underset{\sim}{L}^T$), then the steady-state, hydrodynamically controlled orientation distribution of vectors $\underset{\sim}{r}$, can be described by:

$$\Psi_{st}^{hydro}(\underset{\sim}{r}) = C\exp[R\Phi(\underset{\sim}{r})/D] \qquad (39)$$

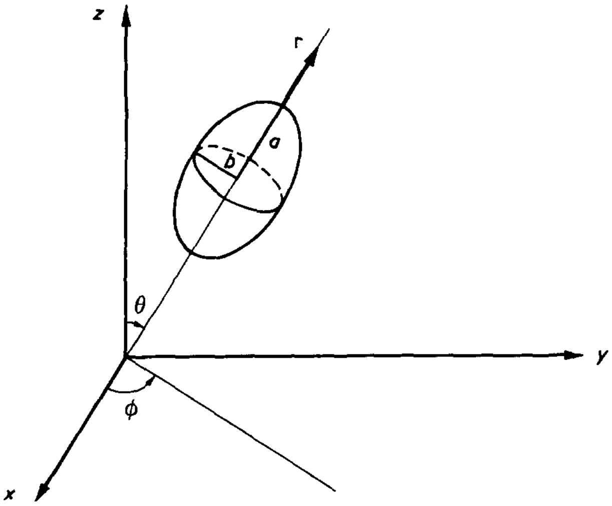

Figure 2 Rotational ellipsoid oriented at θ,ϕ in an external coordinate system. $\underset{\sim}{r}$ is a unit vector of the symmetry axis; *a* and *b* are axes of the ellipsoid

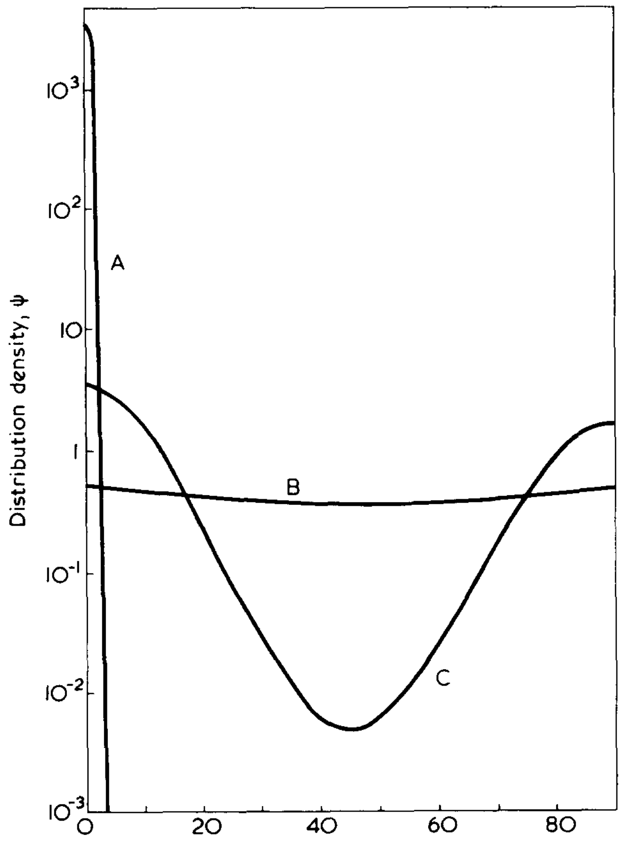

Figure 3 Thermodynamic orientation distributions, $\Psi(\underset{\sim}{\theta})$, of polyethylene crystal *c*-axis under uniaxial stress field, calculated (equation 33) for normal stress differences: A, $|\Delta p| = 10^9$; B, $|\Delta p| = 10^7$; C, $|\Delta p| = 10^8$ dyne/cm^2

where $\Phi(\underset{\sim}{r})$ is the potential of the velocity field and

$$\underset{\sim}{L} = \underset{\sim}{\nabla}(\nabla\Phi)^T \tag{40}$$

For suspensions of rotational ellipsoids subjected to uniaxial elongational flow (along *z*-axis) the distribution density function, Ψ_{st}^{hydro}, reduces to the function of the single angle θ (*Figure 2*). Then the potential Φ for an uncompressible fluid is:

$$\Phi(\theta) = q^*[1 - (3/2)\sin^2\theta]/2 \tag{41}$$

where q^* is the longitudinal velocity gradient.

In the case of a Newtonian fluid, which is characterized by the linear constitutive equation:

$$\underset{\sim}{p} + p_0\underset{\sim}{I} = 2\eta\underset{\sim}{L} \tag{42}$$

the steady-state hydrodynamic distribution, Ψ_{st}^{hydro}, of ellipsoids for the uniaxial elongation flow of fluid is controlled by the difference of normal stress components $\Delta p = p_{33} - p_{11}$, and reads:

$$\Psi_{st}^{hydro}(\theta) = C\exp(A_{hydro}\cos^2\theta) \tag{43}$$

where the dimensionless factor A_{hydro} is proportional to the stress difference Δp:

$$A_{hydro} = \phi(p)V\Delta p/kT \tag{44}$$

and $\phi(p) = R(p)/[4Z(p)]$

The factor A_{hydro} is positive for ellipsoids characterized by $p > 1$ (rods) under extensional stress ($\Delta p > 0$), or for discs ($p < 1$) under compression ($\Delta p < 0$), and negative for rods under compression or discs under extension.

Combination of the thermodynamic and hydrodynamic mechanisms leads to steady-state distribution Ψ_{st} dependent on the crystal free energy $F(\theta)$ and the potential $\Phi(\underset{\sim}{\theta})$:

$$\Psi_{st}^{th,hydro}(\underset{\sim}{\theta}) = C\exp[-F(\underset{\sim}{\theta})/kT + R\Phi(\underset{\sim}{\theta})/D] \tag{45}$$

The hydrodynamic term $kTR\Phi(\underset{\sim}{\theta})/D$ which appears in the equation (45) plays the role of an additional free energy, submitted in steady-state flow by viscous interaction of the potential hydrodynamic field with suspended asymmetric particles (crystals). The hydrodynamic contribution disappears when particles are spherically symmetrical ($R = 0$) or flow potential is zero ($\Phi = 0$), or viscous forces approach zero ($D \rightarrow \infty$).

EXAMPLE CALCULATIONS FOR POLYETHYLENE

Taking into account the elasticity constants estimated for polyethylene crystals by Stachurski and Ward[6], the stress-dependent parameters b_1 and b_2 (equation 32b and 32c) are:

$$b_1 = (31.8\,\Delta p - 0.1\,p_{11})\Delta p \times 10^{-10}\text{cm}^2/\text{dyne} \tag{46a}$$

$$b_2 = -32.4(\Delta p)^2 \times 10^{-10}\text{cm}^2/\text{dyne} \tag{46b}$$

In the case when $|\Delta p|/|p_{11}| \gg 3 \times 10^{-3}$, the parameter b_1 can be approximated by:

$$b_1 \approx 31.8\,(\Delta p)^2 \times 10^{-10}\text{cm}^2/\text{dyne} \tag{47}$$

In the problems concerning crystal orientation, the difference of normal stresses, Δp, usually is high enough for the above condition to be fulfilled. Then the dimensionless factor A_{th} appearing in the thermodynamic distribution function Ψ_{st}^{th} (equation 33) reduces to:

$$A_{th} = \gamma(\Delta p)^2 V/kT \tag{48}$$

where, for polyethylene, $\gamma = 31.8 \times 10^{-10}$ cm^2/dyne. The second coefficient in the distribution (equation 33), for polyethylene crystals amounts to:

$$B = 1.019$$

We have assumed for our calculations that $V/kT = 7.83 \times 10^{-7}$ cm^2/dyne for both thermodynamic (equation 33) and hydrodynamic (equation 43) distributions and an axial ratio of rotational ellipsoids, $p = 2$. Example orientation distributions $\Psi(\underset{\sim}{\theta})$ computed with various stresses Δp, are shown in *Figures 3* and *4* for isolated thermodynamic and hydrodynamic mechanisms. At low stresses, $\Delta p = 10^7$ dyne/cm^2, the separated thermodynamic effect is very weak and leads to almost uniform angular distribution, whereas the hydrodynamic effect is much stronger and practically controls the orientation. At higher stresses, $\Delta p = 10^8$ dyne/cm^2, we observe strong differences between orientation distributions related to separated thermodynamic and hydrodynamic effects. The difference concerns not only the width of the distribution but also its symmetry. The hydrodynamically-controlled distribution exhibits a single maximum at $\theta = 0°$

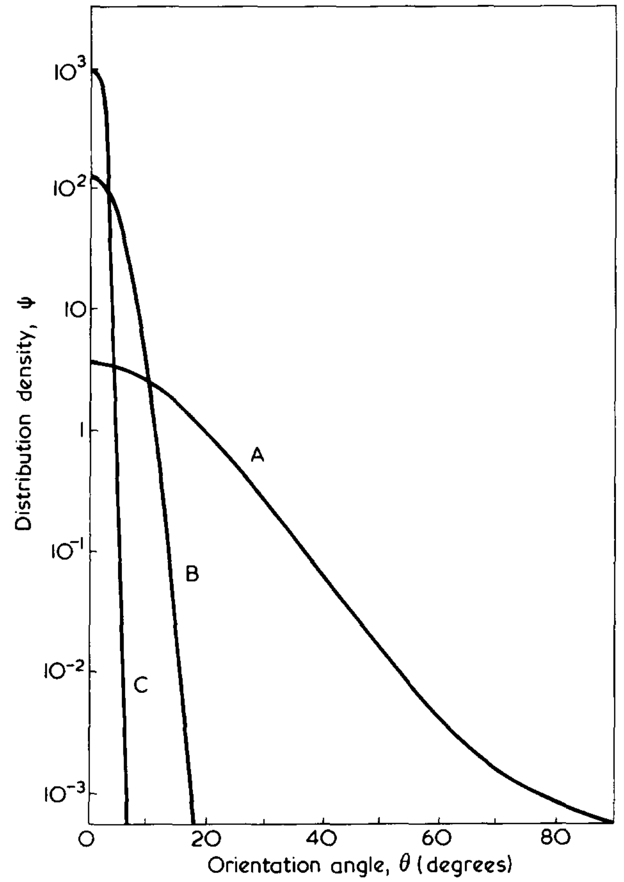

Figure 4 Hydrodynamic orientation distributions, $\Psi(\underset{\sim}{\theta})$, of rotational ellipsoids with axial ratio p = 2 suspended in a viscous, Newtonian fluid under an uniaxial flow field. The distributions are calculated (equation 43) for normal stress differences: A, $|\Delta p| = 10^7$, B, $|\Delta p| = 10^8$; C, $|\Delta p| = 10^9$ dyne/cm²

and a single minimum at $\theta = 90^\circ$, while in the thermodynamic distribution two maxima can be observed: one at $\theta = 0^\circ$ (c-axis parallel to the symmetry axis of the stress field), another maximum at $\theta = 90^\circ$ (c-axis perpendicular), and one minimum at $\theta = 45.53^\circ$. At very high stresses, $\Delta p = 10^9$dyne/cm², the maximum at $\theta = 90^\circ$ practically disappears, while that at $\theta = 0^\circ$ becomes higher and sharper. For very high stresses the thermodynamic factors affect orientation stronger than hydrodynamic ones.

The combined thermodynamic and hydrodynamic steady-state orientation of rotational anisotropic ellipsoids with symmetry axis identical with the crystallographic c-axis of the polyethylene crystal can be described by:

$$\Psi_{st}^{th,hydro}(\underset{\sim}{\theta}) = C\exp[\Delta p(V/kT)\cos^2\theta(\phi - \gamma\Delta p - \gamma B\Delta p\cos^2\theta)] \tag{50}$$

The magnitude of crystal orientation can be discussed in terms of an axial orientation factor, i.e. the second moment of the distribution function which for the symmetry axis of a rotationally symmetric crystals is defined by:

$$f_{or} = (3\langle\cos^2\theta\rangle - 1)/2 \tag{51}$$

where $\langle\cos^2\theta\rangle$ is the square cosine averaged with the actual orientation distribution function, Ψ. For the thermodynamically-controlled orientation, equation (33), it is:

$$\langle\cos^2\theta\rangle = \int_{-1}^{1} x^2\exp[-A_{th}(1 + Bx^2)x^2]\,\mathrm{d}x \Big/ \int_{-1}^{1}\exp[-A_{th}(1 + Bx^2)x^2]\,\mathrm{d}x \tag{52}$$

The numerically determined dependence of the thermodynamically-controlled axial orientation factor f_{or}^{th} vs. parameter A_{th} for polyethylene is shown in *Figure 5*. For not too high stresses satisfying the condition:

$$|\Delta p| < 11(kT/V\gamma)^{1/2} \tag{53}$$

the orientation factor f_{or}^{th} assumes negative values (predominantly perpendicular orientation of c-axes). The dependence in *Figure 5* does not predict, however, an ideal perpendicular orientation ($f_{or} = -0.5$) and the minimum value of f_{or}^{th} does not exceed -0.25. Positive values of the orientation factor (predominantly parallel orientation) appear for stresses higher than the critical value indicated in equation (53).

Stresses in the range:

$$|\Delta p| > 20(kT/\gamma V)^{1/2} \tag{54}$$

lead to practically complete parallel orientation of c-axes with respect to symmetry axis of the stress field, ($f_{or}^{th} \approx 1$).

There is also shown in *Figure 6* a similar master relation for the orientation factor, resulting from hydrodynamic

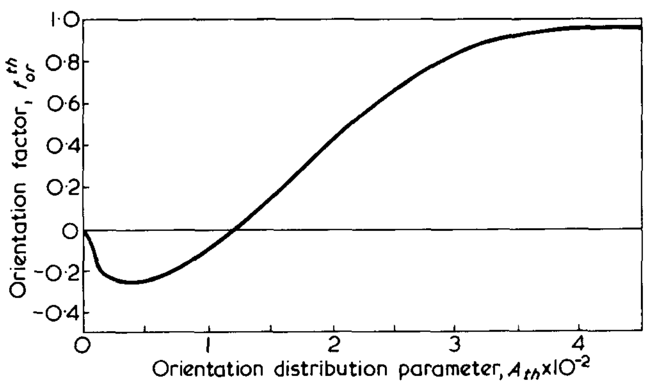

Figure 5 Master relation of axial orientation factor, f_{or}^{th}, of polyethylene crystal c-axis, calculated with thermodynamic distribution (equation 33) vs. dimensionless parameter A_{th}

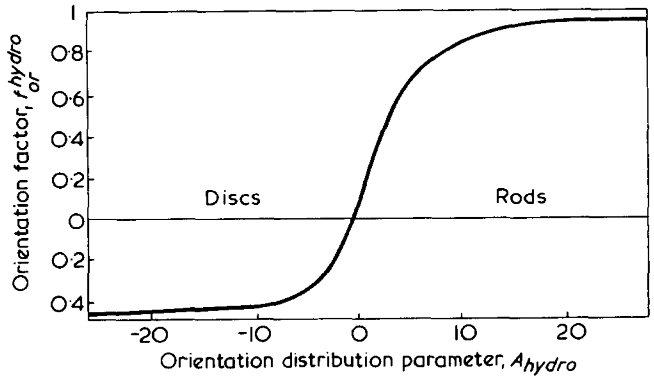

Figure 6 Master relation of axial orientation factor, f_{or}^{hydro} of rotational ellipsoids calculated with hydrodynamic distribution (equation 42) vs. dimensionless parameter A_{hydro}

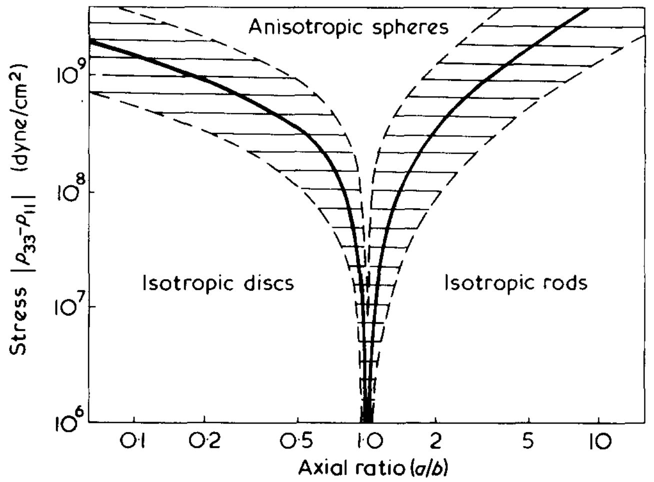

Figure 7 Diagram of anisotropic ellipsoids behaviour under uniaxial, hydrodynamic field

mechanism, f_{or}^{hydro}:

$$f_{or}^{hydro} = 3\{1/W(A_{hydro}^{1/2}) - A_{hydro}^{-1/2}]/(4A_{hydro}^{1/2}) - 1/2 \qquad \text{for } p > 1 \text{ (rods)}$$

$$f_{or}^{hydro} = -3\{2\exp(A_{hydro})/[\pi^{1/2}\mathrm{erf}(|A_{hydro}|^{1/2})] - |A_{hydro}|^{-1/2}\}/(4|A_{hydro}|^{1/2}) \text{ for } p < 1 \text{ (discs)} \qquad (55)$$

where the functions $W(\cdot)$ and $\mathrm{erf}(\cdot)$ are defined as follows:

$$W(x) = \exp(-x^2)\int_0^x \exp(t^2)\mathrm{d}t \qquad (56)$$

$$\mathrm{erf}(x) = 2/(\pi)^{1/2}\int_0^x \exp(-t^2)\mathrm{d}t \qquad (57)$$

The orientation factor of the rotational ellipsoids subjected to a uniaxial hydrodynamic field is always positive for $A_{hydro} > 0$ (rods in compressive field or discs under extension), and converges to unity when $A_{hydro} \to +\infty$. The orientation factor is always negative for $A_{hydro} < 0$ (rods in extensional field or discs under compression) and converges to -0.5 when $A_{hydro} \to -\infty$.

CONCLUSIONS

In the absence of production of new crystals, orientation distribution is controlled by thermodynamic and hydrodynamic factors. The thermodynamic contribution results from an orientation-dependent free energy of a single crystal, $F(\underline{\theta})$. When no other external fields are present, $F(\underline{\theta})$ can result from orientation-dependent strain of anisotropically elastic particles embedded in a continuum with a homogeneous stress field. The hydrodynamic contribution results from viscous interactions between asymmetric particles suspended in the medium subjected to a potential flow.

The isolated thermodynamic and hydrodynamic orientation effects differ in many respects one from another. In the first approximation, the strain energy is a quadratic function of stress, while the hydrodynamic potential is a linear function of stress components. Therefore, strain energy controls orientation at high stresses, while low stresses favour the hydrodynamic effect. In the calculations performed for polyethylene crystals in an extensional flow field both $F(\underline{\theta})$ and $\Phi(\underline{\theta})$ have been found to be approximately dependent on the single stress difference, $\Delta p = p_{33} - p_{11}$. The fact that $F(\underline{\theta})$ is approximately proportional to $(\Delta p)^2$ while the hydrodynamic potential is a linear function of the stress difference Δp multiplied by the shape factor, ϕ, shows that the thermodynamic orientation is invariant to the replacement of extension by compression and vice versa. Hydrodynamic orientation changes orientation axis when Δp is replaced by $(-\Delta p)$ or ϕ by $(-\phi)$.

The other difference concerns the symmetry of the orientation distribution functions. For uniaxially stressed polyethylene, the thermodynamically-controlled orientation function exhibits two maxima (at $\theta = 0°$ and $\theta = 90°$) and a single minimum (at $\theta = 45.53°$) while the hydrodynamic functions show a single maximum at 0° or 90°, and a single minimum at $\theta = 90°$ or 0° dependent on the sign of the product $(\Delta p \cdot \phi)$. The hydrodynamic orientation is strongly dependent on the shape factor ϕ, and reduces to zero when spherically symmetric particles are considered. No effect of shape is encountered in the thermodynamic orientation.

Figure 7 presents the conditions when the thermodynamic and the hydrodynamic effects on crystal orientation become comparable, i.e. when the average free energy $\langle F(\underline{\theta})\rangle$ is equal to the average hydrodynamic potential $\langle kT\Phi(\underline{\theta})/D\rangle$. The results for polyethylene subjected to uniaxial stress field are plotted in the space of stress differences, Δp and axial ratios, p.

Solid lines correspond to the condition: $\langle F(\underline{\theta})\rangle = \langle kT\Phi(\underline{\theta})\rangle/D$. The cross-hatched areas describe transition regions where both mechanisms effectively codetermine the resulting orientation. Far enough from these regions orientation can be approximated by the isolated mechanisms: thermodynamical or hydrodynamical. The first one is effective in the range of high absolute stress differences $|\Delta p|$ and/or small asymmetry of particles (axial ratio p close to unity); the orientation is controlled by crystal strain energy alone and the crystals behave like anisotropic spheres. On the other hand, at small stresses and/or high degree of asymmetry ($p \ll 1$/or $p \gg 1$), the hydrodynamic mechanism is the one controlling orientation, and the crystals behave like isotropic, asymmetric particles.

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