Letters to the Editor

Orientation of Crystallites in Stretched Polyethylene

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THE x-ray diffraction patterns of oriented polyethylene indicate that when the polymer is initially stretched at room temperature, the preferred direction of the crystallite chain axes does not coincide with the direction of elongation but is inclined to it.[1-3] As the elongation is increased, the crystallite orientation changes, until at elongations of about 500 percent the chain axes practically coincide with the stretching direction.[2] From an analysis of the x-ray diffraction patterns, Brown[2] has concluded that at elongations of up to 200 percent the long chain axis of the crystallite is inclined at an angle of 64° to the stretching direction. The purpose of this note is to point out that his analysis is not consistent with an angle of inclination of 64°, but rather the complement of this, *viz.*, about 26°.

After mentioning that the angle of inclination between the stretching direction and the long chain axis of the crystallites is 64°, Brown says, "There is a unique direction in the crystal lattice which is also inclined to the long chain axis at an angle of 64°. This is the 011 direction. Examination of Fig. 7 reveals that this reflection has indeed moved over to the meridian from its normal position in the first layer line. As a consequence of this, the 001 direction, or long chain axis, is inclined to the stretching direction at an angle of 64°."[4] The inconsistency in the above statement arises from a failure to distinguish between a direction in the real lattice, defined in terms of unit cell translations, and one in the reciprocal lattice, defined by the normal to a set of planes. Thus, the angle between the 001 and 011 directions in the real lattice of polyethylene, *viz.*, 62° 48', is not the same as that between the vectors from the origin to the points 001 and 011 in the reciprocal lattice, which is 27° 12'. Therefore the movement of the 011 reflection to the meridian implies a tilt of 27° 12' with respect to the stretching direction.

[1] W. O. Baker, *Advancing Fronts in Chemistry* (Reinhold Publishing Corporation, New York, 1945), Vol. I.
[2] A Brown, J. Appl. Phys. 20, 552 (1949).
[3] S. Krimm and A. V. Tobolsky, J. Polymer Sci. 7, 57 (1951).
[4] See reference 2, p. 555.

Reply to Samuel Krimm's Note

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THE comments made by Dr. Krimm about my paper are quite correct. I erred in the interpretation of the x-ray diffraction pattern. The angle of inclination between stretching direction and long chain axis of the crystallites is 26° (27°) and not 64°.

Distribution of Activation Energies for Viscoelastic Deformation

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ORIGINALLY defined to characterize macroscopic deformational phenomena, the concept of "relaxation time," along with the more recent idea of its distribution, is still in quite general use in the physical theory of polymers, even though more or less detailed models at the molecular level have since been developed. Essentially a mathematical abstraction of large scale effects, relaxation time becomes inadequate as a basic quantity when it is adapted to the molecular picture. The dependence of relaxation time on an over-all activation energy has been suggested by a number of writers[1-4] in accordance with the relationship:

$$\tau = \tau_0 \exp(F^*_{mol}/RT), \tag{1}$$

where τ = relaxation time, τ_0 = constant, F^*_{mol} = activation energy per mole, R = gas constant, and T = absolute temperature. Specific experimental evidence is cited by deBruyne[2] in support of Eq. (1).

For a number of years, also, the distribution of relaxation times has been recognized qualitatively as an implication of the distribution of activation energies, as is suggested by the comments of Huggins.[5] It is the purpose of the present note to call attention to a relationship which (differing slightly from Eq. (1)) refers to the elementary (or unit) deformation process, and to present the distribution of activation energies corresponding to one experimentally derived relaxation-time distribution.

In terms of the reaction-rate theory, the shear modulus is given by Tobolsky, Powell, and Eyring[6] as

$$G = (\lambda_1 2\pi^2 F^*)/(\lambda^2 A), \tag{2}$$

where λ = distance between adjacent equilibrium positions, λ_1 = lateral distance between shearing molecular chains or segments, A = effective area of the deformation unit, and F^* = activation energy per molecule. The coefficient of viscosity is given by

$$\eta = (\lambda_1 h/\lambda^2 A) \exp(F^*/kT), \tag{3}$$

where h = Planck's constant, and k = Boltzmann's constant. If, now, we consider the rates of elastic and viscous shear in the molecular process to be additive, as do Tobolsky *et al.*, there is obtained an equation of the form of the well-known relaxation equation of Maxwell, according to whom the relaxation time is defined $\tau = \eta/G$. Thus, from Eqs. (2) and (3),

$$\tau = (h/2\pi^2 F^*) \exp(F^*/kT). \tag{4}$$

For constant F^*, Eq. (4) gives the same dependence of relaxation time on absolute temperature as does Eq. (1), but it should be noted that Eq. (4) gives the relaxation time of the *elementary* deformation process, whereas Eq. (1) applies to the viscoelastic system as a whole. It is significant that in the derivation of Eq. (4), other molecular parameters cancel out, and τ is dependent only on the activation energy at constant temperature.

In an analysis of dynamic-property and stress-relaxation data on polymers, Tobolsky, Dunell, and Andrews[7] point out that the dynamic modulus E of the whole system as a function of the continuous distribution of the relaxation times of component Maxwell units is given by the relation

$$E = \int_0^\infty E(\tau) d\tau, \tag{5}$$

where $E(\tau)$ is a distribution function such that $E(\tau)d\tau$ expresses the contribution to the total E, from units having relaxation times between τ and $\tau + d\tau$. Tobolsky and co-workers cite experimental results which indicate that

$$\begin{aligned} E(\tau) &= E_0/\tau \quad (\tau_l < \tau < \tau_m), \\ E(\tau) &= 0 \quad (\tau < \tau_l, \tau > \tau_m), \end{aligned} \tag{6}$$

where E_0 = constant. We may suppose each Maxwell unit to correspond to an elementary molecular deformation process. Then, referring to Eq. (4), it can be readily deduced that

$$E(\tau)d\tau = E_0(1/kT - 1/F^*)dF^*. \tag{7}$$

The distribution function for activation energies $\mathscr{E}(F^*)$ $= E_0(1/kT - 1/F^*)$, corresponding to $E(\tau) = E_0/\tau$, is plotted in Fig. 1, for $T = 300°K$, $\mathscr{E}$ being expressed in multiples of E_0. Because of the nature of the function given by Eq. (4), in general two limits on F^* correspond to each of the limits τ_l and τ_m. In the present case, however, two of the F^* limits are superfluous, for they are below the lower limit ($F^* = kT$) which must be imposed if $\mathscr{E}(F^*)$
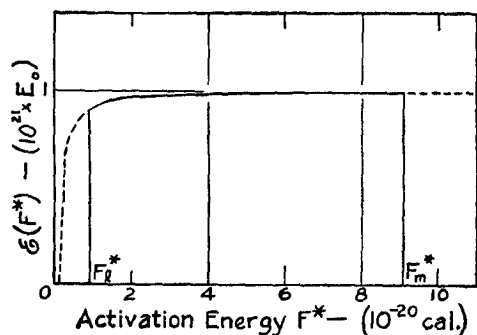
FIG. 1. Distribution function for activation energies, for $T = 300°K$, based on the relaxation-time distribution given by Eq. (6).

is to have only the positive values for which there is ready physical interpretation. The two remaining limits F^*_l and F^*_m, corresponding to τ_l and τ_m, are shown in Fig. 1, being positioned quite generally. It is conceivable that F^*_l coincides with the limit $F^* = kT$, but this does not appear to be generally necessary.

The significance of $\mathcal{E}(F^*)$, as derived here, is analogous to that of $E(\tau)$. $\mathcal{E}(F^*)dF^*$ expresses the contribution to the dynamic modulus of the system from molecular deformation processes having activation energies lying in the interval F^* to $F^* + dF^*$.

[1] J. Frenkl, Z. Physik **35**, 652 (1926).
[2] N. A. deBruyne, Proc. Phys. Soc. (London) **53**, 251 (1941).
[3] Robert Simha, J. Phys. Chem. **47**, 348 (1943).
[4] T. Alfrey, *Mechanical Behavior of High Polymers* (Interscience Publishers, Inc., New York, 1948), p. 77.
[5] M. L. Huggins, J. Appl. Phys. **21**, 518 (1950).
[6] Tobolsky, Powell, and Eyring, edited by Burk and Grummitt, *Chemistry of Large Molecules* (Interscience Publishers, Inc., New York, 1943), p. 133.
[7] Tobolsky, Dunell, and Andrews, Textile Research J. **21**, 404 (1951).

Viscous Energy Dissipated During the Atomization of a Liquid

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WHILE the detailed mechanism of generation of small droplets from bulk liquid is not completely understood, the difficulty in creating them at a high rate is readily apparent. When the liquid changes from the initial continuous state to the final dispersed state, its dimensions change by a factor of about 10^4. We shall assume for this discussion that the continuous state changes shape by flowing from the bulky configuration to a greatly extended thread or film which collapses under surface tension to droplets of various sizes, the mass average of which is at least as great as the thread or film thickness. Since the discrete state does not occur until after the change of shape, viscous energy must be dissipated in creating this extension and we shall show it to be appreciable in the rapid generation of small droplets.

The difficulty of obtaining the necessary rate of change of shape is illustrated by the fact that a one-micron thread would have to be ejected at about 10^8 cm/sec in order to disperse one cubic centimeter in a second. One way to estimate the minimum energy needed to effect the change of shape is to assume first that the liquid flows steadily into a transition region at low velocity and out at high velocity and small cross section. The viscous energy loss can then be computed by integrating the expression for the power loss per unit volume, W', at any point,[1] where

$$W' = \eta\{2(\partial u/\partial x)^2 + 2(\partial v/\partial y)^2 + 2(\partial w/\partial z)^2 + (\partial u/\partial y + \partial v/\partial x)^2 + (\partial u/\partial z + \partial w/\partial x)^2 + (\partial v/\partial z + \partial w/\partial y)^2\}, \quad (1)$$

in which η is the viscosity and u, v, w are the velocity components. If pure viscous flow occurs, a knowledge of the velocity distribution throughout the volume would allow a rather precise evaluation of the energy dissipated.

Since all the terms in Eq. (1) are positive, we shall attempt to estimate the magnitude of the first one, neglecting the others, in order to determine the minimum energy that must be dissipated in atomizing unit volume of liquid. If the liquid enters the large end of a conical transition region of diameter d_1 with a velocity v_1, suffers a constant rate of increase of velocity, and leaves as a thread of diameter d_2, the minimum energy dissipated per unit volume dispersed is of the order of W, given by

$$W = 8\eta d_1^2 R / 3\pi d_2^4 L, \quad (2)$$

where R is the rate of flow and L is the length of the transition region. The proportionality of W to R in Eq. (2) is in agreement with a more general rule, pointed out by J. B. Keller of New York University,[2] that in viscous flow the energy loss is proportional to the mass rate of flow. In order to give an idea of the magnitude of the energy, Eq. (1) has been used to compute the data of Table I.

TABLE I. Minimum viscous energy in calories required to atomize one cubic centimeter of liquid at a rate of one cm³/sec. The viscosity is assumed to be 0.01 poise, the length of the transition region and the diameter of its entrance to be 1 cm.

Thread diameter d_2, microns	Number of threads		
	1	10	100
1	2,000,000	200.000	20.000
5	3200	320	32
10	200	20	2.0
20	13	1.3	0.13

The resulting average droplet size should be at least as large as the thread diameter. Those values below the solid line in Table I probably represent conditions under which viscous energy losses are not a limiting factor in atomization. The existing two fluid atomizers operate under conditions such that this minimum viscous energy loss is not appreciable even though large quantities of energy are used in overcoming the resistance to flow of the propellant. It would therefore seem very difficult to generate a fine dispersion rapidly with the same inefficient method.

The single fluid hydraulic nozzle applies its available energy more efficiently to changing the shape of the liquid, but pressures of the order of 60,000 psi would be needed to supply 100 calories for each cm³ dispersed and much of this must be used in overcoming the resistance to flow caused by the stationary walls of the nozzle.

Although these approximations are very crude, they do seem to indicate the increasing importance of viscous energy losses as the droplet size is decreased. We are attempting to evaluate the magnitude more precisely in some particular cases.

[1] L. M. Milne-Thomson, *Theoretical Hydrodynamics* (Macmillan and Company, Ltd., London, England), second edition, p. 510.
[2] Private communication.

A Note on "Electron Microradiography of Electrodeposited Metals"

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IT was reported by R. Weil and H. J. Read[1] that the electrodeposited thin film of nickel on copper and zinc served for study on electroplating by means of electron microscopy. It is known by electron diffraction investigation[2] that the crystal particles of metal, which are deposited electrolytically on the surface of a metal single crystal, are crystallographically oriented according to the orientation of the boundary faces of substrate. This phenomenon is quite similar to the oxidation taking place on metal; as a matter of fact, the thin oxide film formed on metal is composed of the oriented crystal particles. This oriented oxide film serves as a faithful replica of substrate in electron microscopy.[3] It is, therefore, reasonable to think that the electrode-