

## Flow-Induced Crystallization from Solution: The Relative Effects of Extension and Shearing Flow Fields

ANTHONY J. McHUGH, *Assistant Professor, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

### Synopsis

Calculations have been performed to evaluate the relative effects of extensional and shearing flow fields on both the chain elongation and crystal nucleation rate enhancement for polyethylene crystallizing from xylene solutions. Rheological behavior was evaluated by means of the elastic dumbbell model modified for nonlinear effects at high elongations, and nucleation rate effects were considered from an essentially phenomenological viewpoint. Molecular weight effects were also incorporated explicitly in the computations. Results show that chain elongation and nucleation rate enhancement is far greater for extensional than for shearing flows. Semiquantitative comparisons with experimental results reported in the literature for various aspects of the flow-induced process, including the important fractionation effects, are discussed. Modification of the dumbbell model to account for shear rate effects on the intrinsic viscosity is also discussed.

### INTRODUCTION

The problem of flow-induced crystallization of polymers from solution has been one of relatively high interest in recent years. Investigations reported to date have been almost exclusively experimental in nature, with the principal objectives being elucidation of the morphological features and physical properties of the shishkebab crystals and experimental documentation of the fractionation effect (see references 1 and 2 for more detailed reviews). As a result of the fundamental observations on the fluid mechanics of flow-induced crystallization made by Pennings and co-workers,<sup>3,4</sup> and borne out by later investigations,<sup>1,2,5,6</sup> it seems a firmly established fact that regions of extensional flow are necessary for the nucleation of fibrous crystals from solution and that simple, laminar shearing flow does not induce fibrous nucleation in normal molecular weight systems. Very recent observations, however, indicate that fibrous growth can be enhanced by a laminar shearing flow field.<sup>7</sup>

Kobayashi and Nagasawa<sup>8</sup> have reported calculations to show the effects of chain elongation on crystal thickness, growth, and nucleation rates. Their computations, however, are reported in terms of the change in birefringence on orientation and as such do not give a direct measure of the flow parameters necessary to produce such orientation, nor do they explicitly show the important effects of molecular weight. Their results

are also based on a linear force extension model for the polymer chain network. Hlavacek and Seyer<sup>9</sup> have also shown computations for the relative effects of shear and elongation rates on molecular extension; however, their computations are also based on a linear necklace model and they do not explicitly include molecular weight effects. Their computations also appear to neglect the Brownian motion force.

The purpose of this presentation will be to elucidate in a more exact quantitative fashion, via the elastic dumbbell model, the effects of the fundamental fluid mechanical and molecular parameters (especially molecular weight) on the elongation of a polymer molecule in solution and also, through a basically phenomenological approach, to show how the fluid mechanics will affect the energetics of the nucleation process. The system chosen for computation will be polyethylene in xylene.

### THE ELASTIC DUMBBELL MODEL AND MOLECULAR EXTENSION

Computations to show the various fluid mechanical effects will be based on the well-known elastic dumbbell model modified according to a method developed by Peterlin<sup>10</sup> to account for nonlinear force-extension effects at high elongations. The dumbbell model considers only the motion of the free ends, connected by an elastic force, with the hydrodynamic resistance concentrated in the dumbbell ends. The dumbbell model was chosen over the perhaps physically more realistic necklace model for its relative computational simplicity and since it does allow explicit inclusion of molecular weight effects in a relatively straightforward fashion.

When the polymer molecule is immersed in a flowing medium, various forces act on it to alter the chain end separation and orientation. These forces are the frictional resistance between the molecule and surrounding medium in which it flows, an elastic retractive force which resists chain extension, and a Brownian motion force. Thus to compute the mean square end-to-end separation of the chain ends, one needs to evaluate the diffusion equation for the distribution of lengths and orientations of the dumbbells. The distribution function  $\phi$  is given by<sup>10</sup>

$$\frac{\partial \phi}{\partial t} = - \nabla \cdot [(\mathbf{v} - \mathbf{F}/\zeta)\phi] + D \nabla^2 \phi \quad (1)$$

where  $\mathbf{F}$  is the elastic force in the dumbbell,  $\mathbf{v}$  is the velocity field between the two ends of the dumbbell, and  $\zeta$  is the coefficient of frictional resistance between the beads and surrounding medium. The diffusivity  $D$  is given by the Fokker-Planck relation

$$D = kT/\zeta \quad (2)$$

The elastic retractive force is given by an entropy force<sup>10,11</sup>

$$\mathbf{F} = - T \nabla S(r) \quad (3)$$

where  $r$  is the end-to-end separation. In general, the elastic force components must be computed from Kuhn's expression<sup>12,13</sup>

$$F = \frac{kTu}{L} \quad (4)$$

where  $L$  is the length of an equivalent statistical chain segment and  $u$  is given by the inverse Langevin function

$$\coth u - \frac{1}{u} = r/NL \quad (5)$$

with  $N$  as the total number of statistical segments in the molecule.

In the limit of small extensions, eqs. (4) and (5) reduce to a linear force-separation relation, the evaluation of the diffusion equation for  $\phi$  becomes straightforward, and solutions for the mean square end-to-end distance have been worked out.<sup>10</sup> As pointed out, however,<sup>10</sup> these solutions produce the unrealistic result that at certain critical conditions the mean square separation becomes infinite—a result of the breakdown of the linear force extension relation at moderately high extensions. As eq. (5) predicts, the elastic force constant increases rapidly for moderate to large extensions. Peterlin<sup>10</sup> has given a straightforward modification to account for this non-linear effect by assuming that the elastic force-extension relation can be written as

$$F = 2\mu EkTr \quad (6a)$$

where

$$E = \frac{u}{3 \left( \frac{r}{NL} \right)} \quad (6b)$$

and

$$\mu = \frac{3}{2N L^2} \quad (6c)$$

By assuming that  $E$  is a function only of the final rather than instantaneous chain end separation, the diffusion equation remains linear and solutions in terms of the force constant  $E$  can be obtained by direct modification of the linear results.<sup>10</sup> The force factor  $E$  thus becomes an implicit function of the solvent kinematics and is obtained from a combination of eqs. (5) and (6) where the chain end separation  $r$  is replaced by the root mean square end-to-end distance.

For the evaluation of the elongation and nucleation rate effects, results will be compared for both a simple, steady extensional flow with solvent kinematics in rectangular Cartesian coordinates given by

$$\mathbf{v} = G(x\mathbf{e}_x, -\frac{1}{2}y\mathbf{e}_y, -\frac{1}{2}z\mathbf{e}_z) \quad (7)$$

where  $G$ , the stretch rate, is constant and  $\mathbf{e}_x$ ,  $\mathbf{e}_y$ ,  $\mathbf{e}_z$  are the Cartesian coordinate unit vectors, with the origin of the coordinate system as the center of mass of the dumbbell, and a simple shearing flow field where

$$\mathbf{v} = G (y\mathbf{e}_x, 0, 0) \quad (8)$$

with  $G$  being the shear rate. Expressions for the mean square extension of the dumbbell are derived from

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \quad (9)$$

where the brackets refer to the ensemble average obtained by integrating the appropriate quantity with the distribution function over the dumbbell space  $r(x, y, z)$ . Expressions for the extension have been worked out<sup>10</sup>; and in terms of the extension ratio  $\alpha$  and the nonlinear force factor  $E$ , these become

$$\alpha = \left[ \frac{(E - \theta G)}{(E - 2\theta G)(E + \theta G)} \right]^{1/2} \quad (10)$$

for extensional flow and

$$\alpha = \left[ \frac{3E^2 + 2\theta^2 G^2}{3E^3} \right]^{1/2} \quad (11)$$

for shearing flow. The chain extension  $\alpha$  is just

$$\alpha = \left[ \frac{\langle r^2 \rangle}{\langle r_0^2 \rangle} \right]^{1/2} \quad (12)$$

with  $\langle r_0^2 \rangle^{1/2}$  the r.m.s. distance for the macromolecule at rest. In these expressions, the parameter  $\theta$ , the relaxation time, is equal to<sup>12</sup>  $\zeta \langle r_0^2 \rangle / 6 kT$  and can be directly related to molecular weight through the intrinsic viscosity. For the dumbbell model, the intrinsic viscosity at zero shear,  $[\eta]_0$ , is given by<sup>10</sup>

$$[\eta]_0 = \frac{RT\theta}{\eta_0 M} \quad (13)$$

where  $R$  is the gas constant,  $\eta_0$  is the solvent viscosity, and  $M$  is the macromolecule molecular weight. Combining eq. (13) with the Mark-Houwink equation,<sup>13</sup>

$$[\eta]_0 = KM^a \quad (14)$$

gives  $\theta$  directly as a function of molecular weight:

$$\theta = \frac{\eta_0 KM^{1+a}}{RT} \quad (15)$$

### NUCLEATION RATE EFFECTS

In order to compare the effects of the two flow fields, eqs. (7) and (8), on the nucleation rate of fibrous crystals from solution, a purely phenomenological approach can be taken. If one assumes that nucleation is controlled

by interfacial processes and is not influenced by the transport of molecules to the nucleation site (an assumption for which there appears to be some experimental justification<sup>4</sup>), then the energetics of nucleation turn out to be essentially the same as for quiescent growth with a modification necessary only for the free energy terms.

The nucleation rate expression for the formation of primary nuclei with folds having a rectangular cross section due to Lauritzen and Hoffman<sup>14</sup> is

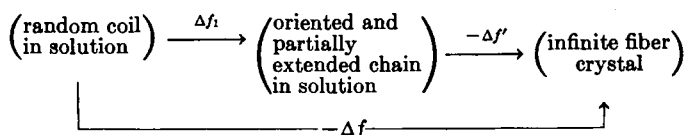
$$I_0 = \frac{K_0 kT}{h} n_0 \exp \left[ \frac{-\Delta F_p^*}{kT} \right] \exp \left[ \frac{-32\sigma_s^2 \sigma_e}{kT(\Delta f)^2} \right] \quad (16)$$

where  $I_0$  is the nucleation rate,  $\sigma_s$  and  $\sigma_e$  are the fold- and side-surface free energies, respectively,  $h$  is Planck's constant,  $n_0$  is the number of molecules per unit volume,  $\Delta F_p^*$  is the free energy associated with the activated jump process at the interface, and  $\Delta f$  is the free energy change per unit volume for the formation of an infinite crystal from a random coil in solution. The preexponential term,  $K_0$ , comes from the modification of the Turnbull-Fisher nucleation theory and contains terms in  $\sigma_e$ ,  $\sigma_s$ ,  $\Delta f$ , and  $a$ , the molecular cross section.<sup>14</sup> Consistent with the assumption that transport processes to the nucleation interface are being neglected, it seems reasonable to assume that the rate expressions developed by Flory<sup>15</sup> and modified by Mandelkern<sup>16</sup> for the nucleation of a bundle-like nucleus can be applied to the formation of the fibrous structures in the flow-induced process. Thus, one can assume that molecules are crystallizing from a solution state in which they are already partially extended as a result of the fluid mechanical forces. We thus have for the nucleation rate of fibrous entities with similar cross section as the folded chain crystal

$$I_b = K_b \left( \frac{kT}{h} \right) n_0 \exp \left[ \frac{-\Delta F_p^*}{kT} \right] \exp \left[ \frac{-32\sigma_s^2 \sigma_e'}{kT(\Delta f')^2} \right] \cdot \exp \left[ \frac{16\sigma_s^2 \ln v_2}{a(\Delta f')^2} \right] \quad (17)$$

where the preexponential term  $K_b$  differs somewhat from  $K_0$  in that it contains terms in  $v_2$ ,  $\sigma_e'$ , and the free energy  $\Delta f'$ . The  $\sigma_e'$  refers to the end-surface free energy for the bundle-like nucleus, a term which in general will differ from  $\sigma_e$ ;  $v_2$  is the volume fraction of polymer and  $\Delta f'$  is the mentioned free energy difference between an infinite fiber crystal and an extended or partially extended chain in solution.

To evaluate  $\Delta f'$  in terms of known quantities, we can consider the process of fibrous crystallization at constant temperature as follows:



where the usual assumption is made that  $\Delta f$  is the same for fibrous and folded chain crystals<sup>14</sup> and is related to the free energy of crystallization from the melt,  $\Delta f^0$ , by<sup>17</sup>

$$\Delta f = \Delta f^0 - \frac{RT}{V_1} [v_1 - (1 - v_2)^2 \chi] \quad (18)$$

where  $V_1$  is the solvent molar volume,  $v_1$  is the volume fraction of solvent, and  $\chi$  is the solvent-polymer interaction parameter which can also vary with molecular weight.<sup>17</sup>

From the diagram, then, we expect

$$\Delta f' = \Delta f + \Delta f_1. \quad (19)$$

To compute the relative effects of folded chain and fibrous nucleation in a flowing field, we take the ratio of eq. (17) to eq. (16):

$$\frac{I_b}{I_o} = \exp \frac{32\sigma_s^2\sigma_e}{kT} \left[ \frac{1}{\Delta f^2} - \frac{1}{\Delta f'^2} \right] \cdot \exp \left[ \frac{16\sigma_s^2 \ln v_2}{a \Delta f'^2} \right]. \quad (20)$$

In eq. (20), the differences in  $K_0$  and  $K_b\sigma_e$  and  $\sigma_e'$  and the  $\Delta F_p^*$  terms have been omitted since as computations will show once a critical elongation is achieved, the nucleation ratio increases catastrophically, with the changes being controlled completely by the very large values of  $\Delta f_1$  which result. This makes the result insensitive to even order-of-magnitude differences in the aforementioned quantities. The change  $\Delta f_1$  is evaluated from the thermodynamic expression for the change in free energy  $F$  of an elastic body acted on by a net tensile force  $f_{ex}$  causing an extension  $dL$ <sup>17</sup>:

$$dF = VdP - SdT + f_{ex}dL. \quad (21)$$

The evaluation of  $f_{ex}$  for both extensional and shearing flows is discussed in the Appendix, where it is shown that at constant  $T$  and pressure,

$$\Delta f_1 = \frac{1}{c} \int_1^\alpha (\tau_{xx} - \tau_{yy}) \frac{d\alpha}{\alpha} \quad (22)$$

where  $\tau_{xx} - \tau_{yy}$ , the first normal stress difference acting along the principle stretch axes, is the net force extending the molecule, and  $c$  is polymer concentration in mass units. The first normal stress difference is evaluated from<sup>12</sup>

$$\tau_{xx} - \tau_{yy} = \frac{2RTc\mu}{M} [\langle x^2 \rangle - \langle y^2 \rangle] \quad (23)$$

with the  $\langle x^2 \rangle$  and  $\langle y^2 \rangle$  terms evaluated from the previously mentioned non-linear modification of the diffusion equation. For a stretching flow field, eq. (7),  $\tau_{xx} - \tau_{yy}$  lies along the direction of motion, i.e., the polymer  $x$ -axis, while for a shearing flow the principal axis of deformation is rotated through an angle  $\beta$  with the direction of flow where<sup>18</sup>

$$\cot 2\beta = \frac{\tau_{xx} - \tau_{yy}}{2 \tau_{xy}} \quad (24)$$

with  $\tau_{xy}$  being the shear stress. Thus, for the shearing flow, the first normal stress difference along the principal axes is<sup>18</sup>

$$(\tau_{xx} - \tau_{yy})_p = (\tau_{xx} - \tau_{yy}) \cos 2\beta. \quad (25)$$

Thus, for the nonlinear dumbbell in an extensional field,

$$(\tau_{xx} - \tau_{yy}) = \frac{3RTcEG\theta}{M(E - 2G\theta)(E + G\theta)} \quad (26)$$

while for a shearing flow field,

$$(\tau_{xx} - \tau_{yy})_p = \frac{2RTc}{M} \left(\frac{G\theta}{E}\right)^2 [\cos 2\beta]^{-1} \quad (27)$$

where<sup>10</sup>

$$\cot 2\beta = \frac{G\theta}{E} \quad (28)$$

### COMPUTATIONS

Calculations were carried out for a 0.2 wt-% polyethylene solution in xylene at temperatures of 95°, 100°, and 105°C for a wide range of stretch and shear rates. Molecular weight effects were incorporated explicitly in the terms for the interaction parameter  $\chi$ , the relaxation time  $\theta$ , and the number of statistically equivalent random links.

For  $\chi$ , the following expression was used<sup>19</sup>:

$$\chi = 0.372 - 25.23M^{-0.5} \quad (29)$$

For the intrinsic viscosity parameters in eq. (15), the following expression for polyethylene fractions in xylene at 105°C was used<sup>20</sup>:

$$[\eta] = 1.65 \times 10^{-4} M^{0.83} \quad (30)$$

For the  $N$  and  $L$  terms needed in eq. (5), the following expression for the mean square end-to-end distance of a polyethylene molecule in a theta solvent<sup>22</sup> was used:

$$\langle r_0^2 \rangle = 6.7nl^2 \quad (31)$$

with  $n$  and  $l$  being the number and length, respectively, of CH<sub>2</sub> repeat units in the chain. From eq. (31), using the standard technique,<sup>17</sup> the statistically equivalent terms were obtained. In eq. (18), the standard expression for  $\Delta f^0$  was used<sup>14</sup>:

$$\Delta f^0 = \Delta h^0 (1 - T/T_m^0) \quad (32)$$

with  $T_m^0$  being the equilibrium melting temperature and  $\Delta h^0$  the enthalpy of crystallization of an infinite crystal from the melt. Numerical constants for the parameters in this expression and the remaining constants needed were taken as follows<sup>21</sup>:

$$\Delta h^0 = 2.80 \times 10^9 \text{ erg/cm}^3, T_m^0 = 145^\circ\text{C}, a = 20 \text{ \AA}^2,$$

$$\sigma_e = 70 \text{ ergs/cm}^2, \sigma_s = 10 \text{ ergs/cm}^2.$$

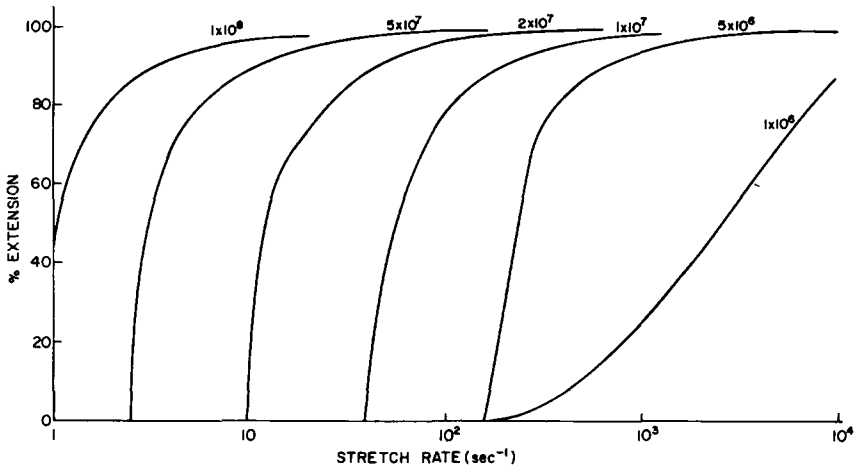


Fig. 1. Per cent extension vs. stretch rate for various molecular weights at 100°C.

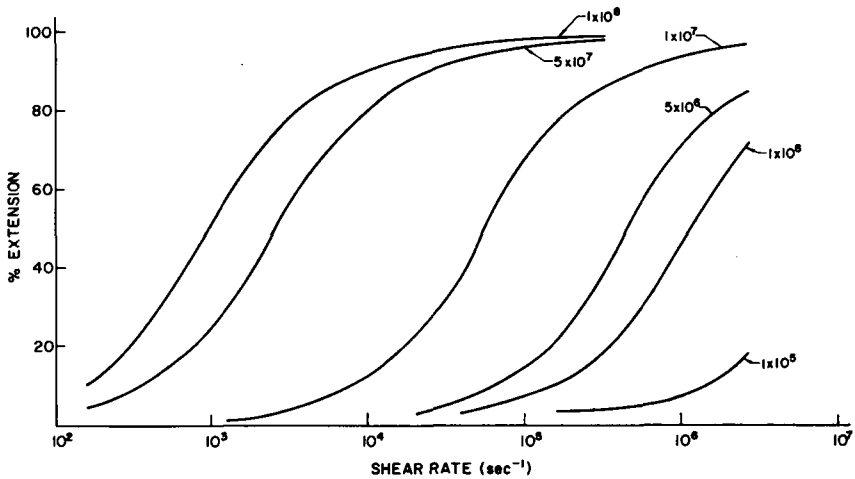


Fig. 2. Per cent extension vs. shear rate for various molecular weights at 100°C.

Figures 1 and 2 show the results for per cent extension (i.e., ratio of chain extension to contour length of completely extended molecule) as a function of solvent stretch or shear rate for various molecular weights. The calculations for per cent extension were essentially insensitive to temperature for the range chosen and so are shown for 100°C. These results show the dramatic effects of molecular weight on the critical stretch or shear rate needed for reasonable molecular extensions and clearly show the greater efficiency for elongation (i.e., more catastrophic stretch rate dependence) of extensional kinematics as opposed to shearing flow.

Figure 1 shows that for polyethylene of molecular weight much above  $5 \times 10^6$ , fairly modest stretch rates can produce large extensions; and, in fact, for molecular weights above  $5 \times 10^7$ , stretch rates even less than 1 in-



inverse second can induce near-complete molecular extension. In contrast, the results seen in Figure 2 show the much less dramatic changes in extension possible with a shearing flow field. Where for the extensional flow chains with molecular weights of  $5 \times 10^6$  and above can readily elongate for reasonable stretch rates, for shearing flow, minimal shear rates on the order of  $10^5 \text{ sec}^{-1}$  are needed; and, in addition, increases in extension for increased shear are much less dramatic. Even for a molecular weight of  $10^8$ , shear rates on the order of  $10^3 \text{ sec}^{-1}$  are seen to be necessary to achieve moderate extensions.

Table I shows the nucleation rate ratios for the various conditions. The values listed for the nucleation rate ratio are the first values at which the rates dramatically increase from values very much less than unity. Several observations are clear: First, at a given temperature and molecular weight, the critical stretch rate for catastrophic increases in the ratio is nearly two full orders of magnitude smaller than the corresponding critical shear rate needed; and, second, the corresponding ratios and hence elongations at the critical ratio are larger and occur over a much narrower range for the extensional kinematics. Also, the rate ratio increases with increasing crystallization temperature. The absolute values of the nucleation rate of course decrease with increasing temperature (and dramatically at these high temperatures). However, as the increased ratio demonstrates, fibrous nucleation becomes even more favorable over folded chain nucleation at the higher temperatures; and, in fact, one can readily explain the reduction in supercooling observed in agitated solutions on this basis.

The clear indication of these results is that extensional flow kinematics are far more conducive to fibrous nucleation from solution than shearing flow; and, in addition, the enhancement of chain elongation and nucleation rates is far more sensitive to molecular weight for the extensional flow.

## DISCUSSION

Two points are worthy of discussion regarding the elongations possible in shearing flow with the elastic dumbbell model, the inclusion of which, as it turns out, would further decrease chain extension. The first is the so-called internal viscosity effect,<sup>10</sup> which has to do with the fact that in a shearing flow field, the polymer coil rotates as well as deforms and for each full rotation is twice compressed and twice extended. Accounting for the dynamic resistance of the molecule to the resulting changes in conformation brings about a further decrease in extension possible at a given shear rate.<sup>10</sup>

Additionally, the dumbbell model does not predict an explicit dependence of intrinsic viscosity on shear rate for low shear rates. The shear rate dependence of  $[\eta]$ , in fact, only shows implicitly through the nonlinear force factor  $E$  and its dependence on shear rate, an effect which is essentially negligible for moderate rates.

A recent modification of the elastic dumbbell equations, proposed by Gordon and Schowalter<sup>23</sup> and discussed in detail elsewhere,<sup>24,25</sup> can, in fact,

TABLE I  
Nucleation Rate Ratios at Critical Conditions

MW =	Elongational flow						Shearing flow						
	$1 \times 10^6$	$5 \times 10^6$	$1 \times 10^7$	$5 \times 10^7$	$1 \times 10^8$	$5 \times 10^8$	$1 \times 10^8$	$5 \times 10^8$	$1 \times 10^9$	$5 \times 10^9$	$1 \times 10^{10}$	$5 \times 10^{10}$	$1 \times 10^{11}$
$G, \text{ sec}^{-1}$	5120	320	80	5	1	$2 \times 10^4$	$10^8$	$2 \times 10^4$	5120	640	320		
$I_b/I_0$													
95°C	$10^{80}$	$10^{59}$	$10^{53}$	$10^{33}$	$10^{88}$	$10^{37}$	$10^{36}$	$10^{34}$	$10^8$	$10^{19}$	$10^{24}$		
100°C	$10^{94}$	$10^{80}$	$10^{89}$	$10^{88}$	$10^{88}$	$10^{82}$	$10^{82}$	$10^{88}$	$10^{33}$	$10^{27}$	$10^{88}$		
105°C	$10^{168}$	$10^{158}$	$10^{155}$	$10^{153}$	$10^{153}$	$10^{111}$	$10^{122}$	$10^{115}$	$10^{43}$	$10^{43}$	$10^{15}$		

account explicitly for the shear rate dependence seen in many systems.<sup>24</sup> The essential implication of the modification shows in the prediction for intrinsic viscosity (at moderate shear rates where linear force extension can be assumed) where<sup>24</sup>

$$\frac{[\eta]}{[\eta]_0} = \frac{1}{1 + B(\theta G)^2} \quad (33)$$

where  $[\eta]_0$  is the zero shear intrinsic viscosity and  $B$ , a term involving the phenomenological parameter  $\epsilon$ , is

$$B = \frac{\epsilon(2 - \epsilon)}{(1 - \epsilon)^2} \quad (34)$$

with  $\epsilon$  having values between 0 and 1. As it turns out, using this approach would not affect the extensional flow computations since in applying the modified dumbbell results to the extensional kinematics, one merely finds the parameter  $\theta$ , shown previously, replaced by the quantity  $\theta(1 - \epsilon)$ ; and since by assumption<sup>25</sup>

$$\theta = \frac{\eta_0 K M^{1+\alpha}}{RT(1 - \epsilon)} \quad (35)$$

the computations remain unchanged. For shearing flow, the results are, however, noticeably different. Carrying through Peterlin's nonlinear approach to the modified dumbbell theory, one finds for the extension ratio  $\alpha$  and first normal stress difference, respectively,

$$\alpha = \left\{ \frac{3E^2 + [2 + \epsilon(2 - \epsilon)]\theta^2 G^2}{3E[E^2 + \epsilon(2 - \epsilon)\theta^2 G^2]} \right\}^{1/2} \quad (36a)$$

and

$$\tau_{xx} - \tau_{yy} = \frac{RTc}{M} \left[ \frac{2(1 - \epsilon)\theta^2 G^2}{E^2 + \epsilon(2 - \epsilon)\theta^2 G^2} \right] \quad (36b)$$

where clearly, for the special case  $\epsilon = 0$ , the above equations reduce to the standard elastic dumbbell results.

Intrinsic viscosity-shear rate data reported for polyethylene solutions in tetralin<sup>26</sup> were compared to eq. (33) and are shown in Figure 3. Evaluation of  $[\eta]$  was not completely straightforward since the specific viscosity-to-concentration ratio did not linearly extrapolate to zero concentration.<sup>26</sup> Nonetheless, allowing even for reasonable errors, one sees that the shear rate dependence can be adequately fit by the model. Using the data from reference 26 along with estimates for the molecular weight, computed from an expression for intrinsic viscosity in tetralin,<sup>20</sup> values for the parameter  $\epsilon$  were obtained and fit to molecular weight via the suggested power law dependence.<sup>24</sup> Using the modified eqs. (36a) and (36b) yielded results for chain extension and nucleation rates which, for all but the very highest molecular weight, were at least an order of magnitude under the critical

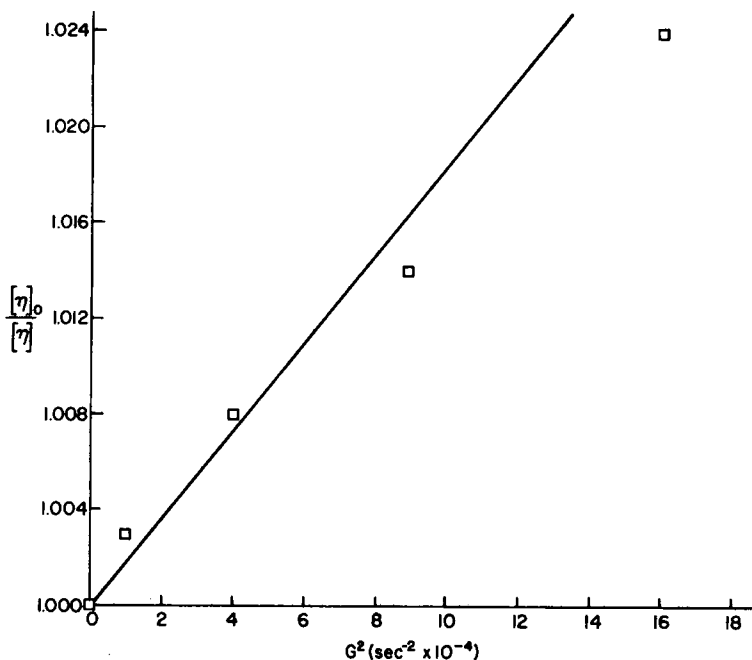


Fig. 3. Intrinsic viscosity ratio vs. square of shear rate. Data points evaluated from ref. 26.

shear rates in Table II for the simple elastic dumbbell model. Thus, one can conclude with some assurance that, for the elastic dumbbell model, shearing flows are clearly far less effective than elongational flows in initiating fibrous crystallization from solution.

Further relative enhancement of the effectiveness of extensional flows in this mode of crystallization arises from the realization that extensional kinematics are far more effective than shearing flows in orienting and bringing together the extended chains,<sup>20,31</sup> an effect which has not been considered in these calculations.

These results, although subject to limitations regarding precise numerical values as a result of extrapolation of eq. (30) beyond the region of its applicability, offer quantitative support to the observations of Pennings and coworkers regarding fractionation effects and the minimum molecular weights needed for fibrous growth from stirred solutions.<sup>3,19,27,28</sup> In one set of experiments, a minimum molecular weight of  $5 \times 10^4$  was needed for fibrous growth from vigorously agitated solutions.<sup>27</sup> Purely laminar shearing flow was also shown to be incapable of inducing fibrous nucleation in a 5 wt-% Marlex solution.<sup>3</sup> Both results are clearly in line with the computations presented here. In the former case, as Figure 2 shows, even for molecular weights as high as  $10^5$ , chain extensions necessary for catastrophic growth of the nucleation rate are only possible for shear rates greater than  $10^6 \text{ sec}^{-1}$ . Further, for the 5% Marlex solution stirred at  $250 \text{ sec}^{-1}$ ,<sup>3</sup> even

considering that a sizable fraction of material above  $10^6$  molecular weight might be present, Figure 2 indicates only minimal extension; and hence essentially zero nucleation rate enhancement would occur.

Figure 1 also lends support to the far greater efficiency observed for fractionation from flow fields with an extensional component.<sup>19</sup> Experimental results have also been reported showing the nucleation capabilities of modest stretch rates (i.e., 5 to 15 sec<sup>-1</sup>) on an unfractionated Fortiflex polyethylene<sup>2</sup> which are also consistent with the results shown here.

As has been pointed out,<sup>2</sup> many questions regarding the precise role of the fluid kinematics in the growth steps and resultant morphology of polyethylene shishkebobs remain. These computations again, however, do lend support to interpretations concerning the high molecular weight, acid-resistant, essentially structureless fibers reported from stirred solutions and seen in melting and gel permeation chromatographic behavior.<sup>32</sup>

The basis for the energetics calculations is, of course, the assumption of completely isolated chains in solution. Although computations were carried out for a 0.2 wt-% solution, only the free energy expression of eq. (18) and the  $\ln v_2$  term in the nucleation rate expression, eq. (20), turn out to have explicit concentration dependence. The catastrophic behavior seen in the nucleation ratio turned out to be independent of the  $\ln v_2$  term in that omitting it completely produced only a relatively minor increase in the ratio at the critical stretch or shear rate. The dumbbell model, strictly speaking from a molecular basis, ought only to be applied to solutions dilute enough that chain entanglements and network formation would not occur. One might expect some entanglement formation for 0.2% polyethylene solutions, particularly for the very high molecular weight fractions (i.e., greater than  $10^6$ ), although without complete rheological data there is no sure way to estimate this effect.<sup>36</sup> Regardless of this fact, however, one finds that the ability of expressions based on dilute solution theory for predicting rheological behavior of polymeric solutions, even for more concentrated systems, is often quite good.<sup>34,35</sup> Exact quantitative details may vary from model to model for more concentrated solutions; however, the general behavior regarding catastrophic nucleation rate effects ought to be the same regardless of the model. A careful analysis,<sup>37</sup> in fact, shows that constitutive equations based on the linear dumbbell and network models have precisely the same form. Both models result in two-constant equations; for the dumbbell model, these are polymer concentration and the relaxation time  $\theta$ ; while for the network model, the constants are for the numbers of and rate of loss of network segments, and both parameters need to be determined empirically.<sup>37</sup>

The elastic dumbbell model presents the obvious advantage of a single parameter which is readily estimated from dilute solution behavior. Thus, one should expect the basic approach taken in these calculations to be equally useful in predicting the general effectiveness of extensional and shearing flow kinematics on fibrous nucleation fairly independently of solution concentration. However, in light of the observation concerning

growth in a purely shearing flow field, it is felt that a simple phenomenological approach of the type presented here would be inappropriate for explaining growth enhancement. In the case of growth, it would appear that perhaps computations based on mechanical entanglement arguments, similar to those proposed elsewhere, may be more appropriate.<sup>29</sup>

## Appendix

### Development of Free Energy-Extension Relation

There does not appear to be a well-defined justification in the literature for the expression presented in eq. (22) for the free energy-extension relation. A similar expression is given in reference 9 on an apparently ad hoc basis. The purpose here will be to present what is believed to be a rigorous development based on a continuum approach.

Consider first the case for the steady extensional kinematics given by eq. (7). In order to compute the net force causing extension of the polymer molecule, we can consider the extension of a cylinder of fluid within the main body of flow consisting of both polymer and solvent. If one then assumes that during the stretching process the dumbbell ends follow the main flow up to the point of their maximum steady state extension, then the development to be presented parallels closely in several details with a previously given derivation for the extension of a viscoelastic cylinder.<sup>33</sup> Transforming the kinematics of eq. (7) to the more natural cylindrical coordinates ( $r, \theta, Z$ ) with  $Z$  as the direction of extension,

$$v = G \left( -\frac{r}{2}, 0, Z \right). \quad (\text{A.1})$$

The net force needed to extend the cylinder is then<sup>33,34</sup>

$$F' = 2\pi \int_0^{R(t)} T_{zz}|_{z=0} r dr \quad (\text{A.2})$$

where  $T_{zz}$  is the total stress acting on the moving end of the cylinder of radius  $R(t)$ .  $T_{zz}$  is related to the deviatoric stress  $\tau_{zz}$  by<sup>34</sup>

$$T_{zz} = -p + \tau_{zz} \quad (\text{A.3})$$

where  $p$  is the isotropic pressure. The problem thus becomes evaluation of eq. (A.3) for this case where the forces on the cylinder sides are non-zero.

The deviatoric stress tensor components for the solution remain diagonal and thus the Cauchy equations of motion for the solution reduce to<sup>33</sup>

$$\rho v_r \frac{\partial v_r}{\partial r} = -\frac{\partial p}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rr}) - \frac{\tau_{\theta\theta}}{r} \quad (\text{A.4a})$$

$$\rho v_z \frac{\partial v_z}{\partial z} = -\frac{\partial p}{\partial z} + \frac{\partial \tau_{zz}}{\partial z} \quad (\text{A.4b})$$

with  $\rho$  the solution density and for the deviatoric stress terms by symmetry  $\tau_{\theta\theta} = \tau_{rr}$ . Substituting the kinematics from eq. (A.1) into eqs. (A.4) and integrating by invoking the standard compatibility arguments, one finds that the isotropic pressure can be written as<sup>33</sup>

$$p = p_d + p_0 \quad (\text{A.5})$$

where  $p_0$  is the so-called static pressure evaluated at  $r = z = 0$  and  $p_d$  is a so-called dynamic pressure<sup>33</sup> where

$$p_d = -\frac{\rho G^2}{2} \left( Z^2 + \frac{r^2}{4} \right). \quad (\text{A.6})$$

By analogy to the development given for the extension of a cylinder under atmospheric conditions,<sup>24</sup> we can take for the total stress acting in the radial direction<sup>25</sup>

$$T_{rr}|_{r=R(t)} = -p_d. \quad (\text{A.7})$$

Combining with

$$T_{rr} = -p + \tau_{rr} \quad (\text{A.8})$$

gives

$$p_0 = \tau_{rr}. \quad (\text{A.9})$$

Substitution into (A.3) along with the kinematics gives

$$T_{zz} = \frac{\rho}{z} (v_z^2 + v_r^2) + (\tau_{zz} - \tau_{rr}). \quad (\text{A.10})$$

Since we are only interested in the forces necessary to overcome the viscous resistance to flow represented by the beads and solvent, we shall neglect the first term which is essentially a kinetic energy arising from the fluid kinematics. We thus have for eq. (A.2)

$$F' = \pi R^2(t)(\tau_{zz} - \tau_{rr}). \quad (\text{A.11})$$

From eq. (21) at constant  $T$  and  $P$ , the total free energy change for the cylinder extended from an initial length  $L_0$  to some final steady state length  $L$  is

$$\Delta F = \int_{L_0}^L F' dz. \quad (\text{A.12})$$

The continuity equation for the cylinder gives<sup>22</sup>

$$R_0^2 L_0 = R^2(t) Z(t) \quad (\text{A.13})$$

which, on substitution with (A.11) into (A.12), gives

$$\Delta F = \pi R_0^2 L_0 \int_1^\alpha (\tau_{zz} - \tau_{rr}) \frac{d\alpha}{\alpha} \quad (\text{A.14})$$

with the extension ratio  $\alpha$  as

$$\alpha = \frac{Z(t)}{L_0}. \quad (\text{A.15})$$

The relative contributions of the solvent and beads to the deviatoric stress tensor are assumed to be additive<sup>25</sup>; and since only the contribution of the beads is desired in the free energy of extension, the stress terms in (A.14) can be taken as the stress due only to the beads, as given in the text of this paper. Finally, dividing by the volume and concentration gives the desired free energy change per unit mass of polymer as

$$\Delta f_1 = \frac{1}{c} \int_1^\alpha (\tau_{zz} - \tau_{\nu\nu}) \frac{d\alpha}{\alpha} \quad (\text{A.16})$$

where the first normal stress difference has been transformed to the original Cartesian system. For the equivalent expression in shearing flow, one need only assume that the same computation is valid for the extension occurring along the principal stress directions where the stress tensor is again diagonal. The relation between the principal stresses and the stresses in Cartesian  $x, y, z$  space are given in eqs. (27) and (28).

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