# Kinetic model of fibre drawing

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A phenomenological model of polymer melt spinning is proposed that allows exact analytical treatment. Using the description of crystallite orientation by means of a simple Ising-type approach, it is possible to follow the crystallization and orientation processes up to rather high draw ratios and large times. Approximate solutions for the strain-rate and time dependences of the fibre temperature, degree of crystallinity and orientation are obtained. It is shown that the early stage of crystallization is described by the Avrami equation with exponent 2.

**(Keywords: fibre drawing; crystallization kinetics; modelling)**

## INTRODUCTION

The problem of fibre spinning kinetics is one of the most intriguing and complex in present-day polymer physics. It was shown [1-5] that in polymer fibres drawn from melt or concentrated solution, very complicated supermolecular structure exists. Even for fibres with rather high draw ratios (*DR*) and, respectively, high degree of crystallinity, the structure is very far from ideal crystal packing. The account of these circumstances requires different and rather complicated models.

At present, there exist many theories explaining the thermodynamics of fibres and their equilibrium properties (e.g. Young's modulus) as a function of initial conditions and characteristics of drawing. Some of them[6,7] are based on the idea that Young's modulus depends only upon molecular orientation, not supermolecular structure. This concept proved to be correct in many cases, but in general the role of structure is important and cannot simply be neglected.

Some theories are devoted especially to polymer crystallization[8]. The kinetics of chain folding, lamellae formation and reorientation are their main subject. Nevertheless, thus far this approach has failed to provide complete analytic results, though a qualitative picture has been provided.

The third kind of description of polymer fibre drawing lies in the hydrodynamic analysis of anisotropic liquid flow. In these theories[9] the viscosity of the liquid is a function determined by local structure, while local temperature and flow velocity are determined from the hydrodynamic equations. So from the molecular point of view this class of theories is a purely phenomenological one.

Between these concepts there exists a large unfilled gap. A possible bridge across this gap must be built on the basis of constructing semi-phenomenological theories of the 'structure–properties' type. It cannot be a molecular theory (in this case it would be very complicated), but it must have as its structural units the small supermolecular structures — crystallites. In this case only the elementary crystallization characteristics are considered as known — they are determined from the experiment and/or molecular theory. The formation of complex structures — shish-kebabs, lamellae, spherulites and fibrils — must be described properly in this 'bridge' theory — as well as the crystallization kinetics. The first step in this direction is made in the paper proposed.

## MODEL

Let us consider a fibre spun from a polymer melt. The problem can be considered as one-dimensional, if transverse effects are not taken into account in the first approximation. The scheme of the process is shown in *Figure 1*.

During the spinning, fibre velocity increases; we suppose this increase to be a linear one:

$$V(x)=V_0+Wx \tag{1}$$

where $W=d\varepsilon/dt$ is a strain rate and $V_0$ is the initial flow velocity.

In our analysis we will look at the kinetics of crystallization. In order to introduce the degree of crystallinity we imagine a three-dimensional lattice. Each site of this lattice is occupied either by an elementary crystallite or by an amorphous polymer. Degree of crystallinity $\Phi$ thus can be defined as the fraction of sites filled by crystallites.

Since drawing determines a specific direction, we can introduce a director and measure the orientation of each crystallite with respect to this director. Let us suppose that crystallites have only two possible orientations — along the $x$ axis (director orientation) or in the $yz$ plane. Let us denote the fraction of former ones as $X$; then the percentage of latter ones is $\Phi-X$.

If we suppose that the orientation of crystallites may occur only through the amorphous state, not directly, then the kinetic mechanism should be as follows:

$$(yz\text{ crystallite})\rightarrow(\text{amorphous phase})\rightarrow(x\text{ crystallite}) \tag{2}$$

Let us consider a not very late stage of crystallization,

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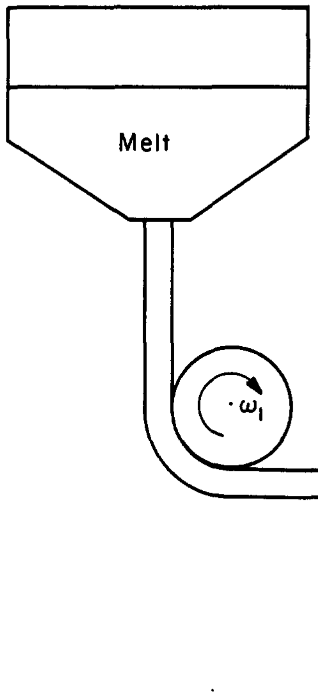

**Figure 1** Mechanical scheme of the process to be modelled

when it is still possible to neglect the inverse 'reaction' of melting and disorientation of crystallites. In this case the kinetic equations are:

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t}=[K_1(T,\varepsilon)+K_2(T,\varepsilon)](1-\Phi) \qquad (3)$$

$$\frac{\mathrm{d}X}{\mathrm{d}t}=K_1(T,\varepsilon)(1-\Phi) \qquad (4)$$

where $K_1$ and $K_2$ are temperature- and strain-dependent kinetic coefficients. To investigate their $T$ and $\varepsilon$ dependences, though, it is necessary to involve some thermodynamic considerations.

Since, below the melting point, crystallization is preferred, the internal energy of the system is a monotonically decreasing function of $\Phi$. Also, as the strain $\varepsilon$ increases, the orientation along the $x$ axis becomes more favourable, so, in total, the internal energy may be written in a form:

$$U=-\sigma A\Phi-b\sigma\varepsilon X \qquad (5)$$

where $A$ and $b$ are empirically introduced parameters (their calculation should be a task of molecular crystallization theory), and $\sigma$ is the polymer linear density. The lattice mixing entropy is given by:

$$S/k_{\mathrm{B}}=-(1-\Phi)\ln(1-\Phi)-(\Phi-X)\ln(\Phi-X)-X\ln X \qquad (6)$$

Minimization of free energy $F=U-TS$ on $\Phi$ and $X$ gives their equilibrium values $\Phi^*$ and $X^*$. They are determined by equations:

$$\frac{\Phi^*-X^*}{1-\Phi^*}=\exp\left(\frac{A}{k_{\mathrm{B}}T}\right) \qquad (7)$$

$$\frac{X^*}{\Phi^*-X^*}=\exp\left(\frac{b\varepsilon}{k_{\mathrm{B}}T}\right) \qquad (8)$$

Let us examine the influence of draw ratio $\lambda$ (or, the same, of strain $\varepsilon=\ln\lambda$) on the kinetics of the crystallization and orientation reaction. The first reaction of scheme (2) 'amorphous phase→$x$ crystallite' is characterized by the direct reaction rate constant $K_1$ and inverse reaction rate constant $K'_1$. They obey the well known relationship:

$$\frac{K_1}{K'_1}=K_{\mathrm{eq}}=\frac{X^*}{1-\Phi^*}=\exp\left(\frac{A+b\varepsilon}{k_{\mathrm{B}}T}\right) \qquad (9)$$

The second reaction 'amorphous phase→$yz$ crystallite' is also characterized by the pair of reaction rate constants $K_2$ and $K'_2$, which depend upon each other in a similar way:

$$\frac{K_2}{K'_2}=K_{\mathrm{eq}}=\frac{\Phi^*-X^*}{1-\Phi^*}=\exp\left(\frac{A}{k_{\mathrm{B}}T}\right) \qquad (10)$$

In the absence of strain ($\varepsilon=0$), $K_1=K_2$, $K'_1=K'_2=K_1\exp(-A/k_{\mathrm{B}}T)$; it is evident because directions $x$, $y$, $z$ are indistinguishable. For the case $\varepsilon>0$ we suppose that $K_2$ and $K'_2$ do not change, while $K_1$ and $K'_1$ must be multiplied respectively by factors $\exp(b\varepsilon/2k_{\mathrm{B}}T)$ and $\exp(-b\varepsilon/2k_{\mathrm{B}}T)$. Also we suppose that $(A/k_{\mathrm{B}}T)>1$, so $K_1\gg K'_1$ and it is possible to disregard the inverse reaction up to very high degree of conversion, as we mentioned earlier.

The temperature dependence of $K_1$ and $K_2$ may be determined from several simple assumptions. At $T=T_{\mathrm{m}}$ (melting point) the crystallization rate is zero, because crystallites of the required size cannot form. At $T=T_{\mathrm{g}}$ (glass transition) it is also zero, because molecular mobility is frozen. That is why crystallization can occur only in the temperature interval between $T_{\mathrm{m}}$ and $T_{\mathrm{g}}$; for the $T$ dependence of $K_2$ we propose the simplest formula:

$$K_2=K\Theta(1-\Theta) \qquad (11)$$

where $\Theta=(T-T_{\mathrm{g}})/(T_{\mathrm{m}}-T_{\mathrm{g}})$, and $K$ is a coefficient that should be determined independently — in this theory it is simply a phenomenological parameter. Thus a system of two equations (3) and (4), with $K_1$ and $K_2$ given by equations (9)–(11), is obtained to describe the behaviour of four variables: deformation $\varepsilon$, temperature $\Theta$, degree of crystallinity $\Phi$ and orientation $X$. To complete this system, it is necessary to add two more equations. These equations can be easily written: they are the mass conservation and the energy conservation equations.

The mass conservation equation can be written in the form:

$$\frac{\partial\sigma}{\partial t}+\frac{\partial}{\partial x}(\sigma V)=0 \qquad (12)$$

If we suppose that the diameter of a fibre does not change significantly during the entire process (of course, it is not always true), then the linear density of lattice sites $\sigma$ is inversely proportional to draw ratio $\lambda$. Let us expand this assumption also for the case of non-constant-diameter drawing and ascribe the diameter changes (unless they are not very large) not to the change of lattice site density, but to difference in orientation and, hence, transverse cross-section for different kinds of crystallites. In this case, since a stationary process is analysed, equation (12) may be rewritten as follows:

$$\frac{W}{\lambda}+(V_0+Wx)\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{1}{\lambda}\right)=0 \qquad (13)$$

Thus, from equation (13) we see that $\lambda = 1 + (Wx/V_0)$, and deformation $\varepsilon$ is therefore given by:

$$\varepsilon = \ln \lambda = \ln[1 + (Wx/V_0)] \tag{14}$$

The last equation necessary to complete the system is the energy conservation law. Taking into account the fibre cooling due to the interaction with the environment, we can write energy balance in the form:

$$\frac{\mathrm{d}}{\mathrm{d}x}[V(x)U(x)] + qk_\mathrm{B}(T - T_0) = 0 \tag{15}$$

with $T_0$ the temperature of the air, $q$ the inverse characteristic cooling time and $U(x)$ the density of internal energy, given by:

$$U = \sigma(cT - A\Phi - b\varepsilon X) \tag{16}$$

where $c$ is heat capacity. (Though heat capacity of any polymer strongly depends on its state, we will nevertheless consider it constant throughout the processing. The justification for this assumption is that the region of temperatures is not very large and that $c$ depends on microstructure, but not on orientation.) From equation (12) it is evident that $V(x)\sigma(x) = V_0\sigma_0$ and therefore equation (16) may be rewritten in the form:

$$\frac{\sigma_0 W}{g}\frac{\mathrm{d}\psi}{\mathrm{d}\varepsilon} + e\varepsilon\psi - \frac{\sigma_0 A}{qk_\mathrm{B}(T_\mathrm{m} - T_0)}\frac{\mathrm{d}\Phi}{\mathrm{d}\varepsilon} - \frac{\sigma_0 b}{qk_\mathrm{B}(T_\mathrm{m} - T_0)}\frac{\mathrm{d}}{\mathrm{d}\varepsilon}(\varepsilon X) = 0 \tag{17}$$

where according to equation (14) transition was made from independent variable $x$ to variable $\varepsilon$. We suppose that both environmental temperature and glass temperature are much lower than $T_\mathrm{m}$.

As a result of the transformations performed, three parameters $X$, $\Phi$ and $\psi$ are described by the complete system of three equations — equation (17) and a pair of kinetic ones:

$$\frac{W}{K}\frac{\mathrm{d}\Phi}{\mathrm{d}\varepsilon} = \psi(1 - \psi)(\mathrm{e}^{\Delta\varepsilon} + 1)(1 - \Phi) \tag{18}$$

$$\frac{W}{K}\frac{\mathrm{d}X}{\mathrm{d}\varepsilon} = \psi(1 - \psi)\mathrm{e}^{\Delta\varepsilon}(1 - \Phi) \tag{19}$$

with $\Delta = (\sigma_0 b / 2k_\mathrm{B} T_\mathrm{m})$. It is important to emphasize again that since equations (18) and (19) do not take into account inverse reactions, they are not valid at very high degrees of conversion 'amorphous phase→crystal'.

If the drawing is conducted under constant strain, not strain rate (i.e. $W = 0$, $V = V_0$, $\varepsilon = \varepsilon_0$), then instead of indirect time dependence via deformation we will have time dependence via $x$ coordinate. Kinetic equations for this case take the form:

$$X = [\mathrm{e}^{\Delta\varepsilon}/(1 + \mathrm{e}^{\Delta\varepsilon})]\Phi \tag{20}$$

$$\frac{\mathrm{d}\Phi}{\mathrm{d}x} = \frac{1}{\Lambda}\psi(1 - \psi)(1 - \Phi) \tag{21}$$

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} + \nu\frac{\psi}{\Lambda} = \kappa\frac{\mathrm{d}\Phi}{\mathrm{d}x} \tag{22}$$

where parameters $\Lambda$, $\nu$ and $\kappa$ are given by:

$$\Lambda = \frac{V_0}{K(1 + \mathrm{e}^{\Delta\varepsilon})} \tag{23}$$

$$\nu = \frac{qk_\mathrm{B}}{\rho c K(1 + \mathrm{e}^{\Delta\varepsilon})} \tag{24}$$

$$\kappa = \frac{A + b\varepsilon\mathrm{e}^{\Delta\varepsilon}/(1 + \mathrm{e}^{\Delta\varepsilon})}{c(T_\mathrm{m} - T_\mathrm{g})} \tag{25}$$

In the next section we will analyse the behaviour of solutions of the system (17)–(19), describing the early stage of fibre drawing from the melt. After that, the process of fibre spinning from solution will also be analysed. The approximate analytic solution of equations (20)–(22) will be found and comparison will be made with experimental data[10]. Emphasis will be put on the deviation from the Avrami law of crystallization.

## MELT DRAWING — SOLUTIONS

### *Small $\varepsilon$*

For drasing from the melt, initial conditions are:

(i) $\psi = 1$, temperature is that of melting;
(ii) $\Phi = 0$, degree of crystallinity is zero;
(iii) $X = 0$, there are no oriented crystallites.

At the beginning of the process all three functions $X$, $\Phi$ and $\psi$ may be expanded into series in $\varepsilon$. It can be easily shown that the series for $\Phi$ and $X$ should start from the term proportional to $\varepsilon^2$, because at $\varepsilon = 0$, $\Phi$, $X$, $(\mathrm{d}\Phi/\mathrm{d}\varepsilon)$ and $(\mathrm{d}X/\mathrm{d}\varepsilon)$ are all equal to zero (it follows from initial conditions and equations (18) and (19) in which the right-hand sides become zero when $\psi = 1$). That is why for small $\varepsilon$:

$$\Phi = \alpha\varepsilon^2 \tag{26}$$

$$X = \beta\varepsilon^2 \tag{27}$$

$$\psi = 1 - \gamma\varepsilon \tag{28}$$

(only leading terms are preserved).

Substitution of the expressions for $\Phi$, $X$ and $\psi$ into equations (17)–(19) gives for $\alpha$, $\beta$ and $\gamma$ the following:

$$\alpha = \frac{Kq}{\sigma_0 c W^2} \tag{29}$$

$$\beta = \frac{Kq}{2\sigma_0 c W^2} \tag{30}$$

$$\gamma = \frac{q}{\sigma_0 c W} \tag{31}$$

Equations (26)–(31) describe the early stage of crystallization with simultaneous cooling. These results also must be taken as asymptotic ones for general solutions.

It is necessary also to point out that $\varepsilon$ is proportional to $t$ (because strain rate is constant) — hence degree of crystallinity and orientation are proportional to $t^2$.

### *Intermediate $\varepsilon$ (an approximate analytic solution)*

To obtain solutions of system (17)–(19) that are valid over a large time scale, it is necessary to simplify this system significantly. First of all, from equations (18) and (19) we can derive the relationship between $\Phi$ and $X$:

$$X(\varepsilon) = \int_0^\varepsilon \frac{\mathrm{d}\Phi}{\mathrm{d}y}\frac{\mathrm{e}^{\Delta\varepsilon}}{1 + \mathrm{e}^{\Delta\varepsilon}}\mathrm{d}y \tag{32}$$

Let us take $\Phi(\varepsilon)$ in the form:

$$\Phi(\varepsilon)=1-\exp[-g(\varepsilon)] \tag{33}$$

This Avrami-type[11] form describes correctly the behaviour of fibre crystallinity for all the range of times, even for very high conversion. But since the model proposed is valid only for small and intermediate degrees of crystallinity, we deal only with the region of $\varepsilon$ where $0<g<1$. Let us expand $g$ into a series in $\varepsilon$ and preserve only two leading terms:

$$g(\varepsilon)=\alpha\varepsilon^2+\mu\varepsilon^3 \tag{34}$$

(here $\alpha$ is given by (29), and $\mu$ will be determined later). Substituting (33) and (34) into (18), we obtain:

$$\psi(1-\psi)=\frac{W(2\alpha\varepsilon+3\mu\varepsilon^2)}{K(1+\varepsilon^{\gamma\varepsilon})} \tag{35}$$

The maximum of the left-hand side of (35) is equal to 0.25, and hence the maximum of the right-hand side must be the same — this gives an equation for the determination of $\mu$. If we denote $\xi=\Delta\varepsilon$ this equation may be written as follows:

$$\frac{W}{K}\max_{\zeta}\left(\frac{2(\alpha/\Delta)\xi+3(\mu/\Delta^2)\xi^2}{1+e^{\zeta}}\right)=0.25 \tag{36}$$

After some transformations and numerical analysis the value of $\mu$ is obtained:

$$\mu\approx\frac{2\alpha\Delta}{3}\left(\frac{K\Delta}{8W\alpha}-0.25\right) \tag{37}$$

On the basis of results obtained, it is possible to describe the behaviour of all three functions $\Phi$, $X$ and $\psi$ in a rather broad interval of times. Near the point $\varepsilon=(2/\Delta)$, where the maximal conversion rate is achieved, the temperature of the polymer decreases sharply — the derivative $(\mathrm{d}\Phi/\mathrm{d}\varepsilon)$, calculated from equation (17), is given by:

$$\lambda=\left(\frac{\mathrm{d}\Phi}{\mathrm{d}\varepsilon}\right)_{\mathrm{m}}=-\tau\left\{0.5\exp(-2/\Delta)-\frac{2K(\rho_0A+4T_{\mathrm{m}})}{\Delta W(T_{\mathrm{m}}-T_0)}\right.$$
$$\times\exp\left[-\frac{Kq}{\rho_0c\Delta^2W^2}\left(\frac{8}{3}+\frac{2\rho_0cW}{3q}\right)\right]$$
$$\left.-\frac{\rho_0bW}{q(T_{\mathrm{m}}-T_0)}X|_{\varepsilon=2/\Delta}\right\} \tag{38}$$

The first term dominates and thus the temperature drop is almost all near the point $\varepsilon=2/\Delta$, as schematically shown in *Figure 2*.

Let us analyse now the fibre crystallinity at the chosen point $x=L_0$, corresponding to the end of the real processing region. If we denote $f=K/W$, $\Theta=q/K$, then the crystallization and orientation at this point should crucially depend upon $f$ and $\Theta$. The deformation $\varepsilon$ at point $L_0$ is given by:

$$\varepsilon(L_0)=\ln[1+(WL_0/V_0)]=\ln[1+(KL_0/fV_0)] \tag{39}$$

and the degree of crystallinity $\Phi(L_0)$ is equal to:

$$\Phi(L_0)=$$
$$1-\exp\{-f^2\Theta\varepsilon^2/c\rho_0-2f^2\theta\Delta\varepsilon_3[(\rho_0c\Delta/8f\theta)-0.25]/3c\rho\} \tag{40}$$

where $\varepsilon=\varepsilon(L_0)$, given by equation (39).

The exponent can be rewritten in a way more convenient for analysis:

$$g=\frac{\Theta}{c\rho_0}\left(\frac{KL_0}{V_0}\right)^2\phi^2\ln^2(1+1/\phi)+\frac{\Delta^2KL_0}{12V_0}\phi\ln^3(1+1/\phi) \tag{41}$$

with $\phi=(fV_0/KL_0)$. Maximization of $g$ on $\phi$ may give us the optimal strain rate (i.e. the strain rate that provides maximal degree of crystallization at point $L_0$).

If we take into account only the first term in equation (40), we can see there is no maximum — function $[\phi\ln(1+1/\phi)]^2$ increases continuously from 0 to 1. On the contrary, the second term has a maximum at point $\phi\approx0.06$. So, the behaviour of the exponent as a whole

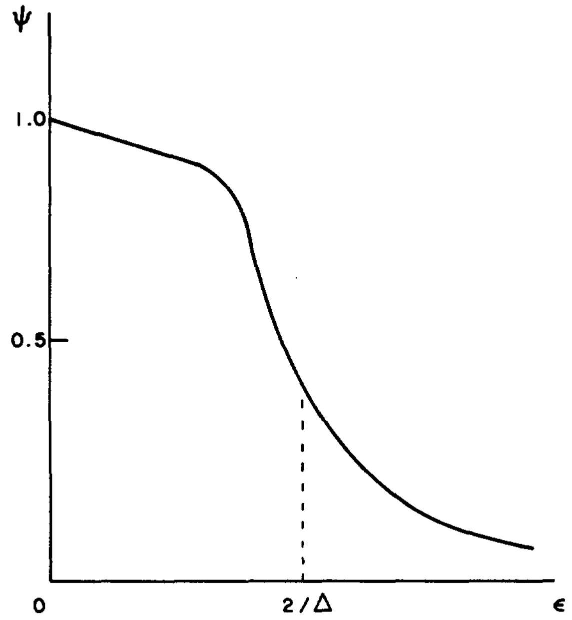

**Figure 2** Dimensionless temperature $\psi=(T-T_0)/(T_{\mathrm{m}}-T_0)$ as a function of deformation $\varepsilon$ or time $t$

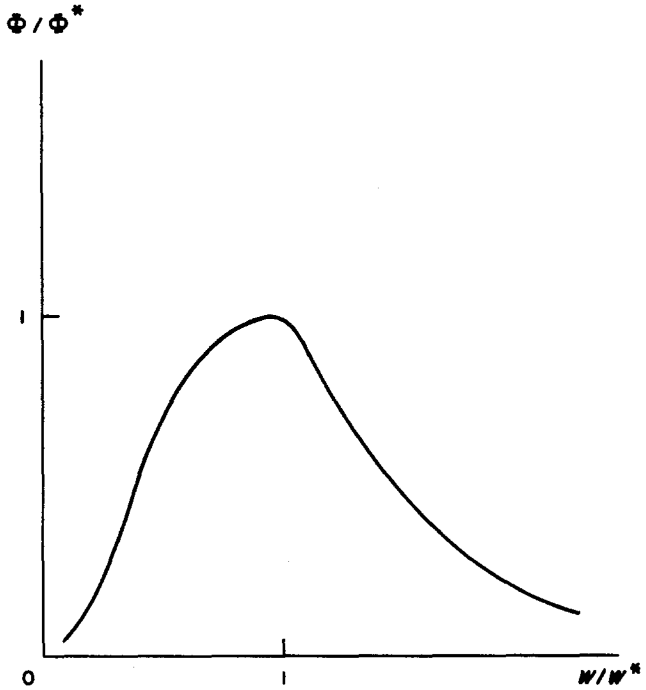

**Figure 3** Degree of crystallinity at point $x=L_0$ vs. strain rate $W$; $W^*$ and $\Phi^*$ are defined by (42) and (43)

is determined by the dimensionless parameter:

$$G = 12\theta K L_0 / c\rho_0 V_0 \Delta^2 \tag{42}$$

If $G \ll 1$, maximal crystallization can be achieved at a strain rate:

$$W^* = 16 V_0 / L_0 \tag{43}$$

and is equal to:

$$\Phi^* = 1 - \exp[-0.12\Delta^2 (K L_0 / V_0)] \tag{44}$$

The dependence of $\Phi(L_0)$ on $W$ in the limit $G \ll 1$ is schematically plotted in *Figure 3*. If $G \gg 1$, there is no maximum in crystallinity and $\Phi$ increases monotonically as $W$ decreases.

## DISCUSSION

The model proposed here and preliminary results of rough calculations in its framework allow us to describe some qualitative regularities of fibre drawing from the melt in the case where the temperature of the polymer is not maintained constant, as in real drawing processes. Unfortunately, most experiments to date have been performed at constant temperature, so direct comparison with experimental data now is difficult. Nevertheless, qualitatively the model proposed gives an acceptable prediction about the possibility of having the optimal strain rate for a drawing process.

In fact, the proposed model is the extension for the case of non-constant temperature of the so-called finite-grain model of crystallization (FGM) (see, e.g., ref. 12). The main idea is that, at some stage of crystallization, when sizes of crystallites are large, they either cannot grow more or this growth is not the main contribution to crystallization kinetics. Thus, the dimensionality of growth changes.

It is important to emphasize that, though the solutions of the kinetic equations obtained in this paper are correct only for low and intermediate degrees of crystallinity, the equations themselves may be easily adapted to the case of arbitrary crystallinity and deformation. Nevertheless, it will be much more difficult to obtain analytic solutions. In particular, the function $\Phi(\varepsilon)$ will be of more generalized Avrami type, with exponent containing more than two terms.

A problem beyond consideration was the structure formation (fibrils, shish-kebabs, etc.). The analysis of this aspect of drawing, nevertheless, is also possible in the framework of the model proposed. The use of modern theories of structural instabilities (e.g. spinodal decomposition[13]) will probably give a means of description of these structures.

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