Viscoelasticity in Shearing and Accelerative Flows: A Simplified Integral Theory

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An explicit, four-constant model for viscosity and normal stresses in simple shear has been developed by simplifying the integral theory of Bernstein, Kearsley, and Zapas. In essence the procedure involves curve-fitting the linear relaxation spectrum. The four constants appear also in equations for the stress distribution and for pressure drop in accelerative flow between flat plates; flow along rays is assumed. The equations reduce to second-order theory and to Newtonian theory as a Deborah number becomes small. Comparison of the predicted stress distributions with previously published stress birefringent data shows good agreement; because of the low shear rates, however, the check is not demonstrating very strong departures from the second-order asymptote. Certain other theoretical results, including pressure drop predictions, are also noted.

A major effort in the field of rheology has been devoted to the development of constitutive equations for viscoelastic fluids. These have been reviewed in some detail in recent papers by Spriggs, Huppler, and Bird (*11*) and Bogue and Doughty (*5*). The present work is an effort to simplify these rather complicated equations to produce explicit results for simple shearing flows and for certain accelerative flows.

Although current research on stress overshoot and other time-dependent experiments may shortly narrow the field of consideration, there does not at the moment appear to be any strong reason for selecting one constitutive equation over another. The present authors prefer the integral theories, as opposed to the differential theories, on the basis that they lead to explicit results once the kinematics is assumed. In the present work, the theory of Bernstein, Kearsley, and Zapas (*3, 4*) (hereafter called the B-K-Z theory) was selected because it seems to have wide utility and because it rests (although not uniquely) on a thermodynamic rationale. It is felt, however, that the basic ideas presented here are not limited to the B-K-Z theory and can be extended to other integral theories.

Several recent applications of the B-K-Z theory have shown its versatility. Zapas (*14*) has brought together solid biaxial stress data with polymer solution data, while Zapas and Craft (*15*) have treated multiple-step stress relaxation. Doughty and Bogue (*7*), in work similar to Zapas' on polymer solutions, have brought together steady shear and linear dynamic data. And finally Fields and Bogue (*9*) have estimated normal stresses in a slowly accelerating flow field near a channel entrance. On the theoretical side White and Tokita (*13*) have shown that the B-K-Z theory can be considered as a special case of an integral expansion of the more general Green-Rivlin framework.

CONSTITUTIVE EQUATION

Bernstein, Kearsley, and Zapas (*3, 4*) have proposed the following integral theory for incompressible and isothermal flows:

$$\tau_{ij} = -pg_{ij} + 2\int_0^\infty \left\{ \frac{\partial U}{\partial I} c^{-1}{}_{ij}(s) - \frac{\partial U}{\partial II} c_{ij}(s) \right\} ds \quad (1)$$

where

$$\left.\begin{aligned} c_{ij}{}^{-1} &= g^{ab} g_{ki} g_{lj} \frac{\partial x^k}{\partial X^a} \frac{\partial x^l}{\partial X^b} \\ c_{ij} &= g_{ab} \frac{\partial X^a}{\partial x^i} \frac{\partial X^b}{\partial x^j} \end{aligned}\right\} \text{relative strain tensors}$$

The x^i are the coordinates of points at the present time; X^i, the coordinates of points at some earlier time; and U, an empirical potential function of time and the invariants of the strain tensors.

The theory involves an integration of memory-weighted strain over all past time. The basic concept is that the present stress depends less on strain in the distant past than on strain in the recent past. The potential function U describes how the strains are weighted over past time. More details of this theory are given in an earlier paper by Bogue and Doughty (*5*). Only the pertinent theoretical results of the general theory will be presented in the following discussion.

To use the B-K-Z theory to solve actual problems of interest, one must specify both the kinematics of the problems, which indicates how coordinate points move in time, and the potential function U, which gives the nonlinear history dependence of strain. Zapas (*14*) has proposed a potential function for low to moderate shear rates which, with some simplifications, is of the form:

$$U = \frac{-m'(s)}{2a} \ln\left\{ 1 + \frac{a}{2}\left[(I-3) + (II-3)\right] \right\} - 12\, m'(s) \ln\left[\frac{I+15}{II+15} \right] \quad (2)$$

where $-m'(s)$ is the linear memory decay function. The constant a in the above equation is an adjustable parameter which probably must be varied somewhat for different fluids. For polyisobutylene solutions a is about 2/9, which is the value presented by Zapas.

Zapas (*14*) points out that his formulation of the function U is empirical and thus is not necessarily unique. However, it is a reasonable one in that it is able to describe both solid viscoelastic behavior as well as nonlinear polymer solution response. It is through the invariants of strain in the potential function that the shear dependence is introduced into the theory.

The other function that needs to be specified is the memory function $m(s)$. If exponential decay functions are used, it is the same function as the relaxation modulus of linear viscoelasticity, $G(t)$. Usually this modulus is expressed in terms of a continuous relaxation spectrum $H(\lambda)$

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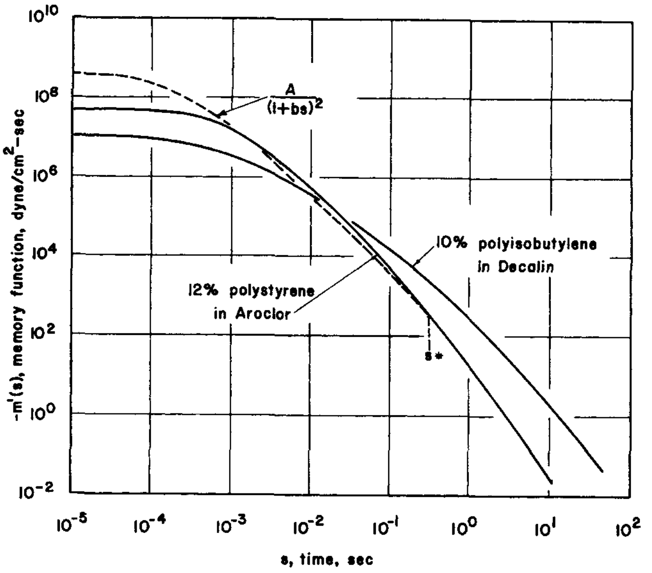

Fig. 1. Memory function.

defined by (8):

$$m(s) = \int_{-\infty}^{+\infty} H(\lambda)\, e^{-s/\lambda}\, d\ln\lambda \qquad (3)$$

or

$$-m'(s) = \int_{-\infty}^{+\infty} \frac{H(\lambda)}{\lambda}\, e^{-s/\lambda}\, d\ln\lambda \qquad (4)$$

There is considerable literature on relaxation spectra coming from the molecular theories and from linear viscoelastic experiments. Ferry (8) presents typical curves for different classes of bulk polymers and polymer solutions. For dilute polymer solutions the discrete spectra of the theories may be represented (except near the maximum relaxation time $\lambda_{\max}$) by continuous spectra of the form

$$H(\lambda) = \frac{\text{const.}}{\lambda^k} \qquad (5)$$

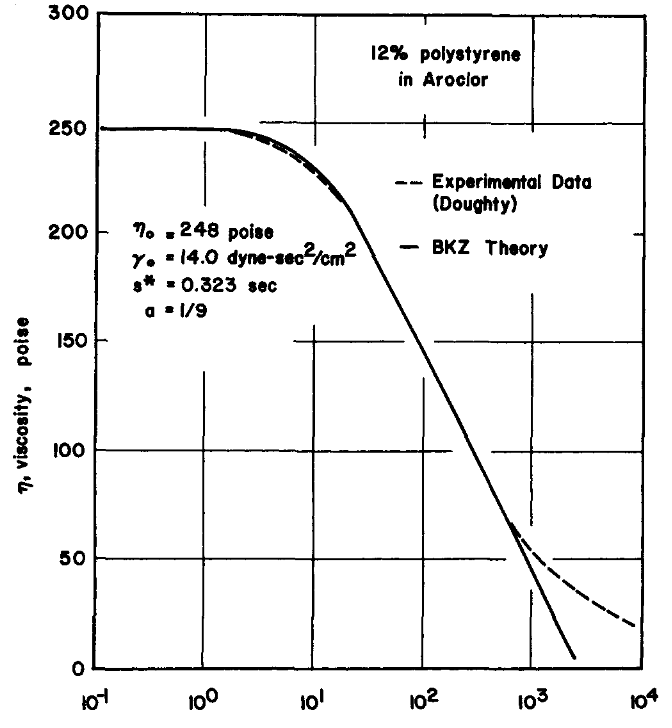

Fig. 2. Comparison of simplified B-K-Z theory with viscosity data in simple shear.

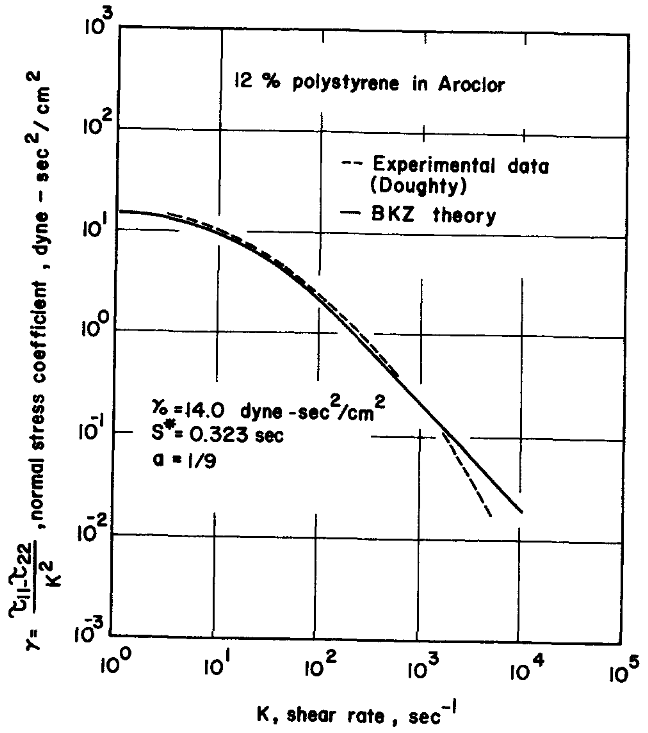

Fig. 3. Comparison of simplified B-K-Z theory with normal stress data in simple shear.

The exponent k has a value of 1/2 in the Rouse theory and a value of 2/3 in the Zimm theory. If one inserts Equation (5) into Equation (4), one obtains, for the range where $s/\lambda_{\max} \to 0$, an equation of the form

$$-m'(s) = \frac{\text{const.}}{s^{k+1}} \qquad (6)$$

This function will drop off as the 1.5 or the 1.67 power in the cases of the Rouse and Zimm theories, respectively. In the present work this result has been generalized slightly and the memory function has been represented by equations of the form

$$-m'(s) = \frac{A}{(1+bs)^n} \quad (\text{for } s < s^*)$$
$$-m'(s) = 0 \quad (\text{for } s > s^*) \qquad (7)$$

where A, b, and s^* are material constants with units of dynes/sq.cm.-sec., sec.$^{-1}$ and sec., respectively. The time constant s^* plays the role of a maximum relaxation time. Physically one need look back only s^* seconds in time to see all relevant strain history. Equation (7) may be thought of finally as an extension of Equation (6) up to large values of $s/\lambda_{\max}$, even though Equation (6) does not hold rigorously there; or simply as a curve-fitting equation for $m'(s)$ data. For mathematical reasons the exponent n is taken as an integer with values typically of the order of 1 or 2.

The solid line in Figure 1 shows plots of $-m'(s)$ for two polymer solutions (12% polystyrene in Aroclor and 10% polyisobutylene in Decalin), the data coming from the work of Doughty (6, 7). These results can be reasonably represented with equations of the form of Equation (7), taking $n = 2$. The dotted line in Figure 1 will be discussed later. This value of n has been used in the subsequent work, although some additional results for other values of n are available in the thesis and will be noted.

SIMPLE SHEAR FLOW

The kinematics of simple shear flow is given by Bogue

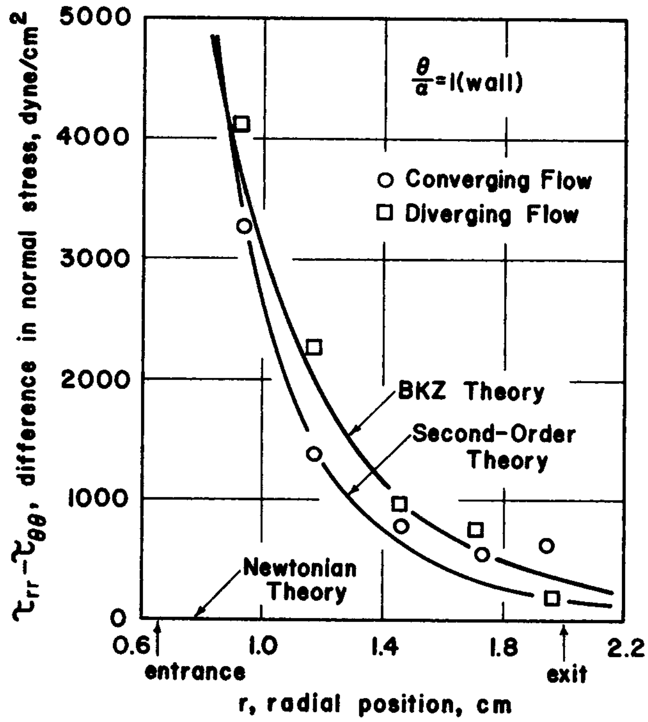

Fig. 4. Normal stress data at the wall in converging-diverging flow.

and Doughty (5). If these results are inserted into the general B-K-Z theory one has

$$\eta \equiv \frac{\tau_{12}}{K} = \int_0^\infty \frac{-m'(s)s\,ds}{1 + aK^2s^2} \tag{8}$$

and

$$\gamma \equiv \frac{\tau_{11} - \tau_{22}}{K^2} = \int_0^\infty \frac{-m'(s)s^2ds}{1 + aK^2s^2} \tag{9}$$

(Note that the symbol γ used here differs by a factor of -2 from that used in our earlier work and in some of the literature on constitutive equations.)

For a memory function of the form of Equation (7) (with $n = 2$), one has the following results for zero shear rate:

$$\eta_0 = \frac{A}{b^2}\left\{\ln(1 + bs^*) + \frac{1}{1 + bs^*} - 1\right\} \tag{10}$$

$$\gamma_0 = \frac{A}{b^2}\left\{s^* - \frac{1}{b^2}\left[2\ln(1 + bs^*) + \frac{1}{1 + bs^*} - 1\right]\right\} \tag{11}$$

The more general results (for higher shear rates) are:

$$\eta = \eta_0 - \frac{\gamma_0}{2s^*}\ln(1 + aK^2s^{*2}) \tag{12}$$

and

$$\gamma = \frac{\gamma_0}{\sqrt{a}Ks^*}\tan^{-1}(\sqrt{a}Ks^*) \tag{13}$$

In obtaining these simple results, one must make the approximations $aK^2/b^2 << 1$ and $bs^* >> 1$. For the polystyrene solution, b has a value of approximately 3,000 sec.$^{-1}$ and a has a value of about 1/9, which means that these equations are valid for shear rates of the order of $K < \sim 5 \times 10^3$ sec.$^{-1}$ Also with $s^* \approx 0.3$ sec., the requirement $bs^* >> 1$ is well satisfied.

Equations (12) and (13) have been fitted to experimental data for a 12% solution of polystyrene in Aroclor (6), as shown in Figures 2 and 3. The constant a was selected *a priori* from previous experience (6, 7) and the other three constants (η_0, γ_0, s^*) were obtained by curve-fitting. As can be seen in the figures, quite good fits are possible.

In simple shear and also in the other problems to be presented, the original constants A and b disappear (that is, becoming lumped into the constants η_0 and γ_0). Thus, in the usual case of having available only viscosity and normal stress data, one does not need to know the memory (relaxation) function in detail, although it is necessary to know its general shape. Nonetheless, it is of interest to back calculate a memory function for comparison with the experimental data. From the above constants and Equations (10) and (11), one can calculate $A = 2.5 \times 10^8$ dynes/sq.cm.-sec. and $b = 2{,}400$ sec.$^{-1}$ Inserting these values into Equation (7), one obtains the dotted line in Figure 1. The fit is good in the range of a which makes a significant contribution to the η and γ coefficients (from about 10^{-4} sec. to s^*). At low values of s there is a discrepancy, although this causes little error in the coefficients in view of the integrands $-m'(s)s$ and $-m'(s)s^2$ Equations (8) and (9). The value of the time constant s^* is probably too small; choosing a larger value would give somewhat less satisfactory fits of the viscosity and normal stress functions. Difference of this magnitude appear to be inherent in the B-K-Z and other integral theories or in the data and not in the approximations made here (7). All factors considered, it is believed that the equations presented provide a reasonable framework for comparing one fluid with another and for undertaking more complicated problems, although the absolute values of the constants probably cannot be interpreted quantitatively in terms of the relaxation spectrum.

CONVERGING AND DIVERGING FLOW

Consider the radial flow of a viscoelastic fluid between converging and diverging flat plates, that is, flow along rays in a polar coordinate system. The appropriate kine-

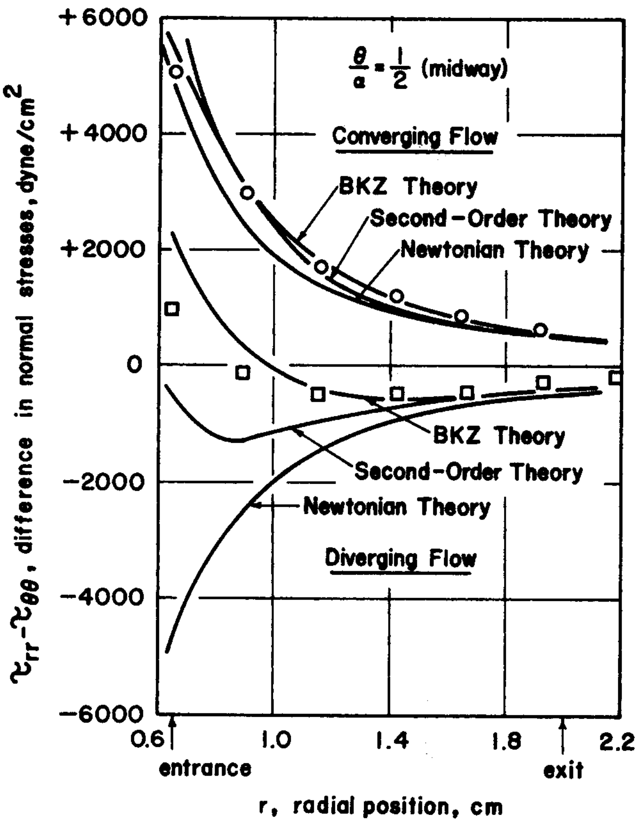

Fig. 5. Normal stress data at the midway point in converging-diverging flow.

matical descriptions are

$$r = \sqrt{R^2 + 2fs}$$
$$\theta = \Theta$$
$$z = Z \qquad (14)$$

where small letters denote coordinates in present time and capital letters denote coordinates at an arbitrary earlier time. The symbol f is defined by

$$f(\theta) = r\,v_r$$

which follows from the radial flow assumption. Writing out the physical components of the strain tensor, one has

$$c_{ij}^{-1} = \begin{pmatrix} \dfrac{R^2 + \dfrac{(f')^2 s^2}{R^2}}{r^2} & \dfrac{f's}{R^2} & 0 \\ \dfrac{f's}{R^2} & \dfrac{r^2}{R^2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (16)$$

The corresponding invariants of strain are

$$\mathrm{I} = \mathrm{II} = 1 + \frac{r^2}{R^2} + \frac{R^2}{r^2} + \frac{(f')^2 s^2}{r^2 R^2} \qquad (17)$$

$$\mathrm{III} = 1 \qquad (18)$$

These equations for the strain and strain invariants can be inserted into the B-K-Z theory and integrated (for the case analogous to $aK^2/b^2 << 1$). The results are quite complicated (*1*) and will not be presented here. Special cases of interest are the stresses at the wall (where $f = 0$):

$$\tau_{r\theta} = \frac{f'}{r^2}\left\{\eta_0 - \frac{\gamma_0}{2s^*}\ln\left(1 + a\frac{f'^2 s^{*2}}{r^4}\right)\right\} \qquad (19)$$

$$\tau_{rr} - \tau_{\theta\theta} = \frac{f'}{\sqrt{a}\,r^2}\,\frac{\gamma_0}{s^*}\tan^{-1}\left(\frac{\sqrt{a}f's^*}{r^2}\right) \qquad (20)$$

and stresses at the centerline (where $f' = 0$):

$$\tau_{r\theta} = 0 \qquad (21)$$

and

$$\tau_{rr} - \tau_{\theta\theta} = \frac{-4f}{r^2}\eta_0 + \frac{2f}{r^2}\,\frac{\gamma_0}{s^*} \ln\left(1 - \frac{2fs^*}{r^2} + 4a\frac{f^2 s^{*2}}{r^4}\right) \qquad (22)$$

In obtaining these simple results, the approximations $|2f/br^2| << 1$ and $a(4f^2 + f'^2)/b^2r^4 << 1$ (analogous to $aK^2/b^2 << 1$) have been made. These results reduce to the second-order theory presented by Adams, Whitehead, and Bogue (*2*) as fs^*/r^2 becomes small. As this group becomes still smaller the result approaches the Newtonian asymptote (the term involving η_0). The group fs^*/r^2, being a ratio of material to system times, may be thought as a local (r-dependent) Deborah number (*10*).

To obtain explicit results from the above equations a velocity profile must be assumed or calculated. For low flow rates and modest angles one can assume a parabolic distribution of the following form (*2*):

$$f = \pm\frac{3}{4}\,\frac{Q}{w\alpha}\left[1 - \left(\frac{\theta}{\alpha}\right)^2\right] \qquad (23)$$

where the plus and minus signs are for diverging and converging flow, respectively.

Calculations for the shear and normal stresses were made using Equations (19) to (22) and their analogs for other angular positions. Representative normal stress data are shown in Figures 4 and 5 for $\theta/\alpha = 1$ (wall) and $\theta/\alpha = ½$ (midway point). The birefringent data shown are those reported by Adams, Whitehead, and Bogue (*2*) for a 12% polystyrene in Aroclor solution. Theoretical lines for Newtonian and Coleman-Noll second-order theory (see *2*) are also presented.

The elastic effects in these low shear rate data are not large ones and thus the full integral (B-K-Z) theory is not greatly different from the second-order theory. It is encouraging, however, that the B-K-Z theory lines are generally in better agreement, especially at small values of r in Figure 5. However, a slight, probably fortuitous, improvement of the analytical [Equations (19) to (22)] over computer results using the full B-K-Z theory (*1*) and the scatter in Figure 4 do not permit one to conclude that the check is definitive.

OTHER RESULTS

The stress results may be combined with a force balance (equation of change) in the r-direction and integrated along this coordinate to obtain predictions for the pressure drop. As before, flow along rays is assumed. Surprisingly simple results were obtained for the total stress $P_{\theta\theta}$ at the wall (that which one would measure with a pressure gauge). Also worked out, but not presented here, are the predictions of the B-K-Z theory in elongational flow and in the sudden inception of a steady shear rate (the stress overshoot experiment).

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NOTATION

A = material constant in Equation (7), dynes/sq.cm.-sec.
a = material constant in potential function, Equation (2), dimensionless
b = material constant in Equation (7), sec.$^{-1}$
c_{ij}, c_{ij}^{-1} = relative strain tensors, Equation (1)
f = $v_r r$, a new velocity variable, sq. cm./sec.
f', f'' = first, second derivatives of f with respect to θ, sq.cm./sec.
g_{ij} = metric tensor
$H(\lambda)$ = relaxation spectrum, Equation (3), dynes/sq.cm.
I, II = first, second invariants of c_{ij}^{-1}, $I = c_{ii}^{-1}$, $II = \frac{1}{2}(c_{ii}^{-1}) - \frac{1}{2}c_{ij}^{-1}c_{ji}^{-1}$
k = exponent in Equation (5)
K = shear rate, sec.$^{-1}$
$m(s)$ = memory function, Equation (3), dynes/sq.cm.
$m'(s)$ = first time derivative of memory function, Equation (4), dynes/sq.cm.sec.
p = scalar stress (pressure), dynes/sq.cm.
$P_{rr}, P_{\theta\theta}$ = total stress components, dynes/sq.cm.
Q = volumetric flow rate, cc./sec.
r = radial position, cm.
s = backward running time, sec.
s^* = maximum relaxation time in memory function, sec.
U = potential function, Equation (2)
v_r = velocity in r-direction, cm./sec.
w = depth of channel
x^i = present coordinates of points
X^i = past coordinates of points

Greek Letters

α = half angle of duct, radians
$\gamma(K)$ = normal stress function, Equation (9), dynes-sec.^{2}/sq.cm.

γ_0 = zero shear normal stress coefficient, dynes-sec.^{2}/sq.cm.
$\eta(K)$ = viscosity function, Equation (8), dynes-sec./sq.cm.
η_0 = zero shear viscosity, dynes-sec./sq.cm.
τ_{ij} = stress tensor
$\tau_{rr}, \tau_{\theta\theta}$ = r and θ components of stress, dynes/sq.cm.
θ = polar coordinate

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Numerical Evaluation of Temperature Profiles and Interface Position in Filaments Undergoing Solidification

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A numerical method has been described for the solution of the general equations which depict solidification in the cylindrical coordinate system. The method has been outlined for cooling and solidification of a moving filament of molten polymer. The solution is given in terms of six dimensionless variables: α_l/α_s, k_l/k_s, hR/k_R, $L/[C_{ps}(T_O\text{-}T_C)]$, T_O/T_C, and $\sigma\epsilon_p R(T_O\text{-}T_C)^3/k_R$. Plots are shown for the solution of the heat transfer equations and associated boundary conditions for several values of the dimensionless variables. The method describes the process of cooling and freezing liquids when convective and/or radiative energy losses are considered. The form of the theoretical equation compares very favorably with experimental data.

Prediction of the temperature profile and solid-liquid interface as a function of time for a freezing medium is of importance in the processing of frozen foods, casting of metals and solid rocket motors, production of plastic components, and spinning of textile fibers. It is important to know the position of the solid-liquid interface as a function of time in order to determine the time for solidification. However, in some instances it is even more important to know the temperature profile as a function of time. In the spinning of many textile fibers, molten polymer is extruded through an orifice and the filament cooled by passing through an inert gaseous atmosphere. The fiber properties are then altered by a drawing process. If the fiber is not sufficiently cooled or large temperature gradients exist during the spinning process, filaments with undesirable properties may result. This paper describes the numerical solution of a set of partial differential equations which describe heat transfer in a freezing filament. Radial temperature profiles and interface position are evaluated as a function of time. The filament is initially liquid and above the freezing point; however, simpler problems such as heat transfer to a saturated solution can also be solved by the technique described.

Several papers have been published on heat transfer in freezing media. London and Seban (*17*) presented an analogue method for prediction of the solid-liquid interface position as a function of time when the specific heat of the two phases was neglected. Their work considered the freezing problem in cartesian, cylindrical, and spherical coordinate systems. Danckwerts (*8*) obtained solutions for heat conduction with a moving boundary in cartesian coordinates, when the change in density was important. Lin (*16*) has presented an analytical solution for the liquid-solid interface position as a function of time for unsteady state freezing problems in the cylindrical and spherical coordinate system, if the cartesian coordinate solution is known. Relaxation methods were used to solve the cartesian coordinate problem in a semi-infinite medium by Allen and Severn (*1*). Hrycak (*11*) has described solidification of a plane-parallel stratified medium. Carslaw and Jaeger (*5*) report a solution for freezing a saturated liquid in a semi-infinite medium in cartesian coordinates. Wilcox and Duty (*22*) have described a numerical technique for evaluation of steady state temperature profiles in a cylindrical crystal being drawn from a liquid melt. Numerical methods for solution of the unsteady state freezing problem

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