c_p = specific heat of liquid phase
D = diffusivity of absorbing component
E = enhancement factor
E_R = activation energy
h_L = liquid phase heat transfer coefficient
K = liquid phase thermal conductivity
$k(T)$ = first-order rate constant at temperature T
k_L = liquid phase mass transfer coefficient
M = group $\sqrt{k(T_b)D/k_L^2}$
M' = group $\sqrt{k(T^*)D/k_L^2}$
T^* = interface temperature
T = temperature
T_b = bulk liquid phase temperature
x = position within liquid film
x_H = thickness of mass transfer film
x_M = thickness of heat transfer film

Greek Letters

α = thermal diffusivity
ΔH_s = heat of solution
ΔH_R = heat of reaction
ρ = density of liquid phase
μ_s = slope of solubility-temperature relationship

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Mechanics of Nonisothermal Polymer Melt Spinning

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Spin line tension, diameter attenuation, and the onset of the draw resonance instability are determined for a viscoelastic polymer melt, taking into account the changes in physical properties resulting from cooling of the filament. The theory predicts the experimentally observed stabilization of very short and very long filaments.

SCOPE

Melt spinning is the process of continuously drawing an extruded polymer melt into a fiber. The influence of melt viscoelasticity on the mechanics and certain aspects of the stability of the process is now reasonably well understood for spinning under isothermal conditions, but prior analyses of spinning under conditions where heat transfer is important have not considered the elasticity of the melt. Neglect of elasticity can result in grossly inaccurate estimates of spin line tension, diameter attenuation rate, and stability.

This paper is an extension of our previous analyses of the mechanics and stability of melt spinning (Denn et al., 1975; Fisher and Denn, 1976) to include the effect of heat transfer between the filament and surroundings as well as melt elasticity. The analysis is restricted to a Maxwell model of fluid viscoelasticity which has a single relaxation time and deformation-rate independent viscosity and modulus. In general, only qualitative results can be expected, but the model appears to be adequate for some polymers, including polyethylene terephthalate of intermediate intrinsic viscosity.

CONCLUSIONS AND SIGNIFICANCE

The effect of cooling is to increase the initial rate of diameter attenuation of a viscoelastic filament. Cooling inhibits the onset of a processing instability known as draw resonance, and the interaction of cooling and viscoelasticity results in a stabilization at high Stanton number which cannot exist for an inelastic liquid. Generally, short spin lines will be stabilized by fluid elasticity and long spin lines by cooling.

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There are little reliable nonisothermal spinning data with which to compare the theoretical model predictions. An indirect comparison with draw resonance data of Ishihara and Kase (1976) on polyethylene terephthalate shows agreement.

Melt spinning is a process in which a polymer melt filament which has been extruded through a spinneret hole is continuously drawn into a fiber by winding up downstream at a speed which is greater than the extrusion velocity. The process is shown schematically in Figure 1. There is a region of die swell just beyond the spinneret, where some of the elastic stresses generated in the extrusion process relax as the axial velocity distribution in the jet becomes uniform. This is followed by the melt drawing zone, where the diameter attenuates as the velocity increases to the take-up speed. Most of the drawing takes place in the melt, and we shall presume in all that follows that the diameter is constant following solidification. The processes of film casting and extrusion coating are nearly identical in a mechanical sense to fiber spinning.

The melt spinning process was first analyzed theoretically by Kase and Matsuo (1965) and Matovich and Pearson (1969). These studies do not account for the large elastic stresses which can be established in extensional flows of high molecular weight liquids, and hence they are often not applicable to commercially interesting polymers. Failure to account for the elastic stresses can result in prediction of too small a take-up tension and too slow an initial rate of diameter attenuation with distance.

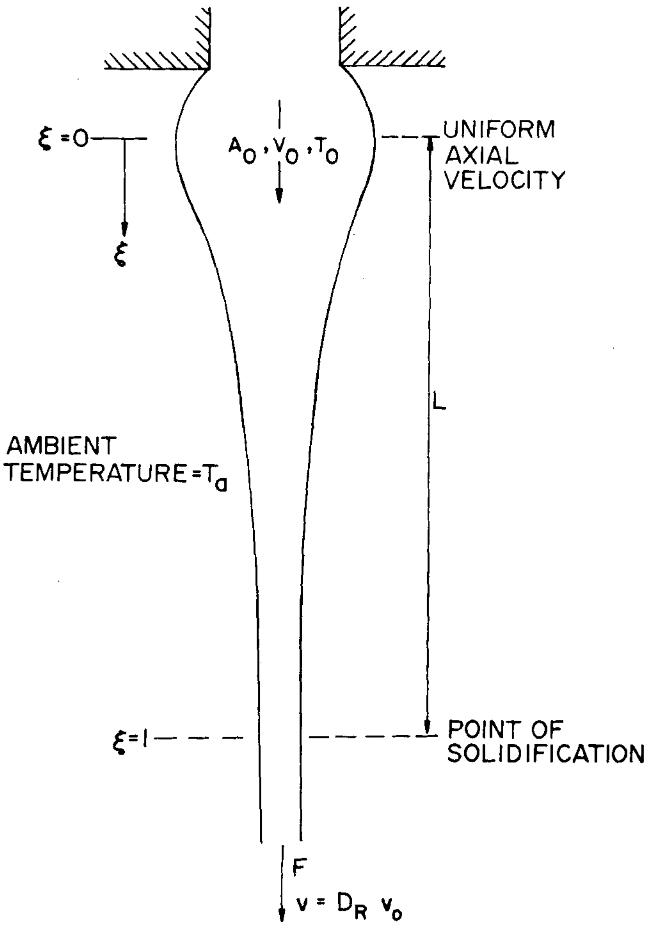

Fig. 1. Schematic of melt spinning process.

We have recently described a simulation of melt spinning in which fluid elasticity is included by means of a single parameter, the shear modulus, which is the ratio of the viscosity to the time characteristic of stress relaxation (Denn et al., 1975; Fisher and Denn, 1976). This work was restricted to isothermal spinning, in which heat transfer from the filament to the surroundings is negligible prior to the point of solidification. The model shows the important characteristics of isothermal spinning experiments, including the large tension and an approach at high stress to a velocity profile which is linear in axial position. Quantitative agreement with experiment requires use of a modulus which is 40 to 80% of the value measured in steady shear experiments, but Denn and Marrucci (1976) have recently shown that this discrepancy is a consequence of attempting to account for the full spectrum of relaxation times in a polymer melt by a single average quantity, and the more detailed calculation for a spectrum can be carried out.

We report here on an extension of our previous work to nonisothermal melt spinning, for which heat transfer from the filament to the surroundings must be explicitly taken into account. The effect of heat transfer on the onset of a process instability known as draw resonance is particularly striking, and we shall emphasize this aspect of the study.

CONSTITUTIVE EQUATION

Melt spinning is a high Deborah number process, in which the residence time and the time characteristic of stress relaxation are comparable. The simplest equation relating the stress to the deformation state which is valid under high Deborah number conditions is the Maxwell model. This model assumes that all elastic response can be accommodated by a single material parameter, and it ignores the fact that most polymer melts must be characterized by a complete distribution of relaxation times. In the form in which we shall use the model, it also assumes physical properties which are independent of deformation rate. For many polymers these are severe restrictions, and we can expect only qualitative results; the assumption of deformation-independent physical properties is particularly restrictive. Some of the best experiments on melt spinning have been done with polyethylene terephthalate (PET) of intermediate intrinsic viscosity, however, which is a polymer for which the Maxwell model appears to be adequate, and our comparison with experiment will be with these data.

The form of the Maxwell model which is appropriate for nonisothermal conditions has been shown by Marrucci (1972) to be

$$\boldsymbol{\tau} + \frac{\mu}{G}\left[\frac{\partial \boldsymbol{\tau}}{\partial t} + \mathbf{v}\cdot\nabla\boldsymbol{\tau} - (\nabla\mathbf{v})\cdot\boldsymbol{\tau} - \boldsymbol{\tau}\cdot(\nabla\mathbf{v})^{\dagger} - \boldsymbol{\tau}\frac{\partial \ln T}{\partial t} - \boldsymbol{\tau}(\mathbf{v}\cdot\nabla\ln T)\right] = \mu\,[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\dagger}] \quad (1)$$

Here $\boldsymbol{\tau}$ is the extra stress, v is the velocity, and T is the absolute temperature. μ is the viscosity, and G is the shear modulus; the ratio μ/G has dimensions of time and is known as the relaxation time, which is the time characteristic of stress relaxation following a cessation of motion. In general, μ and G may be functions of temperature. G is relatively independent of temperature for some polymers, including PET (Gregory, 1973), and we shall treat it as a constant. The viscosity has an Arrhenius form

$$\mu = \mu_o \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{2}$$

For PET of intrinsic viscosity 0.563, which is of experimental interest subsequently, $E/R = 3\,240°\text{K}$ (Gregory, 1973). T_o is a reference temperature which is taken in all that follows to be the temperature at which the melt is extruded.

SPINNING EQUATIONS

The development of the spinning equations has been described in detail elsewhere (Kase and Matsuo, 1965; Matovich and Pearson, 1969; Denn et al., 1975). The dimensionless mass, momentum, and energy balances have the form, respectively,

$$\frac{\partial a}{\partial \sigma} + \frac{\partial}{\partial \xi}(au) = 0 \tag{3}$$

$$\frac{\partial}{\partial \xi}[a(\tau - \varpi)] = 0 \tag{4}$$

$$\frac{\partial \theta}{\partial \sigma} + u\frac{\partial \theta}{\partial \xi} + St\frac{u^{1/3}}{a^{5/6}}(\theta - \theta_a) = 0 \tag{5}$$

while the stress, Equation (1), simplifies to the two-component equations

$$\tau + \alpha\left[\frac{\partial \tau}{\partial \sigma} + u\frac{\partial \tau}{\partial \xi} - 2\tau\frac{\partial u}{\partial \xi} - \tau\frac{\partial \ln\theta}{\partial \sigma} - \tau u\frac{\partial \ln\theta}{\partial \xi}\right] = 2\epsilon\frac{\partial u}{\partial \xi} \tag{6}$$

$$\varpi + \alpha\left[\frac{\partial \varpi}{\partial \sigma} + u\frac{\partial \varpi}{\partial \xi} + \varpi\frac{\partial u}{\partial \xi} - \varpi\frac{\partial \ln\theta}{\partial \sigma} - \varpi u\frac{\partial \ln\theta}{\partial \xi}\right] = -\epsilon\frac{\partial u}{\partial \xi} \tag{7}$$

Here ξ is the axial position, made dimensionless with respect to the length of the melt zone L; σ is time, made dimensionless with respect to L/v_o, where v_o is the initial velocity; u is axial velocity, made dimensionless with respect to v_o; a is filament area, made dimensionless with respect to the initial area A_o; θ and θ_a are filament and ambient temperature, respectively, made dimensionless with respect to T_o; and τ and ϖ are the components of the stress in the axial and normal directions, respectively, made dimensionless with respect to F/A_o, where F is the force required under steady state conditions to draw the filament.

There are three-dimensionless groups which govern the behavior of the system, defined as follows:

$$\alpha = \frac{\mu_o v_o}{GL} \tag{8}$$

$$\epsilon = \frac{\mu_o A_o v_o}{FL} \tag{9}$$

$$St = 1.67 \times 10^{-4}\, L/\rho c_p A_o^{5/6} v_o^{2/3} \tag{10}$$

α embodies the viscoelasticity of the material at the spinneret, while St is a dimensionless heat transfer coefficient. The numerical factor in Equation (10) presumes the use of c.g.s. units.

The boundary conditions for these equations are not well defined, largely because the region of die swell is not understood theoretically. Thus, the origin of the coordinate system, $\xi = 0$, cannot be taken at the spinneret, but is taken instead at the point where the axial velocity has become independent of radial position. This point, in turn, is assumed to be located at the position of maximum die swell. The velocity, area, and temperature are assumed known here; we have already made use of this fact in the nondimensionalization of the variables. Thus, we have

$$a = u = \theta = 1 \quad \text{at} \quad \xi = 0 \tag{11a}$$

We also need a stress initial condition. This condition has been discussed by Denn et al. (1975), who show that the system response is relatively insensitive to the choice, and that a reasonable selection is that corresponding to fully developed spinneret flow,

$$\tau = 1 \quad \text{at} \quad \xi = 0 \tag{11b}$$

Finally, the filament is taken up at a speed which is greater by a factor D_R than the initial velocity. D_R is known as the draw ratio, and under steady operating conditions it corresponds to the area reduction ratio. Thus, our final condition is

$$u = D_R \quad \text{at} \quad \xi = 1 \tag{11c}$$

It should be noted that we have assumed that the length L is known and is constant in time.

STEADY PROCESSING

For steady processing, with all time derivatives equal to zero, numerical solution of Equations (3) through (7) is straightforward. Solution is iterative, since ϵ and D_R cannot be specified independently. By choosing D_R we have chosen the take-up speed; in that case the tension, and hence ϵ, must be calculated as part of the solution.

This last observation is important in understanding the physical behavior, for it means that the solution will depend on the relaxation time (μ/G) but not on the viscosity. In the limit of small Stanton number, the system will approach isothermal behavior with $\theta = 1$, but it should also approach isothermal behavior in the limit $St \to \infty$. In the latter case, however, the effective temperature is θ_a. The velocity and tension will then correspond to those for which α is replaced by $\alpha \exp[-E(1 - 1/\theta_a)/RT_o]$. This will result in a more linear profile for $\alpha > 0$ when $\theta_a < 1$ (Denn et al., 1975).

It is worth noting in passing that at steady state the energy Equation (5) is only weakly coupled to the momentum and stress equations, and a very good approximation to the solution is

$$\theta \sim \theta_a + (1 - \theta_a)\exp(-St\,\xi) \tag{12}$$

We have not made use of this approximation, but it is helpful in locating the position of the point of solidification when that point is not imposed by an air or water bath.

Figure 2 shows a typical set of calculations to illustrate the influence of Stanton number on the steady solution. The overshoot of the profile at intermediate values of St is typical and is more pronounced with some other choices of parameters. We are not aware of any reliable published steady state spinning data taken under controlled nonisothermal conditions which allow comparison with theory. Thus, we turn our attention at once to the transient.

DRAW RESONANCE

Draw resonance is an instability which occurs in spinning, film casting, and particularly extrusion coating under conditions in which L is externally fixed and cannot vary even under transient conditions. The instability is charac-

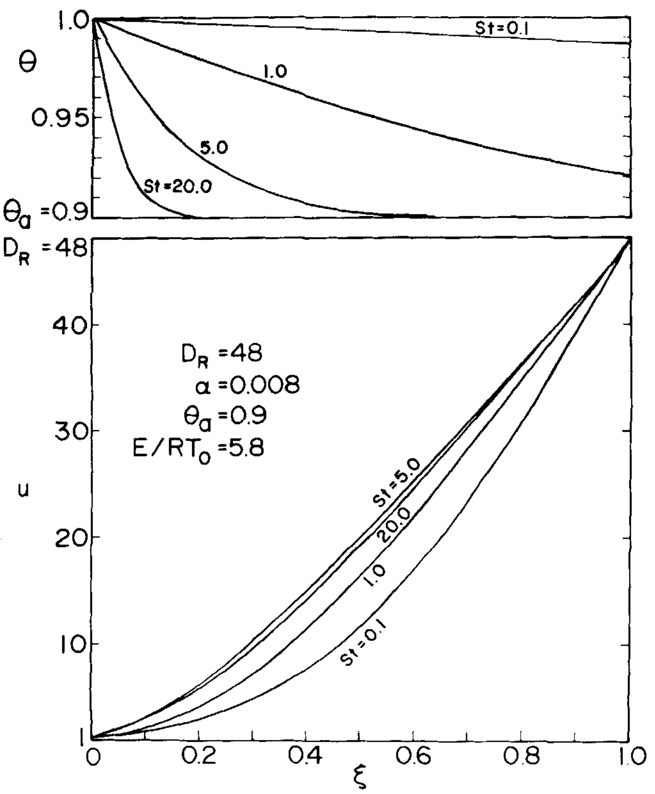

Fig. 2. Temperature and velocity profiles; $D_R = 48$, $\alpha = 0.008$, $\theta_a = 0.9$, $E/RT_0 = 5.8$.

terized by a periodic variation in filament cross section despite a constant extrusion rate and a constant take-up speed. For a given spinning length, the onset of draw resonance occurs when the draw ratio exceeds a critical value, though there is a second critical draw ratio at which resonance disappears. For a given draw ratio above some minimum value, there is a critical length at which resonance occurs, and there appears to be a second length beyond which it disappears. The experimental and theoretical understanding of the phenomenon has been thoroughly reviewed recently (Petrie and Denn, 1976), and the results of Fisher and Denn (1976) appear to describe the phenomenon quite well under isothermal spinning conditions.

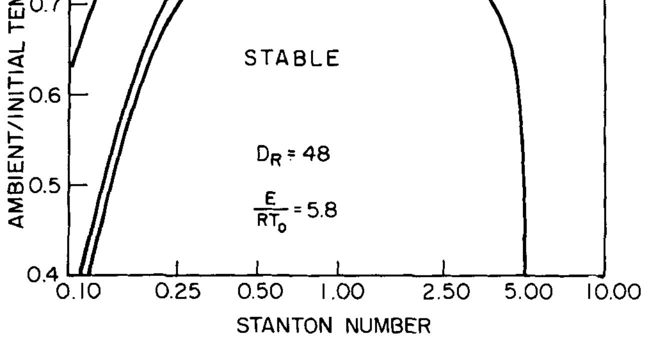

Fig. 3. Stability regions; $D_R = 48$, $E/RT_0 = 5.8$.

Our approach for predicting the onset of draw resonance is to use a linear stability analysis. The procedure is quite conventional and is discussed in texts such as Denn (1975). The nonlinear partial differential equations are linearized about the steady state, and separation-of-variable solutions are sought. These solutions will consist of sums of terms whose time dependence is of the form $\exp(\lambda\sigma)$, where the complex number $\lambda = \lambda_R + i\lambda_I$ is obtained by solution of an eigenvalue problem. The system is stable to infinitesimal disturbances when all eigenvalues λ_R are negative; the system is unstable if any eigenvalue λ_R is positive. The transition occurs at the marginal point $\lambda_R = 0$. The linear stability theory approach is restrictive, but we have shown previously by means of nonlinear theory that the marginal point does correspond to the onset of draw resonance for isothermal systems (Fisher and Denn, 1975, 1976).

Except for the straightforward introduction of an additional equation and some extra terms, the problem is identical to that reported in Fisher and Denn (1976), and we shall not reproduce the details here. Figure 3, following Kase (1974), shows typical results for $D_R = 48$ in the form of stability contours for various values of the viscoelastic parameter α in a temperature $-St$ plane. The region below any contour is stable and above unstable. The curve for the Newtonian fluid ($\alpha = 0$) is computed from a correlation given by Shah and Pearson (1972). The well-known stabilizing effect of cooling is clearly shown. The destabilizing effect at high Stanton number is a consequence of the reverse trend towards isothermal conditions. Since the Newtonian fluid does not have a relaxation time, the limits $St \rightarrow 0$ and $St \rightarrow \infty$ are identical.

The stabilizing effect of elasticity is evident by considering behavior at fixed Stanton number. The stability region is enlarged with increasing α, and it comprises the entire plane for $\alpha = 0.01$. Isothermal spinning is stable at $D_R = 48$ for $\alpha \geqq 0.01$ (Fisher and Denn, 1976).

The asymptotic behavior at large Stanton number is of considerable interest here. The contours evidently become horizontal at some ambient temperature corresponding to each particular α. This is because the cooling is sufficient to produce a flow which approaches isothermality, but with an effective viscoelastic parameter equal to $\alpha \exp[-E(1 - 1/\theta_a)/RT_o]$. Since isothermal spinning is stable at $D_R = 48$ for $\alpha = 0.01$, the asymptote satisfies the equation

$$\theta_a = \left(1 - \frac{RT_o}{E}\ln 100\alpha\right)^{-1} \qquad (13)$$

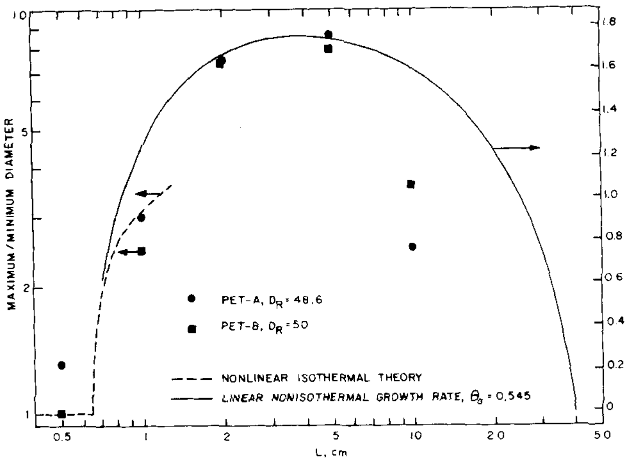

Fig. 4. Intensity of draw resonance and initial growth rate as a function of spinning length; data are from Ishihara and Kase (1976).

The result for other draw ratios follows readily from Figure 5 of Fisher and Denn (1976). This asymptotic behavior at high Stanton number is qualitatively similar to the stabilization noted by Kase (1974) and Pearson et al. (1976) resulting from solidification of the filament and a consequent possible time dependence of the length of the melt zone. Solidification is not included in the present analysis, where it is assumed that the length of the melt zone is fixed at all times.

COMPARISON WITH EXPERIMENT

The only well-defined nonisothermal experiments on draw resonance are those of Ishihara and Kase (1976) on PET of intrinsic viscosity 0.563. These experiments were mostly carried out in the unstable region, with an extrusion temperature of 280° and 285°C and an ambient temperature which is presumed to be 30°C ($\theta_a = 0.545$). The data are shown in Figure 4 in the form of the intensity of the diameter oscillations as a function of the length of the melt zone. The dashed line is an approximate solution to the nonlinear isothermal equations (Fisher and Denn, 1976).

The linear theory cannot give any information about the system response when the instability is fully developed. We hypothesize, however, that there will be a correlation between the ultimate intensity of the oscillation and the initial growth rate of the disturbance. This can be shown to be the case for isothermal spinning if the oscillation intensity is plotted logarithmically and the growth rate linearly.

Figure 4 shows a linear plot of initial growth rate computed from linear theory vs. length for conditions characteristic of the experiments of Ishihara and Kase (1976). The scale was chosen to make the curve pass through the maximum intensity. The only adjustable parameter here is μ_o/G, which is taken from the data of Gregory (1973) to be 10^{-3} s. It is evident that the general features of the data are reproduced, and the system is predicted to stabilize again at a length of about 40 cm.

These data and calculations point up the interesting interplay between heat transfer and viscoelasticity. All other things remaining equal, elasticity will come to dominate as the melt zone is shortened (increasing α, decreasing St), while heat transfer will come to dominate as the melt zone is lengthened (decreasing α, increasing St). A rough first approximation which follows from our previous work (Denn et al., 1975; Fisher and Denn, 1976) and which is consistent with these calculations is that elasticity can safely be neglected as long as αD_R is less than 0.1 to 0.2, but it must otherwise be taken explicitly into account.

It should be noted that this analysis and comparison with data applies only to spinning into an ambient environment of constant temperature and without crossflow. Data on the influence of crossflow air and non-constant environment on filament stability do not show a clear trend. These data are discussed by Petrie and Denn (1976).

CONCLUSION

The effect of cooling of a viscoelastic filament in steady spinning is generally to increase the initial rate of diameter attenuation, though there will be some Stanton number beyond which the rate will start to decrease again. Cooling inhibits the onset of the draw resonance spinning instability, and the interaction of cooling and viscoelasticity results in a stabilization at high Stanton number which cannot occur for an inelastic liquid. Generally, short spin lines will be stabilized by fluid elasticity and long spin lines by the effect of cooling.

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NOTATION

a = dimensionless area
A_o = initial area
c_p = heat capacity
D_R = draw ratio
E = activation energy
F = force for steady spinning
G = shear modulus
L = length of melt zone
R = gas constant
St = Stanton number
t = time
T, T_o = temperature, reference temperature
u = dimensionless velocity
$\mathbf{v}$ = velocity vector
v_o = initial velocity

Greek Letters

α = viscoelastic parameter
ϵ = dimensionless reciprocal force
θ, θ_a = dimensionless temperature, ambient temperature
λ = eigenvalue
λ_R = growth rate (real part of λ)
μ, μ_o = viscosity, reference viscosity
ξ = dimensionless axial position
ϖ = dimensionless stress normal to spinning direction
ρ = density
σ = dimensionless time
τ = dimensionless axial stress
$\boldsymbol{\tau}$ = extra stress tensor
$\dagger$ = (superscript) transpose

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Turbulent Mass Transfer Rates to a Wall for Large Schmidt Numbers

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New measurements are presented on the influence of Schmidt number on the rate of mass transfer between a turbulent fluid and a pipe wall. It is found that for large Schmidt numbers the fully developed mass transfer coefficient is related to the friction velocity and the Schmidt number by the equation

$$K_\infty = 0.0889\, v^*\, Sc^{-0.704}$$

The experiments are accurate enough to rule out the $Sc^{-2/3}$ or the $Sc^{-3/4}$ relations commonly used, deduced from plausible limiting expressions for the eddy diffusivity close to a wall. It is argued that these expressions are valid only over a vanishingly small portion of the concentration field as $Sc \rightarrow \infty$.

SCOPE

Mass transfer between a turbulent fluid and a solid boundary is usually characterized by a large Schmidt number Sc. For this reason, considerable attention has been given to the definition of the limiting relation for the rate of mass transfer as $Sc \rightarrow \infty$. A local mass transfer coefficient characterizing the mass transfer process can be defined as

$$K = \frac{N_0}{C_B - C_W} \qquad (1)$$

In a series of very careful experiments at $Sc = 2\,400$, Son and Hanratty (1967) established that for flow in a pipe, the influence of fluid velocity on the local mass transfer coefficient is defined by the equation

$$K = v^*\, g(Sc, x^+) \qquad (2)$$

For large enough values of x^+, a fully developed condition is reached where K is independent of x^+. That is

$$K_\infty = v^*\, f(Sc) \qquad (3)$$

The usual procedure is to represent $f(Sc)$ as a power law

$$f(Sc) = B\, Sc^m \qquad (4)$$

There has been a considerable difference in opinion as to what is the proper exponent m. The two relations most often considered are $m = -2/3$ and $m = -3/4$. These are usually justified by recognizing that the concentration boundary layer is so thin for large Sc that the velocity field within δ_c can be represented as a Taylor series expansion in terms of the dimensionless distance from the wall y^+. By using an analogy between momentum transfer and mass transfer, it is argued that the eddy diffusivity is given as $\epsilon/\nu^* \sim y^{+n}$, where n is an integer greater than or equal to 3. (See pages 343-7 of the book by Monin and Yaglom, 1965.)

In order to establish the correct exponent m, it is necessary to obtain very precise measurements over a wide range of Schmidt numbers, since the difference between the $Sc^{-2/3}$ and the $Sc^{-3/4}$ relations is not great. A considerable number of experimental studies have been directed toward this goal. However, there is enough disagreement among the results of different investigators that the problem has not been conclusively resolved.

During the course of a study on the influence of Schmidt number on the frequency of mass transfer fluctuations, we obtained the very extensive set of measurements of $f(Sc)$ presented here. Because of the care given to the execution of these experiments, we feel that a greater precision was attained than in previous investigations.

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