Bounds and Approximate Solutions to Linear Problems with Nonlinear Boundary Conditions: Solidification of a Slab

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In solidification, one is primarily interested in the movement of the solid-liquid interface and not in the details of the internal temperature distribution. This is parallelled in many other processes of practical interest. Because of the linearity of the governing equation, one may readily obtain an integral relationship between the system variables, as expressed by the moment equations. By further introducing physically reasonable assumptions, one obtains bounding or approximate solutions, some of which are simple but accurate analytic expressions.

SCOPE

Approximate analytic solutions to problems which cannot be solved by rigid analysis are attractive for engineering purposes because they are easily incorporated in feasibility and optimization studies on complex processes. If two such solutions can be found which not only approximate but also bound the unknown true result, then a numerical or experimental verification becomes redundant as long as the relative difference between the two bounds is sufficiently small. The approach thus provides a built-in error criterion.

When trying a systematic attack on certain classes of such problems, one immediately encounters a difficulty. Tight and hence useful bounds often require specific assumptions concerning the physical rather than the mathematical situation. In consequence, the results will not always be of the desired generality. For this reason, the present study deals only with linear diffusion types of problems containing a nonlinear boundary condition.

More specifically, this paper considers the general problem of unidirectional solidification subject to a known heat flux from the melt and a boundary condition of the third kind (sometimes termed Newton's cooling) at the cold slab surface. Simplified versions of this problem have received continuing attention in the literature, but to our knowledge the above problem has only been dealt with by a few approximate methods, most of which require numerical evaluation and are difficult to assess in their accuracy. Our aim is to generate accurate analytic bounds for the general problem from which the simpler problems treated previously can be extracted as limiting cases.

CONCLUSIONS AND SIGNIFICANCE

Using various types of moments of the governing diffusion equation, one obtains integral relations which can be integrated analytically once suitable approximations to the integrands have been introduced. However, instead of mere approximations, we insert rigid inequalities so that after integration we have bounding solutions for the solidification time as a function of the solid thickness and the system parameters. These inequalities are suggested by physical reasoning, and it is obvious that the tighter the inequality the better will be the bound but the more involved may be the final integration. The limit is reached when we have to resort to numerical integration of the bounding equation.

By comparison with previous numerical results, it is shown that analytic results can be generated which remain sufficiently accurate up to quite extreme values of the system parameters. Typically, the maximum relative error is of the order of 10%, a surprisingly good agreement in view of the simple structure of the equations. Situations of extremely rapid solidification, such as the classical Stefan solidification at a very small ratio of latent-heat to internal-energy removal, give rise to larger errors. But most of these cases have been covered by previous authors, and analytic working equations of good accuracy do exist. Whereas it is primarily the intermediate range of moderate solidification rates and more general boundary conditions which so far have not been covered adequately, we believe that this gap has been closed with the present analysis. For extremely slow solidification processes one may, of course, follow the well-known quasistationary approach to obtain accurate results.

Based on the same philosophy, some approximate results are also derived. They are not rigid mathematical bounds but are believed to form fairly tight upper and lower approximations. Although for the general case numerical integration becomes necessary, the results may still be useful for certain applications. The upper approximation does, in fact, lead to the same equation as a previously published method where the results were claimed to be accurate to within 2.5%.

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With the increasing computation cost attached to a numerical simulation, the development of approximate analytic solutions to complex problems becomes increasingly more attractive. A classical example of such an approach is the boundary-layer concept in fluid mechanics, but over the last two decades, various other methods have been developed. Variational calculus, matched asymptotic expansions, imbedding techniques, and more advanced integral methods have been used successfully to circumvent the complexity without sacrificing too much accuracy.

Although numerical solutions with their generally high accuracy are desirable for comparison purposes and for case studies, they are not quite suitable for many engineering purposes. Here one often requires a compact analytic result for further use in dynamic process investigations and/or in the design of equipment. Accuracy is of minor importance as long as one has an estimate of the maximum possible error inherent in the result. To that end one can either generate a few numerical results at sample points or, rather than develop just one approximate solution, try and find two bounds which form a reasonably tight envelope around the unknown exact solution. Obviously, the latter approach does not require any numerical simulation, since the discrepancy between two such bounding solutions is itself indicative of the maximum possible error. The user can decide immediately whether or not the approximation is acceptable for the particular application in mind.

Approximate solutions with bounding character are well documented in the literature, the most prominent one being perhaps the pseudo steady state solution to a transient problem. However, to find a useful second bound in many cases is not quite as simple and may involve physical arguments that are limited to a particular process. In view of the variety of possible complications arising in the differential equation or in a boundary condition, it is doubtful whether generally valid mathematical rules can be devised at all. In the following we shall therefore limit ourselves to problems where the differential equation is linear but where one of the boundary conditions obstructs a rigid analytic approach. More specifically, we consider the diffusion equation

$$\frac{\partial u}{\partial t} = \nabla^2 u \tag{1}$$

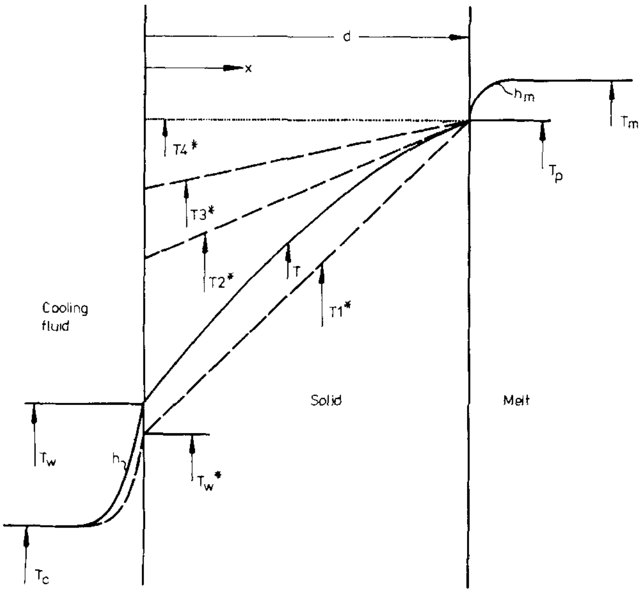

Fig. 1. Illustration of the system and the various approximate temperature profiles.

to be solved subject to a boundary condition of the form

$$\left.\frac{\partial u}{\partial x}\right|_{x_1} = f\left(\frac{\partial u}{\partial x}, \frac{\partial u}{\partial t}, u^n, t^m\right) \tag{2}$$

The latter equation may be seen to include commonly encountered cases such as the heating of a wall due to a time-dependent, heat transfer coefficient

$$k\left.\frac{\partial T}{\partial x}\right|_{x_1,t} = h(t)[T(x_1, t) - T_o] \tag{2a}$$

or due to thermal radiation

$$k\left.\frac{\partial T}{\partial x}\right|_{x_1,t} = C[T(x_1, t)^4 - T_o^4] \tag{2b}$$

These will be dealt with in a later article; here we shall concentrate on the nonlinear boundary condition associated with the problem of unidirectional solidification; that is

$$k\left.\frac{\partial T}{\partial x}\right|_{x_1(t)} = -\rho\lambda\left.\left(\frac{\partial T/\partial t}{\partial T/\partial x}\right)\right|_{x_1(t)} + C \tag{2c}$$

The latter problem, known as the Stefan problem, has received continuing attention in the literature, a consequence of its importance in fields such as food processing, chemical and metallurgical engineering, and space and biological sciences. Apart from a few special solutions (Carslaw and Jaeger, 1959), no exact results are available because of the difficulties connected with Equation (2*c*). Rather than reviewing all the numerical and analytic methods used in this context, we may refer to the book by Ockendon and Hodgkins (1975) and just add a few relevant remarks.

With unidirectional solidification, the boundary condition on the cold side of the slab will commonly be of the third kind, and, in general, we also have to allow for heat flux from the melt to be incorporated in the other boundary condition at the solid-liquid interface. This may be termed the general problem and has been analyzed by Stephan (1969) who assumed a parabolic temperature distribution in the solid and obtained an expression for the rate of solidification which, however, cannot be integrated analytically. Further, a perturbation analysis by Huang and Shih (1975) is available but is limited to large values of the parameter *Ph* (see below) or else numerical integration becomes necessary. Similar reasoning seems to apply to the analysis of Siegel and Savino (1966), although their method does not necessarily converge to the correct answer. To our knowledge, all the other numerical and analytic studies have been limited to simplified versions of the above problem. Either heat flux from the melt was neglected (Goodman, 1958; Hrycak, 1963; Megerlin, 1966; Stephan and Holzknecht, 1974, 1976) or the temperature at the cooling face was assumed constant (Libby and Chen, 1965; Lapadula and Mueller, 1966; Beaubouef and Chapman, 1967; Savino and Siegel, 1969). Making both these assumptions simultaneously, we have, of course, the original Stefan problem for which an exact analytic solution exists. Other boundary conditions such as constant heat flux at the cold or at the warm interface have also been considered (Goodman, 1958; Boley, 1963; Goodling and Khader, 1975), but with a few exceptions they represent cases of minor practical importance.

A disadvantage of all the analytic approximations is the inherent uncertainty about the accuracy of the results. Most authors draw on a selection of numerically exact data to justify their approach and find good agreement at certain stages of the process or for certain combinations of the system parameters. Sometimes improved accuracy is gained by iteration (Siegel and Savino, 1966) or perturbation; in other cases, the basic result is modified to match numerical data. But in spite of the usually more complicated expression, its general reliability remains difficult to assess. In fact, it can be shown that some of the apparently good models break down under extreme and yet practically possible conditions. This unsatisfactory state calls for a self-checking approach, independent of a numerical solution, such as the development of two bounding solutions of the type discussed above.

However, bounding solutions to the present problem are rare. Boley (1963) discusses the melting of a solid slab subject to a constant heat flux condition at the initial or at the instantaneous solid-liquid interface. By imposing a larger or a smaller flux, but in each case one for which an analytic solution can be obtained, he finds bounds. Elmas (1970) considers solidification subject to a constant cooling wall temperature and derives bounds for the rate of solidification, but in the final explicit form the results cease to be bounds in a mathematical sense. Kern (1977) obtains solutions to the above defined general problem and, from the comparison with numerical results, suggests rather than proves their bounding character.

We conclude that simple bounding solutions to the general unidirectional solidification problem are highly desirable from an engineering as well as scientific viewpoint but have not been presented as yet. The basic approach here is to use moment equations as well as physical arguments to derive mathematical bounds which are sufficiently tight so as to be useful for practical application. However, it should be clear that with any bounding solution there is still room for improvement so long as the bound is not identical to the exact solution.

MATHEMATICAL PRELIMINARIES

Assuming constant physical properties of the phases, negligible dilatation effects, convective transfer on both sides of the solid layer, and a well-defined phase-change temperature as well as solid-liquid interface, we describe the general problem by the following nondimensional equations (for symbols see Figure 1 and the notation):

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial X^2}, \quad 0 \le X \le \delta \tag{3}$$

$$\left.\frac{\partial\theta}{\partial X}\right|_{X=0} = Bi\theta|_{X=0} \equiv Bi\theta_w \tag{4}$$

$$\left.\frac{\partial\theta}{\partial X}\right|_{X=\delta(t)} = Ph\frac{d\delta}{d\tau} + \Delta Bi \tag{5}$$

$$\theta(X = \delta) = 1 \tag{6}$$

It is pointed out that the reference length d_o, which enters the Biot modulus, is entirely arbitrary at this stage. However, by performing the final integration from $\delta \equiv d/d_o = 0$ to 1, the solidification time is obtained in the form

$$\tau = f(Bi, Ph, \Delta) \tag{7}$$

where Bi is effectively the space variable. This notation was found to simplify the algebraic manipulations and is, of course, just one of the many possible ones. The phase-change parameter Ph relates the latent heat λ' (which includes any desuperheating of the melt) to the maximum internal energy $c(T_p - T_c)$ per unit mass of solidified material. Its magnitude indicates the relative significance of these two quantities: with $Ph \to \infty$ the process is dominated by latent heat removal, whereas with $Ph \to 0$, the solidification time is controlled by the removal of internal energy. In practice typical values are found in the range $0.2 \le Ph \le 20$. Note that $1/Ph$ (Stefan number) has also been used in the literature. Δ is the flux parameter and relates the heat flux from the melt to the heat flux to the sink. For solidification to proceed, Δ must be smaller than one, but since a frozen layer of thickness Bi offers a thermal resistance, the value of Δ is further limited by

$$\Delta \le \frac{1}{1 + Bi}$$

The nonlinearity in Equation (5), which corresponds to Equation (2c), is known to obstruct a rigid analytic solution of the problem. But even a numerical integration becomes involved because the system boundary moves at a variable speed. Hence, to obtain accurate results, successive readjustment of the grid spacing is necessary (see the discrepancies between the results of Tao, 1967, and those of Stephan and Holzknecht, 1974). This reason and the fact that we deal with a two-parameter system (Ph, Δ) may explain the attractiveness of approximate analyses. However, in order to find bounding solutions, we have to establish inequalities rather than approximate relationships and keep in mind that the former can be integrated but not necessarily differentiated.

Throughout this paper we shall be using one or more of the following expressions:

1. The unknown temperature at the cooling surface θ_w. The backward first moment of Equation (3) is

$$\int_o^\delta (\delta - X)\frac{\partial^2\theta}{\partial X^2}dX = \int_o^\delta (\delta - X)\frac{\partial\theta}{\partial\tau}dX \tag{8}$$

Integration by parts of the left-hand side yields

$$\left\{(\delta - X)\frac{\partial\theta}{\partial X}\right\}\Big|_o^\delta + \int_o^\delta \frac{\partial\theta}{\partial X}dX = -\delta Bi\theta_w + (1 - \theta_w) \tag{9}$$

From the maximum principle $\partial\theta/\partial\tau$, and hence the right-hand side of Equation (8) is shown to be always negative so that

$$-\delta Bi\theta_w + (1 - \theta_w) \le 0$$

or

$$\theta_w \ge \frac{1}{1 + \delta Bi} \equiv \theta_w^* \tag{10}$$

2. The unknown temperature distribution in the solidified slab θ. Since the curvature of the temperature profile is always negative (see above), we write

$$\theta \ge \theta_w + X(1 - \theta_w)/\delta \tag{11}$$

and eliminate θ_w by use of Equation (10). Thus

$$\theta \ge \frac{1 + XBi}{1 + \delta Bi} = \theta_1^* \tag{12}$$

This lower temperature profile $\theta_1^*(T_1^*)$ is included in Figure 1. However, we can also formulate an upper temperature profile by making use of Equation (5):

$$\theta \le 1 - (\delta - X)\left.\frac{\partial\theta}{\partial X}\right|_{X=\delta} \tag{13}$$

From this we derive inequalities of differing tightness (see

Figure 1); that is

$$\theta \leqq 1 - (\delta - X)\left\{ Ph\frac{d\delta}{d\tau} + \Delta Bi \right\} = \theta_2^* \quad (13a)$$

$$\theta \leqq 1 - (\delta - X)\Delta Bi = \theta_3^* \geqq \theta_2^* \quad (14)$$

$$\theta \leqq 1 = \theta_4^* \geqq \theta_3^* \geqq \theta_2^* \quad (15)$$

By employing various combinations of these inequalities in the zero- and first-order moments of Equation (3), we shall be able to perform the second integration and obtain bounding solutions for the solidification time.

BOUNDING SOLUTIONS

Integration of Equation (3) yields

$$\int_0^\delta \frac{\partial\theta}{\partial\tau}dX = \int_0^\delta \frac{\partial^2\theta}{\partial X^2}dX$$

$$= Ph\frac{d\delta}{d\tau} + \Delta Bi - Bi\theta_w \quad (16)$$

The first moment of Equation (3) is used to eliminate the unknown temperature θ_w:

$$\int_0^\delta X\frac{\partial\theta}{\partial\tau}dX = \delta Ph\frac{d\delta}{d\tau} + \delta\Delta Bi - (1 - \theta_w) \quad (17)$$

With this we write Equation (16) as

$$\int_0^\delta (1 + BiX)\frac{\partial\theta}{\partial\tau}dX = Ph(1 + Bi\delta)\frac{d\delta}{d\tau}$$

$$+ Bi(1 + Bi\delta)\Delta - Bi \quad (18)$$

Equation (18) provides the starting point for the generation of the various bounding solutions.

Lower bounds

A first lower bound is obtained by use of Equation (15). Since in that case

$$\frac{\partial\theta}{\partial\tau} \leqq \frac{\partial\theta_4^*}{\partial\tau} = 0$$

it follows that

$$\frac{d\delta}{d\tau} \leqq \left(\frac{d\delta}{d\tau}\right)_4 = \frac{Bi}{Ph}\left[\frac{1 - \Delta(1 + Bi\delta)}{1 + Bi\delta}\right] \quad (19)$$

Separating the variables and integrating over δ from 0 to 1, we obtain

$$\tau \geqq \tau_4 = -\frac{Ph}{Bi\Delta} - \frac{Ph}{(Bi\Delta)^2}\ln\left(1 - \frac{\Delta Bi}{1 - \Delta}\right) \quad (20)$$

This is the well-known quasistationary solution which was first derived by Planck (1932). The assumption of a constant solid temperature $\theta = 1$ implies that only latent heat but no internal energy is removed from the system. The solutions for constant wall temperature ($Bi \to \infty$, $\Delta \to 0$, $Bi\Delta$ finite) and/or no heat flux from the melt ($\Delta \to 0$) are easily extracted from the above result. Equation (20) is, however, known to heavily underpredict the solidification time when Ph is small ($\leqq 1$). It is therefore worthwhile improving the bound by including the removal of at least some internal energy.

Applying Leibniz's rule to the left-hand side of Equation (18), this becomes

$$\frac{d}{d\tau}\int_0^\delta (1 + BiX)(\theta - 1)dX = Ph(1 + Bi\delta)\frac{d\delta}{d\tau}$$

$$+ Bi(1 + Bi\delta)\Delta - Bi \quad (21)$$

Integration yields

$$\int_0^\delta (1 + BiX)(\theta - 1)dX = Ph\delta\left(1 + Bi\frac{\delta}{2}\right)$$

$$+ Bi(\Delta - 1)\tau + Bi^2\Delta\int_0^\tau \delta d\tau \quad (22)$$

The integrals are approximated by use of Equations (14) and (19). From the former it follows that

$$\int_0^\delta (1 + BiX)(\theta - 1)dX \leqq$$

$$-\int_0^\delta (1 + BiX)(\delta - X)\Delta Bi dX =$$

$$-\Delta Bi\delta^2\left(\frac{1}{2} + \frac{Bi\delta}{6}\right) \quad (23)$$

Further, from Equation (19)

$$\int_0^\tau \delta d\tau = \int_0^\delta \frac{\delta'}{\frac{d\delta'}{d\tau}}d\delta' \geqq \int_0^\delta \frac{\delta'}{\left(\frac{d\delta'}{d\tau}\right)_4}d\delta' \quad (24)$$

so that

$$Bi^2\Delta\int_0^\tau \delta d\tau \geqq \Delta Bi Ph\int_0^\delta \frac{\delta'(1 + Bi\delta')}{1 - \Delta(1 + Bi\delta')}d\delta' \quad (25)$$

Performing the integration, rearranging Equation (22), and evaluating between the limits of δ, we finally obtain

$$\tau \geqq \tau_3 = -\frac{Ph}{\Delta Bi} - \frac{Ph}{(\Delta Bi)^2}\ln\left(1 - \frac{\Delta Bi}{1 - \Delta}\right)$$

$$+ \frac{\Delta}{1 - \Delta}\left(\frac{1}{2} + \frac{Bi}{6}\right) \quad (26)$$

Since the last term is always positive, a tighter bound is provided by Equation (26) as compared to Equation (20); that is

$$\tau_3 \geqq \tau_4 \quad (27)$$

However, the improvement is limited to $\Delta \neq 0$ because otherwise $\tau_3 \equiv \tau_4$. Further improvement on this bound is achieved by employing Equation (13a) rather than (14), but then the time τ_2 has to be evaluated by numerical integration:

$$\int_0^\delta (1 + BiX)(\theta - 1)dX \leqq$$

$$-\left(\Delta Bi + Ph\frac{d\delta}{d\tau}\right)\delta^2\left(\frac{1}{2} + \frac{Bi\delta}{6}\right) \quad (23a)$$

and Equation (25) are inserted in Equation (22) to give the nonlinear differential equation

$$\frac{Ph}{Bi}\delta^2\left(\frac{1}{2} + \frac{Bi\delta}{6}\right)\frac{d\delta}{d\tau} \leqq -\Delta\delta^2\left(\frac{1}{2} + \frac{Bi\delta}{6}\right) + (1 - \Delta)\tau$$

$$+ \frac{Ph(1 - \Delta)\delta}{\Delta Bi} + \frac{Ph(1 - \Delta)}{(\Delta Bi)^2}\ln\left(1 - \frac{\Delta Bi\delta}{1 - \Delta}\right) \quad (28)$$

It is easily seen that integration of the equality leads to

$$\tau_2(Bi, \Delta, Ph) \leqq \tau \quad (29)$$

With a numerical integration τ_p, we do lose some of the attractiveness of the basic approach, but, on the other hand, a significant improvement is expected in the case of $\Delta = 0$ and $Ph < 1$.

Finally, another analytic lower bound for τ may be found by rearranging rather than integrating Equation (21) and by using both Equations (12) and (14). From

$$\frac{\frac{1}{Bi}\frac{d}{d\tau}\int_0^\delta (1+BiX)(\theta-1)dX}{1-\Delta(1+Bi\delta)} = \frac{\frac{Ph}{Bi}(1+Bi\delta)\frac{d\delta}{d\tau}}{1-\Delta(1+Bi\delta)} - 1 \qquad (21a)$$

we obtain, after integration over δ between 0 and 1

$$\tau = -\frac{Ph}{\Delta Bi} - \frac{Ph}{(\Delta Bi)^2}\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) - \frac{1}{Bi}\int_0^1 \frac{d\int_0^\delta (1+BiX)(\theta-1)dX}{1-\Delta(1+Bi\delta)} \qquad (30)$$

Since the last term can be integrated by parts

$$\int_0^1 \cdots = \frac{\int_0^1 (1+BiX)(\theta-1)dX}{1-\Delta(1+Bi)} - \Delta Bi\int_0^1 \frac{\int_0^\delta (1+BiX)(\theta-1)dX}{[1-\Delta(1+Bi\delta)]^2}\,d\delta \qquad (31)$$

we have an expression for τ with θ appearing in two different terms of opposite sign. By employing Equation (14) in the first term and Equation (12) in the second term of Equation (31), we add less to the value of τ than is expressed by the integral in Equation (30). The result thus constitutes a lower bound.

Reversing first the integration by parts on the second term of Equation (31), which now contains θ_1^*, we can combine terms such that

$$\tau \geqq -\frac{Ph}{\Delta Bi} - \frac{Ph}{(\Delta Bi)^2}\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) - \frac{\frac{1}{Bi}\int_0^1 (1+BiX)(\theta_3^*-\theta_1^*)dX}{1-\Delta(1+Bi)} - \frac{1}{Bi}\int_0^1 \frac{d\int_0^\delta (1+BiX)(\theta_1^*-1)dX}{1-\Delta(1+Bi\delta)} \qquad (32)$$

With the above expressions for θ_3^* and θ_1^*, all the integrands are seen to be polynomials in X or δ. The integration is tedious but straightforward and leads to

$$\tau \geqq \tau_1 = -\frac{Ph}{\Delta Bi} - \frac{Ph}{(\Delta Bi)^2}\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) - \frac{3+Bi}{6(1+Bi)} - \frac{1}{3Bi(1+Bi)} - \frac{1}{3\Delta Bi} - \frac{\Delta}{3Bi^2}\ln(1+Bi) - \frac{1}{\Delta Bi^2}\left(\frac{1}{3\Delta}-\frac{\Delta^2}{3}\right)\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) \qquad (33)$$

From the approach it is quite clear that this bound is not necessarily tighter than the one given by Equation (20), the quasistationary solution. It is only for larger times, when the frozen layer approaches its maximum thickness, that the last term in Equation (33) dominates the other additional terms, and τ_1 will provide a good lower bound.

Upper bounds

For the purpose of generating an upper bound for the solidification time, we start from Equation (22) and integrate the last term on the right-hand side by parts; that is

$$\int_0^\delta (1+BiX)(\theta-1)dX = Ph\delta\left(1+\frac{Bi\delta}{2}\right) + Bi(\Delta-1)\tau + Bi^2\Delta\left(\delta\tau - \int_0^\delta \tau d\delta'\right) \qquad (22a)$$

Here the integrals can be approximated as follows:
From Equation (12)

$$\int_0^\delta (1+BiX)(\theta-1)dX \geqq \int_0^\delta (1+BiX)(\theta_1^*-1)dX \geqq -\frac{Bi\delta^2}{1+Bi\delta}\left(\frac{1}{2}+\frac{Bi\delta}{6}\right) \qquad (34)$$

and from Equation (26)

$$Bi^2\Delta\int_0^\delta \tau d\delta' \geqq Bi^2\Delta\int_0^\delta \tau_3(\delta')d\delta' \geqq -\frac{PhBi\delta^2}{2} + \frac{Ph\delta}{\Delta} + \frac{Ph}{Bi\Delta^2}[1-\Delta(1+Bi\delta)]\ln\left(1-\frac{\Delta Bi\delta}{1-\Delta}\right) + \frac{\Delta^2(Bi\delta)^3}{1-\Delta}\left(\frac{1}{6}+\frac{Bi\delta}{24}\right) \qquad (35)$$

Rearranging Equation (22a) and evaluating τ between the limits of δ, we obtain an upper bound:

$$\tau \leqq \hat{\tau}_3 = -\frac{Ph}{\Delta Bi} - \frac{Ph}{(\Delta Bi)^2}\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) + \frac{\left(\frac{1}{2}+\frac{Bi}{6}\right)}{(1+Bi)[1-\Delta(1+Bi)]} - \frac{\Delta^2 Bi\left(\frac{1}{6}+\frac{Bi}{24}\right)}{(1-\Delta)[1-\Delta(1+Bi)]} \qquad (36)$$

Equation (22a) indicates that the tighter the lower bound we insert the tighter will be the upper bound we obtain. If we had used Equation (20) instead of (26), the last term of Equation (36) would not have appeared, and a poorer upper bound $\hat{\tau}_4$ would have been obtained. However, even $\hat{\tau}_3$ is found to overpredict significantly the solidification time at large times and small values of Ph. In this region we expect a tighter upper bound to result from the alternative approach discussed above. One may verify that by using Equation (12) in the first term and Equation (14) in the second term of Equation (31), we now obtain an upper bound given by

$$\tau \leqq \hat{\tau}_1 = -\frac{Ph}{\Delta Bi} - \frac{Ph}{(\Delta Bi)^2}\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) - \frac{1}{2Bi\Delta} - \frac{1-\Delta^2}{2(\Delta Bi)^2}\ln\left(1-\frac{\Delta Bi}{1-\Delta}\right) - \frac{1+Bi/2+Bi^2/6}{2Bi(1+Bi)} \qquad (37)$$

The comparison of Equations (36) and (37) indicates that, as before, $\hat{\tau}_1$ is the better long-time bound.

Different boundary conditions

Apart from the general problem characterized by the boundary conditions (4) and (5), there are a number of

Table 1. Summary of Bounding Solutions to the General Problem and its Simplified Versions

	Δ or Δ^* or $Bi^* \neq 0$	Δ or Δ^* or $Bi^* = 0$
Finite heat transfer (Bi, Ph, Δ)	τ_4, Equation (20)	$\tau_4 = Ph\left(\frac{1}{Bi} + \frac{1}{2}\right)$
	τ_3, Equation (26)	$\tau_3 = \tau_4$
	τ_2, Equation (28)	$\tau_2 = \frac{Ph}{Bi}\delta^2\left(\frac{1}{2} + \frac{Bi\delta}{6}\right)\left(\frac{d\delta}{d\tau}\right)_2 + \frac{Ph\delta}{Bi}\left(1 + \frac{Bi\delta}{2}\right)$
	τ_1, Equation (33)	$\tau_1 = \tau_3 = \tau_4$
	$\hat{\tau}_3$, Equation (36)	$\hat{\tau}_3 = \tau_4 + \frac{3 + Bi}{6(1 + Bi)}$
	$\hat{\tau}_1$, Equation (37)	$\hat{\tau}_1 = \tau_3$
Constant heat flux (Ph^*, Δ^*)	$\tau_4 = Ph^*/(1 - \Delta^*)$	$\tau_4 = Ph^*$
	$\tau_3 = (Ph^* + \Delta^*/2)/(1 - \Delta^*)$	$\tau_3 = \tau_4$
	$(1 - \Delta^*)\tau_2 = Ph^*\delta + \frac{\Delta^*\delta^2}{2} + \frac{Ph^*\delta^2}{2}(d\delta/d\tau)_2$	$\tau_2 = Ph^*\delta + \frac{Ph^*\delta^2}{2}(d\delta/d\tau)_2$
	$\tau_1 = \tau_3$	$\tau_1 = \tau_3 = \tau_4$
	$\hat{\tau}_3 = (Ph^* + ½)/(1 - \Delta^*) = \hat{\tau}_1$	$\hat{\tau}_3 = (Ph^* + ½) = \hat{\tau}_1$
Constant wall temperature $(Ph, \Delta Bi = Bi^*)$	$\tau_4 = -\frac{Ph}{Bi^{*2}}[Bi^* + \ln(1 - Bi^*)]$	$\tau_4 = \frac{Ph}{2}$
	$\tau_3 = \tau_4 + Bi^*/6$	$\tau_3 = \tau_4$
	$\tau_2 = \frac{Ph\delta^3}{6}\left(\frac{d\delta}{d\tau}\right)_2 + \frac{Bi^*\delta^3}{6} - \frac{Ph}{Bi^*}\left[\delta + \frac{\ln[1 - Bi^*\delta)}{Bi^*}\right]$	$\tau_2 = \frac{Ph}{4}\left[1 + \sqrt{\left(1 + \frac{4}{3Ph}\right)}\right]$
	$\tau_1 = \tau_4 - \frac{1}{3Bi^*}\left[1 + \frac{\ln(1 - Bi^*)}{Bi^*}\right] - \frac{1}{6}$	$\tau_1 = \tau_3 = \tau_4$
	$\hat{\tau}_3 = \tau_4 + \frac{4 - Bi^{*2}}{24(1 - Bi^*)}$	$\hat{\tau}_3 = \frac{Ph}{2} + \frac{1}{6}$
	$\hat{\tau}_1 = \tau_4 - \frac{1}{2Bi^*}\left[1 + \frac{\ln(1 - Bi^*)}{Bi^*}\right] - \frac{1}{12}$	$\hat{\tau}_1 = \tau_3$

simpler cases for which the results can either be extracted from the above equations or are obtained by an analogous procedure.

If the system is cooled subject to a constant heat flux q at the cold surface of the slab, then the reference temperature difference $(T_p - T_c)$ is replaced by qd_o/k such that

$$Ph^* = \frac{\lambda' k}{q d_o c} \quad \text{and} \quad \Delta^* = \frac{h_m(T_m - T_p)}{q}$$

become the system parameters. Further, when the cold-surface temperature is constant ($h_c \to \infty$), the characteristic parameters become

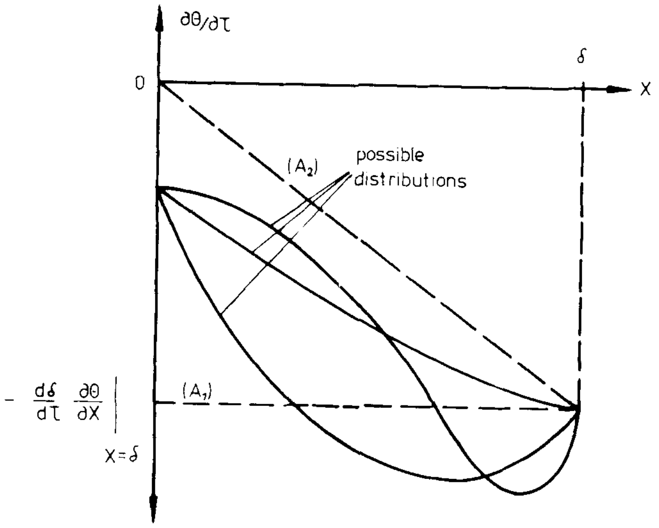

Fig. 2. Approximating the left-hand side of Eq. (18).

$$Ph \text{ and } Bi^* \equiv \Delta Bi = \frac{h_m d_o(T_m - T_p)}{k(T_p - T_c)}$$

Finally, in many situations the melt is at or slightly above the phase change temperature T_p, and convective flux from the melt can be neglected. In that case, the appropriate parameter

$$\Delta \text{ or } \Delta^* \text{ or } Bi^* \to 0$$

and the corresponding results are obtained directly from the more general equations.

For convenience, all the bounding solutions developed in this paper are summarized in Table 1. Throughout the table the notation for τ indicates the type of bound as well as the approach by which the bound is obtained and is consistent with the notation used in the previous sections. Identities such as $\tau_3 = \tau_4$ do, however, hold only within a block of boundary conditions

APPROXIMATE SOLUTIONS

A simple approximate result is obtained from the arithmetic mean of the upper and lower bounding solutions; that is

$$\bar{\tau} = (\tau + \hat{\tau})/2 \tag{38}$$

Then, the maximum possible error is just half the difference between the bounds and will be sufficiently small for many engineering applications (see the subsequent discussion of the results). For extremely small values of Ph and Δ, discrepancies may, however, become quite large because with Equation (38), for the sake of simplicity, we are limited to using the analytic bounds. In such cases we may, rather than derive an approximation by use of a numerically integrated lower bound, follow the more direct approach of approximating $\partial\theta/\partial\tau$ in Equation (18).

Referring to Figure 2, we use either of the two approximations:

$$\int_o^\delta \frac{\partial\theta}{\partial\tau} \cong -\delta\frac{d\delta}{d\tau}\frac{\partial\theta}{\partial X}\Big|_{X=\delta} \quad \text{and}$$

$$\int_o^\delta X\frac{\partial\theta}{\partial\tau} \cong -\frac{\delta^2}{2}\frac{d\delta}{d\tau}\frac{\partial\theta}{\partial X}\Big|_{X=\delta} \tag{39}$$

or

$$\int_o^\delta \frac{\partial\theta}{\partial\tau} \cong -\frac{\delta}{2}\frac{d\delta}{d\tau}\frac{\partial\theta}{\partial X}\Big|_{X=\delta} \quad \text{and}$$

$$\int_o^\delta X\frac{\partial\theta}{\partial\tau} \cong -\frac{\delta^2}{3}\frac{d\delta}{d\tau}\frac{\partial\theta}{\partial X}\Big|_{X=\delta} \tag{40}$$

From the illustration it is seen that Equation (39) tends to overpredict the solidification time because we assume that the temperature of any interior solid element changes at the same rate as at the solid/liquid interface, whereas one would expect the change $|\partial\theta/\partial\tau|$ to be smallest at the wall. Likewise, Equation (40) tends to underpredict the solidification time, particularly when we consider that for the general problem $\partial\theta_w/\partial\tau < 0$. In fact, it can be shown that for constant wall temperature and no heat flux from the melt, the latter approximation leads to a lower bound for τ and thus will, most probably, constitute a lower bound also in the general case. However, we shall not try to prove the bounding nature of the above statements because the general equations cannot be integrated analytically. With Equations (39) and (40) inserted in Equation (18), we obtain after rearrangement

$$\tau \cong \int_o^\delta \frac{2\delta' Ph A_{1,2} d\delta'}{\sqrt{\{[\delta'\Delta Bi A_{1,2} - Ph(1 + \mathrm{Bi}\delta')]^2 + 4\delta' Ph Bi A_{1,2}\}} - \delta' Bi\Delta A_{1,2} - Ph(1 + Bi\delta')} \tag{41}$$

with

$$A_1 = 1 + Bi\delta'/2 \text{ from Equation (39)}$$

and

$$A_2 = 1/2 + Bi\delta'/3 \text{ from Equation (40)}$$

Though easy to integrate numerically, Equation (41) appears to be somewhat inconvenient for practical applications, where a safe result is often preferred to a more accurate but possibly unsafe result. Its use is therefore limited to situations where Equation (38) becomes unsatisfactory.

Justification for the above statement concerning the bounding nature of Equation (41) is drawn primarily from the comparison with the exact Neumann solution. For $\Delta = 0$ and $Bi \to \infty$ we obtain

$$\tau_{A1} = \frac{1}{2[\sqrt{(1 + 2/Ph)} - 1]} \tag{42}$$

and

$$\tau_{A2} = \frac{1}{3[\sqrt{(1 + 4/3Ph)} - 1]} \tag{43}$$

The last equation is identical to the corresponding τ_2 in Table 1 and thus constitutes a lower bound, whereas Equation (42) provides an extremely tight upper bound as long as $Ph \geqq 0.28$, but not in general. Physical reasoning does, however, suggest that in the more general cases the bounding character extends to at least the same values of Ph and is, indeed, likely to hold for all practically occurring Ph values.

We conclude that the approximations (41) developed in this section tend to be bounds and that the upper solution τ_{A1}, if not a bound, constitutes a good approximation to the exact result.

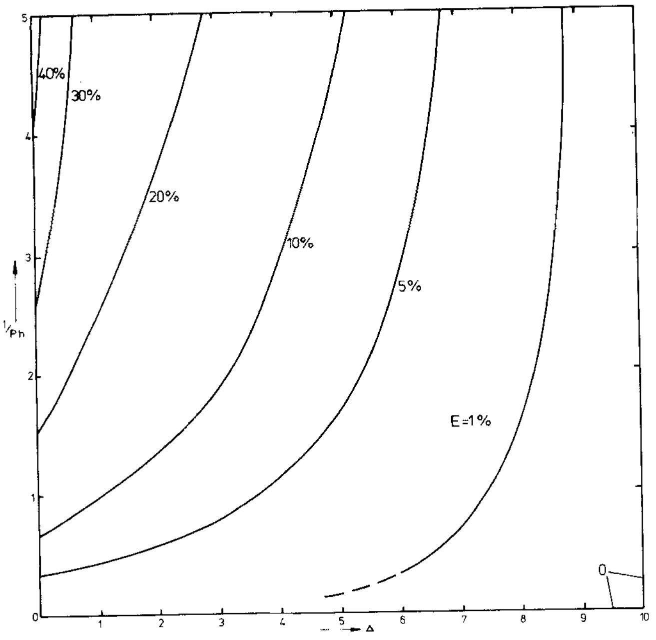

Fig. 3. The maximum possible error involved in using the arithmetic mean of the two best analytic bounds.

DISCUSSION OF RESULTS

It is not the aim here to compare the present solutions with all the analytic and numerical results developed previously for the various versions of the problem. As pointed out before, the advantage of our method is that the results have a built-in accuracy criterion. We can therefore concentrate on the latter and restrict the comparison to areas of large discrepancy. The table shows clearly that for $\Delta = 0$, all the analytic lower bounds are identical to the quasistationary solutions which are known to become increasingly inaccurate with smaller values of *Ph* and larger values of *Bi*. Hence, a similar trend will show up in any result that contains the lower bound.

In Figure 3 lines of constant maximum possible error are plotted as a function of Δ and *Ph*. The error is defined as

$$E = (\hat{\tau} - \tau)/(\hat{\tau} + \tau) \equiv \frac{\hat{\tau} - \tau}{2} / \bar{\tau} \qquad (44)$$

and for each value of *Bi* the largest analytic lower and smallest upper bound have been chosen (see the above discussion on long- and short-time bounds). The quoted errors are, however, conservative in that for any combination of Δ and *Ph*, the maximum discrepancy occurring over the entire range of *Bi* has been considered. Further, we have to keep in mind that the actual error may be significantly smaller than the maximum possible one.

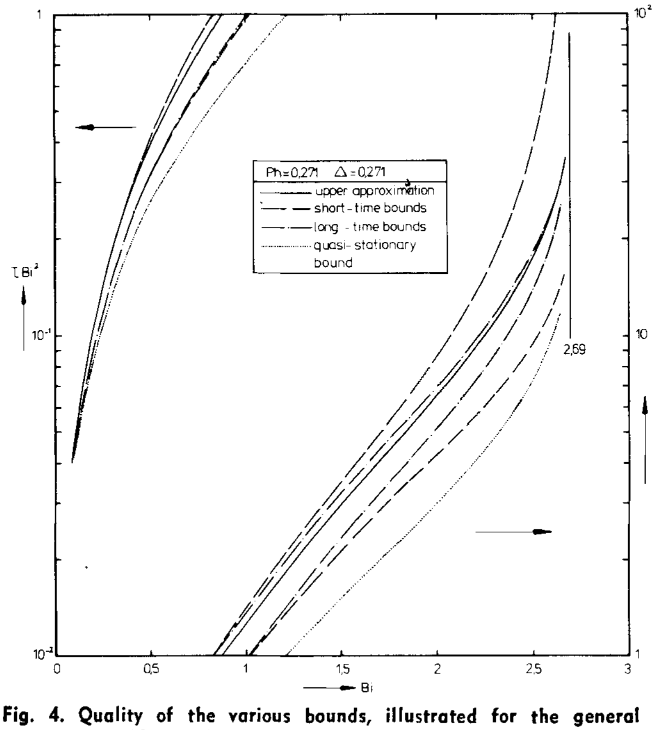

Fig. 4. Quality of the various bounds, illustrated for the general problem and a particular parameter combination.

In order to provide an impression of the quality of the bounding solutions, two examples will be discussed for which Figure 3 predicts rather large errors. The first one is illustrated in Figure 4 and has also been dealt with by Stephan (1969). We point out that his assumption of a parabolic temperature profile satisfying the differential equation only at the solid/liquid interface is equivalent to our approximation (39) and leads, in fact, to the same Equation (41). Since he claims an accuracy better than 2.5%, we may use the numerical solution of Equation (41) (with A_1) as a reference result. Included in the figure are the upper bounds, Equations (36) and (37), and it is seen that for long times $\hat{\tau}_1$ provides a much tighter bound than $\hat{\tau}_3$. Similarly, the lower bound is improved substantially by considering Equation (14) rather than (15). This is evident, since the problem is characterized by a rather large heat flux from the melt and a small phase change parameter. The long-time lower bound τ_1 yields further improvement, particularly at large values of time. Since for this particular parameter combination the other two expressions τ_2 and τ_{A2} are almost identical to τ_3 and τ_1, respectively, they have not been plotted in Figure 4. For other parameter combinations (smaller Δ, larger *Ph*), the numerical integration of Equation (28) in particular may, however, be useful and is conveniently performed by a predictor-corrector method with a series solution for small values of *Bi* as a starting value. Obviously for short as well as very long times one can obtain quite accurate analytic solutions for τ_2 by neglecting in Equation (28) the corresponding terms of first-order smallness and for the remainder assume a series solution with higher terms suppressed.

As a point of interest we note that from Figure 3 the maximum possible error *E* is 16.7% for the present parameter combination, whereas the actual maximum error, from the comparison with Equation (41), turns out to be only 7.5%. This stresses that Equation (44) can be used with quite some confidence. Lastly, we mention that $\hat{\tau}_1$ is always a tighter bound than the one suggested by Kern (1977), thus proving that his approach does in fact yield an upper bound. The discrepancy between his results and those of Stephan (1969) on the above parameter combination appears to be due to an inaccurate numerical integration of Stephan's Equation (36), identical to our Equation (41) with A_1.

Quite a different picture is found for the second example illustrated in Figure 5. With $\Delta = 0$ and $Ph = 0.2$, this is a situation where we expect large errors to occur. Figure 3 indicates a maximum possible error of over 40%. As before, the comparison with numerically exact results (Stephan and Holzknecht, 1974) reveals, however, that Equation (44) predicts the solidification time by a lesser amount, that is between 18% at $Bi \to \infty$ and 11% at $Bi = 0.5$. But the agreement is not really satisfactory and may call for a numerical integration of the improved

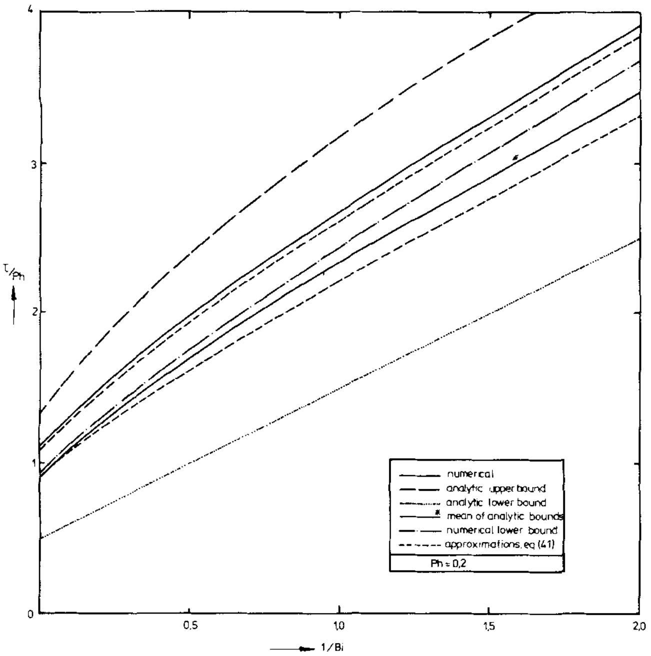

Fig. 5. Quality of the various bounds and approximate results, illustrated for no heat flux from the melt and a small phase change parameter.

lower bound τ_2; as expected, the improvement is seen to be quite significant. As before, a short-time analytic solution for τ_2 can be generated, while for long times τ_2 converges towards $\tau_2(Bi^* = 0)$ as given in the table. On the other hand, Megerlin (1966) has derived an analytic solution to Equation (41) with $\Delta = 0$. The upper approximation (A_1) was found to be accurate to within 1.7%, and although the resulting expression for τ is rather lengthy, it is certainly preferential to any numerical result. If a simpler analytic result is ever required, one may use the upper bound on its own because it constitutes a safe result of about the same accuracy as $\bar{\tau}$ from τ_4. Alternatively, one can employ weighting factors other than the rather arbitrary 0.5 for lower and upper bounds (see Kern, 1977) and obtain accurate and yet simple approximations.

Similar conclusions are drawn when the bounding solutions for constant heat flux at the wall (Ph^*, Δ^*) are compared with available data, but, for conciseness, the discussion has been omitted. In summary, it can be stated that the present approach yields very accurate bounds or approximate solutions as long as the solidification rate is not too large. Since this rate is inversely proportional to the heat influx from the melt as well as to the values of Ph and $(1/Bi)$, the best predictions are expected and indeed found for the general problem, whereas agreement is poorest for the classical Stefan problem ($\Delta = 0$, $Bi \rightarrow \infty$).

NOTATION

Bi = hd_o/k = Biot modulus
Bi^* = ΔBi = modified Biot modulus for $h \rightarrow \infty$
c = specific heat capacity, J/(kgK)
d, d_o = instantaneous, arbitrary thickness of solidified slab, m
E = relative error, Equation (44)
h, h_m = heat-transfer coefficient at the cold, warm side of the solidified slab, W/(m^{2}K)
k = thermal conductivity, W/(mK)
Ph = $\lambda'/(c[T_p - T_c])$ = phase-change parameter
Ph^* = $\lambda' k/(q d_o c)$ = modified phase change parameter for constant heat flux at the cold slab surface
q = heat flux density at the cold slab surface, W/m^2
t = time, s
T = temperature, K
x = coordinate perpendicular to the cooling face, m
X = x/d_o = nondimensional coordinate

Greek Letters

α = thermal diffusivity, m^2/s
δ = d/d_o = nondimensional solid thickness
Δ = $h_m(T_m - T_p)/[h(T_p - T_c)]$ = heat flux parameter
Δ^* = $h_m(T_m - T_p)/q$ = modified heat flux parameter
θ = $(T - T_c)/(T_p - T_c)$ = nondimensional temperature
λ = latent heat of fusion, J/kg
λ' = $\lambda + c_m(T_m - T_p)$ = modified latent heat of fusion, J/kg
ρ = density, kg/m^3
τ = $t\alpha/d_o^2$ = nondimensional time

Subscripts

c = relating to cooling fluid
m = relating to melt
p = at phase change condition
w = relating to cooling face
1, 2, 3, 4 = relating to the various types of approximation

Superscripts

$*$ = in connection with θ referring to an approximated temperature profile
$\wedge$ = upper bound
$-$ = arithmetic mean

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Droplet Size Spectra Generated in Turbulent Pipe Flow of Dilute Liquid/Liquid Dispersions

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Experiments were carried out with water dispersed in hydrocarbons at various flow rates. The measured size spectra can be well represented by either an upper limit log-probability function or a Rosin-Rammler type of equation with constant parameters and only one variable, the maximum drop diameter $d_{\max}$ or d_{95}. The latter can be predicted satisfactorily by a correlation based on the Hinze/Kolmogorov model of droplet breakup.

SCOPE

Reliable estimates of the distribution of droplet sizes in flowing liquid/liquid dispersions are required in many areas of chemical engineering practice, for example, in the design of chemical reactors and of physical separation processes. At present, it is impossible to make such a priori estimates even in common problems, including pipe flow of dilute dispersions, owing to insufficient information about the effect of flow conditions on the size spectrum.

Collins and Knudsen (1970) have published the only available drop size distribution data, obtained in well-defined turbulent pipe flow with water as the continuous phase. These authors reached a rather disturbing conclusion, namely, that their data did not conform to any of the presently available distribution functions, such as the log-normal, upper limit log-normal, etc. In order to interpret the measured size spectra, Collins and Knudsen developed a computer aided stochastic model by postulating a breakup mechanism in which the maximum stable drop size $d_{\max}$ is a basic input parameter. However, the presently available correlations due to Hinze (1955) and Sleicher (1962) predict maximum droplet sizes $d_{\max}$, in turbulent pipe flow, which differ almost by an order of magnitude for flow conditions and liquid properties of practical interest. Moreover, according to the Hinze model, $d_{\max}$ is approximately inversely proportional to the mean velocity $\overline{U}$, whereas in the Sleicher correlation, $d_{\max}$ varies with $\overline{U}^{-2.5}$. It is clear, therefore, that in the problem considered here, the literature provides very little guidance of questionable reliability.

The need to describe dispersions of water in flowing hydrocarbons provided the motivation for this work. The main objective was to make accurate measurements of droplet size spectra generated in turbulent pipe flow. In the absence of a satisfactory theory, such measurements are necessary in order to select the most representative distribution function and to study the influence of flow conditions and liquid properties on some physically significant parameters of the size spectrum, for example, the Sauter mean $\overline{d}_{32}$ or the maximum droplet diameter $d_{\max}$.

CONCLUSIONS AND SIGNIFICANCE

Accurate data of water drop size spectra have been obtained by a relatively new droplet encapsulation technique. Two liquid hydrocarbons of viscosity approximately 2 and 20 mN s/m^2 have been used as the continuous phase in a 5.04 cm ID pipe loop with a straight test section 32 m long. The measured spectra show a remarkable similarity and can be satisfactorily represented by either an upper limit log-probability function or a Rosin-Rammler type of equation with nearly constant parameters (see Tables 2 and 4), the only variable being the characteristic size $d_{\max}$ or d_{95}. The latter can be predicted independently as a function of flow conditions and liquid physical properties.

The maximum drop sizes, or d_{95}, appear to be approximately inversely proportional to the mean flow velocity, in agreement with the theory of Kolmogorov (1949) and Hinze (1955). A correlation proposed by the latter author, essentially untested so far for pipe flow of dilute dispersions, has been reexamined and slightly modified to improve its accuracy at high Reynolds numbers. Our data are generally in good agreement with this correlation

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