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DIFFUSION IN COMPOSITE MEDIA

PART I : STEADY-STATE

by

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The diffusion behaviour of a composite sheet is studied using numerical techniques. The effective diffusion coefficient is obtained for particles of a dispersed phase arranged on a regular lattice in a continuum. Typical concentration and flow patterns are presented. The effects of the shape, size and position of the dispersed phase are investigated and the acceptability of existing approximate models is assessed.

COMPOSITE MEDIA

1.1 Introduction

Many materials in common use are heterogeneous in structure. Their properties are not only of technical importance but also, they present interesting theoretical problems.

Barrer (1968) distinguishes three different types of heterogeneous media. This paper is concerned with the first type, namely, dispersed phase or phases in a continuum. Holliday (1963) presents a number of examples of systems made up of one continuous polymer phase and one dispersed phase. To determine some overall physical property of the system, such as thermal or electrical conductivity, or permeability, detailed knowledge of the different phases is required. For a composite medium of this kind, Holliday (1963) specifies the following parameters

(i) The geometry and distribution of the dispersed phase.

(ii) The composition of the dispersed phase.

(iii) The composition of the continuum.

Laplace's equation

$$\nabla^2 u = 0 \qquad (1)$$

describes many physical processes and, in particular, heat conduction and diffusion. The scalar function, $u(x,y,z)$, represents some quantative aspect of the phenomenon under investigation, for example, temperature, potential or concentration of a diffusing substance. Usually, soma property associated with the material is of interest and in general, this can be defined in terms of u and its derivatives, such as conductivity, permeability, etc. Subsequently, the mathematical solution of equation (1) for a particular situation may be interpreted in a variety of ways. Conversely, researches into different physical properties of composites can be unified.

This paper presents a study in depth of a fundamental problem, using numerical techniques, and discusses the validity of approximate models proposed by recent authors.

In the review that follows the references are chosen to represent the main different mathematical approaches. The nomenclature, as far as possible, relates to the diffusion process.

1.2 Review

In 1873, Maxwell solved the problem of sparsely distributed spheres suspended in a continuum and obtained an effective diffusion coefficient for the composite medium. His work was extended by Burger (1915). Eucken (1932) and Fricke (1931) to deal with the suspension of both ellipsoids and spheroids. Fricke compared his results with existing experimental data for the conductivity of blood and reported excellent agreement. On the other hand, Hamilton and Grosser (1962) correlated Fricke's expression for the effective diffusion coefficient with experimental data relating to aluminium or balsa spheres suspended in rubber with only limited success. They suggest a modification to Fricke's formulation based on the evidence of their empirical studies.

Expressing the solution of equation (1) in terms of Legendre functions. Rayleigh (1892) improved Maxwell's model. In turn, this work was developed further by Runge (1925) and de Vries (1952),

Barrer (1968) quotes several references and formulae and a table from de Vries comparing calculated results for spheres by several authors. These are seen to be consistent when the ratio of the diffusion coefficient of the dispersed phase to that of the continuum is small. Barrer suggests that the formulae may account reasonably well for plastics containing impermeable filler particles, though the question of non-spherical shapes is not resolved.

More recently, the idea that neighbouring parts of a composite may be considered to be in series or parallel has been explored. Jefferson et al.(1958) employed this concept to derive an expression for the effective diffusion coefficient of an array of uniform spheres arranged on a regular lattice. Tsao (1961) and, later, Cheng and Vachon (1969) went much further, extending the series-parallel technique to composites in which the dispersed phase consists of randomly distributed particles of irregular size and shape. Although, in reality, the underlying assumptions of the series-parallel formulation are not strictly time, the attraction of the technique lies in its simplicity and applicability. When the volume of the dispersed phase to that of the continuum is small, the above authors (Jefferson et al., Tsao, and Cheng and Vachon) report favourable agreement between their formulations and experimental, data.

Fidelle and Kirk (1971) have attempted to assess the degree of approximation involved in the series-parallel formulae. They studied Jefferson's model for spheres obtaining numerical solutions of equation (1) by a finite difference method. In their numerical procedure, the spherical surface between the two phases was not reproduced exactly but a best approximation with a rectangular grid was used. They reduced the grid size till no difference in the effective diffusion coefficient of the composite was observed for successively finer grids to the accuracy of working. From a comparison of their results with those of previous authors, they conclude that the series-parallel formulation of Cheng and Vaohon is the best predictor.

A majority of the work discussed so far as been concerned with dilute suspensions of spherical-shaped particles and, as indicated, many adequate formulae exist. The important feature of the series-parallel technique is its adaptability to non-spherical shapes. In the present study it is convenient to compare the results of such approximate models with the numerical and experimental data obtained. From these comparisons it will be possible to assess the limitations of the series-parallel technique regarding the non-sphericity of the dispersed particles and the fractional volume occupied by them.

Keller (1963), on the other hand, was concerned with closely packed spheres and produced an expression for the asymptotic behaviour of the effective diffusion coefficient of the composite as the distance between adjacent spheres decreased. Keller and

Sachs (1964) investigated the validity of this expression by obtaining finite difference solutions to the associated problem of a composite whose dispersed phase consists of closely packed cylinders. Moreover, they present results for the entire range of cylinder radii which allows suitable comparisons to be made with those computed by the present authors.

1.3 Composites in Series and Parallel

Crank(1956) gives the following expression for a composite composed of n sheets of thicknesses ℓ_1, ℓ_2 ,... ℓ_n and diffusion coefficients D_1, D_2,..., D_n, see figure 1(a), placed in series,

$$\frac{\ell_2}{D_1} + \frac{\ell_2}{D_2} + \ldots + \frac{\ell_n}{D_n} = \frac{L}{D} \quad , \tag{2}$$

where D is the effective diffusion coefficient for the composite and L denotes the total width.

Similarly, when the composite consists of n sheets placed in parallel, as in figure 1 (b),the effective diffusion coefficient, D, of the system is given by

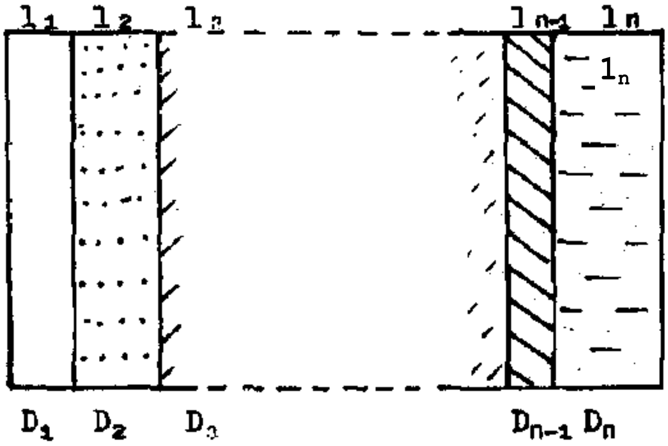
$$\ell_1 D_1 + \ell_2 D_2 + \cdots + \ell_n D_n = LD \ . \tag{3}$$

The equations (2) and (3) are analogous to the formulae for electrical resistances in series and parallel, respectively. The idea exploited by Tsao, and Cheng and Vachon, is to split a composite into thin strips of $\Delta\ell$, as shown in figure 1(c), calculate an effective diffusion coefficient for each strip using (3) and, finally, by summing the strips in series obtain an effective diffusion coefficient for the composite as a whole. Thus,

Figure 1 •

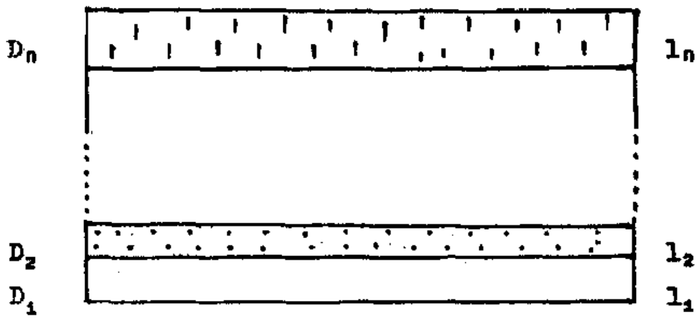
1 (a) Series

Direction of Flow



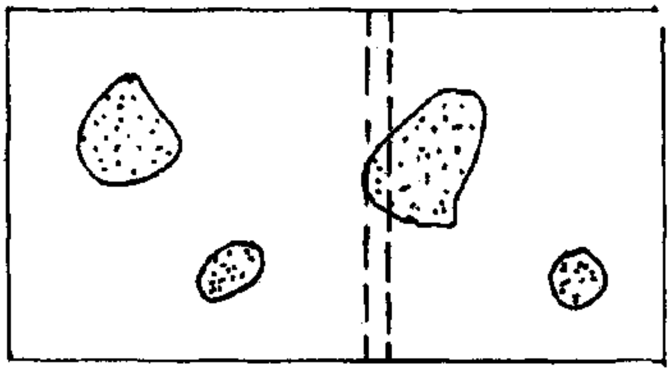
1 (b) Parallel

Direction of Plow



1 (c) Typioal Composite

Direction of Flow



Δl

this technique assumes the validity of equations (2) and (3), which, in turn, implies unidirectional flow. If the flow is not unidirectional then both these relationships are approximate. By applying the above procedure to the problems considered in the following sections the acceptability of such an assumption is assessed.

MODEL PROBLEM

2.1 Idealised Model

Numerical solutions of Laplace's equation are obtained in a region pertaining to identical rectangular blocks dispersed on a regular lattice in a continuum. An extreme case is considered in which the blocks are impenetrable by the diffusing substance, that is,they have aero diffusion coefficient. In particular, the effects of size and arrangement of the blocks are studied.

2.2 Symmetry and Basic Patterns

Figure 2 shows a two-dimensional array of identical rectangular blocks. A typical unit of the repeating pattern lies between the lines AA' and BB', Symmetry about the line XX' leads us to consider the region in figure 3, where, for the moment, only two blocks are included with sizes and spacing as indicated.

A steady-state problem in diffusion through this region is defined by the following system of equations in which u denotes the concentration of the diffusing substance and axes Ox and Oy are as indicated. Typically, the ends $x = 0$, ℓ are held at unit and zero concentrations respectively and all other

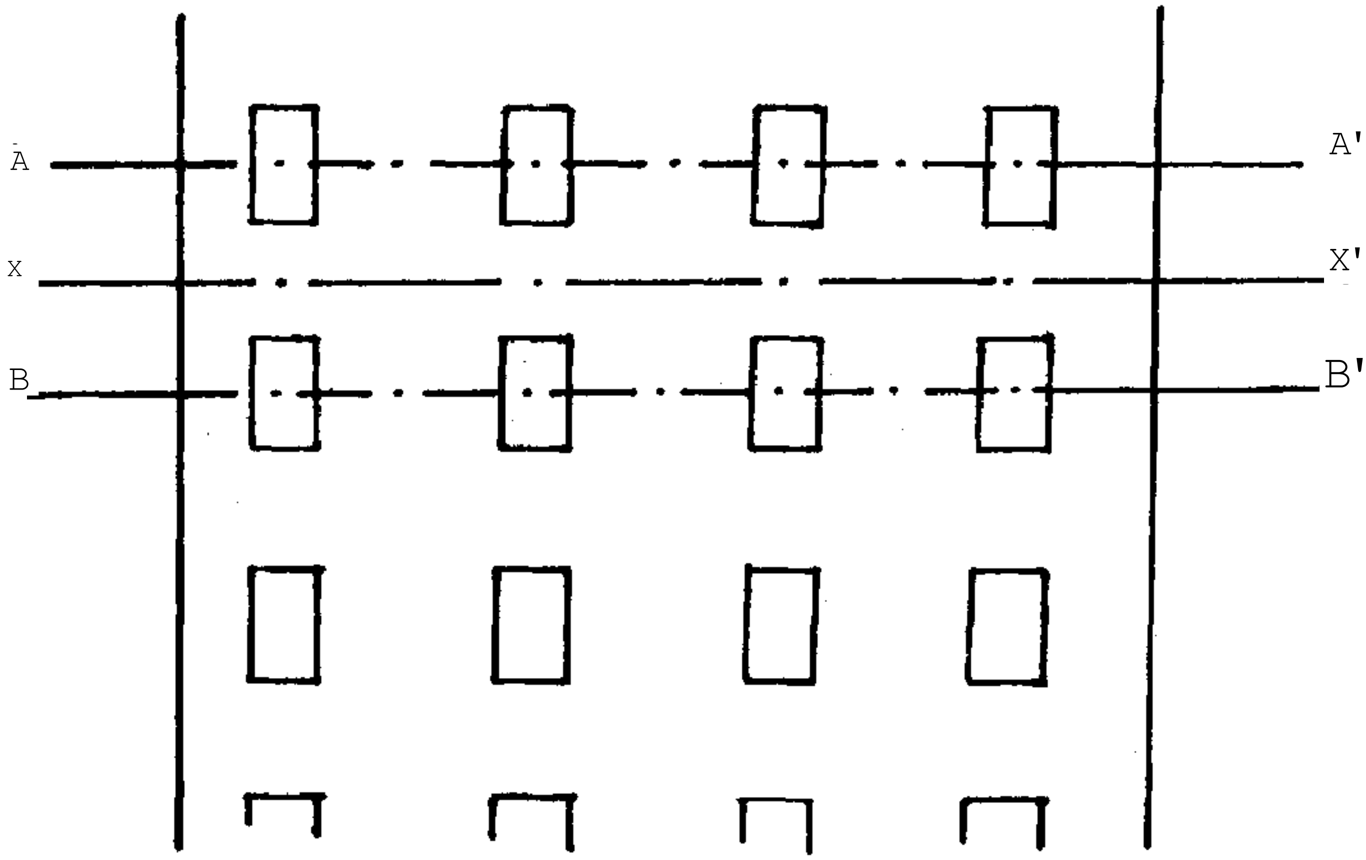


Figure 2

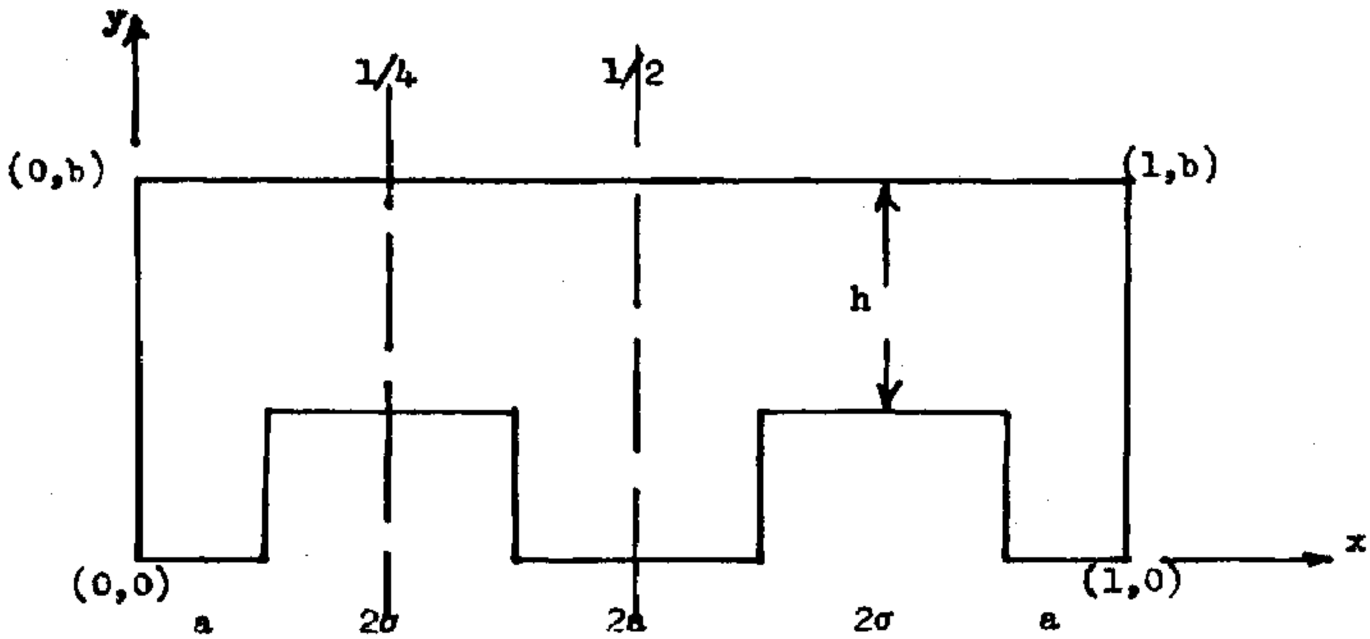


Figure 3

surfaces are impermeable.

$$\nabla^2 u = \frac{\partial^2 u}{\partial x^z} + \frac{\partial^2 u}{\partial y^2} = 0 \quad , \tag{4}$$

$$\begin{aligned} &u = 1 , \quad x = 0 , \quad 0 \le y \le b , \\ &u = 0 , \; x = \ell , \; 0 \le y \le b , \end{aligned} \tag{5}$$

and ,
$$D \frac{\partial u}{\partial \eta} = 0 \quad , \tag{6}$$

on the remaining parts of the boundary, where $\frac{\partial}{\partial \eta}$ denotes differentiation with respect to the outward drawn normal to the boundary and D is the diffusion coefficient of the continuum, assumed constant.

Suppose the solution of equations (4), (5) and (6) is $u = f(x,y)$. Introducing the transformation

$$\left.\begin{aligned} &{}^{v}(x_i, y_i) - 1 - u(x, y) \quad , \\ &\text{where} \\ &x_1 = \ell - x, \text{ and } y_1 = y \quad , \end{aligned}\right\} \tag{7}$$

we obtain
$$\Delta^2 \; v = 0 \quad ,$$

and, also,

$$v = 1 , \quad x_1 = 0, \; 0 \le y_1 \le b ,$$

$$v = 0, \quad x_1 = \ell, \; 0 \le y_1 \le b .$$

These are identical to equations (4) and (5) and, similarly , it can easily be shown that equations (6) remain the same in the new variables. The problem in terms of v, x_1, y, is identical to the original problem in u, x, y.

That is, $v(x_1, y_1) = f(x_1, y_1)$,

and, using (7) gives

$$v = f(\ell - x, y) = 1 - f(x,y) .$$

Therefore, the problem is anti-symmetric about $x = \ell/2$.

In particular, when $x = \ell/2$,

$$u(\ell/2, y) = f(\ell/2, y) = \tfrac{1}{2}, \quad 0 \le y \le b. \tag{8}$$

Similarly, by considering the region between $0 < x < \ell/2$, for $0 < y < b$, we again have symmetry of shape about $x = \ell/4$. If $g(x,y)$ is the solution in this region then

$$g(x,y) + g(\ell/2 - x, y) = 3/2$$

and when $x = \ell/4$, $s(\ell/4, y) = 3/4$.

Thus, for any region with repeated symmetry, it suffices to study the steady-state problem in a rectangular region with a re-entrant corner as in figure 4, provided the number of repeating basic units is an integer power of two.

We note in passing that the blocks need not be rectangular. The argument applies in general, provided a symmetry can be identified.

Furthermore, a staggered arrangement as in figure 5(a) can be studied by solving the problem for the rectangle with two re-entrant corners, as in figure 5(b).

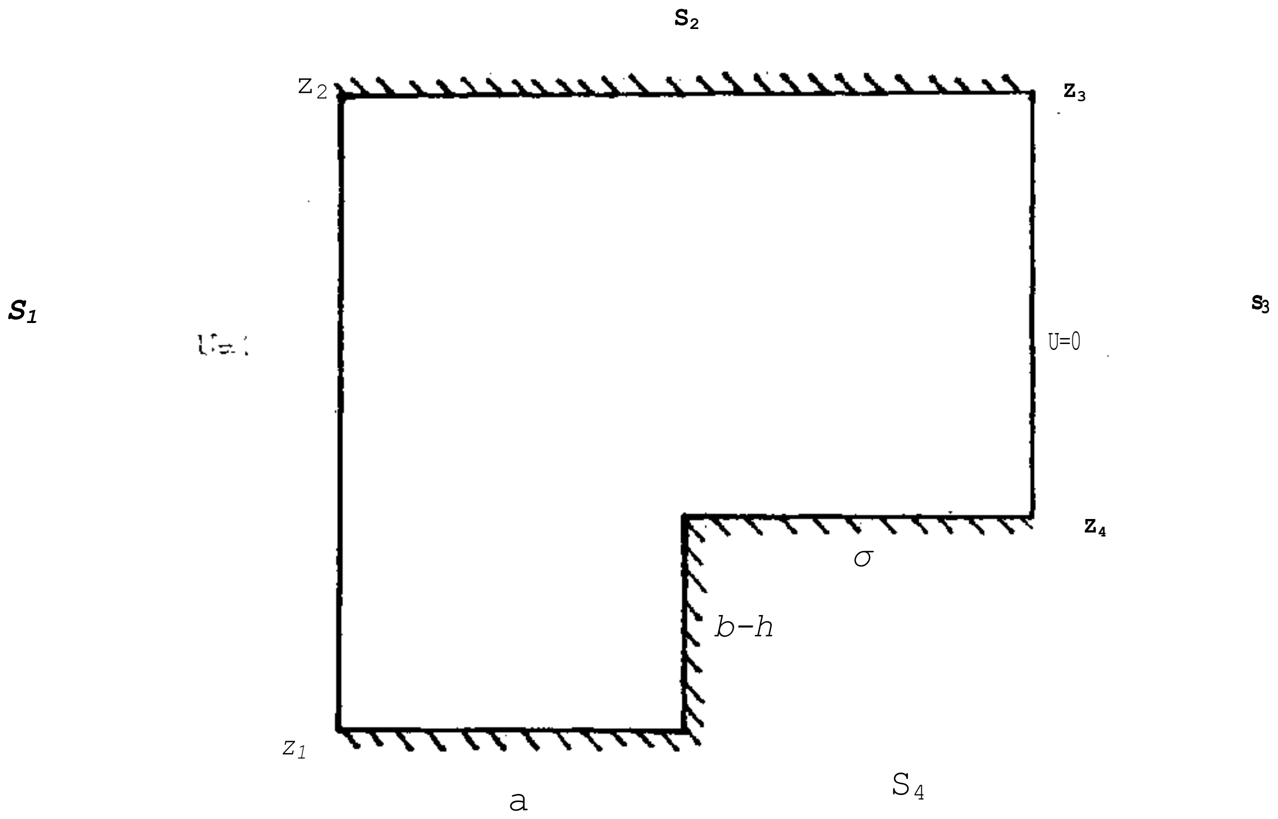


Figure 4. (All shaded lines are impermeable)

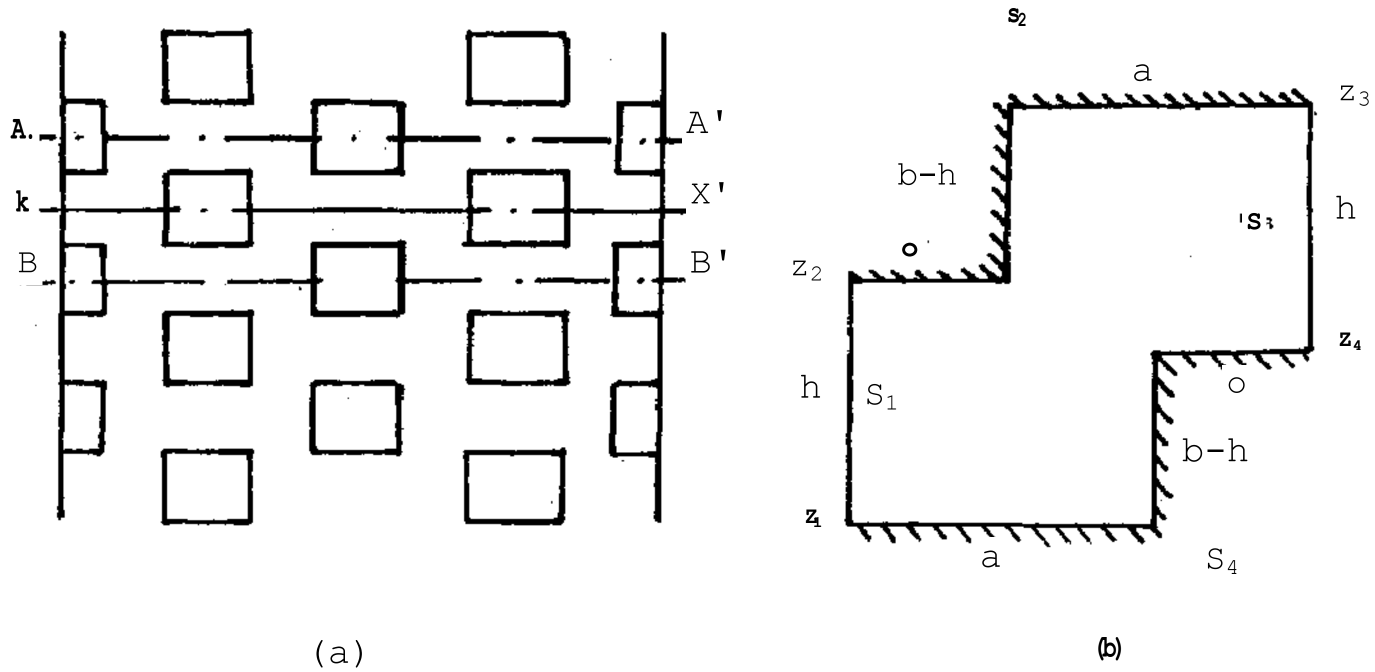


Figure 5.

2.3 Mathematical Procedure

The major mathematical difficulty encountered in attempting to obtain solutions of Laplace's equation in regions illustrated in figures 4 and 5(b) arises from the presence of the re-entrant corners. Singularities occur in the solution at such a corner and some or all of the derivatives are unbounded. Consequently, numerical methods, based on finite-differences or finite elements, tend to produce values of low accuracy near a re-entrant corner. Several methods of overcoming the difficulty have been proposed. The steady-state results quoted in this paper have been obtained by using conformal transformation methods developed by Whiteman and Papamichael (1972, 1975).

They transform, by conformal mapping techniques, the original problems, illustrated in figures 4 and 5(b) into the trivial problem of one-dimensional diffusion in a plane sheet with ends maintained at unit and zero concentrations respectively. This procedure is possible provided the region, G, tinder consideration (fig.4 or 5(b)) is a polygon with boundary S where S consists of adjacent arcs S_1, S_2 , S_3 and S_4 such that,

$$
\begin{aligned}
u(x,y) &= 1, & (x,y) &\in s_1 ,\\
\frac{\partial}{\partial \eta} u(x,y) &= 0, & (x,y) &\in s_3 ,\\
u\ (x,y) &= 0, & (x,y) &\in s_3 ,\\
\frac{\partial}{\partial \eta} u(x,) &= 0, & (x,y) &\in s_4 .
\end{aligned}
$$

and

The transformation is achieved by four successive oonforoal mappings of which the first is performed numerically using an integral equation method due to Symm (1966). Considering G to be in the complex plane, z = x+ iy, with origin 0, within G, then the mappings are :

1. $w = F(z)$,

which maps G onto the unit circle $|w| \leq 1$, in the w - plane.

2. $$t = 1\left[\frac{1+w}{1-w}\right] = T(z) \quad ,$$

which is a bilinear transformation mapping the unit circle in the w -plane onto the upper half t- plane.

3. $$t' = \left[\frac{T(z_4) - T(z_2)}{T(z_4) - T(z_1)}\right] \left[\frac{t - T(z_1)}{t - T(z_2)}\right] = P(t) \quad ,$$

is a second bilinear transformation, where z_1, z_2, z_3 and z_4 are as indicated in figures 4 and 5(b), and denote the leading points of the four arcs S_i, taken in order. This remaps the upper-half t-plane onto itself in preparation for the final transformation.

4. The Schwarz - Christoffel transformation ,

5. $$w' = \frac{1}{K(m)} \quad sn^{-1} \; (\sqrt{t'}\, , m) \quad ,$$

where sn denotes the Jacobian elliptic sine and k(m) is the complete elliptic integral of the first kind with modulus m given by

$$m = \{P(T(z_3))\}^{-\frac{1}{2}}$$

The effect of this final transformation is to map the upper-half t' plane onto a rectangle in the w' -plane and, since Laplace's equation is invariant under conformal transformations, the solution in the rectangle is

$$v(\xi,\eta) = 1 - \xi$$

where $w' = \xi + i\eta$.

The form of F(z) clearly depends on the geometry of the original region. Since, in general, F(z) cannot he written down analytically, the mapping W = F(z) is performed numerically. Therefore, the solution finally obtained is approximate but, by analyzing model problems, Whiteman and Papamichael conclude that this method compares favourably in computing speed and accuracy with other methods.

This technique can be used for obtaining solutions of (4) in any simply-connected domain (see Papamichael and Whiteman, 1973), but for the purpose of this study only the regions illustrated in figures 4 and 5 are considered, For convenience, the dimensions of the basic shapes are given by

$$b = 1, \text{ and } a = 1 - o, \tag{9}$$

h and σ being allowed to vary.

CALCULATED PROPERTIES OF COMPOSITES

3.1 Concentration Distribution

Table 1 shows a typical set of solution values covering a region of the type shown in figure 4, with $h = \sigma = \frac{1}{2}$. In figure 5, the corresponding lines of constant concentration (analogous to isothermals in heat flow) are plotted together with lines of constant flow (analogous to streamlines). Figure 7 presents corresponding plots for a region of the type illustrated in figure 5.

These illustrate two important features of the general problem, the consequences of which are discussed later. Firstly, the variation in concentration along the line x - 0.5 (Table 1 and figure 6) is considerable. Thus, any approximation based on the drop in concentration across different parts of the composite must be formulated in terms of mean drops in concentration. Barrer (1968) realising this, introduced a number of scaling factors into his approach but was unable to determine them explicitly.

Secondly, considering the distance between neighbouring "isothermals" to be an estimate of the local gradient, and hence the flux, it can be seen from figures 6 and 7 that the variation in flux throughout the region is also appreciable.

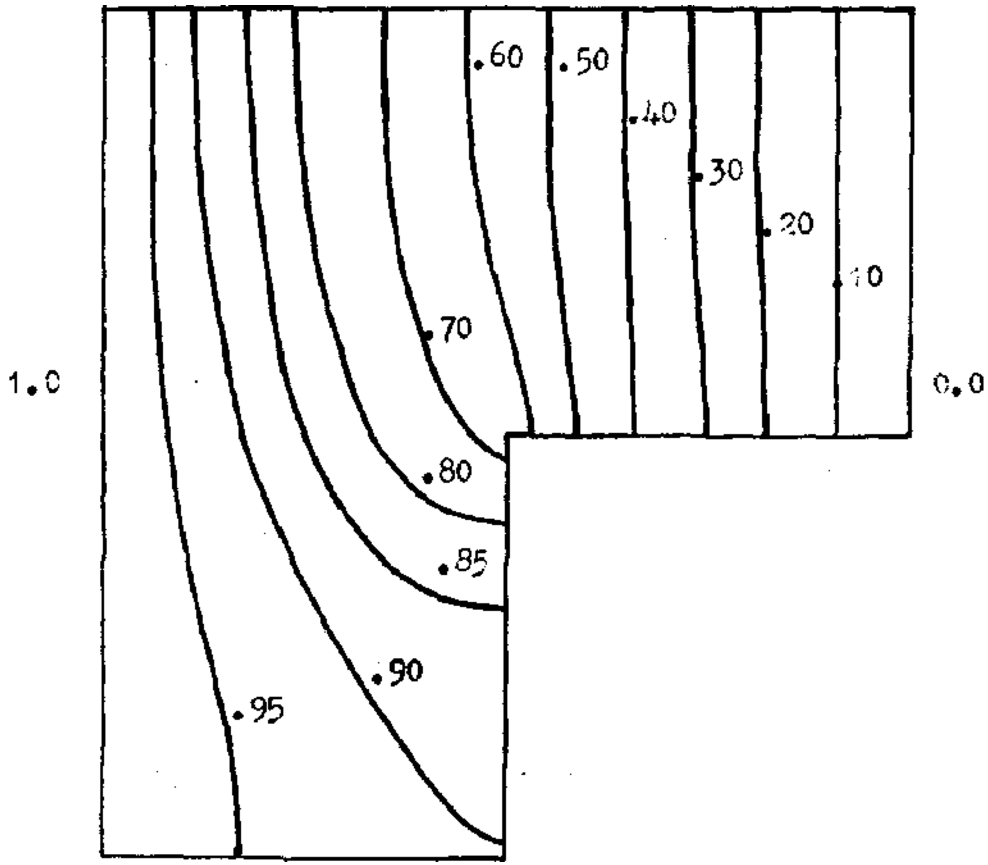
The limitations of unidirectional models are closely related to these two features.

Table 1. Concentration Values for a Typical

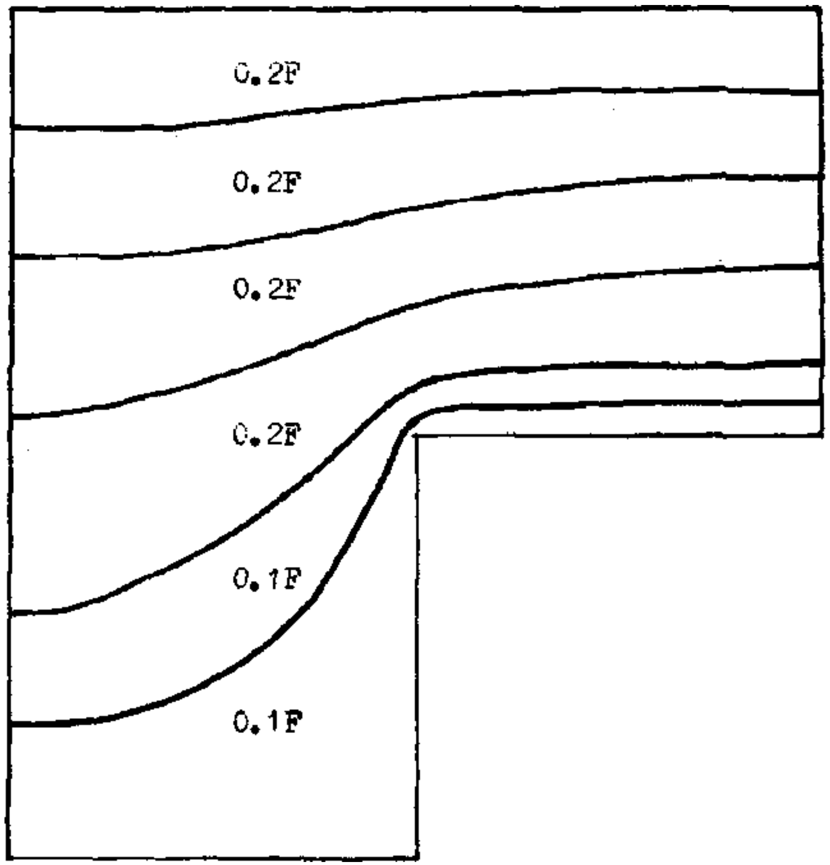
Region. ($h=0.5$, $\sigma=0.5$)

1.000	.916	.832	.743	.649	.550	.445	.333	.226	.114	000
	.918	.833	.745	.652	.552	.448	.339	.227	.114	
1.000	.920	.939	.753	.661	.561	.454	.343	.229	.115	000
	.925	.949	.767	.677	.576	.465	.349	.233	.116	
1.000	.932	.863	.790	.707	.603	.479	.356	.236	.117	000
	.941	.832	.821	.755	.666	.483	.358	.237	.117	
1.000	.950	.901	.355	.815	.795					
	.958	.919	.884	.858	.848					
1.000	.965	.932	.004	.886	.879					
	.969	.940	.916	.901	.895					
1.000	.970	.943	.920	.906	.901					

Figare 6.

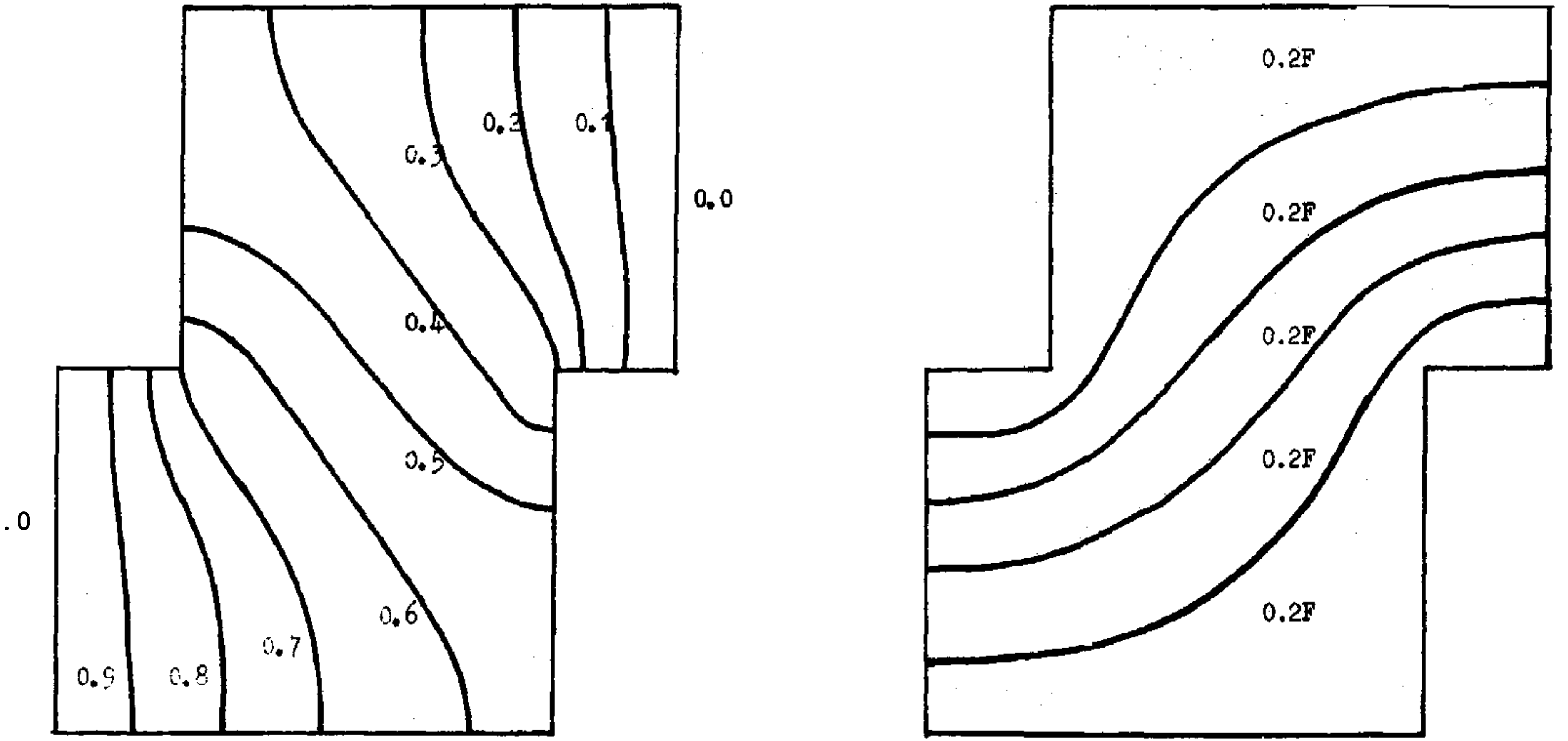


Lines of Constant Concentration



Flow lines (where P is the total flow through the region)

Figure 7.



lines of Constant Concentration

Flow Lines

3.2 Rates of Plow and Effective Diffusion Coefficients

A quantity which is commonly observed in stead-state diffusion experiments is the rate of flow through the medium. From this the diffusion coefficient can readily be deduced if the surface concentrations are known and the flow is unidirectional. Thus, the flow, F, through an area A perpendicular to the x direction is given by

$$F = -DA\frac{\partial u}{\partial x} = -DA\frac{(u_2 - u_2)}{\ell} \quad , \tag{10}$$

where u_1, u_2 are the constant surface concentrations, ℓ *is* the medium thickness and D the diffusion coefficient of the medium, assumed constant.

In two- dimensional flow problems in composites, as illustrated for example in figure 4, equation (10) is replaced by

$$F = -D\int_c^b \frac{\partial u}{\partial x}\partial y \quad , \qquad \text{on } x = 0, \tag{11}$$

or, more generally,

$$F = -D\int_c \frac{\partial u}{\partial \eta}\, ds \quad , \tag{12}$$

where C is any arc S drawn aoross the flow and $\partial / _{\partial \eta}$ implies differentiation normal to S.

The evaluation of the integral in equation (12) along Any two distinct lines, for example $x = 0$ and $x = a + \sigma$, in figure 4, provides a useful check on the numerical integration procedure. Also, in view of' the singularity at the re-entrant corners it is desirable to evaluate F well away from such corners, although, in theory, F is bounded for any arc S.

An experimentalist measuring flow rates through composites will deduce mean or effective diffusion coefficients for the composites by equating the measured flow to the expression in (10). Thus, denoting the effective diffusion coefficient by D_{eff}, and taking the dimensions of the composite to be those specified in (9), we have

$$De_{ff} = -D\int_{o}^{1} (\frac{\partial u}{\partial x})\ \partial y \quad , \tag{13}$$

since $u_1 - u_2 = 1$.

Values of D_{eff} have been obtained from the numerical solutions of Laplace's equation for various sizes of the blocks forming the dispersed phase. The derivatives in (13) were estimated by a central difference approximation and the integration performed using Simpson's Method. This method was found to be adequate for the accuracy required.

The results are presented in graphical form in figures 8, 9 ana 10.

Further results were obtained experimentally and are presented in figure 11. These were obtained by setting up an electrical analogy of the steady-state diffusion process. 'Teledeltos' paper was cut to the required shapes and a constant potential difference established across the appropriate edges. The remaining edges provide a natural 'no flow'