Induced Transport in Pulsating Flow

F. J. M. HORN and R. L. KIPP, JR.
Rice University, Houston, Texas

The dispersion coefficient is evaluated in a general linear chromatographic system in which the velocity field is time periodic. Computations are carried out in detail for two examples. In the first example there are two phases and the flow pattern is simple. In the second example there is only one phase and the flow pattern is complex. The latter example is closely related to Taylor diffusion. Depending on the relative size of certain dimensionless parameters, one can distinguish four regions of different qualitative behavior of the system: molecular diffusion region, Taylor region, constant amplification region, and boundary transport region.

Induced transport is a phenomenon which occurs if there is transport in a space direction x due to a gradient in chemical or electrochemical potential (parent transport) and simultaneously a time- and/or position-dependent flow in a direction z orthogonal to the direction x. The parent transport causes an induced transport in the z direction which sometimes has an important effect on the system which can be utilized in separation techniques or in the determination of transport or equilibrium data. The parent transport can be forced by outside means, for instance, by time varying temperature fields (*11*), or it may be spontaneous as in the case of diffusion. The most important effect in the latter class is Taylor diffusion (*8* to *10*). In this paper Taylor-type effects will be studied which occur if the flow velocity in the z direction is a periodic function of time.

First a slight generalization of the theory of Aris (*1* to *4*) will be presented which allows the calculation of the dispersion coefficient for general chromatographic systems (*6*). This theory will then be applied to two special examples which represent a large class of cases. The main purpose of this paper is to discuss a new phenomenon associated with these examples.

PULSATING FLOW IN A GENERAL CHROMATOGRAPHIC SYSTEM

In this section certain n-dimensional spaces will be considered. These correspond to the cross section of a column, and therefore it might be expected that n equals 2 in any real situation. However, as has been explained in another paper (*6*) it is convenient to take care of the complexities of pore systems and/or of particle-size distributions by mapping the two-dimensional cross section of a real three-dimensional column into the n-dimensional cross section of an $(n + 1)$-dimensional column. In this way the theory can be simplified despite the increase of dimensionality. The special examples treated in this paper have $n = 2$.

A general chromatographic system is defined as follows. The column is generated by a domain X of Euclidean n space (coordinates $x_1, \ldots x_n$) which is translated along the z axis perpendicular to the axes $x_1, \ldots x_n$. The domain may consist of various subdomains which are occupied by different phases. There are several magnitudes defined as functions of the position in the domain X. The velocity vector $\mathbf{v}$ is an n-dimensional vector corresponding to convective transport within X. The scalar v_z denotes the velocity in the z direction. An equilibrium constant K for a linear equilibrium relationship for the tracer concentration is defined as follows. K is a constant within each phase and in case of equilibrium $c/K =$ position independent, where c is the concentration of tracer. It is evident that K (as well as k which will be defined below) is defined only up to an arbitrary factor. This ambiguity, however, has no influence on the final results. The n by n diffusion tensor $\mathbf{D}$ governs the diffusional transport in X and the diffusion constant D_z describes diffusional transport in the z direction.

An interfacial mass transfer resistance is described by a magnitude k which is defined at the interfaces between the phases. That is, the amount of tracer transferred from phase 1 to phase 2 across a unit element of interface per unit time is given by

$$k\left(\frac{c_1}{K_1} - \frac{c_2}{K_2}\right)$$

where K_1 and K_2 are the equilibrium constants in phases 1 and 2, respectively, and c_1 and c_2 are the concentrations of the tracer in phases 1 and 2 at the interface.

STEADY STATE FLOW VELOCITIES

The case where $\mathbf{v}$ and v_z are time independent has been studied in detail in a previously published paper (*6*). If a tracer is introduced in a finite section of the column, the transport of the tracer in the z direction can be described asymptotically by a peak velocity v^* and a dispersion coefficient D^*. These magnitudes are defined as follows. Let c^* denote the amount of tracer per unit length of column. That is

$$c^*(z, t) = \int_X c(z, x, t)\,dV \qquad (1)$$

where dV is the n-dimensional volume element of X. The center z^* of the tracer distribution is defined as

$$z^*(t) = \int_{-\infty}^{+\infty} z\,c^*(z, t)\,dz \Big/ \int_{-\infty}^{+\infty} c^*(z, t)\,dz \qquad (2)$$

F. J. M. Horn is at the University of Rochester, Rochester, New York.

and the width $\sigma(t)$ of this distribution is defined as

$$\sigma^2(t) = \int_{-\infty}^{+\infty} (z - z^*)^2 c^*(z,t)dz \Big/ \int_{-\infty}^{+\infty} c^*(z,t)dz \tag{3}$$

Then the peak velocity v^* is defined as

$$v^* = \lim_{t\to\infty} \frac{dz^*}{dt} \tag{4}$$

and the dispersion coefficient D^* is defined as

$$D^* = \frac{1}{2} \lim_{t\to\infty} \frac{d\sigma^2}{dt} \tag{5}$$

Both quantities can be calculated from the distribution of $\mathbf{v}$, v_z, $\mathbf{D}$, D_z, K, and k over X by application rules described in reference *6*.

Extension to Periodic Flow Velocities

We assume now that v_z and $\mathbf{v}$ are periodic functions of t with period τ

$$v_z(t) = v_z(t+\tau) \tag{6a}$$

$$\mathbf{v}(t) = \mathbf{v}(t+\tau) \tag{6b}$$

The peak velocity and dispersion in this case will be defined as

$$v^* = \lim_{t\to\infty} \frac{1}{\tau} \int_{t'=t}^{t+\tau} \frac{dz^*}{dt'} dt' = \lim_{t\to\infty} \frac{z^*(t+\tau) - z^*(t)}{\tau} \tag{7}$$

and

$$D^* = \lim_{t\to\infty} \frac{1}{2\tau} \int_{t'=t}^{t+\tau} \frac{d\sigma^2}{dt'} dt' = \lim_{t\to\infty} \frac{\sigma^2(t+\tau) - \sigma^2(t)}{2\tau} \tag{8}$$

That is, peak velocity and dispersion coefficient are the averages over a period of the respective quantities as defined in the nonperiodic case.

v^* and D^* can then be calculated with techniques which are described in detail by Aris (*2, 4*) and by Horn (*6*). v^* is given by

$$v^* = \frac{1}{\tau} \int_0^\tau \bar{v}_z(t)\, dt \tag{9}$$

A bar over a quantity denotes the K weighted average of this quantity over X. Thus

$$\bar{v}_z = \int_X K v_z\, dV \Big/ \int_X K\, dV \tag{10}$$

Let $\psi(x,t)$ denote the time periodic concentration of a fictitious tracer, which will be called dispersion substance, under the following conditions

1. There is no transport in the z direction
2. The dispersion substance is generated by sources with density distribution s given by

$$s = K v_{zr} \tag{11}$$

where

$$v_{zr} = v_z - \bar{v}_z \tag{12}$$

3. Diffusional and convective transport of the dispersion substance obey the same laws in X as the respective transport of the real tracer.

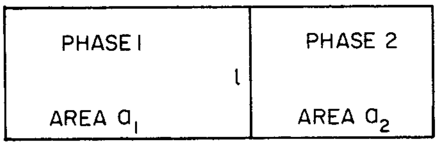

Fig. 1. Cross-sectional space X for the simple model of chromatography (Example I).

4. The boundary conditions for the dispersion substance in X are the same as for the real tracer.

The problem of finding ψ according to these conditions will be called source problem. D^* is then given by

$$D^* = D_T^* + \bar{D}_z \tag{13}$$

with

$$D_T^* = \frac{1}{\tau} \int_0^\tau \overline{\psi v_{zr}/K}\, dt \tag{14}$$

In the case where $\mathbf{v} = 0$ the dispersion coefficient can be easily calculated by means of a Fourier expansion. Here the source problem is defined by the differential equation (and certain boundary conditions)

$$\frac{\partial \psi}{\partial t} = L(\psi) + K v_{zr} \tag{15}$$

where L is a time-independent linear operator acting on ψ. Since v_z is periodic

$$v_z = \sum_{\nu=-\infty}^{+\infty} f_\nu(x) \exp i\nu\omega t \tag{16}$$

f_ν and $f_{-\nu}$ are complex conjugate functions of x. Let g_ν be a solution of

$$i\nu\omega g_\nu = L(g_\nu) + K f_{\nu r} \tag{17}$$

where

$$f_{\nu r} = f_\nu - \bar{f}_\nu \tag{18}$$

g_ν is subject to boundary conditions in X identical to those for ψ. Then a solution of Equation (15) is given by

$$\psi = \sum_{\nu=-\infty}^{+\infty} g_\nu \exp i\nu\omega t \tag{19}$$

where g_ν and $g_{-\nu}$ are complex conjugates. Combining (16) and (19) into (14) yields

$$D_T^* = \sum_{\nu=0}^{\infty} D_{T\nu}^* \tag{20}$$

where

$$D_{T0}^* = \overline{g_0 f_{0r}/K} \tag{21}$$

$$D_{T\nu}^* = 2 \text{ Real } \overline{g_{-\nu} f_{\nu r}/K}, \quad \nu \neq 0 \tag{22}$$

EXAMPLE I: PERIODIC FLOW IN THE SIMPLE MODEL OF CHROMATOGRAPHY

In the simple model of chromatography it is assumed that there are two phases: one occupying the area a_1 and the other area a_2 in the cross section (see Figure 1). There is no resistance against mass transport within the phases. All resistance is lumped into an interfacial resistance described by the mass transfer coefficient k. The magnitude l is equal to the area of interface per unit length of column. We may set

$$K_1 = 1$$

because K_1 is defined only up to an arbitrary position independent factor. The transport across the interface from phase 2 to phase 1 per unit length of column and unit time is then given by

$$kl\left(\frac{c_2}{K_2} - c_1\right)$$

The concentrations are position independent within each phase. Also position independent within each phase are the magnitudes ψ and g. All these magnitudes therefore can be written as two-dimensional vectors with the first element referring to the moving phase (1) and the second one to the stationary phase (2). The operator L becomes a matrix operator. Piston flow is assumed for the moving phase. The effect of irregularities of flow may be lumped, however, into a diffusion constant D_{z1} ($D_{z2} = 0$).

We shall assume that the velocity of the moving phase is sinusoidal. Thus

$$v_z = \begin{pmatrix} b \cos \omega t \\ 0 \end{pmatrix} \tag{23}$$

The vector notation explained before is used here for the flow velocity. From Equation (16) it follows that

$$f_1 = f_{-1} = \frac{b}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{24}$$

All other f magnitudes vanish.

Averaging over the cross section with K as weight yields

$$\overline{f_1} = \frac{b}{2}\,\frac{a_1}{a_1 + K_2 a_2} \tag{25}$$

It follows then that

$$f_{1r} = f_1 - \overline{f_1} = \frac{b}{2}\begin{pmatrix} \beta \\ -\alpha \end{pmatrix} \tag{26}$$

where

$$\alpha = a_1/(a_1 + K_2 a_2), \quad \beta = K_2 a_2/(a_1 + K_2 a_2), \quad \alpha + \beta = 1 \tag{27}$$

α and β are the fraction of the tracer contained in moving and stationary phases, respectively, in case of equilibrium. Let q and r be the values g_1 assumes in the moving and the stationary phases, respectively. Equation (17) then becomes

$$i\omega q = \frac{1}{a_1} kl\left(\frac{r}{K_2} - q\right) + \frac{b}{2}\beta \tag{28a}$$

$$i\omega r = -\frac{1}{a_2} kl\left(\frac{r}{K_2} - q\right) - \frac{b}{2}K_2\alpha \tag{28b}$$

Solving for q and r yields

$$q = -\frac{b}{2}\beta i\left[\omega - ikl\left(\frac{1}{a_1} + \frac{1}{K_2 a_2}\right)\right]^{-1} \tag{29a}$$

$$r = \frac{b}{2}K_2\,\alpha i\left[\omega - ikl\left(\frac{1}{a_1} + \frac{1}{K_2 a_2}\right)\right]^{-1} \tag{29b}$$

So that g_{-1} (= complex conjugate of g) becomes

$$g_{-1} = \frac{bi}{2}\left[\omega + ikl\left(\frac{1}{a_1} + \frac{1}{K_2 a_2}\right)\right]^{-1}\begin{pmatrix} \beta \\ -K_2\alpha \end{pmatrix} \tag{30}$$

From this and from Equation (26) it follows that

$$\overline{g_{-1} f_{1r}/K} = \frac{b^2 i}{4}(a_1 + K_2 a_2)^{-1}$$
$$\left[\omega + ikl\left(\frac{1}{a_1} + \frac{1}{K_2 a_2}\right)\right]^{-1}(\beta^2 a_1 + K_2\alpha^2 a_2) \tag{31}$$

Then according to Equation (22) it follows that

$$D_T^* = \frac{b^2}{2kl}\,\frac{(K_2 a_1 a_2)^2}{(a_1 + K_2 a_2)^3}\,\frac{1}{1 + \omega^2 T^2} \tag{32}$$

where T is given by

$$T = \frac{K_2 a_1 a_2}{(a_1 + K_2 a_2)\,kl} \tag{33}$$

T is the time constant of approach to equilibrium in a (hypothetical) system in which there is no transport in the z direction.

If the period τ is large compared with T we have that

$$\omega^2 T^2 << 1 \tag{34}$$

and Equation (32) becomes

$$D_T^* = \frac{v_m^2}{kl}\,\frac{(K_2 a_1 a_2)^2}{(a_1 + K_2 a_2)^3} \tag{35}$$

Here $b^2/2$ is replaced by v_m which is the root-mean-square of the periodic fluid velocity. Equation (35) shows that in the case $T << \tau$, so that Equation (34) is valid, the dispersion is the same as in a steady state flow system [compare with Equation (92) in reference *6*] in which the fluid velocity is equal to the root-mean-square of the velocity under periodic flow conditions.

The amplitude of the linear displacement Δ of the moving phase is given by

$$\Delta = b/\omega \tag{36}$$

From this and Equation (32) it follows that

$$D_T^* = \frac{\Delta^2 (K_2 a_1 a_2)^2}{2kl(a_1 + K_2 a_2)^3}\cdot\frac{\omega^2}{1 + \omega^2 T^2}$$

If for constant Δ the frequency is increased the dispersion coefficient approaches the value

$$\lim_{\omega \to \infty} D_T^* = \frac{\Delta^2}{2}\,\frac{kl}{a_1 + K_2 a_2} \tag{37}$$

Thus, if $T >> \tau$ the transport in the z direction is proportional to the square of the amplitude of the linear displacement, proportional to the mass transfer coefficient, and proportional to the fraction of the tracer present in the moving phase in the case of equilibrium. If $T << \tau$, on the other hand, it can be seen from Equation (35) that D_T^* is inversely proportional to the mass transfer coefficient.

EXAMPLE II: DISPERSION BETWEEN OSCILLATING FLAT PLATES

We consider now a system consisting of two parallel flat plates infinite in extent which are separated by the distance d (= $2a$) (see Figure 2). The space between the plates is filled with a Newtonian fluid. The plates oscillate sinusoidally with the same frequency ω and amplitude

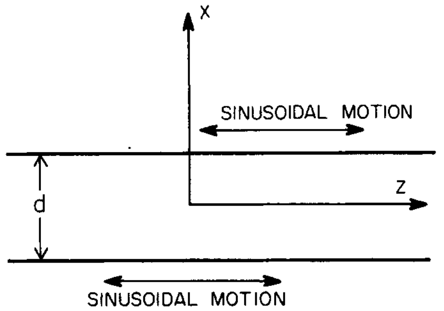

Fig. 2. Oscillating plate system considered in Example II.

such that the difference in phase between the two plates is 180 deg. It will be assumed that the flow field is laminar. Since in this problem there is only one phase we can set:

$$K = 1 \tag{38}$$

Diffusion in the x and z directions is governed by a constant diffusivity D. The function $v_z(x, t)$ is determined by the differential equation

$$\nu \frac{\partial^2 v_z}{\partial x^2} = \frac{\partial v_z}{\partial t} \tag{39}$$

where ν is the kinematic viscosity; and the boundary conditions

$$v_z(a, t) \quad = \quad b \cos \omega t \tag{40a}$$

$$v_z(-a, t) = -\, b \cos \omega t \tag{40b}$$

Integration of Equation (39) yields for the periodic state

$$v_z = \frac{b}{2} \left[\frac{\sinh\,(1 + i)\,\beta x/2a}{\sinh\,(i + 1)\,\beta/2} \exp i\omega t + \frac{\sinh\,(1 - i)\,\beta x/2a}{\sinh\,(1 - i)\,\beta/2} \exp - i\omega t \right] \tag{41}$$

where β is given by

$$\beta = 2a\sqrt{\omega/2\nu} = d\sqrt{\omega/2\nu} \tag{42}$$

Thus, according to Equations (16) and (18), f_1 and f_{1r} is given by

$$f_1 = f_{1r} = \frac{b}{2}\, \frac{\sinh\,(1 + i)\,\beta x/2a}{\sinh\,(1 + i)\,\beta/2} \tag{43}$$

The differential equation for $g_1(x)$ follows from this and from Equation (17)

$$-D\frac{d^2 g_1}{dx^2} + i\omega g_1 = \frac{b}{2}\, \frac{\sinh\,(1 + i)\,\beta x/2a}{\sinh\,(1 + i)\,\beta/2} \tag{44}$$

The boundary conditions for g_1 are

$$\frac{dg_1}{dx} = 0 \quad \text{at} \quad x = \pm\, a \tag{45}$$

The cases $\nu = D$ and $\nu \neq D$ require different treatment. It will be assumed at first that $\nu \neq D$. The result for the other case will be obtained later by taking the limit of this solution as $\nu \rightarrow D$. The solution of Equation (44) under the boundary conditions (45) is given by

$$g_1 = \frac{a^2\, b\, i}{D\alpha(\alpha^2 - \beta^2) \sinh\,(1 + i)\,\beta/2 \cdot \cosh\,(1 + i)\,\alpha/2}\, G(x) \tag{46}$$

where

$$G(x) = \beta \cosh \frac{1 + i}{2}\beta \cdot \sinh \frac{1 + i}{2a}\alpha x - \alpha \cosh \frac{1 + i}{2}\alpha \cdot \sinh \frac{1 + i}{2a}\beta x$$

$D_T{}^*$ can now be calculated from

$$D_T{}^* = 2\,\text{Real}\, \frac{1}{2a} \int_{-a}^{+a} g_{-1} f_{1r}\, dx \tag{47}$$

where g_{-1} is the conjugate complex of g_1. A lengthy but elementary calculation yields the following result:

$$\frac{d^2}{\Delta^2}\, \frac{D^* - D}{D} = h(\alpha, \beta) \tag{48}$$

where

$$h(\alpha, \beta) = \frac{\alpha^3 \beta}{4(\alpha^4 - \beta^4)} \left[\alpha \frac{\sinh \beta + \sin \beta}{\cosh \beta - \cos \beta} - \beta \frac{\sinh \alpha + \sin \alpha}{\cosh \alpha + \cos \alpha} \cdot \frac{\cosh \beta + \cos \beta}{\cosh \beta - \cos \beta} \right] \tag{49}$$

Δ is the amplitude of the relative displacement of the plates; that is

$$\Delta = 2b/\omega \tag{50}$$

and α is given by

$$\alpha = 2a\sqrt{\omega/2D} = d\sqrt{\omega/2D} \tag{51}$$

Several limiting cases are of interest. If the angular frequency ω is small so that

$$\alpha << 1 \quad \text{and} \quad \beta << 1 \tag{52}$$

$h(\alpha, \beta)$ is given approximately by

$$h = \alpha^4/60 + 0(\alpha^8)$$

so that the effective dispersion coefficient D^* is given by

$$D^* = \frac{\Delta^2\, \omega^2\, d^2}{240\, D} + D \tag{53}$$

This result is identical with that obtained for Taylor diffusion in the case where both plates move in different directions with the same constant velocity provided this velocity is equal to the root-mean-square of the plate velocities in the case of periodic motion. The region where $\alpha << 1$ and $\beta << 1$ will therefore be referred to as the Taylor region. In this region the time required to establish Taylor diffusion and a linear velocity profile is small compared to the period of the motion. In the Taylor region one can distinguish between a Taylor region proper where the first term on the right-hand side of Equation (53) dominates and a molecular diffusion region where the second term dominates (see reference 7).

From the definitions (42) and (51) for α and β, it follows that the ratio ν/D, that is, the Schmidt number, is given by

$$N_{Sc} = \alpha^2/\beta^2 \tag{54}$$

If the Schmidt number is large, as is the case for liquids, there is a frequency range such that

$$\beta << 1, \quad \beta << \alpha \tag{55}$$

In this case Equation (48) becomes

$$\frac{d^2}{\Delta^2}\, \frac{D^* - D}{D} = \frac{1}{2} \left(1 - \frac{1}{\alpha}\, \frac{\sinh \alpha + \sin \alpha}{\cosh \alpha + \cos \alpha} \right) \tag{56}$$

This result is given in a previous publication by the authors (7). It was derived under the assumption that the velocity profile is linear in x at all times (corresponding to $\nu \rightarrow \infty$).

If

$$\beta << 1 \quad \text{and} \quad \alpha >> 1 \tag{57}$$

the right-hand side of Equation (48) becomes 1/2 and one obtains

$$D^* = \left[\frac{\Delta^2}{2d^2} + 1 \right] D \tag{58}$$

This region is the constant amplification region of diffusion. If $\Delta^2/2d^2$ is large enough an interesting phenomenon occurs in the transition between the constant amplification region and the Taylor region; for given ω, d, and Δ the apparent dispersion coefficient D^* has a maximum as a function of the molecular diffusivity coefficient. This maxi-

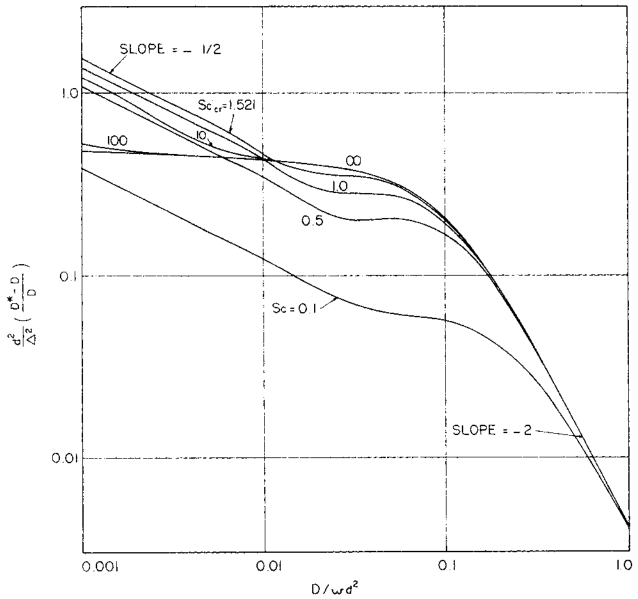

Fig. 3. Dispersion coefficient for the oscillating plate system (Example II) as function of Schmidt number and $D/\omega d^2$.

mum can be made arbitrarily large by choosing Δ/d large enough (see reference 7).

If the frequency ω is large enough one has that

$$\alpha >> 1, \quad \beta >> 1 \tag{59}$$

In this case one obtains from Equations (48) and (49) the result that

$$\frac{d^2}{\Delta^2}\frac{D^*-D}{D} = \frac{1}{4\sqrt{2}}\,\frac{N_{Sc}}{1+\sqrt{N_{Sc}}+N_{Sc}+\sqrt{N_{Sc}^3}}\sqrt{\frac{\omega d^2}{D}} \tag{60}$$

This region will be called the boundary transport region, since in this region $\beta >> 1$ and only a small boundary layer adjacent to the plate is in motion. Because of this a given concentration gradient in the z direction is transformed into a large concentration gradient in the x direction at certain time intervals in the period. This effect causes the difference $D^* - D$ to become proportional to $\sqrt{D}$ in this region (for fixed N_{Sc}).

There are some obvious similarities in the results of this flat plate problem and the case of the simple model of chromatography treated in the previous section. In Example I a counterpart of the boundary transport phenomenon would become apparent if k were made dependent on fluid velocity and diffusion in the liquid in an appropriate way.

The result for the case $\alpha = \beta$ corresponding to

$$N_{Sc} = 1$$

can be obtained from Equation (49) by taking the limit of $h(\alpha, \beta)$ as $\beta \rightarrow \alpha$ which yields

$$h(\alpha, \alpha) = \frac{\alpha(\cosh\alpha + \cos\alpha)(\sinh\alpha + \sin\alpha) - 2\alpha^2(1+\cosh\alpha\cos\alpha)}{16(\cosh^2\alpha - \cos^2\alpha)} \tag{61}$$

In Figure 3 $d^2(D^* - D)/\Delta^2$ is plotted against $D/\omega d^2$ in logarithmic coordinates for various Schmidt numbers. The regions mentioned before can be seen clearly. In the boundary transport region the slope of curves is $-1/2$. The slope is zero in the constant amplification region, and the slope is -2 in the Taylor region.

From Equation (60) it follows that there is a critical value of the Schmidt number for which the asymptote in the boundary transport region lies above any other such asymptote. The critical Schmidt number can be found by differentiating the coefficient depending on N_{Sc} on the right-hand side of Equation (60) with respect to N_{Sc} and setting the result equal to zero. Thus it is found that for the critical Schmidt number

$$(N_{Sc})^{3/2} - (N_{Sc})^{1/2} - 2 = 0 \tag{62}$$

from which it follows that

$$N_{Sc\,\mathrm{crit}} = 1.521 \tag{63}$$

The corresponding critical curve is plotted in Figure 3.

An example similar to this example was investigated by Harris and Goren (5). These authors considered periodic flow in a circular pipe. In this case the splitting of complex functions such as those given by (46) and the integral in (47) into real and imaginary parts does not lead to equations as simple as (48) and (49). Consequently, the mathematical discussion has not been carried out by Harris and Goren in such detail as has been done here. However, these authors have confirmed their theoretical results by experimental evidence. Furthermore, Harris and Goren consider the important case of periodic state transport between two reservoirs with time-invariant concentrations rather than the impulse perturbation investigated here. It can be shown that the dispersion coefficients derived from both types of systems agree if and only if $v^* = 0$. This condition is satisfied in the study by Harris and Goren and in our example. Therefore the results of these authors agree with our results to the extent which can be expected considering the different geometry.

ACKNOWLEDGMENT

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NOTATION

a = one-half the separation of the plates (Example II)
a_i = cross-sectional area of phase i (Example I)
b = amplitude of periodic v_z
c = tracer concentration
d = separation of the plates (Example II)
D = molecular diffusivity (Example II)
$\mathbf{D}$ = diffusion tensor in X space
$D_T{}^*$ = induced transport effective dispersion coefficient
D_z = diffusivity in the z direction
D^* = effective dispersion coefficient
f = Fourier coefficients of v_z
g = Fourier coefficients of ψ
$G(x)$ = function Equation (46)
$h(\alpha, \beta)$ = function Equation (49)
k = interface mass transfer coefficient
K_i = equilibrium constant in phase i
l = area of interface per unit length of column (Example I)
L = time-independent linear operator
N_{Sc} = Schmidt number
q = g_1 in phase 1 (Example I)
r = g_1 in phase 2 (Example I)
s = source distribution in periodic source problem
t = time
T = time constant, Equation (33), Example I
$\mathbf{v}$ = fluid velocity vector in X space
v_z = fluid velocity in z direction

v_{zr} = fluid velocity in z direction relative to the mean velocity in the z direction
v_m = root-mean-square velocity v_z
v^* = asymptotic peak velocity of tracer
X = cross-sectional space
x_i = i^{th} coordinate in cross-sectional space
z = axial coordinate of the system
z^* = first moment of tracer distribution divided by zeroth moment

Greek Letters

α = fraction of tracer in the moving phase at equilibrium (Example I)
β = fraction of tracer in the stationary phase at equilibrium (Example I)
α = dimensionless parameter (Example II) Equation (51)
β = dimensionless parameter (Example II) Equation (42)
Δ = amplitude of the linear displacement of the moving phase (Example I)
Δ = amplitude of the relative displacement of the plates (Example II)
σ = width of tracer distribution, Equation (3)
ψ = concentration of dispersion substance in the periodic source problem
ν = kinematic viscosity
τ = period of oscillation
ω = angular frequency of oscillation

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Nucleate and Film Pool Boiling of Ethane-Ethylene Mixtures

R. D. WRIGHT, L. D. CLEMENTS, and C. P. COLVER
University of Oklahoma, Norman, Oklahoma

Experimental results are presented for saturated nucleate and film pool boiling heat transfer to ethane, ethylene, and three binary ethane-ethylene mixtures containing approximately 25, 50, and 75 mole % ethylene. Data were obtained at reduced pressures from 0.05 to 0.75. The nucleate boiling data are compared with several predictions; the film boiling data are favorably compared with the Sciance, Colver, and Sliepcevich correlation.

This study was initiated to gain further knowledge of saturated pool boiling mixtures in the nucleate and film boiling regimes. The work is part of a continuing series of investigations at the University of Oklahoma on boiling nitrogen (*12*) and pure component liquified hydrocarbon gases (*15, 16*) and their mixtures (*3, 5, 20*).

Probably the earliest nucleate boiling mixture heat transfer data reported in the literature were those of Cichelli and Bonilla (*4*) for several propane–*n*-pentane mixtures. Since that time a limited number of nucleate boiling mixture studies have been reported. However, most of the available data have been obtained at atmospheric pressure for binary mixtures at only one composition or over a very limited composition range. Experimental results have clearly demonstrated that significant differences can exist between the nucleate boiling heat transfer characteristics of pure components and mixtures (*1, 3, 5, 17, 18, 20*). Moreover, it has been suggested (*5, 17*) that mixtures possessing a wide boiling range, that is, mixtures of large relative volatility, can be expected to give considerably higher ΔTs at a given heat flux level than for the mixture's pure components. For two such systems the difference has been shown to be as much as ten- (*3*) to thirtyfold (*17*).