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MATHEMATICAL MODELS FOR SEPARATION BY INDUCED TRANSPORT

by

Chin Houei Lin

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To My Parents
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I. INTRODUCTION

In many systems of interest to chemical engineers coupling occurs between the transport of a substance due to a gradient in chemical or electrochemical potential in one direction and convective transport in another direction. The coupling may induce a transport in a direction different from the potential gradient which fact can be utilized for the separation of a mixture.

A. Parent Transport and Convective Transport

The transport due to a gradient in chemical (electrochemical) potential will be called parent transport. It is difficult to establish a completely satisfactory classification of the nature of the parent transport, but there are two groups which can be fairly well kept apart and which may be called "spontaneous" and "forced". We shall call the parent transport spontaneous if the gradient in potential is caused by the flow field and is not forced by other means. This is the case, for instance, in Taylor diffusion (24,25,26) where the parent transport is molecular diffusion in the direction orthogonal to the flow field. Here, the concentration gradient is set up by the gradient in fluid velocity orthogonal to the direction of flow. For an example with forced parent transport consider a system of two plates as shown in Fig. 1. Both plates move parallel to each other periodically such that the time average convective fluid flow vanishes. The parent transport is forced by a time varying electric field orthogonal to the plates. This apparatus will be discussed in chapter IV. Other example with forced parent transport has been investigated by Wilhelm et al. (28,29,30,18,19,20,23) and will be discussed in Chapter III.
PERIODIC ELECTRIC FIELD

PERIODIC MOTION

UPPER PLATE

LOWER PLATE

d

FIGURE 1: PERIODIC FLOW ELECTROPHORESIS
The parent transport, in general, is related to the potential gradient by phenomenological constants such as diffusivities or electrophoretic mobilities. If the objective is to separate two substances and if the separation is caused by a difference in the transport constants of these substances this difference (or the relative difference) will be called the elementary separation effect.

B. Modes of Operation

Apparatus utilizing induced transport usually is operated in one or the other of two modes. In "impulse operation" a column is operated such that concentration "peaks" move along the axis of the column. This is the case in Taylor diffusion and in chromatography. In "steady operation" the column is operated either at or close to a steady state or a periodic state. That is, the characteristic time constant governing the dynamical behaviour of the column is small compared to the time in which the state or the periodic state of the column changes appreciably. A system will be called to be in the periodic state if both control and state variables are periodic functions of time. The steady state is a special case of a periodic state.

In Table 1 some processes are classified according to natures of parent transport and modes of operation. The starred processes will be discussed in the following chapters. The purpose of this work is to show connections between these processes which are important for economic evaluation and to discuss theoretical aspects of some of less known processes.
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Table 1. Examples for Separation Process Utilizing Induced Transport
II. LINEAR CHROMATOGRAPHIC SYSTEMS WITH PERIODICALLY VARYING TEMPERATURE AND FLOW FIELDS

A. Taylor Diffusion and Chromatographic Systems

Consider a tube in which a steady flow of an incompressible fluid is maintained. If a tracer is injected into the flow, tracer molecules will be transported by molecular diffusion from regions of large axial velocity (near the tube center) to regions of low axial velocity (near the tube wall) and vise versa. This lateral diffusion induces a dispersion of tracer in longitudinal direction. Taylor (24, 25, 26) was the first to study this effect theoretically and experimentally, and a number of studies (1, 2, 3, 12, 13, 27) has been carried out after that. It has shown that the axial transport of the tracer is characterized by a dispersion coefficient $D^*$, where

$$D^* = D + \alpha_p R \overline{v}^2 / D$$

(2.1)

$D$ is the molecular diffusivity, $\overline{v}$ is the average fluid velocity in the tube, and $R$ is a characteristic length associated with the cross-section of the tube (e.g. the diameter for a circular cross-section). The parameter $\alpha_p$ depends on cross-section geometry and shape of velocity profile.

The Taylor effect can be considered as a special case of the dispersion effect occurring in general chromatographic systems. Such a system will be considered as an infinitely long tube generated by translating the regions $C^S$ in $x_1-x_2$ plane along the $z$-axis which is orthogonal to the plane (Fig. 2). This column is filled with one (in case of Taylor diffusion) or more phases which are in motion. The following assumptions will be made:
FIGURE 2: CHROMATOGRAPHIC COLUMN, $C^S$ IS A REGION ON $X_1-X_2$ PLANE.
1. The shapes and positions of subregions of the $C^s$ space occupied by different phases are independent of $z$.

2. The velocity vector in $C^s$ space, $v_\mathbf{x}$ and the axial velocity $v_z$ do not depend on $z$ but may depend on coordinates $x_1$ and $x_2$.

3. The equilibrium and transport relations of the tracer are linear. That is, each phase can be characterized by a constant $K$ such that at equilibrium

$$
\frac{c(x_1', x_2', z)}{K(x_1', x_2', z)} = \text{constant} \tag{2.2}
$$

The equilibrium constants may vary with external conditions such as temperature and pressure.

Then the distribution of concentration $c$ is governed by the following differential equation

$$
\frac{\partial c}{\partial t} = -v_z \frac{\partial c}{\partial z} - v_\mathbf{x} \cdot \nabla c + D_z \frac{\partial^2 c}{\partial z^2} + \nabla D \cdot \nabla c \tag{2.3}
$$

where $D_z$ is the diffusivity matrix assumed to be positive definite and symmetric, and $D_z$ is molecular diffusivity in $z$-direction. The boundary conditions at interfaces are given by

$$
\mathbf{n} \cdot D \cdot \nabla c = -k \Delta c \tag{2.4}
$$

where $\mathbf{n}$ is the unit normal of the interface, $k$ is mass transfer coefficient and $\Delta c$ is linear driving force of mass transfer, for instance, on the interface between phase 1 and phase 2

$$
\Delta c = \left( \frac{c_2}{K_2} - \frac{c_1}{K_1} \right) \tag{2.5}
$$
Aris (2,3) has applied the moment method to investigate the special cases of one and two phase problem with certain geometry. The moment method enables one to compute dispersion coefficient and asymptotic peak velocity (velocity of the center of tracer distribution) without solving (2.3) in detail. The moment transformation is defined by

\[ \mu^{(n)}(x, t) = \int_{-\infty}^{\infty} z^n c(x, z, t) \, dz \]  

(2.6)

where \( n \) is a non-positive integer, \( \mu^{(n)} \) is the \( n \)th moment and the operation will be abbreviated as \( \mu \). The integration of \( \mu^{(n)} \) over the space \( C^s \) is denoted by \( M^{(n)} \), that is

\[ M^{(n)}(t) = \int_{C^s} \mu^{(n)}(x, t) \, dA \]  

(2.7)

Evidently the operation \( \mu \) and the integration are commutable, i.e.

\[ M^{(n)}(t) = \mu \int_{C^s} c(x, z, t) \, dA \]  

(2.8)

Horn (15,16) applied this method to investigate general linear chromatographic system. In his work the center \( z^* \) of the peak is defined by

\[ z^*(t) = \frac{M^{(1)}}{M^{(0)}} \]  

(2.9)

and the width \( \widetilde{B} \) of the peak is defined by

\[ \widetilde{B}^2(t) = \frac{M^{(2)}}{M^{(0)}} - (z^*)^2 \]  

(2.10)

The asymptotic peak velocity \( v^* \) and the dispersion coefficient \( D^* \) are related to \( z^* \) ans \( \widetilde{B}^2 \) as follows

1. For steady state operation

\[ v^* = \lim_{t \to \infty} \frac{dz^*}{dt} \]  

(2.11)
\[ D^* = \frac{1}{2} \lim_{t \to \infty} \frac{dB^2}{dt} \quad (2.12) \]

2. For periodic state operation

\[ v^* = \lim_{t \to \infty} \frac{1}{T} \int_t^{t+T} \frac{ds^*}{dt} \, dt \quad (2.13) \]

\[ D^* = \frac{1}{2} \lim_{t \to \infty} \frac{1}{T} \int_t^{t+T} \frac{dB^2}{dt} \, dt \quad (2.14) \]

It has been shown that the evaluation of \( v^* \) and \( D^* \) of general chromatographic system requires the asymptotic solution of a steady state or periodic state source problem defined on the cross section of the column.

B. Simple Models for Systems with Periodically Varying Temperature and Flow Fields

It will now be assumed that

1. \( v_x = 0 \)

2. \( v_z \) is position independent within each subregion occupied by a phase.

3. There is no mass transfer resistance within those subregions.

That is, the tracer concentration can be assumed position independent in each subregion. Resistance will be lumped into phenomenological coefficients for the mass transfer across interfaces.

Then the differential equation \( (2.3) \) and boundary conditions \( (2.4) \) can be lumped to yield the following equations

\[ a_i \frac{\partial c_i}{\partial t} = -v_{zi} \frac{\partial c_i}{\partial z} + D_{zi} \frac{\partial^2 c_i}{\partial z^2} + \sum_{j=1}^{N} k_{ij} \ell_{ij} \left( \frac{c_i}{k_i} - \frac{c_j}{k_j} \right) \]

\[ i = 1, 2, \ldots, N \quad (2.15) \]
where \( c_i, a_i, v_{zi}, D_{zi} \) and \( K_i \) are tracer concentration, cross-section area, axial velocity, molecular diffusivity and equilibrium constant for \( i \)th phase respectively. \( k_{ij} \) and \( \mathcal{L}_{ij} \) are mass transfer coefficient and area per unit length of column of the interface between \( i \)th and \( j \)th phases. Obviously

\[
\mathcal{L}_{ij} = \mathcal{L}_{ji} \quad (2.16a)
\]

and

\[
k_{ij} = k_{ji} \quad (2.16b)
\]

Furthermore we set

\[
k_{ij} \mathcal{L}_{ij} = 0 \quad \text{if} \quad (1) \ i = j \quad (2.16c)
\]

or \( (2) \ i \)th and \( j \)th phases are not adjacent.

By application of \( \mathcal{M} \) to (2.15) the following equations for the first three moments are obtained

\[
\dot{\mathcal{M}}(0) = \mathcal{V} \mathcal{M}(0) \quad (2.17a)
\]

\[
\dot{\mathcal{M}}(1) = \mathcal{V} \mathcal{M}(1) + \mathcal{V} \mathcal{M}(0) \quad (2.17b)
\]

\[
\dot{\mathcal{M}}(2) = \mathcal{V} \mathcal{M}(2) + 2 \mathcal{V} \mathcal{M}(1) + 2 D_{zi} \mathcal{M}(0) \quad (2.17c)
\]

where \( \mathcal{M}(0), \mathcal{M}(1) \) and \( \mathcal{M}(2) \) are column moment vectors for which the \( i \)th components are the correspondent moments in the \( i \)th phase respectively.

That is

\[
\mathcal{M}^{(n)} = (\mathcal{M}^{(n)}_1, \mathcal{M}^{(n)}_2, \ldots, \mathcal{M}^{(n)}_N)^T \quad (2.18)
\]

The dot refers to derivation with respect to time \( t \). \( \mathcal{V} \) and \( D_{zi} \) are \( N \times N \) matrices given by
\[ v_z = \text{diag}\{ v_{z1}, v_{z2}, \ldots, v_{zN} \} \]  
(2.19a)

\[ D_z = \text{diag}\{ D_{z1}, D_{z2}, \ldots, D_{zN} \} \]  
(2.19b)

\[ Y \] is a \( N \times N \) matrix with its elements given by

\[ Y_{ii} = -\sum_{j=1}^{N} \left( k_{ij} \ell_{ij} / a_i K_i \right) \]  
(2.20a)

\[ Y_{ij} = k_{ij} \ell_{ij} / a_i K_j \]  
(2.20b)

Let \( a \) and \( K \) denote a row vector and a column vector for which the \( i^{th} \) elements are \( a_i \) and \( K_i \) respectively it is easy to see that \( Y \) is singular and that \( a \) and \( K \) are the left and the right hand side null vectors of \( Y \) respectively. That is

\[ a Y = 0, \quad Y K = 0 \]  
(2.21)

It also can be shown that the null space of \( Y \) is one-dimensional (see Appendix I).

The equations (2.17a) and (2.17b) can be interpreted as equations describe the transport of two fictitious sustances in the \( C^5 \) space.

There is source term \( v_z \mu^{(0)} \) in (2.17b) but no source term in (2.17a). Three subcases will be studied, the first and the second subcases can be considered as the special cases of the second and the third subcases respectively;

1. Constant Temperature and Velocity

In this case both \( Y \) and \( v_z \) are constant matrices. It can be shown that all eigenvalues of \( Y \) except 0 are negative real (Appendix I). Therefore, the solution of (2.17a) must approach a multiple of the eigenvector belonging to 0, that is \( K \). Furthermore, since \( a \) is left
eigenvector of \( Y \), \( a \mu^{(0)} \) is time invariant. If \( \mu^{(0)}(0) \) is chosen such that

\[
a \mu^{(0)} = a K
\]

then

\[
\lim_{t \to \infty} \mu^{(0)} = K
\]

In the following development the initial condition (2.22a) is assumed.

We put solution of (2.17a) into (2.17b). Since we are interested only in asymptotic behaviors it will suffice to use the asymptotic value of the solution. That is we study

\[
\mu^{(1)} = Y \mu^{(1)} + \frac{Y}{\alpha} K
\]

The solution of (2.17a) differs from the asymptotic solution by a linear combination of decreasing exponential functions. Such functions generate in the solution of (2.17b) again decreasing exponential functions. Thus solution of (2.23) differs from the true function only by exponential decaying additive terms. Such terms will be denoted by EXP. Premultiplying (2.23) by \( a \) shows that time invariant solution exists only if

\[
a \frac{Y}{\alpha} K = 0
\]

But this is not the general case. In order to find a particular solution of equation (2.23) the following trial function can be used

\[
\mu^{(1)} = \alpha t K + \rho
\]

where \( \alpha \) is a time invariant scalar to be determined and \( \rho \) is a time invariant vector. Putting (2.25) into (2.23) yields
\[
Y \varphi = v_z K - \alpha K \quad (2.26)
\]

According to the main theorem of linear algebra this system has solution \( \varphi \) if and only if each row vector annihilating the left hand side also annihilates the right hand side. Since the rank of \( Y \) is \( N-1 \) (Appendix I) only the left hand side null vector \( a \) has to be considered. That is, solution \( \varphi \) exists if and only if

\[
a ( v_z K - \alpha K ) = 0 \quad (2.27)
\]

This means \( \alpha \) has to be chosen according to

\[
\alpha = a v_z K / a K \quad (2.28)
\]

The right hand side is the average of the axial velocity \( v_z \) over \( C^g \) with \( K \) as weight. From now on it will be denoted by \( \bar{v}_z \), that is

\[
\alpha = \bar{v}_z \quad (2.29)
\]

\( \mathcal{M}^{(1)} \) is then given by

\[
\mathcal{M}^{(1)} = \bar{v}_z t K + \varphi \quad (2.30)
\]

and \( \varphi \) becomes a solution of the equation

\[
Y \varphi = v_{zr} K \quad (2.31)
\]

where \( v_{zr} \) is a matrix given by

\[
v_{zr} = \text{diag} \{ v_{zr1}, v_{zr2}, \ldots, v_{zrN} \} \quad (2.32)
\]

and where the diagonal component \( v_{zr1} \) is defined by
\[ v_{z1} = v_{z1} - \frac{1}{z}, \quad 1 = 1, 2, \ldots, N \] (2.33)

It is obvious that the solution of (2.31) is not unique since \( \bar{z} \) is singular. However it will be shown that the choice of solution does not affect the final result.

From (2.8), (2.22b) and (2.30), \( M^{(0)} \) and \( M^{(1)} \) are given by

\[ M^{(0)} = a \bar{K} + \text{EXP} \] (2.34)

\[ M^{(1)} = -\frac{1}{v_z} \frac{a \bar{K} + a \varphi + \text{EXP}}{a \bar{K} + a \varphi + \text{EXP}} \] (2.35)

As mentioned before EXP stands for linear combination of functions decreasing exponentially with time. Note that EXP does not denote any specific such combination. Obviously, these terms will be different in (2.34) and (2.35). It follows from (2.9) that \( z^*(t) \) is given by

\[ z^*(t) = v_z t + \left( \frac{a \varphi}{a \bar{K}} \right) + \text{EXP} \] (2.36)

where EXP again denotes exponentially decreasing term but has a more general meaning (here it stands for the difference between the terms \( -\frac{1}{v_z} \frac{a \bar{K} + a \varphi + \text{EXP}}{a \bar{K} + a \varphi + \text{EXP}} \) and \( -\frac{1}{v_z} \frac{a \bar{K} + a \varphi}{a \bar{K} + a \varphi} \)).

By putting (2.36) into (2.11) \( v^* \) is obtained and it is given by

\[ v^* = \frac{1}{v_z} \] (2.37)

It is not necessary to integrate the equation (2.17c) to obtain the dispersion coefficient \( D^*_z \). The following procedures may be used; at first premultiplying \( a \) into (2.17c) it yields

\[ \frac{dM^{(2)}}{dt} = 2 \frac{a}{v_z} \mu(1) + 2 \frac{a}{D_z} \mu(0) \] (2.38)
Putting (2.22) and (2.30) into (2.38), and then dividing both sides by \( M^{(0)} \), it follows that

\[
\frac{1}{M^{(0)}} \frac{dM^{(2)}}{dt} = 2v_z^2 t + \frac{2}{a K} (a v_z \varphi + a \frac{D_z}{z}) + \text{EXP} \quad (2.39)
\]

Integrating both sides of (2.39) yields

\[
\frac{M^{(2)}}{M^{(0)}} = v_z^2 t^2 + \frac{2}{a K} (a v_z \varphi + a \frac{D_z}{z}) + \text{EXP} + \text{constant} \quad (2.40)
\]

From (2.10), (2.36) and (2.40) \( \bar{E}^2(t) \) is given by

\[
\bar{E}^2(t) = \frac{2v_z^2 t^2}{a K} (a v_{zr} \varphi + a \frac{D_z}{z}) + \text{EXP} \quad (2.41)
\]

From (2.12) and (2.33) the dispersion coefficient is then given by

\[
D^* = \frac{1}{a K} \left( a v_{zr} \varphi + a \frac{D_z}{z} \right) \quad (2.42)
\]

It can be seen that the choice of solution \( \varphi \) does not affect \( D^* \), because the difference between two solutions of (2.31) is in the null space of \( \Xi \) and thus a multiple of \( K \) and because of the identity

\[
a v_{zr} K = 0 \quad (2.43)
\]

Furthermore \( D^* \) can be split into two parts, that is

\[
D^* = D_T^* + D_z^* \quad (2.44)
\]

where \( D_T^* \) is the Taylor contribution to the dispersion coefficient, it is given by

\[
D_T^* = a v_{zr} \varphi / a K \quad (2.45)
\]
It is easy to see that different choice of initial condition (2.22a) does not affect the results since \( v^* \) and \( D^* \) are computed from the ratios of moments.

2. Constant Temperature and Time Periodic Flow Velocity

In this subcase \( v_z \) is a periodic function of time. The solution (2.22b) for \( \mu^{(0)} \) is still valid since \( Y \) has not been changed. However the first moment equation is now given by

\[
\dot{\mu}^{(1)} = \frac{Y}{c} \mu^{(1)} + v_z(t) \overline{K} \tag{2.46}
\]

This equation does not admit a time periodic solution unless the time average of the total source over one period vanishes. That is

\[
\int_0^T a(v_z(t) \overline{K}) \, dt = 0 \tag{2.47}
\]

Since this is not the case in general, the following trial function is used for the particular solution of (2.46)

\[
\mu^{(1)} = \alpha t \overline{K} + \varphi'(t) \tag{2.48}
\]

where \( \alpha \) is a time invariant scalar. Putting (2.48) into (2.46) yields

\[
\dot{\varphi}'(t) = \frac{Y}{c} \varphi'(t) + (v_z(t) \overline{K} - \alpha \overline{K}) \tag{2.49}
\]

We are only interested in periodic solutions \( \varphi'(t) \). Obviously for such a periodic solution to exist it is necessary that

\[
\int_0^T a(v_z(t) \overline{K} - \alpha \overline{K}) \, dt = 0 \tag{2.50}
\]

It can be shown (Appendix I) that this condition is also sufficient. Therefore, \( \alpha \) must be chosen according to
\[ \alpha = \frac{1}{\tau} \int_0^\tau \frac{a}{K} z(t) \; \frac{v_z(t)}{v_z(t)} \; dt = \frac{1}{\tau} \int_0^\tau \frac{v_z(t)}{v_z(t)} \; dt \quad (2.51) \]

By applying the same procedures employed in the first subcase the asymptotic peak velocity \( v^* \) and Taylor contribution to the dispersion coefficient \( D_T^* \) can be obtained, the results are given by

\[ v^* = \frac{1}{\tau} \int_0^\tau \frac{v_z(t)}{v_z(t)} \; dt \quad (2.52a) \]
\[ D_T^* = \frac{1}{\tau} a \frac{a}{K} \int_0^\tau \frac{v_z(t)}{v_z(t)} \; \varphi'(t) \; dt \quad (2.52b) \]

Here \( \varphi'(t) \) will be related to the periodic solution of the equation

\[ \ddot{\varphi}(t) = \frac{a}{\tau} \varphi(t) + v_{zr}(t) \frac{a}{K} \quad (2.53) \]

by a difference function \( \varphi_D(t) \). That is, \( \varphi_D(t) \) is defined by

\[ \varphi_D(t) = \varphi'(t) - \varphi(t) \quad (2.54) \]

and \( \varphi_D(t) \) is a periodic solution of the equation

\[ \ddot{\varphi}_D(t) = \frac{a}{\tau} \varphi_D(t) + (v_z(t) - \alpha) \frac{a}{K} \quad (2.55) \]

It can be easily verified that \( \varphi_D \) is linear dependent with the particular solution

\[ \varphi_D(t) = \left( \int_0^t (v_z(t) - \alpha) \; dt \right) \frac{a}{K} \quad (2.56) \]

From \((2.54), (2.56)\) and the definition of \( v_z \) the following identity holds

\[ a v_{zr} \varphi' = a v_{zr} \varphi \quad (2.57) \]

\( D_T^* \) is then transformed into the form

\[ D_T^* = \frac{1}{\tau} \frac{a}{\alpha} \int_0^\tau \frac{a}{K} v_{zr}(t) \varphi(t) \; dt \quad (2.58) \]
3. Time Periodic Temperature and Flow Velocity

In this case it is assumed that the temperature of the system varies with time periodically such that \( K \) becomes a periodic function of time, that is

\[
K(t) = K(t + \mathcal{T}) \quad \text{for all } t \tag{2.59a}
\]

Hence both \( Y \) and \( z \) vary periodically with time \( t \). Obviously, the left hand side null vector of \( Y \) is \( a \) for all time, and therefore is time invariant, while the right hand side null vector is time periodic. Since (2.17a) describes the forcing in a closed system (no source term) by periodic temperature variations. It will be assumed, as it is physically plausible, that the solution of this system approaches for \( t \to \infty \) a periodic state, that is

\[
\lim_{t \to \infty} \mu^{(0)}(t) = \psi(t) \tag{2.59b}
\]

where \( \psi(t) \) is a periodic function. Putting (2.59b) into (2.17b) yields

\[
\mu^{(1)} = Y(t) \mu^{(1)} + z(t) \psi(t) \tag{2.60}
\]

This equation will not admit periodic solution unless the condition

\[
\int_{0}^{\mathcal{T}} a z(t) \psi(t) \, dt = 0 \tag{2.61}
\]

is satisfied (see Appendix I). The following function is used to obtain a particular solution for (2.60)

\[
\mu^{(1)}(t) = t \zeta(t) + \varphi'(t) \tag{2.62}
\]

where \( \zeta \) and \( \varphi' \) are both periodic functions. Putting (2.62) into
\[ \dot{\varphi}^t + t \ddot{\varphi}^t + \varphi = t \ddot{\gamma}^t + \varphi \dot{\varphi}^t + \varphi_{z} \varphi \]  

(2.63)

Equalizing the terms with the same order of \( t \) in (2.63) gives two differential equations

\[ \dot{\xi} = \Xi(t) \dot{\xi} \]  

(2.64a)

\[ \dot{\varphi}^t = \Xi(t) \varphi^t + ( \varphi_{z}(t) \varphi(t) - \xi(t) ) \]  

(2.64b)

The periodic solution of (2.64a) will be determined such that the integral source in (2.64b) vanishes equivalent to (2.61). By comparing (2.17a) and (2.64a) it can be seen that a periodic solution of the latter equation is given by

\[ \xi = \alpha \varphi \]  

(2.65)

where \( \alpha \) is a constant. From (2.65) and (2.64b) it follows that

\[ \dot{\varphi}^t = \Xi(t) \varphi^t + ( \varphi_{z}(t) \varphi(t) - \alpha \varphi(t) ) \]  

(2.66)

The condition of vanishing integral source becomes

\[ \int_0^\tau \alpha ( \varphi_{z}(t) \varphi(t) - \alpha \varphi(t) ) \, dt = 0 \]  

(2.67)

This means \( \alpha \) must be chosen according to

\[ \alpha = \int_0^\tau \frac{\alpha}{\varphi(t)} \varphi(t) \, dt / \int_0^\tau \frac{\alpha}{\varphi(t)} \varphi(t) \, dt \]  

(2.68)

From now on \( \varphi_{z} \) will be defined as the average of the axial velocity over the \( C^3 \) space with \( \varphi \) as weight, and it can be seen that \( \frac{\alpha}{\varphi} \) is time invariant. Then \( \alpha \) can be expressed in form of

\[ \alpha = \frac{1}{T} \int_0^\tau \bar{v}_{z}(t) \, dt \]  

(2.69)
By applying the same techniques as in the first two subcases one can obtain the asymptotic peak velocity and the dispersion coefficient

\[ v^* = \frac{1}{T} \int_0^T -v_z(t) \, dt \]  
(2.70a)

\[ D_T^* = \frac{1}{T} a \int_0^T a \nabla_z \varphi(t) \varphi(t) \, dt \]  
(2.70b)

where \( \varphi \) is a periodic solution of the differential equation

\[ \varphi' = \frac{v_z}{\tau} \varphi + v_{zr} \varphi(t) \]  
(2.71)

It can be seen that \( v^* \) is time-space average of the velocity with \( \varphi \) as weight. This is physically plausible since \( \varphi \) can be interpreted as proportional to the probability of finding a tracer molecule in a certain phase at a certain time.

C. Example

If the column contains only two phases, the ratios defined by

\[ a = a_2 / a_1, \quad K = K_2 / K_1 \]  
(2.73)

will be introduced. Here \( K \) as well as \( v_z \) will be assumed to be periodic in time with period \( \tau \). That is

\[ K(t + \tau) = K(t), \quad v_z(t + \tau) = v_z(t) \]  
(2.74)

Then the matrix \( \tilde{Y} \) is given by

\[ \tilde{Y} = \begin{pmatrix} -k\ell K & k\ell \\ k\ell K/a & -k\ell/a \end{pmatrix} \]  
(2.75)
where \( k \ell \) is defined by

\[
k \ell = \frac{k_{12} \ell_{12}}{a_1}
\]  
(2.76)

The equation (2.17a) is easily integrated and the solution is given by

\[
\psi_1(t) = \frac{k \ell}{a(g(T)-1)} \int_0^T \frac{g(t+t_1)}{g(t)} dt_1 
\]  
(2.77a)

\[
\psi_2(t) = \frac{(1 - \psi_1(t))}{a}
\]  
(2.77b)

where \( g \) is defined by

\[
g(t) = \exp\left(\frac{k \ell}{a} \int_0^t (1 + a K(t_1)) dt_1 \right)
\]  
(2.78)

It follows from (2.77) that \( \bar{v}_z \) is given by

\[
\bar{v}(t) = \left( v_{z1}(t) - v_{z2}(t) \right) \psi_1(t) + v_{z2}(t)
\]  
(2.79)

and the two elements of \( v_{zr} \) are then given by

\[
v_{zr1}(t) = S(t) / \psi_1(t)
\]  
(2.80a)

\[
v_{zr2}(t) = -S(t) / (1 - \psi_1(t))
\]  
(2.80b)

where \( S \) is defined by

\[
S(t) = \psi_1(t) \left(1 - \psi_1(t)\right) (v_{z1}(t) - v_{z2}(t))
\]  
(2.81)

Putting (2.80) into (2.71) it becomes

\[
\dot{\psi} = \frac{\bar{v}(t) \psi + S(t) \left( \frac{1}{-a} \right)}
\]  
(2.82)

This equation can be integrated to give the periodic solutions
\[ \phi_1(t) = \frac{1}{g(\tau) - 1} \int_0^\tau S(t+t_1) \frac{g(t+t_1)}{g(t)} \, dt_1 \quad (2.83a) \]

\[ \phi_2(t) = \frac{-1}{a(g(\tau) - 1)} \int_0^\tau S(t+t_1) \frac{g(t+t_1)}{g(t)} \, dt_1 \quad (2.83b) \]

From (2.83a), (2.83b) and (2.70), \( v^* \) and \( D_T^* \) are given by

\[ v^* = \frac{1}{\tau} \int_0^\tau ((v_{z1}(t) - v_{z2}(t))\psi_1(t) + v_{z2}(t)) \, dt \quad (2.84a) \]

\[ D_T^* = \frac{1}{\tau (g(\tau) - 1)} \int_0^\tau \frac{(v_{z1}(t) - v_{z2}(t))}{g(t)} \int_0^\tau S(t+t_1) \frac{g(t+t_1)}{g(t)} \, dt_1 \, dt \quad (2.84b) \]
III. PARAMETRIC PUMPING BY TIME TEMPERATURE FIELD

The transport induced by the coupling of time periodic flow and temperature fields may also be utilized in the process operating in steady mode. Wilhelm et al. (28,29,30,19,20,23) showed that a separation of the components in a mixture can be achieved by the use of time periodic flow and temperature fields in a fixed bed column. He and his collaborators carried out extensive numerical and experimental work for special systems. Lates Pigford, Baker and Blum (18) presented an equilibrium theory of the process for a closed system with special forcing functions. In this chapter equilibrium theory (17) will be developed for a general forcing function and for an open steady state system. The parametric pumping process then will be related to a steady state process which either involves two columns operating at different temperatures or which is identical to a conventional extraction process.

A. Equilibrium Theory

The apparatus considered here consists of three reservoirs $R_p$, $R_m$ and $R_r$ (Fig. 3) which are connected by two column sections $C_p$ and $C_r$, which form the column $C$. The column contains a stationary phase ($v_2 = 0$) and a fluid phase. The following assumptions are being made:

1. The velocity $v_1$ of the fluid phase varies periodically with time $t$ and is independent of position $z$ in the column. That is

$$v_1(t + T) = v_1(t) \quad \text{for all } t \quad (3.1)$$

2. The temperature $\theta$ is, at any given time, uniform throughout
FIGURE 3: SCHEMATIC REPRESENTATION OF SEPARATION APPARATUS (ENRICHMENT).
the system and varies periodically with time. That is

$$\theta(t + \tau) = \theta(t) \quad \text{for all } t$$  \hspace{1cm} (3.2)

3. The reservoirs are sufficiently far apart from each other. A quantitative condition will be given later.

4. If there are two or more solutes in the fluid phase, they will be assumed to be non-interacting and linear relations governing the transport and equilibrium conditions will be assumed. Furthermore, it will be assumed in this moment that there is equilibrium between fluid phase and stationary phase in the column at any time.

5. The flow will be assumed to be non-dispersive.

Under the assumptions made the transport of solute in the column is governed by

$$\frac{\partial}{\partial t}(1 + aK)c_1 = -v_1 \frac{\partial c_1}{\partial z}$$  \hspace{1cm} (3.3)

where $K$ is the ratio of the concentration in phase 2 to that in phase 1 at equilibrium and $a$ is the holdup ratio of phase 2 to phase 1.

Using the new variables

$$\delta(t) = 1 / (1 + aK(\theta(t)))$$  \hspace{1cm} (3.4)

and

$$y = (1 + aK)c_1$$  \hspace{1cm} (3.5)

one obtains the equation

$$\frac{\partial y}{\partial t} + v_1 \delta \frac{\partial y}{\partial z} = 0$$  \hspace{1cm} (3.6)
where \( v_1 \) and \( \mathcal{C} \) are periodic functions of time. This equation can be integrated easily. The general solution is

\[
y(t, z) = G(z - \int_0^t v_1(t) \mathcal{C}(t) \, dt)
\]  

(3.7)

where \( G \) is a function satisfying the necessary differentiability conditions but otherwise arbitrary. Thus the variable \( y \) is constant along characteristics in \( z-t \) plane which are given by

\[
z - \int_0^t v_1(t) \mathcal{C}(t) \, dt = C
\]  

(3.8)

where \( C \) is a constant.

The mean velocity of the tracer will be defined by

\[
\overline{w} = \frac{1}{\Upsilon} \int_0^\Upsilon v_1(t) \mathcal{C}(t) \, dt
\]  

(3.9)

\( \Upsilon \overline{w} \) is the distance over which a discontinuity in the concentration profile travels during the period \( \Upsilon \). It will be shown later that this distance can be considered as the axial displacement of an individual tracer molecule during one period. The characteristics in Fig. 4 give the relation between time and distance for a tracer molecule travelling through the column. The diagonal of the rectangle shown corresponds to the average tracer movement. \( \overline{w} \) is the slope of this diagonal with respect to the ordinate.

It will be assumed that the distances \( L_\ell \) and \( L_\tau \) of \( R_\ell \) and \( R_\tau \) from \( R_m \) satisfy the following conditions:

(a) For a solute for which \( \overline{w} > 0 \)

\[
L_\ell, L_\tau > \max_{t_1 < t_2} \int_{t_1}^{t_2} v_1(t) \mathcal{C}(t) \, dt
\]  

(3.10)
FIGURE 4: CHARACTERISTIC LINES IN $z$-$t$ PLANE, FOR THE EXAMPLE SHOWN $\bar{w} > 0$
(b) For a solute for which \( \overline{w} < 0 \)

\[
L_{\mathcal{L}}, \quad l_1 > \text{Min}_{t_1 < t_2} \int_{t_1}^{t_2} v_1(t) \hat{S}(t) \, dt \quad (3.11)
\]

The right hand side of (3.11) is equal to the horizontal distance between points P and Q in Fig. 4. It is obvious that both (3.10) and (3.11) can be satisfied under the conditions stated if \( L_{\mathcal{L}} \) and \( L_1 \) are made sufficiently large.

From the discussion of characteristics in the z-t plane (Fig. 4) it follows that for a component for which \( \overline{w} > 0 \) the condition of the right section of the column is completely determined by the conditions in \( R_1 \) except for a boundary zone adjacent to \( R_1 \) which does not extend up to \( R_1 \) because of the condition (3.11). Similarly for such a component the state of the left column section is essentially determined by \( R_{\mathcal{L}} \). Assume now that such a component is fed into \( R_1 \) while nothing of it is added to \( R_{\mathcal{L}} \) and to \( R_1 \). Since the average flux of such a component must be non-negative and since nothing is added to \( R_{\mathcal{L}} \) the average flux in \( C_{\mathcal{L}} \) will be zero and the average flux in \( C_1 \) will be determined by the amount of the component fed into \( R_1 \). In other word a component with \( \overline{w} > 0 \) which is added to \( R_1 \) can move only through the right column section. Similarly if \( \overline{w} < 0 \) the component if added to \( R_1 \) can move only through the left column section.

All other properties of such a column can now be derived from a discussion of (3.9) and from simple overall mass balances. We shall now write \( v_1 \) as

\[
v_1 = u + \overline{v_1} \quad (3.12)
\]

where \( \overline{v_1} \) is the time average of \( v_1 \). The part \( u \) of the fluid velocity
satisfies
\[ \int_0^\tau u(t) \, dt = 0 \]  \hspace{1cm} (3.13)

The displacement \( \Delta \) defined by
\[ \Delta(t) = \int_0^t u(t) \, dt \]  \hspace{1cm} (3.14)

then becomes a periodic function of time. That is
\[ \Delta(t + \tau) = \Delta(t) \quad \text{for all } t \]  \hspace{1cm} (3.15)

From (3.9) and (3.12)
\[ \bar{w} = \bar{v}_1 \bar{\delta} + w^* \]  \hspace{1cm} (3.16)

where \( \bar{\delta} \) is the time average of \( \delta \) and where \( w^* \), the induced velocity, is defined by
\[ w^* = \frac{1}{\tau} \int_0^\tau \delta(t) \, u(t) \, dt = \frac{1}{\tau} \int_0^\tau \delta(t) \Delta(t) \, dt \]  \hspace{1cm} (3.17)

The splitting of the mean velocity \( \bar{w} \) into two parts is convenient for the analysis of the apparatus. \( \bar{\delta}\bar{v}_1 \) is the tracer velocity caused by the average fluid velocity \( \bar{v}_1 \), and \( w^* \) is the tracer velocity caused by the periodic part of the fluid movement superimposed on \( \bar{v}_1 \).

The integral in (3.17) can be interpreted as the area of a closed loop traced out by the statepoint of the system in a \( \delta - \Delta \) diagram (see Fig. 5). The area is to be counted positive or negative depending on whether the statepoint moves along the boundary clockwise or counterclockwise, respectively.

Consider the movement of individual tracer molecule in the column.
FIGURE 5: REPRESENTATION OF $W^*$ AS AREA OF A LOOP IN A $\delta - \Delta$ DIAGRAM
By equilibrium assumption there is no resistance for the transfer of the tracer molecule between two phases. Therefore the probability of finding a tracer molecule in the fluid phase or in the stationary phase at time \( t \) is independent of the position of this molecule at previous time. The probability of finding a tracer molecule in the fluid phase or in the stationary phase is then given by

\[
P_1(t) = \frac{1}{1 + a K(t)} \tag{3.18}
\]

or by

\[
P_2(t) = a K(t) / (1 + a K(t)) \tag{3.19}
\]

respectively. \( P_1 \) and \( P_2 \) are identical for every molecule in the system. Thus the space-average axial velocity of the tracer molecule is given by

\[
w(t) = P_1(t) v_1(t) + P_2(t) v_2(t) \tag{3.20}
\]

and the axial displacement of a tracer molecule during a period is given by

\[
s = \int_0^T w(t) \, dt \tag{3.21}
\]

From (3.18) through (3.20) the right hand side of (3.21) is equal to \( \bar{w}T \).

Two basic separation problems will be discussed in what follows. In the one case only a carrier and one component needs to be considered. The objective is to obtain a product in which the concentration of this component is larger than the corresponding concentration in the feed. Such a problem will be called an enrichment problem. In isotope separation, if the isotope of interest has a very small natural
abundance, a part of the process can be considered as enrichment process in this sense. The isotope with relatively large natural abundance then can be taken as carrier phase at least in the first stages of the process (which are also the most costly ones).

The other problem of interest will be called a split problem. Here it is assumed that there are at least two components in a carrier fluid which are difficult to separate from each other, but are easy to separate from the carrier fluid.

B. The Enrichment Problem

It will be assumed that the equilibrium constant $K$ of the component under consideration is not temperature independent. That is, there are two temperatures $\theta_1$ and $\theta_2$ such that

$$K(\theta_1) \neq K(\theta_2)$$

(3.22)

In this case it is always possible to find time periodic functions $\Delta$ and $\delta$ such that the loop traced out in the $\Delta - \delta$ diagram encloses a positive area. This can be achieved by a loop which approximated sufficiently closely a rectangle with sides parallel to the axes and with upper and lower sides at ordinate values $\delta_1$ and $\delta_2$ respectively, where

$$\delta_{1,2} = \frac{1}{1 + aK(\theta_1, \theta_2)}$$

(3.23)

Under such an operation

$$w^* > 0$$

(3.24)

The feed containing the component to be enriched is added to $R_m$ with volumetric flow rate $F_m$. Fluid phase is recovered from
reservoirs \( R_L \) and \( R_R \) with flow rates \( F_L \) and \( F_R \) respectively, where

\[
F_L = F_m (1-\eta), \quad F_R = F_m \eta
\]  

(3.25)

If there is no other fluid added or removed from the system the average fluid velocities in the left and right part of the column are given by

\[
\bar{v}_{1L} = -\frac{F_L}{a_1}, \quad \bar{v}_{1r} = \frac{F_R}{a_1}
\]  

(3.26)

where \( a_1 \) is the cross-sectional area occupied by phase 1 and the mean velocities of the component are

\[
\bar{w}_L = - \left( \frac{F_L}{a_1} \right) \bar{\delta} + w^* \]  

(3.27)

\[
\bar{w}_R = \left( \frac{F_R}{a_1} \right) \bar{\delta} + w^* \]  

(3.28)

Thus by choosing \( F_m \) sufficiently small one can obtain a situation where

\[
\bar{w}_L > 0, \quad \bar{w}_R > 0
\]  

(3.29)

In this situation no component can penetrate the left part of the column. That is the component concentration in the fluid removed at the left reservoir is zero. A simple mass balance over the whole system gives the average component concentration in the fluid removed from the right reservoir,

\[
\bar{c}_{1r} = \frac{c_{1m}}{\eta}
\]  

(3.30)

Since \( \eta \) can be chosen arbitrary in the interval

\[
0 \leq \eta \leq 1
\]  

(3.31)

the concentration \( \bar{c}_{1r} \) can be made arbitrarily large.
Naturally the mathematical model of the process (notably the linearity assumption) will break down if the concentration becomes too large and further analysis needs to be carried out in such a case.

The cyclic process described utilizes the temperature dependence of the equilibrium constant $K$. The same effect is utilized in a steady state process known as dual-temperature process $(4,5,21,22)$. Consider two columns as shown in Fig. 6 which are operated at different temperatures $\theta_L$ and $\theta_R$ respectively. Corresponding to the assumption of negligible dispersion and mass transfer resistance in the cyclic process the assumption will be used here that the two columns are very long so that one can use the approximation of an infinite number of theoretical stages. A linear column then is characterized by the location of its pinch (equilibrium between two phases). If the equilibrium constants are different at the two temperatures one can always choose the flow rates $V_{1m}$, $V_2$ and $F$ such that for both columns the pinch is at the end nearest to point III (see Fig. 6).

To show this we can assume without loss of generality that

$$K(\theta_L) > K(\theta_R)$$

Furthermore the flow rate of phase 1 will be counted positive if the phase in the columns flows from the left to the right (see Fig. 6), and the flow rate of phase 2 will be counted positive if this phase flows from the right to the left in the columns. The conditions for having the pinches at the indicated points are given by

$$V_{1L} - K(\theta_L) V_2 < 0$$  \hspace{1cm} (3.33)

$$V_{1R} - K(\theta_R) V_2 > 0$$  \hspace{1cm} (3.34)
By choosing $V_{1m}/V_2$ such that

$$K(\theta_L) > V_{1m}/V_2 > K(\theta_r)$$

and $F/V_{1m}$ sufficiently small one can always satisfy both conditions (3.33) and (3.34). A mass balance about a region including point III and near ends of both columns together with the pinch condition gives the result that the concentration of point III vanishes. An overall mass balance yields the same result as for the cyclic process. The concentration $c_{1r}$ in the product stream is related to the feed concentration $c_{1m}$ by

$$c_{1r} = c_{1m}/\eta$$

(3.36)

The difference in practical operation between the two processes may be summarized as follows:

In the cyclic process only one phase needs to be transported, which fact may be of advantage if one phase is a solid. However, it should be noted that an opposite flow between two phases through a column can be formally achieved without actually moving one of the phases through the column. This can be done by using a set of compartments in such a way that input and output are switched cyclically from one stage to another. However such a process may become more complicated to design and operate. On the other hand the heat recovery problem is difficult to solve though heat recovery is possible in principle if several systems are operated simultaneously with phase shift.

In the dual-temperature process heat recovery can be achieved simply by using two heat exchangers placed within the loops which
FIGURE 6: SCHEMATIC REPRESENTATION OF DUAL-TEMPERATURE PROCESS
are separated by the two columns.

In both processes the assumption of infinitely many stages (equivalent to no dispersion and no mass transfer resistance) and the requirement of total recovery of the component of interest leads to a bound on the feed rate $F$. It will be shown in the next section that this bound is completely determined by equilibrium properties and by the maximum allowable flow rate through the column.

C. Maximum Allowable Feed Rate for Enrichment Problem

The bound on the feed rate for the cyclic process and for the dual-temperature process will be discussed separately:

1. Cyclic Temperature Process

At first we shall consider the bang-bang operation, that is, the system is operated at temperature $\theta_1$ during subperiod 1 $(0, r\tau)$ and at $\theta_2$ during subperiod 2 $(r\tau, \tau)$. Here $r$ is a positive parameter less than 1. In each subperiod the fluid velocity is chosen to be constant. Furthermore it can be assumed without loss of generality that

$$S_1 > S_2 > 0 \quad (3.37)$$

The state point of this operation will trace out a rectangle on the $\Delta - S$ diagram. In this situation $\bar{S}$ and $w^*$ are given by

$$\bar{S} = r S_1 + (1 - r) S_2 \quad (3.38)$$

$$w^* = u_1 r (S_1 - S_2) = u_2 (r - 1) (S_1 - S_2) \quad (3.39)$$

where $u_1$ and $u_2$ are the values assumed by the periodic function $u$ in the subperiods 1 and 2 respectively, they are assumed to be constants. From the discussion in III.B, it is obvious that the condition to be satisfied in the left column section will impose more severe
restriction on the bound of feed rate. That is, the condition

\[ w^* - \frac{F_\ell}{a_1} \delta \geq 0 \quad (3.40) \]

must be satisfied. In order to have \( w^* > 0 \) which is essential to satisfy the condition (3.40) the condition

\[ u_1 = \frac{(r - 1) u_2}{r} > 0 \quad (3.41) \]

must be met. From (3.38) and (3.39) the condition (3.40) becomes

\[ u_1 \frac{r (\delta_1 - \delta_2)}{a_1} - \frac{F_\ell}{a_1} (r \delta_1 + (1-r) \delta_2) \geq 0 \quad (3.42) \]

The instantaneous flow rate in the left column section is given by

\[ V_{1\ell} = \begin{cases} -F_\ell + a_1 u_1 & \text{for } 0 \leq t < r \tau \\ -F_\ell + a_1 u_2 & \text{for } r \tau \leq t < \tau \end{cases} \quad (3.43) \]

It is obvious that the magnitude of \( V_{1\ell} \) must not be larger than the maximum allowable flow rate \( V_{\text{max}} \) through the column. That is

\[ |V_{1\ell}| \leq V_{\text{max}} \quad (3.44) \]

Therefore, besides the constraint (3.42) it follows from (3.41), (3.43) and (3.44) that the constraints

\[ V_{\text{max}} \geq a_1 u_1 - F_\ell \geq -V_{\text{max}} \quad (3.45) \]

\[ 0 \geq \frac{1}{r - 1} a_1 u_1 - F_\ell \geq -V_{\text{max}} \quad (3.46) \]

must be imposed on the seeking of the allowable average flow rate \( F \)
for the enrichment problem.

It can be shown (Appendix II) that there exist two possible maximum $F_K$ under those constraints for given $\delta_1$, $\delta_2$, $r$ and $V_{\text{max}}$. They are:

(a) in case that $(\delta_1 / \delta_2) \leq (1-r)/r$

$$\max F_K = V_{\text{max}} r \frac{(\delta_1 - \delta_2)}{\delta_2}$$

(3.47a)

(b) in case that $(\delta_1 / \delta_2) \geq (1-r)/r$

$$\max F_K = V_{\text{max}} (1-r) \frac{(\delta_1 - \delta_2)}{\delta_1}$$

(3.47b)

If there is freedom in the choice of the parameter $r$, it can be seen from (3.47a,b) that the optimum value of $r$ for maximizing $F_K$ is given by

$$r = \frac{\delta_2}{(\delta_1 + \delta_2)}$$

(3.48)

and the maximum $F_K$ under this situation is given by

$$\max F_K = V_{\text{max}} \frac{(\delta_1 - \delta_2)}{(\delta_1 + \delta_2)}$$

(3.49a)

Consequently the bound for the feed rate $F_m$ which is relate to $F_K$ by the relation (3.25) is then given by

$$\max F_m = V_{\text{max}} \frac{(\delta_1 - \delta_2)}{(\delta_1 + \delta_2)(1-\eta)}$$

(3.49b)

If $\delta_1$ and $\delta_2$ are the extrema of the function $\delta(\theta)$ with respect to admissible temperature variations, then (3.49b) gives the maximum value for $F_m$ for bang-bang operation, because of

$$\frac{\delta_1 - \delta_2}{\delta_1 + \delta_2} \geq \frac{\delta_3 - \delta_4}{\delta_3 + \delta_4} \Leftrightarrow \delta_1 > \delta_2 > \delta_3 > \delta_4$$

(3.50)
Furthermore, for any admissible cyclic operation it can be shown (Appendix II) that there exists a previously described bang-bang operation which may allow larger or equal feed rate for the same apparatus. This comes from the fact that \( w^* \) can be made larger by bang-bang operation even the amplitude of the function \( \Delta(t) \) does not change. Therefore one may conclude that the bound for the feed rate \( F_m \) for the cyclic temperature process is given by (3.49b).

2. Dual-Temperature Process

From mass balance at point III (Fig. 6), it follows that

\[
V_{1r} + (1 - \eta) F = V_{1l} \tag{3.52}
\]

Combining this with the conditions (3.33) and (3.34) it follows that

\[
F \leq V_2 \left( K(\theta_L) - K(\theta_R) \right) / (1 - \eta) \tag{3.53}
\]

It is obvious that the maximum feed rate is then given by

\[
\text{Max } F = (V_2)_{\text{max}} \left( K(\theta_L) - K(\theta_R) \right) / (1 - \eta) \tag{3.54}
\]

where \((V_2)_{\text{max}}\) is the maximum allowable flow rate in phase 2.

D. The Split Problem

By assumption both components A and B can be easily separated from the carrier fluid. Therefore we may assume the existence of recovery loops as shown in Fig. 7 without further explanation on how the recovery is achieved.

The mixture containing the components to be separated is dissolved in the feed loop connected with the middle reservoir. Components A and B will be recovered from the recovery loops connected with the right and left reservoirs respectively.
In order to obtain a perfect separation, the mean velocities of the components A and B must satisfy the condition

\[ \bar{w}_A > 0 , \quad \bar{w}_B < 0 \]  \hspace{1cm} (3.55)

in both parts of the column. Since the conditions are identical for both parts of the column these parts may be operated in the same way, i.e. it will be assumed that \( \theta \) and \( v_1 \) are the same everywhere in the column at any given time. In general there will be a net flow of carrier \( (\bar{v}_1 \neq 0) \) which explains the connection between left and right recovery loops shown in the figure.

It will be assumed that there are two temperatures such that

\[ \frac{\delta A(\theta_1)}{\delta B(\theta_1)} \neq \frac{\delta A(\theta_2)}{\delta B(\theta_2)} \]  \hspace{1cm} (3.56)

This is satisfied under very general conditions. If there is freedom in the choice of \( a \), then (3.56) can be met if

\[ K_B(\theta_1) \neq K_A(\theta_1) \neq K_A(\theta_2) \]  \hspace{1cm} (3.57)

Furthermore if (3.56) is satisfied it is easy to show that

\[ \left( \frac{w_A^*}{\delta A} \right) > \left( \frac{w_B^*}{\delta B} \right) \]  \hspace{1cm} (3.58)

can be realized, for instance, by a properly chosen cycle which approximates a rectangle in the \( \Delta - \delta \) diagram. Now if (3.58) is satisfied \( \bar{v}_1 \) can be found such that

\[ \bar{w}_A = \frac{\delta A}{\delta A} \bar{v}_1 + w_A^* > 0 \]  \hspace{1cm} (3.59a)

\[ \bar{w}_B = \frac{\delta B}{\delta B} \bar{v}_1 + w_B^* < 0 \]  \hspace{1cm} (3.59b)
FIGURE 7: SCHEMATIC REPRESENTATION OF A SPLITTING PROCESS
Therefore under very general conditions the components A and B can be separated from each other by the cyclic process.

Consider now the ordinary counter-current extraction process shown in Fig. 8. Here the whole system is operated at one temperature at which both equilibrium constants are different. The following differences exist between this conventional process and the cyclic process.

In the cyclic process only one of the two phases needs to be transported in the column and to be processed in the recovery operation. These may be of advantage if one phase is solid or if A and B are easy to recover from one phase but are difficult to recover from other phase. As mentioned previously the disadvantage of the cyclic process is the heat recovery problem.

In the ordinary extraction process the column is operated under constant temperature. Thus a heat recovery problem similar to that in the cyclic process is not encountered.

E. Mean Velocity Under Non-Equilibrium Condition

If the mass transfer resistance between two phases is taken into consideration while the other assumptions are still kept, the differential equations which describe the transport of the solute in the column are then given by

\[
\frac{\partial c_1}{\partial t} = -v_1(t) \frac{\partial c_1}{\partial z} - k_l (k(t)c_1 - c_2) \tag{3.60}
\]

\[
\frac{\partial c_2}{\partial t} = \frac{k_l}{a} (k(t)c_1 - c_2) \tag{3.61}
\]

where \( k \) and \( l \) are mass transfer coefficient and interface area per unit length of column between two phases respectively, they are assumed
FIGURE 8: SPLITTING BY CONVENTIONAL EXTRACTION
to be constant.

In what follows the dependence of the concentration on \( z \) and \( t \) in the column will be discussed qualitatively.

Consider the right column section and the solute for which \( \bar{w} > 0 \), as the operation starts and assume \( v_1 > 0 \) at \( t=0 \), a concentration front emerging from the middle reservoir will move into the column with velocity \( w \). Since \( \bar{w} > 0 \) the front will have a positive displacement at time \( t=T \). As the operation continues, the front will move through the column i.e. in each period by the amount \( \bar{w}T \). After sufficiently many periods the front will reach the right reservoir. From then on the concentration may be considered as \( z \)-invariant except for a region adjacent to the right reservoir. That is as \( v_1 < 0 \) the concentration front will emerge from the right reservoir into the column and retreat again to the reservoir since \( \bar{w} > 0 \). The invariance with respect to \( z \) will be correct only if the amount of component in the middle reservoir is kept constant all the time, that is

\[
c_1(0^-, t) + a c_2(0^-, t) = c_a \quad \text{for all } t \quad (3.62a)
\]

where \( c_a \) is a constant, and the relation governing the interphase mass transfer in the middle reservoir is the same as that in the column, that is

\[
\frac{dc_1(0^-, t)}{dt} = -k' \ell(K(t) c_1(0^-, t) - c_2(0^-, t)) \quad (3.62b)
\]

The conditions (3.62a) and (3.62b) can be met if the reservoir is made sufficiently large and has the same packing as the column. Similar discussion can be held for the solute with \( \bar{w} < 0 \).

Although it is not essential for the solute with \( \bar{w} > 0 \), it is reasonable to assume that in the right reservoir
\begin{align}
c_1(I^+_{r}, t) + a_{c2}(I^+_{r}, t) &= c_b \quad (3.63a) \\
\frac{dc_1(I^+_{r}, t)}{dt} &= k \ell (K(t) c_1(I^+_{r}, t) - c_2(I^+_{r}, t)) \quad (3.63b)
\end{align}

where \(c_b\) is also a constant. The numerical solutions of (3.60) and (3.61) subjected to the conditions (3.62a,b) and (3.63a,b) and to the boundary conditions in the column which are given by

\begin{align}
c_1(0^+, t) &= c_1(0^-, t) \quad \text{when } \nu_1 > 0 \quad (3.64) \\
c_1(I^-_{r}, t) &= c_1(I^+_{r}, t) \quad \text{when } \nu_1 < 0 \quad (3.65)
\end{align}

are calculated. Since the periodic solutions are of interest the solutions which satisfy the periodicity conditions

\begin{align}
c_1(z, t) &= c_1(z, t+\tau) \quad \forall \ t, z \quad (3.66) \\
c_2(z, t) &= c_2(z, t+\tau) \quad \forall \ t, z \quad (3.67)
\end{align}

are sought. One of the results is presented in Fig.9 in which the fluid phase concentration \(c_1\) is plotted against \(z\) at the moments after \(\nu_1 > 0\) and after \(\nu_1 < 0\). It shows that the concentration profiles are almost \(z\)-invariant in the column except in the region near \(z/L_r = 1\) (in this example \(z/L_r > 0.77\)).

If the concentration profile can be considered as \(z\)-invariant in the column, then the column may be described by a pair of ordinary differential equations which are given by

\begin{align}
\frac{dc_1}{dt} &= -k \ell (K(t) c_1 - c_2) \quad (3.68) \\
\frac{dc_2}{dt} &= \frac{k \ell}{a} (K(t) c_1 - c_2) \quad (3.69)
\end{align}

with periodic boundary conditions.
FIGURE 9: SOLUTE CONCENTRATION IN MOVING PHASE VS. AXIAL POSITION Z AT TWO INSTANTS.
\[ c_1(0) = c_1(\tau), \quad c_2(0) = c_2(\tau) \]  \hspace{1cm} (3.70)

The instantaneous flux \( q \) of the component under consideration is given by

\[ q(t) = v_1(t) c_1(t) \]  \hspace{1cm} (3.71)

and the time average flux \( \bar{q} \) is expressible in form of

\[ \bar{q} = \frac{1}{\tau} \int_0^{\tau} v_1(t) c_1(t) \, dt \]  \hspace{1cm} (3.72)

The mean velocity \( \bar{w} \) of the component will be given by

\[ \bar{w} = \bar{q} / \bar{c} (1 + a) \]  \hspace{1cm} (3.73)

where \( \bar{c} \) is the concentration of the component averaged over period and cross-section, that is

\[ \bar{c} = \frac{1}{(1+a)\tau} \int_0^{\tau} (c_1 + a c_2) \, dt \]  \hspace{1cm} (3.74)

By adding (3.68) and (3.69) it can be seen that \( c_1 + a c_2 \) is time invariant, thus \( \bar{c} \) is expressible in form of

\[ \bar{c} = (c_1 + a c_2) / (1 + a) \]  \hspace{1cm} (3.75)

The solution of (3.68) and (3.69) subjected to (3.70) can be easily obtained by elementary method. The result is given by

\[ c_1(t) = \frac{k \ell \bar{c} (1+a)}{a (g(\tau)-1)} \int_0^{\tau} \frac{g(t+t_1)}{g(t)} dt_1 \]  \hspace{1cm} (3.76)

where \( g \) is defined by

\[ g(t) = \exp\left( \frac{k \ell}{a} \tau \right) \int_0^{t} (1 + a K(t_1)) \, dt_1 \]  \hspace{1cm} (3.77)
It is possible to derive from (3.72) through (3.77) the simple expressions for the asymptotic cases $k \to \infty$ and $k \to 0$.

The case for large $k$ will be treated first, the result (derived in Appendix II) is the following

$$
\bar{w} = \bar{v}_1 \delta + \frac{1}{T} \int_0^T \delta(t) \dot{A}(t) \, dt - \frac{a}{2k \ell T} \int_0^T \delta^2(t) \dot{A}(t) \, dt \\
+ O\left(1/k^2\right)
$$

(3.78)

It can be seen that for very large $k$ the mean velocity approaches the value derived previously for the case without mass transfer resistance, which is given by (3.16). The second integral in (3.78) corresponds to the area enclosed by a cycle traced out by the state point in a $\Delta - \delta^2$ diagram. It is plausible that in this term the role of change of $\delta$ enters. Also the sign of the term can be easily made plausible by considering the various combinations of signs of $\dot{\delta}$ and $v_1$ ($\delta > 0$ in any case) and the corresponding effects on the mean velocity $\bar{w}$ of the solute. For instance, if $\dot{\delta} > 0$ the solute is forced out from the stationary phase. Due to the mass transfer resistance, the amount going to the fluid phase is smaller than it would in the case without resistance. If $v_1 > 0$ at this time this means that a smaller amount of solute is transported by the fluid into positive $z$ direction and, therefore, the mean velocity will be reduced. In above argument values of $v_1$ and $\dot{\delta}$ at the same time can be related since $k$ is assumed to be sufficiently large.

In the case that $k$ is small the result (derived in Appendix II) is given by

$$
\bar{w} = \frac{\bar{v}_1}{1+aK} \left(\frac{\ell T}{a}\right) \frac{1}{T} \int_0^T u(t) \int_0^t \left(K(t_1) - K\right) \, dt_1 \, dt \\
+ O\left(k^2\right)
$$

(3.79)
where \( \bar{K} \) is the time average of the function \( K \) and is given by

\[
\bar{K} = \frac{1}{T} \int_0^T K(t) \, dt
\] (3.80)

It can be seen that if \( k \) become very small the mean velocity \( \bar{w} \) will approach the value \( v_1/(1+a\bar{K}) \) which is time-space average of the velocity with \( \bar{K} \) as weight. This is plausible since when \( k \) is very small the ratio of the tracer concentration in phase 2 to that in phase 1 can be approximated by a constant \( \bar{K} \) at any time after sufficiently many periods of operation. The second term on the right hand side of (3.79) is caused by the small concentration perturbation in the fluid phase due to interphase mass transfer.
IV. PARAMETRIC PUMPING BY TIME VARYING ELECTRIC FIELD

A. Electrophoresis

Electrophoresis is the movement of charged particles suspended in a liquid, under the influence of an electric field. If a dc field is applied to a colloidal solution, in a short time the velocity of the particles reaches a constant which is proportional to the strength of the field. The velocity per unit strength of the applied electric field is defined as the electrophoretic mobility of the particles. Usually the mobilities of the individual components in a mixture are different which fact is utilized as the elementary separation effect for the electrophoresis processes.

In recent years, the development of the electrophoresis processes has shown the increasing potential of this method in analysis and separation of biochemical and chemical mixtures, especially for proteins and polymers. A review for the theory and application of the existing electrophoresis processes may be found in references (6,7).

A process which may be considered in the category of induced transport will be briefly discussed here. This forced flow electrophoresis was developed by Bier (6,7) in 1959. The apparatus employed by this process is illustrated in Fig. 10. It shows the expanded side view of a single electrophoretic cell defined by two membranes A and A', and containing the filter B which divides the cell into two compartments. The colloidal solution is fed by a volumetric flow rate \( V_1 \) into the left compartment and part of it is forced by a pressure gradient and suitable pumping arrangement to flow through the filter
FIGURE 10: EXPANDED SIDE VIEW OF A ELECTROPHORETIC CELL FOR FORCED FLOW ELECTROPHORESIS.
and is collected as $V_3$. Simultaneously an electric field is applied in the direction orthogonal to the filter causing all negatively charged particles migrate toward the left compartment of the cell. It is obvious if this electrophoretic flow rate $V_o$ of negatively charged particles is equal to or greater than that along the liquid flowing through the filter $V_f$, no negatively charged particle which is fed into the left compartment will flow through the filter. That is, the outlet $V_3$ will carry only positively charged particles or isoelectric ones, and all negatively charged particles will be carried out through the outlet $V_2$ at the bottom (see Fig. 10).

This separation effect is caused by the transport induced by the coupling of the counter-current flow and the parent transport forced by a time invariant electric field.

B. Electrophoresis with Time Periodic Electric Field - Molecular Approach

The mathematical models for a novel process in which the parent transport is forced by time periodic electric field will be developed. The apparatus of this process consists of two parallel plates with colloidal liquid between them (Fig. 11). The following assumptions are made at first and the effects due to their non-validity will be discussed later.

(a) The velocity profile is linear in the position variable $x$ at any time. This condition is satisfied if the flow is laminar and if $d^2/\nu$ is sufficiently small compared to a characteristic time describing the movement of the plate, where $d$ is the distance between two plates and $\nu$ is the kinematic viscosity of the colloidal liquid. In case of harmonic movement the characteristic time is the primitive period.
FIGURE II  APPARATUS FOR PERIODIC FLOW ELECTROPHORESIS.
(b) Effects due to permeability or impermeability of the plates for charged particles have not to be considered. This condition is satisfied if the amplitude of the displacement of the charged particles in the x-direction is sufficiently small compared to the plate distance d.

(c) Diffusivity of the particles in x and z directions can be neglected. Roughly speaking this condition will be satisfied if the transport due to electrophoresis is sufficiently large compared to the transport due to diffusion. A quantitative condition will be developed later.

Assumed now that these assumptions are satisfied and consider the following operation: the upper plate moves periodically parallel to the lower plate which is at rest such that the displacement $\Delta$ of the upper plate is a periodic function of time, that is

$$\Delta(t + \tau) = \Delta(t) \quad \text{for all } t \quad (4.1)$$

A time periodic electric field $E$ with the same period $\tau$ is maintained between the plates such that at any time the field vector is orthogonal to the plates and independent of position and such that

$$\int_0^\tau E(t) \, dt = 0 \quad (4.2)$$

The relative electrophoretic displacement $\delta$ of a charged particle in the direction orthogonal to the plates is given by

$$\delta(t) = \frac{1}{d} \int_0^t B E(t) \, dt \quad (4.3)$$

where $B$ is the electrophoretic mobility of the charged particles.

Obviously $\delta$ is a periodic function of $t$ with period $\tau$. By assumption
The maximum relative displacement \( |\delta|_{\text{max}} \) is small compared to 1.

The velocity \( v \) of the fluid between the plates is also a periodic function of \( t \) and is, by assumption, linear in \( x \), that is

\[
v(x, t + \tau) = v(x, t) \quad \text{for all } x, t \quad (4.4)
\]

with boundary conditions

\[
v(d, t) = \frac{d\Delta}{dt} \quad (4.5)
\]

\[
v(0, t) = 0 \quad (4.6)
\]

Since \( \Delta \) is a periodic function and because of linearity assumption

\[
\int_0^\tau v(x, t) \, dt = 0 \quad \text{for all } x \quad (4.7)
\]

A charged particle which is at position \( x_0 \) at \( t=0 \) is at position \( x_0 + \delta(t)d \) at time \( t \) due to electrophoretic transport. Because of the linearity of \( v \) in \( x \), the velocity of the particle in \( z \)-direction at time \( t \) is given by

\[
w(x_0, t) = v(x_0, t) + \left( \frac{\partial v}{\partial x} \right)_{x=x_0} + \delta(t) \, d \quad (4.8)
\]

Averaging \( w \) over period and position gives the induced velocity \( w^* \) in \( z \)-direction (Because the average fluid velocity vanishes, the induced velocity of the charged particle is identical with the average velocity of them)

\[
w^* = \frac{1}{d \tau} \int_{t=0}^{\tau} \int_{x=0}^{d} w(x, t) \, dt \quad (4.9)
\]

From (4.5) through (4.9)

\[
w^* = \frac{1}{\tau} \int_{t=0}^{\tau} \delta(t) \Delta(t) \, dt \quad (4.10)
\]
Equation (4.10) is identical to equation (3.17) and the induced velocity \( w^* \) can be represented by the area of a loop in the \( \Delta - \delta \) diagram as in the case discussed in the previous chapter.

The induced transport can be utilized for separation process in two different ways. In case of impulse operation the mixture to be separated would be at \( t=0 \) confined to a small interval of \( z \). If the constituents of the mixture have different electrophoretic mobility, their induced velocity is different and therefore concentration zones corresponding to the pure components of the mixture will separate after sufficiently long operation. It can be seen from (4.10) that the induced velocity can be made arbitrarily large for given electric field strength by making the amplitude of the plate movement sufficiently large provided that the flow is still laminar. The ratios of the induced velocities, however, are given by the ratios of the mobilities. In case of steady operation there will be two reservoirs connected by the plates as shown in Fig. 11. To one reservoir the mixture to be separated is added and products are withdrawn from both reservoirs. It is assumed that the two components to be separated are one charged and the other isoelectric. This situation usually can be obtained by properly adjusting the pH value of the buffer solution used close to the one of the isoelectric points of the components provided that the isoelectric points are not identical for the components to be separated. Then by choosing \( \Delta \) properly, only charged component can move from the feed reservoir to the other reservoir by induced transport and thus to be withdrawn from this reservoir. The isoelectric component will remain in the original reservoir and then to be withdrawn.
C. Continuums Approach

If the effects of diffusion are taken into account, the approach by application of continuums transport theory will be theoretically simpler. The equation governs the transport of the charged component is given by

$$\frac{\partial c}{\partial t} = -BE(t)\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} - v(x,t)\frac{\partial c}{\partial z} + D\frac{\partial^2 c}{\partial z^2} \quad (4.11)$$

where $D$ is the molecular diffusivity.

As discussed in the previous chapter, if the distance between the two reservoirs is far enough, then the condition in the conduit will be determined by the condition in one of the reservoirs, except the perturbation zone adjacent to the other reservoir. That is, for a component with $w^* > 0$ the average concentration of this component in the conduit will be decided by that in the left reservoir. Of course, this argument will be correct only if the concentration in the reservoir is kept constant. Therefore $c$ may be considered as $z$-invariant in $(4.11)$. That is, the equation $(4.11)$ can be replaced by

$$\frac{\partial c}{\partial t} = - BE(t)\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} \quad (4.12)$$

If the plates are impermeable for the particles the boundary conditions are given by

$$BE(t)\frac{\partial c}{\partial x} - D\frac{\partial c}{\partial x} = 0 \quad \text{at } x = 0, x = d \quad (4.13)$$

Of these equations, solutions periodic in $t$ are of interest, i.e.

$$c(x, t+\tau) = c(x, t) \quad \text{for all } x, t \quad (4.14)$$
The induced transport \( \bar{q} \) associated with such a solution is given by

\[
\bar{q} = \frac{1}{d \tau} \int_{t=0}^{\tau} \int_{x=0}^{d} v(x, t) c(x, t) \, dx \, dt
\]

(4.15)

The induced velocity \( \bar{w} \) is given by

\[
\bar{w} = \frac{\bar{q}}{\bar{c}}
\]

(4.16)

where \( \bar{c} \) is the average concentration in the conduit, that is

\[
\bar{c} = \frac{1}{d \tau} \int_{t=0}^{\tau} \int_{x=0}^{d} c(x, t) \, dx \, dt
\]

(4.17)

For the approximate integration of the partial differential equation (4.12) the following transformations are introduced

\[
\xi = d - x
\]

(4.18)

\[
y = (c - \bar{c}) / \bar{c}
\]

(4.19)

From this, (4.12) and (4.13) one obtains

\[
\frac{\partial y}{\partial t} = B E(t) \frac{\partial y}{\partial \xi} + D \frac{\partial^2 y}{\partial \xi^2}
\]

(4.20)

\[
B E(t) y + D \frac{\partial y}{\partial \xi} = - B E(t) \quad \text{at} \quad \xi = 0, d
\]

(4.21)

For the following discussion, we should move the plate at \( \xi = d \) to \( \xi = \infty \) and it will be shown later how this modified problem is connected with the real one. The second boundary condition for the modified problem is then assumed to be

\[
\lim_{\xi \to \infty} y(\xi, t) = 0
\]

(4.22)

Physically equations (4.20) and (4.21) describe a system in which
there is a time periodic source at $\xi = 0$ with time average source strength equal to zero. Material is transported to and from this source by diffusion and by a convective mechanism (term $BEy$) in which the time average of the convective velocity ($BE$) is zero. One should expect that in such a situation at any time $|y|$ decreases with increasing $\xi$ very fast if $\xi$ is larger than a critical value. This value will depend on $D$, $\tau$, and on the amplitude of $BE$. This assumption will be justified later by the numerical solution of (4.20).

In any practical situation of interest the conditions

$$\frac{D \tau}{d^2} \ll 1 \quad \frac{BE_m \tau}{d} \ll 1 \quad (4.23)$$

are always satisfied and therefore $|y|$ is not very small only in intervals adjacent to the plates which are small compared to $d$. That is the concentration is affected by the forcing only in small intervals adjacent to the plates, $c$ is constant in the bulk of the liquid between the plates. For this reason the perturbation in the fluid associated with each plate does not interact each other and the situation near the plate can be studied by assuming semi-infinite system.

The differential equation (4.20) and boundary condition (4.21) are made dimensionless and then integrated numerically to obtain the periodic solution. The result of an example in which $E$ is a sinusoidal function is shown in Fig. 12. It shows that in the region of which $\xi$ is larger than a critical value (about 2.5 times of $BE_m \tau$ in this case, where $E_m$ is the amplitude of function $E$) $y$ is almost zero at any time. The value of $y$ inside the perturbation region of which $\xi$ is less than $BE_m \tau$ oscillates vigorously due to the source term at $\xi = 0$ and the convective mechanism. This result is quite consistent
FIGURE 12: CONCENTRATION PERTURBATION NEAR UPPER PLATE ($\xi = 0$)
with the previous discussion.

As the assumption is valid, the induced velocity can be calculated without analytically integrating the partial differential equation (4.20). From (4.15) and (4.19) it follows that

\[
\bar{q} = \frac{c}{d \tau} \left[ \int_0^\tau \int_0^d v(x, t) y(d-x, t) \, dx \, dt \right. \\
+ \left. \int_0^\tau \int_0^d v(x, t) \, dx \, dt \right] 
\]

(4.24)

The second integral vanishes since \( v \) is the time derivative of a time periodic function. Because \( y \) approaches zero outside a small interval next to \( x=d \) and because of \( v=0 \) at \( x=0 \), one can write

\[
\bar{q} = \frac{c}{d \tau} \int_0^\tau v(d, t) \int_{\xi=0}^{\xi=\infty} y(\xi, t) \, d\xi \, dt 
\]

(4.25)

By integrating (4.20) with respect to \( \xi \) from \( \xi=0 \) to \( \xi=\infty \) under conditions of (4.21) and (4.22) it yields

\[
\frac{d}{dt} \int_{\xi=0}^{\xi=\infty} y(\xi, t) \, d\xi = B E(t) 
\]

(4.26)

Recall that the relative electrophoretic displacement is defined by (4.3), then it follows that

\[
\int_{\xi=0}^{\xi=\infty} y(\xi, t) \, d\xi = \delta(t) \, d + \text{constant} 
\]

(4.27)

By putting (4.27) into (4.25) \( \bar{q} \) is expressible in form of

\[
\bar{q} = \frac{c}{d \tau} \left( \int_0^\tau \delta(t) \, v(d, t) \, dt + \text{constant} \right. \int_0^\tau v(d, t) \, dt \left. \right) 
\]

(4.28)

Once again the second integral vanishes and \( v(d, t) \) is identical to \( \Delta(t) \), therefore it follows from (4.16) and (4.28) the equation (4.10) appears again.
It will be noted that in the molecular approach the velocity of an individual particle is averaged over the period and that this result is an induced velocity for every particle in the conduit. In the continuums approach the flux of particles is averaged at a fixed position and this result is an average flux which is zero everywhere except in the small region adjacent to the upper plate. There is, of course, no contradiction in this since the averaging procedure is different in both cases. This situation is made clear in Fig. 13 where ideal paths of two individual particles during a period are traced out for bang-bang forcing. The transports indicated by a and b cancel each other in the continuums approach.

D. Effects of Plate Permeability

The molecular approach is employed to study effects on the induced velocity due to plate permeability. It is assumed that the size of the charged particles under consideration is small compared to that of the pores of the plates such that the particles can penetrate freely through the plates. Furthermore if a particle has penetrated one of the plates it will be assumed that this particle possesses the same velocity in z-direction as the plate does. The particles which are able to reach the upper plate are which have their initial x-position between \( d(1 - \delta_{\text{max}}) \) and \( d \), and the particles which are able to reach the lower plate are which have their initial x-position between \( 0 \) and \( -d \delta_{\text{min}} \), where \( \delta_{\text{max}} \) and \( \delta_{\text{min}} \) are the maximum and minimum of the function \( \delta \). These two groups are shown in Fig. 14 by two shadow areas adjacent to the plate which they can reach.

Therefore the velocity of the particles which have the initial
FIGURE 13: IDEAL PATHS FOR TWO PARTICLES (A,B) DURING A PERIOD BY BANG-BANG FORCING.
FIGURE 14: THE REGIONS IN WHICH CHARGED PARTICLES MAY REACH THE ADJACENT PLATE.
position \( x_0 \) and can reach the upper plate is given by

\[
w(x_0, t) = v(x_0, t) + \left( \frac{\partial v}{\partial x} \right)_{x=x_0} \delta(t) \quad \text{for } 0 \leq t \leq t_1(x_0)
\]

\[
= \Delta(t) \quad \text{for } t_1(x_0) \leq t \leq t_2(x_0)
\]

\[
= v(x_0, t) + \left( \frac{\partial v}{\partial x} \right)_{x=x_0} \delta(t) \quad \text{for } t_2(x_0) \leq t \leq \tau
\]

\[(4.29)\]

where \( t_1(x) \) and \( t_2(x) \) are the solutions of algebraic equation

\[
\delta(t) = (d - x) / d \quad \text{(4.30)}
\]

Similarly, for the particles which may reach the lower plate, the velocity is given by

\[
w(x_0, t) = v(x_0, t) + \left( \frac{\partial v}{\partial x} \right)_{x=x_0} (t) \quad \text{for } 0 \leq t \leq t_3(x_0)
\]

\[
= 0 \quad \text{for } t_3(x_0) \leq t \leq t_4(x_0)
\]

\[
= v(x_0, t) + \left( \frac{\partial v}{\partial x} \right)_{x=x_0} (t) \quad \text{for } t_4(x_0) \leq t \leq \tau
\]

\[(4.31)\]

where \( t_3(x) \) and \( t_4(x) \) are the solutions of algebraic equation

\[
\delta(t) = -x / d \quad (4.32)
\]

Certainly it must be assumed that each of the equations (4.30) and (4.32) has at most two non-identical solutions in one period, otherwise a complicate situation will be involved. The velocity of the particles which do not reach the plates during the period is still given by (4.8). Again averaging the velocity over the period and position gives the induced velocity. Putting (4.29), (4.31) and (4.8) into (4.9) yields that
\[
w^* = \frac{1}{dT} \left( \int_0^{\delta_{\text{min}}} \int_0^{t_3} (v(x,t) + \frac{\partial v}{\partial x} \delta(t) dt) dx + \int_{t_4}^{\delta_{\text{max}}} \int_0^T (v(x,t) + \frac{\partial v}{\partial x} \delta(t) dt) dx \\
+ \int_0^{d(1-\delta_{\text{max}})} (v(x,t) + \frac{\partial v}{\partial x} \delta(t) dt) dx \\
+ \int_0^{d(1-\delta_{\text{min}})} (\int_0^{t_1} (v(x,t) + \frac{\partial v}{\partial x} \delta(t) dt) + \int_{t_1}^{t_2} \Delta(t) dt) dx \\
+ \int_{t_2}^T (v(x,t) + \frac{\partial v}{\partial x} \delta(t) dt) dx \right)
\] (4.33)

After a mathematical manipulation has been carried out on the right hand side of (4.33) (see Appendix III) the result is given by

\[
w^* = \frac{1}{\tau} \int_0^\tau \delta(t) \Delta(t) dt - \frac{1}{2\tau} \int_0^\tau \delta(t) |\delta(t)| \Delta(t) dt
\] (4.34)

Comparing with (4.10) the effect due to the plate permeability is given by

\[
w_p^* = \frac{1}{2\tau} \int_0^\tau \delta(t) |\delta(t)| \Delta(t) dt
\] (4.35)

This integral may be interpreted as the area enclosed by a loop on \(\delta|\delta| - \Delta\) plane. This area is of second order of \(\delta\) compared to that \(w^*\) is of first order of \(\delta\). Since \(|\delta|_{\text{max}}\) is small compared to 1, the permeability of the plates has only considerable small effects on induced velocity.

E. Interaction between Reservoirs

It is interesting to study the case of that the distance \(L\) between two reservoirs connected by the plates is smaller than the amplitude of the plate movement \(\Delta\). In this situation the charged particles in the boundary zone adjacent to the upper plate may travel from one reservoir to the other one even without completing a period.
of operation. Therefore the averaging procedures utilized previously can no longer be applied. It is objective of this section to study the method in evaluating the net flow of a charged component between two reservoirs in this situation at steady state. The following assumptions are being made in addition to those made in IV.B.

1. Both reservoirs are large enough and well mixed such that the bulk concentrations in the reservoirs are kept constant all the time.

2. The fluid velocity is linear in $x$ over the whole range at any time, that is

$$v(x, t) = x \Delta(t) / d$$  \hspace{1cm} (4.36)

3. For the component under consideration the induced velocity $w^*$ defined by (4.10) is positive.

From the second assumption the velocity $w$ of the charged particle which enters the conduit from the left reservoir $R$ at position $x_0$ and at time $t_0$ is given by

$$w(x_0, t_0, t) = \Delta(t) \left( \frac{x_0}{d} + \delta(t) - \delta(t_0) \right)$$ \hspace{1cm} (4.37)

Integrating both sides of (4.37) from $t_0$ to $t$ gives the displacement $s$ of this particle in $z$-direction at time $t$, that is

$$s(x_0, t_0, t) = \left( \frac{x_0}{d} - \delta(t_0) \right) (\Delta(t) - \Delta(t_0))$$

$$+ \int_{t_0}^{t} \delta(t) \Delta(t) \, dt$$ \hspace{1cm} (4.38)

It can be seen from (4.38) that $s$ is linear in $x_0$ and that

$$s(x_0, t_0, t_0 + \tau) = w^* \tau > 0$$ \hspace{1cm} (4.39)

Since $s$ is an integration of a periodic function, from (4.39) the condition
\[ s(x_0, 0, t) \geq 0 \] \hspace{1cm} (4.40)

can be met after a proper transformation on \( t \) coordinate has been made. This means that the particles which are in the conduit \( (x_0 \geq 0) \) at time \( t=0 \) will have non-negative displacement at any time \( t \geq 0 \), and will have a positive displacement \( w^* \tau \) after a period of operation. As the operation continues these particles will move through the conduit and enter the right reservoir \( R_r \).

Therefore as the periodic state is approached the charged particles which leave \( R_\ell \) in the period \([0, \tau]\) and will not return to \( R_\ell \) can be categorized into two groups:

(a) The particles which leave \( R_\ell \) and enter \( R_r \) during the period. That is, for the particle which enters the conduit at position \( x_0 \) and at time \( t_0 \), there exists a \( t_\ell \) in the interval \([t_0, \tau]\) such that the conditions

\[ s(x_0, t_0, t_\ell) \geq L \] \hspace{1cm} (4.41a)

and

\[ s(x_0, t_0, t) \geq 0 \hspace{1cm} \text{for all} \hspace{0.5cm} t \in [t_0, t_\ell] \] \hspace{1cm} (4.41b)

are met.

(b) The particles which leave \( R_\ell \) and remain in the conduit at the end of the period. These particles will eventually enter the right reservoir \( R_r \) after sufficient time of operation. For these particles the condition

\[ s(x_0, t_0, t) \geq 0 \hspace{1cm} \text{for all} \hspace{0.5cm} t \in [t_0, \tau] \] \hspace{1cm} (4.42)

must be met.
Thus the fate of every particle which leaves $R_\ell$ in the period $[0, \tau]$ is characterized by a pair of numbers $(x_0, t_0)$. On $x_0-t_0$ plane the areas corresponding to the particle groups (a) and (b) are denoted by $A_a$ and $A_b$, respectively (see Fig. 15). The amount of the charged component lost by the left reservoir $R_\ell$ in a period of operation is then given by

$$M_\ell = W \int_{A_a} c_\ell v(x_0, t_0) \, dA + \int_{A_b} c_\ell v(x_0, t_0) \, dA$$  \hspace{1cm} (4.43)

where $W$ is the width of the conduit and $c_\ell$ is the bulk concentration of the component in $R_\ell$.

Similarly the particles which leave the right reservoir $R_\tau$ in the period and will not return to it are the particles which are able to reach $R_\ell$ in the period. That is, if a particle leaves $R_\tau$ at position $x_0$ and at time $t_0$, then there exists a $t_\tau$ in the interval $[t_0, \tau]$ such that for this particle

$$s(x_0, t_0, t_\tau) \leq -L$$  \hspace{1cm} (4.44a)

and

$$s(x_0, t_0, t) \leq 0 \quad \text{for all } t \text{ in } [t_0, t_\tau]$$  \hspace{1cm} (4.44b)

The particles which leave $R_\tau$ and remain in the conduit at the end of the period will eventually return to $R_\tau$ and will not be counted as lost by $R_\tau$. Thus the amount of the charged component lost by $R_\tau$ in a period of operation is given by

$$M_\tau = - W \int_{A_0} c_\tau v(x_0, t_0) \, dA$$  \hspace{1cm} (4.45)

where the area $A_0$ on $x_0-t_0$ plane (Fig. 15) corresponds to the particle group which satisfies the conditions (4.44 a,b), and $c_\tau$ is the bulk
FIGURE 15: AREAS SATISFYING CONDITIONS (4.41), (4.42) AND (4.44) RESPECTIVELY.
concentration of the component in \( R_\tau \). The net mass transfer of the component between two reservoirs at periodic state is then given by

\[
M_{\ell R} = M_{\ell} - M_R
\]  

(4.46)

It has been demonstrated here that the mass transfer in this operation can be evaluated without the detailed knowledge of the concentration distribution in the conduit.

In general the integrations of (4.43) and (4.45) may involve the difficulty in formulating the boundaries of the areas \( A_a, \ A_b \) and \( A_c \) which correspond to the curves \( aa' \), \( bb' \) and \( cc' \) in Fig. 15. However for some cases such as bang-bang or simple harmonic forcing of which the boundaries may be formulated explicitly the integrations may be performed by conventional method. For instance, if the forcing functions are given by

\[
\Delta(t) = \Delta_m (1 - \cos \omega t) \tag{4.47}
\]

\[
E(t) = E_m \cos \omega t \tag{4.48}
\]

Then the equations for the curves \( aa' \), \( bb' \) and \( cc' \) are given by

\[
x_0(t_0) = \frac{dL}{\Delta_m} \frac{BE_m}{2\omega} \frac{(1 - \cos \omega t_0 + 2) \sin \omega t_0 - \omega t_0}{\cos \omega t_0 + 1} \tag{4.49}
\]

\[
x_0(t_0) = \frac{BE_m}{\omega} \left( \sin \omega t_0 + \frac{(\cos \omega t_0 \sin \omega t_0 + 2\pi - \omega t_0)}{2(1 - \cos \omega t_0)} \right) \tag{4.50}
\]

\[
x_0(t_0) = \frac{dL}{\Delta_m} \frac{BE_m}{2\omega} \frac{(2 - \cos \omega t_0) \sin \omega t_0 + 2\pi - \omega t_0}{(1 - \cos \omega t_0)} \tag{4.51}
\]
respectively. The integrations can be performed by numerical method.

In case that the boundaries can not be formulated explicitly, a simple Monte Carlo method (11) can be used to approximated the integrations. \( N \) pairs of numbers \((x^i_{0}, t^i_{0})\) with rectangular distribution in the rectangle \(0 \leq x_{0} \leq d, 0 \leq t \leq \tau\) are chosen as random numbers. The relative maximums and minimums of the displacement \( s(x^i_{0}, t^i_{0}, t) \) with respect to time \( t \) in the interval \((t^i_{0}, \tau)\) are then located and their values are calculated. If \( w \) is continuous, these relative extrema will be at \( t = \varepsilon^i \) such that the condition

\[
w(x^i_{0}, t^i_{0}, \varepsilon^i) = 0
\]

is met, since \( w \) is the time derivative of \( s \). Let \( \varepsilon^1, \varepsilon^2, \ldots, \varepsilon^{p-1} \) denote the increasing sequences of the solutions of (4.52) in the interval \((t^i_{0}, \tau)\) and \( \varepsilon^p \) be the end of the period \( \tau \), where \( p \) is an integer depends on the values of \( x^i_{0} \) and \( t^i_{0} \). The decision function associated with \((x^i_{0}, t^i_{0})\) is defined by

\[
\Phi^i = 1 \quad \text{if (1) there exists an } \varepsilon^i \text{ such that}
\]

\[
s(x^i_{0}, t^i_{0}, \varepsilon^i) \geq L \text{ and that}
\]

\[
s(x^i_{0}, t^i_{0}, \varepsilon^j) \geq 0 \text{ for all } j < n
\]

or \( (2) \ L > s(x^1_{0}, t^1_{0}, \varepsilon^j) \geq 0 \text{ for all } j \leq p \)

\[
\Phi^i = 0 \quad \text{if } \Phi^i \neq 1
\]

Then \( M_{\ell} \) may be approximated by the summations

\[
M_{\ell} = \frac{dW_{\ell}}{N} \sum_{i=1}^{N} \Phi^i \ell (x^i_{0}, t^i_{0})
\]

Similarly the other decision function which is correspondent to \( M_{\tau} \) is defined by
\[ \psi^1 = 1 \quad \text{if there exists an } \varepsilon_n^1 \text{ such that} \\
\quad s(x_0^1, t_0^1, \varepsilon_n^1) \leq -L \text{ and that} \\
\quad s(x_j^1, t_0^1, \varepsilon_j^1) \leq 0 \quad \text{for all } j < n \]
\[ \psi^1 = 0 \quad \text{if } \psi^1 \neq 1 \quad (4.54a) \]

\[ M_r \text{ then may be approximated by} \]
\[ M_r = -\frac{dW_T}{N} \sum_{i=1}^{N} \psi^1 c_r v(x_0^1, t_0^1) \quad (4.54b) \]

F. Heating Effects

The heat generated by the passing of electric current through electrolyte usually is a main problem encountered in the scaling up of an electrophoresis process. Since it becomes increasingly difficult to dissipate the heat generated as the size of apparatus becomes larger. Especially in the case that the substances to be separated are sensible to heat and in the case that an undesired convective current may appear due to irregular heating which makes separation impossible. Therefore an adequate cooling is necessary to the utilization of electrophoresis process.

To study the heating effects associated with parametric pumping by electrophoresis, it is assumed that the temperature at both plates may be kept at the same constant temperature \( \theta_p \) by some cooling method. The temperature distribution between two plates is governed by
\[ \rho c_p \frac{\partial \theta}{\partial t} = h \frac{\partial^2 \theta}{\partial x^2} + H(t) \quad (4.55) \]
and subjected to the boundary conditions
\[ \theta = \theta_p \quad \text{at } x = 0, d \quad (4.56) \]
It is also assumed that \( H \), the heat generated per unit time and unit volume is position independent. \( h \) is the thermal conductivity, \( \rho \) is the density and \( C_p \) is the heat capacity of the electrolyte, they are all assumed to be constant. \( H(t) \) is relative to \( E(t) \) by

\[
H(t) = \sigma E^2 / J
\]  

(4.57)

where \( \sigma \) denotes the electric conductivity of the fluid and \( J \) is the Joule's constant.

Suppose \( E(t) \) is harmonic, for instance, it is given by (4.48). The periodic solution of (4.55) subjected to (4.56) is given by

\[
\theta(t, x) = \theta_p + \frac{\sigma E_m^2 d^2}{16 h J} \left( (1 - (2x - d)^2)/(2d F_o) \right) + 4F_o \Re(e^{i2\omega t} \mathcal{F}(x) e^{i2\omega t})
\]  

(4.58)

where \( \mathcal{F}(x) \) is defined by

\[
\mathcal{F}(x) = \frac{\cosh((1+i)(2x-d)/(2d F_o))}{\cosh((1+i)/(2d F_o))} - 1
\]  

(4.59)

and where \( i^2 = -1 \) and \( F_o \) is Fourier constant defined by

\[
F_o = \frac{h}{\omega \rho C_p \omega^2}
\]  

(4.60)

The maximum temperature difference, \( \Delta \theta_m \), between plate temperature and temperature of the electrolyte is then given by

\[
\Delta \theta_m = \frac{E_m^2 d^2}{16 h J} \left( 1 + 4\sqrt{2} F_o \frac{\cosh(1/2 \sqrt{F_o}) - \cos(1/2 \sqrt{F_o})}{(\cosh(1/\sqrt{F_o}) - \cos(1/\sqrt{F_o}))^{3/2}} \right)
\]  

(4.61)

The expression in the bracket approaches 1 if \( F_o \) is small and approaches 2 if \( F_o \) is large. For any \( F_o \) (see Fig. 16)
\[
\left( \frac{16\hbar J}{\sigma E^2 m d^2} \right) \Delta \theta_m
\]

**Figure 16: Maximum Temperature Difference vs. \( F_0 \)**
\[
\frac{\int E_m^2 \, d^2}{16 \, h \, J} < \Delta \theta_m < \frac{\int E_m^2 \, d^2}{8 \, h \, J}
\] (4.62)

G. Chapter Conclusions

In this chapter, different models (molecular approach and continuum approach) have been established to study the proposed process - parametric pumping by time periodic electric field. The results obtained by different approaches are identical; there is an induced velocity in z-direction due to periodic forcing and it is given by \((4.10)\). Furthermore, it is interesting to note that in each model the net mass transfer can be evaluated without detailed knowledge of the concentration distribution in the conduit. This may avoid the difficulty in solving the partial differential equation which governs the transport of the charged component in the conduit.
<table>
<thead>
<tr>
<th>Roman Letters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Hold up ratio of phase 2 to phase 1</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Cross-sectional area occupied by the $i^{th}$ phase. See text under (2.15)</td>
</tr>
<tr>
<td>$a$</td>
<td>Row vector with the elements $a_i$</td>
</tr>
<tr>
<td>B</td>
<td>Electrophoretic mobility</td>
</tr>
<tr>
<td>$\hat{B}$</td>
<td>Width of concentration peak</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Concentration of the tracer in the $i^{th}$ phase</td>
</tr>
<tr>
<td>$\bar{c}_i$</td>
<td>Average of $c_i$ over one period</td>
</tr>
<tr>
<td>$\bar{c}$</td>
<td>Average concentration of the tracer over period and cross-section of the column</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity</td>
</tr>
<tr>
<td>d</td>
<td>Distance between two parallel plates</td>
</tr>
<tr>
<td>D</td>
<td>Molecular diffusivity</td>
</tr>
<tr>
<td>$D^*$</td>
<td>Diffusivity Matrix</td>
</tr>
<tr>
<td>$D^*_T$</td>
<td>Dispersion coefficient</td>
</tr>
<tr>
<td>$D_T$</td>
<td>Taylor contribution to dispersion coefficient</td>
</tr>
<tr>
<td>E</td>
<td>Strength of electric field</td>
</tr>
<tr>
<td>$E_m$</td>
<td>Amplitude of the function $E$</td>
</tr>
<tr>
<td>F</td>
<td>Volumetric feed or product flow rate</td>
</tr>
<tr>
<td>$F_0$</td>
<td>Fourier constant defined by (4.60)</td>
</tr>
<tr>
<td>g</td>
<td>Function defined by (2.78)</td>
</tr>
<tr>
<td>H</td>
<td>Heat generated by electric current per unit time and unit volume</td>
</tr>
<tr>
<td>J</td>
<td>Joule constant</td>
</tr>
<tr>
<td>$k_{ij}$</td>
<td>Mass transfer coefficient of the interface between the phases i and j</td>
</tr>
</tbody>
</table>
\( K \)  
Ratio of tracer concentration in phase 2 to that in phase 1 at equilibrium

\( \overline{K} \)  
Time average of \( K \)

\( K_i \)  
Equilibrium constant associated with the \( i \)th phase

\( K \)  
Column vector with the elements \( K_i \)

\( L \)  
Distance between two reservoirs

\( n^{(n)} \)  
See equation (2.7)

\( M_{\xi r} \)  
Mass transfer between the reservoirs \( R_\xi \) and \( R_r \)

\( N \)  
Number of the phases in the column

\( n \)  
Unit normal of the interface

\( P_i \)  
Probability of finding a tracer molecule in phase \( i \)

\( q \)  
Flux of the solute in the column

\( \overline{q} \)  
Time average of \( q \)

\( r \)  
A positive parameter less than 1

\( s \)  
Displacement of tracer molecule

\( S \)  
Function defined by (2.19a)

\( t \)  
Time

\( u \)  
Periodic part of \( v_1 \)

\( u_1 \)  
Value assumed by \( u \) in subperiod 1

\( u_2 \)  
Value assumed by \( u \) in subperiod 2

\( v_{zi} \)  
Axial velocity of the \( i \)th phase

\( \overline{v_z} \)  
Diagonal matrix defined by (2.19a)

\( v_z \)  
Average of axial velocity over the cross section of the column with \( K_i \) as weight

\( v_{zri} \)  
Relative axial velocity of the \( i \)th phase with respect to a reference phase with velocity \( v_z \)

\( \overline{v_{zr}} \)  
Diagonal matrix defined by (2.32)

\( v^* \)  
Asymptotic peak velocity of tracer concentration distribution
\( v_i \) Axial velocity of fluid phase in the fixed bed column
\( \overline{v_i} \) Time average of \( v_i \)
\( V \) Volumetric flow rate
\( w \) Axial velocity of the tracer
\( \overline{w} \) Mean velocity of the tracer
\( w^* \) Induced velocity of the tracer
\( W \) Width of the conduit
\( x \) Axis orthogonal to \( z \)
\( x_0 \) Initial \( x \)-position of charged particle
\( y \) Concentration variable
\( Y \) Matrix defined by \((2.20a,b)\)
\( z \) Axis along the column

**Greek Letters**

\( \alpha \) A constant scalar
\( \delta \) Function defined by \((3.5)\)
\( \overline{\delta} \) Time average of \( \delta \)
\( \Delta \) Periodic movement of fluid phase or of upper plate
\( \Delta_m \) Amplitude of \( \Delta \)
\( \xi_n^i \) Solutions of the equation \((4.52)\)
\( \zeta \) See \((2.62)\)
\( \theta \) Temperature
\( \mu^{(n)} \) \( n \)th moment
\( \nu \) Kinematic viscosity
\( \xi \) See \((4.18)\)
\( \rho \) Density
\( \sigma \) Electric conductivity
$\tau$ Period of the periodic forcing functions

$\psi$ Periodic solution of the equation (2.53)

$\psi'$ Periodic solution of the equation (2.49)

$\phi^1$ Decision function

$\psi$ Periodic solution of the equation (2.17a)

$\psi^1$ Decision function

**Script Letters**

$\mathcal{F}$ Function defined by (4.59)

$\mathcal{L}_{ij}$ Area of the interface between the phases $i$ and $j$ per unit length of column
REFERENCES


APPENDIX I. SOME ASPECTS OF THE LINEAR SYSTEMS IN CHAPTER II

A. Eigenvalues and Null Space of $Y$

The matrix $Y$ can be written as

$$ Y = A \ R \ F $$

(I.1)

where the matrices $A$ and $F$ are given by

$$ A = \text{diag} \left\{ \frac{1}{a_1}, \frac{1}{a_2}, \ldots, \frac{1}{a_N} \right\} $$

(I.2)

$$ F = \text{diag} \left\{ \frac{1}{K_1}, \frac{1}{K_2}, \ldots, \frac{1}{K_N} \right\} $$

(I.3)

and where $R$ is a $N \times N$ symmetric matrix with its elements given by

$$ R_{ij} = k_{ij} \ell_{ij} $$

(I.4a)

$$ R_{ii} = - \sum_j k_{ij} \ell_{ij} $$

(I.4b)

Evidently $R$ has $\underline{e}$ as left and $\underline{e}^T$ as right eigenvectors associated with the eigenvalue 0, where $\underline{e}$ is given by

$$ \underline{e} = (1, 1, \ldots, 1) $$

(I.5)

From (I.1) it can be seen that the vectors $a$ and $k$ which are given by

$$ a = e A^{-1} , \quad k = F^{-1} e^T $$

(I.6)

are the left and right eigenvectors associated with eigenvalue 0 of $Y$ respectively. Introduce the diagonal matrices $A^{\frac{1}{2}}$ and $F^{\frac{1}{2}}$ defined by

$$ A^{\frac{1}{2}} A^{\frac{1}{2}} = A , \quad A^{\frac{1}{2}} = \text{diag} \left\{ \frac{1}{\sqrt{a_1}}, \frac{1}{\sqrt{a_2}}, \ldots, \frac{1}{\sqrt{a_N}} \right\} $$

(I.7a)

$$ F^{\frac{1}{2}} F^{\frac{1}{2}} = F , \quad F^{\frac{1}{2}} = \text{diag} \left\{ \frac{1}{\sqrt{K_1}}, \frac{1}{\sqrt{K_2}}, \ldots, \frac{1}{\sqrt{K_N}} \right\} $$

(I.7b)
It follows from (I.7) and (I.1) that

\[ F^{\frac{1}{2}} A^{\frac{1}{2}} Y F^{\frac{1}{2}} A^{\frac{1}{2}} = F^{\frac{1}{2}} A^{\frac{1}{2}} R F^{\frac{1}{2}} A^{\frac{1}{2}} \]  \hspace{1cm} (I.8)

where \( F^{\frac{1}{2}} \) and \( A^{\frac{1}{2}} \) are the inverses of the matrices \( F^{\frac{1}{2}} \) and \( A^{\frac{1}{2}} \) respectively.

Let the matrices \( T \) and \( U \) be defined by

\[ T = F^{\frac{1}{2}} A^{\frac{1}{2}} \] \hspace{1cm} (I.9a)

\[ U = F^{\frac{1}{2}} A^{\frac{1}{2}} R A^{\frac{1}{2}} F^{\frac{1}{2}} \] \hspace{1cm} (I.9b)

then there exists a similarity transformation (note that diagonal matrices commute)

\[ T^{-1} Y T = U \] \hspace{1cm} (I.10)

This means that \( Y \) and \( U \) will have the same eigenvalues. From (I.9b) it follows that \( U \) is symmetric because \( R \) is symmetric and \( A^{\frac{1}{2}} \) and \( F^{\frac{1}{2}} \) are diagonal. Therefore \( Y \) as well as \( U \) has only real eigenvalues.

Furthermore, \( R \) is negative semi-definite since

\[ b^T R b = -\frac{1}{2} \sum_i \sum_j k_{ij} \ell_{ij} (b_i - b_j)^2 \]  \hspace{1cm} (I.11)

Since \( U \) is congruent to \( R \) it is also negative semi-definite so that all eigenvalues of \( U \) and consequently of \( Y \) must be non-positive.

The multiplicity of the zero eigenvalue will now be studied. Since \( R \) and \( Y \) are equivalent to each other the dimension of their null spaces must agree. It will be shown that \( R \) has one-dimensional null space if a certain assumption concerning the connection of the subregions is made. The assumption which will be made is that there is no proper subset of subregions which is isolated in the sense that it does not
interact with its complement. In other words there is $k_{ij} \ell_{ij} > 0$ with $i$ being an index belonging to subset considered and $j$ belonging to the complement. It will be shown later that every vector in the null space of $R$ must be either zero (all elements zero), positive (all elements positive) or negative (all elements negative). From this it immediately follows that the dimension of the null space is one. For let $b$ be a non-zero vector in the null space of $R$, then by the above statement $b_i \neq 0$. Since $e$ is a vector in the null space so is $(1/b_i)b - e$, and this vector must be zero because its first element is zero. Thus $b$ is linearly dependent with $e$. In what follows it will be shown that every non-zero vector in the null space of $R$ is either positive or negative. If a vector is non-zero there is at least one non-zero element, if this element is negative we multiply the vector by $-1$ and obtain a positive element. Thus we obtain a null vector $b$ with at least one positive element. It is sufficient to show that all other elements in $b$ are also positive. It will be proceeded by contradicting the opposite assumptions. Assume that the indices of the positive elements form a proper subset $Q$ of the set of the indices. Let $\underline{p}$ denote the vector obtained from summing the row vectors in $R$ belonging to the index set $Q$. Since $b$ is in the null space of $R$

$$p \cdot b = 0 \quad (I.12)$$

The elements of $p$ belonging to indices in $Q$ cannot be all zero since otherwise the collection of subregions corresponding to $Q$ is isolated. The elements with these indices are, of course, all non-positive. Thus

$$p_i \leq 0 \quad i \in Q \quad (I.13a)$$
\[ p_j < 0 \quad \text{for some } j \in Q \quad (I.13b) \]

Also, it is easily seen that

\[ p_i > 0 \quad i \in Q' \quad (I.13c) \]

where \( Q' \) is the complement of \( Q \). According to the assumption

\[ b_i > 0 \quad i \in Q \quad (I.14a) \]
\[ b_j \leq 0 \quad j \in Q' \quad (I.14b) \]

It follows that

\[ p \cdot b < 0 \quad (I.15) \]

which contradicts \( (I.12) \). Therefore the subset of the indices of the positive elements of \( b \) must agree with the index set of \( b' \), and \( b' \) must be positive. From this it follows that \( U \) has one-dimensional null space since it is equivalent to \( R \). Furthermore, since \( U \) is symmetric the algebraic multiplicity of any eigenvalue of \( U \) is equal to its geometric multiplicity and therefore the algebraic multiplicity of the zero eigenvalue of \( U \) is one. Since \( Y \) is similar to \( U \), it must have a zero eigenvalue with geometric and algebraic multiplicity equal to one.

B. The Existence of Periodic Solution for the System \( \dot{\varphi} = Y(t) \varphi + f(t) \)

If \( \Phi(t) \) denotes the principal matrix solution of the homogeneous system

\[ \dot{\varphi} = Y(t) \varphi \quad (I.16) \]

in which \( Y(t) \) is a periodic function of \( t \), the necessary and sufficient condition for \( (I.16) \) to have a periodic solution is that \( \Phi(t) \)
has an eigenvalue of 1 (see Ref. 14). From the definition of the principal matrix solution it follows that

\[ \dot{\Phi}(t) = Y(t) \Phi(t) , \quad \Phi(0) = I \]  \hspace{1cm} (I.17)

where \( I \) is unit matrix. Since \( a \) is the left hand side null vector of \( Y \), it follows from (I.17) that

\[ a \Phi(t) = 0 \]  \hspace{1cm} (I.18)

Integrating both sides of (I.18) from 0 to \( T \) (\( a \) is time invariant) yields

\[ a (\Phi(T) - I) = 0 \]  \hspace{1cm} (I.19)

Since \( a \) is non-zero \( \Phi(T) - I \) must be singular. That is, 1 is an eigenvalue of the matrix \( \Phi(T) \). Therefore there exists a non-trivial periodic solution of period \( T \) for the homogeneous system (I.16).

In what follows it will be assumed that the null space of \( \Phi(T) - I \) is one-dimensional.

The solution of the system

\[ \dot{\varphi} = Y(t) \varphi + f(t) \]  \hspace{1cm} (I.20)

can be written as

\[ \varphi(t) = \varphi_p(t) + \Phi(t) m \]  \hspace{1cm} (I.21)

where \( \varphi_p \) is a particular solution of (I.20) and \( m \) is a time invariant vector. From (I.21) it is easily seen that

\[ \varphi(T) - \varphi(0) = \varphi_p(T) - \varphi_p(0) + (\Phi(T) - I) m \]  \hspace{1cm} (I.22)
The necessary and sufficient condition for the system (I.20) to have a periodic solution of period $T$ is that there exists a non-trivial vector $m$ such that

$$\left( \Phi (T) - I \right) m = - \left( \varphi (T) - \varphi (0) \right) \quad (I.23)$$

It follows from the main theorem of linear algebra that (I.23) will have solution if and only if the condition

$$a \left( \varphi (T) - \varphi (0) \right) = 0 \quad (I.24)$$

is satisfied. Since $\varphi$ satisfies the equation (I.20) it is obvious

$$a \left( \varphi (T) - \varphi (0) \right) = \int_{0}^{T} a \; f(t) \; dt \quad (I.25)$$

This means, the system (I.20) will have a periodic solution of period $T$ if and only if the following condition is met

$$\int_{0}^{T} a \; f(t) \; dt = 0 \quad (I.26)$$
A. Maximum Allowable Average Flow Rate in Left Column Section

Since only the situation that both $u_1$ and $F_\ell$ are positive is of interest, the inequalities (3.42), (3.45) and (3.46) may be interpreted as three convex regions on the first quarter of $F_\ell - u_1$ plane (Fig. 18). The boundaries of these regions are given by the following linear equations:

\[ a_1 u_1 r (\delta_1 - \delta_2) - F_\ell (r \delta_1 + (1-r) \delta_2) = 0 \quad (\text{II.1}) \]

\[ a_1 u_1 - F_\ell + V_{\text{max}} = 0 \quad (\text{II.2a}) \]

\[ a_1 u_1 - F_\ell - V_{\text{max}} = 0 \quad (\text{II.2b}) \]

\[ a_1 u_1 r/(1-r) - F_\ell - V_{\text{max}} = 0 \quad (\text{II.3}) \]

and the ordinates. The straight lines on the $F_\ell - u_1$ plane which correspond to the linear equations (II.1), (II.2a), (II.2b) and (II.3) are denoted by OA, DE, FG and DC\(^1\) (or DC\(^2\), depending on the value of $r \delta_1/(1-r) \delta_2$). The regions which satisfy the inequalities (3.42), (3.45) and (3.46) are the regions under OH, between DE and FH and under DC\(^1\) (or DC\(^2\)) respectively. There are two possible locations for maximum $F_\ell$ in the intersection of these regions, they are:

1. When $\delta_1/\delta_2 \geq (1-r)/r$.

In this situation the equation (II.3) corresponds to DC\(^2\) on Fig. 18, and the intersection of the regions satisfying the inequalities is the triangle OAF. Therefore the maximum $F_\ell$ is equal to the $F_\ell$-ordinate value of point A, which is given by
FIGURE 17: REPRESENTATIONS OF LINEAR EQUATIONS (II.1), (II.2a), (II.2b), AND (II.3).
\[
\left( \frac{F_{\ell}}{\ell} \right)_A = \min r \left( \delta_1 - \delta_2 \right) / \delta_2 \quad (II.4)
\]

2. When \( \delta_1 / \delta_2 \leq (1-r)/r \)

In this situation the equation (II.3) corresponds to DC1 on Fig. 13, and the intersection of the regions satisfying the inequalities is the triangle \( \text{OB}_1C_1 \). Similarly the maximum \( F_{\ell} \) is equal to the \( F_{\ell} \), ordinate value of point \( B_1 \), which is given by

\[
\left( \frac{F_{\ell}}{\ell} \right)_{B1} = \min (1-r) \left( \delta_1 - \delta_2 \right) / \delta_2 \quad (II.5)
\]

A given cyclic operation is characterized by two forcing functions \( \delta(t) \), \( u(t) \) and average flow rate \( F_{\ell} \). If \( \delta_1 \) and \( \delta_2 \) now denote the maximum and the minimum values of the function \( \delta(t) \) that is,

\[
\delta_1 = \max_t \delta(t), \quad \delta_2 = \max_t \delta(t) \quad (II.6)
\]

then there exists a periodic function \( r' \) such that

\[
\delta(t) = \delta_2 + r'(t) \left( \delta_1 - \delta_2 \right) \quad \text{for all } t \quad (II.7a)
\]

and

\[
0 \leq r'(t) \leq 1 \quad \text{for all } t \quad (II.7b)
\]

Consider a bang-bang operation described in III.C of which \( \theta_1, \theta_2 \) and \( r \) are selected such that

\[
\delta(\theta_{1,2}) = \delta_{1,2} \quad (II.8a)
\]

and

\[
r = \frac{1}{T} \int_0^T r'(t) \, dt \quad (II.8b)
\]

The values of \( u_1 \) and \( u_2 \) for this bang-bang operation are chosen such the induced velocity \( w^* \) of the bang-bang operation is equal to that of the given operation, that is
\[ w^* = u_1 r(\delta_1 - \delta_2) = u_2 (r-1)(\delta_1 - \delta_2) = \frac{1}{t} \int_0^T \delta(t) u(t) dt \]  

(II.9)

If this bang-bang operation also bears an average flow rate \( F_e \) then the condition (3.40) is satisfied for both operations. From (II.7a) and (3.13) it follows that

\[ w^* = \frac{(\delta_1 - \delta_2)}{\tau} \int_0^\tau r'(t) u(t) dt \]  

(II.10)

and from (II.7b), (II.8b) and (II.10) it can be shown that

\[ w^* \leq (\delta_1 - \delta_2) r u_{\max} \]  

(II.11a)

\[ w^* \leq (\delta_1 - \delta_2)(r - 1) u_{\min} \]  

(II.11b)

where \( u_{\max} \) and \( u_{\min} \) are the maximum and minimum of the function \( u \) of the given operation, respectively. By putting (II.11) into (II.9), the following conditions are satisfied by the bang-bang operation

\[ u_1 \leq u_{\max} \]  

(II.12a)

\[-u_2 \leq -u_{\min} \]  

(II.12b)

This means, the bang-bang operation described here may allow the same \( F_e \) as the given operation does, but the fluid velocity in the bang-bang operation is always smaller than or equal to the maximum fluid velocity in the given operation. Furthermore, since this bang-bang operation is not necessary the optimal one in its own class, a bang-bang operation which allows larger or equal \( F_e \) can be realized for the same apparatus.
B. Existence of Perfect Separation Operation for Split Problem

It is the object of this section to show that the condition (3.58) can be met by certain operation if the condition (3.56) is satisfied. It will be assumed that $\delta_A(\theta_1) > \delta_A(\theta_2)$ and that a bang--bang operation as described in the section III.C can be approximated. Then the quantities $\frac{w^*_A}{\delta_A}$ and $\frac{w^*_B}{\delta_B}$ are given by

$$w^*_A = \frac{\frac{u_1}{\delta_A}(\delta_A(\theta_1) - \delta_A(\theta_2))}{(r \delta_A(\theta_1) + (1-r) \delta_A(\theta_2))} \quad (II.13a)$$

$$w^*_B = \frac{\frac{u_1}{\delta_B}(\delta_B(\theta_1) - \delta_B(\theta_2))}{(r \delta_B(\theta_1) + (1-r) \delta_B(\theta_2))} \quad (II.13b)$$

by subtracting (II.13b) from (II.13a) it follows that

$$\frac{w^*_A}{\delta_A} - \frac{w^*_B}{\delta_B} = \frac{u_1(r \delta_A(\theta_2) \delta_B(\theta_1) - \delta_A(\theta_1) \delta_B(\theta_2))}{\delta_A \delta_B} \quad (II.14)$$

It should be noted here that $u_1$, the value assumed by the function $u$ in the subperiod 1, can be chosen to be either positive or negative.

If the condition (3.56) is satisfied it is easy to see that the right hand side of (II.14) is non-zero. By properly choosing the sign of $u_1$ the right hand side of (II.14) can be always made positive. That means the condition (3.58) can be met.

C. Asymptotic Expansions for Mean Velocity Under Non-Equilibrium Condition

The cases of very large mass transfer coefficient $k$ and of very small $k$ will be treated separately:

1. In case that $k$ is very large, the asymptotic expansions for
mean velocity can be obtained by a classical method, i.e., repeated integrations by parts. At first the functions \( \psi_0 \) and \( \varphi \) defined by

\[
\psi_0(t, t_1) = \delta(t+t_1) \quad (\text{II.15})
\]

\[
\varphi(t, t_1) = \exp\left(\frac{k \ell}{a} \int_t^{t+t_1} \frac{1}{\delta(t_2)} \, dt_2\right) \quad (\text{II.16})
\]

will be introduced, where \( \delta \) is defined by equation (3.4) and it will be assumed to be \( N^{th} \) order differentiable. From (3.76), (II.15) and (II.16) it follows that

\[
c_1 = \frac{\bar{c}(1+a)}{g(c)} \int_{t_1=0}^{T} \psi_0(t, t_1) \frac{\partial \varphi}{\partial t_1} \, dt_1 \quad (\text{II.17})
\]

Integrating by parts yields

\[
c_1 = \frac{\bar{c}(1+a)}{g(c)} \left( \delta(t+c) \varphi(t, t) - \delta(t) \varphi(t, 0) \right)
\]

\[- \int_{t_1=0}^{T} \varphi(t, t_1) \frac{\partial \psi_0}{\partial t_1} \, dt_1 \quad (\text{II.18})
\]

From the fact that \( \delta \) is a periodic function of \( t \) and from the identities

\[
\varphi(t, T) = g(c), \quad \varphi(t, 0) = 1 \quad (\text{II.19})
\]

it follows that

\[
c_1 = \bar{c}(1+a) \left( \delta(t) - \frac{1}{g(c)} \int_{t_1=0}^{T} \varphi(t, t_1) \frac{\partial \psi_0}{\partial t_1} \, dt_1 \right)
\]

(II.20)

Again the function \( \psi_1 \) defined by

\[
\psi_1(t, t_1) = \delta(t+t_1) \frac{\partial \psi_0}{\partial t_1} \quad (\text{II.21})
\]

will be introduced. It is obvious that \( \psi_1 \) is a periodic function of both \( t \) and \( t_1 \). From (II.16) and (II.21) it is easy to show that
\[
\int_{t_1=0}^{T} \varphi(t, t_1) \frac{\partial \psi_0}{\partial t_1} dt_1 = \frac{a}{k \ell} \int_{t_1=0}^{T} \psi_1(t, t_1) \frac{\partial \varphi}{\partial t_1} dt_1
\]  
(II.22)

Integrating the right hand side of (II.22) by parts and putting the result into (II.20) yield

\[
c_1 = \delta(1+a) \delta(t) + (-\frac{a}{k \ell}) \psi_1(t, 0)
\]
\[-\frac{-a/k \ell}{g(\tau)-1} \int_0^{\tau} \psi(t, t_1) \frac{\partial \psi_1}{\partial t_1} dt_1 \]  
(II.23)

Now introduce the functions defined by

\[
\psi_{n+1}(t, t_1) = \delta(t+t_1) \frac{\partial \psi_n}{\partial t_1}, \quad n=1, 2, \ldots, N
\]  
(II.24)

which are assumed to be continuous and bounded, and repeat the described process N times. The asymptotic expansions of function \(c_1\) can be obtained and are given by

\[
c_1 = \delta(1+a) \delta(t) + (-\frac{a}{k \ell}) \psi_1(t, 0) + (-\frac{a}{k \ell})^2 \psi_2(t, 0) + \cdots + (-\frac{a}{k \ell})^N \psi_N(t, 0) + R_N(t, k)
\]  
(II.25a)

where \(R_N\) is the remainder of the expansions which is given by

\[
R_N = (-\frac{a}{k \ell}) \frac{1}{g(\tau)-1} \int_{t_1=0}^{\tau} \psi_N(t, t_1) \frac{\partial \varphi}{\partial t_1} dt_1
\]  
(II.25b)

In what follows the convergence of the expansions will be discussed.

For the situation \(k \to \infty\) it is obvious that

\[
g(\tau) = \exp\left( \frac{k \ell}{a} \int_0^{\tau} (1+aK(t)) dt \right) \gg 1
\]  
(II.26)

From the definition of \(\varphi\) the following approximation will hold
\[
R_N(t,k) = \left(\frac{a}{k\xi}\right)^N \int_{t_1=0}^{\tau} \psi_N(t,t_1) \delta(t+t_1) \exp\left(\frac{k\xi}{a} \int_{t_1}^{t+t_1} (1+aK(t_2)) dt_2\right) dt_1
\]

(II.27)

Since the integration with respect to \(t_1\) is over the interval \([0, \tau]\) and \(1+aK\) is always positive, it is obvious that

\[
0 \leq \frac{k\xi}{a} \exp\left(\frac{k\xi}{a} \int_{t_1}^{t+t_1} (1+aK(t_2)) dt_2\right) \leq \exp((t-\tau)(1+aK_{\min}))
\]

(II.28)

where \(K_{\min}\) is the minimum of the function \(K\). From (II.27) and (II.28) it follows that

\[
\left|\frac{R_N(t,k)}{(-\frac{a}{k\xi})^N}\right| \leq \int_{t_1=0}^{\tau} \left|\psi_N(t,t_1) \delta(t+t_1) \exp\left(\frac{k\xi}{a} (t_1-\tau)(1+aK_{\min})\right)\right| dt_1
\]

(II.29)

By assumption \(\psi_N(t,t_1) \delta(t+t_1)\) is bounded, that is

\[
\left|\psi_N(t,t_1) \delta(t+t_1)\right| < M_N
\]

(II.30)

where \(M_N\) is a finite constant which may depend on \(N\). Putting (II.30) into (II.29) yields

\[
\left|\frac{R_N(t,k)}{(-\frac{a}{k\xi})^N}\right| \leq \frac{a}{k\xi} \frac{M_N}{1+aK_{\min}} (1 - \exp\left(-\frac{a\tau}{k\xi(1+aK_{\min})}\right))
\]

(II.31)

This means \(R_N\) is of \((N+1)^{th}\) order of \(1/k\) as \(k\) becomes very large.

However, for given value of \(k\), there is no way to show that \(R_N\) will approach zero as \(N\) increases. Therefore the conventional convergence condition for asymptotic expansions will not be satisfied and the expansions are semi-convergent (8).
If only the terms which are of less than second order of $1/k$ are of interest, the asymptotic expansions may be written as

$$c_1 = \bar{c}(1+a)\delta(t) - (\frac{k}{a\ell}) \delta(t) \dot{\delta}(t) + \mathcal{O}(1/k^2)) \quad (II.32)$$

From this and from (3.71) through (3.73) it is easy to obtain the asymptotic expansions for mean velocity for the case of very large mass transfer coefficient $k$, and it is given by

$$\bar{w} = \frac{1}{\tau} \int_0^\tau \delta(t) v_1(t) \, dt - (\frac{a}{2k\ell}) \frac{1}{\tau} \int_0^\tau \dot{\delta}^2(t) v_1(t) \, dt \quad + \mathcal{O}(1/k^2) \quad (II.33)$$

2. In case that $k$ is very small, the following Taylor expansions will be used to approximate the exponential terms in (3.76), that is

$$\exp\left(\frac{k\ell}{a} \int_t^{t+t_1} (1+aK(t_2)) dt_2\right) = 1 + \frac{k\ell}{a} \int_t^{t+t_1} (1+aK(t_2)) dt_2 + \mathcal{O}(k^2) \quad (II.34)$$

and

$$\frac{k\ell}{a}(g(\tau)-1) = \tau (1+aK) + \frac{1}{2}\left(\frac{k\ell}{a}\right) \tau^2 (1+aK)^2 + \mathcal{O}(k^2) \quad (II.35)$$

where $\overline{K}$ is the time average of the function $K$ and is defined by (3.80). From (3.76), (II.34) and (II.35) $c_1$ may be approximated by

$$c_1 = \frac{\bar{c}(1+a)(\int_{t_1=0}^{\tau} (1+\frac{k\ell}{a} \int_t^{t+t_1} (1+aK(t_2)) dt_2) dt_1)}{(1+a\overline{K})(1+\frac{1}{2} (k\ell/a) \tau^2 (1+a\overline{K}))} \quad (II.36)$$

Furthermore, since $k$ is very small, (II.36) can be simplified to give the approximation

$$c_1 = \frac{\bar{c}(1+a)}{1+a\overline{K}} (1 + \frac{k\ell \tau}{a} (\frac{1}{\tau^2} \int_{t_1=0}^{\tau} \int_t^{t+t_1} (1+aK(t_2)) dt_2 dt_1 - \frac{1}{2} (1+a\overline{K}))) \quad (II.37)$$
It follows from Leibnitz formula that
\[
\frac{d}{dt} \int_{t_1=0}^{T} \int_{t_2=t_1}^{t+t_1} (1+aK(t_2)) dt_2 dt_1 = -T a(K(t) - \bar{K}) \tag{II.38}
\]

Integrating both sides of (II.38) with respect to \( t \) yields
\[
\int_{t_1=0}^{T} \int_{t_2=t_1}^{T} (1+aK(t_2)) dt_2 dt_1 = \int_{t_1=0}^{T} \int_{t_2=0}^{t_1} (1+aK(t_2)) dt_2 dt_1 \\
- T a \int_{0}^{t} (K(t_1) - \bar{K}) dt_1 \tag{II.39}
\]

where the last integral in (II.39) is a periodic function of \( t \), that is
\[
\int_{0}^{t+T} (K(t_1) - \bar{K}) dt_1 = \int_{0}^{t} (K(t_1) - \bar{K}) dt_1 \quad \text{for all} \quad t \tag{II.40}
\]

From (II.37) and (II.39) it follows that
\[
c_1 = \frac{\bar{c}(1+a)}{1+a\bar{K}} \left( 1 + \frac{k \ell T}{a} \frac{1}{T^2} \int_{t_1=0}^{T} \int_{t_2=0}^{t_1} (1+aK(t_2)) dt_2 dt_1 \\
- \frac{a}{T} \int_{0}^{t} (K(t_1) - \bar{K}) dt_1 - \frac{1}{2}(1+a\bar{K}) \right) \tag{II.41}
\]

By integrating both sides of (II.41) with respect to \( t \) over a period, the time average \( \bar{c}_1 \) is given by
\[
\bar{c}_1 = \frac{\bar{c}}{1+a} / (1+a\bar{K}) \tag{II.42}
\]

From (II.40) through (II.42) the mean velocity \( \bar{w} \) for the case of very small \( k \) can be approximated by the expansions
\[
\bar{w} = \frac{\bar{v}_1}{1+a\bar{K}} + \frac{k \ell T}{a} \frac{1}{T^2} \int_{0}^{T} u(t) \int_{0}^{t} (K(t_1) - \bar{K}) dt_1 dt + O(k^2) \tag{II.43}
\]
APPENDIX III. DERIVATION OF THE EQUATION (4.34)

It is easy to show that the equation (4.33) can be rearranged to give

$$ w^* = \frac{1}{t} \int_0^T \delta(t) \dot{\Delta}(t) \, dt - w_p^* $$  \hspace{1cm} (III.1) 

where $w_p^*$ is defined by

$$ w_p^* = \frac{1}{dt} \left( \int_0^{-d} \delta_{min} \int_{t_3}^{t_4} (v(x,t) + \frac{\partial v}{\partial x} \delta(t)d) \, dt \, dx \right. $$

$$ \left. + \int_d^{d(1-\delta_{max})} \int_{t_1}^{t_2} (v(x,t) + \frac{\partial v}{\partial x} \delta(t)d - \dot{\Delta}(t)) \, dt \, dx \right) $$ \hspace{1cm} (III.2) 

In the regions near $x=0$ and $x=d$, $v$ may be approximated by or is equal to the first two terms of its Taylor expansions, that is

$$ v(x, t) = \dot{\Delta}(t) + (x - d) \frac{\partial v}{\partial x} \quad \text{for } x \approx d $$

$$ = x \frac{\partial v}{\partial x} \quad \text{for } x \approx 0 $$ \hspace{1cm} (III.3) 

Putting (III.3) into (III.2) it follows that

$$ w_p^* = \frac{1}{dt} \left( \int_0^{-d} \delta_{min} \int_{t_3}^{t_4} \frac{\partial}{\partial x} ((x+d)v) \, dt \, dx \right. $$

$$ \left. + \int_d^{d(1-\delta_{max})} \int_{t_1}^{t_2} \frac{\partial}{\partial x} ((x+d)v) \, dt \, dx \right. $$

$$ \left. + \int_0^{-d} \delta_{min} \int_{t_3}^{t_4} v(x,t) \, dt \, dx - \int_d^{d(1-\delta_{max})} \int_{t_1}^{t_2} v(x,t) \, dt \, dx \right) $$ \hspace{1cm} (III.4) 

In what follows, the four double integrals on the right hand side of (III.4) will be denoted by $I_1$, $I_2$, $I_3$ and $I_4$ respectively and will
be discussed one by one;

1. From Leibnitz formula the first double integral can be expressed in form of

\[ I_1 = \int_0^d \delta_{\min} \left( \frac{d}{dx} \int_{t_3}^{t_4} (x + \delta d) v \, dt - t_3'(x) (x + \delta (t_4) d) v ight) \\
+ t_3'(x) (x + \delta (t_3) d) v \, dx \quad (\text{III.5}) \]

where \( t_3' \) and \( t_4' \) are the derivatives of \( t_3 \) and \( t_4 \) with respect to \( x \) respectively. From the definitions of \( t_3 \) and \( t_4 \), the identities

\[ \delta(t_3) \, d = \delta(t_4) \, d = -x \quad (\text{III.6}) \]

hold. This means the last two terms on the right hand side of (III.5) vanish. The first term may be integrated to yield

\[ I_1 = \int_{t_3}^{t_4} (x + \delta d) v(x, t) \, dt \bigg|_{x=0}^{x=-d} \delta_{\min} \quad (\text{III.7}) \]

Since from the definition

\[ t_3(-d \delta_{\min}) = t_4(-d \delta_{\min}) \quad (\text{III.8a}) \]

and since

\[ v(0, t) = 0 \quad (\text{III.8b}) \]

it can be shown that the right hand of (III.7) vanishes. Therefore

\[ I_1 = 0 \quad (\text{III.9}) \]

2. By applying the similar manipulation to the second double integral of (III.4), it can be shown that

\[ I_2 = d \int_{t_4(d)}^{t_2(d)} \Delta(t) \delta(t) \, dt \quad (\text{III.10}) \]
3. From (III.3), it follows that the third integral of (III.4) is expressible in form of

\[ I_3 = \frac{1}{2} \int_0^{t_3} \int_{t_3}^{t_4} \delta_{\min} \left( \frac{\partial}{\partial x}(x \nu(x, t)) \right) dt \, dx \]  

(III.11)

By applying Leibnitz formula the right hand side of (III.11) can be integrated to yield

\[ I_3 = \frac{1}{2} \int_{t_3}^{t_4} x \, \nu \, dt \left|_{x=0}^{x=d \delta_{\min}} + \frac{1}{2} \int_0^{d \delta_{\min}} (t_3'(x) \nu(x, t) - t_4'(x) \nu(x, t)) \, dx \right. \]  

(III.12)

The first term on the right hand side of (III.12) vanishes because of (III.8a) and (III.8b). From (III.6) the remained terms may be transformed and integrated to yield

\[ I_3 = (F(t_3(0)) - F(t_4(0))) / 2 \]  

(III.13)

where the function \( F \) is defined by

\[ F(t) = d \int_0^t \delta(t_1) \nu(-d \delta(t_1), t_1) \, dt_1 \]  

(III.14)

Therefore from (III.13) and (III.14), the third integral in (III.4) is expressible in form of

\[ I_3 = -\frac{d}{2} \int_{t_3(0)}^{t_4(0)} \delta(t) \nu(-d \delta(t), t) \, dt \]  

(III.15)

It follows from (III.3) and (III.15) that

\[ I_3 = \frac{d^2}{2} \int_{t_3(0)}^{t_4(0)} (\delta(t))^2 \frac{\partial \nu}{\partial x} \, dt \]  

(III.16)

4. The similar technique is applied to the fourth double integral in (III.4), the result is given by
\[ I_4 = d \int_{t_1(d)}^{t_2(d)} (\delta(t) \dot{\delta}(t) - \frac{d}{2} \delta^2(t) \frac{\partial v}{\partial x}) \, dt \quad (III.17) \]

From (III.4), (III.9), (III.10), (III.16) and (III.17) it follows that

\[ w^* = \frac{d}{2T} \left( \int_{t_1(d)}^{t_2(d)} (\delta(t))^2 \left( \frac{\partial v}{\partial x} \right)_{x=-d} \delta(t) \, dt \right. \]
\[ \left. - \int_{t_3(0)}^{t_4(0)} (\delta(t))^2 \left( \frac{\partial v}{\partial x} \right)_{x=d} \delta(t) \, dt \right) \quad (III.18) \]

It is assumed that the function \( \delta(t) \) has only two zeros in a period, therefore from the definitions of \( t_1, t_2, t_3 \) and \( t_4 \) it is obvious that

\[ t_1(d) = 0, \ t_2(d) = t_3(0), \ t_4(0) = T \quad (III.19) \]

and

\[ \delta(t) \geq 0 \quad \text{for} \quad t \in [t_1(d), t_2(d)] \]
\[ \delta(t) \leq 0 \quad \text{for} \quad t \in [t_3(0), t_4(0)] \quad (III.20) \]

Then the equation (III.18) can be rewritten as

\[ w^* = \frac{d}{2T} \left( \int_{0}^{t_2(d)} \delta(t) |\delta(t)| \left( \frac{\partial v}{\partial x} \right)_{x=-d} \delta(t) \, dt \right. \]
\[ \left. + \int_{t_2(d)}^{T} \delta(t) |\delta(t)| \left( \frac{\partial v}{\partial x} \right)_{x=d} \delta(t) \, dt \right) \quad (III.21) \]

In case that the velocity profile is linear over the whole range of \( x \), \( \frac{\partial v}{\partial x} \) is independent of \( x \), that is

\[ \frac{\partial v}{\partial x} = \frac{1}{d} \dot{\delta}(t) \quad \text{for all} \quad x, t \quad (III.22) \]

In this situation \( w^* \) is given by

\[ w^* = \frac{d}{2T} \int_{0}^{T} \delta(t) |\delta(t)| \dot{\delta}(t) \, dt \quad (III.23) \]

Combining this and (III.1) the equation (4.34) appears.
APPENDIX IV. COMMENTS ON NUMERICAL METHODS FOR INTEGRATIONS OF THE
PARTIAL DIFFERENTIAL EQUATIONS

For both systems of (3.61) and (3.62) and of (4.20) the solutions
which satisfy a time periodicity condition were sought. Such solu-
tions were calculated by assuming physically realizable initial values
for dependent variables and solving the initial value problems until
the limit cycle for state variables had been approached. The periode-
city criterion is tested at the end of each period for each computation.
The periodicity error $E_N$ was taken as, at the end of $N$th period, the
maximum relative error between correspondent values of dependent var-
ables at $t=(N-1)\tau$ and at $t=N\tau$. That is $E_N$ was defined by

$$E_N = \max_z \left( \frac{|c_1(z,N\tau) - c_1(z,(N-1)\tau)|}{c_1(z,N\tau)}, \frac{|c_2(z,N\tau) - c_2(z,(N-1)\tau)|}{c_2(z,N\tau)} \right)$$

(IV.1)

for the system of (3.60) and (3.61), and was defined by

$$E_N = \max_{\xi} \left| \frac{y(\xi,N\tau) - y(\xi,(N-1)\tau)}{y(\xi,N\tau)} \right|$$

(IV.2)

for the system of (4.20). The simulation was ceased when $E_N$ was
smaller than a prescribed value.

In what follows the methods for the integrations of both systems
will be discussed separately;

1. The dimensionless equations for the system of (3.60) and (3.61)
can be obtained by the following transformations:

$$z^* = \frac{z}{L_x}, \quad t^* = \frac{t}{\tau}, \quad v_1^* = \frac{v_1}{\tau / L_x}$$

(IV.3,4,5)

$$k^* \xi^* = k \xi \tau, \quad c_1^* = \frac{c_1}{c_a}, \quad c_2^* = \frac{c_2}{c_a}$$

(IV.6,7,8)
The results after eliminating the stars are given by

\[ \frac{\partial c_1}{\partial t} = -v_1(t) \frac{\partial c_1}{\partial z} - kL (K(t)c_1 - c_2) \quad \text{(IV.9)} \]

\[ \frac{\partial c_2}{\partial t} = kL (K(t)c_1 - c_2) / a \quad \text{(IV.10)} \]

The corresponding dimensionless boundary conditions are given by

\[ c_1(0^-, t) + a c_2(0^-, t) = 1 \quad \text{(IV.11a)} \]

\[ \frac{dc_1(0^-, t)}{dt} = -kL (K(t)c_1(0^-, t) - c_2(0^-, t)) \quad \text{(IV.11b)} \]

\[ c_1(1^+, t) + a c_2(1^+, t) = c_b/c_a \quad \text{(IV.12a)} \]

\[ \frac{dc_1(1^+, t)}{dt} = -kL (K(t)c_1(1^+, t) - c_2(1^+, t)) \quad \text{(IV.12b)} \]

\[ c_1(0^+, t) = c_1(0^-, t) \quad \text{when } v_1(t) \geq 0 \quad \text{(IV.13)} \]

\[ c_1(1^-, t) = c_1(0^+, t) \quad \text{when } v_1(t) < 0 \quad \text{(IV.14)} \]

Equations (IV.9) and (IV.10) are linear, first order hyperbolic partial differential equations and can be numerically integrated along their characteristics. The characteristics are given by

\[ z - \int_0^t v_1(t) \, dt = \alpha_1 \quad \text{(IV.15)} \]

\[ z = \alpha_2 \quad \text{(IV.16)} \]

for the equations (IV.9) and (IV.10) respectively, where \( \alpha_1 \) and \( \alpha_2 \) are constants. Along these characteristics the equations (IV.9) and (IV.10) can be replaced by a pair of ordinary differential equations

\[ \frac{dc_1}{dt} = -kL (K(t)c_1 - c_2) \quad \text{(IV.17)} \]
\[ \frac{dc_2}{dt} = k \mathcal{L} \left( K(t)c_1 - c_2 \right) / a \] (IV.18)

Equations (IV.15) and (IV.16) form a network on z-t plane of which the mesh points are the intersections of the characteristics with constant increment \( \Delta z \) and time dependent increment \( \Delta t_1 \) which satisfies the equation

\[ \Delta z = \int_{t_1}^{t_1 + \Delta t_1} v_1(t) \, dt \] (IV.19)

This means the displacement of fluid phase during each time step is equal to the length \( \Delta z \). Equations (IV.17) and (IV.18) are then integrated along the network to give the values of \( c_1 \) and \( c_2 \) at the mesh points by using Runge-Kutta method.

2. The dimensionless equations for (4.20) and (4.21) are obtained by using the transformations

\[ t^* = \frac{t}{\tau} , \quad \xi^* = \frac{\xi}{(B E_m \tau)} \] (IV.20)

and then eliminating the stars. The results are given by

\[ \frac{\partial y}{\partial t} = \frac{E(t)}{E_m} \frac{\partial y}{\partial \xi} + \frac{D}{(B E_m)^2 \tau} \frac{\partial^2 y}{\partial \xi^2} \] (IV.21)

\[ \frac{E(t)}{E_m} y + \frac{D}{(B E_m)^2 \tau} \frac{\partial y}{\partial \xi} = -\frac{E(t)}{E_m} \quad \xi = 0 \] (IV.22)

where \( E_m \) is the amplitude of the function \( E \). This second order parabolic partial differential equation can be approximated by a system of difference equations. Two difference methods, i.e. the backward difference and the Crank-Nicholson type difference, have been used. The former gave the better result since the greater smoothness was required of the solution to insure convergence for the Crank-Nicholson method. Incidentally this was not the case for system (IV.21) and (IV.22).
Therefore only the backward difference method will be discussed in what follows.

The intervals \([0,1]\) on \(t\) axis and \([0, \xi_L]\) on \(\xi\) axis are divided into \(N\) and \(K\) equal increments \(\Delta t\) and \(\Delta \xi\) respectively, where \(\xi_L\) is a relatively large value such that the behavior of the dependent variable \(y\) at \(\xi = \xi_L\) may approach that at \(\xi \to \infty\). Letting \(y^n_k\) be the solution \(y\) calculated at \(t = t_n\) and \(\xi = \xi_k\), the equation (IV.21) is approximated by

\[
\frac{y_{k+1}^n - y_k^n}{\Delta t} = \frac{E(t_{n+1})}{E_m} \frac{y_{k+1}^{n+1} - y_{k-1}^{n+1}}{2 \Delta \xi} + \frac{D}{(B E_m)^2 \tau} \frac{y_{k+1}^{n+1} - 2y_k^{n+1} + y_{k-1}^{n+1}}{(\Delta \xi)^2}
\]

(IV.23)

The second order approximation (9) for \(\frac{\partial y}{\partial \xi}\) is used for the boundary condition (IV.22), the result is given by

\[
\frac{E(t_{n+1})}{E_m} y_0^{n+1} + \frac{D}{(B E_m)^2 \tau} (- \frac{y_2^{n+1} - 4y_1^{n+1} + 3y_0^{n+1}}{2 \Delta \xi})
\]

(IV.24)

The equations (IV.23) and (IV.24) are rearranged to form a system of linear algebraic equations which are then solved by computer.

The initial condition

\[ y(\xi, 0) = 0 \quad \text{for all } \xi \]

(IV.25)

is adapted because it is physically realizable. The system (IV.21) and (IV.22) describes a source problem of which the time average source strength vanishes. It follows from (IV.25) that the condition
\[
\int_0^\infty y(\xi, M) \, d\xi = 0, \quad M=1, 2, 3, \ldots \quad (IV.26)
\]

must be satisfied by the solution \(y(\xi, t)\) computed from (IV.23) and
(IV.24) at the end of \(M^{th}\) period. Practically the integration on
the left hand side of (IV.26) was carried out over the range \([0, \xi_L]\)
in computation. The average \(\overline{y}_M\) of \(y(\xi, M)\) over this range was defined by

\[
\overline{y}_M = \frac{1}{\xi_L} \int_0^{\xi_L} y(\xi, M) \, d\xi, \quad M=1, 2, \ldots \quad (IV.27)
\]

The value of \(\overline{y}_M\) were very small but not exactly zero. In order to
satisfy the condition (IV.26) the solution \((y(\xi, M)-\overline{y}_M)/(1+\overline{y}_M)\), which
satisfied (IV.21) and (IV.22) as \(y(\xi, M)\) did, was used instead of
\(y(\xi, M)\) as the initial condition for the computation of the next
(i.e. the \(M+1^{th}\) period). This self-adjusting procedure eventually
insured the convergence of the algorithm.