

A FUNDAMENTAL STUDY OF SOLIDS MIXING

by

SEE HEE SHIN

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Department of Chemical Engineering

Kansas State University

Manhattan, Kansas 66506

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Approved by

L. J. Fran
Major Professor

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1. INTRODUCTION	1-1
2. CHARACTERIZATION OF SOLIDS MIXTURES BY THE DISCRETE FOURIER TRANSFORM	
2.1 INTRODUCTION	2-1
2.2 THEORETICAL	
2.2.1 Properties of the Discrete Fourier Transform	2-3
2.2.2 Mixture Pattern Classification	2-9
2.3 COMPUTER SIMULATION	2-11
2.4 RESULTS	2-13
2.5 DISCUSSION	
2.5.1 Mixing Index	2-14
2.5.2 Characteristics of Ordered Mixtures	2-14
2.5.3 Characteristics of Random Mixtures	2-15
2.5.4 Fourier Transform vs. Walsh-Hadamard Transform	2-17
2.6 CONCLUDING REMARKS	2-18
NOTATIONS	2-19
REFERENCES	2-21
APPENDIX	2-23
3. STOCHASTIC DIFFUSION MODEL OF NON-IDEAL MIXING IN A HORIZONTAL DRUM MIXER	
3.1 INTRODUCTION	3-1
3.2 THEORETICAL	
3.2.1 Kolmogorov Diffusion Equation	3-4
3.2.2 Simultaneous Determination of the Diffusion Coefficient and the Drift Velocity	3-10
3.2.3 Methods of Solving the Kolmogorov Equation	3-12
3.3 EXPERIMENTAL	3-13

3.4	RESULTS	3-14
3.5	DISCUSSION	3-15
3.6	CONCLUSION	3-17
	NOTATIONS	3-18
	REFERENCES	3-19
	APPENDICES	3-21
4.	SUMMARY AND RECOMMENDATION	4-1
	ACKNOWLEDGMENTS	

1. INTRODUCTION

Mixing or blending operations are carried out on particulate solids in chemical, metallurgical, pharmaceutical and food industries. Despite its obvious importance, the mixing of solids is far from completely understood. A considerable need exists for fundamental work to delineate the mixing process and to characterize the resulting mixtures on the basis of fundamental theory.

In general, investigations of solids mixing are concerned with two broad aspects; those concerned with the characterization of mixtures and those dealing with mechanisms by which the state of a mixture is changed. Both aspects are equally important; therefore, the work described in this thesis is concerned with both.

Because of the development of various modern technologies, e.g., the fiber optic probe method, continuous detection of particle distribution inside a mixer has become feasible. Under this circumstance the discrete Fourier transform, which is a digitized version of the Fourier transform, may be employed to interpret the data collected from a sampler for the purpose of mixture characterization. The present study aims at determining the relationship between the homogeneity of a solids mixture and its discrete Fourier transform power spectrum for ordered mixtures as well as random ones.

Mixing of particulate solids in a horizontal drum mixer has been the subject of many investigations because of its theoretical as well as practical importance. When non-ideal particles which are different in size and/or density are mixed, their mixing behavior is very random and thus difficult to visualize. Practically no attempt has been made to

elucidate the temporal change of particle distribution along the axial direction of the mixer. In the present work this has been modeled by means of the Kolmogorov diffusion equation. Using the model, the non-uniform equilibrium concentration profile, which is a typical phenomenon occurring when non-ideal particles are mixed in a horizontal drum mixer, could be fairly well described.

2.1 INTRODUCTION

The most widely used criterion for the measure of homogeneity of a solids mixture is based on the variance of spot samples. The variance, however, reveals little as to the internal nature or structure of the mixture because it is a statistical quantity which depends largely on the size as well as the number of samples taken from the mixture. A survey of the literature (Bourne, 1967; Harnby, 1971/72; Kristensen, 1973; Poole et al., 1964; Williams, 1969/70) shows that extensive studies of characterization of the mixture homogeneity have been carried out, which emphasize the investigation of the analysis of variance of spot samples.

The concentration of reference or key particles must be measured at many position in the mixture to test its homogeneity. If the problem of accurate determination of homogeneity is critical, as in the pharmaceutical production industry, continuous sampling over the entire mixture batch is necessary. When the mixture content is likely to deteriorate severely during sampling, special technologies must be exercised in sampling. If the major ingredient in the mixture is sensitive to a certain wavelength, the fiber optic probe technique may be used (Ashton et al., 1966). Harwood et al., (1971) have reported a device to monitor compositional changes in a mixture batch, which employs the fiber optic probe. The signal from its photo multiplier is displayed on a recorder. The measured quantity is the reflectance of the powder mixture at the position under investigation. Compositions can be recovered from a calibration curve. Several probes can be inserted into the mixture batch to obtain the concentration distribution in the mixture batch. For a three-dimensional mixture batch, the disturbance caused by inserting the probes cannot be completely eliminated. However, when a photographic method is used, this difficulty can be minimized

as long as the mixture is well mixed in the direction perpendicular to the exposed surface. For further information on the sampling techniques, readers are referred to the recent review by Schofield (1976).

If any of the continuous sampling techniques mentioned above is applicable, the Fourier transform (FT) is one of the convenient orthogonal transforms that can be used to interpret the data collected from a sampler. These transforms include Walsh, Hadamard, Rademacher and Haar functions (see, e.g., Ahmed and Rao, 1975 for the definitions and properties of these transforms). The FT has been extensively used as a means to characterize images, to reconstruct the data, and to carry out many other related tasks (see, e.g., Crowther et al., 1970; DeRosier and Klug, 1968).

Cooper (1974) investigated the mixture pattern of metal powders which were subjected to chemical diffusion during sintering or melting. He attempted to approximate the concentration distribution of the key particle by a series of sinusoidal fluctuations from the mean value. Though the FT was not explicitly used by him, his approach (an expansion in sine series) is similar to the FT technique.

The discrete Fourier transform (DFT) is the discrete version of the FT. A continuous signal obtained from the sampler is digitized and the FT is performed in a discrete manner, and then the input signal is interpreted on the transform domain. Since efficient DFT algorithms are available (see, e.g., Cooley and Tukey, 1965; Ahmed and Rao, 1975), rapid treatment of the collected data or signals is relatively easy. The present study has been carried out to determine the relationship between the homogeneity of a solids mixture and its DFT power spectrum.

2.2 THEORETICAL

There are at least two distinct ways to carry out photographic or visual sampling. In a continuous mixing process, the product mixture marches in line, and the sampler, which is fixed in position over the mixture stream, measures the concentration of the key particles passing beneath it (Fig. 1). On the other hand, the sampler itself moves along the mixture in a batch process (Fig. 2). The video signal which represents the concentration of the key particles appears on the displayer as a function of time in Fig. 1, and as a function of the spatial position in Fig. 2. For a two-dimensional batch mixture, the scanning is performed horizontally and vertically.

To obtain a digitized form of signal, N equidistant positions are located along the abscissa of the video signal as shown in Figs. 1 and 2. At each position there is a corresponding value of the concentration, $\{X(m)\}$, $m = 0, 1, 2, \dots, N-1$. $\{X(m)\}$ is termed a data matrix; more precisely, $\{X(m)\}$ is a vector for the present one-dimensional case.

2.2.1 Properties of the Discrete Fourier Transform

Suppose that $\{X(m)\}$ is a set of data of N finite numbers ($m = 0, 1, 2, \dots, N-1$) obtained from the signal; then its DFT is defined as (see, e.g., Ahmed and Rao, 1975; Cooley et al., 1967):

$$\begin{aligned} C_x(k) &= \frac{1}{N} \sum_{m=0}^{N-1} X(m) \left[\cos\left(\frac{2\pi km}{N}\right) - i \sin\left(\frac{2\pi km}{N}\right) \right] \\ &= \frac{1}{N} \sum_{m=0}^{N-1} X(m) W^{km} \end{aligned} \quad (1)$$

where

$$N = 2^n$$

$$W = e^{-i \frac{2\pi}{N}}$$

$$j = \sqrt{-1}$$

$$k = 0, 1, 2, \dots, N-1$$

The DFT power spectrum is defined as

$$p(k) = |C_x(k)|^2, \quad k = 0, 1, 2, \dots, N/2 \quad (2)$$

One of the properties of the DFT, known as the shift theorem, can be expressed as follows (see, e.g., Ahmed and Rao, 1975):

If

$$Z(m) = X(m+h), \quad h = 0, 1, 2, \dots, N-1,$$

then

$$C_z(k) = W^{-hk} C_x(k) \quad (3)$$

This theorem indicates that the power spectrum is invariant with respect to the shift of the elements of $\{X(m)\}$.

To illustrate the significance of the shift theorem in relation with the solid mixture homogeneity, let us consider a completely segregated mixture composed of 8 particles. These particles are positioned linearly forming a one-dimensional mixture. Let us denote this by $[X]_1$, i.e.,

$$[X]_1 = [11110000] \quad (4)$$

By performing the DFT on $[X]_1$ we obtain

$$[Y]_1^t = [T][X]_1^t \quad (5)$$

where the subscript t denotes the transpose, $[T]$ is the DFT matrix, and $[Y]_1$ is the transformed vector of $[X]_1$. Generally when N particles are involved the component of $[T]$ is given by

$$T_{m,k} = \frac{1}{N} W^{km}, \quad m, k = 0, 1, 2, \dots, N-1 \quad (6)$$

Suppose that the particles of $[X]_1$ are shifted to the right by bulk movement to form another mixture $[X]_2$ such that

$$[X]_2 = [00111100] \quad (7)$$

As far as the mixture homogeneity and pattern are concerned, $[X]_1$ and $[X]_2$ are essentially identical in the sense that in each mixture the key particles are clustered together, and hence both are in the completely segregated state. By virtue of the shift theorem, the DFT power spectrum of the two mixtures can be shown to be identical. This is one reason why the DFT is more advantageous than other orthogonal transformations in the characterization of mixture patterns.

The physical meaning of the DFT power spectrum of a mixture can be further elucidated by considering a completely random mixture. It must be noted that the first DFT power spectrum component is the square of the average concentration, as can be shown from Eqns. (1) and (2). In fact when $k = 0$, we have

$$\begin{aligned} C_x(0) &= \frac{1}{N} \sum_{m=0}^{N-1} X(m) \\ &= q \end{aligned}$$

and thus

$$p(0) = q^2 \quad (8)$$

Suppose that a binary mixture is in the completely random state. Then the expected value of concentration at each sampling position is identical to the average concentration q , irrespective of the size and/or number of samples. Since the autocorrelation function $R(m)$ is defined as

$$R(m) = \frac{1}{N-m} \sum_{i=0}^{N-1-m} E[X(i) X(i+m)], \quad i = 0, 1, 2, \dots, N-1 \quad (9)$$

the autocorrelation function of the completely random mixture is given by

$$R(m) = q^2 \quad (10)$$

The DFT power spectrum can be obtained by the inverse discrete Fourier

transform (IDFT) of the autocorrelation function (see, e.g., Ahmed and Rao, 1975). This yields

$$p(k) = \sum_{m=0}^{N-1} R(m) W^{-mk}, \quad k = 0, 1, 2, \dots, N/2 \quad (11)$$

Therefore,

$$\begin{aligned} p(0) &= q^2 \\ p(k) &= 0, \quad k = 1, 2, \dots, N/2 \end{aligned} \quad (12)$$

This implies that the power spectrum of a completely random mixture is essentially the delta function. Since $p(0)$ is independent of the mixture homogeneity, it can be conveniently used to normalize the power spectrum. Hereafter, we shall denote the normalized power spectrum by $\bar{p}(k)$, $k = 0, 1, 2, \dots, N/2$.

A completely random mixture is statistically equivalent to a uniform mixture in the sense that the expected value of concentration at every sampling position is identical. Assuming that the concentration is uniformly distributed, i.e.,

$$X(0) = X(1) = \dots = X(N-1) = q, \quad (13)$$

the power spectrum of a uniform mixture can be shown to be the same as that given in Eqn. (12) because of Eqn. (10). The concept of uniformity and randomness, therefore, can be interchangeable in solids mixtures as far as the power spectrum is concerned. In this context it is interesting to establish correspondences between the correlograms and the power spectrum. The former has been introduced by Danckwerts (1953) and extended by Schofield (1970). Danckwerts defined the correlogram as the correlation coefficient $\rho(m)$ with a distance lag m , i.e.,

$$\rho(m) = \frac{\frac{1}{N-m} \sum_{i=0}^{N-1-m} E[(X(i) - q)(X(i+m) - q)]}{\sigma^2} \quad (14)$$

where

$$m = 0, 1, 2, \dots, N-1$$

$$\sigma^2 = \text{sample variance}$$

Since the expected value of concentration at each sampling position is identical for a completely random mixture, it can be shown that

$$\begin{aligned} \rho(0) &= 1 \\ \rho(m) &= 0, \quad m = 1, 2, \dots, N-1 \end{aligned} \quad (15)$$

The area under the correlogram up to the point where it first crosses the m-axis is defined as the scale of segregation. The characteristics of the correlogram and the DFT power spectrum are identical for a completely random mixture as can be seen by comparing Eqns. (12) and (15).

Another property of the DFT, known as Parseval's theorem, states that

$$\frac{1}{N} \sum_{m=0}^{N-1} X^2(m) = C_x^2(0) + \sum_{k=1}^{N-1} [C_x(k)]^2 \quad (16)$$

when Eqn. (1) holds true. From Eqns. (2) and (8), we have

$$C_x^2(0) = p(0) = q^2$$

and, therefore, Eqn. (16) can be rewritten as

$$\frac{1}{N} \sum_{m=0}^{N-1} X^2(m) - q^2 = \sum_{k=1}^{N-1} [C_x(k)]^2 \quad (17)$$

or

$$\sigma^2 = \sum_{k=0}^{N-1} p(k) - p(0) \quad (18)$$

Eqn. (18) shows that the DFT power spectrum represents a mode by which

the key particle distribution contributes to the variance, σ^2 . In other words it contains more physical information about the mixture than the variance itself.

The fundamental concepts of the DFT power spectrum presented so far in one dimension can be extended to higher dimensions. For the two-dimensional case, the DFT is defined as

$$C_{xx}(k_1, k_2) = \frac{1}{N_1 N_2} \sum_{m_2=0}^{N_2-1} \sum_{m_1=0}^{N_1-1} X(m_1, m_2) W_1^{k_1 m_1} W_2^{k_2 m_2} \quad (19)$$

where

$$W_\ell = e^{-\frac{2\pi i}{N_\ell}} \quad \ell = 1, 2$$

$\{X(m_1, m_2)\}$ is the two-dimensional data matrix with $(N \times N)$ elements.

The power spectrum can be defined similar to that in Eqn. (2), i.e.,

$$P_{xx}(k_1, k_2) = [C_{xx}(k_1, k_2)]^2, \quad (20)$$

$$k_1 = 0, 1, 2, \dots, N_1/2$$

$$k_2 = 0, 1, 2, \dots, N_2/2$$

For further information on the FT and DFT, readers are referred to

Ahmed and Rao (1975), Arsac (1961), Bracewell (1965), and Goodman (1968).

2.2.2 Mixture Pattern Classification

The patterns of solids mixtures can be classified according to the concentration distribution of the key component. To be more specific, we shall distinguish mixture patterns from mixture structures (Lai, 1976). The structure of a mixture refers to the packing arrangement of the particles. For example, cubic and hexagonal packings are typical ordered structures for a two-dimensional mixture. A mixture with an ordered pattern may or may not have an ordered structure in microscopic scale. In other words, inside each clump of the ordered pattern, the packing structure of the particles may be random.

The mixing of particulate solids proceeds by two major mechanisms: convection and diffusion. These two mechanisms usually yield different patterns. Ordered pattern mixtures are created as a result of convective mixing in an ordered manner, i.e., successive subdivision of clumps followed by orderly displacements. Diffusive mixing leads to a random mixture.

Even though the importance of ordered mixing has been neglected by solids mixing investigators, Hersey (1976) points out that in producing pharmaceutical mixtures, ordered mixing is sometimes more effective than random mixing, especially for highly cohesive materials.

Ordered mixtures can be subdivided into two groups, striated and checkered pattern mixtures, according to the layout of key particles (see Fig. 3). One- and two-dimensional striated pattern mixtures have essentially the same pattern. The latter is an elongation of the former in one direction. Checkered pattern mixtures only exist in two-dimension. For an ordered mixture, the number of striations or checks completely specifies the pattern while this is not the case for a random mixture.

To identify the pattern of a mixture, it is necessary to sample it. Studies in sampling theory and practice have been centered mostly on the random sampling. If, however, the pattern and homogeneity of a mixture need to be simultaneously determined, the systematic sampling may be more effective than the random sampling. This is due to the fact that an ordered mixture cannot be distinguished easily from a random one only by random sampling.

obtained after 20 random exchanges of particle locations. A one-dimensional random mixture which obeys the simple Fickian diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (23)$$

was also simulated, where c is the concentration of the key particles and D is the diffusion coefficient. For this purpose, the following analytic solution for the boundary conditions that no transport of particles takes place at both ends of the mixer was employed (Lacey, 1960):

$$c - q = \frac{2}{\pi} \sum_{n=1}^{\infty} e^{-n^2 \pi^2 \tau} \cdot \frac{\sin(nq\pi)}{n} \cdot \cos(n\pi y) \quad (24)$$

where

$$\tau = Dt/L^2$$

L = length of the mixer

q = initial proportion of key particles

$y = \frac{x}{L}$ = normalized or dimensionless mixer position

A fixed number of samples with the same size (same number of particles per sample) was systematically withdrawn from each generated mixture. For a one-dimensional ordered mixture, the number of samples was 32, and each sample contained 8 particles, while 256 samples, each containing a single particle, were withdrawn from a one-dimensional (random) or two-dimensional (ordered or random) mixture. The sampled data were arranged in a one- or two-dimensional matrix array, and the DFT power spectrum for it was calculated by using Eqn. (2) or (20). The maximum component of the DFT power spectrum was identified and defined as the mixing index, M_1 , the reason for which will be discussed later. For a random mixture, random sampling was also conducted by withdrawing a fixed number of samples of equal size to calculate the sample variance, σ^2 .

2.4 RESULTS

Figure 4 sketches one-dimensional ordered mixtures in the order of increasing number of striations together with their maximum power spectrum components (M_1). Fig. 5-A shows the power spectrum of the completely segregated mixture corresponding to the first mixture in Fig. 4, while Fig. 5-B is that of the most uniform mixture corresponding to the last one in Fig. 4. Figure 6 illustrates several checkered pattern mixtures and the corresponding values of M_1 .

The sample variances of one- and two-dimensional random mixtures, and their maximum power spectrum components are tabulated in the order of increasing number of particle exchanges in Tables 1 and 2, respectively. Note that mixture 1 is in the completely segregated state while mixture 10 is almost in the completely random state.

2.5 DISCUSSION

Several observations can be made from the numerical results of the simulation. They are detailed in the following.

2.5.1 Mixing Index

Although all power spectrum components can be used to characterize some features of a mixture, it is extremely difficult to employ all of them in characterizing its homogeneity or in computing its mixing index.

For illustration, let us consider the following binary mixture $[X]_3$.

$$[X]_3 = [00010000011011111001101011100110] \quad (25)$$

The power spectrum components of this mixture are tabulated in Table 3.

For this mixture, the predominant power spectrum components, excluding $\bar{p}(0)$, are $\bar{p}(6)$, $\bar{p}(10)$ and $\bar{p}(1)$ in decreasing order. All of them can be considered to be parameters characterizing the homogeneity of mixture $[X]_3$. Therefore, to select a single mixing index, the ensemble average of several predominating power spectrum components or only the maximum component, M_1 , can be used, as long as selection is consistent. The latter is selected in the present study as a mixing index. The results of numerical simulation indicate that M_1 possesses desirable characteristics including stability from change in the average composition, sensitivity, and efficiency.

2.5.2 Characteristics of Ordered Mixtures

Figure 4 shows that the DFT power spectrum can characterize an ordered mixture. M_1 increases as the striation number increases or as the mixing process of an ordered mixture proceeds.

The power spectrum of an ordered mixture has a particular shape. As can be seen in Figs. 5-A and 5-B, the most uniform (ordered) mixture has a

symmetrical power spectrum, and all components of the power spectrum have zero values except at the two ends while the power spectrum components of the completely segregated mixture ($k = 0$ and $k = N/2$) exponentially decreases down to zero with the increase in the wave number. Other intermediate state mixtures lie between these two extremes. We can expect that M_1 of a two-dimensional checkered pattern mixture has a similar property since such a mixture is also an ordered mixture (Fig. 6)

The degree of mixedness of a checkered pattern mixture may be investigated by other methods, for example, by contact number sampling (Lai, 1974).

2.5.3 Characteristics of Random Mixtures

An actual mixing process is often accompanied by random movements of individual particles. The DFT power spectrum of a resulting random mixture has a different structure from that of an ordered one. As a mixing process proceeds or the randomness increases, M_1 decreases. This is in sharp contrast to the characteristics of an ordered mixture for which M_1 increases with an increase in uniformity or homogeneity. As the mixture approaches completely random state, M_1 approaches zero, thereby confirming Eqn. (12) (also see Tables 1 and 2).

The variance of a one-dimensional mixture which undergoes a mixing process of the Fickian diffusion type, Eqn. (23) or (24), can be written as (Lacey, 1960):

$$\sigma^2 = \frac{2}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{\sin(nq\pi)^2}{n} \right] e^{-2n^2\pi^2\tau} \quad (26)$$

When τ is large (> 0.1), only the first term ($n = 1$) is of importance, and Eqn. (26) is reduced to

$$\sigma^2 = \frac{2}{\pi^2} e^{-2\pi^2 \tau} \sin^2 q\pi \quad (27)$$

The DFT power spectrum of this mixture exhibits a special feature. M_1 is always equal to $\bar{p}(1)$ and the rest of the power spectrum components are significantly lower than $\bar{p}(1)$. In fact, the exact relationship between M_1 and τ can be shown to be (see the Appendix)

$$-\ln M_1 = 2\tau \quad (28)$$

From Eqns. (27) and (28), therefore, we can conclude that

$$\ln M_1 = \text{constant} + \ln \sigma^2 \quad (29)$$

This shows that a linear relationship exists between $\ln M_1$ and $\ln \sigma^2$.

A similar result can be obtained for the two-dimensional case.

The mixing process simulated previously by randomly interchanging particles at different locations is essentially a diffusive mixing process, considering that the mixing time is proportional to the number of exchanges of individual particles. Consequently, we can expect that a linear relationship exists between $\ln M_1$ and $\ln \sigma^2$ as derived in Eqn. (29). The data in Tables 1 and 2 for one- and two-dimensional random mixtures plotted in Fig. 7 show such a linear relationship.

The maximum DFT power spectrum, M_1 , has a resolving power to distinguish the ordered pattern from the random one including the homogeneity of the mixture. In contrast, the sample variance, σ^2 , does not possess such a resolving power. Therefore, this property of M_1 may be useful when a product mixture, which must have a specific ordered pattern, needs to be identified.

2.5.4 Fourier Transform vs. Walsh-Hadamard Transform

Using the Walsh-Hadamard power spectrum Wang, et al. (1977) developed a similar technique to assess the random mixture homogeneity. In their work, model mixtures employed for the computer simulation were two-dimensional binary random mixtures represented by a (16x16) matrix. The method of generating a random mixture was identical to that previously described in the present work. After each fixed number of interchanges, the two-dimensional Walsh-Hadamard transform(WHT) was performed, and the corresponding two-dimensional power spectrum was computed.

The results show that the mixing index, based on the WHT power spectrum component which has a predominating variance, is linearly correlated with that based on the sample variance, σ^2 . This is somewhat similar to the present observation for M_1 shown in Fig. 7. No attempt was made by Wang, et al. (1976) to apply their approach to ordered mixtures. Therefore, it is not certain whether the WHT possesses the resolving power similar to the DFT for ordered mixtures.

2.6 CONCLUDING REMARKS

Continuous sampling techniques are being rapidly developed, and to keep pace with this, a fast and reliable technique for determining and classify mixture homogeneity is needed. The present study was carried out to test the applicability of the DFT power spectrum for this purpose. The DFT is particularly useful when the homogeneity and pattern of a mixture are to be simultaneously determined. A fast sampler and a well-trained classifier are required for an efficient characterization of the mixture quality by means of the DFT. The training procedure of the classifier depends on the method of sampling as well as the specific criterion of product quality.

The DFT technique can also be applied to multicomponent particle systems. While training procedures for a multicomponent mixture would be substantially different from these for a binary mixture, the results of the present work would be useful in guiding development of such procedures.

NOTATIONS

c	=	concentration of key particles
$\{C_x(k)\}$	=	one-dimensional DFT of $\{X(m)\}$
$\{C_{xx}(k_1, k_2)\}$	=	two-dimensional DFT of $\{X(m_1, m_2)\}$
D	=	diffusion coefficient
E	=	expectation or expected value
$F(\xi, \tau)$	=	FT of c with respect to y
$F_0(\xi)$	=	$F(\xi, 0)$
h	=	sampling lag
k	=	wave number
L	=	length of the mixer
m	=	sample sequence in one-dimensional mixtures
m_1, m_2	=	sample sequences in two-dimensional mixtures
M_1	=	value of the maximum DFT power spectrum component
N	=	number of samples in one-dimensional mixtures
$N_1 \times N_2$	=	total number of samples in two-dimensional mixtures
$\{p(k)\}$	=	one-dimensional DFT power spectrum
$\{\bar{p}(k)\}$	=	normalized one-dimensional DFT power spectrum
q	=	average concentration or initial proportion of key particles
$R(m)$	=	autocorrelation function with distance lag m
$[T]$	=	DFT matrix
W	=	$e^{-i \frac{2\pi}{N}}$, a complex constant
W_ℓ	=	$e^{-i \frac{2\pi}{N_\ell}}$, a complex constant
$[X]_i$	=	digitized one-dimensional solid mixtures
$\{X(m)\}$	=	one-dimensional data matrix

$\{X(m_1, m_2)\}$	=	two-dimensional data matrix
$[Y]_1$	=	DFT transformed vector of $[X]_1$ mixture
σ^2	=	variance
τ	=	dimensionless time
ξ	=	dummy variable
$\rho(m)$	=	correlation coefficient with distance lag m

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APPENDIX, DERIVATION OF EQUATION (28)

From Eqn. (23) we have

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (\text{A.1})$$

In dimensionless form

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} \quad (\text{A.2})$$

where

$$\tau = Dt/L^2$$

$$y = \frac{x}{L}$$

Let F be the Fourier transform of c with respect to y , i.e.,

$$F(\tau, \xi) = \int_{-\infty}^{\infty} c(y, \tau) e^{-i\xi y} dy \quad (\text{A.3})$$

Then Eqn. (A.1) can be transformed into

$$\frac{dF}{d\tau} + \xi^2 F = 0 \quad (\text{A.4})$$

The solution to Eqn. (A.4) is given by

$$F(\xi, \tau) = F_0(\xi) e^{-\xi^2 \tau} \quad (\text{A.5})$$

where $F_0(\xi)$ is the Fourier transform of c at $\tau = 0$. The power spectrum at a given τ is, by definition,

$$\begin{aligned} p(\xi, \tau) &= [F(\xi, \tau)]^2 \\ &= [F_0(\xi)]^2 e^{-2\xi^2 \tau} \end{aligned} \quad (\text{A.6})$$

The discrete version of the above equation is

$$p(k) = [F_0(k)]^2 e^{-2k^2\tau} \quad (\text{A.7})$$

where

$$k = 0, 1, 2, \dots, \frac{N}{2}$$

The normalized power spectrum is given by

$$\bar{p}(k) = \frac{p(k)}{p(0)} = e^{-2k^2\tau} \quad (\text{A.8})$$

Since M_1 is equal to $\bar{p}(1)$, we can conclude that

$$M_1 = e^{-2\tau}$$

or

$$-\ln M_1 = 2\tau$$

This is Eqn. (28) in the text.

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

**THIS IS AS
RECEIVED FROM
CUSTOMER.**

TABLE 1. One-dimensional random mixture classification.

Mixture	Number of Exchanges	M_1	σ^2
1	0	0.4053	0.2500
2	20	0.2019	0.1344
3	40	0.1443	0.0967
4	60	0.0631	0.0444
5	80	0.0502	0.0400
6	100	0.0381	0.0356
7	120	0.0206	0.0422
8	140	0.0175	0.0244
9	160	0.0159	0.0256
10	180	0.0153	0.0256

TABLE 2.. Two-dimensional random mixture classification.

Mixture	Number of Exchanges	M_1	σ^2
1	0	0.1026	0.2500
2	20	0.0524	0.1896
3	40	0.0277	0.1364
4	60	0.0126	0.0895
5	80	0.0101	0.0727
6	100	0.0061	0.0667
7	120	0.0050	0.0505
8	140	0.0055	0.0440
9	160	0.0046	0.0365
10	180	0.0047	0.0321

TABLE 3. Normalized power spectrum of $[X]_3$ mixture in Eqn. (25).

Wave Number, k	Normalized Power Spectrum, p(k)
0	1.0000
1	0.0670 *
2	0.0418
3	0.0159
4	0.0023
5	0.0046
6	0.1379 *
7	0.0237
8	0.0078
9	0.0164
10	0.0911 *
11	0.0082
12	0.0133
13	0.0211
14	0.0104
15	0.0304
16	0.0156

* Stars represent the three predominating power spectrum components.

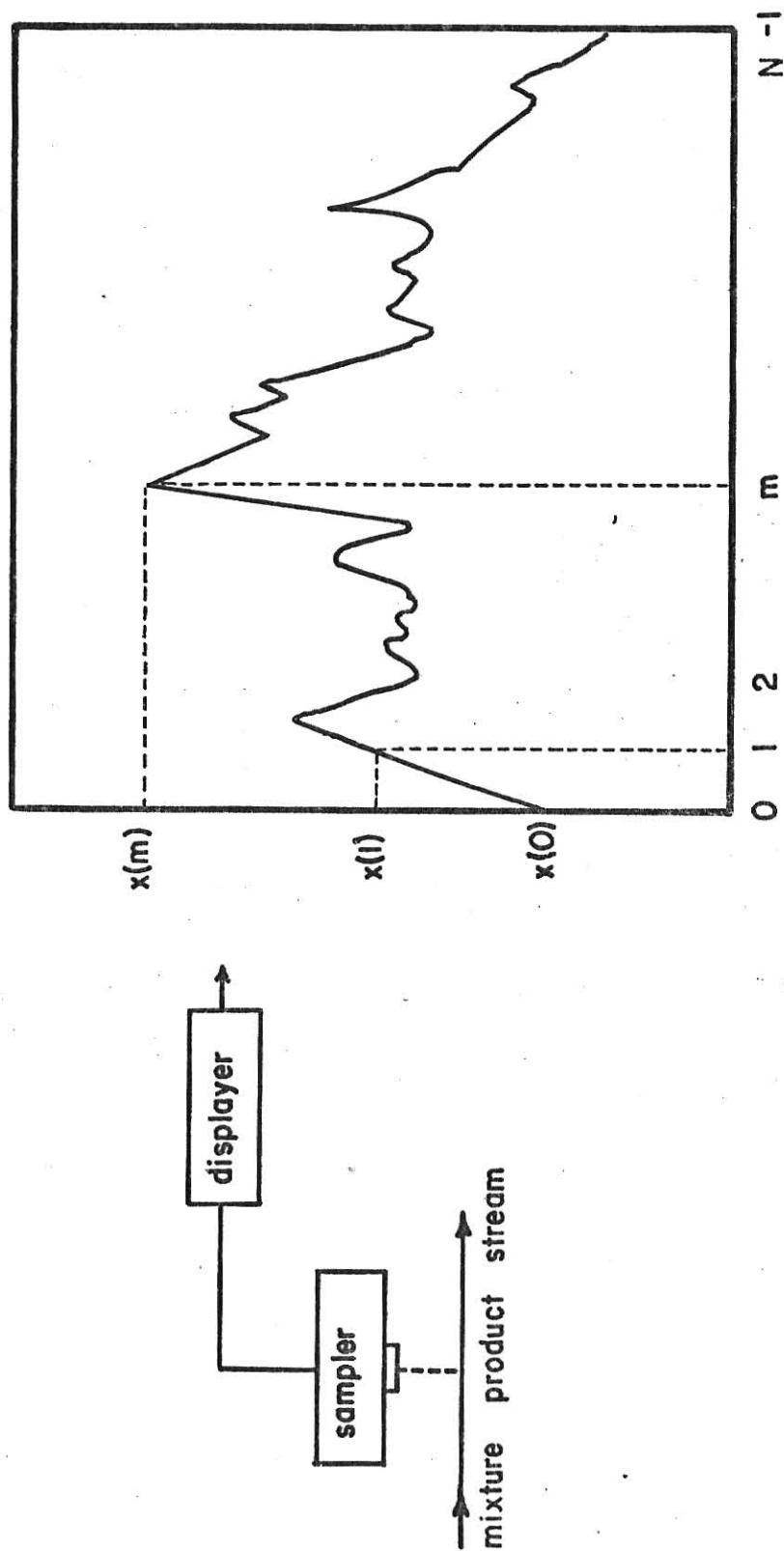


Fig. 1 Signal from a sampler in fixed position. (The curve on the right is the video signal).

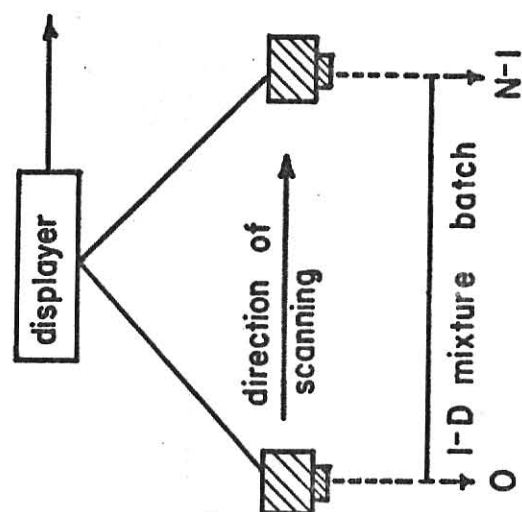
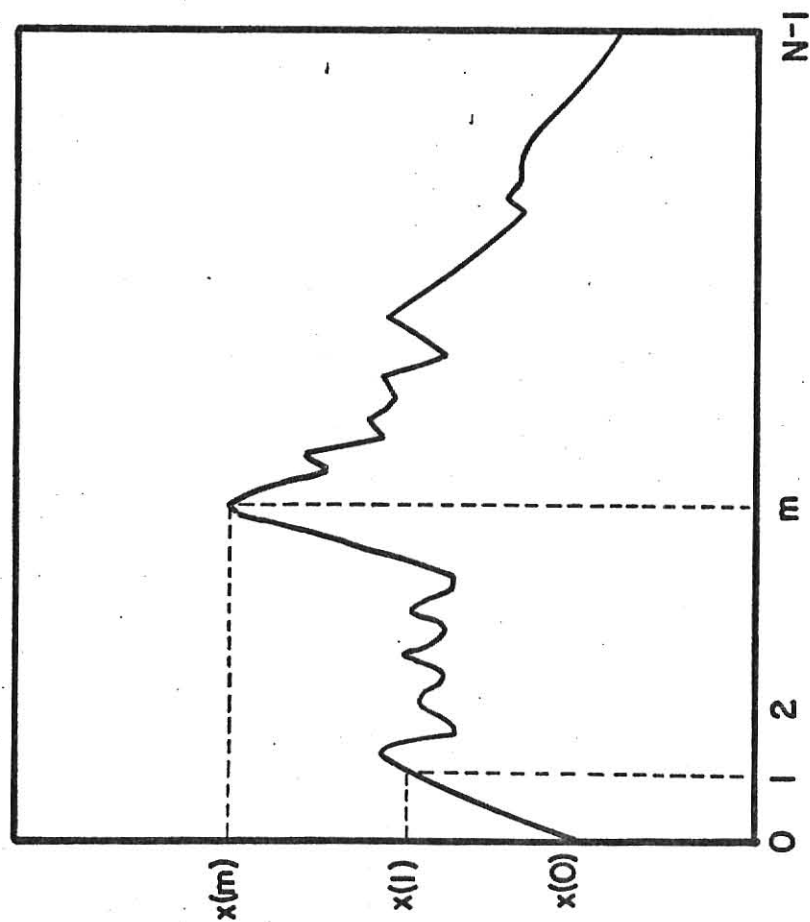


Fig. 2 Signal scanned over a one-dimensional mixture.

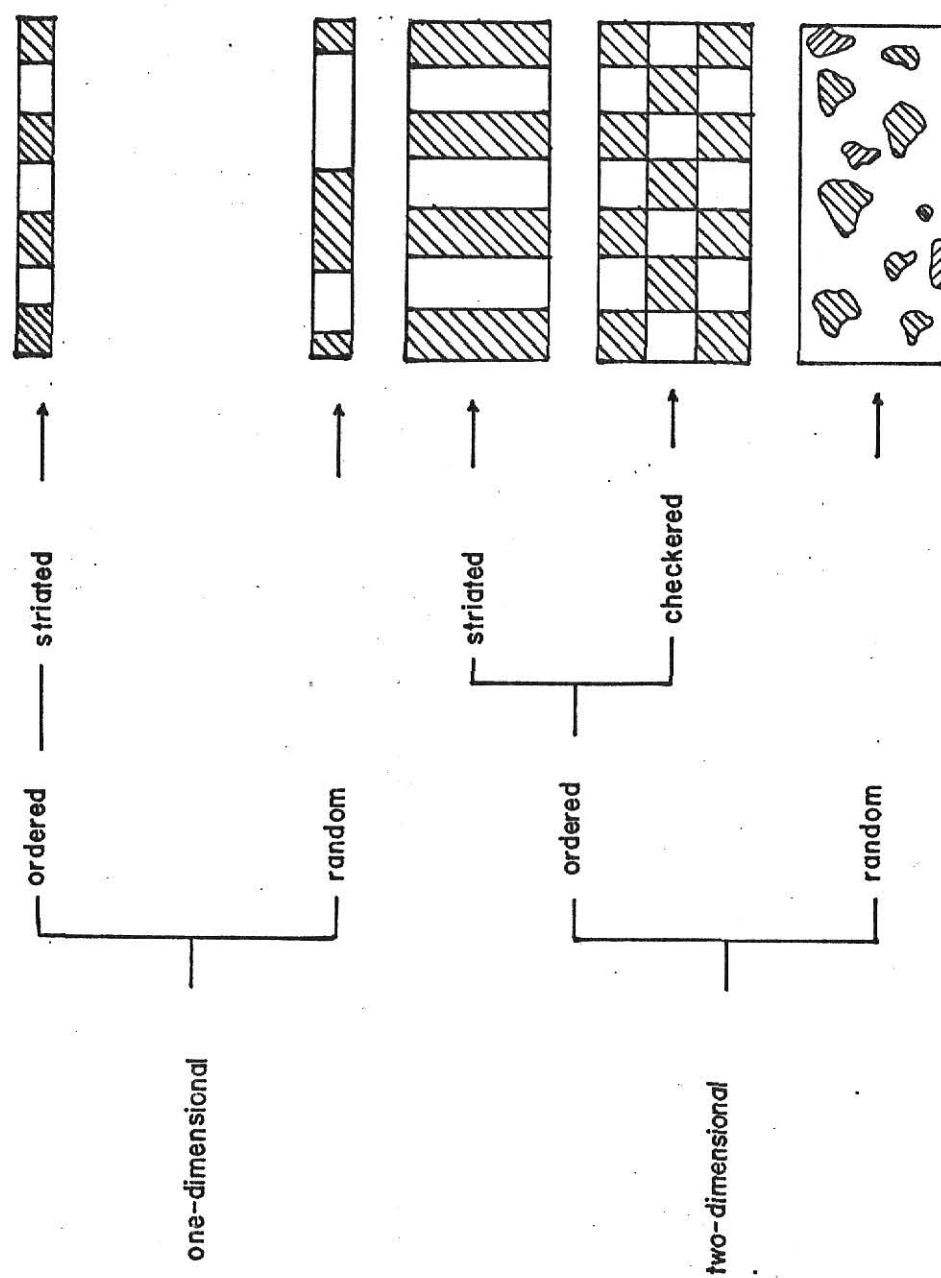


Fig. 3 One- and two-dimensional mixture pattern classification.

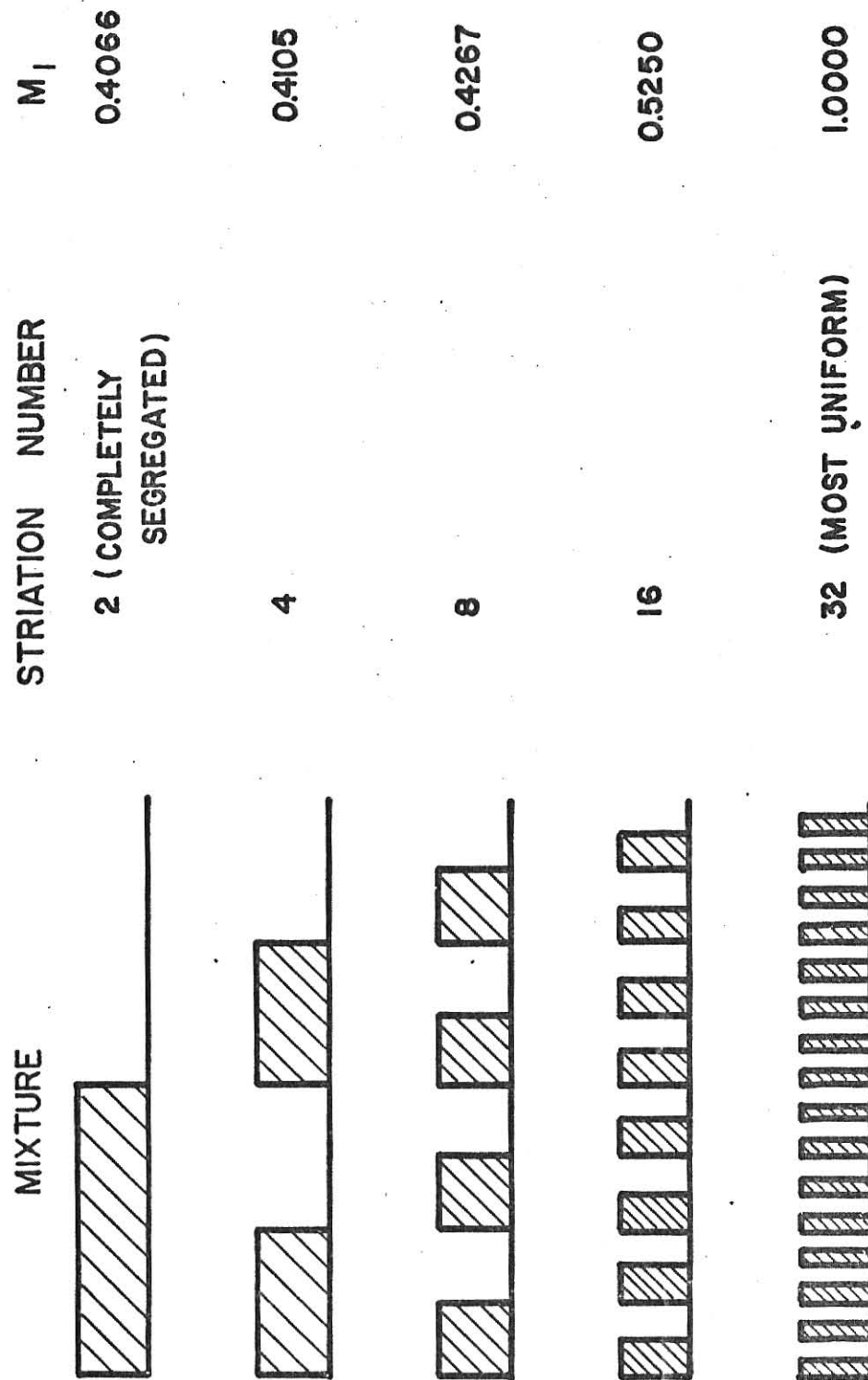


Fig. 4 Maximum power spectrum of one-dimensional ordered mixtures.

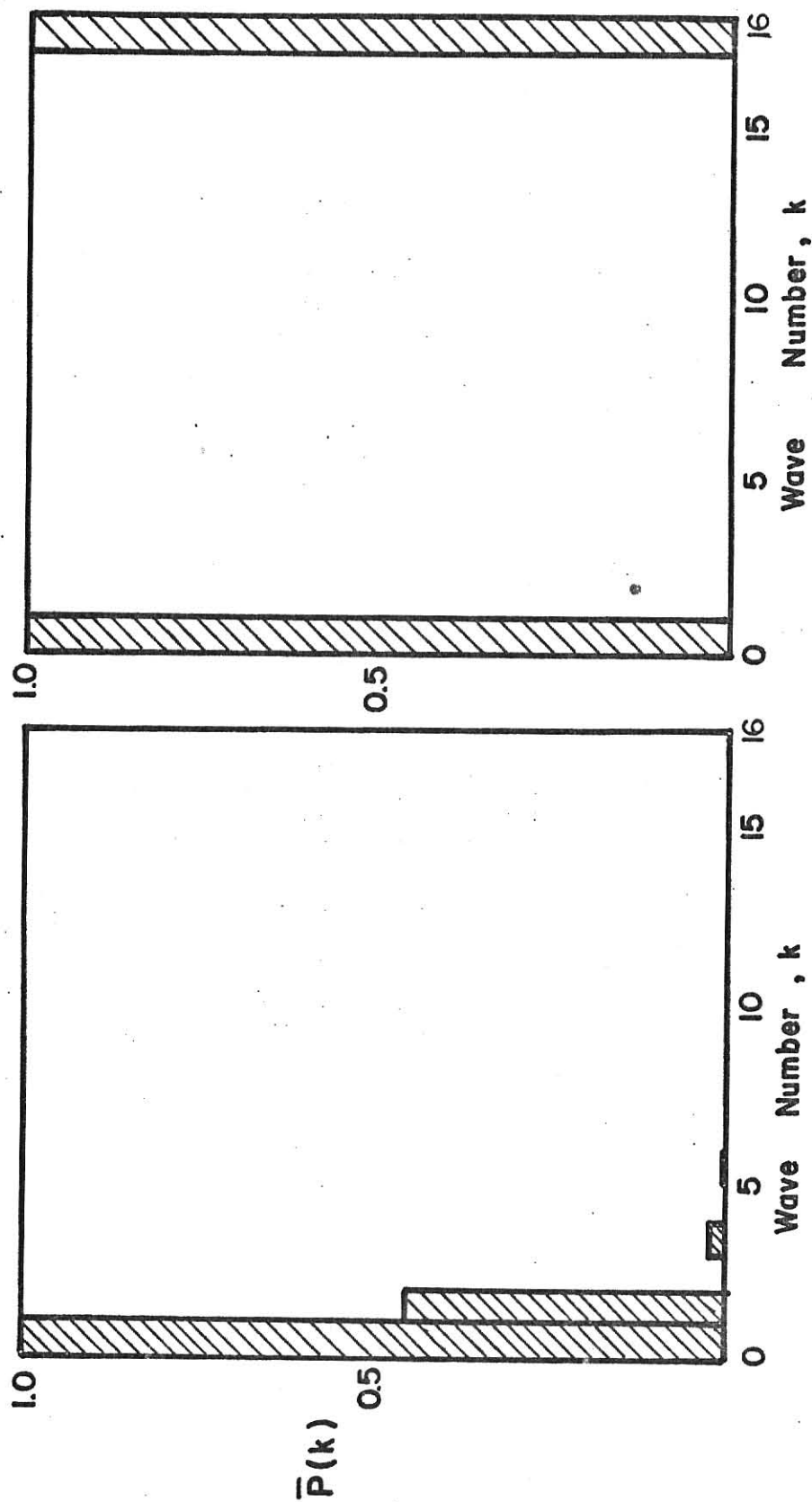
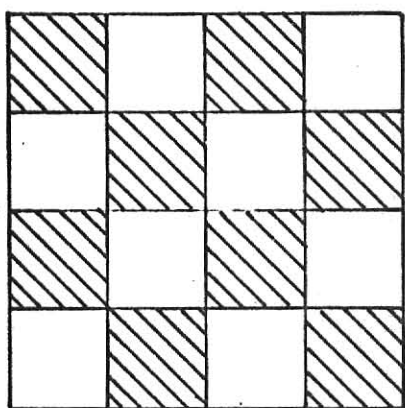


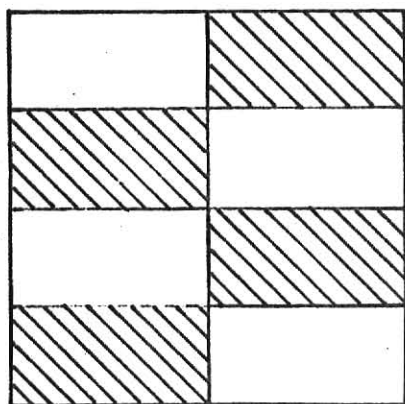
Fig. 5 - B

Fig. 5-A

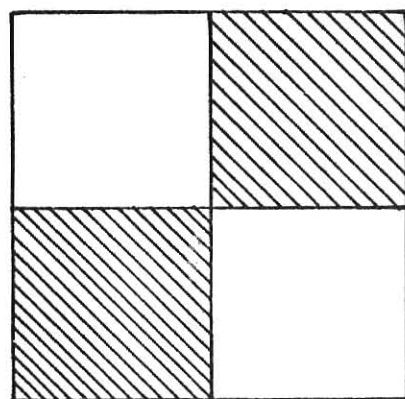
Fig. 5 Normalized power spectrum vs. wave number for a completely segregated mixture (5-A) and for a most uniformly ordered mixture (5-B).



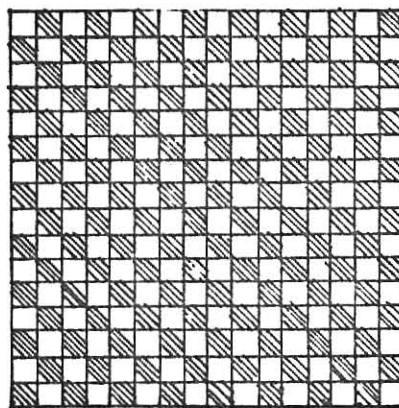
$$M_l = 0.0455$$



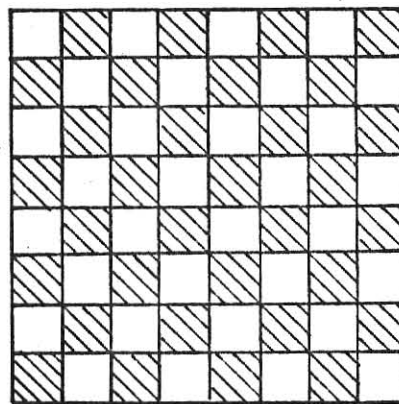
$$M_l = 0.0438$$



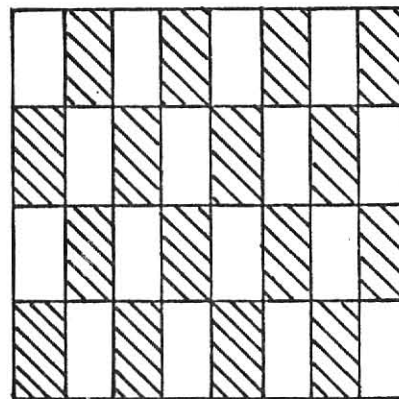
$$M_l = 0.0421$$



$$M_l = 0.2500$$



$$M_l = 0.1250$$



$$M_l = 0.01067$$

Fig. 6 Checkerboard pattern mixtures and corresponding maximum power spectrum.

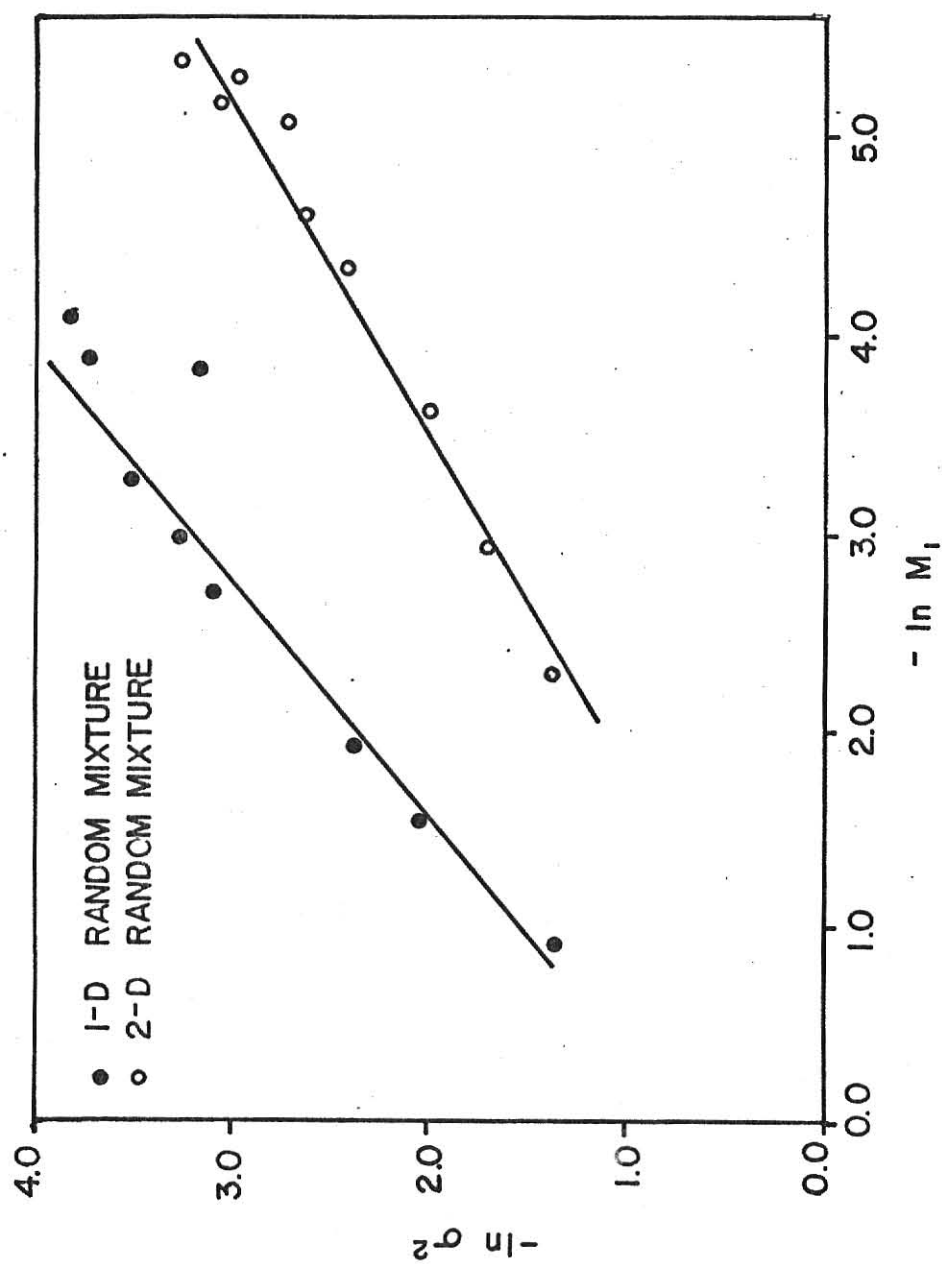


Fig. 7 Plot of $-\ln M_1$ vs. $-\ln q_2$ for random mixtures.
(Note the linear relationships.)

3. STOCHASTIC DIFFUSION MODEL OF NON-IDEAL MIXING IN A HORIZONTAL DRUM MIXER

3.1 INTRODUCTION

A study of solids mixing usually involves two basic aspects; one is elucidation of the rate and mechanism of the mixing process itself and the other is characterization of the resulting mixture including its homogeneity (Bridgwater, 1975; Cooke et al., 1976; Fan et al., 1970; Weidenbaum, 1958). Studies on the rate and mechanism of mixing have mainly been concerned with the establishment of expressions or models for the rate of mixing. Some of the models deal only with the overall rate of mixing without regard to the spatial distribution of particles (see, e.g., Brothman, 1945; Coulson and Maitra, 1950; Rose, 1959; Weidanz, 1960); others take into account both temporal change and spatial distribution of the particle concentration (see, e.g., Hogg et al., 1966; Lai and Fan, 1975; Oleniczak, 1962; Wang and Fan, 1976). The models of the former class are expressed in terms of variance or degree of mixedness which is subjectively defined; those of the latter class are based on the Fickian diffusion or stochastic equations. Obviously, from the fundamental point of view, the change of the particle concentration distribution along the mixer position should be of primary importance.

The modeling of axial mixing in a horizontal drum mixer was first attempted by Lacey (1954) using the following Fickian diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial c}{\partial x} \right] \quad (1)$$

where D is the diffusion coefficient which is generally a function of t , x and c . For an ideal particle system containing particles with identical physical properties except color, the solution of Eqn. (1) with a constant D yields an expression which is in reasonable agreement with experimental data (see, e.g., Hogg et al., 1966). However, Eqn. (1) is

not directly applicable to a segregating or non-ideal particle system which may give rise to a band formation.

The band formation was observed by Donald and Roseman (1962) when particles of different sizes were mixed in a horizontal drum mixer. Bands were first formed at the ends and then moved to the center. They attributed this to axial variation of the radial velocity profile. Bridgwater, Sharpe and Stocker (1969) suggested that the interparticle percolation and differences in void fraction are the probable reasons for such a phenomenon. Lloyd, Yeung and Freshwater (1970) observed that the equilibrium concentration distribution depended on the speed of mixer rotation for a given particle system. Compared with these efforts to analyze and interpret the band formation qualitatively, practically no attempt has been made to describe it quantitatively. Hogg (1969) suggested that the deviation from ideality could be handled by incorporation of concentration dependent D in Eqn. (1). As will be shown later, Eqn. (1) yields a flat equilibrium profile in a batch mixer independent of the functional form of D .

Because of its complexity, stochastic approaches may be advantageous in modeling the rate and mechanism of non-ideal mixing and in predicting the concentration distribution inside a mixer. While most of the stochastic modeling efforts are concerned with ideal mixing, Wang and Fan (1976) applied the Markov chain to a non-ideal particle system. The objective of this work is to examine the applicability of another stochastic model, i.e., the stochastic or Kolmogorov diffusion equation, to such a system which may give rise to a band formation. While this equation was proposed by earlier investigators (Molerus, 1966; Müller and Rumpf, 1967), no attempt has been made so far to apply it in its original or rigorous form.

Suppose that a binary mixture containing different size particles is mixed in a horizontal drum mixer. It can be visualized that both large and small particles move randomly or stochastically in the mixer. In the vicinity of an end of the mixer, however, the probability for smaller particles to migrate toward the center of the mixer is larger than that of larger particles. This is due to the higher mobilities of the smaller ones which tend to move through the interstices of the larger ones. Consequently, as mixing proceeds, the larger particles tend to remain in the end region while a band of smaller ones moves away from it.

3.2 THEORETICAL

First we shall assume that a particle being mixed undergoes a Markov process, i.e., the probability for a particle to migrate from one position to another in a drum mixer is independent of the intermediate steps.

This gives rise to the Kolmogorov diffusion equation.

3.2.1 Kolmogorov Diffusion Equation (see, e.g., Bharucha-Reid, 1960; Seinfeld and Lapidus, 1974).

Suppose that a particle of the key component or simply a key particle was initially observed at x_0 ($0 \leq x_0 \leq 1$), and that after a certain period of mixing the particle is found at x ($0 \leq x \leq 1$). x_0 and x are normalized or dimensionless axial mixer positions which are variables.

Let us define a random variable $\{X(t); t \geq 0\}$ associated with x , which obeys a continuous stochastic process of the Markov type defined on the real line segment between 0 and 1. Furthermore, let us define a conditional probability and its density function such that

$$\begin{aligned} F(x_0, t_0; x, t) &\equiv \Pr[X(t) \leq x | X(t_0) = x_0] \\ f(x_0, t_0; x, t) &\equiv \frac{\partial F}{\partial x} \end{aligned} \quad (2)$$

In this expression, $F(x_0, t_0; x, t)$ is the conditional probability that a key particle originally at x_0 migrates to x during the time period $\Delta t = t - t_0$. Since $f(x_0, t_0; x, t)$ is a probability density function, we have

$$\int_0^1 f(x_0, t_0; x, t) dx = 1 \quad (3)$$

Another assumption necessary for the derivation of the Kolmogorov diffusion equation is that the probability of particle motion during an infinitesimal time interval Δt is negligible compared to Δt . Mathematically,

$$\begin{aligned}
& \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|x'-x| \geq \delta} f(x, t; x', t+\Delta t) dx' \\
& = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|x'-x| \geq \delta} f(x, t-\Delta t; x', t) dx' \\
& = 0
\end{aligned} \tag{4}$$

where

$$\delta > 0, \quad 0 \leq x' \leq 1$$

From the assumption of the Markov property for the random variable, $X(t)$, we have

$$f(x_0, t_0; x, t) = \int_0^1 f(x_0, t_0; x', \tau) f(x', \tau; x, t) dx' \tag{5}$$

where

$$0 \leq x' \leq 1$$

$$t_0 \leq \tau \leq t$$

Equations (4) and (5) give rise to the Kolmogorov or stochastic diffusion equation of the following form (See Appendix 1 for the derivation):

$$\frac{\partial f}{\partial t} = \frac{\partial^2 (Df)}{\partial x^2} - \frac{\partial (Vf)}{\partial x} \tag{6}$$

where

$$f \equiv f(x_0, t_0; x, t)$$

$$D(x, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|x''-x| < \delta} \frac{1}{2} (x''-x)^2 f(x, t; x'', t+\Delta t) dx'' \tag{7}$$

$$V(x, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|x''-x| < \delta} (x''-x) f(x, t; x'', t+\Delta t) dx'' \tag{8}$$

In Eqns. (7) and (8), x'' is a dummy variable in the neighborhood of x , and $D(x, t)$ and $V(x, t)$ are respectively the diffusion coefficient and the drift velocity. Equation (6) is written in terms of the transition

probability density function. In practice, however, it is convenient to express it in terms of concentration. Let $N(x', t_0)$ be the number density (number/unit volume) of key particles at x' and t_0 , and $N(x, t)$, that at x and t . Then from the definition of the transition probability, we can write

$$N(x, t) = \int_0^1 N(x', t_0) f(x', t_0; x, t) dx' \quad (9)$$

Since

$$c(x', t_0) = \frac{N(x', t_0)}{N_t}$$

where

N_t = total number of particles in the mixture

$c(x', t_0)$ = number concentration distribution of the key particles at time t_0

$c(x, t)$ = number concentration distribution of the key particles at time t ,

Eqn. (9) can be rewritten as

$$c(x, t) = \int_0^1 c(x', t_0) f(x', t_0; x, t) dx' \quad (10)$$

By substituting Eqn. (10) into Eqn. (6), we obtain the following Kolmogorov equation in terms of concentration (See Appendix 2):

$$\frac{\partial c}{\partial t} = \frac{\partial^2 (Dc)}{\partial x^2} - \frac{\partial (Vc)}{\partial x} \quad (11)$$

Note that in Eqn. (9) the transition probability $f(x', t_0; x, t)$ must be expressed in terms of the number fraction of key particles which migrate from x' to x during the time interval between t_0 and t . When the concentration is expressed in terms of another variable such as weight or volume,

the value of the transition probability is accordingly changed. In the present study the weight concentration is used instead of the number.

To simplify the model, we shall assume that the mixing process is a stationary Markov process which depends only on the time interval Δt , but not on t . Under this assumption, we have

$$\begin{aligned} D(x,t) &= D(x) \\ V(x,t) &= V(x) \end{aligned} \quad (12)$$

The initial condition for Eqn. (11) is

$$c(x,0) = c_0(x) \quad (13)$$

The boundary conditions are obtained from the conservation of mass at the two boundaries. In a closed (batch) system the mass flux, $J(x)$, vanishes at either boundary, i.e.,

$$J(x) = - \frac{\partial(Dc)}{\partial x} + vc = 0, \quad \text{at } x = 0 \text{ and } x = 1 \quad (14)$$

The variance, $\sigma^2(t)$, and the degree of mixedness, $M(t)$, can be calculated, respectively, by

$$\sigma^2(t) = \int_0^1 [c(x)-q]^2 dx \quad (15)$$

where

$$q = \int_0^1 c_0(x) dx$$

and

$$M(t) = 1 - \frac{\sigma^2(t)}{\sigma_0^2} \quad (16)$$

where

$$\sigma_0^2 = q(1-q)$$

If the drift velocity, V , vanishes for a closed or batch system, Eqn. (11) reduces to

$$\frac{\partial^2 c(x,t)}{\partial t} = \frac{\partial^2 [D(x) c(x,t)]}{\partial x^2} \quad (17)$$

Note that this equation is not identical to the Fickian diffusion equation with a non-constant D , i.e., Eqn. (1), which is repeated below

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[D(x) \frac{\partial c(x,t)}{\partial x} \right] \quad (1)$$

These two equations reduce to an identical form only when D is invariant with respect to x and t for a closed system. Under the equilibrium or steady state condition, Eqn. (17) becomes

$$\frac{\partial^2 [D(x) c_e(x)]}{\partial x^2} = 0 \quad (18)$$

Solving the equation subject to the boundary conditions

$$J = 0, \text{ at } x = 0 \text{ and } x = 1 \quad (19)$$

or

$$\frac{\partial [D(x) c_e(x)]}{\partial x} = 0, \text{ at } x = 0 \text{ and } x = 1 \quad (20)$$

we obtain

$$c_e(x) = \frac{\gamma}{D(x)}, \text{ for all } x \quad (21)$$

where γ is a positive constant and $c_e(x)$ is the equilibrium concentration profile. This indicates that the functional form of $D(x)$ can be determined from the equilibrium profile. On the other hand, the equilibrium profile based on Eqn. (1) with the same boundary conditions as before leads to

$$D(x) \frac{\partial c_e(x)}{\partial x} = 0, \text{ at } x = 0 \text{ and } x = 1 \quad (22)$$

Therefore,

$$c_e(x) = q, \text{ for all } x \quad (23)$$

Comparing Eqns. (21) and (23) we can see that the Fickian equation always results in a flat equilibrium profile independent of $D(x)$, while the Kolmogorov equation gives different equilibrium profiles depending on $D(x)$. The Kolmogorov equation reduces to the Fickian only when

$$D = \gamma/q = \text{constant}$$

as stated previously.

Another distinction between the Kolmogorov equation and the Fickian equation is that the diffusivity coefficient appearing in the former is a derived quantity which has an explicit physical meaning while that in the latter is essentially an empirical parameter.

In the preceeding paragraphs the drift velocity has been neglected to simplify the discussion. To understand its significance, let us consider a mixing process as depicted in Fig. 1. In this figure curve A is the key particle distribution at time t_0 , which is assumed to be the delta function. Curves B and C are the distributions at time t_1 and t_2 , respectively, which are monitored in the subsequent time intervals. Furthermore, let us assume that distributions B and C have finite means and variances. The means of distributions B and C are denoted by x_1 and x_2 , respectively, and the variances by $\sigma^2(t_1)$ and $\sigma^2(t_2)$ respectively. Obviously, distribution A has a mean x_0 and the variance

$$\sigma^2(t_0) = 0 .$$

According to Eqn. (7), the average diffusion coefficient in the region between x_0 and x_1 , and that between x_0 and x_2 are, respectively,

$$\begin{aligned} \bar{D}(x_0 \rightarrow x_1) &= \frac{1}{2} \sigma^2(t_1) \\ \bar{D}(x_0 \rightarrow x_2) &= \frac{1}{2} \sigma^2(t_2) \end{aligned} \quad (24)$$

According to Eqn. (8), the corresponding drift velocities, are, respectively,

$$\begin{aligned} \bar{V}(x_0 \rightarrow x_1) &= \frac{x_1 - x_0}{t_1 - t_0} \\ \bar{V}(x_0 \rightarrow x_2) &= \frac{x_2 - x_0}{t_2 - t_0} \end{aligned} \quad (25)$$

When \bar{V} is negligible, the initial concentration distribution A undergoes a transition to B' and eventually to C' as shown in Fig. 1; however, when \bar{V} is not negligible, distribution A becomes B and eventually becomes C.

It must be noted that the overall average $V(x)$ inside a batch mixer must vanish since there is no net transport of particles out of the mixer ends. Thus,

$$\int_0^1 V(x) dx = 0 \quad (26)$$

However, for a continuous mixer with continuous feeding and removal of particles, a net velocity of the particles through the mixer, V_b , is finite and non-zero, i.e.,

$$\int_0^1 V(x) dx = V_b > 0 \quad (27)$$

3.2.2 Simultaneous Determination of the Diffusion Coefficient and the Drift Velocity

The diffusion coefficient $D(x)$ and the drift velocity $V(x)$ are continuous functions of the dimensionless mixer position x , and their experimental determinations are extremely difficult, thus they can be approximately accomplished at best by discretizing x .

Suppose that the mixer is divided into n hypothetical sections in the axial direction. Assuming that the mixing process is a discrete stationary stochastic process, each section can be considered as the states of the Markov chain (see, e.g., Parzen, 1962; Lai and Fan, 1975; Wang and Fan, 1976). Furthermore, let P_{ij} denote the probability that the state value undergoes a transition from the i -th section to the j -th in one-step time interval or one trial. Then we can write the one-step transition matrix as

$$[P_{ij}] = \begin{bmatrix} P_{11} & P_{12} & \cdot & \cdot & \cdot & P_{1n} \\ P_{21} & P_{22} & \cdot & \cdot & \cdot & P_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ P_{n1} & P_{n2} & \cdot & \cdot & \cdot & P_{nn} \end{bmatrix} \quad (28)$$

If the tracer key particles have been layered originally in the i -th section of the mixer as shown in Fig. 2-A, they will disperse throughout the mixer interior after a short mixing time, as shown in Fig. 2-B.

Even though there exists a local concentration gradient inside the j -th section, we can assume that the average weight fraction of the key particles in the j -th section be approximately P_{ij} . Note that, for this tracer experiment, the displacements of the tracer particles from the initial position to the neighborhood are relatively small since the mixing time is short, and thus, the condition $|x'' - x| < \delta$ in Eqns. (7) and (8) must be approximately valid. Furthermore, under the assumption of the stationary Markov process, we have

$$\begin{aligned} D(x) &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|x''-x|<\delta} \frac{1}{2}(x''-x)^2 f(x, t; x'', t+\Delta t) dx'' \\ &= \int_{|x''-x|<\delta} \frac{1}{2}(x''-x)^2 f(x, t; x'', t+\Delta t) dx'' \end{aligned} \quad (29)$$

and

$$\begin{aligned} V(x) &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|x''-x|<\delta} (x''-x) f(x, t; x'', t+\Delta t) dx'' \\ &= \int_{|x''-x|<\delta} f(x, t; x'', t) dx'' \end{aligned} \quad (30)$$

These equations can be approximated, respectively, by writing them in discrete forms as

$$D(x_i) \approx \sum_{j=1}^n \frac{1}{2}(x_j - x_i)^2 P_{ij} \frac{1}{n} \quad (31)$$

$$V(x_i) \approx \sum_{j=1}^n (x_j - x_i) P_{ij} \frac{1}{n} \quad (32)$$

where

$$\Delta x'' = \frac{1}{n}$$

$$0 \leq x_i, x_j \leq 1$$

Equations (31) and (32) are essentially numerical integration formulas for Eqns. (29) and (30), respectively.

3.2.3 Methods of Solving the Kolmogorov Equation

As can be seen from Eqn. (11), the Kolmogorov equation is a parabolic partial differential equation, and any method for solving such a differential equation can be used. An analytic solution may be obtained by the separation of variables or Laplace transform. The solution strategy should depend on the functional form of $D(x)$. $\frac{1}{D(x)}$ which is not analytic at the boundaries gives rise to a singular diffusion problem. The solution of the singular diffusion problem is not straightforward. To eliminate this difficulty, it is assumed here that $D(x)$ is continuous, twice-differentiable, and finite in the closed interval $[0, 1]$.

Since the analytic solution of Eqn. (11) is usually difficult a numerical approach, e.g., the method of lines, can be employed. A computer package, the PDESOL (Sincovec and Madsen, 1975), is available for executing numerical calculations based on the method of lines which converts, by means of a finite difference method, the original partial differential equation dependent on x and t into a set of ordinary differential equations dependent only on x .

3.3 EXPERIMENTAL

The mixer used for the experiments was constructed from a 0.14 m diameter lucite tube, 0.37 m long, fitted with 0.28 m diameter lucite flangs. The tube was separable so that the upper portion could be removed for loading and smpling. Particles used were spherical lucite with an average diameter of 0.16 cm, 0.32 cm, or 0.48 cm with an average density of 1.156 gr/cm³. For each particle system the smaller ones were identified as the key particles.

Prior to each experimental run, determination of the one-step transition matrix $[P_{ij}]$ was carried out independently at a specified rotational mixer speed. This was accomplished by loading the key particles into one compartment of the mixer by using a templet which was designed to divide the mixer into ten equal sections and measuring the key particle distribution at each section after rotating the mixer for one minute. The diffusion coefficient and drift velocity were calculated according to Eqns. (31) and (32), respectively.

The mixer was loaded end to end with 50% by weight of key particles, which were initially layered on the left half of the mixer. 500 grams of particles were loaded in the mixer at a time which was equivalent to filling approximately 25% of the total mixer volume. Concentration change along the axial mixer position with time was monitored by using the same templet as mentioned previously. At predetermined time intervals the particles were completely removed by suction from each compartment, and the weight fractions of the key particles were measured. The mixer was rotated at a speed of 15, 30, or 45 rotations per minute.

3.4 RESULTS

Figures 3 and 4, respectively, show the variations of the diffusion coefficient and the drift velocity with respect to the dimensionless mixer position x . In these figures S/M stands for the system containing particles with diameters 0.32 cm-0.48 cm and M/L stands for that containing particles with diameters 0.32 cm-0.48 cm. We shall use these notations in the succeeding paragraphs.

The functional forms of $D(x)$ and $V(x)$ were determined by means of the least square method. Substituting these into the governing differential equation, i.e., Eqn. (11), numerical solutions were obtained subject to the boundary condition, Eqn. (14), by using the PDESOL package.

Figures 5-A, 5-B and 5-C show the concentration profiles for the S/M system rotated at 15 r.p.m. Figures 6-A, 6-B and 6-C are the profiles for the same particle system with a rotational speed of 45 r.p.m. In these figures the solid lines represent the experimentally observed data and the broken lines are those predicted based on the model. The solid circles drawn in Figs. 5-C and 6-C are the predicted equilibrium concentration data based on the model. Note that the prediction based on the model did not involve the fitting of the model to the experimental data through adjustable parameters. It was based on the $D(x)$ and $V(x)$ which were independently determined through one-step tracer experiments.

3.5 DISCUSSION

As can be seen in Figs. 3 and 4, $D(x)$ and $V(x)$ are not constant but vary significantly with x . The diffusivity coefficients at both ends and at the center of the mixer appear to be higher than those of other positions. Figure 3 shows that increases in the rotational speed and density difference tend to induce an increase in the diffusivity coefficient.

In contrast to the strong dependence of the diffusivity, $D(x)$, on the rotational speed and size difference, the drift velocity, $V(x)$, was found to be nearly independent of the particle system and the rotational speed. Figure 4 shows that the rotational speed does not appreciably affect the velocity distribution of the S/M system. In this figure, a positive $V(x)$ indicates that the average local movement of the key particles is toward the right in the axial direction of the mixer, and a negative $V(x)$ indicates it is in the opposite direction. Since the system investigated in this work was a batch system, the net particle flow inside the mixer must be negligible as previously indicated. Note that the area under the curve $V(x)$ vanishes approximately, i.e., Eqn. (26) is approximately valid. The dependence of $V(x)$ and $D(x)$ on the density difference has not been investigated in the present study. This is because a horizontal drum mixer is a non-free-fall or packed type mixer in which each particle being mixed is in close contact with the surrounding particles and the particle size difference mainly induces demixing due to the percolation through the interstices of the larger ones. Therefore, the effect of density difference on $D(x)$ and $V(x)$ is relatively unimportant.

The calculated distribution profiles in Figs. 5-A through 6-C are in reasonably good agreement with the experimental results. The discrepancies between the model and the experiment may be due to the assumption of the

stationary Markov process. As can be seen in these figures the mixing rate in the initial stage is faster than expected. However, a generally good agreement between the model and the experiment, especially near the equilibrium state, indicates that the present model is useful for modeling the non-ideal solids mixing in a horizontal drum mixer.

3.6 CONCLUSION

The significant conclusions of this work are listed below.

1. The Kolmogorov or stochastic diffusion equation can describe quantitatively the non-ideal mixing behavior in a horizontal drum mixer.
2. The Fickian diffusion equation, even in its most general form, cannot describe the band formation in the mixer.
3. The diffusion coefficient, $D(x)$, and the drift velocity, $V(x)$, can be determined simultaneously from the one-step tracer experiment under the assumption of the stationary Markov process.
4. $D(x)$ as well as $V(x)$ in a non-ideal mixing system can vary significantly with the axial mixer position.
5. The average value of $V(x)$ over the entire mixer must vanish for a batch system.
6. $D(x)$ is affected by the nature of the particle system being mixed and the rotational speed of the mixer while $V(x)$ is relatively unaffected by them.
7. The Kolmogorov equation gives different equilibrium concentration profiles depending on the functional dependence of D on x , and thus $D(x)$ can be determined from the equilibrium profile if $V(x)$ is negligible.

It should be noted that the Kolmogorov equation is useful for modeling not only particulate mixing but also other systems such as fluidized beds or flow reactors where the diffusion mechanism predominates.

NOTATIONS

$c(x;t)$	= concentration of the key particles
$c_0(x)$	= initial concentration of the key particles
D	= diffusion coefficient, (L^2/θ)
$F(x_0, t_0; x, t)$	= cumulative conditional probability for a key particle to move from x_0 to x during $\Delta t = t - t_0$
$f(x_0, t_0; x, t)$	= conditional density function of $F(x_0, t_0; x, t)$
J	= instantaneous mass flux, $(M/L^2\theta)$
$M(t)$	= degree of mixedness
$N(x, t)$	= number density distribution of key particles at x and t
N	= total number of particles
$[P_{ij}]$	= transition probability matrix
q	= average concentration of the key component
x_0	= initial position of a key particle
x, x', x''	= dummy variables which assume values between 0 and 1
v	= drift velocity, (L/θ)
v_b	= bulk velocity of solids, (L/θ)
γ	= a positive constant
δ	= infinitesimal positive number
$\sigma^2(t)$	= variance

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APPENDIX 1 DERIVATION OF THE KOLMOGOROV DIFFUSION EQUATION (Bharucha - Reid, 1960)

Let $R(x)$ be a nonnegative continuous function such that

$$R(0) = R(1) = \dot{R}(0) = \dot{R}(1) = 0 \quad (A1-1)$$

In terms of the function $R(x)$, it is clear that

$$\begin{aligned} & \lim_{\Delta t \rightarrow 0} \int_0^1 \frac{f(x_0, t_0; x, t+\Delta t) - f(x_0, t_0; x, t)}{\Delta t} R(x) dx \\ &= \int_0^1 \frac{\partial f(x_0, t_0; x, t)}{\partial t} R(x) dx \end{aligned} \quad (A1-2)$$

Replacing t by $t+\Delta t$ and τ by t in Eqn. (5) of the text, we have

$$f(x_0, t_0; x, t+\Delta t) = \int_0^1 f(x_0, t_0; x', t) f(x', t; x, t+\Delta t) dx' \quad (A1-3)$$

Substitution of Eqn. (A1-3) into the left hand side of Eqn. (A1-2) yields

$$\begin{aligned} & \int_0^1 \frac{\partial f(x_0, t_0; x, t)}{\partial t} R(x) dx \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left[\int_0^1 \int_0^1 f(x_0, t_0; x', t) f(x', t; x, t+\Delta t) R(x) dx dx' \right. \\ & \quad \left. - \int_0^1 f(x_0, t_0; x, t) R(x) dx \right] \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left[\int_0^1 f(x_0, t_0; x', t) \left\{ \int_0^1 f(x', t; x, t+\Delta t) R(x) dx \right\} dx' \right. \\ & \quad \left. - \int_0^1 f(x_0, t_0; x, t) R(x) dx \right] \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left\{ \int_0^1 f(x_0, t_0; x, t) \int_0^1 f(x, t; x', t+\Delta t) R(x') dx dx' \right. \\ & \quad \left. - \int_0^1 f(x_0, t_0; x, t) R(x) dx \right\} \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left\{ \int_0^1 f(x_0, t_0; x, t) \int_0^1 f(x, t; x', t+\Delta t) R(x') dx' - R(x) \right\} dx \quad (A1-4) \end{aligned}$$

Note that in the above derivation we interchanged x and x' since they are dummy variables. Expansion of $R(x')$ in the neighborhood of x gives

$$R(x') = R(x) + (x'-x)\dot{R}(x) + \frac{1}{2}(x'-x)^2\ddot{R}(x) + O[(x'-x)^2] \quad (A1-5)$$

By truncating the higher order terms of the above equation when $|x'-x| < \delta$, we obtain

$$R(x') = R(x) + (x'-x)\dot{R}(x) + \frac{1}{2}(x'-x)^2\ddot{R}(x) \quad (A1-6)$$

Multiplying both sides of Eqn. (A1-6) by $f(x,t;x',t+\Delta t)dx'$ and performing term by term integrations of the resulting expression, we obtain

$$\begin{aligned} & \int_0^1 f(x,t;x',t+\Delta t)R(x')dx' \\ &= R(x) \int_0^1 f(x,t;x',t+\Delta t)dx' \\ & \quad + \dot{R}(x) \int_0^1 (x'-x)f(x,t;x',t+\Delta t)dx' \\ & \quad + \frac{1}{2}\ddot{R}(x) \int_0^1 (x'-x)^2 f(x,t;x',t+\Delta t)dx' \end{aligned} \quad (A1-7)$$

Eqn.(3) in the text states that

$$\int_0^1 f(x,t;x',t+\Delta t)dx' = 1 \quad (3)$$

Thus the second term on the right side of Eqn. (A1-7) can be written as

$$\begin{aligned} & \int_0^1 (x'-x)f(x,t;x',t+\Delta t)dx' \\ &= \int_{|x'-x| \geq \delta} (x'-x)f(x,t;x',t+\Delta t)dx' \\ & \quad + \int_{|x'-x| < \delta} (x'-x)f(x,t;x',t+\Delta t)dx' \end{aligned} \quad (A1-8)$$

Since

$$\int_{|x'-x| \geq \delta} f(x,t;x',t+\Delta t)dx' = O(\Delta t)$$

from Eqn. (4) of the text, we can rewrite Eqn. (A1-8) as

$$\int_0^1 (x'-x)f(x,t;x',t+\Delta t)dx' = \int_{|x'-x| < \delta} (x'-x)f(x,t;x',t+\Delta t)dx' \quad (A1-9)$$

The third term of the right hand side of Eqn. (A1-7) can be derived in an identical manner to yield

$$\int_0^1 (x'-x)^2 f(x,t;x',t+\Delta t) dx' = \int_{|x'-x|<\delta} (x'-x)^2 f(x,t;x',t+\Delta t) dx' \quad (A1-10)$$

By substituting Eqns. (A1-9) and (A1-10) into Eqn. (A1-7) and using Eqn. (3), we obtain

$$\begin{aligned} & \int_0^1 f(x,t;x',t+\Delta t) R(x') dx' - R(x) \\ &= R(x) \int_{|x'-x|<\delta} (x'-x) f(x,t;x',t+\Delta t) dx' \\ &+ \frac{1}{2} R(x) \int_{|x'-x|<\delta} (x'-x)^2 f(x,t;x',t+\Delta t) dx' \end{aligned} \quad (A1-11)$$

Substituting Eqn. (A1-11) into the integrand of Eqn. (A1-4) gives

$$\begin{aligned} \int_0^1 \frac{\partial f}{\partial t} R dx &= \int_0^1 f \{VR + DR\} dx \\ &= \int_0^1 fVR dx + \int_0^1 fD\ddot{R} dx \end{aligned} \quad (A1-12)$$

where f stands for $f(x,t;x',t+\Delta t)$; V and D are identical to those defined in Eqns. (7) and (8) of the text.

Integration by parts with respect to x gives

$$\begin{aligned} \int_0^1 fVR dx &= [fVR]_0^1 - \int_0^1 \frac{\partial [fV]}{\partial x} R dx \\ \int_0^1 fV\ddot{R} dx &= [fV\ddot{R}]_0^1 + \int_0^1 \frac{\partial^2 [fV]}{\partial x^2} R dx \end{aligned} \quad (A1-13)$$

Since $R(0) = R(1) = \dot{R}(0) = \dot{R}(1) = 0$, the above equations can be simplified to

$$\begin{aligned} \int_0^1 fVR dx &= - \int_0^1 \frac{\partial [fV]}{\partial x} R dx \\ \int_0^1 fV\ddot{R} dx &= \int_0^1 \frac{\partial^2 [fV]}{\partial x^2} R dx \end{aligned} \quad (A1-14)$$

Substituting Eqn. (A1-14) into Eqn. (A1-12), we obtain

$$\int_0^1 \left\{ -\frac{\partial f}{\partial t} - \frac{\partial [fV]}{\partial x} + \frac{\partial^2 [fV]}{\partial x^2} \right\} R dx = 0 \quad (A1-15)$$

Since $R(x)$ is an arbitrary function, we can conclude

$$\frac{\partial f}{\partial t} = \frac{\partial^2 [Df]}{\partial x^2} - \frac{\partial [Vf]}{\partial x}$$

This is the Kolmogorov equation, Eqn. (6), in the text.

APPENDIX 2 DERIVATION OF EQUATION (11)

From Eqn. (10) we have

$$\frac{\partial c}{\partial t} = \int_0^1 c(x', t_0) \frac{\partial f}{\partial t} dx'$$

$$\frac{\partial^2 (Dc)}{\partial x^2} = \int_0^1 c(x', t_0) \frac{\partial^2 (Df)}{\partial x^2} dx'$$

$$\frac{\partial (Vc)}{\partial x} = \int_0^1 c(x', t_0) \frac{\partial (Vf)}{\partial x} dx'$$

Substituting these expressions into Eqn. (6) we obtain

$$\int_0^1 c(x', t_0) \left[\frac{\partial c}{\partial t} - \frac{\partial^2 (Dc)}{\partial x^2} + \frac{\partial (Vc)}{\partial x} \right] dx' = 0$$

This must be satisfied for arbitrary $c(x', t_0)$. Therefore Eqn. (11) follows.

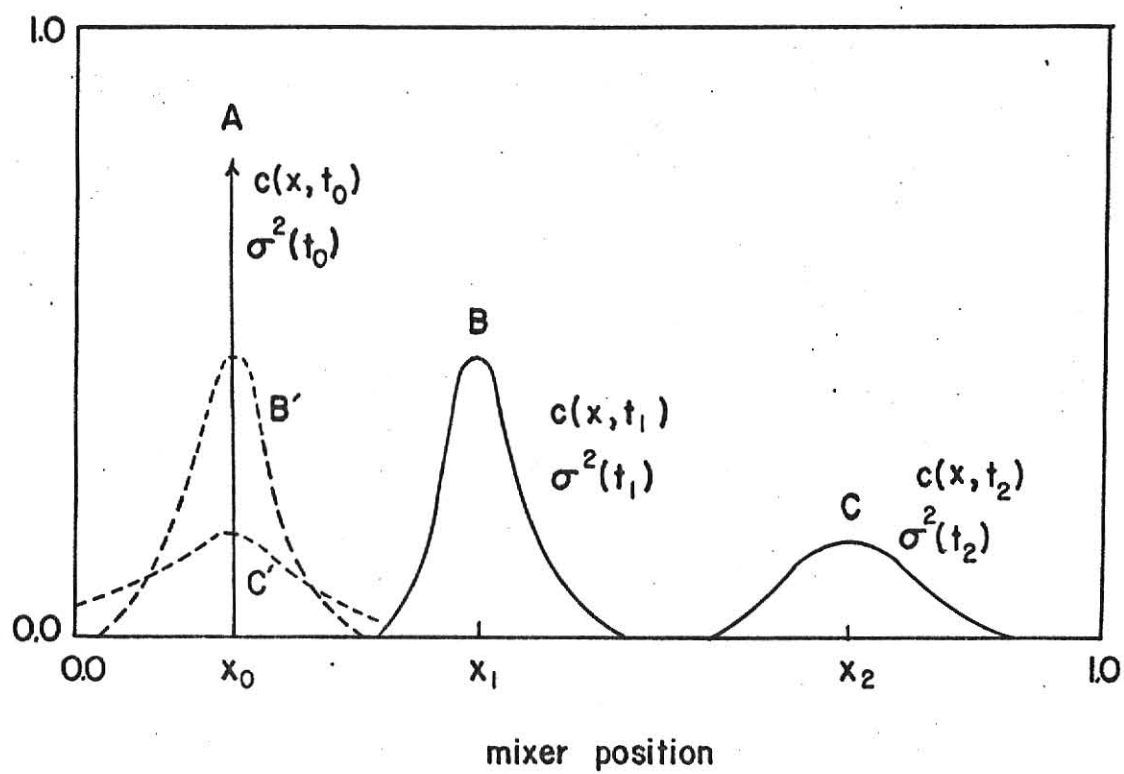


Fig. 1. Schematic diagram for illustrating the physical significances of $D(x)$ and $V(x)$.

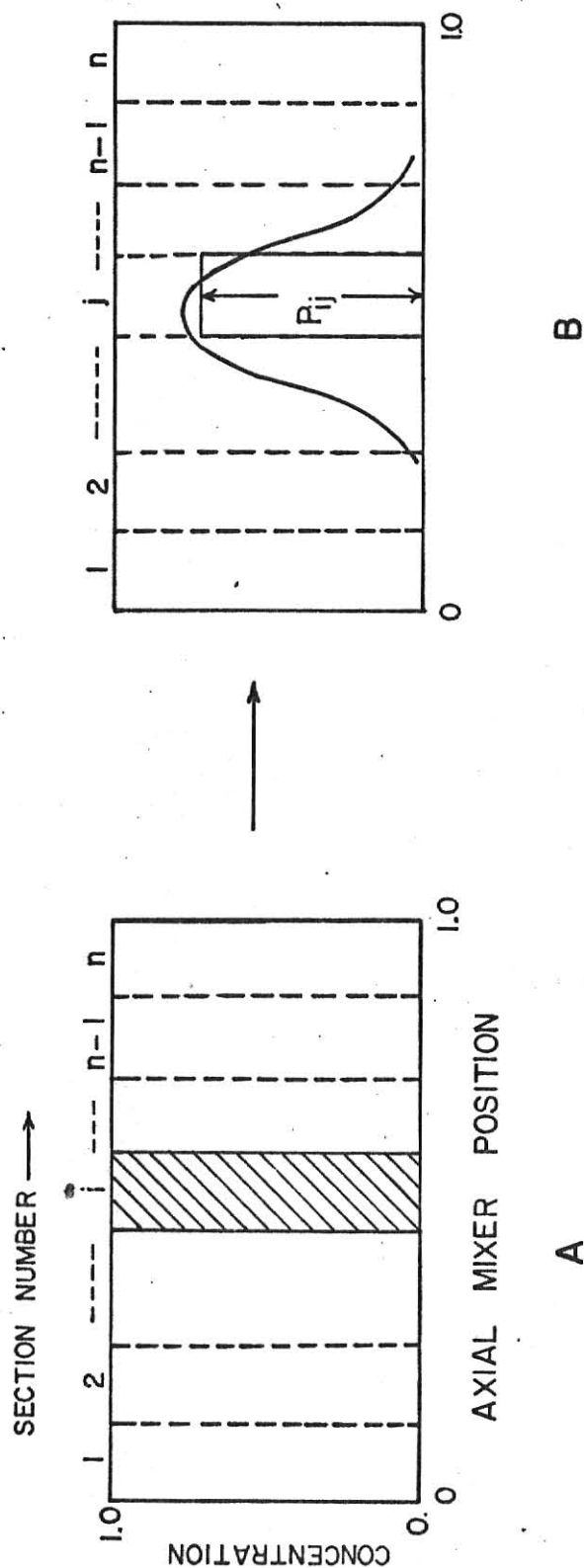


Fig. 2. Tracer experiment to determine $[P_{ij}]$. A is the initial concentration profile at $t=t_0$ and B is the profile at $t=t_0+\Delta t$.

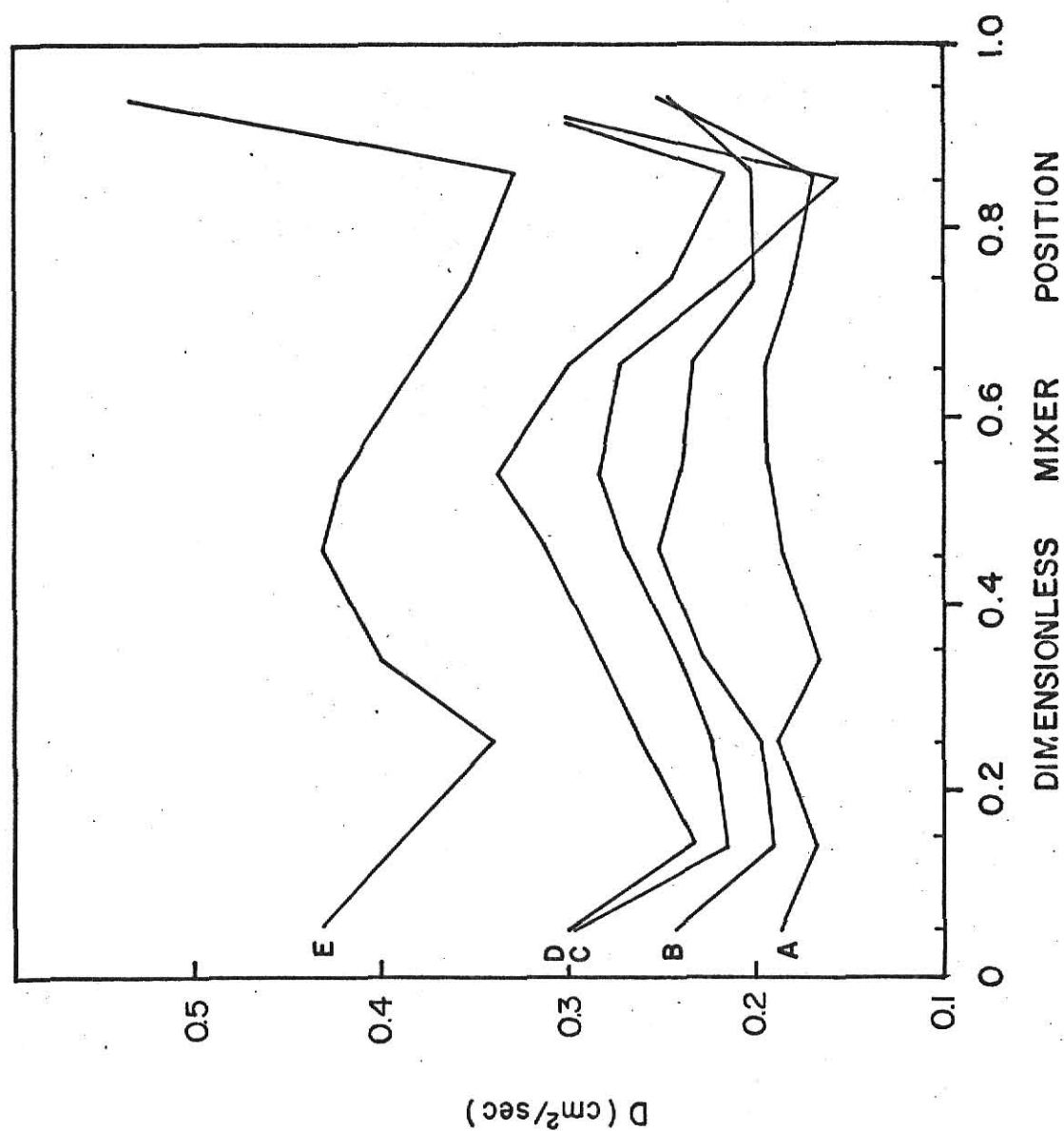


Fig. 3. Variations of diffusion coefficients with axial mixer position.

A: S/M at 15 r.p.m. B: S/M at 30 r.p.m.
 C: S/M at 45 r.p.m. D: M/L at 15 r.p.m.
 E: M/L at 30 r.p.m.

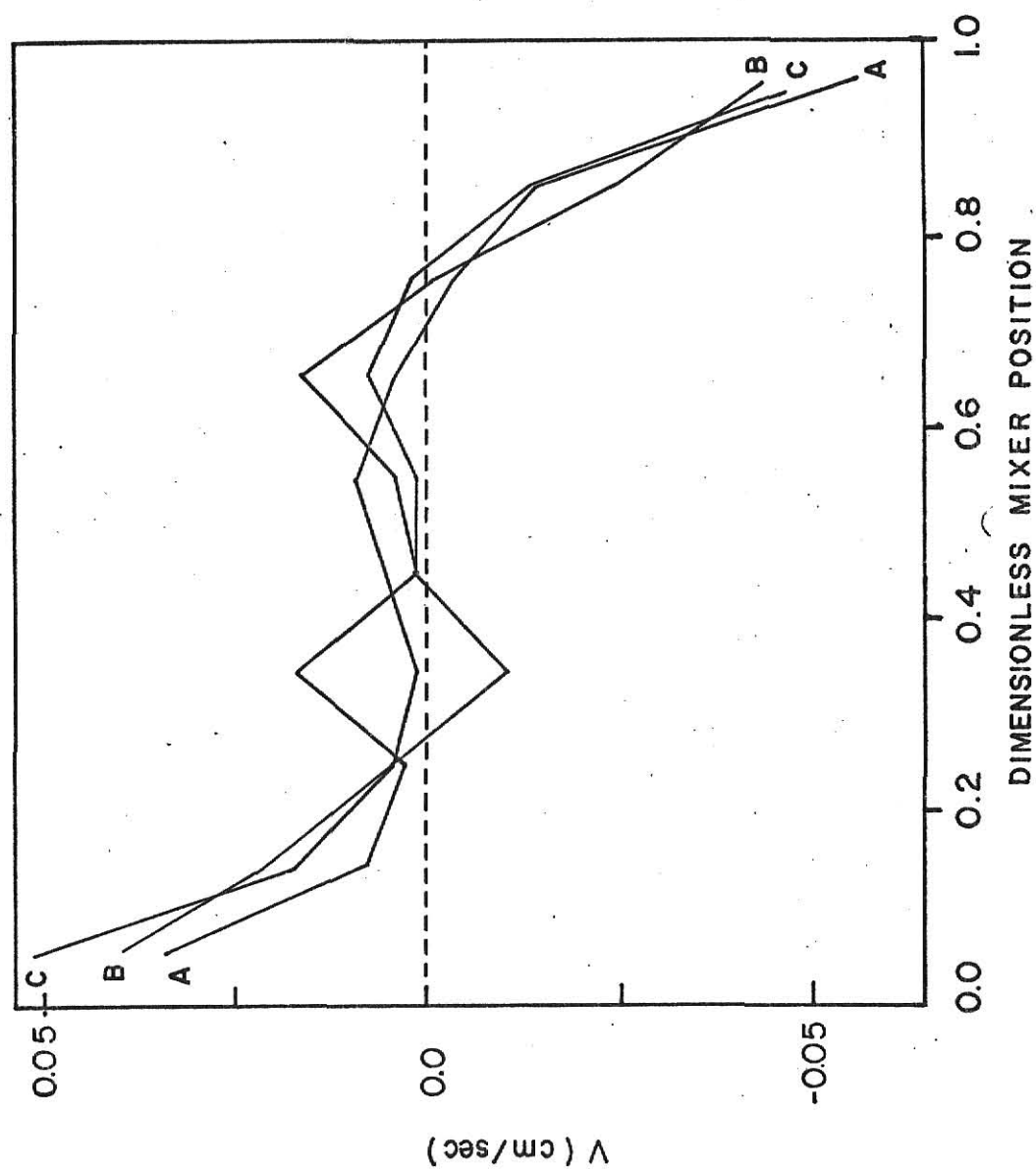


Fig. 4. Variations of drift velocities with axial mixer position.
A: S/M at 15 r.p.m. B: S/M at 30 r.p.m.
C: S/M at 45 r.p.m.

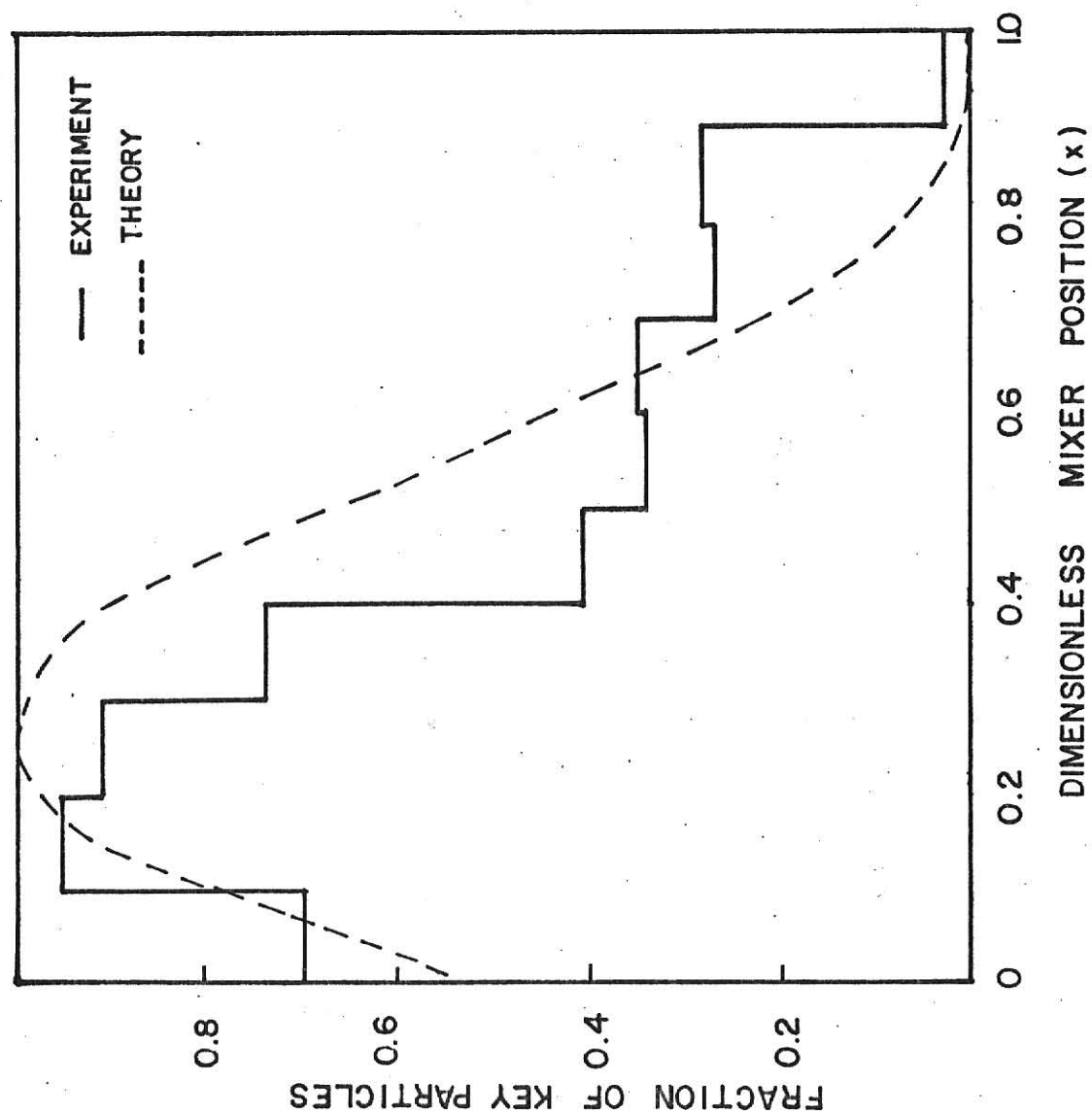


Fig. 5-A. Concentration profile of the S/M system.
r.p.m. = 15. Time = 0.5 hr.

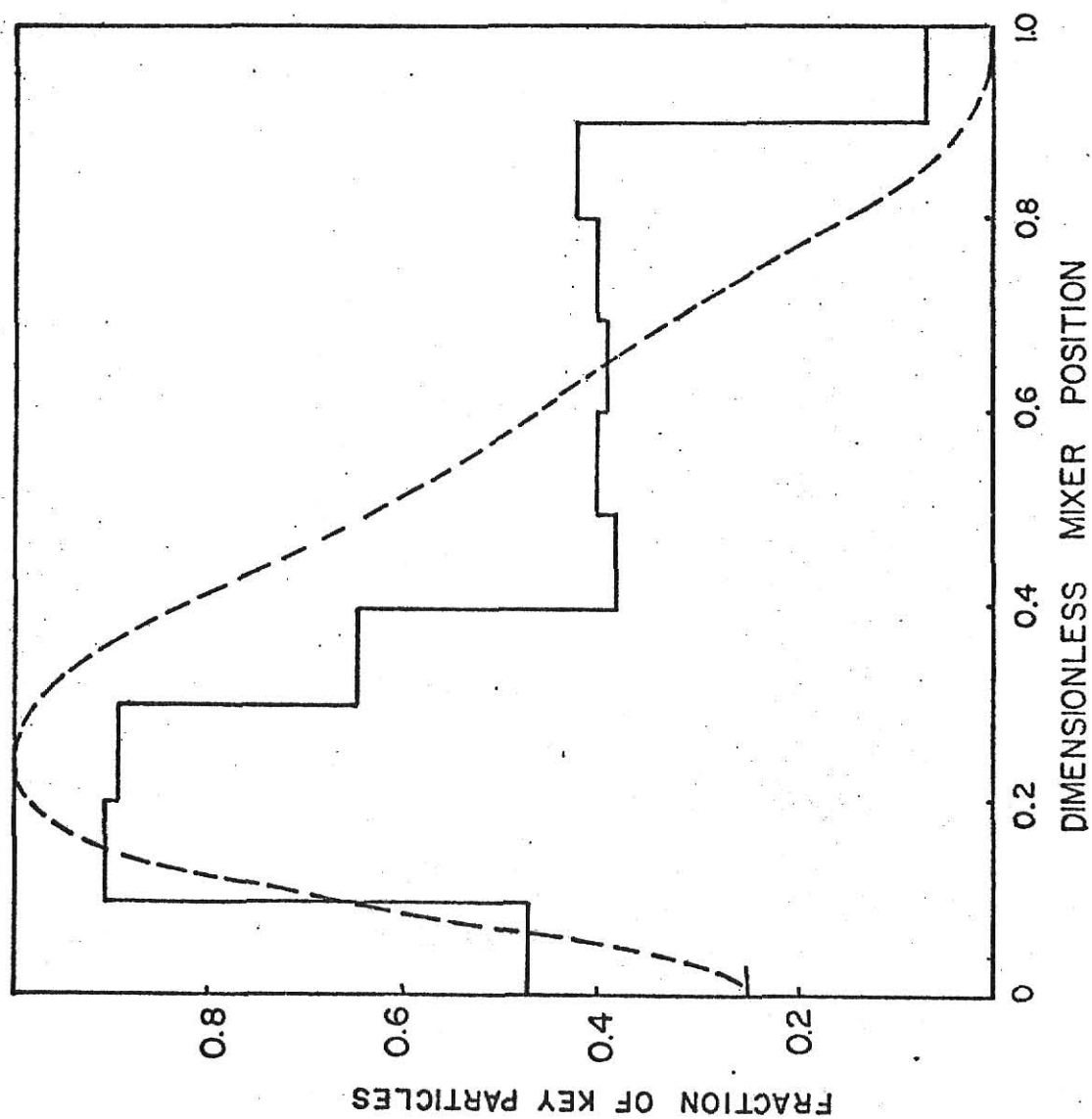


Fig. 5-B. Concentration profile of the S/M system.
r.p.m. = 15. Time = 1 hr.

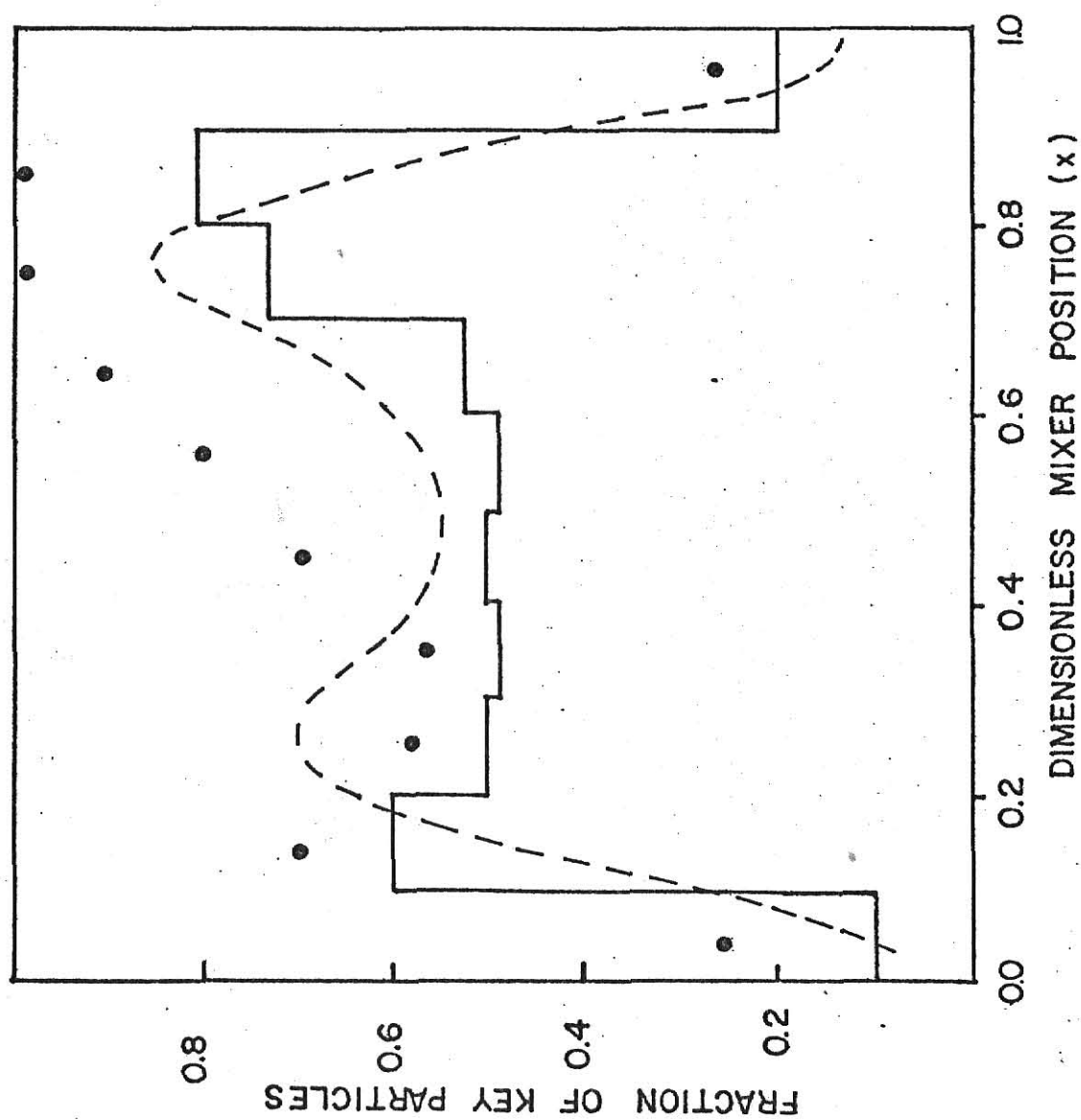


Fig. 5-C. Concentration profile of the S/M system.
r.p.m. = 15. Time = 6 hrs. Solid circles

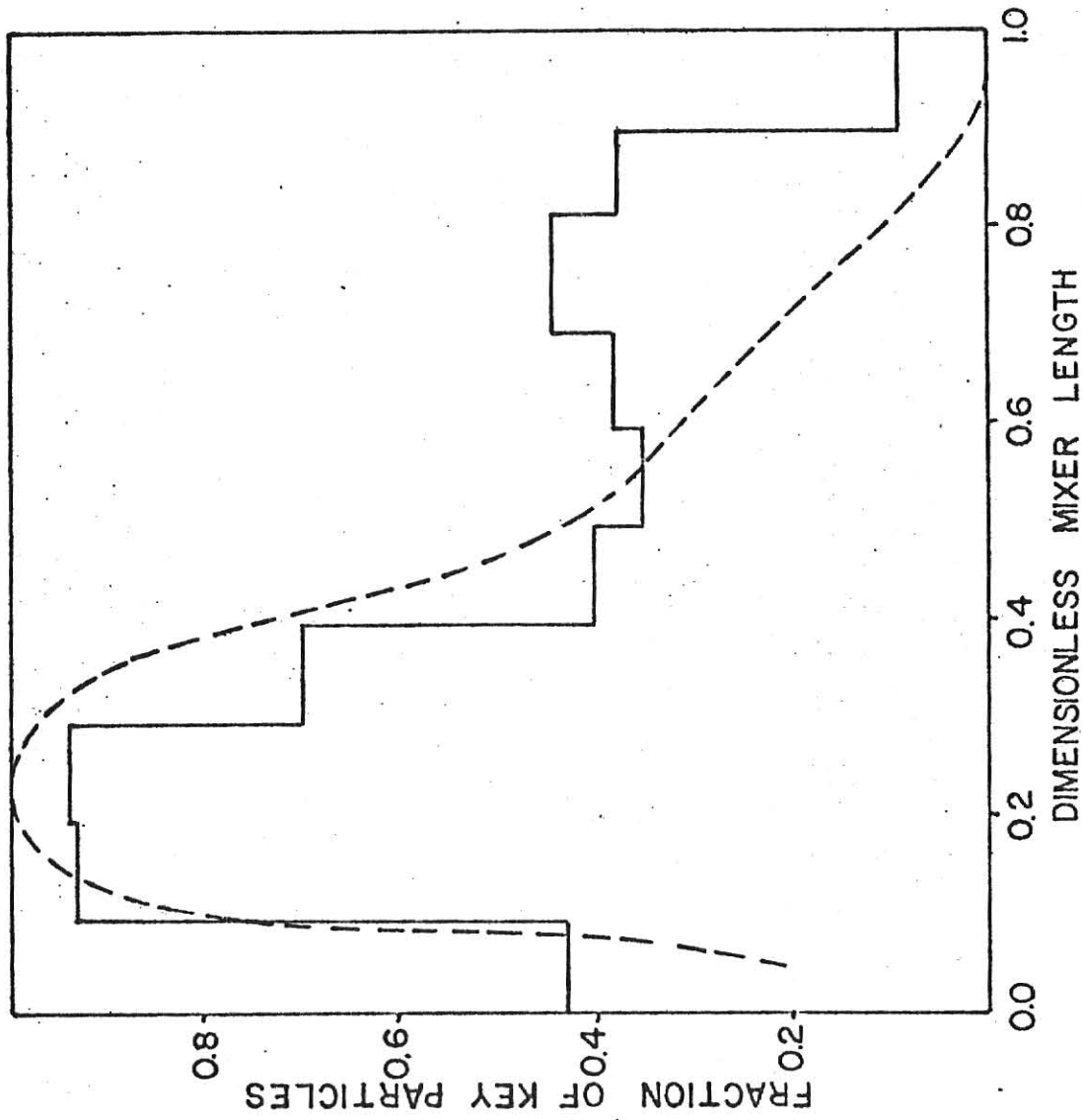


Fig. 6-A. Concentration profile of the S/M system.
r.p.m. = 45. Time = 0.5 hr.

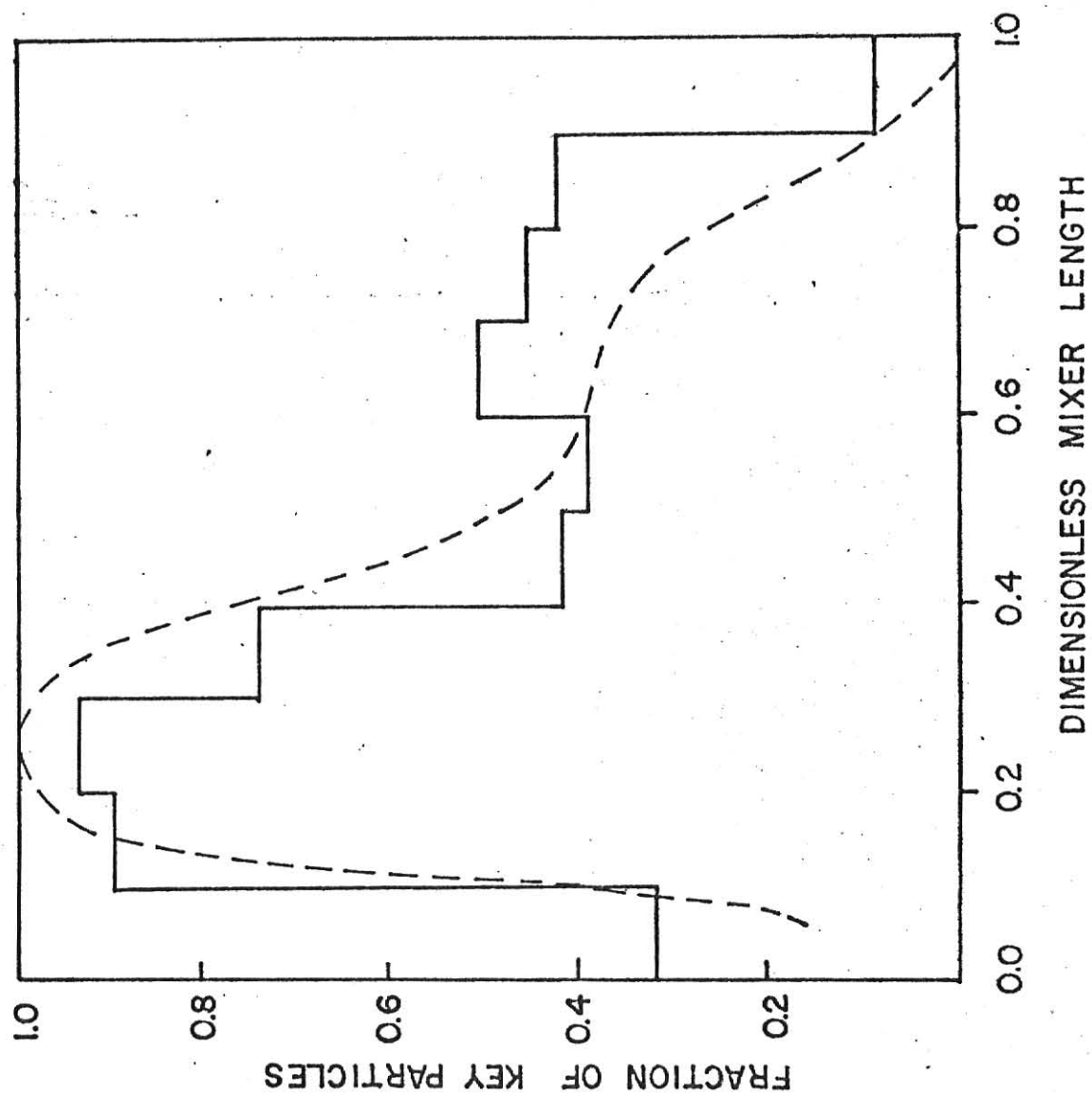


Fig. 6-B. Concentration profile of the S/M system.
r.p.m. = 45. Time = 1 hr.

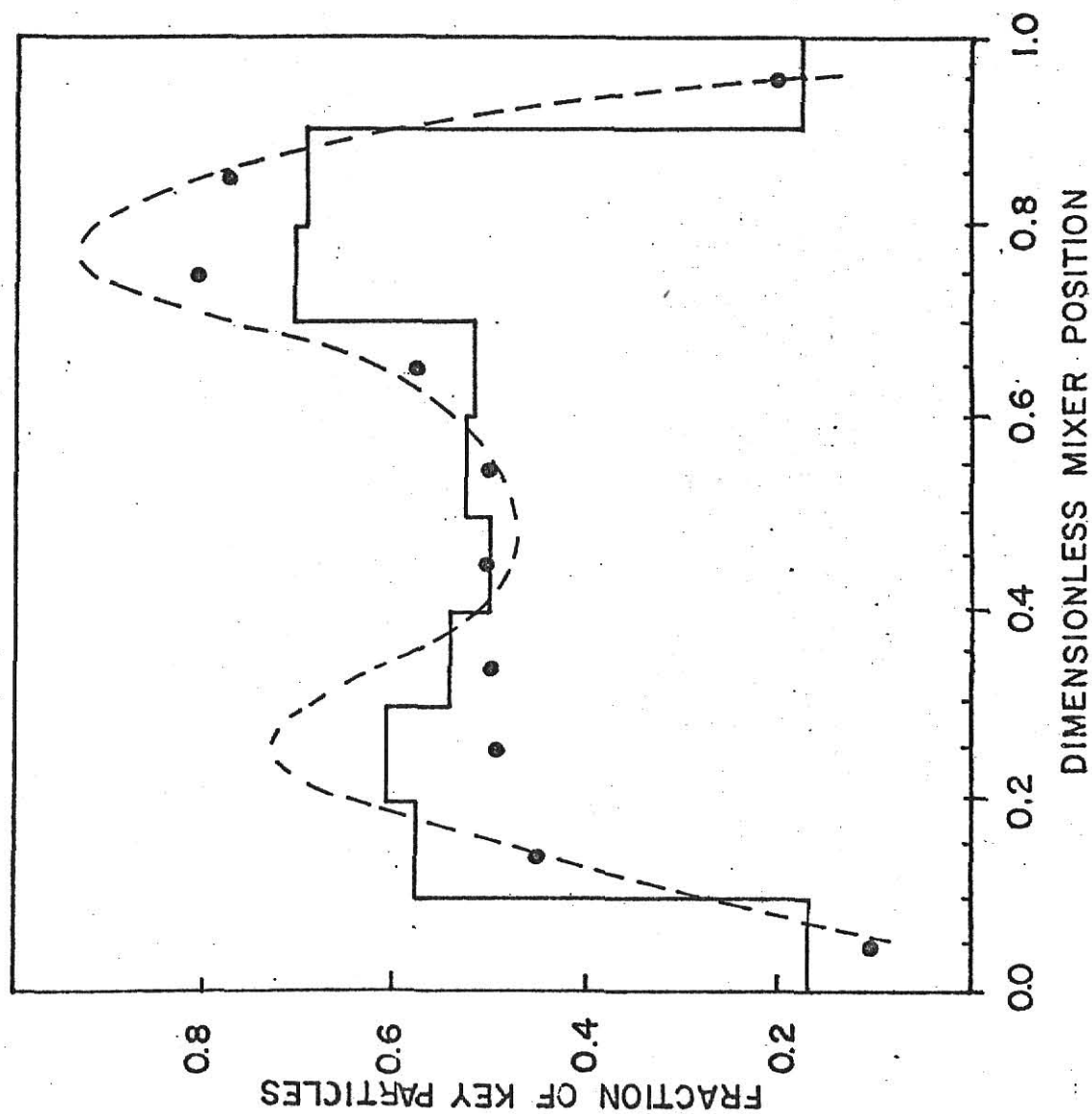


Fig. 6-C. Concentration profile of the S/M system. r.p.m. = 45. Time = 6 hrs. The solid circles represent the equilibrium profile

4. SUMMARY AND RECOMMENDATIONS

In Section 2 the discrete Fourier transform (DFT) power spectrum has been employed as a means to characterize a solids mixture. The DFT power spectrum has been shown to represent the mode by which the key or reference particle distribution contributes to the variance, σ^2 . In other words, it contains more physical information about the mixture than the variance itself.

Computer simulated results show that the maximum component of the DFT power spectrum (M_1) can be employed as a mixing index; this index can distinguish random mixtures from ordered ones. As the mixing process of an ordered mixture proceeds, the maximum power spectrum component increases. This has been shown to be true for any ordered mixture (striated or checkered mixture). On the other hand, it decreases as mixing proceeds for a random mixture. This resolving power of M_1 to distinguish ordered and random mixtures according to their homogeneities is remarkable in contrast to σ^2 which does not have it.

It has been confirmed theoretically that for a mixture undergoing a mixing process according to the Fickian diffusion equation, the maximum DFT power spectrum component, M_1 , is related with σ^2 as

$$\ln M_1 = \text{const} \times \ln \sigma^2$$

In section 3 modeling of non-ideal mixing in a horizontal drum mixer was attempted using the Kolmogorov equation of the following form

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial^2 [D(x) c(x,t)]}{\partial x^2} - \frac{\partial [V(x) c(x,t)]}{\partial x}$$

The Kolmogorov diffusion equation can describe quantitatively the non-ideal mixing behavior in a horizontal drum mixer, while the Fickian diffusion

equation, even in its most general form, cannot do so. The diffusion coefficient, $D(x)$, and the drift velocity, $V(x)$, which appear in the above equation can be determined simultaneously by discretizing the dimensionless mixer position, x . These are obtained from the one-step tracer experiment under the assumption of the stationary Markov process. Experiments show that $D(x)$ and $V(x)$ vary significantly with x and that $D(x)$ is affected by the nature of the particle system being mixed and the rotational speed of the mixer while $V(x)$ is relatively unaffected by them. The Kolmogorov equation gives a fixed equilibrium concentration profile depending on the functional dependence of D on x , and thus $D(x)$ can be determined from the equilibrium profile if $V(x)$ is negligible.

Recommendations for further studies are listed below:

- (1) The DFT technique developed in section 2 can also be applied to a multicomponent particle system. While training procedures for a multicomponent mixture would be substantially different from those for a binary mixture, the results of the present work should be useful in guiding the development of such procedures. A practical sampling method for two-dimensional real mixtures may be accomplished by using the T.V. camera. In this case the DFT technique combined with the image processing technique can yield a fruitful result in characterizing the pattern and homogeneity of the mixture.
- (2) The applicability of the Kolmogorov diffusion equation described in section 3 is not restricted to solids mixing; it can be applied to any system in which the diffusion mechanism is predominant, especially when the diffusion takes place in a non-uniform field.

It is recommended that an experimental method to determine the temporal dependence of $D(x)$ and $V(x)$ be developed, so that the stationary assumption used in this work can be removed. We may apply this model to multi-component and non-ideal mixing in a horizontal drum mixer, which is far from being understood at the present time.

In the present study the axial mixer position of a particle during the mixing process was assumed to be a continuous random variable. In carrying out solids mixing experiments, however, the concentration of the key particles is usually measured in a discrete manner with respect to the spatial coordinate. To be compatible with such experimental measurements, a discrete-in-space stochastic model (e.g., continuous Markov chain) seems to be more convenient in simulating the mixing process in a horizontal drum mixer. Such a model can be developed as a supplementary one to the Kolmogorov diffusion model.

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A FUNDAMENTAL STUDY OF SOLIDS MIXING

by

SEE HEE SHIN

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MASTER OF SCIENCE

Department of Chemical Engineering

Kansas State University

Manhattan, Kansas 66506

1977

ABSTRACT

In this thesis two important aspects of solids mixing have been studied; elucidation of the mixing process and characterization of a solids mixture.

The applicability of the discrete Fourier transform (DFT) for the characterization of random and ordered solids mixtures has been tested. It has been found that the DFT power spectrum possesses more significant physical meaning than the variance itself. Computer simulated results show that the maximum component of the DFT power spectrum can be employed as a mixing index; this index can distinguish random mixtures from ordered mixtures. It has also been confirmed theoretically that, for mixing processes obeying the Fickian diffusion equation, there exists a linear relationship between the logarithmic plot of the variance and the maximum DFT power spectrum component.

Because of the complex and stochastic nature of a solids mixing process which involves a non-ideal particle system containing particles of different size and/or density in a horizontal drum mixer, the stochastic or Kolmogorov diffusion equation in its rigorous form can be applied to modeling such a process. Furthermore, the Kolmogorov diffusion equation can describe the non-uniform concentration profile in the mixer in contrast to the Fickian diffusion equation which cannot do so.

Two parameters appearing in the Kolmogorov diffusion equation, the diffusion coefficient and drift velocity, have been experimentally determined in this work from one-step tracer experiments, and their physical significances have been discussed. A good agreement between the model and the experimental data, has been observed. In general this model can be applied to any system in which the diffusion mechanism is predominant.