Polydisperse Particulate Solids Mixing and Segregation: Nonstationary Markov Chains

C. H. CHOU, J. R. JOHNSON *, and E. G. RIPPIE [x]

Abstract ☐ The feasibility of analyzing interparticulate translocations within agitated beds of polydisperse particulate solids in terms of Markov chains was investigated. A binary mixture of spherical particles subjected to vertical sine wave vibration is shown to behave in accordance with a nonstationary Markov chain having singly stochastic transition matrixes. The transition probability elements of such matrixes, calculated from a knowledge of the initial and final occupancy vectors, agree with those estimated using tracer particles. With appropriate restrictions, the former method, based on the solution of simultaneous equations, permits a quantitative evaluation of particle mobilities throughout the bed.

Keyphrases ☐ Solids, polydisperse particulate—agitated beds, interparticulate translocations in terms of Markov chains ☐ Interparticulate translocations—polydisperse particulate solids, agitated beds, in terms of Markov chains ☐ Markov chains—polydisperse particulate solids, agitated beds, interparticulate translocations

The mixing of solid particles is a key step in many industrial and technical processes. Its pharmaceutical importance related to the manufacture of solid dosage forms is obvious, and the field of solids mixing has developed an extensive literature. Most of this literature deals with the statistical nature of the mixing process in its various forms, with the result that numerous degrees of mixedness (1) have been defined. These quantities are scalar and do not uniquely represent the composition tensors that would otherwise rigorously characterize the total state of mix. Such approaches, while of significant value in characterizing overall kinetic behavior (2), are necessarily incomplete.

A more comprehensive description of the translocations of particles within dynamic particulate beds can be achieved by the analysis of such systems in terms of stochastic theory. Some advantages of this approach are that both particle distributions and particle mobilities can be studied simultaneously and the processes of mixing and segregation can be examined in detail throughout the systems.

Oyama and Ayaki (3) considered the theoretical aspects of a Markov chain, having stationary transition matrixes, applied so as to describe the mixing of monodisperse particles, but they did not verify their results experimentally. The motion of monodisperse solids in a two-dimensional twin-shell mixer was studied, and the applicable stationary transition matrix of a Markov process was established by using single tracer particles (4). Good agreement was found between predicted and measured results using this technique.

The axial mixing of solid particles in a motionless mixer was studied in terms of a Markov chain (5). The transition probabilities were determined by measuring the distribution of tracer particles before and after passage of the bed through the mixer. Good agreement between experiment and theory was found for up to seven mixing passes, assuming the chain to be homogeneous.

The purpose of the present paper is to extend the application of Markov chains to polydisperse solids systems in which the transition matrixes are both nonstationary and singly stochastic. While such systems proceed to equilibrium states, these states represent nonuniform distributions of particles in general; the applicable Markov chains provide insight into the mixing–segregation process. The experimental system was selected to demonstrate the practical applicability of the theory and the experimental approach to polydisperse systems in general.

THEORY

Transition matrixes arising from Markov chains describing the mixing of monodisperse solids are, of necessity, stationary, since the magnitude of the elements representing the probabilities of particle movements from location to location are independent of local bed compositions. This condition is a result of the physical similarity of all particles in the system except for some superficial identifying feature of the tracer particles.

A further simplification results for such systems if, for purposes of analysis, the particulate mass is divided into cells containing equal numbers of particles. The transition matrix then becomes doubly stochastic, since both row and column sums are unity. For such finite, irreducible, aperiodic chains having doubly stochastic transition matrixes, it follows that all states become equally probable in the limit, and the system ultimately assumes a state of random mix. Since such systems are not subject to segregation, they can be mixed satisfactorily by any method, and their study is of somewhat limited practical utility.

Polydisperse particulate solids, in contrast, are subject to segregation; both mixing and segregation occur simultaneously when such systems are agitated. This result is a direct consequence of the fact that the motion of a given particle is affected significantly by the composition gradient it experiences in its immediate neighborhood. As mentioned previously, the transition matrixes of Markov chains applied to these systems are both nonstationary and singly stochastic. In the present paper, binary mixtures of spherical particles are subjected to vertical sine wave oscillation and the resultant particle translocations are analyzed.

A finite, discrete, first-order Markov chain is appropriate for processes where particles move among a finite number of imaginary cells within the bed over arbitrary time intervals and where the transition probabilities for movement depend solely on the state of the system and on the length of the time interval corresponding to a unit step. Mathematically, such a Markov chain can be expressed as the matrix product of a cell occupancy or distribution probability vector with a transition probability matrix. The resultant row vector represents the new occupancy or distribution probability following one or more steps in the chain. Thus:

$$a_i P_{ij} = a_j \qquad \text{(Eq. 1)}$$

where a_i denotes the ith occupancy or distribution probability vector for a system divided into n cells:

$$a_i = [a_1 a_2 \ . \ . \ . \ a_n]_i \qquad \text{(Eq. 2)}$$

$$P_{ij} = \begin{bmatrix} p_{11}p_{12} \cdots p_{1n} \\ p_{21}p_{22} \cdots\cdot \\ \cdot \quad \cdot \quad \cdots\cdot \\ \cdot \quad \cdot p_{kl} \cdot\cdot \\ \cdot \quad \cdot \quad \cdots\cdot \\ p_{n1} \cdot \quad \cdots p_{nn} \end{bmatrix}_{ij} \qquad \text{(Eq. 3)}$$

P_{ij} is the transition matrix corresponding to the step(s) between the states that exist after steps i and j, respectively; p_{kl} is the probability of movement of a particle from cell k to cell l. Since the matrixes P_{ij} are nonstationary:

$$P_{a,a+2} = P_{a,a+1} P_{a+1,a+2} \neq P^2_{a,a+1} \qquad \text{(Eq. 4)}$$

From the definition of p_{kl}, it is apparent that $\Sigma_{l=1}^{n} p_{kl} = 1$ for all k whereas $\Sigma_{k=1}^{n} \neq 1$ in general. These relationships correspond to the singly stochastic condition.

With successive steps in the chain, $P_{i,i+1}$ approaches a limit having as an eigenvector the equilibrium occupancy or distribution vector and also having a corresponding eigenvalue of unity.

In the event the system is divided into cells of unequal volume, Eq. 1 must be written in the more general form:

$$a_i \Pi P_{ij} \Pi^{-1} = a_j \qquad \text{(Eq. 5)}$$

where:

$$\Pi = \begin{bmatrix} x_1 & 0 & . & . & . & 0 \\ 0 & x_2 & 0 & . & . & . \\ . & . & . & . & . & . \\ . & . & 0 & x_k & 0 & . \\ . & . & . & . & . & 0 \\ 0 & . & . & . & 0 & x_n \end{bmatrix} \qquad \text{(Eq. 6)}$$

and where x_k represents the relative volume of cell k. However, in the present paper, all cells are of the same volume so that Π and Π^{-1} cancel and Eq. 5 can be simplified to Eq. 1.

If it is assumed that the values of p_{kl} are unknown for a given step but that the corresponding initial and final occupancy vectors are known, then from the definition of p_{kl} it is apparent that n linear independent equations exist. Also, because the sum of the elements in any occupancy vector is a constant, an additional $n - 1$ linear independent equations can be written. That is, for a given step in the Markov chain under discussion, $2n - 1$ elements in the corresponding transition matrix can be determined from a knowledge of the states of the system before and after a given step. The remainder of the n^2 elements of the nth-order transition matrix either must be zero or must otherwise be known by some independent means. Unless this latter requirement is met, no unique solution can be found for Eq. 1.

It has been shown, by the experimental means discussed later, that all but $2n - 1$ of the n^2 elements p_{kl} of the transition matrix have negligible values and may be assumed to be zero for suitably short transition time intervals. The transition matrixes corresponding to these observations have the general form:

$$P_{ij} = \begin{bmatrix} p_{11} & 0 & . & . & . & 0 \\ p_{21} & p_{22} & 0 & . & . & . \\ 0 & p_{32} & p_{33} & 0 & . & . \\ . & 0 & p_{43} & p_{44} & 0 & . \\ . & . & . & . & . & . \\ 0 & . & . & 0 & p_{nn-1} & p_{nn} \end{bmatrix}_{ij} \qquad \text{(Eq. 7)}$$

The $2n - 1$ unknowns in P_{ij} can be determined from the solutions of the $2n - 1$ linear independent simultaneous equations, which have been shown to result from the stochastic condition of the transition matrix and from Eq. 1.

EXPERIMENTAL

A segmented brass cylinder, 2.54 cm i.d. and 30 cm in height, containing the particulate system under study was mounted vertically on a specially designed shaking device (2). This shaker imparted a vertical sinusoidal motion to the cylinder and was capable of precise adjustment of both the frequency and amplitude of the shaking motion.

The binary mixture used in this study was comprised of 112.5 g each of 2.38- and 5.56-mm chrome steel balls and was loaded into the cylinder in a randomly mixed state prior to each shaking sequence. A random mixture was achieved by the successive addition of mixtures of equal weights of both components in small increments of less than 8% of the total bed. The adequacy of this mixing method was verified by sampling.

The particulate bed was approximately 14 cm in depth and was permitted to expand freely during shaking. Shaking was conducted at a frequency of 17.08 Hz, with a peak to peak amplitude of 5.08 mm. Maximum expansion was estimated at 1–2 cm within each oscillation of the shaker.

Following agitation for various periods, the occupancy vectors of the bed were determined by sequentially removing the six 2.3-cm segments of the cylinder, one at a time, and noting the weight of the bed contained in each and the corresponding weight of the larger component. The fractional composition of each cell thus corresponded to the components a_j of the occupancy vector following agitation. The components a_i of the initial occupancy vector were taken as 0.5 where the bed was randomly mixed initially. Where the bed was partially segregated at the beginning of the transition time segment of interest, the components a_i were those found by measurement after independent runs of the proper duration. This procedure was necessary since the system was disrupted by the sampling method employed.

Transition Matrixes Determined by Tracer Particles—One-sixth of both the large and small components were marked by being blued with a commercial cold process gun bluing solution. The randomly mixed bed was loaded into the segmented cylinder so that the marked particles were located within a given segment. After being vibrated for a predetermined period, the system was analyzed as previously described. The relative movement of the large and small marked components into cylinder segments other than those in which they were located originally corresponds to the transition probabilities p_{kl}. By repeated experiments in which the marked particles are placed in the various cylinder segments, it is possible to construct the transition matrix.

Transition Matrixes Determined by Solution of $2n - 1$ Simultaneous Equations—As discussed previously, Eq. 1 and the singly stochastic transition matrixes define $2n - 1$ linear independent equations whose coefficients correspond to the transition probability elements, p_{kl}, as indicated in Eq. 7. Sets of equations corresponding to various initial and final occupancy vectors were solved on a digital computer[1] using a double precision program based on the Gauss–Jordan method of condensed elimination with partial pivoting. This approach provides a convenient method of obtaining the transition matrixes for any component of a polydisperse mixture without the need for tedious multiple measurements of tagged particles.

Table I—Transition Probability Elements for Tracer-Estimated and Computed Transition Matrixes

	0–5 sec		0–10 sec		0–15 sec	
p_{kl}	Estimated[a]	Computed[b]	Estimated	Computed	Estimated	Computed
p_{11}	1.000	1.000	1.000	1.000	1.000	1.000
p_{21}	0.229	0.198	0.338	0.272	0.474	0.324
p_{22}	0.771	0.802	0.662	0.728	0.526	0.676
p_{32}	0.263	0.296	0.504	0.564	0.560	0.631
p_{33}	0.737	0.704	0.496	0.436	0.440	0.369
p_{43}	0.303	0.288	0.582	0.620	0.729	0.847
p_{44}	0.697	0.712	0.418	0.380	0.271	0.153
p_{54}	0.155	0.238	0.557	0.578	0.807	0.851
p_{55}	0.845	0.762	0.443	0.422	0.193	0.149
p_{65}	0.092	0.136	0.428	0.423	0.521	0.600
p_{66}	0.908	0.864	0.572	0.577	0.479	0.400

[a] Elements estimated from the movements of tracer particles. [b] Elements computed from simultaneous equations.

RESULTS AND DISCUSSION

Transition matrixes for the large component were determined using tracer particles for transition time periods of 5, 10, 15, and 20 sec, beginning in each case with randomly mixed particulate beds. In no case were marked large particles found in bed segments below their initial location; however, after 20 sec of shaking some particles were found to have moved into the second segment above their original position. This latter movement corresponds to a transition giving rise to a positive value of $p_{k,k-2}$, where the six cylinder segments are serially numbered starting at the top. These results indicate that, for sufficiently short time intervals, transitions can be represented by matrixes of the type given in Eq. 7. However, as the system approaches its equilibrium state, other transitions become significant even for short time intervals. Results of the tracer particle studies are presented in Table I.

An indication of the accuracy of tracer-estimated transition matrixes can be obtained by comparing occupancy vectors computed from Eq. 1 with those obtained by direct bed analysis. Figure 1 displays bed compositions determined by direct measurement together with those predicted by Eq. 1. Errors are within probable statistical limits, and the accuracy permits prediction of the distribution of a component within approximately 3% based on total content. Correspondingly lower percent errors will result where samples contain larger numbers of particles due either to larger sample size or smaller average particle size.

[1] Control Data Corp. Cyber 74.

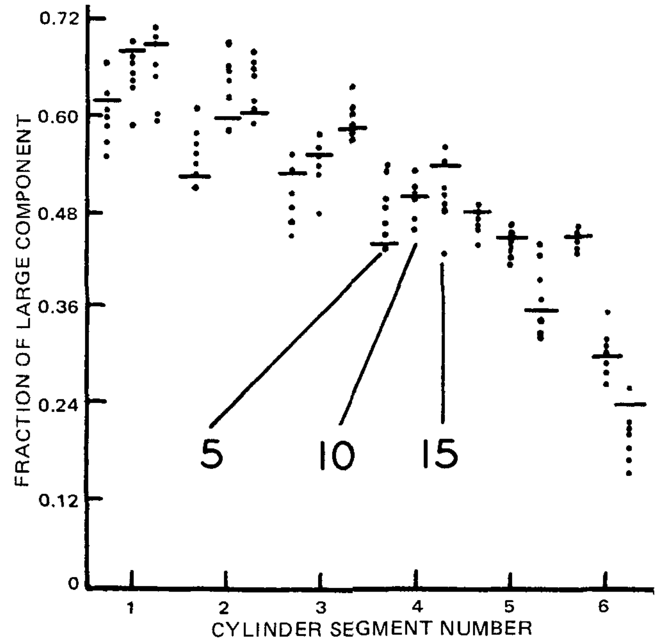

Figure 1—*Fraction of the large component as a function of bed location and time of agitation. Data are shown for 5-, 10-, and 15-sec periods of agitation for each of the six bed positions, numbered from the top. Points represent compositions by analysis, and lines represent calculated values based on the transition matrixes.*

Occupancy vectors, representing the averages of seven identical runs in each case, were used to compute transition matrixes corresponding to those determined by tracer methods. These are presented in Table I as a list of their component transition probability elements. Good agreement can be seen between transition probabilities determined by the two alternative methods used.

The average occupancy vectors were also used to compute P_{ij} for four successive 5-sec time intervals. The inequality expressed by Eq. 4 holds, and the chain is nonstationary (Table II).

Table II—Transition Probability Elements Computed for Successive 5-sec Time Intervals

p_{kl}	0–5 sec	5–10 sec	10–15 sec	15–20 sec
p_{11}	1.000	1.000	1.000	1.000
p_{21}	0.198	0.068	0.040	0.088
p_{22}	0.802	0.932	0.960	0.912
p_{32}	0.296	0.270	0.064	0.131
p_{33}	0.704	0.730	0.936	0.869
p_{43}	0.288	0.350	0.236	0.181
p_{44}	0.712	0.650	0.764	0.819
p_{54}	0.238	0.379	0.323	0.363
p_{55}	0.762	0.621	0.677	0.637
p_{65}	0.136	0.331	0.308	0.428
p_{66}	0.864	0.669	0.692	0.572

Mention should be made concerning the transition matrixes related to the movement of the second component. While it is true that the occupancy vectors of the first component uniquely define those of the second component, the same cannot be said of the respective transition matrixes. Experimentally, the blue 2.38-mm tracer balls had significantly greater mobility than the 5.56-mm balls. The smaller balls moved in both directions from their original locations, and their tracers could be found in as many as five segments after a single 5-sec period of agitation. Since more than $2n - 1$ transition probability elements were nonzero in this case, the transition matrixes could not be calculated from the occupancy vectors but could only be estimated *via* tracer particles.

CONCLUSIONS

The mixing and segregation that occur within vibrated polydisperse particulate beds can be studied as a nonstationary Markov chain. Transition matrixes corresponding to relatively short agitation time intervals can be satisfactorily computed from a knowledge of the initial and final occupancy vectors.

In a binary mixture, a single large particle moving into or out of a given cell does not uniquely imply a corresponding movement of either another single large particle or of several small particles. Hence, the transition matrix established for one component limits, but does not define, the transition matrix of the second component. This limitation is not serious, however, since the occupancy vectors of the two components are complementary. The general methods used in the present study can be applied to the analysis of movement of a given component in a complex polydisperse mixture regardless of the number of components.

The transition probability elements provide a quantitative indication of a given component's mobility as a function of time and location. It is particularly significant that the mechanisms responsible for the observed mobilities are not explicitly implied by the transition matrixes but are accurately manifested by them. Thus, the approach permits the *a posteriori* investigation of a variety of possible mechanistic models. The likelihood of wall effects in the system presented in this paper does not invalidate the analysis but can be investigated in depth using these methods.

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* Present address: Ayerst Laboratories, Rouses Point, NY 12979.

[x] To whom inquiries should be directed.