# Part II. Techniques for Measurement of Age Distribution at Transport Surfaces

**Methods are developed to estimate the mean residence time and the average transport coefficient of elements at a transporting surface from observations of only total element counts, rather than from specific observations of individual elements. The accuracy of the methods is demonstrated in Monte Carlo simulated processes and experimentally at the wall of a gas-fluidized bed.**

In Part I general relations between average transport coefficients and age distributions were presented. In the present paper, a new technique for measurement of the age distribution is presented and its applications are discussed and illustrated.

The technique is to be developed for application to a system where the age distribution of transporting elements is to be determined at a transporting surface. Typical examples of the transporting elements are the fluid eddies or packets in the penetration model of transport, or the fluidized particles in a fluidized bed. The transporting surface may be a heater, a dissolving solid, etc. The characteristic of such systems that has made measurement of age distributions more difficult than in the corresponding problem in reaction vessels is the uncontrollability and difficulty of observation of the element arrival or departure process. Thus, while one can apply a pulse input of tracer to a reaction vessel and observe the exit tracer concentration behavior, no such experiment is readily conducted in the transport surface problem.

However, another possibility exists for such systems. If it is possible to tag some of the elements in such a way that the total number of tagged elements at the surface may be observed as a function of time, then the statistical properties of this time signal will be demonstrated to give information about the age and residence time distributions. It is important to note that identification of individual elements and their times of entrance to and exit from the transporting surface is *not* being proposed, although such a technique would give direct measures of the residence time distribution (if it were possible). Instead, the proposed measurement process has been reduced to total element counts. This measurement simplification will, as usual, come at the expense of additional computational effort and decreased accuracy of the derived age distribution based on the same total number of particles. It will be demonstrated that the reduced accuracy is nevertheless sufficient for engineering purposes.

Examples of tagged elements are colored particles in fluidized beds (to be used for experimental verification in the present work); radioactively tagged particles; colored, immiscible droplets suspended in a flowing fluid of identical density and viscosity; etc. Also, extensions of this technique to determination of age distributions in reaction vessels are clearly possible.

In the context to be used in the ensuing derivations, entrance will signify arrival of a tagged element at the test surface and exit will signify its departure. For convenience, tagged elements will be simply referred to as elements.

## THEORY

### Assumptions

The following assumptions are made:

1. There is a great number $\mathcal{N}$ of elements available for entrance. This number remains essentially unchanged in time, as do the probability laws describing the entrance process.

2. The population of available elements which have not yet entered has an associated a priori distribution of residence times with unknown density function $f(\tau)$. This distribution remains constant in time.

3. Elements are mutually independent; entrance or exit of an element has no effect on the probability of entrance or exit of any other element.

4. If re-entrance is possible after exit, the re-entering element is identical in all respects to the other elements in the population available for entrance.

5. The class of elements to be considered is restricted to those which enter at some time during the interval $-K\bar{\tau} < t < K\bar{\tau}$, where $K \rightarrow \infty$ and $\bar{\tau}$ is the average residence time.

### Probability Description of the Entrance Process

Define $b\Delta t$ as the probability that any particular element from the chosen class will enter during the time interval $(t, t + \Delta t)$. Then

$$2Kb\bar{\tau} = 1 \tag{1}$$

and it follows that $b\bar{\tau}$ is very small compared to unity. The probability $g(n)$ that $n$ elements will enter in a time interval equal to one average residence time is then

$$g(n) = \binom{\mathcal{N}}{n} (b\bar{\tau})^n \, (1 - b\bar{\tau})^{\mathcal{N}-n} \tag{2}$$

The average entrance number $R$ is therefore

$$R = b\bar{\tau}\mathcal{N} \tag{3}$$

expressed as the number of elements which enter in an average residence time. Since $\mathcal{N}$ is large and $b\bar{\tau}$ is small, Equation (2) may be approximated by a Poisson distribution:

$$\lim_{\substack{\mathcal{N} \rightarrow \infty \\ b\bar{\tau} \rightarrow 0 \\ \mathcal{N}b\bar{\tau} \rightarrow R}} g(n) = \frac{e^{-R\bar{\tau}}(R\bar{\tau})^n}{n!} \tag{4}$$

The required largeness of $\mathcal{N}$ and $K$ may now be interpreted to mean that the entrance distribution is Poisson.

### Probability Description of the Element Counts

The probability $p_t$ that a particular element will be in residence at a specified time $t$ is:

$$p_t = \int_{-K\bar{\tau}}^{t} p_{t/\theta} \, b d\theta \tag{5}$$

where $p_{t/\theta}$ is the probability that the element will be in residence at $t$ given that it entered at time $\theta$, $\theta <$ t. The probability $p_{t/\theta}$ is equivalent to the fraction of all entering particles which attain ages of (are in residence for) at least $(t - \theta)$:

$$p_{t/\theta} = \int_{t-\theta}^{\infty} f(\tau) d\tau \tag{6}$$

By substituting Equation (6) into Equation (5) and interchanging the order of integration

$$p_t = \int_0^\infty f(\tau)d\tau \int_{t-\tau}^{t} b d\theta = b\bar{\tau} \quad (7)$$

Note that the lower limit on the integral in Equation (5) has been changed to $-\infty$, as allowed by the condition on $t$. Also note that $p_t$ is independent of $t$, as it must be by the assumptions.

The distribution of the number $N(t)$ of elements in residence at a specified time is therefore binomial with mean $\bar{N} = \mathcal{N} b\bar{\tau}$. Let $h[N(t)]$ denote the probability that $N$ elements will be in residence at time $t$:

$$h(N) = \binom{\mathcal{N}}{N} (b\bar{\tau})^N (1 - b\bar{\tau})^{\mathcal{N}-N} \quad (8)$$

Since $N$ is to be an experimentally observed quantity, it must be much smaller than $\mathcal{N}$; in particular, $\bar{N}$, the expected value of $N$, must be much smaller than $\mathcal{N}$. This is guaranteed by Equation (1), which shows that $b\bar{\tau}$ is small. Again, a Poisson approximation is indicated:

$$\lim_{\substack{\mathcal{N} \to \infty \\ b\bar{\tau} \to 0 \\ \mathcal{N} b\bar{\tau} \to \bar{N}}} h(N) = \frac{e^{-\bar{N}}(\bar{N})^N}{N!} \quad (9)$$

Also, we have established the relation

$$R = \bar{N} \quad (10)$$

#### Estimation of Average Residence Time from Average Entrance Rate

In the experiments to determine the residence time distribution, it is assumed that we have $M + 1$ equally spaced observations of $N(t)$, at times $t_0 + j\Delta t$; $j = 0, 1, 2, \ldots, M$. An estimator of $\bar{N}$ is constructed as

$$X_0 = \frac{1}{M+1} \sum_{j=0}^{M} N(t_0 + j\Delta t) \quad (11)$$

and it is easily demonstrated that

$$E\{X_0\} = \bar{N} = R \quad (12)$$

where $E\{\ \}$ denotes the expected value. Since $X_0$ is also an estimator of $R$, it follows that a knowledge of the rate $r$, entrance of elements in number per unit time, is sufficient to estimate the average residence time from

$$\bar{\tau} = \frac{R}{r} \approx \frac{X_o}{r} \quad (13)$$

An alternative demonstration of Equation (13) may be constructed as follows: Consider any particular element in residence at time $t$. Its probability of exit depends upon its age, through the intensity function of Naor and Shinnar (*4*). This function, denoted by $\lambda(a)$, is defined so that $\lambda(a)dt$ is the probability that an element in residence at time $t$, of age $a$, will exit before time $t + dt$. The intensity function was demonstrated by Naor and Shinnar to be related to the residence time distribution through the relation

$$\lambda(a) = \frac{f(a)}{\bar{\tau}\phi(a)} \quad (14)$$

Since we are observing only the total number of elements, and not their individual times of entrance, the probability $p_e dt$ of exit before $t + dt$ of an arbitrary element in the population in residence at $t$ must be found by integrating $\lambda(a)dt$ over the age distribution $\phi(a)$.

$$p_e dt = dt \int_0^\infty \lambda(a)\ \phi(a) da = \frac{dt}{\bar{\tau}} \quad (15)$$

Therefore, the average number $D$ of elements which exit in an interval of one average residence time may be calculated as

$$D = \sum_{N=0}^{\infty} N p_e \bar{\tau} h(N) = \bar{N} \quad (16)$$

Since at steady state the average exit rate and average entrance rates are equal, Equation (16) leads directly to Equation (13) by virtue of Equation (10).

#### Estimation of Average Entrance Rate

In some experiments, such as reactor residence time measurements, $r$ is an experimental variable set by the experimenter and thus is a known quantity. Therefore, Equations (11) to (13) provide a direct estimate of the average residence time from the average population. However, in other experiments such as the measurement of residence times at transporting surfaces in agitated vessels or fluidized beds, the average entrance rate $r$ is unknown. It should still be possible to estimate $r$ by observation of the changes in the element count $N(t)$.

If one can observe $N(t)$ infinitely often, that is, continuously, then each time $N(t)$ increased by one would correspond to the time of entrance of some element; conversely, each time the count decreased by one would correspond to the time of exit of some element. (The probability of simultaneous entrance and exit of two or more elements is vanishingly small. This is another form of the Poisson assumption.) At steady state the *average* entrance and exit rates $r$ and $e$ must be equal. Hence, the observed frequency of entrance and exit yields $r$ directly.

It is frequently impossible or undesirable to observe $N(t)$ continuously. We next demonstrate that it is usually unnecessary, and that acceptably accurate estimates of $r$ may be obtained from the discrete observations $N(t_0 + j\Delta t)$.

If $N(t)$ is not observed continuously, then when a net increase of $k'$ elements is observed between the counts at two successive observations, all that can be asserted is that the number of entrances which occurred between the observations exceeded the number of exits by $k'$. If $k'$ is negative, the exits exceeded the entrances by $k'$. Let the value of $k'$ observed between observations $j$ and $j + 1$ be denoted $k'_j$. Furthermore, define the random variables $k_j$ and $k$ by

$$k_j = |k'_j| \quad (17)$$

$$k = \sum_{j=0}^{M-1} k_j \quad (18)$$

We next demonstrate that

$$E\{k\} = Mxe^{-x}[I_0(x) + I_1(x)] \quad (19)$$

where $x = 2r\Delta t$. Equation (19) shows that $k$ provides an estimator for $r$, since $M$ and $\Delta t$ are known parameters of the experiment. $I_0$ and $I_1$ are the Bessel functions of complex arguments and are tabulated in standard references (*2*).

To prove Equation (19) we consider the distribution of the random variable $k_j$. Let $p_n(\Delta t)$ be the probability that $n$ elements will exit during a time interval $\Delta t$; then from Equations (15) and (9)

$$p_n(\Delta t) = \sum_{N=n}^{\infty} \frac{e^{-\bar{N}}(\bar{N})^N}{N!} \begin{bmatrix} N \\ n \end{bmatrix} \left(\frac{\Delta t}{\bar{\tau}}\right)^n \left(1 - \frac{\Delta t}{\bar{\tau}}\right)^{N-n} \quad (20)$$

In Equation (20), the probability of $n$ exits for each possible value of population $N$ at the beginning of the interval $t$, is summed over the distribution of $N$, since we desire the distribution of $k_j$ without regard to $N$. Equation (20) may be summed to yield

$$p_n(\Delta t) = \frac{e^{-r\Delta t}(r\Delta t)^n}{n!} \quad (21)$$

This shows that the exit distribution is also Poisson.

Suppose a value $q$ is observed for $k_j$. This may happen in either of two equally likely ways: the number of exits exceeded the number of entrances (during $\Delta t$) by $q$, or the number of entrances exceeded the number of exits by $q$. Let $p_q(\Delta t)$ be the probability that the random variable $k_j$ will assume the value $q$. Then

$$p_q(\Delta t) = \begin{cases} 2e^{-x} \sum_{j=0}^{\infty} \frac{(x/2)^{2j+q}}{(j!)(j+q)!} = 2e^{-x} I_q(x) & q > 0 \\ e^{-x} \sum_{j=0}^{\infty} \frac{(x/2)^{2j}}{(j!)^2} = e^{-x} I_0(x) & q = 0 \end{cases} \quad (22)$$

By definition

$$E\{k_j\} = \sum_{q=0}^{\infty} q p_q(\Delta t) = 2e^{-x} \sum_{q=1}^{\infty} q I_q(x) \quad (23)$$

By using the identity (3)

$$q I_q(x) = \frac{x}{2} [I_{q-1}(x) - I_{q+1}(x)] \quad (24)$$

in Equation (23) results directly in Equation (19).

Some asymptotic expressions for $E(k)$ are of interest. For very short times between observations, $x \to 0$, and

$$\lim_{x \to 0} E(k) = 2rT \quad (25)$$

where $T$ is $M\Delta t$, the total period of observation. Equation (25) verifies that in the limit all entrances and exits will be observed. The ratio of Equation (19) to Equation (25) provides a measure $L(x)$ of the information retention possible with the finite time interval between observations

$$L(x) = e^{-x} [I_0(x) + I_1(x)] \quad (26)$$

For large values of $x$

$$L(x) \to \sqrt{\frac{2}{\pi x}} \quad (27)$$

The quantities $E(k_j)$ and $L(x)$ are plotted as functions of $x$ in Figure 1. To use this figure, one takes the observed value of $k$, divides by $M$ to form an estimator of $E\{k_j\}$, finds $x$ on Figure 1, which estimates $r = x/2\Delta t$.

We next calculate the variance of $k_j$, to obtain a measure of the scatter to be expected in use of Equation (19) to estimate $r$ and the dependence of this scatter on $x$. The calculations in the Appendix* demonstrate that

$$Var\ (k_j) = E\{k_j^2\} - E^2\{k_j\} = x - E^2\{k_j\} \quad (28)$$

where $E\{k_j\}$ is given by Equation (19). Of more interest is the ratio of the standard deviation $\sigma$ (positive square root of the variance) to the mean:

$$\frac{\sigma\{k_j\}}{E\{k_j\}} = \sqrt{\frac{1}{xL^2(x)} - 1} \quad (29)$$

*Deposited as document 8878 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

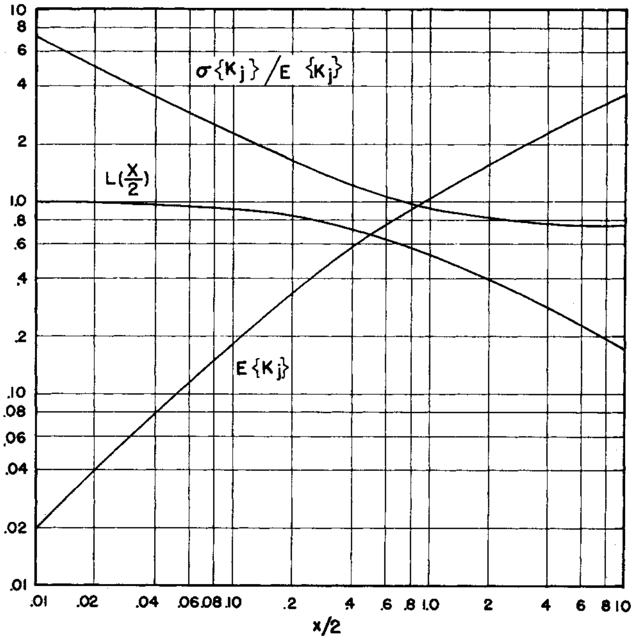


Fig. 1. Dependence of $E\{k_j\}$, $L(x/2)$, and $\sigma\{k_j\}/E\{k_j\}$ on $x$.

By using the asymptotic expression for $L(x)$ given in Equation (27), this is found to approach $\sqrt{\pi/2 - 1}$ as $x$ becomes large and to increase as $x^{-1/2}$ for small $x$. The value for $\sigma\{k_j\}/E\{k_j\}$ is plotted vs. $x/2$ in Figure 1. It may be seen that if one wishes to take more frequent observations, that is, to observe as many of the entrances and exits as possible, it will be necessary to take more total observations to obtain a good estimate of $E\{k_j\}$, because fewer entrances and exits will occur per observation. In fact, Figure 1 suggests that to obtain favorable ratios of $\sigma\{k_j\}/E\{k_j\}$ one should take observations no more often than a time interval corresponding to $r\Delta t = 1$.

The statistic $k$ is a sum of *dependent* random variables. This is because the value of $k_j$ at one observation affects the distribution of $k_{j+1}$ and to a decreasing extent distributions of all subsequent observations. Hence, it is not strictly correct to compute the variance of $k$ as $M$ times the variance of $k_j$. However, if the number of observations is large, the greater share will be essentially mutually independent and this provides justification for the approximation

$$\frac{\sigma\{k\}}{E\{k\}} \approx \frac{1}{\sqrt{M}} \frac{\sigma\{k_j\}}{E\{k_j\}} \quad (30)$$

Equation (19) will be demonstrated in a later section to estimate the entrance rate $r$, and the estimate of $r$ will be used to estimate $\bar{\tau}$ for simulated and real lifetime distributions. Since Part I showed that in many cases $\bar{\tau}$ is sufficient to calculate $\overline{N}_{Nu}$, the relations given by Equations (19) and (30) will suffice for many applications. Equation (30) allows estimation of the number of observations required to obtain a desired accuracy in the estimate of $r$.

#### Reconstruction of Age Distribution from Element Counts

However, in some applications it may be desirable to reconstruct as far as possible, the age distribution from the counts, in order to compute average transport coefficients. An example of a pulselike dependence of the instantaneous transport coefficient on age was cited in Part I.

Consider the quantity

$$A(j\Delta t) = E\{N_i(t)\ N_{i+j}(t)\} \quad (31)$$

where $N_i(t) \equiv N(t_0 + i\Delta t)$. The quantity $A(j\Delta t)$ will be termed the autocorrelation of the discrete signal $N(t)$, and we derive here the relation between $A(j\Delta t)$ and $\phi(j\Delta t)$.

Define $H(\theta)$ and $S(\theta, t)$ so that

$$N(t+\theta) = H(\theta) + S(\theta, t) \tag{32}$$

where $S(\theta, t)$ is the number of elements which enter prior to time $t$ and are still in residence at time $(t + \theta)$, and $H(\theta)$ is the number of elements which arrive after time $t$ and are still in residence at time $(t + \theta)$. Now

$$\begin{aligned} A(j\Delta t) &= E\{[N_i(t) - \overline{N}]\, N_{i+j}(t)\} + \overline{N}^2 \\ &= E\{[N_i(t) - \overline{N}]\, [H(j\Delta t) + S(j\Delta t, t)]\} + \overline{N}^2 \end{aligned}$$

But $N_i(t)$ and $H(j\Delta t)$ are independent. Hence

$$A(j\Delta t) = E\{[N_i(t) - \overline{N}]\, S(j\Delta t, t)\} + \overline{N}^2 \tag{33}$$

To take the expectation required in Equation (33) requires the joint distribution of $S$ and $N$. Define $p_{j\Delta t/t}$ as the probability that an element will be in residence at time $t + j\Delta t$, *given* that it is in residence at time $t$. Then

$$p_{j\Delta t/t} = \frac{p_{j\Delta t, t}}{p_t} \tag{34}$$

where $p_{j\Delta t, t}$ is the probability that an element will be in residence at time $t$ and at time $t + j\Delta t$, and $p_t$ is as defined in Equation (5). Note the difference between $p_{t/\theta}$ in Equation (5) and $p_{j\Delta t/t}$. The former relates to a more specific event, implying entrance at a given time, while the latter is defined for entrance anytime before a specified time. Now $p_{j\Delta t, t}$ is calculated by the following reasoning: The element may have entered at any time $\theta < t$. For a given entrance time $\theta$, the characteristic of the element is that it has a residence time of at least $t + j\Delta t - \theta$. Since any entrance time less than $t$ is permitted, it follows that

$$p_{j\Delta t, t} = \int_{-\infty}^{t} b\, d\theta \int_{t+j\Delta t-\theta}^{\infty} f(\tau)\, d\tau \tag{35}$$

Interchange of the order of integration and substitution of Equations (35) and (7) into Equation (34) give

$$\begin{aligned} p_{j\Delta t/t} &= \frac{1}{\overline{\tau}} \int_{j\Delta t}^{\infty} f(\tau)\, d\tau \int_{t+j\Delta t-\tau}^{t} d\theta \\ &= \frac{1}{\overline{\tau}} \int_{j\Delta t}^{\infty} (\tau - j\Delta t)\, f(\tau)\, d\tau \end{aligned} \tag{36}$$

Note that $p_{j\Delta t/t}$ is independent of $t$, as it should be by virtue of the stationary nature of the process.

If there are $N(t)$ elements in residence at time $t$, the probability $p_{S/N}$ that $S(\theta, t)$ of them are still in residence at time $t + \theta$ is therefore given by

$$p_{S/N} = \binom{N}{S} p^S_{j\Delta t/t}\, (1 - p_{j\Delta t/t})^{N-S} \tag{37}$$

The joint distribution of $N$ and $S$ is the probability $p_{S,N}$ that there are $N$ elements present at time $t$ and that $S$ of these elements are still in residence at time $t + \theta$. This is therefore given by

$$p_{S,N} = p_{S/N}\, h(N) \tag{38}$$

where $h(N)$ is given in Equation (9). From Equation (33)

$$A(j\Delta t) = \sum_{N=0}^{\infty} \sum_{S=0}^{N} [(N - \overline{N}) S(j\Delta t, t)]\, p_{S,N} + \overline{N}^2 \tag{39}$$

Substituting Equations (37) and (38) into Equation (39) and performing the indicated summations, one obtains

$$A(j\Delta t) = \overline{N}\, p_{j\Delta t/t} + \overline{N}^2$$

Use of the relation in Equation (36) gives

$$A(j\Delta t) = \frac{\overline{N}}{\overline{\tau}} \int_{j\Delta t}^{\infty} (\tau - j\Delta t) f(\tau)\, d\tau + \overline{N}^2 \tag{40}$$

Equation (40) is one form of the relationship between $A(j\Delta t)$ and the residence time distribution.

Although values for $A(j\Delta t)$ can only be estimated for discrete separation intervals, if the intervals are sufficiently small then $A(j\Delta t)$ may be regarded as essentially continuous, and quantities such as the derivative of $A$ may be estimated from the differences between values of $A$ for increasing separations. Hence, we replace the discrete separation $j\Delta t$ with a continuous variable $a$, and define for later convenience $\psi(a) = A(a) - \overline{N}^2$ to obtain

$$\psi(a) = \frac{\overline{N}}{\overline{\tau}} \int_{a}^{\infty} (\tau - a) f(\tau)\, d\tau \tag{41}$$

Differentiation of Equation (41) with respect to $a$ yields

$$\frac{d\psi}{da} = -\frac{\overline{N}}{\overline{\tau}} \int_{a}^{\infty} f(\tau)\, d\tau \tag{42}$$

Therefore, from the definition of $\phi$, it follows that

$$\phi(a) = -\frac{1}{\overline{N}} \frac{d\psi}{da} \tag{43}$$

A second differentiation gives

$$f(a) = \frac{\overline{\tau}}{\overline{N}} \frac{d^2\psi}{da^2} \tag{44}$$

Equations (43) and (44) form the basic relations between $\psi(a)$, which may be estimated from only the element counts without identification of the individual elements, and the age and residence time distributions.

Since by definition

$$\phi(0) = 1/\overline{\tau}$$

Equation (43) yields an immediate relation for the average residence time:

$$\overline{\tau} = \frac{-\overline{N}}{\left(\dfrac{d\psi}{da}\right)_{a=0}} \tag{45}$$

Since we have only discrete estimations for $\psi$, in practice Equation (45) would be used in the form

$$\overline{\tau} \simeq \frac{\overline{N}\Delta t}{\psi(0) - \psi(\Delta t)} \tag{46}$$

to estimate the average residence time. Since Equation (41) shows

$$\psi(0) = \overline{N} \tag{47}$$

an alternate to Equation (46) is available:

$$\overline{\tau} \simeq \frac{\Delta t}{1 - \psi(\Delta t)/\psi(0)} \tag{48}$$

However, since the quantities $\overline{N}$ and $\psi$ are not available except as estimates from the given sample of population counts, there will be a statistical difference between the estimates of $\psi(0)$ and $\overline{N}$. While no proof is currently available, it seems reasonable to assume that $\overline{N}$ is better estimated by $X_0$ than by the estimator $Y_0$ of the variance $\psi(0)$:

$$Y_0 = \frac{1}{M+1} \sum_{j=0}^{M} (N_j - X_0)^2 \tag{49}$$

Hence, Equation (46) will be used in preference to Equation (48).

Estimates of $\psi(j\Delta t)$ are available from the sample moments $Y_j$, where

$$Y_j = \frac{1}{M+1-j} \sum_{i=0}^{M-j} (N_i - X_0)(N_{i+j} - X_0) \tag{50}$$

These sample moments may be made unbiased by multiplication by appropriate factors. Hence we have

$$Y'_j = K_j Y_j \tag{51}$$

where $K_j$ are the unbiasing factors, and $Y'_j$ are unbiased estimators. The factors $K_j$ may be calculated by computing $E\{Y_j\}$. However, $Y_j$ and $Y'_j$ were never significantly different in the present studies, so no further details of this computation are given.

In some applications such as radioactive tracer counts, it may not be possible to assign an absolute level to $N$, but rather one can measure only fluctuations in counts about some average level which has no simple relation to $\overline{N}$. In this case, Equation (47) may be used to define a scaled autocorrelation function $\Omega(a)$ by

$$\Omega(a) = \frac{\psi(a)}{\psi(0)} \tag{52}$$

Note that $\Omega(a)$ varies from unity to zero as $a$ varies from zero to infinity. Equations (43), (44), and (45) become

$$\phi(a) = -\frac{d\Omega(a)}{da} \tag{53}$$

$$f(a) = -\frac{d^2\Omega(a)/da^2}{[d\Omega(a)/da]_{a=0}} \tag{54}$$

$$1/\overline{\tau} = -\left[\frac{d\Omega(a)}{da}\right]_{a=0} \tag{55}$$

#### Calculation of Average Transport Coefficients

In the usual case for studies of transport phenomena (or reactor conversions), the age or residence time dis-

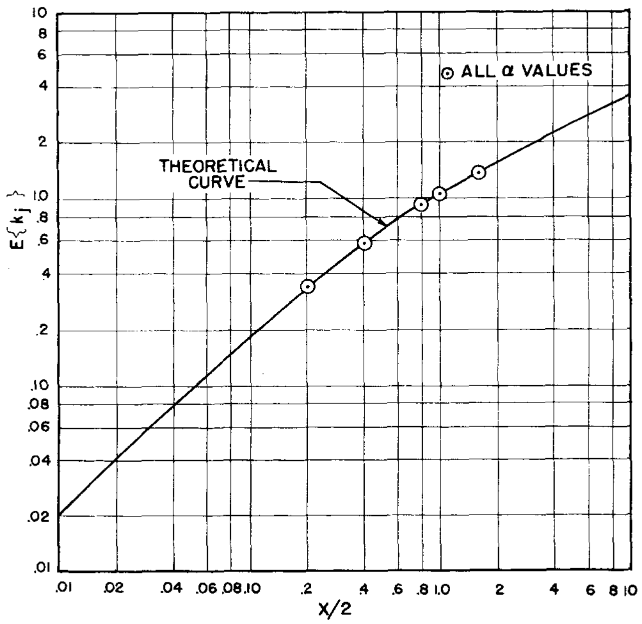


Fig. 2. Comparison of theoretical $E\{k_j\}$ with estimators from computer simulation.

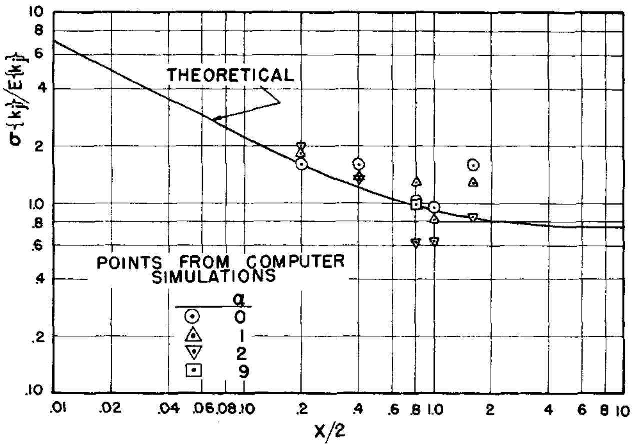


Fig. 3. Comparison of theoretical $\sigma\{k_j\}/E\{k_j\}$ with estimators from computer simulation.

tributions are not quantities of primary interest. Rather, one is interested in integrals of these distributions with the instantaneous transport coefficient, denoted by $N_{Nu}(a)$, to compute average transport coefficients:

$$\overline{N}_{Nu} = \int_0^\infty \phi(a)\, N_{Nu}(a)\, da$$

For convenience, we use Equation (53) for $\phi(a)$, but the resulting relations in $\Omega(a)$ are easily converted to the corresponding relations in $\psi(a)$. Then

$$\overline{N}_{Nu} = -\int_0^\infty \frac{d\Omega}{da} N_{Nu}(a)\, da \tag{56}$$

There are two computational alternates from Equation (56). In the first case, assume $N_{Nu}(0)$ is zero or finite, implying some form of contact resistance in the transport process. Then Equation (56) may be integrated by parts to yield

$$\overline{N}_{Nu} = \int_0^\infty \Omega(a) \frac{dN_{Nu}(a)}{da} da - N_{Nu}(0) \tag{57}$$

Equation (57) is more suitable for computation than is Equation (56), because $\Omega$ is a derived quantity, available only at discrete values of the argument, while $N_{Nu}(a)$ is an analytic form. However, this relation is inapplicable if $N_{Nu}(0)$ is infinite, as is true for the typical penetration model $N_{Nu}(a) = 1/\sqrt{\pi a}$. In this case, it is recommended that Equation (56) be used in the equivalent form

$$\overline{N}_{Nu} = \int_0^1 N_{Nu}[a(\Omega)]\, d\Omega \tag{58}$$

for computational purposes.

## RESULTS

The relations derived in the Theory section were tested on computer-simulated element counts, where the residence times of the elements were drawn from a known distribution. In addition, tests were made on a fluidized-bed system. The results of these tests are described below.

#### Computer Simulation

The process of exit and entrance of elements was simulated by a Monte Carlo technique. For this purpose a computer program was prepared for use on a CDC 3600 digital computer. In essence, the program uses the given residence time distribution (always taken in the gamma form for the present studies) to generate element counts as a function of time and then computes the estimators $Y_j$. The input data are $\alpha$, $M$, $r$, $\Delta t$, and $\overline{\tau}$; in all cases here $\overline{\tau} = 1$.

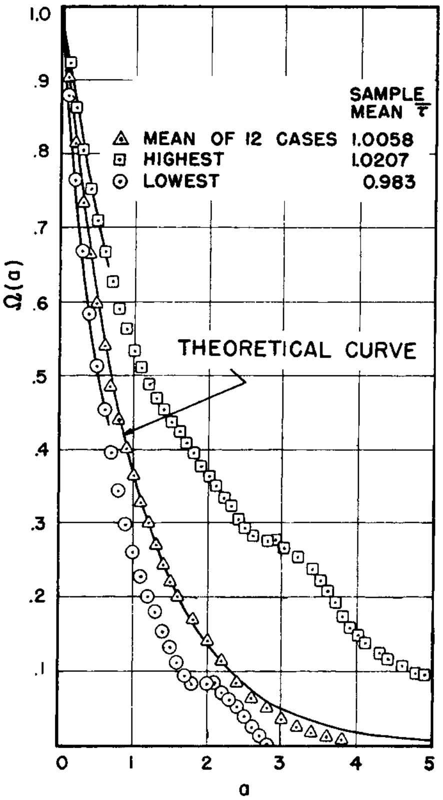


**Fig. 4. Normalized theoretical autocorrelations and sample-estimated autocorrelations, $\alpha = 0$.**

The output from the computer includes:

1. The sample mean, variance, and third moment of the residence times assigned to the elements.
2. The $M + 1$ counts at intervals of $\Delta t$ and the mean of these counts [from Equation (11)].
3. The sample moments $Y_j$ of the counts obtained from Equation (50).
4. $k$, the total changes in elements observed between counts, from Equation (18).
5. The average transport coefficient $\overline{N}_{Nu}$ computed from Equation (58) for the model $\overline{N}_{Nu}(a) = 1/\sqrt{\pi a}$.

*Observed Changes Method.* For each of the values $\alpha =$ 0, 1, 2, several values of $r\Delta t$ were used: 0.2, 0.4, 0.8, 1.0, and 1.6; in addition, for $\alpha = 9$ the value $r\Delta t = 0.8$ was run. For all the runs, $M + 1 = 1{,}500$.

For each case, the sample mean and variance of $k_j$ were determined. The quantity $\frac{\sigma\{k_j\}}{E\{k_j\}}$ was estimated by Equation (30). As can be seen from Figure 2, the sample means computed from the simulated runs show very close agreement with the theoretical values calculated from Equation (19). Equation (30) for $\frac{\sigma\{k_j\}}{E\{k_j\}}$ shows greater deviation from the sample variances, plotted in Figure 3, probably because of the dependence between individual $k_j$'s, as explained in the derivation of Equation (19). The individual cases for the different $\alpha$ values cannot be shown in Figure 2 because all points fall close to the theoretical line.

*Autocorrelations.* A new set of computer-simulated runs was conducted. Sample normalized autocorrelations were computed for twelve cases with $\alpha = 0$, $r\Delta t = 2.0$, $\Delta t = 0.1$; in addition, one case each using $\alpha = 1$, 2, and 9 with $r\Delta t = 2.0$, $\Delta t = 0.1$, were examined. The results discussed in the remainder of this section refer to these fifteen cases and not to the cases used to verify the $k_j$ method. For $a = 5.0$, since $M + 1 = 1{,}500$, only thirty independent samples were available in the estimate of $\Omega$ (5). Hence the estimator has a high variance for large values of $a$.

In Figures 4 and 5, the theoretical normalized autocorrelations, $\Omega(a)$, computed by integrating Equation (53) are plotted together with the estimated values from the simulated counts. For the twelve cases with $\alpha = 0$, only the mean of the twelve cases and the two worst cases (highest and lowest) are shown in Figure 4. For $\alpha = 0$, Figure 4 shows that deviations of sample estimates from $\Omega(a)$ increase with $a$, as expected. Figure 5 indicates a similar result for the other $\alpha$ values.

Table 1* gives values of estimates of $\Omega(a)$ for all cases. Also given are: the mean, variance, and modified third central moment of the actual residence times drawn from the theoretical population; $\bar{\tau}$ estimated from Equations (46) and (48) and from the observed changes method; and sample estimates of $\psi(0)$ and $\overline{N}$. (The means of the actual residence times are indicated for the two cases shown in Figure 4, as well as the overall mean for the twelve cases.) Table 1 shows that the actual sample population of residence times, upon which the estimates of $\Omega(a)$ are based, differ considerably in their higher moments from the theoretical population on which the theoretical $\Omega(a)$ curves are based. Hence, at least part of the scatter between the twelve estimates of $\Omega(a)$ is due to this source. This is a result of the inevitable inability to reconstruct exactly any distributions, or functions of these distributions, from finite samples.

Figure 5 shows that as $\alpha$ is increased the estimated $\Omega(a)$ observes the correct general trend. A theoretical plot for $\alpha = 9$ is not included because the integrations

*See footnote on page 949.

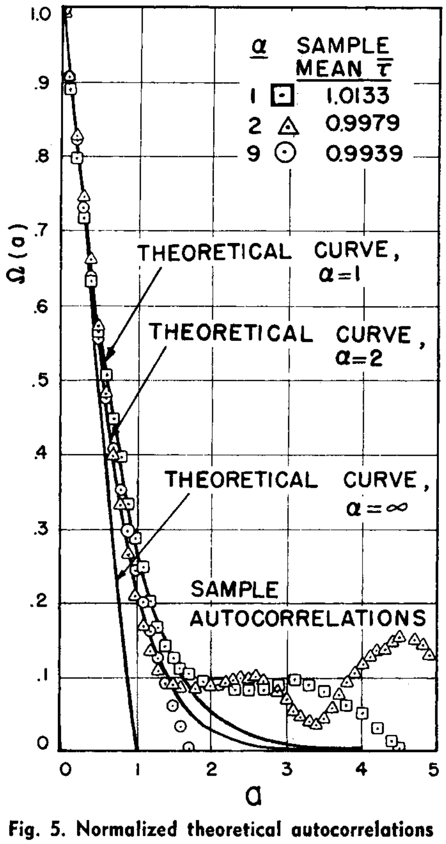


**Fig. 5. Normalized theoretical autocorrelations and sample-estimated autocorrelations, $\alpha = 1$, 2, 9, $\infty$.**

TABLE 2. $r\Delta t = 2.0, \bar{\tau} = 1.0$

| $\alpha$ | $\overline{N}_{Nu}$ | Ratio of standard deviation to $\overline{N}_{Nu}$ | $\overline{N}_{Nu}$ (theor) | $\bar{\tau}$ Sample mean |
|---|---|---|---|---|
| 0 | 0.9754* | 0.078† | 1.000 | 1.0058 |
| 1 | 0.933 | — | 1.061 | 1.0133 |
| 2 | 1.098 | — | 1.081 | 0.9979 |
| 9 | 1.128 | — | 1.114 | 0.9939 |

* Mean of cases 1 to 12.
† Standard deviation of cases 1 to 12.

and computations become excessively tedious. Instead, the limiting case for $\alpha = \infty$ is shown.

The case for $\alpha = 0$ represents the residence time distribution with the largest variance for the gamma form for all $\alpha \geqq 0$. Hence, it is to be expected that statistical estimators for the $\alpha = 0$ case will show greater variance than those for any other $\alpha$. In fact, this is the reason that twelve cases were taken for $\alpha = 0$ and only one each for the other $\alpha$ values. Table 1 and Figures 4 and 5 verify this result. In no case for the higher $\alpha$ values were the sample estimates of the autocorrelation in serious error.

*Mean Transport Coefficients.* For the transport model $N_{Nu} = 1\sqrt{\pi a}$, the mean transport coefficient $\overline{N}_{Nu}$ was found by using Equation (58) for all fifteen cases. The results are shown in Table 2. It should be noted that the normalized sample autocorrelations [that is, estimators of $\Omega(a)$] were computed only up to $a = 5.0$, and the integrations to obtain $\overline{N}_{Nu}$ were truncated at this point. The theoretical values of $\Omega(a)$ are negligible beyond this point and make no contribution to the integral in Equation (58).

As can be seen from Table 2 there is good agreement between the theoretical and simulated values for $\overline{N}_{Nu}$. For $\alpha = 0$, the standard error is only 7.8%. Thus, although the sample autocorrelations sometimes deviate considerably from the theoretical values, the integral of Equation (58) is not overly sensitive to these deviations.

*$\bar{\tau}$ from $\Delta\psi$.* The mean residence time $\bar{\tau}$ was estimated for all cases by using both Equations (46) and (48). For $\alpha = 0$, the sample means of the twelve cases estimated $\bar{\tau} = 1.073$ and $\bar{\tau} = 1.060$, by using Equation (46) and (48), respectively. These agree closely with the true $\bar{\tau} = 1$. The corresponding sample standard deviations were 0.034 and 0.170. Hence both methods yield values of $\bar{\tau}$ which will allow acceptably accurate predictions of $\overline{N}_{Nu}$ from, for example, Equation (19) of Part I.

*$\bar{\tau}$ from Observed Changes.* The values of $\bar{\tau}$ estimated for the twelve cases with $\alpha = 0$, by using the observed changes method showed good agreement with the theoretical $\bar{\tau} = 1.0$. The sample mean of the twelve estimates was 1.053 and the sample standard deviation of these values was 0.043. The total number of elements which contributed to each estimate of $\bar{\tau}$ is approximately $Mr\Delta t$, in this case 3,000. If we were able to observe the residence times of individual elements directly from the same population, the standard deviation of the sample mean estimate of $\bar{\tau}$ would be $1/\sqrt{P}$, where $P$ is the number of elements observed. To obtain the same value of 0.043 would therefore require observation of only 544 elements, less than one-fifth the number involved in the observed changes method. However, the total period of experimental observation is $M\Delta t = 150$ residence times in the observed changes method, compared with a minimum (no time loss between elements) expected value of 544 residence times in the direct method. Hence, by considering many particles at once, the total count method offers a significant reduction in the time of the experiment.

The method was also successfully used to compute $\bar{\tau}$ for the other $\alpha$ values, yielding estimates of 1.001, 1.007, and 0.942 for the case $\alpha = 1$, $\alpha = 2$, and $\alpha = 9$, respectively.

The major difference between the present results and those presented in Figures 2 and 3 on the observed changes method is that the latter were used to check the predicted variation with $r\Delta t$ rather than to compute $\bar{\tau}$ as was done for the present results.

#### Fluidized-Bed Experiments

The experimental system investigated was the entrance and exit of particles at a specific area on the wall of a fluidized bed. The equipment consisted of a 4-in. I.D. stainless steel pipe with a 2½-in. wide Lucite plate mounted as a chord along the entire column length in a slot cut in the pipe. The pipe, mounted vertically, served as the fluid-bed column. Air distribution was through a sintered bronze distributor plate. The fluidized particles were ⅛-in. diameter acetate spheres, with density slightly greater than that of water. A few black spheres among the otherwise white spheres served as tagged elements. The purpose of using round, large particles was to facilitate identification of a tagged particle in photographs of the wall of the bed.

The column was filled to a height of 8 in. with the spheres. A 2-in. × 1 1/3-in. section of the Lucite plate, referred to in the following as the test area, was photographed with a 35-mm. Arriflex movie camera with variable shutter. An example of a typical frame in the film record obtained is shown in Figure 6.

It was found that the bed tended to slug excessively, even at low air velocities. This produced a film record difficult to interpret, since the voids produced by slugging could not be easily distinguished from the black particles, which appeared as light circles on the negatives. To elim-

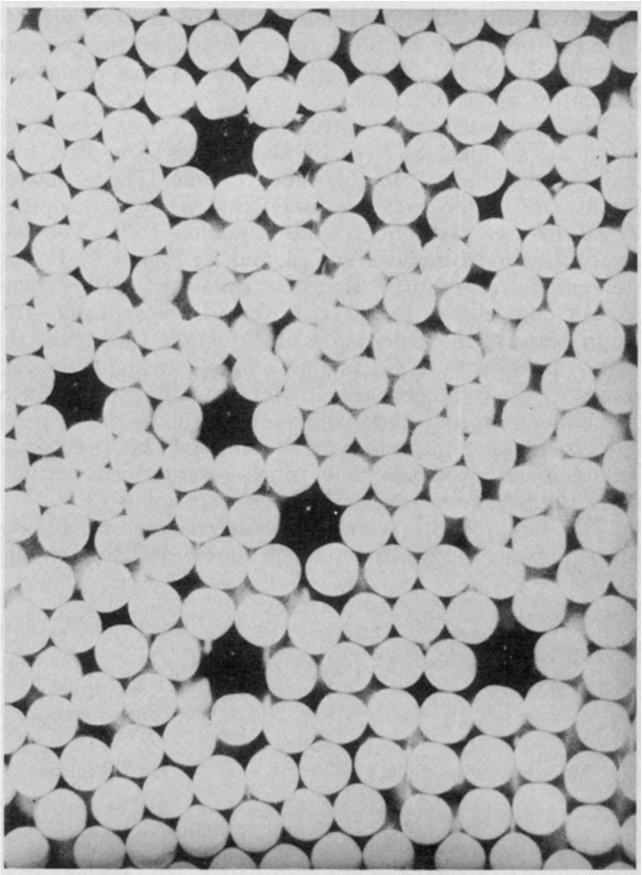

Fig. 6. Typical frame from film of fluidized-bed experiment.

inate the slugging, a stirrer was installed in the bed. This was a ¼-in. stainless steel rod with no impeller, but with its end bent slightly to produce a whip as it was rotated. This device proved satisfactory in causing the particles to move from the bed into the test area and back, as well as along the test area itself, with no slugging and with only infrequent bubbles.

With the bed operating satisfactorily, the test area was photographed at 20 frames/sec. Illumination was from two 150-w. photofloods. The film record so obtained was analyzed as follows:

The film was projected frame-by-frame onto a screen of Mylar plastic. Black particles were identified by numbers marked on the plastic. As the film was advanced, particles exited and entered, their respective numbers being erased or added. A record was kept from frame-to-frame of particles entering and leaving. Thus the residence time of each particle was obtained as well as the number of particles on each frame of the film. It should be noted that for the particles on the first and last frames, only their minimum residence times were obtained, because their times of entrance or exit were unknown.

Five hundred fifty four frames were so analyzed, accounting for forty-nine particles, fourteen of which appeared in the first or last frames, so that for these fourteen only their minimum residence times were known. The time required for this analysis was 10 man-hr., primarily because individual particles were observed. To obtain only total counts requires approximately one-tenth this amount of time, this being a primary advantage of the total counts method. However, for the present research, direct observations were required to check the total counts method.

The cumulative sample distribution of observed residence times [an estimate of $F(\tau)$] was prepared from these data, and the sample autocorrelations for the counts were computed. For the latter, since there were only 554 frames counted, the maximum value of $a$ used was 40 frames, providing approximately fourteen independent samples for $\psi(40)$. (The unit of time for this run is one frame, or about 1/20 sec.)

The estimated age distribution $\phi(a)$ was computed from the estimate of $F(\tau)$ by Equation (1) in Part I by using the sample average residence time. The estimated normalized autocorrelation function $\Omega(a)$ was computed from this age distribution with Equation (53). The several estimated functions are plotted in Figure 7. It may be noted in Figure 7 that the estimated $\Omega(0)$ [from $\phi(a)$] does not go to 1.0 as it should theoretically. This is so because the integration of Equation (53) over the entire interval of $a$ did not give unity, owing to inaccuracies in the estimated age distribution. The sample mean minimum residence time was found from the direct particle observations to be fifty-eight frames. (This is the minimum mean residence time, since for fourteen particles only the minimum residence times were known.)

The total counts were then analyzed to provide information on the mean residence time $\bar{\tau}$ and the average

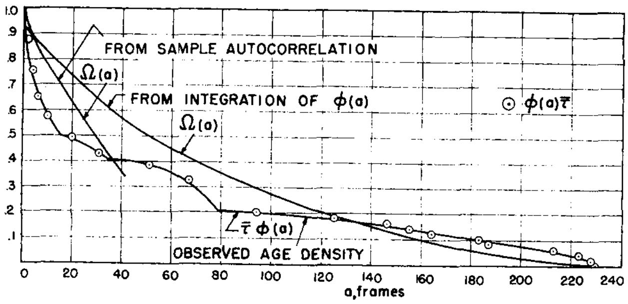


**Fig. 7. Age distribution and autocorrelations for fluidized-bed experiment.**

transport coefficient by using the same techniques applied to the computer simulated runs.

*Observed Changes Method.* The sum $\sum_{j=0}^{553} k_j$ of the observed changes in count between successive frames was computed. This was found to be 80, the mean of the counts being 5.1. Hence

$$r\bar{\tau} = 5.1$$

$$E\{k_j\} = \frac{80}{554} = 0.144$$

From Figure 1, we estimate $r\Delta t = 0.078$; since $\Delta t = 1$, the estimated mean residence time $\bar{\tau} = \frac{5.1}{0.078} = 65$ frames.

*$\bar{\tau}$ from $\Delta\psi$.* The sample autocorrelations for the counts were computed, yielding as *estimators*

$$\overline{N} = 5.1$$
$$\psi(0) = 18.4$$
$$\psi(1) = 17.6$$

(Note that the estimate of $\psi(0)$ here is a poor estimator of the variance in the counts $N(t)$ because of the small number of samples.)

Equation (46) estimates $\bar{\tau} = 61$ frames, Equation (48) estimates $\bar{\tau} = 219$ frames, while $\bar{\tau}_{\text{expt}} \geqq 58$. The result from Equation (48) is poor, as expected.

*Average Transport Coefficient.* Since the age distribution $\phi(a)$ was estimated, Equation (9) of Part I could be used to give $\overline{N}_{Nu}$ directly. This yielded $\overline{N}_{Nu} = 0.0841$, for the transport model $N_{Nu} = 1/\sqrt{\pi a}$.

However, the sample autocorrelations were computed to $a = 40$ frames only, since beyond this point there were insufficient samples to give meaningful results. If the upper limit in the integral in Equation (9) of Part I is taken to be 40, then $\overline{N}_{Nu} = 0.0515$.

By using the sample autocorrelations and Equation (58), the mean transport coefficient $\overline{N}_{Nu}$ was computed again. This provided a low estimate of the true $\overline{N}_{Nu}$, since the autocorrelation was estimated only to forty

TABLE 3.

| | By direct measurement | By estimator | Remarks |
|---|---|---|---|
| 1. Mean residence time $\bar{\tau}$ | >57.9 frames | 65.6 | Observed changes method |
| | | 60.9 | Equation (46) |
| | | 219 | Equation (48) |
| 2. Mean transport coefficient | 0.0841 | | Integration to ∞; Equation (58) |
| | 0.0515 | 0.0563 | Integration to $a = 40$ only |
| 3. Autocorrelations | see Figure 7 | | |

frames. For an integration up to $a = 40$, $\overline{N}_{Nu} = 0.0563$ shows good agreement with the value computed directly from the age distribution.

Table 3 summarizes the results obtained.

## CONCLUSIONS

1. For typical penetration transport models, knowledge of the average residence time at the transport surface is sufficient for estimation of average transport coefficients without knowledge of the shape of the age distribution.

2. The average residence time may be accurately estimated from total element counts. The length of experiment necessary when using total element counts may be made significantly less than the length of experiment necessary to achieve the same confidence limits by using observation of individual elements. Furthermore, the total count technique is applicable in situations where individual observation is difficult or impossible. However, a greater total number of elements must be observed by using the total element counts technique.

3. For situations where it is desirable to reconstruct the age distribution, the sample autocorrelation function of the total counts was shown to provide reasonable statistical estimators for the age distribution. In addition, integration of this reconstructed age distribution with the transport model gave good estimates of the average transport coefficient.

4. In the test on a fluidized-bed system, the autocorrelation method gave satisfactory estimates of the residence time distribution, particularly in view of the small number of particles in the statistical sample.


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## NOTATION

$A(j\Delta t)$ = autocorrelation of signal $N(t)$
$a$ = dimensionless age
$b$ = probability of entrance of an element in unit time
$D$ = average number of elements which exit in an interval of one average residence time
$E\{\ \}$ = expected value
$e$ = exit rate of elements in elements per unit time
$F$ = cumulative distribution resulting from residence time density function
$f$ = residence time density function
$g(n)$ = probability that $n$ elements will enter in a time interval of one average residence time
$H(\theta)$ = number of elements which arrive after time $t$ and are still in residence at time $(t + \theta)$
$h[N(t)]$ = probability that $N$ elements will be in residence at time $t$
$I_p$ = Bessel functions of complex arguments of order $p$
$K$ = constant in Equation (1)
$K_j$ = unbiasing constants in Equation (51)
$k$ = sum of $k_j$ (random variable)
$k'$ = increase in count of elements between two successive observations (random variable)
$k_j'$ = increase in count of elements between observations $j$ and $j + 1$ (random variable)
$L$ = measure of information retention possible with finite time interval
$M + 1$ = number of equally spaced observations
$N(t)$ = number of elements in residence at time $t$
$N_i(t)$ = $N(t_0 + i\Delta t)$
$\overline{N}$ = expected value of $N$
$\mathfrak{N}$ = great number of elements available for entrance
$N$ = number of elements
$N_{Nu}$ = instantaneous transport coefficient
$\overline{N}_{Nu}$ = average transport coefficient
$p_e$ = probability of exit of an element at time $t$ in a unit time interval
$p_n(\Delta t)$ = probability that $n$ elements will exit during a time interval $\Delta t$
$p_q$ = probability that the random variable $k_j$ will assume the value $q$
$p_t$ = probability that a particular element will be in residence at time $t$
$p_{j\Delta t/t}$ = probability that $n$ elements will be in residence at time $t + j\Delta t$, *given* that it is in residence at time $t$
$p_{S,N}$ = probability that there are $N$ elements present at time $t$ and that $S$ of these are still in residence at time $t + \theta$
$p_{S/N}$ = probability that $S$ out of $N$ elements are still in residence at time $t + \theta$, *given* that $N$ are in residence at time $t$
$p_{t/\theta}$ = probability that an element will be in residence at time $t$ given that it entered at time $\theta$, $\theta < t$
$q$ = number by which exits exceed the entrances
$R$ = average number of elements which enter in an average residence time
$r$ = rate of entrance of elements in number per unit time
$S(\theta, t)$ = number of elements which arrive prior to time $t$ and are still in residence at time $(t + \theta)$
$T$ = $M\Delta t$ the total period of observation
Var( ) = variance
$X_0$ = estimator for $\overline{N}$
$x$ = $2r\Delta t$
$Y_j$ = estimator for $\psi(j\Delta t)$
$Y_j'$ = unbiased estimator for $\psi(j\Delta t)$

### Greek Letters

$\alpha$ = shape parameter in gamma distribution
$\Delta t$ = time interval between observations
$\Delta\psi$ = difference between first and second modified autocorrelations $\psi(0) - \psi(\Delta t)$
$\theta$ = time
$\lambda(a)$ = probability that element of age $a$ will exit before a unit time interval
$\sigma\{\ \}$ = standard deviation
$\tau$ = residence time (random variable)
$\overline{\tau}$ = mean residence time
$\phi$ = age density function
$\psi(a)$ = modified autocorrelation = $A(a) - \overline{N}^2$
$\Omega(a)$ = normalized $\psi = \dfrac{\psi(a)}{\psi(0)}$

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