Number of Passage Distribution Functions with Application to Dispersive Mixing

Number of passage distribution (NPD) functions in batch and continuous recirculating systems are presented, and their application to dispersive mixing of plastics and rubber is discussed. Dispersive mixing requires a process of repeated ruptures of the dispersed phase. This is accomplished by repeated passages in special regions of the system where stress levels above a given threshhold value are imposed on the liquid. The application of NPD functions to certain batch and continuous mixers and compounders is discussed.

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Introduction

Consider physical systems, such as mixers and reactors, which contain recirculating fluids. Within these systems some physical or chemical change takes place in one or a number of well-defined regions of the system. In order to characterize such systems, we may wish to know:

- The cycle or passage time,
- The number of cycles or passages,
- The time spent in these regions

of any given fluid element in the system.

Passage times and dispersion of passage times in recirculating systems were first considered by Shinnar et al. (1970) in their analysis of residence time distribution in closed-loop systems. The most important such system is that of the blood circulation, but their analysis is also relevant to engineering systems such as fluidized-bed reactors. The main objective of their work was the analysis of tracer experiments in recirculating systems. The renewal theory discussed by Cox (1962) served as the theoretical framework for their analysis.

The first published work on passage, or cycle time distribution functions is due to Mann and coworkers. First Mann and Crosby (1973) and Mann et al. (1974) defined cycle time distribution (CTD) functions in batch systems, which characterize circulating systems in the same manner as residence time distribution (RTD) characterizes continuous systems. They also defined for these systems the number of cycle distribution (NCD) functions $G_k(t)$ as the probability that the particle completes no more than k cycles during time t, and $g_k(t)$ as the probability that it completes exactly k cycles during time t. When all fluid particles are identical, these are also the corresponding fractions of material in the system that experience no more than k cycles, and exactly k cycles during time t, respectively. Next, Mann et al. (1979) extended the definition to continuous recycle systems, and defined the functions $F_k(\theta)$ and $f_k(\theta)$ [in their nomenclature $Q(n)$ and $q(n)$] as, respectively, the probability of a fluid element to experience no more than k cycles in the system of mean residence time θ, and the probability to experience exactly k cycles. Once again, for identical fluid elements these become identical to exiting flow rate fractions experiencing no more than k cycles, and exactly k cycles, respectively. Finally, Rubinovitch and Mann (1983a, b, 1985) extended these functions to characterize general arbitrary continuous flow systems, with multiple number of flow regions visited, and multiple flow inlets and outlets, and expressed them using Markov chain representation.

The physical processes they considered relevant to this type of analysis include particle coating in air suspension, fluidized catalytic reactor generator systems, granulation, and crystallization.

In this paper, the number of cycle distribution functions or number of passage distribution (NPD) functions are derived and are applied to batch and continuous dispersive mixers. The terminology of NPD is preferred over NCD for these systems, to stress the point that the dispersion process occurs during the *passage* of the particle in the specified region. It will be shown that the NPD functions are not only useful for dispersive mixers, but that the operation of these mixers can be quantified only in terms of these functions.

Dispersive Mixing

Dispersive mixing is associated with the reduction *in size of* one component having a cohesive character, within a continuous liquid phase. The component may be an agglomerated solid, a noncompatible liquid droplet, or a gas bubble. The cohesive character of the agglomerated solids is due primarily to the van der Waals forces between the particles forming the agglomerates (e.g., carbon black, organic and inorganic pigments); whereas, that of the liquid droplet (e.g., noncompatible polymeric blends and alloys) and the gas bubbles (e.g., molten polymeric foams) is due to surface tension and elastic properties.

One of the most characteristic and industrially important dispersive mixing process is that of carbon black into rubber. It is well known, for example, that the quality of tires depends to a large extent on the quality of the carbon black dispersion in the rubber matrix. Although the detailed physical mechanisms associated with the breakdown process are not fully understood, it is generally agreed that the stress level in the continuous phase must exceed a critical value, in order to rupture the dispersed phase via interfacial hydrodynamic forces (Manas-Zloczower et al., 1982, 1984; Tadmor, 1985; Chohan et al., 1987).

Mixers for rubber and plastics, be they batch or continuous, cannot be designed to impose high stress levels throughout their volume due to power and heat transfer limitations. Such dispersive mixers are therefore designed to have:

1. High stress regions of relatively small volume with good heat removal characteristics
2. An overall geometrical configuration which insures that all fluid elements within the mixer pass repeatedly through the high stress region

Repeated passage is required in order to reduce the dispersed phase to the desired size via repeated ruptures.

In the classical Banbury type batch mixer, the high stress region is the radial clearance between the tip of the rotating blade and the wall of the mixer. In continuous-screw type mixers it is the clearance between the tip of a flight or a kneading type element and the barrel surface, or any other geometrical configuration with narrow clearance.

The number of passages of a fluid element over the high stress region, in a given time in batch mixers, or within a given residence time in a continuous mixer, depends on the particular pathline the fluid element follows. Different fluid elements experience, therefore, different numbers of passages over the high stress region, and consequently the dispersed phase within the fluid element experiences a different rupture history and hence acquires different ultimate sizes. The NPD functions therefore must be defined and applied to the mixers to quantitatively characterize the dispersion process in both batch and continuous mixers.

Theory of Number of Passage Distribution Functions

Both Shinnar et al. (1970) and Mann et al. (1974), have shown that the NPD functions can be evaluated from the passage time distribution function, which in turn can be obtained from the renewal theory (Cox, 1962). Thus, following Shinnar et al., consider a fluid element at time $t = 0$, at site A in the recirculating fluid. The passage time of the fluid element from site A to another site B is a continuous random variable, with probability density function $f_{AB}(t)$. Site B for our purpose is the region where the physical or chemical change takes place. This site need not be a single point, nor a single fixed region, but any fixed fraction of volume of the system. Next we assign the probability density function $f_{BB}(t)$ for the fluid element at site B to return to site B. The two passage times are independent, and therefore the probability density function of moving from site A (at $t = 0$) to site B, and one cycle is the convolution of the two densities $f_{AB}(t) \cdot f_{BB}(t)$. In a similar way we can deduce the density function of k cycles as $f_{AB}(t) \cdot f_{BB}(t)^{*k}$. By making the assumption that $f_{AB}(t) = f_{BB}(t) = f(t)$, the density function becomes $f(t)^{*(k+1)}$, that is, the $(k + 1)$ in order convolution operator of $f(t)$. Next, in terms of probabilities we can state that the probability of a single fluid particle, of k cycles, going through site B in a time period between t and $t + \Delta t$ is $f(t)^{*(k+1)}\Delta t$. The total volume of fluid particles (with k cycles) to go through site B is $f(t)^{*(k+1)}V\Delta t$, where V is the material volume in the system. If we let q be the total volumetric flow rate through site B, then the total volume going through site B in the period from t to $t + \Delta t$ is $q\Delta t$. We now can define the NPD, $g_k(t)$, as the fraction of volume in the system that has experienced k passages in time t

$$g_k(t) = \frac{f(t)^{*(k+1)}V\Delta t}{q\Delta t} = \theta f(t)^{*(k+1)} \tag{1}$$

where θ is the mean passage time between successive passages. The NPD function $g_k(t)$ is, of course, also the probability of any fluid particle in the system to have k passages.

In terms of the renewal theory, $g_k(t)$ is the probability of k renewals of the *same* fluid element in time interval t. In all fluid elements are identical this is also the fraction of material volume in the system that has experienced k passages.

It is convenient to take the Laplace transform of Eq. 1 to give:

$$g_k(s) = \mathcal{L}\left[\theta f(t)^{*(k+1)}\right] = \theta f(s)^{(k+1)} \tag{2}$$

and thus, $g_k(t)$ is the inverse of $g_k(s)$

$$g_k(t) = \mathcal{L}^{-1}\left[\theta f(s)^{(k+1)}\right] \tag{3}$$

Consider a simple density function $f(t) = \rho e^{-\rho t}$, describing a Poisson process with a constant age-specific passage rate of $1/\rho = \theta$. This implies that the probability of an additional passage is constant, and independent of either location or passage history; that is, in physical terms, perfect mixing is involved. The Laplace transform of this density function is $\rho/(\rho + s)$, and by Eq. 3 $g_k(t)$ becomes

$$g_k(t) = \frac{\lambda^k}{k!}e^{-\lambda} \tag{4}$$

where λ is the dimensionless time

$$\lambda = \frac{t}{\theta} \tag{5}$$

Equation 4 is equivalent to Eq. 16 of Mann et al. (1974).

NPD Functions in Batch and Flow Recirculating Systems

We defined $g_k(t)$ as the fraction of material volume in circulating batch systems that has experienced exactly k passages in a volume region of interest. The function is continuous in t and discrete in k. The cumulative NPD function, $G_k(t)$, follows from the definition of $g_k(t)$:

$$G_k(t) = \sum_{j=0}^{k} g_j(t) \tag{6}$$

and its physical interpretation is the fraction of material volume in the system that has experienced no more than k passages in the volume region of interest. Clearly, $G_\infty(t) = 1$. Of special interest is the mean number of passages $\bar{k}(t)$, given by

$$\bar{k}(t) = \sum_{j=0}^{\infty} j g_j(t) \tag{7}$$

and associated with it are the fraction of material volume characterized by passage number less than or equal to the mean $G_{\bar{k}}$, and that characterized by $k > \bar{k}$, $G^*_{\bar{k}}$, where

$$G^*_{\bar{k}} = 1 - G_{\bar{k}} \tag{8}$$

The variance of the distribution $g_k(t)$ is given by

$$\sigma^2(t) = \sum_{j=0}^{\infty} (j - \bar{k})^2 g_j(t) \tag{9}$$

The moments of the distribution are defined as

$$\mu_r = \sum_{j=0}^{\infty} j^r g_j(t) \tag{10}$$

and in term of the moments $\bar{k} = \mu_1$ and $\sigma^2 = \mu_2 - \mu_1^2$. Of special interest is the relative measure of breadth, defined as the square of the coefficient of variation, σ^2/μ_1^2.

Higher moments of the distribution are useful in characterizing other features of the distribution such as skewness and kurtosis.

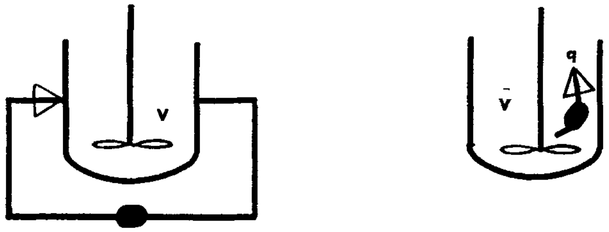

Figure 1. Batch well-stirred vessel.
V, volume; q, internal or external recycle stream

We can conveniently generate the moments of the distribution via the generating function

$$g(Z) = \sum_{j=0}^{\infty} g_j Z^{-j} \tag{11}$$

where Z is the transform variable, by using the following equation,

$$\mu_r = \lim_{Z \to 1} (-1)^r \left[\left(Z \frac{\partial}{\partial Z} \right)^r g(Z) \right] \tag{12}$$

Next, we define a parallel set of NPD functions in flow recirculating systems. We restrict our discussion to steady flow systems. Here we distinguish between external and internal NPD functions. We define f_k and i_k as the fraction of exiting volumetric flow rate and the fraction of material volume, respectively, that have experienced exactly k passages in the specified region of the system. The respective cumulative distribution functions,

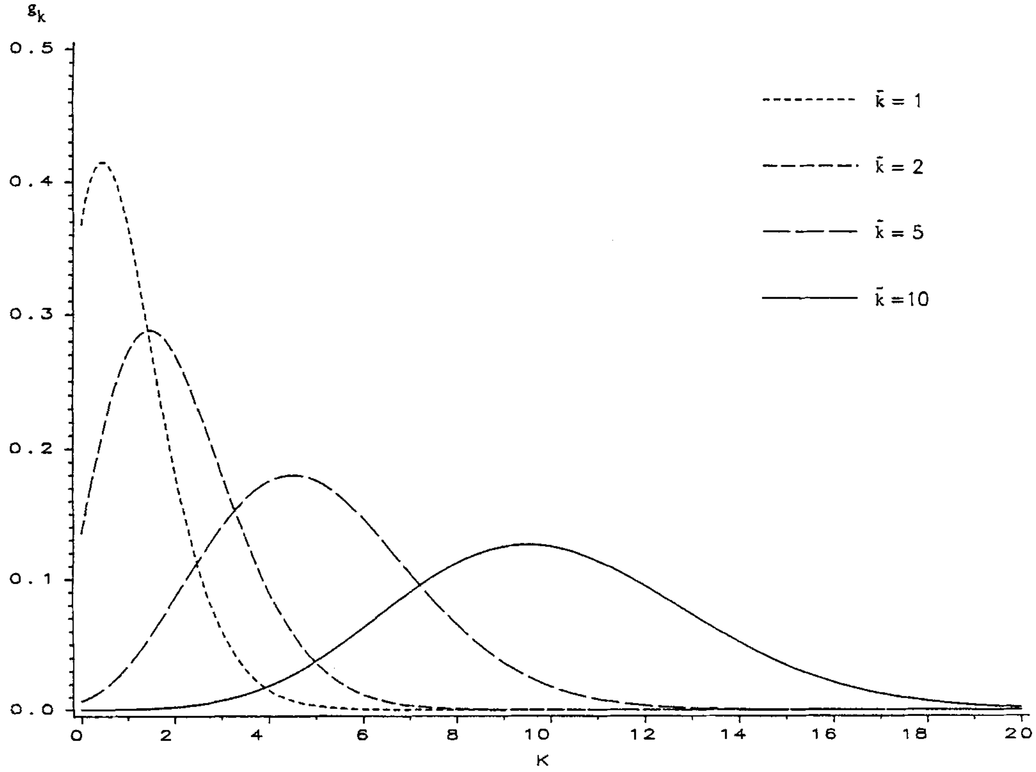

Figure 2. NPD function g_k of system in Figure 1, with mean number of passages $\bar{k}$ as a parameter.

Table 1. NPD Functions, Means, Variances, and Moments of Some Model Batch and Flow Systems with Recirculation

	Well-stirred Batch Vessel	Plug-flow System	Well-stirred Flow System
NPD	$g_k = \frac{\lambda^k}{k!} e^{-\lambda}$	$f_k = \frac{\lambda^k}{k!} e^{-\lambda}$	$f_k = (1 - \alpha)\alpha^k$
Cumulative NPD	$G_k = \Gamma(1 + k, \lambda)/k!$	$F_k = \Gamma(1 + k, \lambda)/k!$	$F_k = \alpha(1 - \alpha^k) + (1 - \alpha)$
Mean no. of passages	$\bar{k} = \lambda = t/\theta$	$\bar{k} = \lambda = \frac{q}{Q}$	$\bar{k} = \frac{\alpha}{1 - \alpha} = \frac{q}{Q}$
Generating function	$g(z) = e^{-\lambda} e^{\lambda/z}$		$f(z) = (1 - \alpha)\left(\frac{z}{z - \alpha}\right)$
First moment	$\mu_1 = \lambda$		$\mu_1 = \alpha/(1 - \alpha)$
Second moment	$\mu_2 = \lambda + \lambda^2$		$\mu_2 = \alpha(1 + \alpha)/(1 - \alpha)^2$
Variance	$\sigma^2 = \mu_2 - \mu_1^2 = \lambda$		$\sigma^2 = \mu_2 - \mu_1^2 = \alpha/(1 - \alpha)^2 = \bar{k}(1 + \bar{k})$
Coeff. of variation	$\frac{\sigma^2}{\mu_1^2} = \frac{1}{\lambda}$		$\frac{\sigma^2}{\mu_1^2} = \frac{1}{\alpha} = 1 + \frac{1}{\bar{k}}$

t = mixing time
V = volume of system
q = volumetric recirculation rate
Q = volumetric flow rate
$\theta = V/q$ mean circulation time
$\Gamma(a, b)$ = incomplete Beta function

F_k and I_k, the means of the distributions, the variances, and the moments of distributions, parallel the former definitions given for the batch system.

For steady, constant-density flow systems, the internal and external NPD's can be easily shown to be related as follows:

$$i_k = \frac{Q}{q}(1 - F_k) \tag{13}$$

where Q and q are the volumetric flow rate of the system and the recirculation rate, respectively.

NPD Functions in Some Model Systems

Well-stirred batch vessel with recirculation

One of the simplest batch systems of interest is the well-stirred vessel of volume V, with an internal or external circulation rate q, as shown in Figure 1. The well-stirred vessel, or perfectly mixed vessel, is characterized by a probability distribution function $f(t) = pe^{-pt}$. The NPD functions that can be derived either by population balance models or from probabilistic consideration, are given in Table 1 together with the moments of the distribution, the mean number of passages, and the variance. The NPD function g_k is plotted in Figure 2 with $\bar{k} = \lambda$ as a parameter. Clearly, the absolute breadth of the distribution, as measured by σ^2, increases with increasing mixing time, but the relative breadth, as measured by σ^2/μ_1^2 decreases with increasing mixing time.

For example, Manas-Zloczower et al. (1982) adopted the well-stirred vessel with recirculation as a model for internal Banbury type mixtures. They derived the NPD function, combined it with a physical and hydrodynamic model to describe the rupture of an individual freely suspended axisymmetric solid particles, and derived the ultimate particle size distribution of the solids. They tested the model with experimental results on carbon black dispersion in rubber, and showed very good agreement. The good agreement was explained by the fact that the NPD function captured the key element of the very complex mixing process. Indeed they have suggested (Manas-Zloczower and Tadmor, 1984) as a mixer scale-up criterion the mean number of passages coupled with securing a given threshold shear stress value in the high shear region between the tip of the rotor and the chamber wall.

Plug flow with recirculation

The equations derived for the batch vessel with recirculation also hold for a plug-flow system, with perfect mixing over a finite slice perpendicular to the main flow direction, and recirculation, as diagramed in Figure 3.

In this case the mixing time t is replaced by the residence time V/Q, where V is the volume of the flow system and Q is the volumetric flow. Hence λ, in the equation listed in Table 1, is given by

$$\lambda = \frac{V/Q}{V/q} = \frac{q}{Q} \tag{14}$$

which is the ratio of the recirculating flow rate to the flow rate of the system. Thus, the net flow rate in the recirculating region is simply the product of the net flow rate and the mean number of passages. This result was also derived by Rubinovitch and Mann (1982) for any general steady continuous system.

Manas-Zloczower and Tadmor (1983), modeled the single screw extruder as such a continuous plug-flow system with recir-

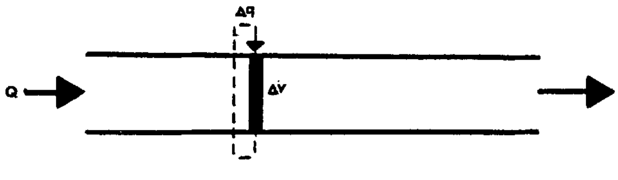

Figure 3. Plug-flow system with internal recycle.
Q, total flow rate; Δq, local recycle rate of an element of volume ΔV
ΔV element moves with constant velocity in main flow direction

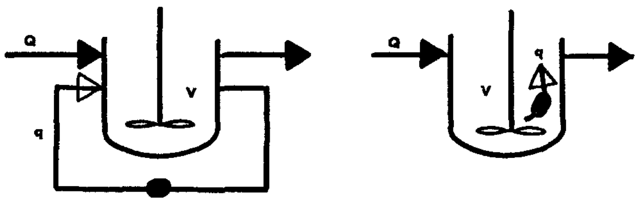

Figure 4. Continuous well-stirred vessel.
V, volume; Q, flow rate; q, recirculatory internal or external flow

culation, and using the NPD function showed that most of the exiting fluid in the extruders experienced no passages over the screw flight. And, since the flight clearance is the only high shear region of these machines, single screw extruders are inherently poor dispersive mixers.

Well-stirred continuous vessel with recycle

This system is shown in Figure 4 and the NPD functions are listed in Table 1. The function f_k is plotted in Figure 5 with the mean number of passages as a parameter. The NPD is identical in form to Flory's (1953) most probable distribution of polymer chains in a stepwise addition polycondensation. This is not surprising because from a probability point of view the processes are identical.

The model system represents certain types of continuous mixers, or certain types of mixing sections in continuous compounders. It is interesting to note that the mean number of passages of this model is identical to that of the plug flow with recycle, yet the NPD functions are very different (compare Figures 2 and 5). The former is a relatively narrow distribution, whereas the latter is a wide distribution. Thus the mean number of passages, though easily computable, cannot serve as the sole quantitative criterion for dispersive mixers and there is a need to derive, or experimentally measure, the whole distribution.

Discussion

The rupture of the solids agglomerates in a polymeric matrix, and that of a liquid droplet in a noncompatible polymeric blend, takes place during the passage of the mixture in high stress regions of mixers and compounders. Repeated ruptures, and hence repeated passages, are needed in order to reach the desirable final size of the dispersed phase. Commercial batch and continuous mixers and compounders are designed and operated so as to generate within them complex chaotic flow patterns. Consequently, different fluid elements within the batch mixers, and in the exiting stream in continuous mixers, have experienced different numbers of passages in the high stress region. Therefore, only via NPD functions can the dispersive mixing process be formulated quantitatively.

Although the foregoing model systems capture important elements of certain types of real mixers, it is unfortuante that there are no general experimental techniques for measuring NPD function. Such techniques would be of very great utility to characterize and evaluate dispersive mixers and compounders. In the absence of such techniques, it would be worthwhile to consider experimental techniques that would only measure the f_0 or g_0 values of the NPD function, that is, the fractions that experienced no passages over high stress regions. These fractions for the two flow systems discussed above (i.e., continuous mixed vessel and plug flow with recycle) result in $f_0 = e^{-\bar{k}}$ and $f_0 =$

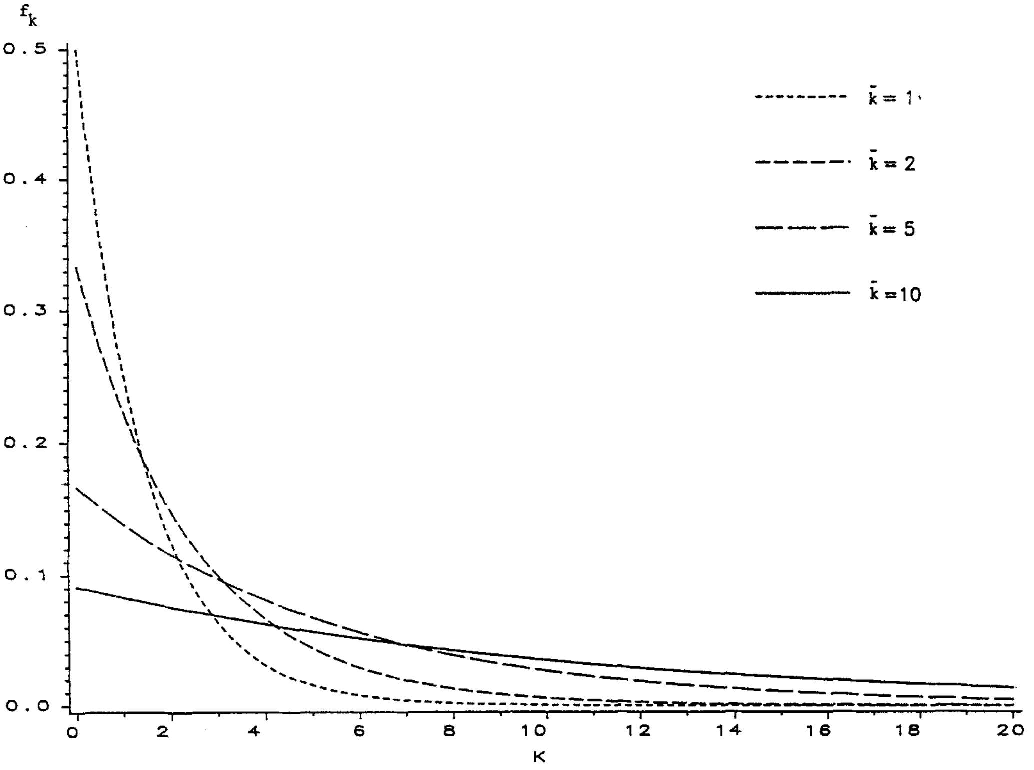

Figure 5. NPD function f_k of system in Figure 4, with mean number of passages $\bar{k}$ as a parameter.

$1/(\bar{k}+1)$, respectively. The former for any $\bar{k} > 1$ is much smaller and hence is distinguishable from the latter. In principle, this fraction could be evaluated with tracer particles, such as microballoons of a given strength, by measuring the fraction of unbroken particles after a given mixing time in batch mixers, or in the exit stream in continuous mixers.

However, unlike RTD functions in chemical reactors, the utility of the NPD functions in polymer processing does not hinge solely on the availability of experimental measurement techniques. The flow in these systems is always laminar, the velocity fields are deterministic, and it therefore is possible, in principle, to compute these functions numerically. This can be done by tracking a sufficient number of passive fluid particles along their trajectories and recording each passage in the high stress regions. The numerical technique and methodology for this procedure is the same as the one developed and used recently to study chaotic streamlines and compute Poincarè sections in time-dependent two-dimensional flows (Aref, 1984; Aref and Balachander, 1986; Chaiken et al., 1986, 1987) and in steady three-dimensional flows (Dombre et al., 1986). In fact the same computation in real mixers will yield Poincarè sections reflecting extensive mixing behavior, and NPD functions reflecting intensive mixing behavior. Work along these lines is in progress in these laboratories.

Acknowledgment

This research was supported by a grant from the National Council for Research and Development, and the KFA Juelich, West Germany. It is part of a joint research project on dispersive mixing with G. Menges, A. Limper, and J. Grajewski from the Institut fur Kunststoffverarbeitung in Aachen. The author wishes to thank M. Rubinovitch and A. Nir for their comments.

Notation

f_k = fraction of exiting volumetric flow rate that experiences k passages
$F_k = \Sigma_{j=0}^{k} f_j$ = fraction of exiting volumetric flow rate that experiences a number of passages $\leq k$
$F_k^* = 1 - F_k$
$g(z)$ = generating function, Eq. 11
g_k = fraction of material volume in circulating batch systems that has experienced k passages
$G_k = \Sigma_{j=0}^{k} g_j$ = fraction of material volume in circulating batch systems that has experienced a number of passages $\leq k$
$G_k^* = 1 - G_k$
i_k = fraction of material in a circulating flow system that has experienced k passages
I_k = fraction of material in a circulating flow system that has experienced a number of passages $\leq k$
$\bar{k}$ = mean number of passages
q = volumetric recirculating flow rate
Q = volumetric flow rate
V = material volume in system

Greek letters

$\alpha = q/(q+Q)$
$\Gamma(a, s)$ = incomplete Beta function
$\theta = V/q$ mean circulation time
$\lambda = t/Q$ or q/Q, Table 1
μ_r = moments of distribution, Eq. 10
σ^2 = variance of distribution

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Manuscript received Mar. 24, 1988, and revision received July 22, 1988.