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Alena Kukukova, Joelle Aubin, Suzanne Kresta. A new definition of mixing and segregation: Three dimensions of a key process variable. *Chemical Engineering Research and Design*, 2009, 87 (4), pp.633-647. <10.1016/J.CHERD.2009.01.001>. <hal-03562913>

HAL Id: hal-03562913

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To link to this article: DOI:10.1016/J.CHERD.2009.01.001
URL: <http://dx.doi.org/10.1016/J.CHERD.2009.01.001>

To cite this version: Kukukova, Alena and Aubin, Joelle and Kresta, Suzanne (2009) A new definition of mixing and segregation: Three dimensions of a key process variable. *Chemical Engineering Research and Design*, vol. 87 (n° 4). pp. 633-647. ISSN 0263-8762

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A new definition of mixing and segregation: Three dimensions of a key process variable

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A B S T R A C T

Although a number of definitions of mixing have been proposed in the literature, no single definition accurately and clearly describes the full range of problems in the field of industrial mixing. An alternate approach is proposed which defines segregation as being composed of three separate dimensions. The first dimension is the intensity of segregation quantified by the normalized concentration variance (CoV); the second dimension is the scale of segregation or clustering; and the last dimension is the exposure or the potential to reduce segregation. The first dimension focuses on the instantaneous concentration variance; the second on the instantaneous length scales in the mixing field; and the third on the driving force for change, i.e. the mixing time scale, or the instantaneous rate of reduction in segregation. With these three dimensions in hand, it is possible to speak more clearly about what is meant by the control of segregation in industrial mixing processes. In this paper, the three dimensions of segregation are presented and defined in the context of previous definitions of mixing, and then applied to a range of industrial mixing problems to test their accuracy and robustness.

Keywords: Mixing; Segregation; Exposure; Stirred tank; Static mixer; Micromixer; Multiscale processes; Spatial statistics; Multiphase mixing; Chaotic mixing; Turbulent mixing; Laminar mixing

1. Early definitions of mixing

The study of mixing dates back many years before the first journal publications, and the idea of “well mixed” is easily discarded as intuitively obvious. A search of the early literature provides a range of qualitative concepts and limiting cases. These papers marked the beginning of three major areas of investigation: mixing in reaction engineering, solids mixing, and polymer processing. Starting from the late 1950s, Danckwerts (1952, 1958) and Zweitering (1959) discussed the difference between complete segregation and perfect mixing in the context of reactor design, particularly for binary mixtures of liquids. Danckwerts (1952) defined the intensity of segregation:

$$I = \frac{\sum_{m=1}^M (\bar{x}_A - x_{Am})^2}{M(\bar{x}_A(1 - \bar{x}_A))} = \frac{\overline{(\bar{x}_A - x_A)^2}}{\bar{x}_A(1 - \bar{x}_A)} \quad (1)$$

where x_A is the fraction of the component A at a point in space and an instant in time, \bar{x}_A is its average fraction in a binary mixture and M is the number of measurement locations. In this context, a point is defined in the continuum sense: large enough to contain a meaningful number of molecules, but small enough to have uniform concentration. The molecules in a homogeneous mixture are uniformly distributed down to the molecular scale and I is equal to 0; in a completely segregated mixture, as defined at a fixed scale of investigation, I is equal to 1. When the mean concentrations of component A and B are equal, $\bar{x}_A = 0.5$, the denominator is the biggest and the intensity of segregation the smallest. The limit of perfectly mixed allows instantaneous contact of two reagents, A and B, on a molecular scale throughout the reactor. The limit of completely segregated is best illustrated as drops of A and drops of B, both suspended in an inert C, with no possibility for dissolution or diffusion of A or B in C. These two limiting definitions are useful, but fail to describe any realistic

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Nomenclature

a	interfacial area (m^2)
a_{ij}	contact area
A, B, C	species or reagents
b	constant
\dot{B}_d	birth rate (s^{-1})
AR_{tr}	threshold aspect ratio
c	constant
C	concentration (mol/m^3)
C_{mean}	average concentration (mol/m^3)
CoV	coefficient of variation
D	dissimilarity index
D_{BA}	molecular diffusivity (m^2/s)
\dot{D}_d	death rate (s^{-1})
D_f	fractal dimension of the cluster
D_r	impeller diameter (m)
E	exposure (mol/s)
i, j	measurement location index, drop interval index or number of particles in a cluster
I	intensity of segregation or index of dispersion
i_{max}	maximum cluster mass in the system
k	Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$)
k_{imp}	constant
K	strength of interaction
$k_L a$	volumetric mass transfer coefficient ($\text{mol}/(\text{s m}^3)$)
L_i	drop size in interval i (m)
L_1, L_2	crystal width and length (m)
n	normal vector or crystal number density ($1/(\text{m}^3 \text{ m m})$)
N	impeller rotational speed (rps or rpm)
N_b	number of neighbouring squares
N_B	molar flow rate (mol/s)
n_d	number of drops (particles)
N_i	number of drops in interval i
$N_i(t)$	number of aggregates of mass i at time t
N_{js}	just-suspended impeller speed (rps or rpm)
N_{jd}	just drawn down impeller speed (rps or rpm)
n_r	impeller rotation frequency (rps)
N_t	total number of measurement locations
t_m	constant
\vec{U}	velocity vector (m/s)
V	volume of crystallizer (m^3)
W	Fuchs stability ratio
x_A	volume fraction of component A at a given point and instant
\bar{x}_A	average volume fraction
<i>Greek letters</i>	
Γ	incomplete gamma function
ε	turbulence kinetic energy dissipation rate per mass ($\text{J}/(\text{kg s})$)
ϕ	volume fraction of dispersed phase
η	kinematic viscosity (m^2/s)
ρ_c	continuous phase density (kg/m^3)
σ	surface tension (N/m)

industrial mixing problem. Danckwerts (1952) also discussed the scale of segregation in some detail. He recognized the difficulty of defining striations when the concentration varies continuously due to diffusion, and discussed in some detail

the use of the autocorrelation of concentration, which he calls the coefficient of correlation, or the correlogram. Several early papers on solids mixing (Lacey, 1954; Lacey and Mirza, 1976a,b; Harnby, 1967; Hersey, 1970) also discuss the intensity and scale of segregation, using the normalized coefficient of variance and addressing the problem of selecting the best sample size (Lacey, 1954; Harnby, 1967), and later considering the scale of segregation, particularly with respect to the auto and cross-correlation functions (Lacey and Mirza, 1976a,b). At that time, it was extraordinarily labor intensive to collect the data densities needed to calculate scales of segregation, and the authors concluded that this measure was not accessible for the solution of realistic problems. Mohr et al. (1957) attempted to relate the rate of reduction in striation thickness to the shear rate in laminar flow systems, with applications to polymer processing, thus marking the beginning of a third parallel path in the history of mixing in the process industries.

During the 1970s, Chemineer published the Chemscale (Gates et al., 1975) as a qualitative description of the intensity of mixing in a tank and this concept was widely used for process design for many years. From the 1960s to the 1980s, Bourne, Villermaux and others (Baldyga and Bourne, 1999) developed more refined ideas about macromixing, mesomixing, and micromixing, but again the definitions are somewhat indirect: clear to the expert, but difficult to explain to a novice. Concurrently, Corrsin (1957, 1964), Toor (1969), and Brodkey (Lee and Brodkey, 1964; McKelvey et al., 1975) all investigated the impact of turbulence on mixing through measurements of concentration fluctuations at a point, sometimes calling this the segregation, with the idea that as the variance in concentration drops to zero, the fluid approaches perfect homogeneity. In the early 1990s, chaos theory examined laminar chaotic mixing with a fresh analytical perspective (Ottino, 1989), and computational fluid dynamics promised numerical solutions to many complex problems (Paul et al., 2004, Chapter 5). In spite of this increasing body of work, the field of industrial mixing lacks a single definition of mixing that allows one to proceed directly from:

1. a rigorous conceptual definition to,
2. experiments which directly measure “mixing,” and
3. equations and theory which quantify the definition.

Fig. 1 shows a selection of important mixing problems encountered in industry. In all of these problems, there is global progress from a segregated state toward a more homogeneous state, but the physical phenomena vary widely. Fig. 1a is the concentration field in a turbulent jet, measured using Planar Laser-Induced Fluorescence (PLIF). The dispersion of minor species by turbulent eddies is evident, as is the range of length scales. This concentration field underlies the problem of by-product formation in a feed plume, known as the mesomixing limit. The critical mixing objective is to achieve dilution of the feed plume before the undesired reaction has time to proceed. Fig. 1b shows mixing in a pipeline at a high laminar Reynolds number. The feed jet is efficiently dispersed using an SMV static mixer. The mixer elements are yellow. Fig. 1c shows the concentration field in a cross-section of an SMX static mixer in laminar flow. Again, the initial objective is to achieve homogeneity in the fluid, but there can also be tight process specifications on the smallest allowable striation. Striations larger or smaller than the specified size can lead to unacceptable final products, particularly where optical clarity or color are key properties. Fig. 1d is a composite material

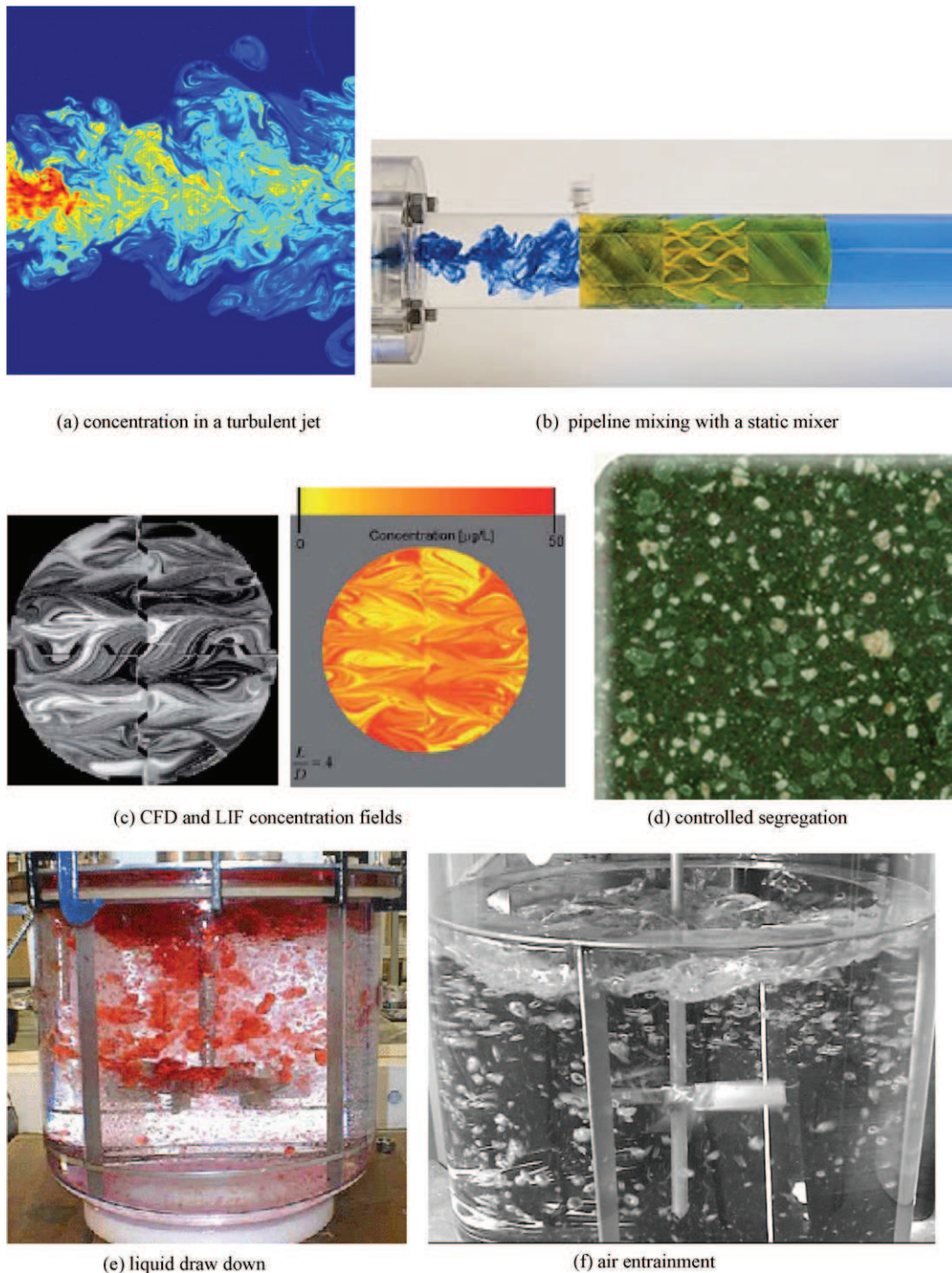


Fig. 1 – Illustrations of the range of mixing objectives encountered in industrial applications, (a) concentration in a turbulent jet, (b) pipeline mixing with a static mixer, (c) CFD and LIF concentration fields, (d) controlled segregation, (e) liquid draw down, (f) air entrainment.

(Corian™ counter top) where several minor phases must be evenly but randomly dispersed in the final product. This is an example of a mixing specification that requires attention to the spatial organization of the minor phase. Fig. 1e shows the initial stages of liquid drawdown in a liquid–liquid mixing application. For this application, the optimal geometry and the rotational speed required to draw down the liquid are needed. The final process specification may involve the rotational speed and time required to achieve some final drop size. This application may also require the addition of surfactants or stabilizers, kill solution to stop a reaction, phase inversion, and/or mass transfer in a mixer settler or liquid–liquid extrac-

tion application. Fig. 1f shows the entrainment of gas bubbles from the surface of a stirred tank. In gas–liquid mixing, the objective is most often gas–liquid mass transfer, but the problem can be substantially complicated by loss of power due to flooding of the impeller and changing conditions in boiling or coalescing systems. In many of these applications, several mixing objectives occur simultaneously in a single vessel or application. These objectives can be grouped into three categories:

- blending of miscible liquids, with possible complications due to high viscosity or non-Newtonian behavior,

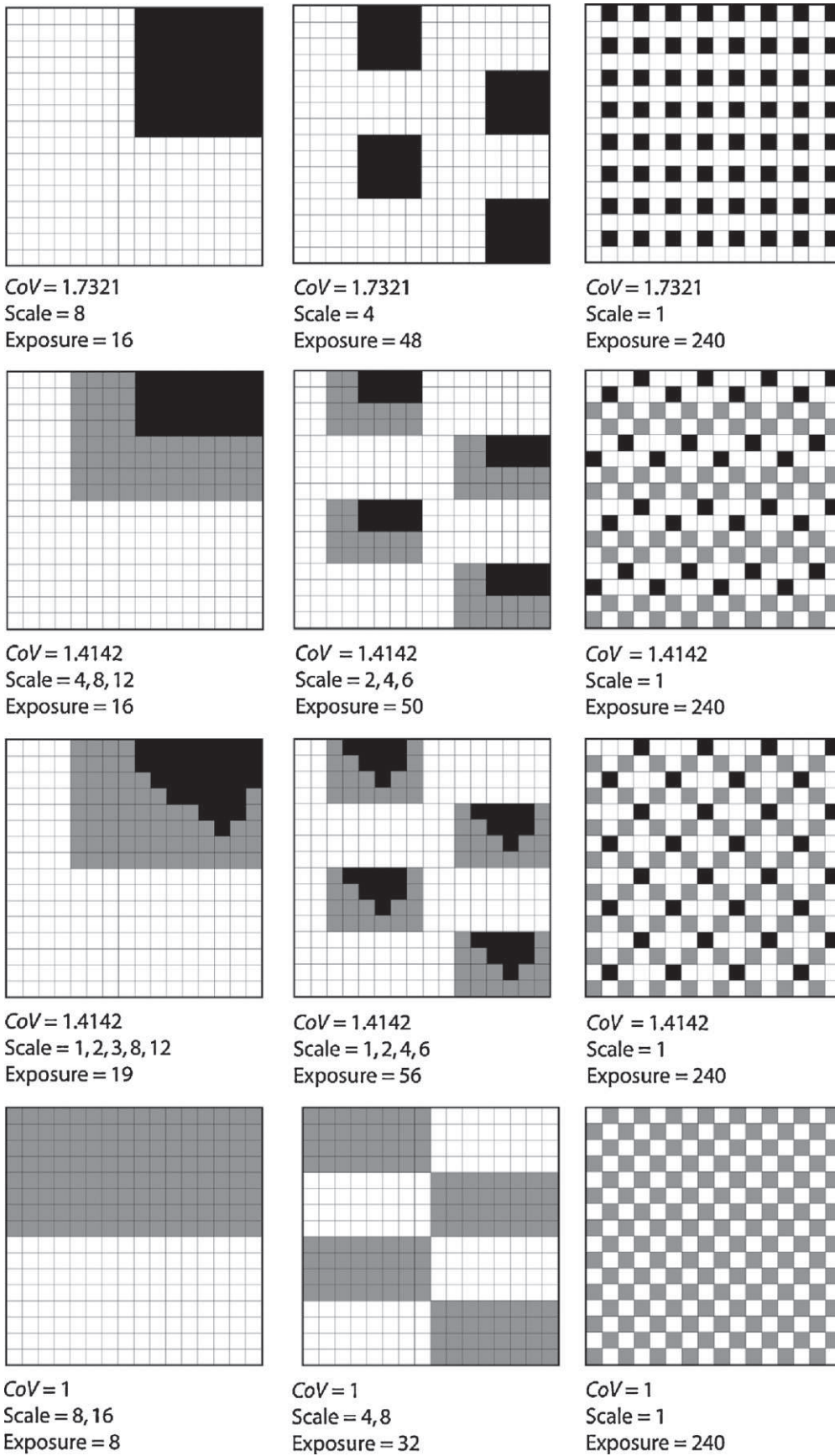


Fig. 2 - Three dimensions of mixing and segregation: intensity of segregation (CoV), scale of segregation (striation thickness) and exposure (rate of change in segregation).

- multiphase mixing with at least one of several objectives: “just contacted”, completely distributed throughout the vessel, size reduction, or mass transfer,
- reaction: either homogeneous or heterogeneous.

A closer examination of these applications, and a number of others, reveals three variables which are directly related to mixing: a reduction in the segregation of concentration; a reduction in the scale of segregation; and/or a mixing time scale that must be accomplished or predicted.

In Danckwerts’ (1958) perfectly mixed limit, all three variables approach zero, and in the simplest mixing problems, the measurement of one variable (e.g. homogeneity of concentration) is often used to infer information about the others. In a second class of problems, for example liquid–liquid dispersions, the concentration remains infinitely segregated but a specific scale of segregation (e.g. drop size) must be achieved. For more difficult mixing problems, there may be a limiting time scale or mixing rate needed to reach homogeneity of concentration over a sub-volume of the vessel (e.g. the mesomixing and reaction problem, or the heterogeneous reaction problem with simultaneous mass transfer). In this case the intensity of segregation, the scale of segregation, and the local mixing time are all important, but the relationship between these variables is not as straightforward as our intuition suggests.

In this paper, a definition of mixing is proposed which provides a bridge between our current understanding of industrial mixing and more theoretical models of mixing (Fox, 2003; Paul et al., 2004 (Ch3)) to give a framework for further research, development, and design. The proposed definition is based on a literature review of theories of segregation in a number of other disciplines: spatial statistics, population ecology, segregation of human populations, geostatistics, and image analysis. The definition is introduced with a thought experiment which illustrates the three key concepts: intensity of segregation, scale of segregation, and exposure.

Fig. 2 shows 12 checkerboard patterns which are organized from left to right by the size of the pattern, and from top to bottom by the variation in concentration. The mean concentration is the same for all 12 checkerboards: black squares have $C_i = 1$, white squares have $C_i = 0$, gray squares have $C_i = 0.5$ and the mean concentration $C_{mean} = 0.25$. The intensity of segregation for each checkerboard is calculated as the CoV:

$$CoV = \sqrt{\frac{1}{N_t} \sum_{i=1}^{N_t} \left(\frac{C_i - C_{mean}}{C_{mean}} \right)^2} \quad (2)$$

The CoV is identical in each row, with the middle two rows showing a change in pattern with no change in the number of black, gray and white squares. The scales of segregation start with the largest possible scales on the left, reducing to

the smallest possible scales on the right of each row. As the patterns become more complex, the number of scales present in a single checkerboard increases. The exposure is calculated from:

$$E \cong \sum_{i=1}^{N_t} \sum_{j=1}^{N_b} \frac{1}{2} K a_{ij} (C_i - C_j) \quad (3)$$

where $N_t = 256$ = total number of squares in the checkerboard, $N_b = 2, 3, \text{ or } 4$ = number of neighbouring squares, $K = 1$ is the strength of interaction, $a_{ij} = 1$ is the contact area per side, and $(C_i - C_j)$ is the concentration difference between two consecutive neighbors. This is analogous to a simplified calculation of the rate of mass transfer across an interface.

A non-expert observer would undoubtedly say that the mixing improves from left to right in Fig. 2. The intensity of segregation (CoV); however, remains constant. It is the scale of segregation which decreases from left to right. The intensity of segregation quantifies how widely the concentration varies, but contains no information about the arrangement of black and white squares. A second look at the equation for the coefficient of variance makes this point clear. From this we conclude that the intensity of segregation is not enough to completely define mixing. The scale of segregation also plays an important role.

It is also possible to normalize the CoV to remove effects of initial concentration by dividing by the initial CoV. In the checkerboard case, the initial CoV is 1.73, giving $CoV/CoV_0 = 1.0$ for the first row, indicating complete segregation. For the second and third rows, $CoV/CoV_0 = 0.709$, and for the last row, $CoV/CoV_0 = 0.578$.

The exposure dimension is related to both the concentration variance and the scales of segregation, but in quite a complicated way. Before discussing the exposure results in Fig. 2, consider the illustration of exposure in Fig. 3. In this figure, the exposure increases from left to right. In (a) both the contact area and the concentration difference are at a minimum, while in (f), both the area and concentration difference are at a maximum. The intermediate pairs (b and c) and (d and e) must have at least a doubling of the total interfacial area to overcome the drop in concentration difference from 1.0 to 0.5. Because the interface has been distorted and folded, the exposure will increase slightly from (b) to (c) and from (d) to (e). Fig. 3 differs from what we would see in an experiment, where the contact area increases rapidly under the influence of turbulent mixing at the same time as the concentration difference continuously drops due to convective mass transfer. The counteracting local effects of scale and intensity make the exposure dimension behave in ways that can be quite complex.

In the first row of Fig. 2, the exposure increases from 16 to 48 to 240 as the scale of segregation drops. Comparing the top and bottom rows suggests that the exposure decreases when the CoV decreases, but as the scale of segregation gets

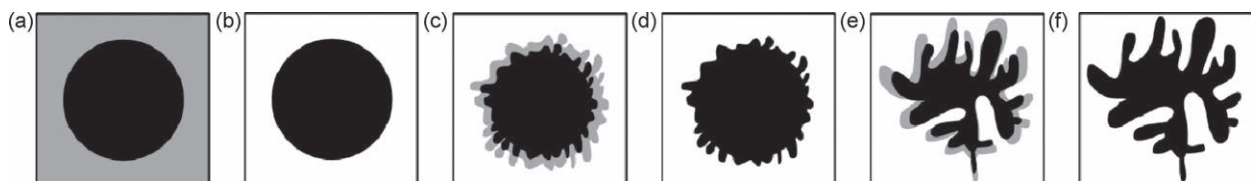


Fig. 3 – Example of increasing exposure showing the effects of concentration difference and area of contact between the two populations. Each pair, moving from left to right, has an increasing area of contact. The first image in each pair (a, c, e) has less exposure than the second (b, d, f), because the concentration difference is smaller.

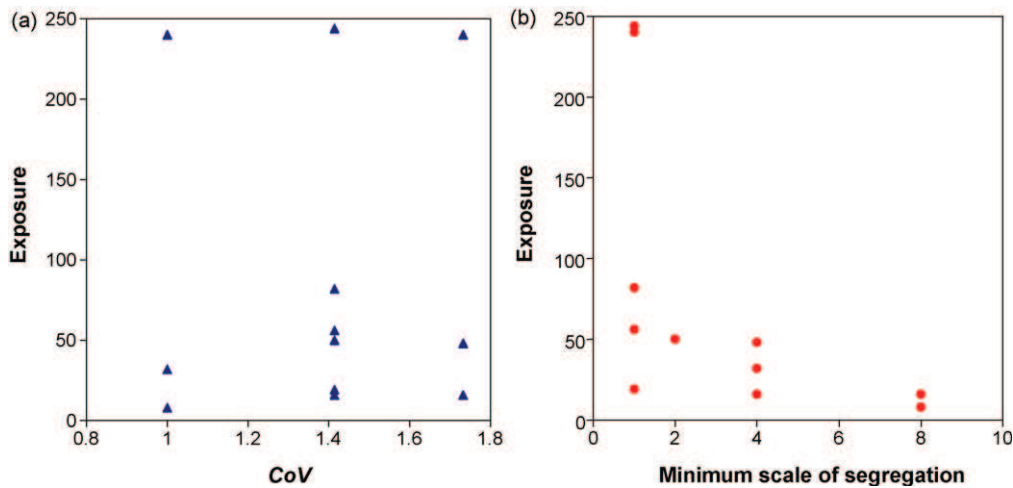


Fig. 4 – Relationship between exposure and (a) intensity of segregation and (b) minimum scale of segregation for the checkerboard patterns in Fig. 2.

smaller, the effect of concentration variance becomes less important. A closer look shows that at intermediate values of CoV with slightly more complicated patterns and a range of length scales, the relationship between CoV and exposure is unpredictable due to the coupling between interfacial area and concentration difference. Decreasing the scale of segregation rapidly increases the exposure for all values of CoV. These results are collected in Fig. 4 where the exposure dimension is plotted against the intensity and minimum scale of segregation. This figure clearly illustrates the need for a third dimension: in Fig. 4a the relationship between CoV and exposure alone is random; in Fig. 4b the exposure decreases rapidly as the minimum scale increases, but there is a wide range of results for exposure at small scales. This thought experiment clearly shows that the exposure dimension is not a simple linear combination of intensity and scale of segregation. The scales of segregation are distributed over a range of values, and are correlated to the interfacial contact area in a complex and non-linear way. In the calculation of exposure, the interfacial area is further coupled with local concentration differences. The exposure dimension combines these effects to describe a third dimension of mixing and segregation, the rate of change of segregation.

In summary, the CoV (intensity of segregation) tells us nothing about the scale of mixing because the definition contains no information about the characteristic length scales or the arrangement of the fluid volumes in the mixing field. This requires a second dimension, the scale of segregation. Exposure is proposed as a third variable, which is a non-linear function of both the intensity and scale of segregation. All three variables play an important role in industrial mixing problems, which are becoming more and more focused on the control of segregation, often at intermediate length scales. This is a more complex problem than the classical perfectly mixed limit.

2. Segregation studies in other disciplines

A literature search reveals that segregation has been studied in a number of fields, and a broad spectrum of useful knowledge has developed in parallel with industrial mixing. A mathematical foundation is defined primarily by the field of spatial statistics. The fields of geostatistics and image anal-

ysis describe segregation in data sets that are fixed in time, but may require three-dimensional reconstruction from limited data sets (e.g. geological core samples). Both population ecology and forest management grapple with interactions between populations, and with extracting meaningful information from limited data. The population ecologists focus on quadrat samples, originally a 1 m × 1 m square area, and the foresters use transect sampling (typically a 2 m wide line sample) extensively. The tendency of populations to cluster, and the opportunities for species to interact with their environment and with other species are both central questions in these fields. This has led to some very useful ways to reconstruct the scale of segregation from limited data sets. Finally, the study of segregation in human populations considers both the instantaneous distribution of populations, and their potential for integration. All of these fields have well developed theory and formalisms, including partial definitions of segregation (Diggle, 2003), but the work by Massey and Denton (1988) is the most complete and quantitative analysis of the dimensions of segregation, integrating all of the key ideas in one overarching definition.

Massey and Denton (1988) reviewed the literature in population segregation and identified 20 different proposed measures of segregation. They applied these measures to 180 independent data sets and used principal components analysis (PCA) to determine which measures contain the most information, which measures are highly correlated with each other, and which measures contain a negligible amount of information. PCA, or partial least squares (PLS) is a regression technique applied to large multivariate data sets to determine which input variables describe the principle dimensions of variance in the results (Kresta et al., 1991). Variables grouped together in a single dimension are collinear and contain similar information (e.g. tray temperatures in a distillation column). Variables appearing in separate dimensions are orthogonal and contain information which pushes the result in a different direction. Massey and Denton's analysis revealed that the data sets contain independent information about 5 distinct dimensions of segregation. The remaining 15 measures did not provide any additional information. The PCA analysis is very significant because it provides a quantitative measure of which variables contribute significantly to the variance in the data. The fact that 5 dimensions are

required reflects the complexity of the underlying data sets; the fact that only 5 of the 20 proposed measures of segregation provided independent information gives us some confidence that the 5 proposed dimensions enable a complete description of segregation. We have retained the meaning of Massey and Denton's 5 proposed dimensions, but reworded them to obtain rigorous definitions that can be applied to a wide range of problems:

1. *Evenness* is the uniformity of concentration of the minor species. Evenness is defined relative to the volume of investigation and the scale of resolution of the measurement.
2. *Clustering* is the degree of spatial continuity or adjacency of members of a population, and is highly correlated to the spatial proximity of members of the population. Clustering is inversely correlated to the degree of spatial dispersion of the species.
3. *Exposure* determines the rate of reduction in segregation. It depends on the deviation from the minimum state of segregation, the physical contact between populations, and the strength of interaction between members of the populations (either attractive or repulsive). Exposure may be thought of as the driving force for change.
4. *Density* is the population density expressed as (number or mass) per (volume or area). The population density includes all species, not just the minor species, so it is distinct from evenness and clustering.
5. *Centralization* is the tendency of a population to concentrate spatially around some central or specified point.

Each of these measures applies at a single instant in time. The five dimensions of segregation are now discussed in more detail and evaluated for their usefulness and applicability to the field of industrial mixing.

Evenness is the first and simplest definition of "good mixing"—perfect homogeneity of the concentration field. The intensity of segregation measures the deviation from homogeneity at an instant in time. The cleanest measure of evenness in the mixing literature is the CoV (coefficient of variation) which is the standard deviation over the mean. The spatial statistics literature provides two other measures: I , the index of dispersion, which is the variance of the population relative to the variance of a completely random distribution; and D , the dissimilarity index, which is the fraction of the minor population that would have to move to eliminate segregation and achieve perfect homogeneity. The index of dispersion is interesting, because in a perfectly random Poisson distribution, the variance is equal to the mean ($I = \text{variance}/\text{mean}$) and $I = 1$ if the distribution is perfectly random. An index of dispersion, $I < 1$, indicates a more regular or homogeneous distribution, and $I > 1$ when there is significant clustering in the population (Diggle, 2003). This provides a more physically meaningful interpretation of the intensity of segregation, should the user be willing to address the issue of units. In multiphase mixing, evenness is achieved when the second phase is homogeneously distributed over the volume of the vessel. This does not require that the bubbles, drops, or particles be monodisperse or small, only that the volume fraction of the minor phase be the same everywhere. The interaction of the scale of segregation with the scale of measurement remains important: as the size of the dispersed particles increases, the size of the averaging volume must also increase in order to retain a meaningful volume averaged concentration. As in the checkerboard example, a large intensity

of segregation contains no information about where the non-homogeneity appears in the vessel, or how large the areas of segregation are. In this case, the intensity of segregation only reveals that the concentration is not uniform.

Clustering appears in the mixing literature as the instantaneous scales of segregation. The study of clustering is well developed in chaotic mixing (Szalai et al., 2004); in population ecology where the clustering of populations is a key indicator of behavior, food sources, and mating (McGarvey et al., 2005; Mugglestone and Renshaw, 2001; Keeling et al., 1997); in geostatistics, where the location of ore bodies from limited data is the main objective (Cressie, 1993), and in image analysis (Mattfeldt, 2005; Anson and Gruzleski, 1999). Measures of clustering include the striation thickness distribution, the stretching distribution, and a family of nearest neighbor methods from spatial statistics. Partial sampling of the scales of segregation in a population can be done using either a transect (line scan) across the volume of interest, or using nearest neighbor analysis over a regular sampling grid. In the past, it was very difficult to obtain enough data to accurately capture all of the scales of segregation in a process, but with increasing resolution in both computational and experimental data, it is now frequently possible to obtain a whole plane of data at quite high resolution, so these methods deserve renewed consideration. In multiphase flow, clustering can characterize bubble swarms, stratified flow, slugging, and other meso-scale phenomena. Direct measures of clustering may provide the means to quantify these different flow regimes. Drop size, particle size, and bubble size distributions are also measures of the scale of segregation, and where the objective is dispersion of a minor phase to a specific scale of segregation, this dimension defines the process.

Exposure is a way of seeing mixing that is implicit in most multi-mechanism models of mixing, but is usually not explicitly addressed. It quantifies the physical contact between two (or more) populations, the strength of interaction between members of the populations (either attractive or repulsive), and the instantaneous departure from the state of maximum mixedness. Together, these terms determine the rate of change of segregation. As an illustrative first example, exposure can be related to Fick's first law for mass transfer:

$$\text{Exposure} = N_B = \int_a D_{BA} \nabla C_B \cdot n da = \int_V D_{BA} \nabla^2 C_B dV$$

where the rate of mass transfer (N_B in moles/s) equals the molecular diffusivity (D_{BA} in m^2/s) times the interfacial area (a in m^2) and the concentration gradient (c_B in $\text{mol}/(\text{m}^3 \text{m})$). While the mixing literature is quite distinct from the large literature on mass transfer, the creation of surface area, a , is certainly a key role of mixing equipment. Exposure measures postulated by Wong and others for racial segregation studies also use concentration differences and areas of contact between populations, combined with distance weights and estimated interaction functions between humans (Wong, 2002, 2005). Their interaction function is directly analogous to the molecular diffusivity. In the design of process equipment the objective is mass transfer. Detailed local measurements of area and concentration are usually not possible. The engineering solution is to lump everything into a single empirical mass transfer coefficient, $k_L a$, which depends on the equipment used, and use a single average concentration driving force. Returning to an understanding based on the underlying

ing physics, however, often leads to improved understanding and better designs. Exposure can also be related to the rate of reaction, drop breakup and coalescence kernels in population balance equations, and the Corrsin model of scalar dispersion by turbulence.

Density is the total population density, or the mass density. It is distinct from the concentration, or fraction, of the minor species. Both total density and concentration may vary locally, as is the case for high density housing in low income areas vs. low density housing in higher income suburbs. In population studies, there may be a correlation between the concentration of a minority group and the total population density, but this is not necessarily the case. The situation is quite different in industrial mixing. In liquid mixing problems, the total population density per volume (e.g. molecules/ml or kg/m³) is constant and the density dimension is not useful as a measure of segregation. In multiphase mixing problems, the mass density may vary substantially over the vessel due to spatial variations in the concentration of the dispersed species. Local concentration measurements, however, will exactly track density changes, so the density dimension of segregation does not provide any new and useful information for a definition of segregation in industrial mixing.

Centralization is the tendency of a population to concentrate spatially at some central point. It can be expressed in physical terms as the centroid or the moment of mass. In population studies this has relevance for the location of populations relative to the city center. In terms of process objectives, this dimension of segregation could be calculated for demixing problems in, for example, centrifuges, cyclones, and rotary kilns, but again, it does not add information about the mixing problem beyond the scale and intensity of segregation.

In summary, the first two dimensions of segregation, evenness and clustering, are directly analogous to the intensity and the scale of segregation. Exposure can be related to the rate of mass transfer, reaction, drop breakup, and a number of other phenomena where the mixing field interacts with some other property to achieve a process objective over some elapsed time. Density and centralization are not useful for a definition of segregation in industrial mixing.

3. Definiton of segregation in industrial mixing

Building on the reviews of mixing and segregation literature, the following definition of industrial mixing is proposed:

Industrial mixing is the control of segregation in unit operations. The instantaneous segregation of a minor species has three dimensions, the intensity of segregation, the scale of segregation, and the rate of change of segregation. The intensity of segregation is the uniformity of concentration of the minor species. Intensity of segregation is defined relative to a fixed volume of investigation and scale of measurement. The scale of segregation is the degree of spatial proximity, or clustering, of members of a population, and is inversely correlated with the degree of spatial dispersion of the minor species. The rate of change of segregation is determined by the exposure, or potential for reduction in segregation. The exposure is determined by three factors: the deviation from the minimum state of segregation, the physical contact between populations, and the strength of interaction between members of the populations (either attractive or repulsive).

In summary, three variables are needed to characterize the state of segregation:

Intensity of segregation = variance in concentration

Scale of segregation = distribution of length scales

*Exposure = rate of change of segregation=(strength of interaction)
× (distance from minimum segregation)
× (opportunity to interact)*

Before evaluating the definition more closely, we recall why definitions are useful and important. In any field of study, definitions provide a foundation for the development of questions, theory, and design. In engineering, it is often said that defining the right problem is halfway to the solution. A good definition of mixing forces us to clarify the way we define the field. It will allow us to classify problems more easily, to describe problems more clearly, and to explain mixing problems unambiguously to non-experts. Clear definition naturally leads to fruitful mathematical modeling and more focussed and powerful experimental investigations because it identifies the key variables for a particular unit operation and their place in the problem definition. In short, a strong definition of mixing and segregation will provide clarity, focus and insight for teaching, research, and engineering applications.

4. Tests of the adequacy of the definition

The definition is tested against the three following criteria:

1. A good conceptual definition will clarify what is mixing, and what is not mixing. It will allow problems to be clearly described and classified, with specifications and explanations which are unambiguous.
2. A physically grounded definition identifies the key variables and their place in the problem definition, providing a structure for the design of experiments.
3. A strong theoretically based definition can be expressed as an equation.

The definition of segregation in industrial mixing is now tested conceptually through application to the body of industrial mixing problems, illustrated by application to three test cases, and placed in the context of existing mathematical models of mixing. At each stage, the definition is evaluated for its usefulness, rigor, and completeness using the criteria identified above.

4.1. Conceptual

Table 1 provides a classification of all of the classical industrial mixing problems in terms of the intensity, scale, and exposure dimensions. Each problem is first identified as either a rate problem, or a state of mixing problem. The dominant dimension of mixing is then highlighted, and all of the important dimensions are with the dominant dimension bolded. Multiphase mixing problems have been grouped together, rather than separating them into gas-liquid, liquid-liquid, solid-liquid, and solid-solid classes. The scale of segregation dimension has been subdivided into the familiar macro-meso- and micromixing subclasses. The physical meaning

Table 1 – Range of industrial mixing applications with dominant dimension(s) of segregation.

Mixing operation	Process specification		Intensity of segregation (CoV → 0)	Scale of segregation			Exposure
	State	Timescale		Macro-	Meso-	Micro-	
Blending of miscible liquids							
Turbulent		Blend time	X			X	X
Laminar		Blend time	X		X	X	X
Non-Newtonian	Caverns fill volume			X			
Multiphase mixing							
Size reduction	Specified size	Equilibrium time			X→	X	X
Just contacted	N_{js}, N_{jd}			X			
Homogeneous	N for uniform suspension		X		X		
Mass transfer		Dissolution time	X			X	X
Mixing sensitive reactions							
Single phase	Minimum by-product or maximum yield	Feed time	X		X→	X	X
Multiphase	Minimum by-product or maximum yield	Mass transfer limited	X		X→	X	X

Bold values indicate the dominant variable.

of these subclasses emerges from exploring the definition of mixing. Macromixing is the volume filling stage of mixing, which takes place at the scale of the vessel. Mesomixing is the scale reduction stage, which in turbulent mixing occurs over the inertial convective scales of turbulence and in laminar mixing occurs over the full range of length scales. Micromixing occurs at the smallest scales of mixing, where molecular diffusivity plays a controlling role in the rate of reduction of segregation. For the applications where the exposure plays a role, Table 2 sets out the process objective, the two populations which interact, and the exposure terms for strength of interaction, minimum segregation, and contact between populations.

Taking the major applications in turn, turbulent blend time is dominated by a reduction in CoV. The blend time is defined as the point where the CoV drops below a fixed threshold, usually 5% from the perfectly mixed state. The injected minor species is dispersed throughout the vessel through interaction with turbulent eddies. While the mean flow plays a role in the volume filling, or macromixing stage, it is the inertial convective eddies which reduce the scale of segregation below the required limit. This explains why the Corrsin scaling approach gives a better result for the blend time correlation than a fixed number of tank turnover times.

For laminar blending, the process specification often involves a minimum scale of segregation. Chaotic mixing analysis has repeatedly shown that the stretching distribution function for a particular mixer geometry determines the rate of reduction in scale of segregation (Zalc et al., 2002; Alvarez et al., 1998). Laminar blending is an interesting process specification because the scale of mixing is the process objective, but the exposure determines the length of pipe, or the mixing time, required to achieve that objective. In contrast, cavern formation in yield stress fluids is strictly a macro-scale mixing problem, where the mixer must be designed to eliminate dead volumes in the mixer. No time scales or concentration scales come into play, so the exposure dimension and the intensity of segregation are less interesting.

Multiphase mixing provides the largest challenges to a general definition of mixing, because the mixing objectives are so

varied. The first objective of multiphase mixing occurs at the largest scale of mixing. The just contacted objective (just suspended solids, just drawn down buoyant liquids and solids, the point of air entrainment from the head space, and the flooding point of a gassed impeller) identify a macro-scale segregation. The design criterion is the point at which the macro-scale segregation is disrupted, but this is far from the point of complete homogeneity of the second phase. The second objective is the complete dispersion. In this state of mixing, the CoV (measured on a meso-scale significantly larger than a single bubble, drop, or particle) drops to zero and the volume averaged concentration is uniform throughout the vessel. The third objective of multiphase mixing considers size reduction, particularly of liquid drops in emulsions and suspensions, but sometimes also of solids (e.g. milling machines), and possibly of gases in foams. In the drop break-up application, the exposure dimension appears in the breakage and coalescence kernels of population balances, giving the instantaneous rate of change of the drop size distribution as it moves toward the final equilibrium drop size. The strength of interaction between the drops and the turbulent eddies is associated with the turbulent energy dissipation rate, the opportunity for contact between drops and eddies is given by the number of drops in the sample volume, and the distance from equilibrium is associated with the distance from the equilibrium drop size, usually given by some kind of exponential decay function where the probability of a change in drop size gets smaller as the drops approach the final equilibrium size. The process objective is the scale of segregation, but the design specification is the strength of interaction (dissipation, or power per mass) required to achieve a fixed scale of segregation (drop size). The fourth objective identified for multiphase mixing is the mass transfer requirement. In this step, the dissolution time (for solids) or the rate of mass transfer (for liquids and gases) is the key mixing specification, and the exposure is the dominant dimension. When the solids are completely dissolved, the scale of segregation and the intensity of segregation both drop to zero. The rate of mass transfer and the dissolution time are determined by the mass transfer coefficient (the strength of interaction), the interfacial area (contact

Table 2 – Exposure definitions for mixing applications involving a timescale or rate.

Mixing operation	Process objective	Population 1	Population 2	Strength of interaction given by	Minimum segregation occurs at	Contact of populations is given by
Turbulent blending	CoV \rightarrow 0	Minor species	Eddies of major species	Turbulent diffusivity	CoV = 0	Time in high ϵ zone
Laminar blending	Scale \rightarrow 0	Minor species	Shear field of major species	Stretching distribution	Scale = 0	Surface area of lamellae
Liquid-liquid dispersion (size reduction)	Specified drop size	Drops of dispersed phase	Eddies of continuous phase	Interfacial tension and attractive forces	Equilibrium drop size	Time in high ϵ zone
Solids dissolution (mass transfer)	Large exposure \rightarrow MTF	Particles	Eddies of continuous phase	MTF coefficient, k_i	Saturation or complete dissolution	Interfacial surface area, a
Homogeneous reactions	Minimum by-product	Limiting reactant B (feed)	Excess reactant A (bulk)	Competing reaction rates	CoV = 0 or scale = 0 or complete consumption of B	Time in high ϵ zone or surface area of lamellae
Heterogeneous reactions (mass transfer limited)	Minimum by-product	Dispersed species B	Continuous species A	Mass transfer coefficient	Saturation or complete consumption of B	Interfacial surface area, a

between phases), and the concentration difference (distance from minimum segregation).

The final class of industrial mixing problems involves mixing sensitive reactions. This is the most varied and complex class of mixing problems, as these reactions typically encompass multiple mixing objectives, often simultaneously. The single phase homogeneous reaction problem is considered first. In this problem, the objective is to minimize by-product formation by ensuring that the reagents are well mixed at a rate that is much faster than the rate of undesired reaction. When meso-scales of segregation are present, more by-product is formed. Increasing exposure quickly and eliminating meso-scales ensures the success of the mixing operation. The equations for the exposure dimension for homogeneous reactions are discussed in more detail in the next section. Heterogeneous reactions are a second class of mixing sensitive reactions, with most of the more difficult problems limited by mass transfer or contact between the two phases. Once the reaction is mass transfer limited, the exposure dimension reduces to the same terms as discussed earlier under multiphase mass transfer, with the added possibility of having zero concentration in the continuous phase if the reaction goes to completion as soon as the dispersed species B is able to contact with the bulk species A.

Heat transfer in mixing vessels is not consistent with this definition of mixing problem, because no minor species is present. All of the core problems identified in Chapters 9–15 of the Handbook of Industrial Mixing (2004) are encompassed by the new definition, thus satisfying criterion 1. The definition provides a clearer focus for identifying the key design criteria, and also allows us to consider secondary design criteria and primary variables in the problem definition.

4.2. Physical and experimental

Three quantitative examples have been chosen to illustrate the dimensions of segregation. The first two focus on blending problems, the first for turbulent dispersion of dissolving particles in a stirred tank, where the intensity of segregation dominates, the second is the maximum striation thickness in a laminar micromixer, and the third is the break up and dissolution of dissolving drops in a stirred tank, where the exposure dimension is of greatest interest. These three examples illustrate the different approaches to analysis of mixing problems that can be taken when different dimensions of segregation dominate. They also illustrate how the three dimensions interact in practical applications.

4.2.1. Intensity of segregation

Fig. 5 shows the reduction in intensity of segregation for turbulent dissolution of particles in a tank (Hartmann et al., 2006). The last four images illustrate the reduction in scale of segregation (mesomixing), while the first two clearly illustrate the volume filling stage (macromixing). Time steps beyond 60 rotations of the impeller complete the micromixing and dissolution stage. The CoV analysis is reported more extensively in Kukukova et al. (2008a,b), who showed the sensitivity of CoV to the scale of measurement. Note that the reduction in CoV is very rapid for macromixing, but slower for mesomixing. Attempts to track the scale of segregation for this problem were less successful because turbulent dispersion rapidly smears out striation boundaries.

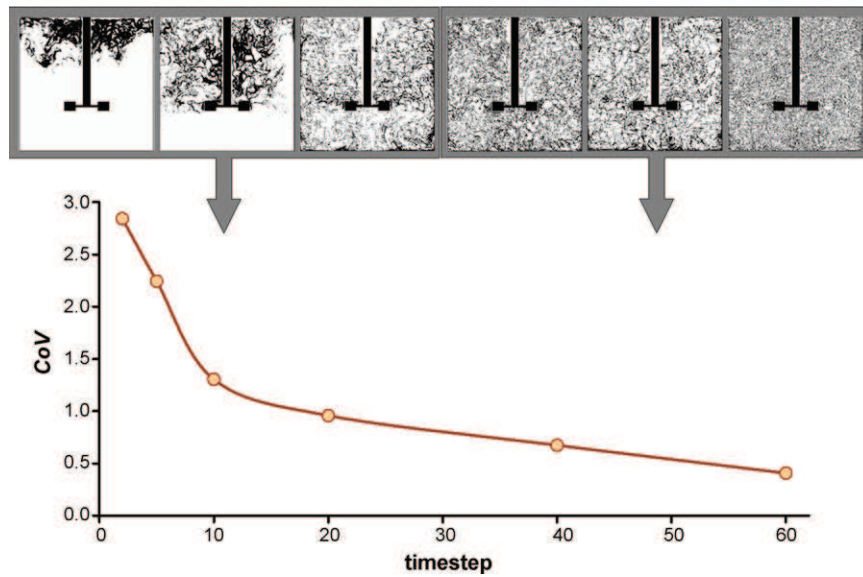


Fig. 5 – Turbulent dissolution in a stirred tank: two-stage process showing the volume filling, or macromixing stage, and the scale reduction, or mesomixing stage.

4.2.2. Scale of segregation

Fig. 6 illustrates the importance of the scale of segregation in laminar mixing. For this work (Aubin et al., 2005), the CoV was not able to accurately track the differences in performance for three different micromixers, but a transect of the striation thicknesses shows the smooth reduction in maximum striation thickness (s) and accurately characterizes the different mixers. In this case, the volume filling and scale reduction stages occur simultaneously, so the meso-scale dominates. Because the mixing is laminar, the striations remain coherent and accurate measurement of the CoV requires measurement resolution at the scale of individual striations. As the smallest scales of segregation shrink, this becomes impractical.

4.2.3. Exposure

Fig. 7a illustrates the interaction of the three dimensions of segregation in a mixing and dissolution problem. In this example, an additive is injected close to the impeller. The amount injected is equal to the solubility limit of the additive. On each pass through the impeller, the drop size is reduced, initially

very rapidly, but then much more slowly as the equilibrium drop size is approached. As the drops travel through the bulk of the tank, they dissolve and the bulk concentration in the tank increases. Fig. 7b shows snapshots of the volume of fluid as time progresses. The steps (1 → 2, 3 → 4, 5 → 6, and 7 → 8) show drop break-up at the impeller. The steps (2 → 3, 4 → 5, 6 → 7, 8 → 9 and 9 → 10) show dissolution in the bulk. The values for time, drop size, CoV, and exposure are given in the table below, and then plotted in Fig. 7c. The values for drop size and dissolution rate used for this illustrative example are based on the work by Ibemere and Kresta (2007).

In this example, the intensity, scale, and rate of change of segregation all drop to zero over time. The scale drops in a step-wise way, the CoV drops off smoothly, and the exposure shows a sawtooth behavior as the concentration difference drops, but the interfacial area increases. On the first pass through the impeller, the exposure more than doubles from its initial value and stays quite high over most of the dissolution time. As the drops approach their equilibrium size, the functions for both scale and exposure become smoother. This complicated

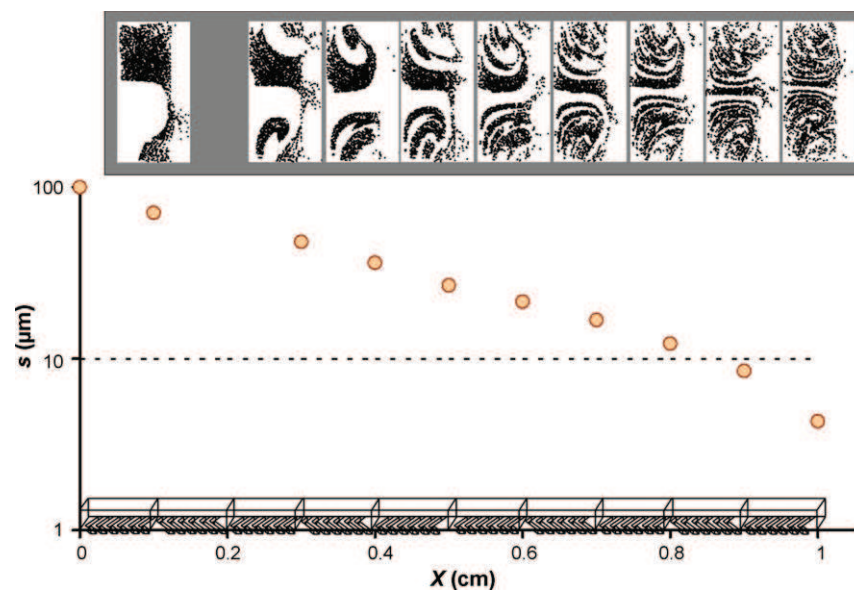
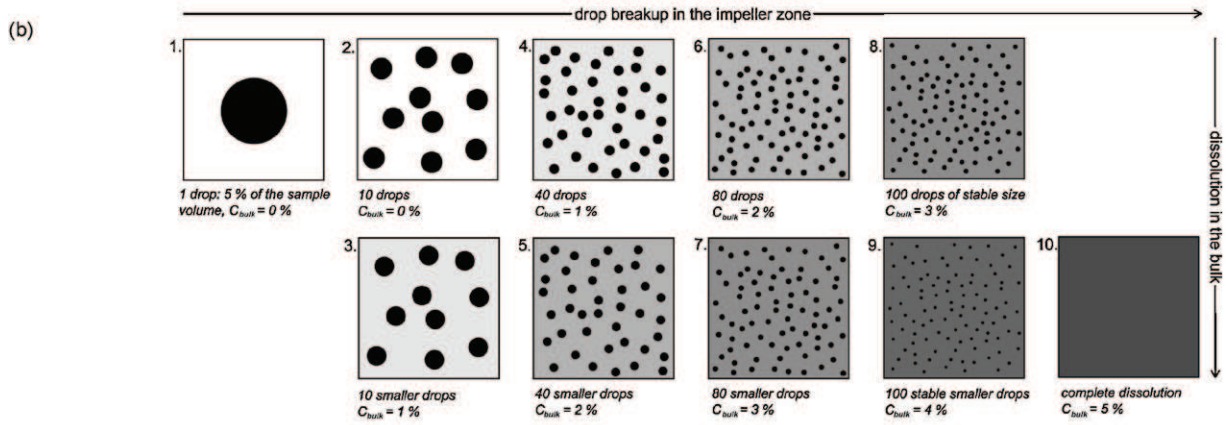
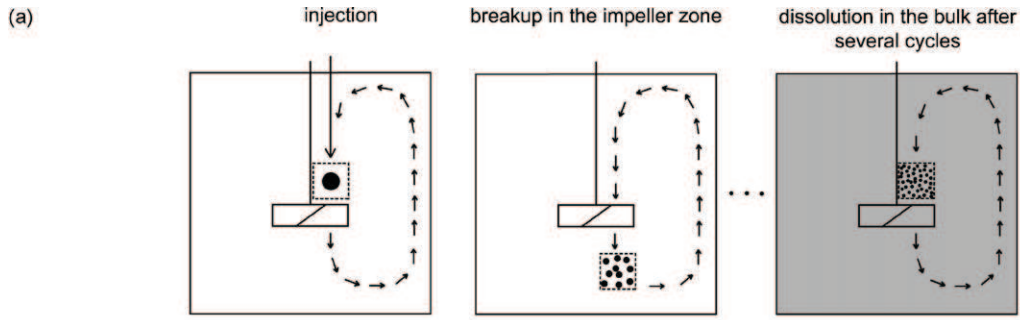


Fig. 6 – Maximum striation thickness (s) on a transect for a laminar micromixer.



time (s)	0	0.09 5.38	5.47 10.77	10.85 16.15	16.24 24.54	∞
drop size/scale of segregation (μm)	457	212 197	124 113	89 78	73 58	0
CoV (-)	4.36	4.36 0.68	0.68 0.24	0.24 0.09	0.09 0.02	0
exposure $\times 10^7$ (kg/s)	3.28	7.07 4.87	7.74 4.79	6.03 3.07	3.31 1.04	0

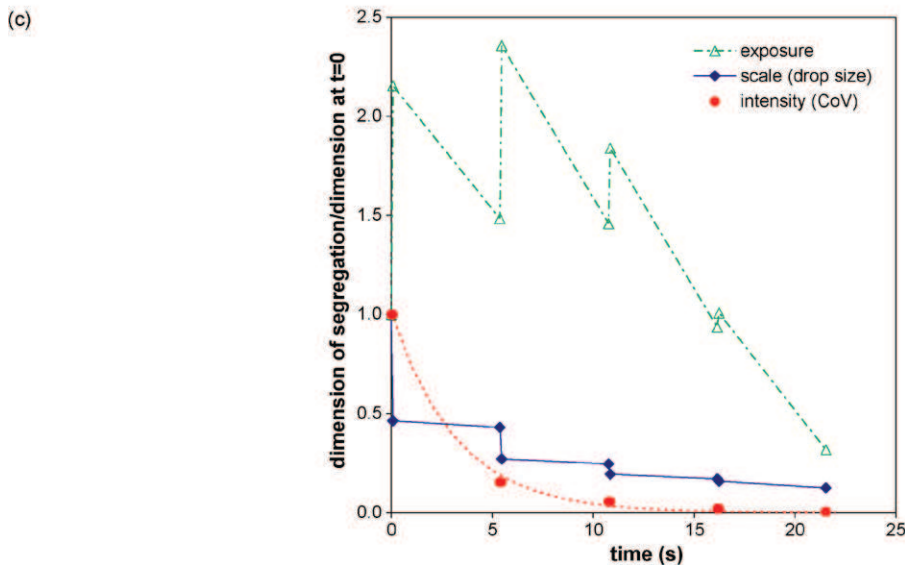


Fig. 7 – (a) Progress of an injected additive as drops break up and dissolve over time. Drop break-up is restricted to the impeller zone, and dissolution is restricted to the bulk. (b) Snapshots of the sample volume over the dissolution process. Dissolution steps are from the top row to the bottom row, and the corresponding values of time, drop size, CoV, and exposure are given in table. (c) Comparison of the scale, intensity, and rate of change of segregation as they change over time, all normalized with the initial values in step 1.

interaction between drop size reduction and concentration difference may explain the wide variation in the drop size exponent reported in liquid–liquid mass transfer correlations for stirred tanks (Ibemere, 2005).

4.3. Mathematical

Criterion 3 requires that the three dimensions of mixing have direct translations to physically meaningful equations which describe industrial mixing problems. The full range of equations that have been proposed to describe the dimensions of segregation across all mixing applications is enormous, with new attempts appearing in the literature on a regular basis. The reader is referred to individual review papers and texts presented earlier in the paper for the full mathematical details of specific applications. In this section, the objective is to illustrate how the core concepts of the dimensions of segregation consistently appear in the most successful model equations.

Taking the three dimensions in turn, the intensity of segregation is described by Eq. (2) for the CoV. Many other variations of a coefficient of variation have been proposed in the literature. All of the equations contain the same essential features, with the key differences being the variable used to normalize the variance, and whether the variance or the standard deviation is reported. Kukukova et al. (2008a,b) have discussed the impact of sampling on the value of CoV, and considered the impact of the classical MAUP (modifiable areal unit problem) on measurements of the variance in mixing applications. Both of these principles, developed for other applications of segregation, provided new insights for the measurement of mixing.

The scale of segregation is a rich problem with more work needed on mathematical descriptions of the scale of segregation, particularly now that experimental techniques and computational power are able to capture the full complexity of coupled multiscale mechanisms. Early researchers (e.g. Danckwerts, 1952 and Lacey and Mirza, 1976b) recognized methods that can only recently be fully exploited as experimental data moves to high resolution full field instruments. As these new instruments come into play, the field of spatial statistics provides a rich new selection of measures and methods that can extract useful information in a mathematically sound way (see the review under Clustering in Section 4 for references). Diffusion and turbulence lead to systems where the concentration varies continuously and the edges of striations are diffuse rather than sharp. In many of these problems, it will be the time scale related to the reduction in segregation, rather than the scale of segregation, which is the defining variable. Equations also exist to describe the diffusing case (Danckwerts, 1952; Cressie, 1993). The timescale, or exposure dimension, is discussed below.

The reader may also legitimately ask what is to be done with the full spectrum of scales of segregation often observed in realistic problems. First, the physics often offers an elegant simplification, returning self-similarity in drop size distributions (Mishra et al., 1998), striation thickness distributions and stretching distributions (Alvarez et al., 1998; Hobbs and Muzzio, 1998), aggregate and crystal size distributions (Marchisio et al., 2003a,b) and many others. This means that given an initial distribution and the correct scaling parameters over time (e.g. decay of the mean drop size), the distributions all collapse onto a single line. This enormously simplifies the modelling and computational demands, since the complete distribution can be tracked using a small number of vari-

ables (e.g. Marchisio et al., 2003a,b). The scale of segregation is increasingly used as a specification for consumer products, cosmetics, crystals, polymer composites, and some pharmaceuticals, so the industrial need for solutions will undoubtedly drive further research in this area.

Finally, the rate of change of segregation, or the exposure dimension, appears in many existing models of mixing processes. Typical mixing variables are related to the exposure dimension in Table 2. Taking three illustrative examples from mass transfer, population balances, and the reaction-diffusion equation, the model equations are shown to follow the form of the exposure definition:

1. *Mass transfer*: in this case, the exposure is related to the flow of component A in moles/s through the standard diffusion equation:

$$\text{Exposure} = \int_A D_{AB} \nabla c_A \cdot n \, dA$$

The diffusivity D_{AB} is the strength of interaction, or the willingness of the two populations to interact; the minimum segregation is complete homogeneity and the concentration gradient ∇c_A gives the distance from minimum segregation; and the interfacial area, A provides the opportunity for molecules to interact. Note that A is not always the surface of a sharp striation, but can also be the surface of a computational cell or control volume of interest where the concentration varies continuously throughout the system.

2. *Population balances*: the literature on population balance modeling is extensive, and has applications over a wide range of processes. The general form of the population balance for a flow system is (Paul et al., 2004):

$$\frac{\partial n_d}{\partial t} + \nabla \cdot (\bar{U} n_d) - \dot{B}_d + \dot{D}_d = 0$$

where n_d is the number of drops or particles being balanced, so the first two terms are the accumulation and convection terms, and \dot{B}_d and \dot{D}_d are the birth and death rates, respectively. The exposure dimension is found in the birth and death terms of the population balance. To illustrate this, three examples of the birth or death terms in drop breakup, aggregation kinetics, and crystallization are examined in more detail.

- a) *Drop breakup* (Ibemere and Kresta, 2007):

$$\begin{aligned} \text{Death term} = & - \sum_{j=1}^{i-1} \frac{1}{2} \frac{-2.4738(1-\phi)}{b^{8/11}} \left(\frac{\varepsilon}{L_j^2} \right)^{1/3} \\ & \times \left\{ \begin{aligned} & [\Gamma(8/11, t_m) - \Gamma(8/11, b)] + \\ & + 2b^{3/11} [\Gamma(5/11, t_m) - \Gamma(8/11, b)] + \\ & + b^{6/11} [\Gamma(2/11, t_m) - \Gamma(2/11, b)] \end{aligned} \right\} \Delta L_j \\ & \times N(L_i, t) \end{aligned}$$

The death term of this drop breakup model represents the death by drop breakage. By close examination of the expression, all three components of exposure can be observed. The term in front of the curly brackets combines the physical properties of drops, the dispersion characteristics and the hydrodynamic conditions to find the strength of interaction; the term inside the brackets and including ΔL_j represents the distance from the

equilibrium drop size with the gamma function showing how the drops are increasingly likely to break when they are much larger than the equilibrium drop size; and the number of drops of size i , present at time t ($N(L_i, t)$) determines the opportunity for drops to interact with the flow and break up.

b) Aggregation kinetics (Lattuada et al., 2004):

$$\text{Birth term} = \frac{1}{2} \sum_{j=1}^{i-1} \frac{8kT}{3\eta W} \frac{(i^{1/D_f} + j^{1/D_f})(i^{-1/D_f} + j^{-1/D_f})}{4} N_{i-j}(t)N_j(t)$$

In this example of aggregation kinetics, the birth by aggregation also has a form of exposure. The first fraction term again represents the strength of interaction by including the fluid physical properties, temperature and hydrodynamic and Van der Waals interactions in the system. The second fraction term contains the fractal dimension D_f , together with the sizes of interacting clusters (i and j are the numbers of particles in the cluster) which defines the distance from aggregate equilibrium size. The last term describes the number of clusters of particular sizes in the system ($N_{i-j}(t)N_j(t)$) and quantifies the opportunity clusters have to interact with each other.

c) Crystallization (Sato et al., 2008):

$$\text{Death term} = k_{\text{imp}} \frac{\rho_s n_r^3 D_r^5}{V} L_1^2 L_2 \times \frac{1}{2} \left(\tanh \left(k \left(\frac{L_2}{L_1} - AR_{\text{tr}} \right) \right) + 1 \right) \times n(L_1, L_2)$$

This death term represents the death by breakage of crystals with width L_1 and length L_2 . All exposure components can again be found in this expression. The strength of crystal interaction is given by the hydrodynamic conditions in the system described by the impeller diameter and rotational frequency, properties of the mixture like crystal dimensions, crystallizer volume V and crystal density, all included in the first term before the multiplier. The middle term describes the distance from equilibrium crystal size: AR_{tr} is the threshold aspect ratio and crystals are only prone to breakage when their aspect ratio exceeds this value; the tanh function again adds the increasing probability for breakage as the crystal size moves further away from the equilibrium point. The last term, the number of crystals, again quantifies their opportunity to meet and interact.

3. Reaction kinetics: When studying the mixing time scale for reactions, two types of exposure can be identified. When all reactants are present in sufficient quantities and the only concern is to get them into molecular contact in order for the reaction to proceed, the reaction is mass-transfer limited and the exposure expression that dominates this problem is the mass transfer exposure defined in 1. If, on the other hand, reactant A is limiting, e.g. for a reaction:



the time scale of the process is given by the reaction rate term which also has a form of exposure:

$$\text{Reaction rate} = \int_V k \cdot c_A \cdot c_B dV$$

Here, the strength of interaction is represented by the rate constant k , the concentration of reactant A, c_A , is the distance from the equilibrium state with the reaction no longer proceeding

after the reactant A has been depleted, and the concentration of reactant B, c_B , is the opportunity for reactants to interact if A is present. The field of mixing sensitive reactions is a complex one. No consideration is given here to the question of continuous systems with the added complication of backmixing in time. From a mathematical perspective, this is treated as a fourth dimension in the data, but the practical application of this fourth dimension can be very challenging.

The reaction rate equation, break up and coalescence kernels in population balance equations for crystals, aggregates, and drops, Corrsin's model for the dispersion of scalar in a turbulent mixing field, and as illustrated in this paper, the mass transfer equation, all follow the form suggested by the definition of exposure. Additional examples are available in a number of detailed models where direct computation of the interaction between the scale and intensity of segregation with reaction and/or mass transfer have been carried out through high resolution computations (see Fox, 2003; Kresta et al., 2004; Alvarez et al., 1998, and many others). More work is warranted here, particularly using experimental data where the key scales of segregation can be measured. The concept of exposure provides a clearer path to model development and validation, and may help to identify the problems where detailed modeling of many scales with coupled mechanisms will prove most productive.

5. Conclusions

A definition of industrial mixing is proposed based on three dimensions of segregation: intensity of segregation (concentration scale), scale of segregation (length scale), and exposure (rate of change of segregation). A series of checkerboard patterns are used to illustrate the three dimensions. These variables are well established in the fields of spatial statistics, population ecology, and population segregation both conceptually and mathematically, and provide an expanded theoretical and experimental toolkit for the analysis of mixing problems.

The proposed definition satisfies three criteria for a good definition: conceptual, physical and mathematical; and provides a direct path from the definition to equations and measurements. Three examples are used to illustrate how the definition can improve our understanding of mixing problems. The first two examples clarify the distinction between macro- and micromixing, and highlight the utility of considering the scale of segregation instead of intensity of segregation for laminar mixing problems. The exposure dimension is introduced through an example of drop break up and dissolution, showing both the distinct behavior of exposure, and its dependence on the scale and intensity of segregation. The exposure dimension is essential for mixing problems that are dominated by a mixing time scale, such as mixing sensitive reactions and mass transfer.

Given a strong definition, the physical phenomena and process objectives can be framed in ways that match both the complexity of the problem and our intuitive understanding. This provides clarity, focus, and insight for teaching, research, and engineering applications. While this definition may subsequently prove to be incomplete or require clarification, it is our hope that it is general enough to encompass the full range and complexity of industrial mixing problems, but specific enough to be clear.

Acknowledgements

The authors would like to thank CNRS and NSERC for financial support.

Image credits for Fig. 1 are as follows:

a) Paul et al., 2004, cover image courtesy of Chiharu Fukushima and Jerry Westerweel, Laboratory for Aero and Hydrodynamics, Delft University of Technology, The Netherlands.

b and c) Sultzer ChemTech: <http://www.sulzerchemtech.com>, July 15, 2008.

d) DuPont Corian Products http://www2.dupont.com/Surfaces/en_US/products/corion, Sept 29, 2008.

e) Paul et al., 2004, Fig. 4.24b, BHR Group.

f) Bhattacharya et al., 2007, Fig. 4c.

References

- Alvarez, M.M., Muzzio, F.J., Cerbelli, S., Adrover, A. and Giona, M., 1998, Self-similar spatiotemporal structure of intermaterial boundaries in chaotic flows. *Phys Rev Lett*, 81: 3395.
- Anson, J.P. and Gruzleski, J.E., 1999, The quantitative discrimination between shrinkage and gas microporosity in cast aluminum alloys using spatial data analysis. *Mater Char*, 43: 319–335.
- Aubin, J., Fletcher, D.F. and Xuereb, C., 2005, Design of micromixers using CFD modelling. *Chem Eng Sci*, 60: 2503–2516.
- Baldyga, J. and Bourne, J.R., (1999). *Turbulent Mixing and Chemical Reactions*. (Wiley).
- Bhattacharya, S., Hebert, D. and Kresta, S.M., 2007, Air entrainment in baffled stirred tanks. *Chem Eng Res Des*, 85: 654–664.
- Corrsin, S., 1957, Simple theory of an idealized turbulent mixer. *AIChE J*, 3: 329–330.
- Corrsin, S., 1964, The isotropic turbulent mixer. 2. Arbitrary Schmidt number. *AIChE J*, 10: 870–877.
- Cressie, N., (1993). *Statistics for Spatial Data*. (Wiley, New York).
- Danckwerts, P.V., 1952, The definition and measurement of some characteristics of mixtures. *Appl Sci Res A*, 3: 279–296.
- Danckwerts, P.V., 1958, The effect of incomplete mixing on homogeneous reactions. *Chem Eng Sci*, 8: 93–102.
- Diggle, P.J., (2003). *Statistical Analysis of Spatial Point Patterns*. (Hodder Arnold, London).
- Fox, R.O., (2003). *Computational Models for Turbulent Reacting Flows*. (Cambridge Univ Press, New York).
- Gates, L.E., et al., 1975, Select the optimum turbine agitator. *Chem Eng*, 8(December): 110–114.
- Harnby, N., 1967, A comparison of the performance of industrial solids mixers using segregating materials. *Powder Technol*, 1: 94–102.
- Hartmann, H., et al., 2006, Numerical simulation of a dissolution process in a stirred tank reactor. *Chem Eng Sci*, 61: 3025–3032.
- Hersey, J.A., 1970, Sampling and assessment of powder mixtures for cosmetics and pharmaceuticals. *J Soc Cosmet Chem*, 21: 259–269.
- Hobbs, D.M. and Muzzio, F.J., 1998, Reynolds number effects on laminar mixing in the Kenics static mixer. *Chem Eng J*, 70: 93–104.
- Ibemere, S., 2005, Dissolution Kinetics of Liquid–Liquid Dispersions using Local Rates of Turbulent Dissipation, MSc Thesis, University of Alberta, Canada.
- Ibemere, S. and Kresta, S.M., 2007, Modeling the mixing and dissolution kinetics of partially miscible liquids. *Chem Eng Res Des*, 85: 710–720.
- Keeling, M.J., Mezic, I., Hendry, R.J., McGlade, J. and Rand, D.A., 1997, Characteristic length scales of spatial models in ecology via fluctuation analysis. *Phil Trans R Soc Lond B*, 352: 1589–1601.
- Kresta, J.V., MacGregor, J.F. and Marlin, T.E., 1991, Multivariate statistical monitoring of process operating performance. *Can J Chem Eng*, 69: 35–47.
- Kresta, S.M., Anthieren, G.L. and Parsiegla, K., 2004, Mixing effects in silver halide precipitation: linking theory with practice using a multi-mechanism model. *Chem Eng Res Des*, 82: 1117–1126.
- Kukukova, A., Shah, S.I.A., Aubin, J. and Kresta, S.M., 2008, Quantifying mixing: the exposure dimension, In *6th International Symposium on Mixing in Industrial Processes* Niagara Falls, August 17–21,
- Kukukova, A., Noel, B., Kresta, S. and Aubin, J., 2008, Impact of sampling method and scale on the measurement of mixing and the coefficient of variance. *AIChE J*, 54: 3068–3083.
- Lacey, P.M.C., 1954, Developments in the theory of particle mixing I. *J Appl Chem*, 4: 257–268.
- Lacey, P.M.C. and Mirza, F.S.M.A., 1976, A study of the structure of imperfect mixtures of particles. Part I. Experimental technique. *Powder Technol*, 14: 17–24.
- Lacey, P.M.C. and Mirza, F.S.M.A., 1976, A study of the structure of imperfect mixtures of particles. Part II. Correlational analysis. *Powder Technol*, 14: 25–33.
- Lattuada, M., et al., 2004, Modelling of aggregation kinetics of colloidal systems and its validation by light scattering measurements. *Chem Eng Sci*, 59: 1783–1798.
- Lee, J. and Brodkey, R.S., 1964, Turbulent motion and mixing in a pipe. *AIChE J*, 10: 187–193.
- Marchisio, D.L., Vigil, R.D. and Fox, R.O., 2003, Quadrature method of moments for aggregation-breakage processes. *J Coll Int Sci*, 258: 322–334.
- Marchisio, D.L., Piktorna, J.T., Fox, R.O., et al., 2003, Quadrature method of moments for population-balance equations. *AIChE J*, 49: 1266–1276.
- Massey, D.S. and Denton, N.A., 1988, The dimensions of residential segregation. *Soc Forces*, 67: 281–315.
- Mattfeldt, T., 2005, Explorative statistical analysis of planar point processes in microscopy. *J Microsc*, 22: 131–139.
- McGarvey, R., Byth, K., Dixon, C.D., Day, R.W. and Feenstra, J.E., 2005, Field trials and simulations of point-nearest-neighbor distance methods for estimating abalone density. *J Shellfish Res*, 24: 393–399.
- McKelvey, K.N., et al., 1975, Turbulent motion, mixing and kinetics in a chemical reactor configuration. *AIChE J*, 21: 1165–1176.
- Mishra, V., Kresta, S.M. and Masliyah, J.H., 1998, Self-preservation of the drop size distribution function, and variation in the stability ratio for rapid coalescence of a polydisperse emulsion in a simple shear field. *J Colloid Interf Sci*, 197: 57–67.
- Mohr, W.D., Saxton, R.E. and Jepsen, C.H., 1957, Mixing in laminar flow systems. *Ind Eng Chem*, 49: 1855–1856.
- Mugglestone, M.A. and Renshaw, E., 2001, Spectral tests of randomness for spatial point patterns. *Environ Ecol Stat*, 8: 237–251.
- Ottino, J.M., (1989). *The Kinematics of Mixing: Stretching, Chaos, and Transport*. (Cambridge University Press, New York).
- Paul, E.L., Atiemo-Obeng, V.A., & Kresta, S.M. (eds) 2004, *Handbook of Industrial Mixing: Science and Practice*.
- Sato, K., et al., 2008, Two-dimensional population balance model with breakage of high aspect ratio crystals for batch crystallization. *Chem Eng Sci*, 63: 3271–3278.
- Szalai, E., Alvarez, M., Muzzio, F.J., 2004, Laminar Mixing: A Dynamical Systems Perspective, Chapter 3 in Paul et al., 2004.
- Toor, H.L., 1969, Turbulent mixing of two species with and without chemical reaction. *I&E C Res*, 8: 655–659.
- Wong, D.W., 2002, Modeling local segregation: a spatial interaction approach. *Geogr Environ Model*, 6: 81–97.
- Wong, D.W., 2005, Formulating a general spatial segregation measure. *The Prof Geogr*, 57: 285–294.
- Zalc, J.M., Szalai, E.S., Muzzio, F.J. and Jaffer, S., 2002, Characterization of flow and mixing in an SMX static mixer. *AIChE J*, 48: 427–436.
- Zweitering, T.H., 1959, The degree of mixing in continuous flow systems. *Chem Eng Sci*, 11: 1–12.