Steady-State Segregation in Diffusion-Limited Reactions

Katja Lindenberg,(1,2) Bruce J. West,(2,3) and Raoul Kopelman(1,2,4)
(1)*Department of Chemistry, B-040, University of California at San Diego, La Jolla, California 92093*
(2)*Institute for Nonlinear Science, R-002, University of California at San Diego, La Jolla, California 92093*
(3)*Division of Applied Nonlinear Problems, La Jolla, California 92038*
(4)*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109*(a)

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The conditions for a macroscopic segregation of A and B in a steady-state $A+B\rightarrow 0$ reaction are studied via a finite continuum model. Segregation occurs in $d=1$, is marginal for $d=2$ (critical dimension), and is absent for $d\geq 3$. Results for infinite systems are also mentioned.

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The nonclassical kinetics of diffusion-limited reactions are of much current interest.[1-9] The reaction $A+A\rightarrow$ products is of relevance to exciton annihilation in molecular crystals,[7] polymers,[10] and photosynthetic antennas.[11] Its nonclassical behavior for few-dimensional ($d\leq 2$) and fractal systems has been widely documented.[1-10] The reaction $A+B\rightarrow$ products is of interest in chemical kinetics and in solid-state reactions: electron-hole, soliton-antisoliton, and defect-antidefect recombinations. It is also of potential interest to charge recombination in clouds and to matter-antimatter annihilation in the universe.[8]

Zeldovich and co-workers[1] have demonstrated how the density fluctuations during an $A+B$ reaction lead to long-time anomalous kinetics and to reactant segregation. This effect has been demonstrated in simulations by Toussaint and Wilczek[3] and others.[4,6] The upper critical dimension for this behavior is $d=4$.[1,3,5] We emphasize that the above discussed reactions are of the "big-bang" type (also called "batch," "transient," or "pulsed"), that is, particle creation occurs only at the origin of time. The initial, relatively small, density fluctuations translate into relatively large long-time density fluctuations, even though they are quite small in absolute terms.

Another fluctuation-segregation effect has been demonstrated very recently for *steady-state* $A+B$ reactions occurring over a wide density range.[8] Here the simulations start from zero density, but a steady rate of particle creation leads to segregated, high-density, steady states. Timewise, there is *no* fluctuation in the global densities ($\rho_A^G-\rho_B^G=0$). However, spacewise, the steady-state realizations are drastically segregated, i.e., there are large regions where $\rho_A-\rho_B\approx\rho_A$ and others where $\rho_A-\rho_B\approx -\rho_B$. It is noteworthy that the upper critical dimension for this steady-state effect appears to be[8,12] $d=2$ (compared with $d=4$ for the Zeldovich effect). As the Zeldovich approach sheds no light on this new effect it has attracted much recent interest[9,12,13] and is the subject of this paper. Our results differ from those obtained recently with different methods.[9]

Our reactant segregation measure[14] involves both the density-difference ($\rho_A-\rho_B$) correlations and the density-sum ($\rho_A+\rho_B$) correlations. A previous measure,[9] employing only the difference terms, is not meaningful: For there to be segregation there must be a large *relative* excess of one species over the other, e.g., $\rho_A\gg\rho_B$ (or $\rho_B\gg\rho_A$). This in turn implies that $|\rho_A-\rho_B|\approx\rho_A+\rho_B$. However, large-amplitude long-range correlations in $\rho_A-\rho_B$ are prerequisite for macroscopic segregation. We show that segregation in finite systems does occur for $d=1$, occurs marginally for $d=2$, and does not occur at all for $d=3$.

Let $\rho_A(\mathbf{r},t)$ and $\rho_B(\mathbf{r},t)$ respectively denote the local concentrations of species A and B at time t. A and B react and annihilate one another, $A+B\rightarrow 0$. Both species can diffuse with coefficient σ, and are created at random locations and times. The equations that might describe the rate of change of the two concentrations then are of the form

$$\dot{\rho}_i(\mathbf{r},t)=\sigma\nabla^2\rho_i(\mathbf{r},t)-F(\rho_A,\rho_B)+\eta_i(\mathbf{r},t),\qquad i=A,B, \tag{1}$$

where $\eta_A(\mathbf{r},t)$ and $\eta_B(\mathbf{r},t)$ are the random source terms. $F(\rho_A,\rho_B)$ is a function symmetric in its arguments, i.e., $F(\rho_A,\rho_B)=F(\rho_B,\rho_A)$, that describes the local reaction. A and B molecules are deposited at spatially random locations that change every τ units of time, but the total number of A and B molecules is kept equal at all times.

It is convenient to deal with the sum and difference variables $\gamma(\mathbf{r},t)=\frac{1}{2}[\rho_A(\mathbf{r},t)-\rho_B(\mathbf{r},t)]$ and $\rho(\mathbf{r},t)=\frac{1}{2}[\rho_A(\mathbf{r},t)+\rho_B(\mathbf{r},t)]$ with corresponding definitions for $\eta_\gamma(\mathbf{r},t)$ and $\eta_\rho(\mathbf{r},t)$. The difference variable then obeys the linear equation (unaffected by the reaction)

$$\dot{\gamma}(\mathbf{r},t)=\sigma\nabla^2\gamma(\mathbf{r},t)+\eta_\gamma(\mathbf{r},t), \tag{2}$$

while the sum variable evolves according to the nonlinear equation

$$\dot{\rho}(\mathbf{r},t)=\sigma\nabla^2\rho(\mathbf{r},t)-F(\rho+\gamma,\rho-\gamma)+\eta_\rho(\mathbf{r},t). \tag{3}$$

Note that

$$\int \gamma(\mathbf{r},t)d^3r=\int \eta_\gamma(\mathbf{r},t)d^3r=0 \tag{4}$$

at all times.

Chemical segregation might arise as a consequence of the detailed interplay of the three counteracting mechanisms implicit in (1). Diffusion tends to mix the species. Reaction annihilates the thoroughly mixed regions, thus favoring spatially separated regions. The sources tend to create spatially nonuniform patches on a scale determined by the density of sources (this latter scale is, in general, much smaller than the macroscopic scales of interest for segregation). For sufficiently many dimensions, one expects diffusion to dominate and the long-time spatial distribution of species to be uniform. The interesting question is whether there exists a critical dimension below which macroscopic segregation occurs.

A measure of the spatial variations in the difference variable is the correlation function $C_\gamma(\mathbf{r}-\mathbf{r}',t)\equiv l^{2d}\langle\gamma(\mathbf{r},t)\gamma(\mathbf{r}',t)\rangle$, where l^d is the volume of a unit cell in the corresponding d-dimensional discrete problem[15] and the brackets denote an average over an ensemble of the possible realizations of the random source terms η_A and η_B. To evaluate the correlation function C_γ it is necessary to specify the first and second moments of the source term η_γ. We introduce a number of parameters as follows. One might envision A molecules (or B molecules) being deposited from a "source" into a given unit cell for a time interval of average duration τ after which that source is "turned off." During the time τ, n molecules on the average are deposited in a unit cell. At any instant of time A molecules are being deposited into an average of N unit cells. The total rate of deposition of A's in the entire system is Nn/τ and the rate of deposition of A's (or of B's) per unit cell is $R\equiv Nnl^d/L^d\tau$, where L^d is the total system volume. For the first moment (4) clearly implies $\langle\eta_\gamma(\mathbf{r},t)\rangle=0$. For the second moment one obtains

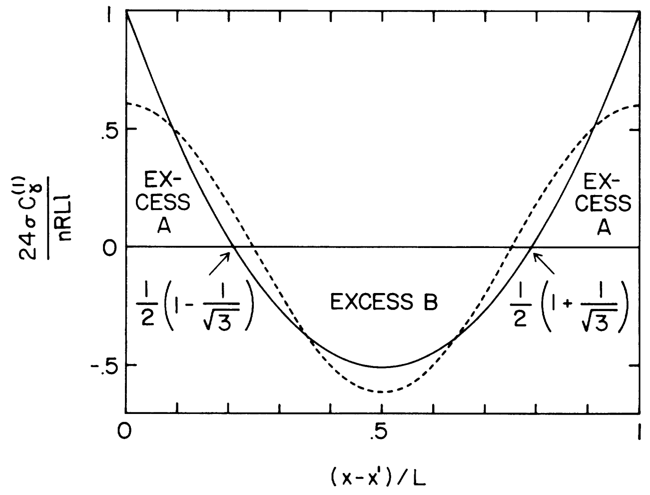

FIG. 1. Steady-state difference-variable correlation function for $d=1$. Solid curve, exact results (Ref. 8); dashed curve, first term approximation. Note that any conclusions about segregation require additional information about the sum variable.

$$\langle\eta_\gamma(\mathbf{r},t)\eta_\gamma(\mathbf{r}',t')\rangle=(Rn/l^d)\delta(t-t')[\delta(\mathbf{r}-\mathbf{r}')-L^{-d}]. \tag{5}$$

The L^{-d} factor subtracted from the spatial δ function in (5) is a direct consequence of the constraint (4).

Use of standard Fourier-transform techniques for linear equations leads to the result

$$C_\gamma(\mathbf{r}-\mathbf{r}',t)=\frac{Rnl^d}{2\sigma L^d}\sum_{\mathbf{k}\neq 0}e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\frac{(1-e^{-2\sigma k^2 t})}{k^2}, \tag{6}$$

where the initial densities of A and B have been set to zero (we assume periodic boundary conditions; the results we obtain are insensitive to this choice). The $\mathbf{k}$ values in the sum (6) are given by $\mathbf{k}=2\pi\mathbf{m}/L$, where $\mathbf{m}$ is a vector of nonnegative integers ($\mathbf{m}\neq 0$). Note that the exclusion of $\mathbf{k}=0$ is a consequence of the conservation condition (4). Such a term would have contributed a spatially homogeneous configuration whose intensity grows linearly with time.

We are interested in the behavior of the correlation function at long times. From (6) we see that a steady state is achieved as $t\to\infty$ only because the $\mathbf{k}=0$ term is absent. In one dimension the $t\to\infty$ sum can be evaluated exactly with the result (see Fig. 1)

$$C_\gamma^{(1)}(x-x')=(RnLl/24\sigma)[1-(6/L)(x-x')+6(x-x')^2/L^2],\quad 0\le(x-x')\le L, \tag{7}$$

where the superscript denotes $d=1$. The species observed at x' is dominant over a length $(1-1/\sqrt{3})L$ while the other species spreads over a length $L/\sqrt{3}$. This long-range correlation indicates an excess of one species over the other over a macroscopic distance. Whether this excess is macroscopically significant depends on the relative densities, i.e., segregation is observed if either $\rho_A\gg\rho_B$ or $\rho_B\gg\rho_A$. Note that the maximum value of the correlation function is proportional to L, the size of the system. Figure 1 also shows the lowest term in the sum, i.e.,

$$C_{\gamma,1}^{(1)}=(RnL/4\pi^2\sigma)\cos[2\pi(x-x')/L].$$

In dimensions higher than $d=1$ the sum (6) cannot be done exactly. The $d=1$ case suggests that the contribution to the sum from the smallest $|\mathbf{k}|$ values might be an adequate representation of the essential features of the sum when $t \to \infty$. In two dimensions with $\mathbf{r}=(x_1,x_2)$ we distinguish between those terms that have one component of $\mathbf{k}$ vanish and those for which neither k_1 nor k_2 vanishes. The former contribute to striped configurations and the latter to configurations that vary in both directions. We retain only the lowest contribution of each of these qualitatively distinct types of terms:

$$C_\gamma^{(2)}(\mathbf{r}-\mathbf{r}') \approx \frac{Rnl^2}{4\pi^2\sigma}\left[\sum_{i=1}^{2}\cos\left[\frac{2\pi}{L}(x_i-x_i')\right]+\tfrac{1}{2}\cos\left[\frac{2\pi}{L}(x_1-x_1'+x_2-x_2')\right]\right]. \tag{8}$$

In three dimensions we similarly distinguish terms with two k components equal to zero, one k component equal to zero, and all nonvanishing components. Again retaining only the lowest-order contribution to each of these types of terms, we obtain

$$C_\gamma^{(3)}(\mathbf{r}-\mathbf{r}') \approx \frac{Rnl^2}{4\pi^2\sigma L}\left[\sum_{i=1}^{3}\cos\left[\frac{2\pi}{L}(x_i-x_i')\right]+\tfrac{1}{2}\sum_{\substack{i,j=1\\ i<j}}^{3}\cos\left[\frac{2\pi}{L}(x_i-x_i'+x_j-x_j')\right]\right.$$
$$\left.+\tfrac{1}{3}\cos\left[\frac{2\pi}{L}(x_1-x_1'+x_2-x_2'+x_3-x_3')\right]\right]. \tag{9}$$

As in one dimension, the spatial patterns implicit in (8) and (9) are also persistent over macroscopic length scales. The big difference between the one- and higher-dimensional correlation functions lie in their amplitude: Whereas $C_\gamma^{(1)}(0) \propto L$, $C_\gamma^{(2)}(0)$ is independent of the volume of the system and $C_\gamma^{(3)}(0)$ decreases with increasing system volume as $V^{-1/3}=L^{-1}$. *Note that the above results are not in themselves sufficient to determine whether or not observable segregation will occur.* However, the system volume dependence of the amplitudes does suggest a greater likelihood of segregation for decreasing dimensionality d. Also note that the sum variable $\rho(\mathbf{r},t)$ must satisfy the obvious constraint $\langle\rho^2(\mathbf{r},t)\rangle \geq \langle\gamma^2(\mathbf{r},t)\rangle$ in all dimensions; in one dimension $\langle\rho^2(\mathbf{r},t)\rangle$ must therefore grow at least linearly with system volume, contrary to classical chemical kinetics results.

One calculationally tractable measure of the degree of macroscopic segregation is the ratio $S(t) \equiv \langle\gamma^2(\mathbf{r},t)\rangle / \langle\rho^2(\mathbf{r},t)\rangle$. The ratio $S(t) \to 1$ when only one chemical species is present at any $\mathbf{r}$, and $S(t) \to 0$ when the relative excess of one species over the other is small. To find the steady-state segregation index

$$S \equiv \lim_{t\to\infty} S(t)$$

we must determine the L dependence of $\langle\rho^2(\mathbf{r},t)\rangle$. To do so we must first specify a form for the reaction function F in Eq. (1). We choose the form $F(\rho_A,\rho_B)=K\rho_A^X\rho_B^X$, where K is a rate constant. The order X is positive and is usually chosen to be unity. We require that $X>\frac{1}{2}$ but need not specify its value any further. Equation (3) then becomes

$$\dot\rho(\mathbf{r},t)=\sigma\nabla^2\rho(\mathbf{r},t)-K[\rho^2(\mathbf{r},t)-\gamma^2(\mathbf{r},t)]^X+\eta_\rho(\mathbf{r},t). \tag{10}$$

In the steady state we thus set $\langle\dot\rho(\mathbf{r},t)\rangle=0$ and use $\langle\eta_\rho(\mathbf{r},t)\rangle=R/l^d$ to write

$$0=\sigma\nabla^2\langle\rho(\mathbf{r},t)\rangle-K\langle[\rho^2(\mathbf{r},t)-\gamma^2(\mathbf{r},t)]^X\rangle+R/l^d. \tag{11}$$

We replace $\langle[\rho^2(\mathbf{r},t)-\gamma^2(\mathbf{r},t)]^X\rangle$ with $\langle\rho^2(\mathbf{r},t)-\gamma^2(\mathbf{r},t)\rangle^X$: Although unknown errors are introduced by this replacement, it is unlikely that the system-size dependence of $\langle\rho^2(\mathbf{r},t)\rangle$ will be affected.

Consider then the L dependence of the terms in (11). The source term is $O(L^0)$ and $\langle\gamma^2(\mathbf{r},t)\rangle$ is $O(L^{2-d})$. Suppose that $\langle\rho(\mathbf{r},t)\rangle=O(L^\alpha)$ with α to be determined, and that correspondingly $\langle\rho^2\rangle=O(L^{2\alpha})$. The diffusion term $\nabla^2\langle\rho\rangle$ is then $O(L^\beta)$ with $\beta\leq\alpha$. Purely schematically the leading L dependences in (11) then are expressed by

$$0 \sim -L^\beta-(L^{2\alpha}-L^{2-d})^X+L^0. \tag{12}$$

We focus on the balance of the largest contributions, and we do so for each dimension.

When $d=1$ the leading contributions are in the parentheses, i.e., we must have $2\alpha=2-d=1$ or $\alpha=\frac{1}{2}$ regardless of the value of $X>\frac{1}{2}$. Thus for $d=1$ $\langle\rho^2(\mathbf{r},t)\rangle \sim L$ and consequently the segregation index $S=O(L^0)$, i.e., $S\to 1$. Therefore, spontaneous macroscopic segregation occurs in one dimension.

On the other hand, when $d=3$ the leading terms that must balance are $L^{2\alpha X}$ and L^0 from which it follows that $\alpha=0$. Thus for $d=3$ we find the classical behavior $\langle\rho^2(\mathbf{r},t)\rangle \sim L^0$ and since $\langle\gamma^2(\mathbf{r},t)\rangle \sim 1/L$, the segregation index vanishes with increasing L, i.e., $S\to 0$. Therefore, there is no macroscopic segregation in three dimensions.

When $d=2$ then there are two terms $O(L^0)$ in (12) which must be balanced by the $\langle\rho^2\rangle$ term, i.e., we must again have $\alpha=0$. We can write from (11) $\langle\rho^2(\mathbf{r},t)\rangle \approx \langle\gamma^2(\mathbf{r},t)\rangle + (R/K)^{1/X}$ and both terms on the right are $O(L^0)$. With the results obtained earlier for $\langle\gamma^2(\mathbf{r},t)\rangle$ we thus have for the segregation index

$$S=\left[1+(R/l^2)^{(1-X)/X}\frac{4\pi^2\sigma}{nCK^{1/X}}\right]^{-1}, \qquad (13)$$

$$C\equiv\sum_{j,m\neq 0}(j^2+m^2)^{-1}.$$

The behavior of S is clearly dependent on detailed parameter values. If $X=1$ (classical case), then S becomes independent of the deposition rate R. If $X\neq 1$, then a higher deposition rate favors segregation if $X>1$ and inhibits it if $X<1$. For a given n, efficient diffusion relative to reaction ($\sigma l^2 \gg nK^{1/X}$) inhibits segregation while efficient reaction relative to diffusion ($nK^{1/X}\gg\sigma l^2$) promotes segregation. Finally, note that increasing n, the number of A's or B's deposited in a unit cell in the time interval τ, promotes segregation. Thus we conclude that for the critical dimension $d=2$ segregation is marginal and depends sensitively on the detailed parameter values.

In summary, we have shown for finite systems that macroscopic segregation occurs in one dimension, occurs marginally in two dimensions, and does not occur in $d\geq 3$ dimensions. For $d=2$ in the simplest cases ($n=1$, $X=1$) the segregation index is completely determined by the ratio $\sigma l^2/K$, i.e., by the relative rates of diffusion and reaction. In one dimension the correlation length of a pattern is of order $L/2$. In two dimensions this length depends on the detailed parameter values. Numerical simulations carried out on finite systems yield results that are not only in qualitative agreement but also in quantitative agreement with ours.[13]

In an infinite system (detailed elsewhere[15]) analogous (but different) conclusions about segregation can be drawn: There is segregation in one and two dimensions, and marginal segregation in three dimensions.

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[a] Permanent address.

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