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Diffusion-limited reactions: Effect of strong space disorder on segregation

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The effect of strong space disorder in a one-dimensional medium on the macroscopic segregation of A and B in the $A+B\rightarrow 0$ reaction is studied via an effective-medium approximation. The strongest disorder (percolative medium) shows an increase of the segregation due to the existence of isolated diffusive regions. Poisson strong disorder shows a slowing down both in the extinction and segregation. In the presence of sources a disorder-induced transition from bounded to unbounded growth is observed.

Quite recently the nonclassical kinetics of the diffusion-limited reaction processes for two-species annihilation $A+B\rightarrow C$ (where C is the inert species), has attracted considerable attention.[1–7] Such a process has been studied as a model of several different physical and chemical systems (ionic, electron-hole, and defect recombination, matter-antimatter annihilation, etc.). An aspect pointed out over a decade ago by Orchinnikov and Zeldovich was the possibility of macroscopic segregation.[8] Several recent reviews have analyzed this and related aspects of such systems.[9–12] Among other problems, workers have been concerned with the influence of dimensionality, initial conditions, sources, conservation laws, etc.[1,5,6,12] The form of the kinetic or rate equations has also received some attention.[4,7,11–13]

In this paper we would like to address the effect of spatial disorder on the diffusive properties of the above-mentioned systems and consequently its effect on the macroscopic-segregation characteristics. Basically two mechanisms, reaction and diffusion, govern the evolution of the system. The reaction process alone, in our case annihilation, already produces segregation. The diffusion process leads to homogenization of species and in this way reduces segregation. However, when diffusion stirring is inefficient, as in low-dimensional systems, macroscopic segregation occurs.[12] In this framework the effect of disorder can be understood by considering changes in the diffusive behavior of particles. A direct method of analysis can be achieved by considering an effective-medium approximation (EMA). Such an approximation gives an equivalent time-dependent diffusion coefficient calculated from the statistical properties of the random disordered field. Then we can use a standard analysis of the reaction diffusion equation with an effective diffusion coefficient that takes into account the effect of disorder.

The EMA has been used only for discrete systems. In this case, and based on operator projection techniques and ordered cumulants, a systematic way of obtaining an EMA and perturbations around it has been developed in Ref. 14. Although it is usually thought that EMA is only valid for discrete models, it is possible to generalize such approximation to a continuous medium. This generalization has been made in the case of weak disorder[15] and can be extrapolated, in general, to strong disorder.[16] We will apply here this procedure discussing only the one-dimensional problem. The higher-dimensional situation will be considered in the future.

From Ref. 15, it is clear that the effect of weak disorder will not alter the conclusions of Refs. 6 and 12, since the resulting effective diffusion constant only implies a change in its magnitude but not a time dependence. We then concentrate on the most interesting case of strong disorder.[14,15,17] We follow the approach of Refs. 6 and 12. Then we assume the reaction diffusion equations for the sum and difference variables $\rho(x,t)=\frac{1}{2}[\rho_A(x,t)+\rho_B(x,t)]$ and $\gamma(x,t)=\frac{1}{2}[\rho_A(x,t)-\rho_B(x,t)]$ to be valid, where ρ_A and ρ_B are the local densities of the A and B reactants, respectively. The equations are

$$\dot{\gamma}(x,t)=\partial_x\eta(x)\,\partial_x\gamma(x,t)+R_\gamma(x,t)\,, \tag{1a}$$

$$\dot{\rho}(x,t)=\partial_x\eta(x)\,\partial_x\rho(x,t)-k(\rho^2-\gamma^2)+R_\rho(x,t)\,, \tag{1b}$$

where R_γ and R_ρ are the associated source terms, k is the rate coefficient, and the diffusion coefficient $\eta(x)$ is a random field. Applying the continuous version of the EMA (Ref. 15) to (1a) we arrive at

$$\dot{\bar{\gamma}}(x,t)=\int_0^t D(t-t')\,\partial_x^2\bar{\gamma}(x,t')dt'+R_\gamma(x,t)\,, \tag{2}$$

where the overbar indicates average over field configurations. The effective time-dependent diffusion coefficient is given in the Laplace-transformed space, $t\rightarrow s$ (hereafter Laplace-transformed functions are written as the same functions with argument s instead of t), but the self-consistent condition[16]

$$\left\{\frac{\eta - D(s)}{1+1/[D(s)][\eta - D(s)][1-lG_1(0,s)]}\right\}=0\,, \quad (3)$$

where {} indicates average over field configurations, l is the correlation length of the field $\eta(x)$, and G_1 is the one-point Green function of the ordered case. This condition is equivalent to the EMA condition in a discrete medium with statistically independent sites separated a distance l. This is a very useful condition because in this way it is easy to generalize known results from the equivalent discrete medium.

As shown in Refs. 6 and 12 one way to obtain information regarding the degree of segregation is through the analysis of the correlation function $C(x-x',t) = \langle\gamma(x,t)\gamma(x',t)\rangle$. From the knowledge of the initial correlation $\langle\gamma(x,0)\gamma(x',0)\rangle$ and correlation of sources $\langle R_\gamma(x,t)R_\gamma(x',t)\rangle$ we can obtain $C(x-x',t)$ as

$$C(x-x',t)=\int dx_1\int dx_2\overline{G_2}(x,x',t/x_1,x_2,0)\langle\gamma(x_1,0)\gamma(x_2,0)\rangle + \int_0^t dt'\int dx_1\int dx_2\overline{G_2}(x,x',t/x_1,x_2,t')\langle R_\gamma(x_1,t')R_\gamma(x_2,t')\rangle\,. \quad (4)$$

$\langle\,\rangle$ means average over all possible randomness. We have assumed that disorder is independent of initial conditions and sources. $\overline{G_2}(x,x',t/x_1,x_2,0)$ is the disorder-averaged two-point Green function. Here we make the following ansatz for such a Green function:

$$\overline{G_2}(x,x',t/x_1,x_2,0)\approx\overline{G_1}(x,t/x_1,0)\overline{G_1}(x',t/x_2,0)\,, \quad (5)$$

where $\overline{G_1}(x',t/x,0)$ is the one-point averaged Green-function solution of (2) with $R_\gamma=0$ and $\delta(x-x')$ as initial conditions. A thorough discussion of this ansatz and other related aspects will be given elsewhere.[16] We will next consider two kinds of strong disorder given by a percolative and a generalized Poisson models of disorder. In both cases we study the influence of initial random conditions and of random source terms.

We first analyze the percolative disorder. In this case the random field η is defined by a two-level process with values $\eta=\Delta$ and $\eta=0$ with probability α and $1-\alpha$, respectively. For the sake of simplicity we take an exponential correlated field with a correlation length l:

$$\langle\eta(x)\eta(x')\rangle=\Delta^2\alpha(1-\alpha)\exp(-|x-x'|/l)+(\Delta\alpha)^2\,. \quad (6)$$

The field can be thought of as regions that are exponentially distributed in which diffusion is possible or not possible. This field has the strongest disorder. The stationary solution of (1a) is trivially obtained for a given realization. In the case of $R=0$ we have

$$\gamma_{\rm st}(x)=\begin{cases}\dfrac{1}{a-b}\displaystyle\int_b^a\gamma(x,0)dx, & \text{if } x\in(a,b) \text{ where } \eta=\Delta\,,\\ \gamma(x,0), & \text{if } x\in(c,d) \text{ where } \eta=0\,.\end{cases} \quad (7)$$

Other exact calculations are also possible. In particular it is not difficult to obtain the long-time limit of the equivalent diffusion coefficient defined, in terms of the Laplace variable s, as $D=\frac{1}{2}s^2\langle x^2(s)\rangle$. It reads

$$D(s)=\tfrac{1}{6}\,al^2s\,. \quad (8)$$

This exact result can be compared with the one obtained with the EMA condition (3). As in the discrete case, the EMA deals with the correct time dependence but does not lead to a correct coefficient.[18]

Inserting $D(s)$ from (8) into (2) and Fourier transforming we obtain for $\overline{G_1}$

$$\lim_{t\to\infty}\overline{G_1}(k,t/0)\sim\frac{1}{1+D_1k^2} \quad (9)$$

with $D_1=\frac{1}{6}\,al^2$. Then the ansatz of Eq. (5) gives (neglecting sources)

$$\langle\gamma(k,t)\gamma(k',t)\rangle\approx\overline{G_1}(k,t/0)\overline{G_1}(k',t/0)\times\langle\gamma(k,0)\gamma(k',0)\rangle\,. \quad (10)$$

Following Refs. 6 and 12 we can choose uncorrelated (u) or correlated (c) initial conditions. In the first case

$$\langle\gamma(k,0)\gamma(k',0)\rangle_u=\tfrac{1}{2}N(\delta_{k+k',0}-\delta_{k,0}-\delta_{k',0})\,,$$

which leads to

$$\lim_{t\to\infty}\langle\gamma(x,t)\gamma(0,t)\rangle_u\approx\frac{n}{2D_1^{1/2}}\left[\left(1+\frac{|x|}{D_1^{1/2}}\right)\times\exp\left(-\frac{|x|}{D_1^{1/2}}\right)\right], \quad (11)$$

from which results

$$\lim_{t\to\infty}\langle[\gamma(x,t)]^2\rangle_u=\frac{n}{2D_1^{1/2}}\,. \quad (12)$$

We remark that our analysis follows the method of Refs. 6 and 12, thus the density n appearing in (11) and (12) is obtained as N/V in the thermodynamic limit.

From the stationary solution of Eq. (1b), we arrive at $\langle[\rho_{\rm st}(x)]^2\rangle=\langle[\gamma_{\rm st}(x)]^2\rangle$. Then the segregation parameter introduced in Refs. 6 and 12 turns out to be

$$\lim_{t\to\infty}S(t)=\frac{\langle\gamma^2\rangle}{\langle\rho^2\rangle}=1\,.$$

The result (12) clearly indicates that the subdiffusive behavior due to the percolative disorder increases the segregation with respect to the ordered case. In this last case, segregation is only reached in the extinction limit. On the other hand, if we consider a correlated initial condition, with c the geminate correlated placement,[6,12] we have for the initial correlations

$$\langle\gamma(k,0)\gamma(k',0)\rangle=\tfrac{1}{2}N\delta_{k+k',0}(1-\cos(kc))\,. \quad (13)$$

This leads to

$$C_c(x,t)=C_u(x,t)-\tfrac{1}{2}[C_u(x-c,t)+C_u(x+c,t)] \tag{14}$$

so that

$$\langle[\gamma(t)]^2\rangle_c=C_c(0,t)\underset{t\to\infty}{\sim}\frac{n}{2D_1^{1/2}}\left[1-\left(1+\frac{c}{D_1^{1/2}}\right)\exp(-c/D_1^{1/2})\right] \tag{15}$$

indicating a reduction of the segregation due to the initial correlation. We find a kind of competition between the effective diffusion length $D_1^{1/2}$ and the initial geminate placement c. If $c\gg D_1^{1/2}$ correlated particles are in different diffusive regions and this is equivalent to the uncorrelated situation, so we recover the previous result (12). In the opposite case, $c<D_1^{1/2}$, the probability of extinction of the correlated particles is larger and consequently the number of segregated particles is reduced.

From (11) and (14) it is possible to do an estimation of a segregation length. In the uncorrelated case it is clear that a length scale given by $l_s=D_1^{1/2}$ exists. In the correlated case a possible estimation can be given by the length in which the correlation is zero. When $D_1^{1/2}>c$, this length is given by

$$l_s=\frac{c[\exp(c/D_1^{1/2})-\exp(-c/D_1^{1/2})]}{\exp(c/D_1^{1/2})+\exp(-c/D_1^{1/2})-2}\,, \tag{16}$$

which tends to $2D_1^{1/2}$ if $D_1^{1/2}\gg c$. In the case $c>D_1^{1/2}$ it is evident that the correlations in the correlated and uncorrelated initial condition cases are very similar.

Now we consider Poisson disorder. In this case the random field $\eta(x)$ is given by a spatial distribution of random pulses separated by an exponentially distributed random distance of mean λ. For the sake of simplicity we take exponential pulses with a height ω and decay parameter $1/l$ being ω a random variable exponentially distributed with mean ω_0. Strong disorder appears when $\lambda l<1$, so that the mean distance between pulses is greater than its width.[15] Poisson strong disorder is weaker than percolative disorder because the space remains connected. This corresponds to a disorder of class c,[18] i.e., with a probability distribution, $P(\eta)\sim\eta^{\lambda l-1}$, for η close to zero. Diffusive regions (exponential pulses) are only connected by an exponentially small diffusion coefficient. This is the cause of the subdiffusive behavior found with this kind of disorder. Applying the EMA condition (3) to this case we obtain an equivalent diffusion coefficient for small s (long time) given by

$$D(s)=D_2s^{\nu}\,, \tag{17}$$

where

$$\nu=\frac{1-\lambda l}{1+\lambda l}\,, \tag{18}$$

and

$$D_2=\left[\frac{1}{2\Gamma(1-\lambda l)}\right]^{2/(1-\lambda l)}(2\omega_0)^{2\lambda l/(1+\lambda l)}l^{2(1-2\lambda l)/(1+\lambda l)}\,. \tag{19}$$

With this coefficient in Eq. (2) we obtain

$$\langle\gamma^2(t)\rangle_u\approx\frac{n\Omega(\nu+1/2)}{4D_2^{1/2}\Gamma(\nu+1/2)}t^{-(1-\nu)/2} \tag{20}$$

for the uncorrelated initial condition and

$$\langle\gamma^2(t)\rangle_c\approx\frac{nc^2\Omega(\nu)}{8D_2^{3/2}\Gamma(3\nu-1/2)}t^{-3(1-\nu)/2} \tag{21}$$

for the correlated case. Ω is the function

$$\Omega(z)=\frac{1}{2\pi i}\int_{r-i\infty}^{r+i\infty}\frac{[u(1-u)]^{-z}}{(1-u)^{(1-\nu)/2}+u^{(1-\nu)/2}}du\,. \tag{22}$$

For the segregation parameter an analysis similar to the one of the percolative case gives for the long-time limit $S\to1$, so the segregation is reached in the limit of extinction. The difference with the ordered case is that segregation and extinction are slowed down due to the subdiffusive behavior induced by the disorder. This slowing down is more intense when disorder is stronger, i.e., when $\lambda l\to0$.

Finally we study the case of strictly conservative sources in the correlated and uncorrelated cases. The correlation of sources are[12]

$$\langle R_\gamma(x,t)R_\gamma(x',t')\rangle_{u,c}=\frac{4R}{n}\delta(t-t')\times\langle\gamma(x,0)\gamma(x',0)\rangle_{u,c}\,, \tag{23}$$

which leads to the following relation between correlation with sources, $C_R(x,t)$, and without sources, $C(x,t)$, given by

$$C_R(x,t)=\frac{4R}{n}\int_0^t C(x,t')dt'\,. \tag{24}$$

From the asymptotic expressions of $\langle\gamma^2(t)\rangle$ given in Eqs. (12), (15), (18), and (19), we can deduce immediately whether $\langle\gamma^2(t)\rangle_R$ remains finite or not in the $t\to\infty$ limit. It grows without bound in the correlated and uncorrelated percolative cases [(12) and (15)] and in the correlated Poisson disorder with $\nu>\frac{1}{3}$, that is, $\lambda l<\frac{1}{2}$. $\langle\gamma^2(t)\rangle_R$ remains finite in the uncorrelated Poisson case (20) and also in the correlated one with $\lambda l>\frac{1}{2}$. Here we observe a kind of transition induced by disorder. When $\lambda l>\frac{1}{2}$ diffusion is large enough to connect the correlated sources and a similar behavior to the one observed in the ordered situation occurs. If $\lambda l<\frac{1}{2}$ the subdiffusive behavior is so strong that correlated sources appear as isolated, the recombination time of the particles is long enough to produce an infinite growth. In the percolative case the sources are actually disconnected and this is the cause of the infinite growth.

Let us summarize the effect of disorder on the time evolution and segregation of the diffusing particles. When disorder is weak only a quantitative change of the diffusion coefficient is possible and no important changes with respect to the ordered situation appear. When the disorder is so strong that it produces subdiffusive behavior but not strong enough to disconnect diffusive regions, we obtain a slowing down of the reaction process and also of the segregation (Poisson disorder). In the percolative case, where disorder is so strong that it produces isolated diffusive regions, extinction is not possible and a segregated steady state appears. The effect of disorder in the case with sources is similar. We observe an infinite growth if disorder is able to isolate correlated sources. In the Poisson case a transition from bounded to unbounded growth is observed at $l = 1/2\lambda$.

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