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Equilibrium of two-species annihilation with input

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We provide necessary conditions for the equilibrium of the process $A+B\rightarrow C$ where there is a steady input of A and B particles, or when back reactions $C\rightarrow A+B$ are allowed. There is an important distinction between inputs which conserve or do not conserve the particle number difference (N_A-N_B). For nonconserving input in finite volume or in low enough dimensions, the system never reaches equilibrium. For conserving input, as in the case of back reactions, the system may or may not reach equilibrium.

The diffusion-limited reaction process for two-species annihilation, $A+B\rightarrow$ (inert species) has been studied as a model for several physical and chemical systems, including ionic recombination,[1,2] electron-hole recombination in a variety of condensed matter systems,[3–7] and recombination of magnetic monopoles in the early universe.[8] The anomalous decay of the concentration of the reactants observed in experiments is nicely explained by the predictions based on theoretical and numerical analyses of the two-species annihilation model. For equal initial concentrations of the two species, the total concentration decays as $t^{-d/4}$ for dimensions $d\leq 4$. As the process evolves, A-rich and B-rich domains are formed. Reactions between particles occur only along the domain boundaries, slowing down the total reaction rate and resulting in anomalous kinetics. This segregation into domains takes place only in low space dimensions. For $d\geq 4$ domains do not form and the resulting $1/t$ decay is satisfactorily explained by classical rate equations.

The usefulness of the two-species annihilation model is greatly increased by relaxing the restriction that the species react *irreversibly*. Allowing for back reactions $(A+B\rightleftharpoons C)$ the model becomes suitable for the study of many more systems where equilibrium and the approach to equilibrium are important features.[9] Similarly, equilibrium can be studied in an open system model where there is a continuous external input of A and B particles. Anacker and Kopelman[10] have recently shown that when the two-species annihilation process *with input* takes place on the Sierpiński gasket there is segregation of A and B in the equilibrium state, but there is no such segregation for the same process on the cubic lattice. Zhang[11] looks into the question of the necessary conditions for the occurrence of segregation phenomena.

In this Rapid Communication, we question the existence of an equilibrium itself. An important distinction has yet to be made between external inputs which conserve the particle number difference N_A-N_B, and those which do not. We show that the existence of an equilibrium state depends crucially on these factors, as well as on the dimension of the system and whether it is of finite or infinite volume. Our conclusions are based on an *exact* solution of the stochastic partial differential equation for the evolution of the difference in concentrations of the two species.

Let us consider two-species annihilation with random input. As a possible starting point, we may look at a continuum version of the process, represented by

$$\begin{aligned}\dot{A}(\mathbf{x},t)&=D\Delta A(\mathbf{x},t)-kA(\mathbf{x},t)B(\mathbf{x},t)+\eta_A(\mathbf{x},t)\ ,\\ \dot{B}(\mathbf{x},t)&=D\Delta B(\mathbf{x},t)-kA(\mathbf{x},t)B(\mathbf{x},t)+\eta_B(\mathbf{x},t)\ .\end{aligned}\tag{1}$$

Here $A(\mathbf{x},t)$ and $B(\mathbf{x},t)$ are the concentrations of A and B particles. The first terms represent diffusion with a diffusion coefficient D, the second terms represent reaction, and η_A and η_B are stochastic variables representing the random inputs of A and B. An important consequence of Eq. (1) is that the difference in concentrations $\gamma(\mathbf{x},t)\equiv A(\mathbf{x},t)-B(\mathbf{x},t)$, obeys a *linear* partial differential equation

$$\dot{\gamma}(\mathbf{x},t)=D\Delta\gamma(\mathbf{x},t)+\eta_\gamma(\mathbf{x},t)\ ,\tag{2}$$

where $\eta_\gamma(\mathbf{x},t)\equiv\eta_A(\mathbf{x},t)-\eta_B(\mathbf{x},t)$. It should be noted that Eq. (2) is insensitive to the explicit form of the reaction term because of the symmetry between A and B when their diffusion coefficients are the same. This is important in view of the claim that for diffusion-reaction systems the reaction is of an effective order different than that simply implied by classical rate equations.[12] For the case that

there is no input ($\eta_\gamma=0$), Eq. (2) reflects the fact that the particle number difference, N_A-N_B, is conserved upon each single reaction, and consequently throughout the whole process.

Much depends on the properties of the stochastic variables η_A and η_B. We will generally require that

$$\langle\eta_A(\mathbf{x},t)\rangle=\langle\eta_B(\mathbf{x},t)\rangle=R\ , \tag{3}$$

where $\langle\cdots\rangle$ denotes an ensemble average. Thus, R is the average number of particles (of either species) introduced to the system per unit volume per unit time. Furthermore, we consider the case of uncorrelated inputs of particles,

$$\langle\eta_A(\mathbf{x},t)\eta_A(\mathbf{x}',t')\rangle=R^2+R\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')\ , \tag{4}$$

and likewise for η_B. There are two general assumptions which enter into this structure of the input correlations: (1) the input process is assumed Poissonian, so that the variance is proportional to the mean (R), and (2) the size of the particles is neglected, resulting in a neglect of a short wavelength cutoff.[13]

From Eq. (3) it follows that $\langle\eta_\gamma(\mathbf{x},t)\rangle=0$. We distinguish between two cases of interest. In the first case, the input of A particles is completely independent from the input of B particles. In this case,

$$\langle\eta_\gamma(\mathbf{x},t)\eta_\gamma(\mathbf{x}',t')\rangle=2R\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')\ . \tag{5}$$

This is a nonconserving input, as it violates conservation of the particle number difference. The other case of interest is when the A and B particles are introduced simultaneously as, for example, with back reactions $C\rightarrow A+B$. Then,

$$\langle\eta_\gamma(\mathbf{x},t)\eta_\gamma(\mathbf{x}',t')\rangle=2R[\delta(\mathbf{x}-\mathbf{x}')-p(\mathbf{x}-\mathbf{x}')]\delta(t-t')\ , \tag{6}$$

where $p(\mathbf{x}-\mathbf{x}')$ is the probability density that an $A-B$ pair is introduced a displacement $\mathbf{x}-\mathbf{x}'$ apart. Back reactions are conveniently represented in this way by interpreting $p(\mathbf{x}-\mathbf{x}')$ as the probability of *creating* a pair of particles separated by the displacement $\mathbf{x}-\mathbf{x}'$. Since $\int d^d\mathbf{x}p(\mathbf{x})=1$, we see that $\int d^d\mathbf{x}\eta_\gamma(\mathbf{x},t)=0$ with probability one and the particle number difference is conserved.

The solution of Eq. (2) is straightforward. Since we are interested in the long-time behavior we may neglect the initial condition and take $\gamma(\mathbf{x},0)=0$. Fourier transforming the equation, one finds

$$\begin{aligned}\gamma(\mathbf{k},t)&=\int\frac{d^d\mathbf{x}}{(\sqrt{2\pi})^d}e^{-i\mathbf{k}\cdot\mathbf{x}}\gamma(\mathbf{x},t)\\&=\int_0^t\eta_\gamma(\mathbf{k},t')e^{-Dk^2(t-t')}dt'\ ,\end{aligned} \tag{7}$$

so that

$$\langle\gamma(\mathbf{k},t)\gamma(\mathbf{k}',t)\rangle=\int_0^t dt_1\int_0^t dt_2 e^{-Dk^2(t-t_1)-Dk'^2(t-t_2)}\langle\eta_\gamma(\mathbf{k},t_1)\eta_\gamma(\mathbf{k}',t_2)\rangle\ . \tag{8}$$

We first treat the case of independent A and B inputs, Eq. (5). In this case,

$$\langle\eta(\mathbf{k},t)\eta(\mathbf{k}',t')\rangle=2R\delta(\mathbf{k}+\mathbf{k}')\delta(t-t')\ , \tag{9}$$

and

$$\langle\gamma^2(\mathbf{x},t)\rangle=\frac{R}{D}\int\frac{d^d\mathbf{k}}{(2\pi)^d}\frac{(1-e^{-2Dk^2t})}{k^2}\ . \tag{10}$$

The divergence of this integral for $|\mathbf{k}|\rightarrow\infty$ in $d\geq 2$, i.e., the ultraviolet (UV) divergence, is due to the neglect of the short-distance cutoff (the size of the particles or an underlying lattice spacing) and is not of concern here. What is of concern is the behavior of the integrand as $|\mathbf{k}|\rightarrow 0$, i.e., the infinite volume infrared (IR) behavior. For $d\leq 2$ the usual IR problems of field theory appear and we find

$$\langle\gamma^2(\mathbf{x},t)\rangle\sim\begin{cases}\text{const}, & d>2\ ,\\ \ln t, & d=2\ ,\\ t^{(2-d)/2}, & d<2\ .\end{cases}\quad\text{(infinite volume)} \tag{11}$$

If the difference in concentrations never reaches a stationary state, as is the case for infinite volume and $d\leq 2$, then *no* equilibrium is possible. For *finite* volume the wave numbers are discrete and one can study the long-time behavior of the solution by simply looking at the $\mathbf{k}=0$ component of $\gamma(\mathbf{k},t)$. For any dimension, we find that for $t\rightarrow\infty$,

$$\langle\gamma^2(\mathbf{x},t)\rangle\sim t,\ \text{(finite volume)}. \tag{12}$$

These results are understood by observing that the particle number difference is described by a simple random walk constrained only by the spatial diffusion. Diffusion tends to dissipate any local buildups of excess particles. When the volume of the system is finite, the excess particles are bound to stay inside the system and $\langle\gamma^2\rangle$ grows linearly with t in a pure random-walk fashion. In contrast, when the system is infinite, diffusion can control the growth of $\langle\gamma^2\rangle$ by spreading buildups over an arbitrarily large region if the space dimension is large enough ($d>2$). Even in low dimensions ($d\leq 2$), the buildup of $\langle\gamma^2\rangle$ in infinite volume is *slower* than linear.

We now turn to the case of conserving input and of back reactions. Instead of (9), we have, from Eq. (6),

$$\langle\eta_\gamma(\mathbf{k},t)\eta_\gamma(\mathbf{k}',t')\rangle=2R\delta(\mathbf{k}+\mathbf{k}')[1-p(\mathbf{k})]\delta(t-t')\ , \tag{13}$$

where $p(\mathbf{k})$ is the characteristic function (Fourier transform) of $p(\mathbf{x})$. Thus,

$$\langle\gamma^2(\cdot,t)\rangle=\frac{R}{D}\int\frac{d^d\mathbf{k}}{(2\pi)^d}[1-p(\mathbf{k})]\frac{1-e^{-2Dk^2t}}{k^2}\ . \tag{14}$$

Because p is a probability density, the Riemann-Lesbegue

theorem ensures that the characteristic function $p(\mathbf{k})$ must approach the value 1 continuously as $|\mathbf{k}| \to 0$. For the borderline dimension, $d=2$, this will generically imply the IR convergence of the integral in Eq. (14) uniformly in t as $t \to \infty$, rather than the logarithmic divergence observed for a nonconserving input [Eq. (11)]. For $d<2$, IR convergence is possible only if

$$|1-p(\mathbf{k})| < (\text{const})\,|\mathbf{k}|^{\alpha}, \quad \alpha > 2-d \ , \tag{15}$$

as $|\mathbf{k}| \to 0$. This is equivalent to the requirement that

$$p(\mathbf{x}) < (\text{const})\,|\mathbf{x}|^{-\beta}, \quad \beta > 3-d \ , \tag{16}$$

as $|\mathbf{x}| \to \infty$. Thus, for $d<2$ equilibrium may not be achieved even for a "conserving" time-correlated input of $A-B$ pairs, if the spatial correlation of this input is not localized enough. The diffusion in $d<2$ is not strong enough to overcome the disordering effect of widely separated inputs. For example, in $d=1$ a stationary state can exist only if the mean particle-input separation is finite.

In finite volume a stationary state is realized in all dimensions for the conserving input. When the wave numbers are discrete, the correlated input contains *no* $\mathbf{k}=0$ components.

In summary, we have shown that the mere existence of an equilibrium state for the diffusion limited two-species annihilation process with input depends on the space dimension, on whether the system is finite, and on the character of the stochastic input. We have given necessary conditions for the existence of a stationary state in low-dimensional systems. While we disagree with the results of Ref. 11, similar results to our own have recently been derived independently by Lindenberg, West, and Kopelman,[14] who also study the question of spatial segregation.

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