Stochastic clustering of reacting particles and kinetics of their loss

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Analysis is carried out of the spectrum of the fluctuations which an external source with a Poisson distribution excites in a system of particles which react with each other. Asymptotic results describing the decay of the concentration of reacting particles after the source is turned off are derived for the cases of neutral and charged particles.

Fluctuations in the spatial distribution of reacting particles and, in particular, thermodynamic fluctuations lead to distinctive features in the long-term kinetics of the relaxation of the average concentrations of these particles to equilibrium values. In the case of the irreversible reaction $A + B \to C$, for example, we have[1] $c_A \sim t^{-3/4}$, where the concentrations of the particles of species A and B, i.e., c_A and c_B, are equal. This asymptotic behavior is determined by the initial fluctuations of the random (Poisson) distribution of particles. If the reaction is reversible, the relaxation to the equilibrium values is described by the power-law asymptotic expression[2] $t^{-3/2}$, which is sharply different from the exponential (in time) decay predicted by formal kinetics. A common result of Refs. 1 and 2 was the assertion that the long-term dependence is determined by the diffusive smoothing over of the fluctuations of the original distribution of reacting particles.

In the present letter we show that if a system of reacting particles of species A and B (present in equal concentrations) is prepared by a steady stream of these particles, as a result of, for example, their production in a radiation field or spontaneous radioactive decay with a normal Poisson distribution in space, the steady-state distribution of the particles of species A and B which is established will no longer have Poisson properties. There will be a sort of spatial clustering of like particles, and when the particle source is turned off, the concentrations will tend toward zero in accordance with $t^{-1/4}$ for the uncharged particles or by some other law for charged particles.

A clustering of like particles in a steady stream was also predicted in Refs. 3–6, but the fluctuation spectrum was not derived there.

The system of equations controlling the production and loss of neutral particles A and B with equal diffusion coefficients, $D_A = D_B = D$, is

$$\begin{cases} \partial c_A(r,t)/\partial t = D\Delta c_A(r,t) - \kappa c_A(r,t)c_B(r,t) + i_A(r,t) \\ \partial c_B(r,t)/\partial t = D\Delta c_B(r,t) - \kappa c_A(r,t)c_B + i_B(r,t) \end{cases} \tag{1}$$

The particle fluxes $i_A(r,t)$ and $i_B(r,t)$ have Poisson statistical properties:

$$\begin{cases} \langle i_A(r,t)\rangle = \langle i_B(r,t)\rangle = i_0\,; \qquad \langle i_a i_b\rangle = 0 \\ \langle i_A(r,t)i_A(r',t')\rangle = \langle i_B(r,t)i_B(r',t')\rangle = i_0\delta(r-r')\delta(t-t') \end{cases} \tag{2}$$

where κ is the rate constant for a bimolecular loss of particles.

For the difference $c_A(r,t) - c_B(r,t) = z(r,t)$ we have the equation

$$\partial z/\partial t = D\Delta z(r,t) + \delta i(r,t)\,, \tag{3}$$

The Fourier components of the solution of this equation have the correlation functions

$$g = \langle z_k(t) z_{k'}(t)\rangle = \frac{2i_0\delta_{k+k'}}{Dk^2}\, e^{-Dk^2|t-t'|} \tag{4}$$

At small values of k, g becomes large, telling us that the particles of species A and B become separated at a large scale. Expression (4) holds for any dimensionality. The complete spectrum of fluctuations, $z_k(t)$, diverges in one or two dimensions, telling us that the regions along which the phases of the like particles are spread out in these cases are comparable to the total dimensions of the system.

When the source of particles is turned off, the particles are initially lost in accordance with the bimolecular decay law $c_A \sim (\kappa t)^{-1}$, but the long-term kinetics is determined by the diffusive equalization of the difference (z) between the numbers of particles of species A and B in large volumes. In the latter stage, the concentration is actually equal to the average value of the modulus of $z(r,t)$:

$$c_A = c_B = \frac{1}{2}\langle |z(r,t)|\rangle. \tag{5}$$

The average $\langle |z(r,t)|\rangle$ with the spectrum of initial $(t = t' = 0)$ fluctuations in (4) is evaluated by analogy with Ref. 1; the result is

$$c_A = \frac{1}{2}\langle |z(r,t)|\rangle = \frac{1}{2\pi}\left(\frac{i_0}{(2\pi)^3 D}\int \frac{d^3k}{k^2}\, e^{-2Dk^2 t}\right)^{1/2}. \tag{6}$$

For three dimensions we have

$$c_A \sim i_0^{1/2} D^{-3/4} t^{-1/4}. \tag{7}$$

The relative number of particles which are consumed according to (7) is $\delta c_0/c_0 \approx r_0 c^{1/3}$, where r_0 is the reaction radius of the particles. This relative number can be observed experimentally. For two dimensions, the integral in (6) is cut off at $k \sim S^{-1/2}$, where S is the area of the entire surface, and the particles disappear completely over a time $\sim S/D$. In the case of instantaneous production of particles, the faster asymptotic results in Refs. 1 and 2 would apply.

A more interesting case is that of unlike charged particles. Long-wave fluctuations $z(r,t)$ are suppressed by the Coulomb field of the particles. In our original system, (1), we acquire a force term with a potential φ satisfying the Poisson equation[7]:

$$\Delta\varphi = \frac{4\pi e}{\epsilon}(c_A(r) - c_B(r)). \tag{8}$$

The behavior of charged particles changes substantially when we go from three to two dimensions. We will give here the results for a three-dimensional space. The spectrum of steady-state fluctuations is

$$\langle z_k(t) z_{k'}(t') \rangle = \frac{2 i_0 \delta_{k+k'}}{D(k^2 + a_d^{-2})} e^{-D(k^2 + a_d^{-2})|t-t'|}, \tag{9}$$

where $a_d = (8\pi c_A e^2/T)^{-1/2}$ is the Debye length of the system in its steady state. It is a simple matter to derive the spectrum of fluctuations of the potentials and fields. The average-modulus field in the sample is thus

$$|\bar{E}| \approx e(T/e^2)^{1/8}(i/D)^{3/8} \tag{10}$$

and can reach a large value in a large flux or if the diffusion coefficients are small. This effect has been observed experimentally.[8]

Since the fluctuations of $z(r,t)$ do not have a singularity at small k, the long-term asymptotic loss of particles when the source is turned off is essentially consistent with the laws predicted by formal kinetics.

Some interesting features arise in the two-dimensional case when, for example, a stream of particles is incident on a plane. The electric fields are not particularly long-range fields, and the long-wave fluctuations are screened only partially by these fields.

The spectrum of fluctuations z is

$$\langle z_k(t) z_{k'}(0) \rangle = \frac{2 i_0 \delta_{k+k'}}{D(k^2 + |k| q)} e^{-D(k^2 + |k| q)t}, \tag{11}$$

where $q = 2\pi\sigma_0 e^2/T$ (an alalog of the reciprocal of the Debye length in two dimensions), and σ_0 is the two-dimensional particle density. We note in connection with (11) an interesting property of the temporal spectrum of fluctuations of the charge, $Q(t)$, at a point on a plane:

$$\eta_\omega = \int \langle Q(t)Q(0)\rangle e^{i\omega t} dt = 2i_0 \int \frac{d^2k}{D^2(k^2 + q\,|k|)^2 + \omega^2}$$

At small values of ω with $q = 0$, we have $\eta_\omega \sim 1/\omega$; i.e., there is a singularity of the flicker-noise type.

Finally, we state without proof the law describing the decay of the density of particles when the source is turned off: $c_A \sim t^{-1/3}$.

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