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LETTER TO THE EDITOR

Recombination processes in disordered media with external field

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Abstract. A recombination of charged particles in disordered media in the presence of a strong external field, which causes the non-classical drift of particles, is considered. It is shown that the particles spend most of the time in randomly distributed regimes, impenetrable for diffusing particles, stretched along the field. Positively and negatively charged particles are hidden in different cavities and this causes a reduction of the recombination rate.

It is well known that the long-time behaviour of the recombination process $A+B\to 0$ at equal concentration of A and B components cannot be described using a standard approach:

$$\frac{\mathrm{d}C_{\mathrm{A,B}}}{\mathrm{d}t}=-KC_{\mathrm{A}}C_{\mathrm{B}}. \tag{1}$$

If the initial distribution of particles is random, in any part of the system of size L there is an excess of particles of one kind or another of the order of $\delta N_{\mathrm{A,B}}\simeq(C_0L^d)^{1/2}$, where C_0 is the initial concentration of particles and d is the dimensionality of the space. These particles can only annihilate if they diffuse into a region which is rich in particles of another kind. The time required for this process is $t\sim L^2$; thus [1–3]

$$C_{\mathrm{A,B}}=C\simeq C_0^{1/2}\left(\frac{1}{t}\right)^{d/4}\qquad d<4. \tag{2}$$

In homogeneous media the main effect of the external electric field would result in a drift of particles of different kinds in opposite directions. This is an additional intermixing factor with a characteristic scale in the direction of the field $L_{\mathrm{drift}}=Et$. If L_{drift} becomes larger than $L_{\mathrm{dif}}=t^{1/2}$ then $\delta N_{\mathrm{A,B}}\simeq(c_0L_{\mathrm{dif}}^{d-1}L_{\mathrm{drift}})^{1/2}$ and [4]

$$C\simeq c_0^{1/2}E^{1/2}\left(\frac{1}{t}\right)^{(d+1)/4}. \tag{3}$$

The upper critical dimension in this case is $d_c=3$ $(c\sim 1/t)$. It should be noted that particle concentrations (1) and (2) are independent of the value of the reaction constant (diffusion-controlled regime).

Much more interesting is the case of inhomogeneous media with randomly distributed regions which are impenetrable for diffusing particles. We shall assume that the largest characteristic scale of the these inhomogeneties is l_0. If an external field is strong enough, so that $el_0E>kT$, the single-particle motion deviates from the classical

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drift [5]. Most important in this case are random traps, which are the cavities accidentally formed by impenetrable regions stretched in the field direction. The possibility of finding a large cavity of size $l \gg l_0$ is exponentially small:

$$P(l) \sim \exp(-|l|/l_0)$$

but if the particle falls into the trap it stays there for an exponentially long time

$$\tau(l) = \tau_0 \exp(eEl/kT). \tag{4}$$

For the observation time t starting from the beginning of the process the size of the deepest trap is

$$l_m = l_0 \frac{E_c}{E} \ln t/\tau_0 \qquad E_c = \frac{kT}{el_0}. \tag{5}$$

The typical number of steps which is needed to fall into this trap is

$$n(t) \simeq e^{l_m/l_0} \simeq \left(\frac{t}{\tau_0}\right)^{E_c/E} \qquad E > E_c. \tag{6}$$

The particles A and B are oppositely charged and hidden in cavities which have opposite directions $\pm \boldsymbol{E}/|E|$†. This causes a decrease of the effective recombination rate constant. A partition of A and B particles between different cavities can be described as

$$C_A(l) = C_B(-l)$$

$$C_A(l)\,\mathrm{d}l = C_A P(l)\tau(l)\,\mathrm{d}l \left(\int_{-l_m}^{l_m} P(l')\tau(l')\,\mathrm{d}l'\right)^{-1}$$

$$\simeq \frac{E-E_c}{E_c} \exp\left(\frac{E-E_c}{E_c}\frac{l_m-|l|}{l_0}\right)\begin{cases} 1 & l>0 \\ \exp(-2El/E_c l_c) & l<0. \end{cases} \tag{7}$$

It is clear that particles A and B become more and more separated from each other inside the system. This separation differs in principle from the large-scale separation of particles in a homogeneous medium (2) or (3). The recombination rate is reduced to

$$K(t) = K_0 \int_{-l_m}^{l_m} P(l)\tau(l)\tau(-l)\,\mathrm{d}l \left[\int_{-l_m}^{l_m} P(l)\tau(l)\,\mathrm{d}l\right]^{-2} \simeq K_0\left(\frac{\tau_0}{t}\right)[2(E-E_c)/E]. \tag{8}$$

From (1) we get

$$\begin{aligned} C &\sim \frac{1}{K_0}\, t(E-2E_c)/E && \text{if} \quad E_c < E < 2E_c \\ C &\to \text{constant} && \text{if} \quad E > 2E_c. \end{aligned} \tag{9}$$

At large times this regime will be superseded by another one in which all the deepest traps are occupied. In this case the typical length of the trap can be defined through the condition that the concentration of these traps is equal to the particle concentration $C \sim \exp(-l_m/l_0)$, or

$$l_m(c) = l_0 \ln(1/c). \tag{10}$$

† We shall distinguish these cavities by the sign + or −.

Using (1), (8) and (10) we get for this asymptotic regime

$$K(c) \simeq \left(\frac{E-E_c}{E_c}\right) K_0 C[2(E-E_c)/E_c] \qquad t \sim \frac{1}{K_0} t - E_c/(2E-E_c). \tag{11}$$

The crossover between (9) and (11) occurs at t^* defined by $l_m(t^*) = l_m(c)$:

$$t^*(c) = \tau_0 \left(\frac{1}{c}\right)^{E/E_c}. \tag{12}$$

The results (9) and (11) were obtained under the assumption that the recombination process is controlled by a diminishing reaction rate. In order to check this assumption we shall evaluate a rate for the diffusion-controlled process. It deviates from (3) because of the anomalous character of drift in disordered media [5]. Using (6) we get $L_{\text{drift}} = L_0(t)$, $L_{\text{dif}} = L_0(n(t))^{1/2}$ and

$$C = l_0^{-d} \left(\frac{\tau_0}{t}\right) [(d-1)/4](E_c/E). \tag{13}$$

At large t when all the deepest traps are occupied, $n(t)$ can be written as

$$\int_0^t \frac{\partial n(t')}{\partial t'} \, \mathrm{d}t'$$

where $\partial n(t')/\partial t'$ depends on the concentration of particles at time t':

$$\frac{\partial n}{\partial t'}(t') \simeq \left. \frac{n(c)}{t^*(c)} \right|_{c=c(t')}. \tag{14}$$

Here $n(c) = \mathrm{e}^{l_m(c)}$ is a typical number of steps between two traps of size $l_m(c)$. Making a self-consistent estimate for c we obtain

$$C = l_0^{-d} \left(\frac{\tau_0}{t}\right)^{[(d+1)E_c]/[4E_c+(d+1)(E-E_c)]}. \tag{15}$$

It is clear that at $d = 3$ the reaction-controlled asymptotics (9) and (11) are the dominant ones because (13) and (15) predict a more rapid decrease of the particle concentration. In two dimensions the situation is more complicated. In this case each regime (9), (11), (13) or (15) can be obtained by a proper choice of E and t. The corresponding conditions can easily be given. We notice only that near E_c the diffusion-controlled mechanism is dominant, whereas far away from E_c the reaction-controlled one is dominant. It has been assumed in the above considerations that the particle concentration is low enough and the effects of their local fields are negligible. At high concentrations of particles these fields can themselves lead to effects of particle trapping without any external field. We shall consider these effects elsewhere.

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