PHYSICA A

Self-organization in the A + B → 0 reaction of charged particles

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The formalism of many-particle densities developed earlier by the authors is applied to the study of the self-organization phenomena occurring during the course of the bimolecular A + B → 0 reaction between charged particles, interacting via the Coulomb law. Unlike the Debye–Hückel theory, charge screening has an essentially non-equilibrium character. It is shown that for the asymmetric mobility of reactants ($D_A = 0$, $D_B \neq 0$) similar immobile reactants A form aggregates characterized by a sharp maximum, observed at short distances, in the joint correlation function $X_A(r, t)$. Such an aggregation leads to the accelerated particle recombination $n \propto t^{-5/4}$ ($n_A = n_B = n$) instead of the generally accepted algebraic law $n \propto t^{-1}$.

1. Introduction

In the last years great attention in the kinetics of bimolecular reactions was paid to many-particle effects and pattern formation [1–9]. In the particular case of the A + B → 0 reaction both analytical theories [1–7] and computer simulations [5–9] have demonstrated a *reduction* of the reaction rate at long times. In the diffusion-controlled regime the asymptotic law is $n(t) \propto t^{-d/4}$ (d is the spatial dimension) instead of the generally accepted result $n(t) \propto t^{-1}$, in formal chemical kinetics [10]. Such a delayed reaction rate results due to *pattern formation*: during the reaction a whole volume is divided into domains with distinctive sizes $\xi(t) = \sqrt{Dt}$ (the so-called *diffusion length*, D is the diffusion coefficient); each domain contains predominantly either particle A or B only, that is similar particles tend to aggregate and thus a well-stirred system is replaced in time by a self-organized aggregate structure. If one of the partners (reactants) is immobile (say, $D_A = 0$), the reduction in the reaction rate is even larger; for $d = 3$, $n(t) \propto t^{-1/2}$ [3,11]. In this case the spatial distribution of particles A becomes singular, unlike particles B where local inhomogeneities in their spatial distribution are smoothed out at the scale of the diffusion length $\xi(t)$, among *immobile* particles A survive only those rare which statistically existed in isolated groups, so we observe something like raisins (A) in a dough (B).

These results are valid for the reaction between *neutral* particles and it was

generally accepted that self-organization does not occur in the reactions between charged particles interacting through long-range Coulomb forces. In particular, the asymptotic $(t \to \infty)$ concentration decay incorporating many-particle effects was found to be $n(t) \propto t^{-1}$ [3,12], i.e. the same as in standard chemical kinetics [10]. However, for *intermediate* times the reaction rate reveals a certain acceleration due to *non-equilibrium charge screening*. This is caused by both relatively slow diffusive motion of reactants and by their disappearance due to reaction. But what was missed in refs. [3,12] is the peculiarity of the asymmetric case when one of the reactants is *immobile*, $D_A = 0$. We will demonstrate below that in this (degenerate) situation the unique decay asymptotics takes place, $n(t) \propto t^{-5/4}$, corresponding to the *accelerated reaction* (in contrast to the above-discussed reduced reaction rate observed for neutral particles). The kinetics under study is actual for the Frenkel defects in irradiated alkali halide crystals where vacancies are immobile below room temperature whereas their complementary interstitial ions are mobile already above 20–30 K [13,14]. These defects interact via Coulomb potentials and their concentration after prolonged irradiation could be large enough to demonstrate many-particle effects [3].

2. The formalism of many-point particle densities

The quantitative analysis of the problem is based on a set of kinetic equations presented in a review paper [3] (eqs. (2.1), (2.11) to (2.13)). In this paper the effective Coulomb interaction is treated in terms of Debye–Hückel theory [15]. The relevant partial differential equations for the *joint densities* (correlation functions) of both similar (A–A, B–B) and dissimilar (A–B) reactants were solved in this paper by numerical methods; these results are completed below with a qualitative analytical estimate of the decay kinetics. We start from the equation for the macroscopic reactant concentrations

$$\frac{dn(t)}{dt} = -K(t)\, n^2(t) , \tag{1}$$

with the time-dependent reaction rate $K(t)$. Both sets of equations derived in refs. [3,12] and taking into account many-particle effects (provided $D_A, D_B \neq 0$), as well as equations of the formal chemical kinetics [10] neglecting these effects, demonstrate the existence of the limiting $(t \to \infty)$ reaction rate $K(\infty) = K_0 = 4\pi D R_{eff}$ where D is the coefficient of the relative diffusion $(D = D_A + D_B)$, and the effective reaction radius is described by the Debye equation [16], which reads for the black sphere model (AB pairs disappear when particles

approach each other to within a critical distance r_0)

$$R_{\mathrm{eff}} = r_0 \frac{L}{1 - \exp(-L)} .$$ (2)

The dimensionless parameter $L = R/r_0$ contains the *Onsager radius* $R = |e_A e_B|/$ $\varepsilon k_B T$ at which the Coulomb interaction energy equals the thermal energy $(k_B T)$ and the survival probability of a pair is rather small. Therefore, the Onsager radius R is defined by a product of particle charges; the electroneutrality of a whole system is secured by the conditions $n = n_A = n_B$, $e = e_A = -e_B$ so that $R = e^2/\varepsilon k_B T$. Note that for $L \gg 1$, $K_0 \propto R_{\mathrm{eff}} \approx R$ and $K_0 \propto |e_A e_B|$.

Let us estimate analytically the effect of the non-uniform distribution of immobile particles A which, as is shown below, form in time compact aggregates ("raisins") existing on the uniform background of B particles ("dough") (strictly ·speaking, due to their Coulomb repulsion there are no pairs of B particles at relative distances $r \leq R$). Such A-rich aggregates resemble super-particles with effective charges $e_{\mathrm{eff}} \approx N_A e_A$ (where N_A is the number of A particles in an aggregate); therefore the effective recombination radius is roughly $R_{\mathrm{eff}} \approx N_A R$. Making a qualitative estimate, we take into account that diffusive motion of B particles destroys small A aggregates, so that at long time t we have the number of large A-aggregates each occupying the distinctive volumes $V \approx \xi(t)^3$, ξ is the diffusion length. The upper limit estimate of N_A is the mean number of particles A in a volume V, i.e. $N_A = n(t) \xi(t)^3$. Substitution of the reaction rate $K(t) \approx 4\pi D R_{\mathrm{eff}}$ with $R_{\mathrm{eff}} = N_A R$ into eq. (1) leads to the asymptotic law sought for: $n(t) \propto t^{-5/4}$, indicating that the reaction is *accelerated* as compared to the standard result of chemical kinetics, $n \propto t^{-1}$. (It could be attributed to the increase in time of the effective radius R_{eff}.) It is easy to see that both $K(t)$ and R_{eff} increase proportionally to $t^{1/4}$, i.e. as $t \to \infty$, there is *no* limiting magnitude! Note that for neutral particles, when $L = 0$, the reaction rate, in contrast, strives for zero, as $t \to \infty$ [3].

Such an unusual result is confirmed by numerical calculations of the many-particle kinetic equations derived in ref. [3]. Fig. 1 shows the dimensionless non-steady-state reaction rate as a function of time. (The chosen value of $L = 1$ corresponds to the weak electrostatic field; the Onsager radius is small and close to the recombination sphere radius r_0.) The broken curve is the result of standard chemical kinetics [10]; for large t it corresponds to the Debye equation [16]. The kinetics incorporating many-particle effects (not shown) reveals the same limit but provided *both* reactants are mobile; $D_A, D_B \neq 0$! Lastly, the full curve corresponds to our treatment of many-particle effects in the asymmetric case $(D_A = 0)$ – it has *no* steady-state at long reaction times!
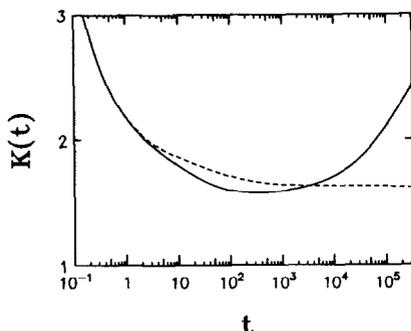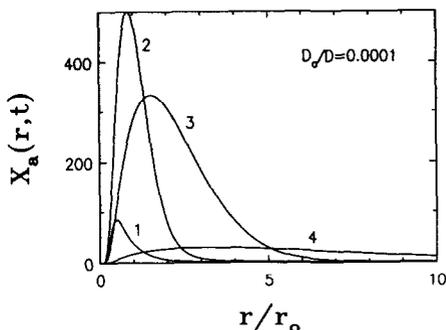
Fig. 1.   Fig. 2.

Fig. 1. The time dependence of the reaction rate $K = K(t)$ in the asymmetric case, $D_A = 0$. K is in dimensionless units $4\pi D r_0$, time in r_0^2/D. The full line is a numerical solution of many-particle equations [3]; the broken line is for the standard chemical kinetics [9]. Parameters are $4\pi n(0) r_0^3 = 0.1$, $L = 1$.

Fig. 2. The joint correlation function of a similar immobile particle A. Parameters are $4\pi n(0) r_0^3 = 0.1$, $L = 1$, $D_A/D = 0.0001$. The curves 1 to 4 correspond to reaction times (in units Dt/r_0^2): 10^1 (1), 10^2 (2), 10^3 (3), 10^4 (4), respectively.

Fig. 2 demonstrates a peculiarity of this problem for very slow-mobile particles A $(D_A/D = 0.0001)$ in terms of the joint correlation function $X_A(r, t)$ for similar particles. This function means physically a ratio of the probability density to find some A particle at a certain distance r from another A to that at their infinite separation, $r \rightarrow \infty$. For short times, $t < 10^2$, aggregates of particles A remind of small compact raisins in a dough (B) but since particles are mobile, at long times their mutual Coulomb repulsion leads to the diffusive destruction of these aggregates, which results finally in the standard *asymptotic* decay law $n(t) \propto t^{-1}$.

3. Conclusion

It is demonstrated that many-particle effects can lead to the unusual *accelerated* decay of reactant concentrations, $n(t) \propto t^{-5/4}$, if two kinds of particles A, B interact via Coulomb forces, participate in the 3D bimolecular $A + B \rightarrow 0$ reaction, and one kind of them is immobile (e.g. $D_A = 0$, which is the actual case for Frenkel defects in alkali halide crystals).

Acknowledgements

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