PATTERN FORMATION AND UNUSUAL $A + B \rightarrow 0$ REACTION KINETICS BETWEEN CHARGED REACTANTS IN LOW DIMENSIONS

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Abstract

The effect of non-equilibrium charge screening in the kinetics of the one-dimensional, diffusion-controlled $A + B \rightarrow 0$ reaction between charged reactants in solids and liquids is studied. Incorrectness of static, Debye-Hückel theory is shown. Our microscopic formalism is based on the Kirkwood superposition approximation for three-particle densities and the self-consistent treatment of the electrostatic interactions defined by the nonuniform spatial distribution of similar and dissimilar reactants treated in terms of the relevant joint correlation functions. Special attention is paid to the pattern formation due to a reaction-induced non-Poissonian fluctuation spectrum of reactant densities. This reflects a formation of loose domains containing similar reactants only. The effect of asymmetry in reactant mobilities ($D_A = 0$, $D_B > 0$) contrasting the traditional symmetric case, i.e. equal diffusion coefficients, ($D_A = D_B$) is studied. In the asymmetric case concentration decay is predicted to be *accelerated*, $n(t) \propto t^{-\alpha}$, $\alpha = 1/3$ as compared to the well-established critical exponent for fluctuation-controlled kinetics in the symmetric case, $\alpha = 1/4$ and/or the prediction of the standard chemical kinetics, $\alpha = 1/2$. Results for the present microscopic theory are compared with the mesoscopic theory.

1 Introduction

Bimolecular $A + B \rightarrow 0$ reactions are quite common in condensed matter physics and physical chemistry; e.g. they occur between primary radiation defects of two types, A and B, which recombine when they approach each other during diffusion walks to within some critical distance r_0. These particles (called Frenkel defects in solids and/or electrons and radicals in liquids) could be neutral or charged.

Many-particle effects caused by the spatial fluctuations of the reactant densities have been intensively studied in recent years in the kinetics of bimolecular chemical reactions, including the above-mentioned $A + B \rightarrow 0$ reaction. A number of quite different techniques and methods were developed for this purpose, including direct computer simulations, a mesoscopic approach, the scaling, as well as microscopic theory - see review articles [1, 2], a monograph [3]) and proceedings of the conference [4]. These studies clearly demonstrated that the kinetic laws established long ago in standard chemical kinetics [5] could be violated, usually at high particle concentrations/long reaction times. In particular, the asymptotic ($t \rightarrow \infty$) concentration decay rate turns out to be $n(t) \propto t^{-d/4}$, where $d \leq 4$ is the spatial dimension, i.e. it is *slower* than the one in standard chemical kinetics, $\alpha = 1/2, 1$ and 1 for $d = 1, 2$ and 3, respectively. This effect, called sometimes 'abnormal kinetics' - abnormal from the standard point of view - is directly related to the reaction-induced non-uniform reactant distribution wich is in contrast to the main prediction of chemical kinetics that all reactants are well stirred and the reaction volume is homogeneous. As a result, modern chemical kinetics uses the language of *critical exponents, correlation lengths, etc* similar to the physics of critical phenomena.

Presently almost all studies of fluctuation-controlled effects deal with neutral, non-interacting particles thus neglecting effects caused by their interaction. In this paper, we study *many-particle effects between charged reactants* focusing on the *dynamical* Coulomb potential screening in the $A + B \rightarrow 0$ reaction.

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2 Kinetic equations

The basic equations of our microscopic theory for interacting particles have been derived and discussed recently for $d = 3$ for the cases of Coulomb [6] and elastic ($U(r) \propto 1/r^3$) [7] interactions. Now, based on results of our review article [2], we generalize these equations for arbitrary space dimension d. This helps to show peculiarities in the transition to low dimensions.

Use of the Kirkwood superposion approximation [8] for decoupling the infinite hierarchy of equations for the correlation functions leads to a minimum set of variables describing the fluctuation-controlled reaction kinetics. They are: macroscopic concentrations, $n_A = n_B = n(t)$, and three kinds of *joint correlation functions* [1, 2] - two for similar particles, $X_\nu(r,t)$, $\nu = A, B$ and a third one for dissimilar particles, $Y(r,t)$, where r is the relative distance between two particles. These functions describe a spatial distribution of pairs AA, BB and AB, respectively and are analogous to the radial distribution function in statistical physics of dense gases and liquids [8]. The physical meaning of these correlation functions is the following [2, 6]: $C_A^{(a)}(r,t) = n(t)X_A(r,t)$ and $C_B^{(a)}(r,t) = n(t)Y(r,t)$ are mean densities of particles A and B, respectively at the relative distance r provided that a probe particle A is in the coordinate origin. Introducing for simplicity a new function $X(r,t) = (X_A(r,t) + X_B(r,t))/2$ the basic set of kinetic equations read:

$$\frac{dn(t)}{dt} = -K(t)n^2(t)\ ,\ K(t) = \gamma_d\ r_0^{d-1}\ |\mathrm{j}(r_0,t)|\ , \tag{1}$$

$$\partial Y(r,t)/\partial t = \nabla \mathrm{j}(r,t) - 2n(t)K(t)Y(r,t)J_d[X]\ , \tag{2}$$

$$\mathrm{j}(r,t) = (D_A + D_B)\left\{\nabla Y(r,t) + \beta \nabla U'_{AB}(r,t)Y(r,t)\right\}, \tag{3}$$

$$\partial X_\nu(r,t)/\partial t = \nabla \mathrm{j}_\nu(r,t) - 2n(t)K(t)X_\nu(r,t)J_d[Y], \tag{4}$$

$$\mathrm{j}_\nu(r,t) = 2D_\nu\left\{\nabla X_\nu(r,t) + \beta \nabla U'_{\nu\nu}(r,t)X_\nu(r,t)\right\}\ . \tag{5}$$

In Eqs.(1) to (5) the black-sphere recombination model is assumed implicitly: any AB pair recombines instantly when two reactants during their diffusive walks approach each other to within some critical distance r_0 [1, 2]. This fact is incorporated into the (Smoluchowski) boundary condition for the correlation function of dissimilar particles; $Y(r \le r_0, t) = 0$ in Eq.(2). This correlation function defines the quantity of primary importance - the *reaction rate* $K(t)$ which is a flux of particles over the recombination sphere's surface ($\gamma_d = 2, 2\pi, 4\pi$ for $d = 1, 2, 3$, respectively). For a finite r_0 the reaction rate reads

$$K(t) = \gamma_d r_0^{d-1} \partial Y(r,t)/\partial r|_{r=r_0}.$$

The non-linear terms in Eqs. (2), (4) containing the functionals $J_d[Z]$ arise directly from the Kirkwood approximation [3, 8]. Their expressions for $d = 1, 2, 3$ are given in ref.[2]. In particular,

$$J_1[Z] = (Z(r + r_0, t) + Z(|r - r_0|, t))/2 - 1\ . \tag{6}$$

Expressions for the flux densities j(r,t) and j_ν(r,t) ($\beta = 1/k_BT$) are also non-linear since the effective potential energies $U'_{\lambda\mu}(r,t)$ have contributions of both direct ($\lambda\mu$ pair) and indirect, lateral particle interactions through surrounding particles. The technique for their calculation in the case of a short-range potential has been discussed in ref.[7], whereas that for the Coulomb potentials in ref.[6].

Low-dimensional ($d = 1, 2$) systems with Coulomb interaction reveal a peculiarity which allows us to reduce the number of independent variables and to simplify the kinetic equations. Namely,

we can do the limiting transition $r_0 \to 0$ retaining the finite reaction rate. Physically this means that the reaction rate is governed by the effective radius. This radius is the largest one of the scale lengths in the system. For the Coulomb systems such a scale is called the *Onsager radius*, $R = e^2/\varepsilon k_B T$ [6]. This is a distance at which the thermal energy equals the attraction energy; when approaching to within R two reactants cannot separate and thus inevitably recombine. Usually $R >> r_0$ and thus R determines the reaction rate. Neglecting many-particle effects, the latter has a very simple form: $K = 4\pi D R_{eff}$ [2, 5]. In the limiting case of $r_0 \to 0$ the functional $J_d[Z]$ in eqs.(2),(4) is greatly simplified, $J_d[Z]$=Z(r,t)-1.

The recombination kinetics is defined by the following dimensionless parameters: (i) the initial particle concentration $n(t=0) = n(0)$, (ii) the *partial* diffusion coefficient $\kappa = D_A/D$ (note that dimensionless diffusion coefficients are related by the condition $D_A + D_B = 2$, i.e. $D_A = 2\kappa$, $D_B = 2(1-\kappa)$), (iii) the capillary radius r_c (in the $1d$ case). For more details see [3, 10].

3 Results

3.1 Concentration decay

The kinetics of the concentration decay has been calculated for high initial concentration $n(0) = 1$ and long dimensionless time, $t = 10^8$. At this moment particle concentration drops by three orders of magnitude. (Further concentration decay hardly could be measured experimentally.) To make results more obvious, in Fig.1 we plotted not the very kinetic curves, $n = n(t)$, but their slopes on a logarithmic scale which defines the so-called *current critical exponents*

$$\alpha(t) = -\frac{d\ \ln n(t)}{d\ \ln t}. \tag{7}$$

To demonstrate the importance of the effect of *non-equilibrium* charge screening neglected in many previous studies, we present results for three different approximations as follows.

(i) The traditional, Debye-like treatment of the reaction kinetics with unsreened Coulomb interaction [8].

Many-particle effects are neglected, the kinetic equations arise due to linearization of equations for the correlation functions. As a result, the equation for the correlation function of *similar* particles $X_\nu(r,t)$ no longer affects the kinetics. In fact, the latter is defined entirely by the joint correlation function of dissimilar particles obeying the simple kinetic equation

$$\frac{\partial Y(r,t)}{\partial t} = \frac{\partial}{\partial r}\left\{\frac{\partial}{\partial r}Y(r,t) + Y(r,t)\frac{\partial}{\partial r}U(r)\right\}, \tag{8}$$

where $U(r) = -1/r$ is the unscreened Coulomb potential. After linearization of a set of kinetic equations, their solution no longer depends on the partial diffusion coefficient κ (solid and dashed lines in Fig.1). At long times the solution of Eq.(8) is practically defined by the diffusion length $\xi = \sqrt{t}$, i.e. the decay kinetics obeys the 'classical' algebraic law, $n(t) \propto t^{-\alpha}$, $\alpha = 1/2$.

(ii) The complete set of Eqs. (1) to (6) incorporating many-particle effects (via non-linear terms) but with linearized potentials, $U_A(r,t) = U_B(r,t) = -U(r,t) = 1/r$.

In this intermediate approximation the kinetics under study begins to depend on the mobility parameter κ but asymptotically it still follows the kinetics known for neutral, non-interacting particles with $U(r) = 0$.

(iii) The complete set of kinetic equations is combined with non-equilibrium treatment of charge screening making now no linearization.

The dimensionless capillary radius was chosen as $r_c = 0.1$. (Its reduction to the value of 0.01 results in a small, logarithmic correction which does not affect the critical exponent.) Curve 1 in Fig.1 shows that in the time interval considered the critical exponent rather rapidly approaches

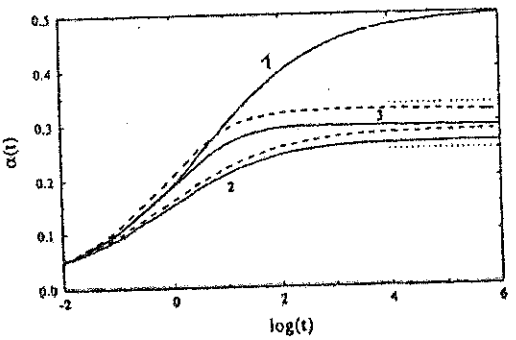

FIG. 1. The critical exponent characterizing the algebraic concentration decay, Eq. (7), as a function of dimensionless reaction time. Solid curves—symmetric reactant mobilities, $D_A = D_B$; dashed curves—asymmetric mobilities, $D_A = 0$. Dotted lines show the two expected asymptotes: $\alpha = \frac{1}{4}$ and $\frac{1}{3}$. Curves 1 correspond to the Debye theory, curves 2 to a solution of the kinetic Eqs. (1)–(6) incorporating spatial reactant correlations but neglecting dynamical charge screening, and curves 3 to the case when all screening effects are incorporated.

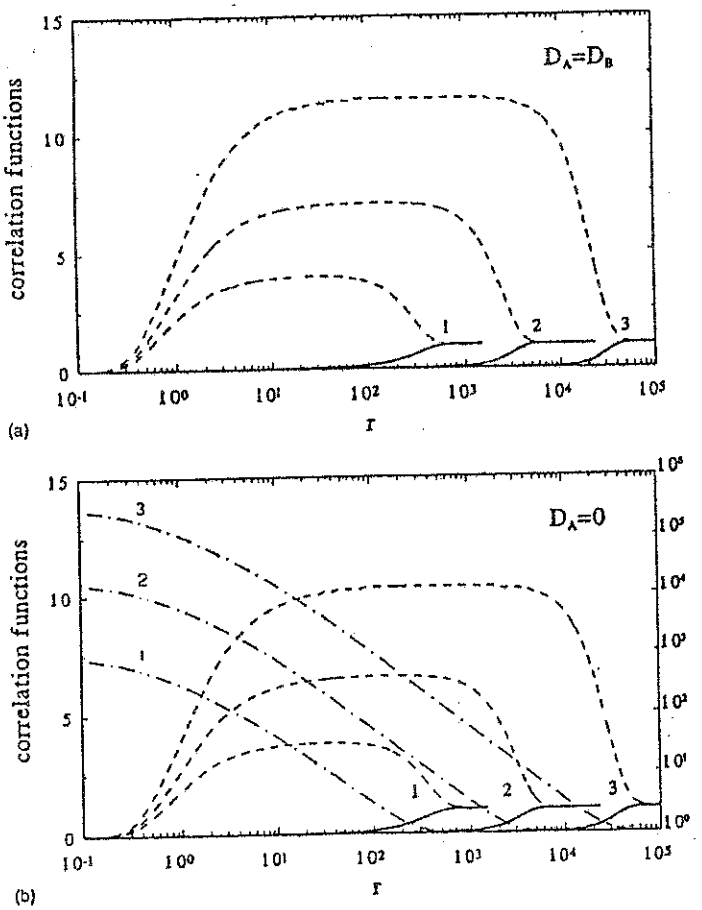

FIG. 2. The joint correlation function of dissimilar particles, $Y(r,t)$ (solid curve), and that of similar particles, $X_A(r,t)$ (dot-dashed curve) and $X_B(r,t)$ (dashed curve). Curves 1–3 correspond to the dimensionless times 10^4, 10^6, and 10^8, respectively. (a) Symmetric mobility case, $D_A = D_B$. (b) Asymmetric case, $D_A = 0$. Note that in case (a) $X_A(r,t) = X_B(r,t) = X(r,t)$; in case (b) $X_A(r,t)$ is plotted on a logarithmic scale.

its limiting 'classical' value of 1/2. Curves 2, incorporating many-particle effects, approach their *quasi*-steady-state after nearly the same time but their further approach from above to another asymptote wich $\alpha = 1/4$ has a logarithmically slow character. For example, for the symmetrical mobilities $\alpha(t = 10^8) = 0.264$. In the asymmetric mobility case the deviation from the asymptote is larger, $\alpha(t = 10^8) = 0.280$. Such a behaviour results from the long-range nature of the Coulomb interaction between particles.

Strictly speaking, the $\alpha = 1/4$ law of the fluctuation-controlled kinetics in $d = 1$ is proved only for non-interacting particles [1, 2, 4]. It was generalized for interacting particles *provided* that their interaction potential is short-range and does not lead to the similar-particle collapse [3]. In fact, this law has been proved for the case when the largest length parameter in the problem is the diffusion length, which is the case if the interaction potential was a Debye- Hückel like. However, the uncreened Coulomb potential, $U(r) = -1/r$, has an *infinite* interaction radius and thus defines the asymptotics of the correlation functions at large distances. The approach to the asymptotic character is very slow, it has diffusion-controlled character. Moreover, in the asymmetric case there is no mechanism of smoothing the fluctuations of the immobile particle distribution at all. This is why the results of our case (ii) are far from trivial.

Lastly, curves 3 in Fig.1 show a considerable difference for the symmetric and asymmetric mobilities which is more pronounced than that in curves 2. However, due to a very slow approach to their limiting values it is not clear whether and by how much the relevant critical exponents differ as $t \to \infty$. Analytical arguments are given in ref. [10] that in the symmetric case $\alpha = 1/4$ (as for non-interacting particles), whereas for asymmetric mobilities the critical exponent is *larger* and the reaction occurs respectively faster, $\alpha = 1/3$. Note that a similar *reaction acceleration* between charged particles with asymmetric mobilities was predicted earlier in the $3d$ case [6]. We found there that $\alpha = 5/4$, to be compared with $\alpha = 1$ known in the standard chemical kinetics, and $\alpha = 3/4$ in the fluctuation-controlled theory. Analogously, in $2d$ [9] we predict $\alpha = 1/2$ and $3/4$ for symmetric and asymmetric mobilities, respectively. Consider now briefly the kinetics of the pattern formation in the particle spatial distribution.

3.2 Spatial reactant distributions

Figure 2 shows the time development of the joint correlation functions (note the logarithmic scale on the x axis and the same scale for immobile similar particles X_A). A key role of the diffusion length $\xi(t) = \sqrt{t}$ is evident here: the characteristic relative distance ξ' at which no AB pairs exist ($Y(r < \xi', t) << 1$) increases in time as $\sqrt{t}$: ξ' increases by an order of magnitude as time increased by *two* orders of magnitude, $\xi' = \xi(t)$.

Irrespective of the κ value, the correlation functions of mobile particles, $X_\nu(r, t)$, have a plateau at the same scale $r < \xi'$ and decrease rapidly to zero at $r < 1$. (This comes from the repulsion of similar particles at the relative distances which are short compared to the Onsager radius). In the asymmetric case the correlation functions of similar immobile particles have singularities at short r, where $X_A(r, t)$ drops by several orders of magnitude in a narrow interval $r \in (0, 1)$.

A comparison of these results with earlier findings for non-interacting particles [11] shows their remarkable similarity. The main difference lies in the depletion in the correlation functions of similar mobile particles at short relative distances caused by particle repulsion, whereas for neutral particles the correlation functions are finite as $r \to 0$. For non-interacting particles and symmetric diffusion such a behaviour of the correlation functions led to the conclusion that the *pattern formation* occurs in a form of alternating *domains* of similar particles, A or B, with linear size $\xi(t)$ [1, 2, 3]. This reaction-induced reactant-structure greatly differs from the basic assumption of standard chemical kinetics about well-stirred and homogeneous reactant distribution. In the domain structure reaction occurs only at the boundaries of the domains of particles of different type. In the asymmetric diffusion case for both non-interacting and interacting particles mobile B reactants remain randomly

distributed within their domains, whereas immobile A reactants form compact clusters - a kind of "raisins in dough" [6, 11]. The $2d$ case will be discuss in detail in ref. [9].

4 Conclusions

We compare in the conclusion the main results of the mesoscopic [3] and the present, microscopic formalism for the diffusion-controlled $A + B \to 0$ reaction between charged particles in the $1d$ case. The former theory claims that the critical exponents in the concentration algebraic decay is the same for charged and neutral particles *provided*:

(i) similar particles (AA, BB) repel each other, and (ii) the pair interaction potential is not divergent (e.g. the Debye- Hückel potential).

Our microscopic theory generalizes this result (valid for the case of symmetric particle mobilities) for the *unscreened* (divergent) Coulomb potential. Moreover, we have studied here the case of asymmetric mobilities ($D_A = 0$, $D_B > 0$) and predicted reaction *acceleration*, i.e. an existence of a new critical exponent, $\alpha = 1/3$. We have also demonstrated that this peculiarity is a direct consequence of the *specific spatial distribution of reactants* studied by us in terms of the joint correlation functions for both similar and dissimilar reactants. A large discrepancy between the two approaches takes place for the accumulation kinetics under permanent particle source [9, 10].

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