

# The kinetics of the bimolecular $A + B \rightarrow 0$ reaction in condensed matter: Effects of non-equilibrium charge screening

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(Received 22 May 1996; accepted 22 August 1996)

The kinetics of the bimolecular  $A + B \rightarrow 0$  reaction between charged reactants is studied in two dimensions, i.e., on a surface. The theory is based on the Kirkwood superposition approximation for three-particle densities and the self-consistent treatment of the electrostatic interactions defined by the non-uniform spatial distribution of similar and dissimilar reactants. Special attention is paid to pattern formation and many-particle effects arising from reaction-induced formation of loose domains containing similar reactants only. It is shown that the critical exponent  $\alpha$  characterizing the algebraic concentration decay law,  $n(t) \propto t^{-\alpha}$ , differs strongly between symmetric ( $D_A = D_B$ ) and asymmetric ( $D_A = 0$ ) reactant mobilities. This effect is abnormal from the point of view of standard chemical kinetics. It arises directly from the specific spatial distribution in the system as in ‘raisons  $A$  in a dough  $B$ .’ At long reaction times the asymptotics of the interaction potentials is of non-equilibrium type at large relative distances. The accumulation kinetics in the presence of a permanent source is studied. Results of the microscopic formalism are compared with a previous mesoscopic theory. © 1996 American Institute of Physics. [S0021-9606(96)51144-X]

## I. INTRODUCTION

The theory of diffusion-controlled chemical reactions initiated long ago by Smoluchowski (1917)<sup>1</sup> attracted in recent years new attention after the discovery of the important role of the *reactant density fluctuations*.<sup>2-9</sup> Unlike well-studied elementary bimolecular reactions, e.g.,  $A + B \rightarrow 0$ , between non-interacting particles, many-particle effects in the reaction between *interacting* reactants remain a poorly studied problem. In the above reaction ‘0’ denotes the neutral reaction product which is supposed not to influence the reaction any further. We also consider an irreversible reaction. Such studies could be classified qualitatively into two categories: *mesoscopic* and *microscopic ones*. The former approach<sup>10-12</sup> contains only one additional interaction parameter, as compared to the mesoscopic theory for neutral reactants; the reaction event itself is not treated directly. Moreover, additional assumptions about the interaction potential symmetry,  $U_{AA}(r) = U_{BB}(r) = -U_{AB}(r)$ , and integrability of  $U_{AB}(r)$  are made. This approach is suited to the study of the reaction *asymptotics* as  $t \rightarrow \infty$  which is determined by large-scale density fluctuations and is independent of the details of the short-range interaction between the particles; the main factor here is the spatial dimension. However, this formalism is no longer valid for the case of *attraction* between similar particles, where small-scale density fluctuations become a key factor.<sup>10</sup>

The alternative, microscopic approach<sup>13-15</sup> takes into account all details of the reactant interactions. One can thus

treat the kinetics at *all* reaction times and for all possible situations including the colloid formation due to attraction of similar reactants.<sup>15</sup> The bottleneck of this approach is the necessity of a numerical solution of a set of integro-differential equations.

The main effort of the mesoscopic approach is focused on the derivation of a non-linear stochastic equation allowing an analytical solution. For this purpose additional symmetry conditions are imposed on the diffusion coefficients ( $D_A = D_B$ ) and the interaction potentials since this reduces the number of kinetic equations to be solved, whereas the potential integrability condition permits one to exclude the appearance of non-local terms in the equations. However, these conditions are often inadequate for real situations, e.g., in describing the reaction between point (Frenkel) defects in solids, where the mobility of vacancies is many orders of magnitude less than that of interstitial atoms, and the elastic interaction between vacancies differs from that between interstitial atoms.<sup>16</sup>

More important is the problem of the integrability of the interaction potential. The kinetics of bimolecular reactions between interacting particles with an unscreened Coulomb potential was considered for the first time in 1942.<sup>17</sup> In the 1970's, it was suggested<sup>18</sup> to take into account the reactant *charge screening effects* in the spirit of the statistical physics of dense systems, i.e., by substituting the singular Coulomb potential with an infinite radius by the Debye-Hückel potential having a finite action radius. Recently, it has been

shown<sup>13</sup> that charge screening in chemical reactions is a *non-equilibrium* effect and depends essentially on the reactant spatial distribution (*pattern formation* developed in the course of a chemical reaction).

The use of the Debye–Hückel potential corresponds to the physical situation of a probe reactant surrounded by a cloud of oppositely charged particles such that its effective potential drops much faster than  $1/r$ . Many-particle effects in a system of neutral particles reveal themselves through the effective aggregation of *similar* particles.<sup>2–9</sup> If this is also the case for charged reactants, i.e., a probe reactant is surrounded by particles of the *same* charge, its effective charge seen from a long distance can be larger than the charge of a single reactant and the effective potential is stronger than  $1/r$ . The relevant modification of the reactant interactions, in its turn, can affect the reaction kinetics and their asymptotics.

The previous microscopic study for the three-dimensional ( $3d$ ) case<sup>13</sup> has demonstrated that the non-equilibrium charge screening indeed takes place, i.e., the static, Debye–Hückel model is not adequate for chemical reactions. In the case of the asymmetric reactant mobilities,  $D_A = 0$ ,  $D_B > 0$ , the concentration decay is *accelerated*,  $n(t) \propto t^{-5/4}$ , as compared to the fluctuation-controlled reaction between neutral particles,  $n(t) \propto t^{-3/4}$ . (For the symmetrical mobility case,  $D_A = D_B$ , the decay law of standard chemical kinetics,  $n(t) \propto t^{-1}$ , is found.) The effect of elastic interaction between neutral defects in solids ( $U_{AB} \propto 1/r^3$ ) has been discussed for the  $3d$  case in Ref. 14.

In this paper, we extend the study of Ref. 13 to the two-dimensional ( $2d$ ) case (surface processes) and the particle accumulation in the presence of a permanent source. In Section II we consider the effective particle interaction for spatial dimensions  $d \leq 2$ . In Sections III and IV the basic kinetic equations are discussed for the cases of concentration decay and accumulation, respectively. Reaction kinetics for the  $2d$  case and symmetric/asymmetric reactant mobilities are presented in Section V. The main results are summarized in Section VI. It is shown that the peculiarity of low dimensional systems of interacting particles is a considerable simplification of the reaction event model. Unlike the  $3d$  case, where the reaction event is described in terms of the reaction sphere of a given radius  $r_0$ ,<sup>6,9,13</sup> in low dimensional systems this radius can be put to be zero because the reaction rate is defined by the effective (Onsager) radius. This allows one to reduce the number of independent parameters and to compare directly the results of the microscopic approach with the mesoscopic theory.

## II. EFFECTIVE INTERACTION OF CHARGED PARTICLES

Our microscopic theory of bimolecular chemical reactions<sup>6,9,13–15</sup> is based on the Kirkwood superposition approximation for three-particle densities and thus operates with the time development of macroscopic reactant concentrations (macroscopic, one-particle densities)  $n_\nu(t)$  ( $\nu = A, B$ ) and with only the joint correlation functions for similar particles,  $X_\nu(r, t)$ , and for dissimilar particles,

$Y(r, t)$ . The joint correlation functions are normalized to unity as  $r \rightarrow \infty$ . In electro-neutral system concentrations of both kinds of particles coincide,  $n(t) = n_A(t) = n_B(t)$  and  $e = e_A = -e_B$ .

The joint correlation functions have a very clear and transparent physical meaning. For a probe particle of the type  $\nu$  in the origin of the coordinate system, the function  $C_\nu^a(r, t) = n(t)X_\nu(r, t)$  gives the average concentration of similar particles at a distance  $r$  from the origin.  $C_b^a(r, t) = C_b^a(r, t) = n(t)Y(r, t)$  is the concentration of particles of the other type. This is why  $\sigma_\nu(r, t) = e_\nu n(t) \times (X_\nu(r, t) - Y(r, t))$  can be interpreted as the mean *charge density* induced by a probe charge in the coordinate origin. This quantity is used below in the calculation of the effective potentials in the spirit of the Debye–Hückel theory.<sup>19</sup> Note that the treatment of low dimensional systems ( $d \leq 2$ ) requires a modification of the problem. Let us start with the Poisson equation (in its integral form) for the potential produced by a probe charge

$$\varphi_\nu(x, y, z, t) = \frac{e_\nu}{\varepsilon r} + \int \frac{\rho_\nu(\mathbf{r}', t) dx' dy' dz'}{\varepsilon |\mathbf{r} - \mathbf{r}'|}. \quad (1)$$

Here  $\varepsilon$  is the dielectric constant and  $\rho_\nu$  the density of induced charge. Assume that the surface ( $2d$ ) reaction under study occurs in the  $x, y$  plane, whereas the reaction in a capillary ( $1d$ ) takes place on the  $x$ -axis. In the former case we are interested only in the potential at  $z = 0$ ,  $\phi_\nu(r, t) = \varphi_\nu(x, y, z = 0, t)$  with  $r = \sqrt{x^2 + y^2}$ . It can be obtained from Eq. (1) with the evident substitution,  $\rho_\nu(x, y, z, t) = \sigma_\nu(x, y, t) \delta(z)$ , where  $\delta$  is Dirac delta-function. As a result, we obtain the integral relation

$$\phi_\nu(r, t) = \frac{e_\nu}{\varepsilon r} + \int \frac{\sigma_\nu(\mathbf{r}', t) dx' dy'}{\varepsilon |\mathbf{r} - \mathbf{r}'|}, \quad (2)$$

which permits us to calculate the interaction energies for reactant pairs in the framework of the Debye–Hückel theory:

$$U_{\nu\nu}(r, t) = e_\nu \phi_\nu(r, t), \quad (3)$$

$$U_{AB}(r, t) = -(U_{AA}(r, t) + U_{BB}(r, t))/2. \quad (4)$$

The  $1d$  case is more problematic. A formal substitution  $\rho_\nu(x, y, z, t) = \sigma_\nu(x, t) \delta(y) \delta(z)$  is not sufficient since the potential on the  $x$  axis is logarithmically divergent as follows from Eq. (1). This effect can be avoided if one assumes that the capillary has a small but finite radius. Analysis of this problem shows that the results depend on this additional parameter only weakly.

## III. KINETIC EQUATIONS

A detailed derivation of the basic kinetic equations has been given in Refs. 13, 14. However, the  $3d$  presentation of these equations is not convenient in the present study. Therefore we will rewrite these equations taking into account results of our previous studies.<sup>6,9</sup> The concentration development has the standard form of the law of mass action:

$$dn(t)/dt = -K(t)n(t)^2. \quad (5)$$

Here  $K(t)$  is the time-dependent *reaction rate* which is defined usually by the flux of particles through the surface of the black sphere of radius  $r_0$

$$K(t) = \gamma_d r_0^{d-1} |\mathbf{j}(r_0, t)|, \quad (6)$$

where  $\gamma_d$  is the surface of the unit sphere. In particular,  $\gamma_d = 2, 2\pi$  and  $4\pi$  for  $d = 1, 2, 3$ , respectively. To calculate the particle flux, the following set of equations for the correlation functions should be solved

$$\partial Y(r, t) / \partial t = \nabla \mathbf{j}(r, t) - 2n(t)K(t)Y(r, t)J_d(X), \quad (7)$$

$$\mathbf{j}(r, t) = D(\nabla Y(r, t) + \beta Y(r, t)\nabla U_{AB}(r, t)), \quad (8)$$

$$\partial X_\nu(r, t) / \partial t = \nabla \mathbf{j}_\nu(r, t) - 2n(t)K(t)X_\nu(r, t)J_d(Y), \quad (9)$$

$$\mathbf{j}_\nu(r, t) = 2D_\nu(\nabla X_\nu(r, t) + \beta X_\nu(r, t)\nabla U_{\nu\nu}(r, t)). \quad (10)$$

Here  $U_{\lambda\nu}(r, t)$  are the effective interaction energies defined in Section II,  $\beta = 1/k_B T$ ,  $X(r, t) = (X_A(r, t) + X_B(r, t))/2$ , and  $D_\nu$  are partial diffusion coefficients,  $D = D_A + D_B$ . The kinetic equations contain also some functionals of the correlation functions,  $J_d(Z)$ , which depend on the spatial dimension. Their explicit expressions for  $d = 1, 2, 3$  are given in the review paper.<sup>9</sup>

For low dimensional systems ( $d \leq 2$ ) the kinetic equation can be significantly simplified by the limiting process,  $r_0 \rightarrow 0$ . The recombination flux, Eq. (6), remains finite due to the peculiarity of the Coulomb potential at small  $r$ . As is well known<sup>13,17</sup> in the system of Coulomb particles the predominant role is played by the *Onsager radius*,  $R = e^2/\epsilon k_B T$ . This is a distance at which the energy of Coulomb attraction equals the thermal energy. When two particles approach each other to this radius, they unavoidably react. In the limit  $r_0 \rightarrow 0$  the functionals  $J_d(Z)$  are greatly simplified by

$$J_d(Z) = Z(r, t) - 1. \quad (11)$$

To solve numerically the above-given set of kinetic equations, it is convenient to use the following standard dimensionless variables  $r' = r/R$ ,  $t' = Dt/R^2$ ,  $n'(t') = \gamma_d n(t)r_0^d$ ,  $D'_\nu = 2D_\nu/D$ . In the new variables the equations read (primes are omitted hereafter)

$$K(t) = \lim_{r \rightarrow 0} r^{d-1} |\mathbf{j}(r, t)|, \quad (12)$$

$$\partial Y(r, t) / \partial t = \nabla \mathbf{j}(r, t) - 2n(t)K(t)Y(r, t)(X(r, t) - 1), \quad (13)$$

$$\mathbf{j}(r, t) = \nabla Y(r, t) + Y(r, t)\nabla U(r, t), \quad (14)$$

$$\partial X_\nu(r, t) / \partial t = \nabla \mathbf{j}_\nu(r, t) - 2n(t)K(t)X_\nu(r, t)(Y(r, t) - 1), \quad (15)$$

$$\mathbf{j}_\nu(r, t) = D_\nu(\nabla X_\nu(r, t) + X_\nu(r, t)\nabla U_\nu(r, t)). \quad (16)$$

This set of equations should be extended by the effective interaction energies, Eqs. (2)–(4). These latter quantities can be written in the form

$$U_\nu(r, t) = 1/r + n(t) \int L_d(r, r')(X_\nu(r', t) - Y(r', t)) dr', \quad (17)$$

$$U(r, t) = -(U_A(r, t) + U_B(r, t))/2, \quad (18)$$

where  $L_d(r, r')$  is a kernel which depends on the spatial dimension only.

Therefore, the kinetic problem is reduced to the numerical treatment of a set of non-linear integro-differential equations. In low dimensional system the most time-consuming step is the calculation of the integral relations for potentials, Eq. (17), whereas the solution of Eqs. (13)–(16) is less difficult, e.g., using their quasi-linearization.<sup>9</sup> Note that in the  $3d$  case the Poisson equation could be presented in differential form which greatly simplifies its solution.<sup>13</sup>

Surface reactions need the following parameters to be defined: initial (dimensionless) concentration  $n(0)$ , relative diffusion coefficient  $\kappa = D_A/D$  (in the dimensionless units  $D_A + D_B = 2$ ,  $D_A = 2\kappa$ ,  $D_B = 2(1 - \kappa)$ ). In standard chemical kinetics the parameter  $\kappa$  does not appear at all, the reaction rate for the  $3d$  recombination (in dimensional units) is well-known to be  $K_0 = K(\infty) = 4\pi(D_A + D_B)r_0$ . Note that the dimensionless equations no longer contain the Onsager radius  $R$ , which does not affect the reaction asymptotic. However, the kinetic equations contain several hidden parameters of the dimension of a length. One of them is the so-called *diffusion length*,  $\xi(t) = \sqrt{Dt}$  ( $\xi(t) = \sqrt{t}$  in the dimensionless units) affecting the reaction kinetics.<sup>2-6,8-10,12-15</sup> Other length parameters could be derived via the particle interaction energy at long distances, e.g.,  $U(r, t) = -\xi_U(t)/r$  as  $r \rightarrow \infty$ . We show below that an analysis of the relation between these lengths leads to a better understanding of the obtained results.

#### IV. GENERALIZATION FOR THE ACCUMULATION KINETICS

The above-given kinetic equations could be easily generalized for the case of particle *accumulation* under permanent source. Note that because of the limiting process  $r_0 \rightarrow 0$  the accumulation reaction remains completely diffusion-controlled. If the reaction has a finite reaction radius (e.g., in the  $3d$  case) a problem arises due to particle creation inside the recombination spheres of pre-existing particles.<sup>9,20</sup> In the limiting case of zero recombination radius Eqs. (5), (13), (15) should be extended by the additional production terms<sup>20</sup>

$$dn(t)/dt|_g = \zeta, \quad (19)$$

$$\partial Y(r, t) / \partial t|_g = 2\zeta(1 - Y(r, t))/n(t), \quad (20)$$

$$\partial X_\nu(r, t) / \partial t|_g = 2\zeta(1 - X_\nu(r, t))/n(t), \quad (21)$$

where a new dimensionless parameter  $\zeta = \gamma_d p R^{d+2}/D$  contains the dimensional creation rate of particles  $p$  (per unit time/“volume”).

#### V. RESULTS

##### A. The kinetics of concentration decay

We present and discuss below the reaction kinetics for the  $2d$  case. The initial dimensionless reactant concentration is taken to be  $n(0) = 1$ ; its value does not affect the asymp-

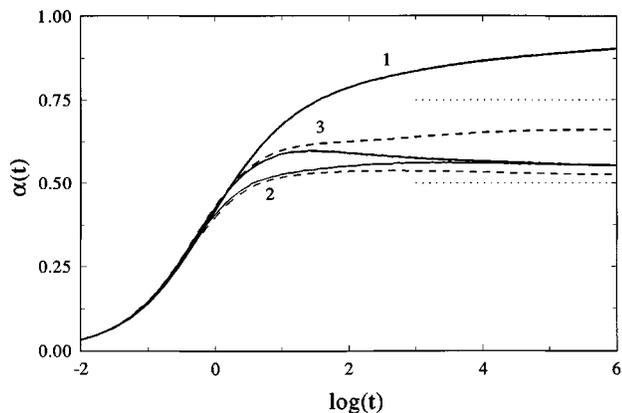


FIG. 1. The critical exponent characterizing algebraic concentration decay, Eq. (22), as a function of reaction time. Full curves—symmetric reactant mobilities,  $D_A = D_B$ , dashed curves—asymmetric mobilities,  $D_A = 0$ . Dotted lines show the two expected asymptotes:  $\alpha = 1/2$  and  $\alpha = 3/4$ . Curves 1 correspond to the Debye theory, curves 2—solution of the kinetic Eqs. (12)–(16) incorporating spatial reactant correlations but neglecting dynamical charge screening, curves 3—all screening effects incorporated, Eq. (17).

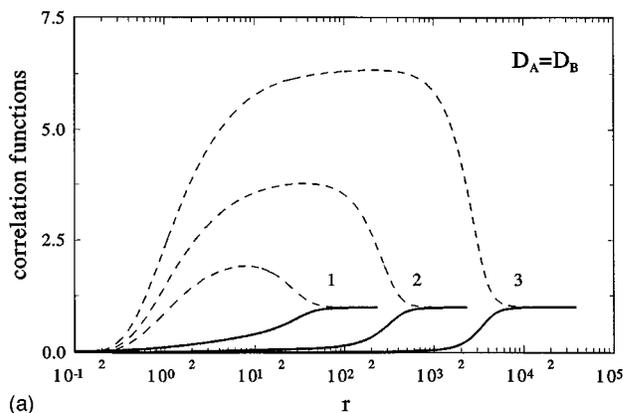
otic decay law. We monitored the reaction kinetics up to  $t = 10^6$  (in dimensionless units) when the reactant concentration has dropped by 4 orders of magnitude, irrespective of the diffusion coefficient. It is convenient to characterize the concentration kinetics by the slope of the current concentration vs time taken in double logarithmic coordinates,<sup>6,9</sup> the so-called current *critical exponent*:

$$\alpha(t) = -d \log n(t) / d \log t \equiv K(t)n(t)t. \quad (22)$$

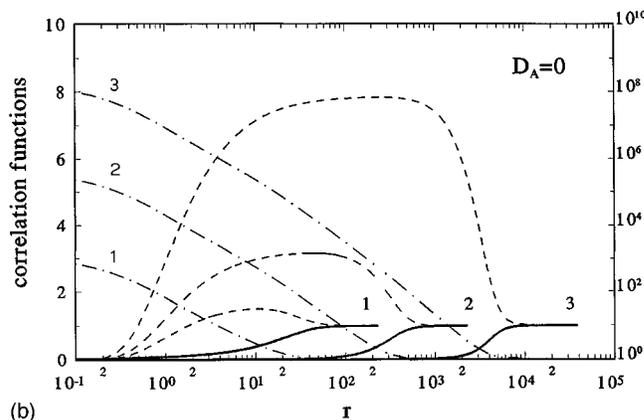
The fundamental feature of the kinetics is its limiting value,  $\alpha = \alpha(t \rightarrow \infty)$  corresponding to the algebraic concentration decay law,  $n(t) \propto t^{-\alpha}$ . The standard chemical kinetics predicts for  $d = 2, 3$   $\alpha = 1$ .

Figure 1 presents results of several approximations in the decay kinetics between charged particles. Curve 1 corresponds to the standard Debye theory.<sup>17</sup> This is the particular case of our kinetic Eqs. (5), (12)–(14) with non-linear terms omitted. Here the partial diffusion coefficient  $\kappa$  does not arise and thus only one kinetic curve is presented. The current critical exponent approaches monotonically (logarithmically) the above-mentioned “classical” value of  $\alpha = 1$ . It is evident that the saturation occurs only at very long reaction times which practically cannot be reached either in analytic calculations or in computer simulations. We can only extrapolate the results obtained here for  $t \leq 10^6$ .

Curves 2 show results of our non-linear kinetics in which many-particle effects in the Coulomb interactions are neglected. In other words, the *unscreened* potentials,  $U_{\nu}(r, t) = 1/r$ , are used here. Almost irrespective of the partial diffusion coefficient  $\kappa$ , the critical exponent logarithmically approaches  $\alpha(t \rightarrow \infty) = 1/2$  (dotted line). It is important to note that the same asymptotics follows from our kinetic equations for non-interacting (neutral) reactants ( $U_{\lambda\nu}(r) = 0$ ). Their fundamental asymptotic behavior follows the universal law established in recent years for the fluctuation-controlled chemical kinetics,  $n(t) \propto t^{-d/4}$ , with  $d$



(a)



(b)

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  $10^2$ ,  $10^4$ , and  $10^6$ , respectively. (a) Symmetric 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 in the logarithmic scale.

the space dimension.<sup>2–6</sup> In other words, incorporation of the long-range Coulomb interactions is not sufficient to change the asymptotic behavior of the reaction. (For neutral reactants the limiting value of  $\alpha$  is reached much faster<sup>6,9</sup> than for charged reactants.)

Last, curves 3 present a solution of our complete set of kinetic equations making *no* approximations. The effect of partial diffusion coefficients is obvious here: the full curve for the symmetric diffusion coefficients ( $D_A = D_B$ ) asymptotically approaches the curves 2 ( $\alpha = 1/2$ ), whereas the critical exponent for the asymmetric diffusion ( $D_A = 0$ ) (dashed line) tends to increase up to the value  $\alpha = 3/4$  obtained earlier for non-interacting particles in the  $3d$  case.<sup>13</sup> Let us analyze now the *spatial distribution* of reactants in terms of the joint correlation functions.

Figure 2 shows the time development of the correlation functions for the symmetric (a) and asymmetric (b) mobility cases. It should be remembered that in the case of non-interacting particles involved in the bimolecular  $A + B \rightarrow 0$  reaction—irrespective of the spatial dimension—the pattern formation takes place. Alternating aggregates (*domains*) containing only similar particles,  $A$ 's or  $B$ 's<sup>2–9</sup> are formed. Each domain has the characteristic size  $\xi = \sqrt{Dt}$  (the above-

mentioned diffusion length). That is, instead of a reaction in a homogeneous medium with well-stirred reactants we have here the reaction between  $A$ -rich and  $B$ -rich domains. It follows from Fig. 2(a) that the same is true for the symmetric case of *interacting* particles. The relevant correlation functions for dissimilar reactants  $Y(r, t)$  reveal a step-like shape, i.e.,  $Y(r < \xi'(t), t) = 0$  at short relative distances (where there are no  $AB$  pairs) and rapidly reaches unity at  $r > \xi'(t)$ . It is also clear from Fig. 2(a) that  $\xi'(t)$  is nothing but the diffusion length,  $\xi'(t) = \xi(t)$ : an increase in time by two orders of magnitude increases  $\xi'(t)$  by one order of magnitude. The correlation functions for similar reactants in the same interval,  $1 < r < \xi(t)$ , have a plateau, i.e., pairs  $AA$  and  $BB$  are randomly distributed. The only difference to the case of the neutral reactants is observed at distances small compared to the Onsager radius,  $r \leq R$ , where the correlation functions are affected by the Coulomb repulsion of similar reactants. The asymptotic reaction kinetics is determined by the largest length-scale parameter in the system, i.e., the diffusion length, and thus is not affected by the mentioned peculiarity in the spatial distribution at short distances ( $r \ll \xi(t)$ ).

Quite different patterns are found in the case of asymmetric diffusion [Fig. 2(b)]. The correlation functions for  $AB$  and  $BB$  pairs ( $B$  particles are mobile) reveal the same behavior as for the symmetric case, whereas the correlation function for *immobile* particles  $A$  has a singularity at short distances  $r$  (shown in the logarithmic scale). This is not caused by the reactant electrostatic interaction since it is also observed for neutral immobile particles.<sup>6,9</sup> Unlike mobile  $B$  particles are essentially delocalized inside their domains, immobile  $A$  particles form very compact aggregates, reminding a kind of "raisins in dough."<sup>13</sup> Assuming that each domain contains a single "raisin" inside, we can estimate the number of particles in the domain as  $N = n(t)\xi(t)^d$ .

Let us discuss the role of different length-scale factors in the kinetics for charged particles. Debye<sup>17</sup> was the first who analyzed the  $3d$  case with two characteristic scale factors, the contact radius  $r_0$  at which the reaction event happens and the Coulomb trapping  $R$  (later called Onsager radius). The effective reaction radius  $R_{\text{eff}}$  is a function of these two parameters. If  $R > r_0$ ,  $R_{\text{eff}} \approx R$ ,<sup>17</sup> i.e., the reaction kinetics is governed by the *largest* length parameter. Physically this means that when  $AB$  pairs approach to within a distance  $R$ , they unavoidably react. In our low dimensional problem we excluded the contact radius  $r_0$  from consideration and thus the kinetics under study is controlled only by the parameter  $R$ . (This is always true for low and intermediate temperatures.) In the asymmetric diffusion case a "raisin" consisting of immobile  $A$  reactants is seen by other remote particles as a super-particle with net charge  $Ne$ . The relevant length scale of its interaction with other particles is  $R_{\text{eff}} \approx NR$ .

After these comments let us look again at curves 2 in Fig. 1 for the unscreened Coulomb interactions. The limiting critical exponent  $\alpha = 1/2$ , corresponds to the reaction rate  $K \propto t^{-1/2}$ , as follows from Eq. (22). Since the initial reactant concentration  $n(0)$  plays no role in the asymptotics of the reaction kinetics,<sup>6,9</sup> the reaction rate reflecting the spatial

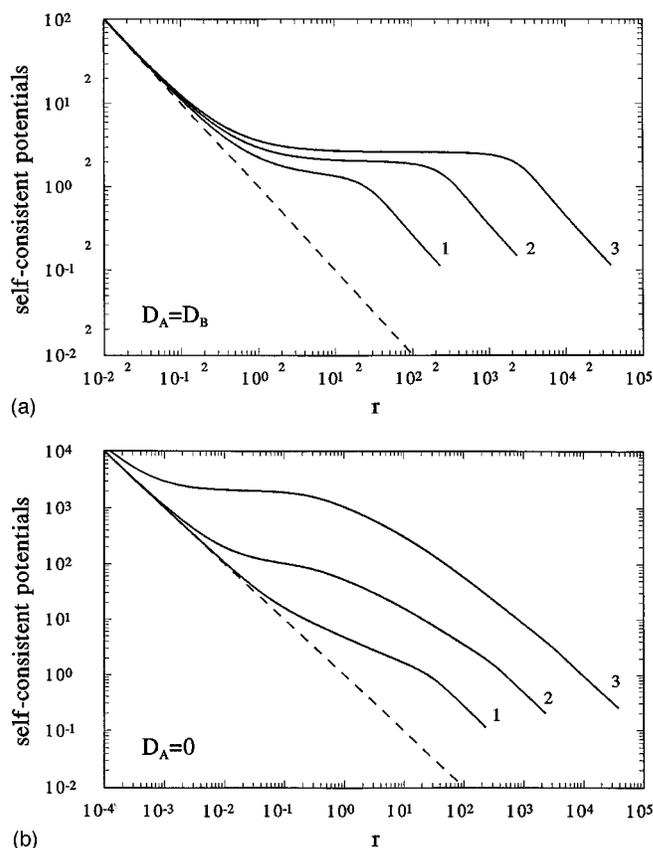


FIG. 3. Calculated self-consistent potentials as a function of the distance  $r$ . Solid curves 1–3 correspond to the reaction time  $t = : 10^2, 10^4, 10^6$ , respectively. Dashed curve  $-U(r) = 1/r$ . (a) Symmetric case,  $D_A = D_B$ . Potential  $-U(r, t) = U_A(r, t) = U_B(r, t)$ . (b) Asymmetric case,  $D_A = 0$ . Potential  $-U(r, t)$  is plotted.

structure of reactants depends on the combination of the two length scale factors,  $R$  and  $\xi(t)$ . From dimensional arguments, in the  $2d$  case the reaction rate can be presented only in the form of  $K(t) \propto DR/\xi(t)$  revealing the correct asymptotic behavior.

Incorporation of many-particle effects into the interaction potentials for the symmetric case does not change the situation, reactant trapping remains determined by the Onsager radius and thus its asymptotics is the same. Contrary to this, in the asymmetric case the effective reaction radius turns out to be  $R_{\text{eff}} \approx NR$ . Substitution into the kinetic Eq. (5) of  $K(t) \propto DR_{\text{eff}}/\xi(t)$  and  $R_{\text{eff}} = n(t)\xi(t)^2$  leads to the new asymptotics  $n(t) \propto t^{-3/4}$ . This critical exponent lies between  $\alpha = 1/2$  observed for the fluctuation-controlled kinetics between neutral reactants, and the prediction of the standard chemical kinetics,  $\alpha = 1$ . At the reaction time  $t = 10^6$  (the maximum value calculated) the deviation of the critical exponents from their limiting values in both the symmetric and asymmetric cases are of the same order of magnitude (Fig. 1).

These qualitative arguments can be illustrated by the effective, self-consistent interaction potentials shown in Fig. 3. In the symmetric case [Fig. 3(a)] the relation  $U_A(r, t) = U_B(r, t) = -U(r, t)$  which is given here in a

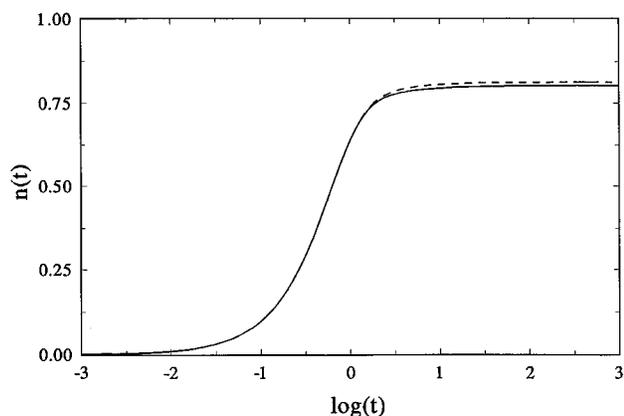


FIG. 4. The accumulation kinetics for the symmetric case,  $D_A = D_B$  (solid curve) and asymmetric case,  $D_A = 0$  (dashed curve).

double logarithmic plot (a dashed line corresponds to the unscreened potential,  $-U(r) = 1/r$ ). The behavior of the effective potentials is quite simple: at short distances, less than the Onsager radius  $R$ , potentials are unscreened and thus coincide with the dashed line. At larger distances  $r > R$  potentials are nearly constant up to  $r = \xi(t)$ , and then change to the asymptotics well fitted to  $U(r, t) = -\xi_U(t)/r$ . In the plateau region the potential is nearly constant, i.e., forces acting on particles are zero. In other words, similar reactants in their domains of size  $\xi(t)$  behave as *neutral* particles. The potential is changed abruptly at the boundary of these domains, at  $r = \xi(t)$ , where dissimilar reactants attract each other. The relevant length scale  $\xi_U(t)$  coincides with the earlier introduced effective radius,  $R_{\text{eff}}$ , since it is also related to the net charge,  $Ne$ , in the domain. For the given critical exponent  $R_{\text{eff}}$  is not an independent parameter since it is easy to see that  $R_{\text{eff}} \propto \xi(t)$ , i.e., at long reaction times the asymptotics of the interaction potentials is of non-equilibrium type at large  $r$ . Particles remain spatially correlated even at very long relative distances which results indirectly from the fact that the observation of the asymptotic reaction law is delayed.

In the asymmetric case shown in Fig. 3(b) the behavior of the potential for mobile reactants,  $U_B(r, t)$ , is similar to that in Fig. 3(a), whereas  $U_A(r, t)$  plays no role. (This is why only  $-U(r, t)$  is plotted here.) The distance  $r$ , where the potential is unscreened, is shifted towards the coordinate origin as time increases. That is, already at  $r = R$  the reactant interaction could be characterized by the effective reaction radius  $R_{\text{eff}}$ .

## B. Accumulation kinetics

Figure 4 shows the calculated accumulation kinetics for particle production rate  $\zeta = 1$  and zero initial concentration,  $n(0) = 0$ . The reactant concentration rapidly approaches the saturation level. Moreover, unlike the concentration decay regime discussed above, there is practically (within an accuracy of one percent) no difference here between symmetric and asymmetric reactant mobilities. Note that this saturation is a *real* steady-state since not only the reactant concentrations but also the correlation functions are time-independent.

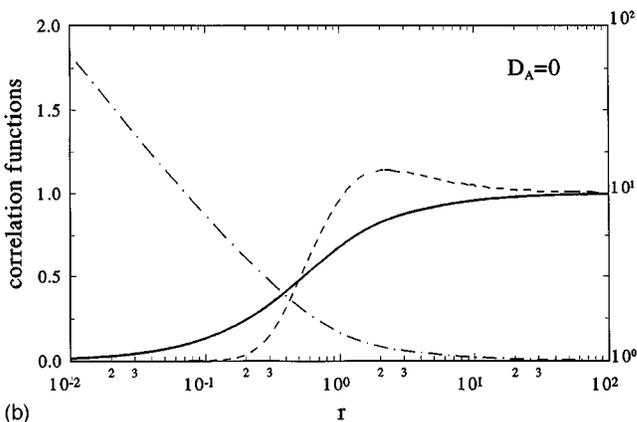
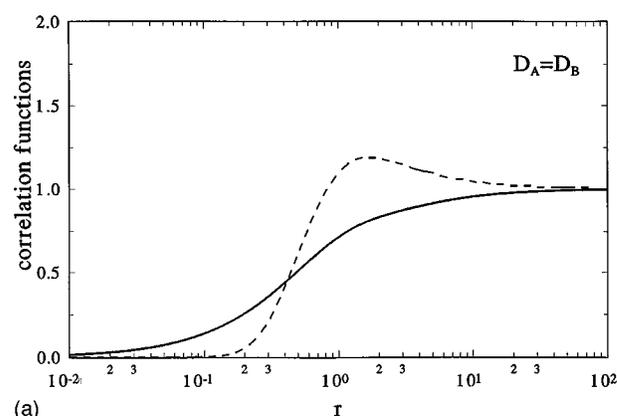


FIG. 5. The joint correlation function of dissimilar particles,  $Y(r, t)$  (solid curve), and that of similar particles,  $X_A(r, t)$  (dot-dashed curve) and  $X_B(r, t)$  (dashed curve). (a) Symmetric case,  $D_A = D_B$ . (b) Asymmetric case,  $D_A = 0$ . Note that for case (a)  $X_A(r, t) = X_B(r, t) = X(r, t)$  whereas for case (b)  $X_A(r, t)$  is plotted in the logarithmic scale.

This is in contrast to the  $2d$  accumulation kinetics for *neutral* particles, where the concentration grows logarithmically and the correlation functions develop in time in the same way as the diffusion.<sup>20</sup>

The steady-state correlation functions are presented in Fig. 5. They approach the asymptotic value of unity at finite distance, i.e., the diffusion length no longer determines their behavior. There is certainly a difference between symmetric and asymmetric cases but this does not affect the concentration kinetics. Moreover, unlike the difference in the correlation functions, the effective interaction potentials (Fig. 6) practically do not depend on the partial diffusion coefficient  $\kappa = D_A/D$ . This is why we have plotted results for the symmetric case only. Peculiarities of the one-dimensional accumulation will be discussed elsewhere.<sup>21</sup>

## VI. CONCLUSION

Let us compare results of our microscopic theory with those obtained in the framework of the mesoscopic approach.<sup>10-12</sup> The latter approach predicts for the concentration decay (no particle source) in the case of symmetric diffusion and with short-range (integrable) interaction potential the same critical exponent  $\alpha = 1/2$  as has been earlier

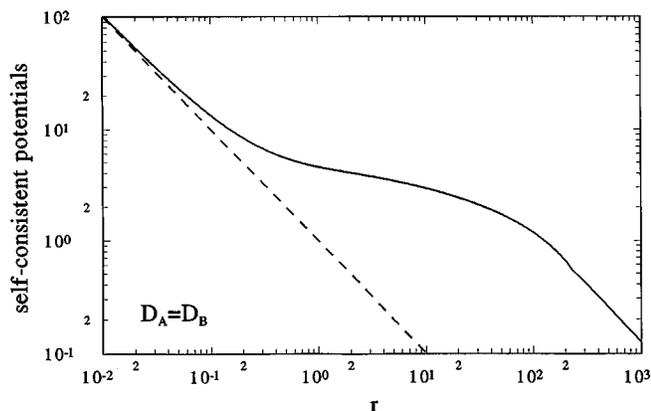


FIG. 6. Self-consistent potentials in the accumulation kinetics at the concentration saturation and for symmetric reactant mobilities.

obtained in the fluctuation-controlled reactions of *non-interacting* particles.<sup>2-9</sup> Our microscopic approach confirms this result and generalizes it for the case of the long-range (singular) Coulomb potential which is far from obvious.

Another important conclusion of the microscopic formalism is that asymmetry in diffusion coefficients of reactants *can change qualitatively the reaction asymptotics*, the reaction becomes *accelerated* ( $\alpha = 3/4$  for  $2d$ ) compared to the asymptotics for neutral particles ( $\alpha = 1/2$ ). This conclusion was arrived at previously for the  $3d$  case.<sup>13</sup>

A comparison of the  $3d$  and  $2d$  cases demonstrates clearly their essential difference: in the  $2d$  case and for symmetric reactant mobilities the critical exponent is the same for charged and neutral particles, whereas in the  $3d$  case the critical exponent for charged reactants coincides with that predicted by standard chemical kinetics ( $\alpha = 1$ ) rather than with the fluctuation-controlled kinetics for neutral particles ( $\alpha = 3/4$ ).

For the accumulation kinetics a mesoscopic theory<sup>10-12</sup> predicts a decrease of the critical exponent,  $n(t) \propto t^\alpha$  only in the one-dimensional case ( $\alpha = 1/5$  vs  $1/4$  for neutral particles), whereas for the  $2d$  case it is the same as for neutral particles ( $\alpha = 0$ , the concentration grows logarithmically and the correlation functions reveal the diffusion length). This is

in contrast with our findings presented above—the concentration reaches a real saturation and a steady-state is confirmed by the stationary correlation functions.

As we have shown, in the accumulation regime the interaction potential remains a long-range one and thus, in contrast to the assumption in Refs. 10–12 is never screened. This is why the use of model short-range potentials (e.g., Debye–Hückel potential) is not justified here.

## ACKNOWLEDGMENTS

This research was supported by the Deutsche Forschungsgemeinschaft (via a fellowship for V. N. Kuzovkov), by the EC HCM network on the Solid State Atomic Scale Simulations (associated Contract No. ERB CIPDCT 940008), and in part by the Fonds der Chemischen Industrie. The authors are indebted to A. Blumen and I. Sokolov for stimulating discussions.

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