

DEVELOPMENT OF THE NEW APPROACH TO THE DIFFUSION-LIMITED REACTION RATE THEORY

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Received July 20, 2011

The new approach to the diffusion-limited reaction rate theory, recently proposed by the author, is further developed on the base of a similar approach to Brownian coagulation. The traditional diffusion approach to calculation of the reaction rate is critically analyzed. In particular, it is shown that the traditional approach is applicable only in the special case of reactions with a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$ (where \bar{r}_A and \bar{r}_B are the mean inter-particle distances), and becomes inappropriate in calculating the reaction rate in the case of a relatively small reaction radius, $R_{AB} \ll \bar{r}_A, \bar{r}_B$. In the latter case, most important for chemical reactions, particle collisions occur not in the diffusion regime but mainly in the kinetic regime characterized by homogeneous (random) spatial distribution of particles on the length scale of the mean inter-particle distance. The calculated reaction rate for a small reaction radius in three dimensions formally (and fortuitously) coincides with the expression derived in the traditional approach for reactions with a large reaction radius, but notably deviates at large times from the traditional result in the planar two-dimensional geometry. In application to reactions on discrete lattice sites, new relations for the reaction rate constants are derived for both three-dimensional and two-dimensional lattices.

1. INTRODUCTION

We refine and further develop the new approach to the diffusion-limited reaction rate theory proposed in our paper [1].

For many chemical processes, the reaction proceeds from a reaction complex formed by collision of two or more reactants. Each reaction rate coefficient K has a temperature dependence, which is usually given by the Arrhenius equation $K = K_0 \exp(-E_a/kT)$, where the pre-exponential factor K_0 determines the collision frequency of reacting species and the exponential factor determines the number of collisions with the energy greater than the activation energy E_a of the complex (i. e., corresponds to the sticking probability of collisions).

Diffusion-limited (or diffusion-controlled) reactions are reactions in which collisions of the reactants (determining the pre-exponential factor K_0) are controlled by their diffusion migration in suspending solvent (rather

than by free-molecule collisions typical for molecular reactions in gas mixtures). Diffusion-limited reactions between two different species A and B ($A + B \rightarrow C$, where C does not affect the reaction) show up in a vast number of applications including not only chemical (see, e. g., [2]) but also biological (e. g., [3–5]) and ecological (e. g., [6]) processes that have been studied over many decades. This may also apply to the reaction of vacancies and interstitials ($V + I \rightarrow 0$), and annihilation in crystals [7] produced by means of high-energy particles or electrons.

A method for calculating the reaction rate of reaction partners migrating via three-dimensional diffusion was developed in [8, 9] by generalizing the Smoluchowski theory for coagulation of colloids [10]. In this method, the radius of the activated complex (or the “reaction radius”) corresponds to the “influence-sphere radius” in the Smoluchowski theory (roughly equal to the sum of the radii of two colliding Brownian particles, $R_{12} \approx R_1 + R_2$), which in the continuum approach is assumed to be large in comparison with elementary drift (or jump) distances $a_{1,2}$ of particles migrating via

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random walks, $R_{12} \gg a_1, a_2$. In the opposite limit case, $R_{12} \ll a_1, a_2$, the continuum diffusion approach is not anymore valid, and therefore the so-called “free-molecule” (or “ballistic”) approximation can be used for colliding Brownian particles [11]. This approach is a generalization of the classical consideration of bimolecular collisions in gas mixtures within the Boltzmann gas-kinetic theory.

In formulating a reaction–diffusion model, a d -dimensional Euclidean space on which A and B particles at initial mean concentrations (number of particles per unit volume) n_A and n_B diffuse freely is usually considered in the continuum approach (see, e. g., [12–14]). In this approach, the reactant particles are represented as points or spheres undergoing spatially continuous Brownian motion, with chemical reactions $A + B \rightarrow C$ occurring instantly when the particles pass within a specified reaction radius R_{AB} between their centres.

The continuum approach was further applied to diffusion-limited reactions in one and two dimensions (see, e. g., [15, 16]); the latter case also has wide applications in the membrane biology (see a review in [17]). The diffusion-limited bimolecular reactions between mobile vacancies and interstitials in strongly anisotropic crystals in the case where the mobile species is constrained to migrate in one plane only may also be well approximated over a wide range of the reaction by a two-dimensional second-order rate equation [18].

In this approach, the same shortcomings of the Brownian coagulation theory that were recently critically analyzed in our papers [19–21] are generally inherited by the diffusion-limited reaction rate models. Namely, it was shown that the diffusion approach [10, 22] to the calculation of the collision rate function, based on the assumption that the local collision rate is equal to the diffusive current of particles, is applicable only in the special case of coalescence between large and small Brownian particles, $R_1 \ll \bar{r} \ll R_2$ (where $\bar{r} \approx n^{-1/3}$ is the mean interparticle distance), and becomes inapplicable to the calculation of the coalescence rate for particles of comparable sizes, $R_1, R_2 \ll \bar{r}$.

In the latter, more general case of comparable-size particles, coalescences occur mainly in the kinetic regime (rather than in the diffusion one) characterized by a homogeneous (random) spatial distribution of particles (rather than by their concentration profiles) [19–21]. This kinetic regime is realized in virtually the entire range of particle concentrations obeying the basic (“dilution”) assumption of the theory, $R/\bar{r} \ll 1$, and can be subdivided into different modes (continuum, free molecular, and transient).

In the continuum mode of the kinetic regime,

$R_{12} \gg a_1, a_2$, the formal expression for the collision frequency of particles (of comparable sizes) coincides (in fact, fortuitously) with that derived in [10, 22] for the diffusion regime (being relevant only in the particular case of coalescence of large particles with small ones). This formal coincidence apparently explains why the traditional approach correctly describes numerous experimental measurements of the coagulation rate of Brownian particles.

The new approach developed in [19–21] is also applicable in the case of diffusion-limited reaction kinetics in continuum media [1], if the characteristic reaction distance R_{AB} for the $A \leftrightarrow B$ complex formation (i. e., the reaction radius) is small in comparison with the mean interparticle distances, $R_{AB} \ll \bar{r}_A, \bar{r}_B$, where $\bar{r}_A \approx n_A^{-1/3}$ and $\bar{r}_B \approx n_B^{-1/3}$ (see Sec. 2), which particularly corresponds to reactions between comparable-size particles (i. e., the most important case). This range can be subdivided into two intervals of the model parameters, $R_{AB} \gg a_A, a_B$ and $R_{AB} \ll a_A, a_B$, corresponding to different modes (continuum and free molecular) of the kinetic regime. For the continuum mode, $R_{AB} \gg a_A, a_B$, the reaction rate calculated in the new approach in the three-dimensional case (see Sec. 3.1) formally (and, again, fortuitously) coincides with the traditional result, valid only for reactions with a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$. But in the two-dimensional case, the traditional approach leads to considerable deviations of the reaction decay $n_{A,B}(t)$ at large times t from that calculated in the new approach in the base case $a_A, a_B \ll R_{AB} \ll \bar{r}_A, \bar{r}_B$ (see Sec. 4).

In the case $R_{AB} \ll a_A, a_B$, the free molecular (or ballistic) regime is realized. This case can be considered similarly to the Brownian particles coagulation problem in the corresponding regime, as well as the case of the transition regime, $R_{AB} \approx a_A, a_B$ (Sec. 3.2).

The new approach can be further generalized to consideration of reaction kinetics for particles migrating via random walks on discrete lattice sites (with a lattice spacing a). Because the case of a large reaction radius $R_{AB} \gg a$ is properly reduced to the continuum medium limit, the opposite case $R_{AB} < a$, with reactions occurring when two particles occupy the same site (see, e. g., [23]), is of most concern. We show in Sec. 5 that the traditional approach [16, 23] to consideration of this important case preserves the main deficiencies of the continuum medium approach and therefore results in erroneous predictions for the reaction kinetics (even in three dimensions). For this reason, new relations for the reaction rate constants are derived for three-dimensional (Sec. 5.1) and two-dimensional (Sec. 5.2) lattices. The discrepancy between the new and tra-

ditional approach predictions increases further when a more complicated case of catalytically activated reactions is considered (Sec. 5.3). The main results are summarized in Sec. 6.

2. RATE EQUATIONS

In the approximation $R/\bar{r} \ll 1$, only pairwise collisions of particles during their diffusion migration can be taken into consideration, and collisions that occur among any combinations consisting of more than two particles can be ignored.

In the rate theory for a continuous distribution of particles $N(r)dr$, the number of particles of a radius R to $R + dR$ per unit volume, under the assumption that collided particles of radii R_1 and R_2 immediately coalesce to form a new particle of the radius $(R_1^3 + R_2^3)^{1/3}$, the Smoluchowski coagulation equation takes the form [10]

$$\begin{aligned} \frac{\partial N(R, t)}{\partial t} = & \frac{1}{2} \int_0^\infty \int_0^\infty N(R_1, t)N(R_2, t) \times \\ & \times \delta \left[R - (R_1^3 + R_2^3)^{1/3} \right] \beta(R_1, R_2) dR_1 dR_2 - \\ & - N(R, t) \int_0^\infty N(R_1, t) \beta(R, R_1) dR_1, \quad (1) \end{aligned}$$

where $\beta(R_1, R_2)$ is the collision frequency function, which, being defined as the collision frequency between two particles randomly located in the unit volume, does not depend on time explicitly. Therefore, $\partial N(R, t)/\partial t$ should be calculated from the analysis of pairwise collisions during a time step δt relatively short for the variation in the concentration densities $N(R_1, t)$ and $N(R_2, t)$ to be neglected, on the one hand, and long enough for $\beta(R_1, R_2)$ to attain the steady state value, on the other hand.

For the kinetics of an irreversible reaction $A + B \rightarrow C$ (where C does not affect the reaction) in the mean-field approximation, Eq. (1) applied to the two-size (R_A and R_B) particle distribution function reduces to

$$\frac{dn_A}{dt} = \frac{dn_B}{dt} = -K_{AB}n_A(t)n_B(t), \quad (2)$$

where n_A and n_B are the mean concentrations of the reacting A and B particles and

$$K_{AB} = \beta(R_1, R_2)\delta(R_1 - R_A)\delta(R_2 - R_B)$$

is the rate function (or reaction constant) directly corresponding to the collision frequency function β for two

particles of different types (A and B). In accordance with the Smoluchowski rate theory, K_{AB} is defined as the collision frequency of two particles randomly located in the unit volume, and it should therefore be regarded as a quantity explicitly independent of time. In a self-consistent approach, the reaction rate dn_A/dt should be calculated with the time step dt chosen short enough to neglect variation of the mean concentrations n_A and n_B in the interval dt , and long enough for a steady state value of $K_{AB}(dt) \approx \text{const} = K_{AB}$ to set in. This is an important difference from the traditional models of diffusion-limited reaction kinetics (even though they are often called the Smoluchowski-type models), where, under the assumption that the local reaction rate is equal to the diffusive current of particles, the “effective” reaction rate is calculated as an explicit time-dependent function $K_{AB}(t)$ (rather than $K_{AB}(dt)$ in the Smoluchowski theory).

Similarly to the analyses of the coagulation problem in [19–21], we show below that this difference is connected to unjustified application of the diffusion approach to the calculation of the effective reaction rate (as the diffusive current of particles) for particles with a relatively small reaction radius, $R_{AB} \ll \bar{r}_A, \bar{r}_B$, which becomes especially critical in the two-dimensional case. Such an approach is valid in the case of small particles A diffusing into large circular traps B (so-called agglomeration), $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$ (with a time-dependent $K(t)$ properly entering the agglomeration rate equation), but it fails in the base case $R_{AB} \ll \bar{r}_A, \bar{r}_B$ (corresponding, in particular, to comparable-size particles, $R_A \approx R_B \ll \bar{r}_A, \bar{r}_B$).

2.1. Applicability of the diffusion approach to particle collisions

The diffusion equation for an ensemble of particles is derived (similarly to the consideration of other relaxation processes in weakly inhomogeneous fluids, such as the heat transfer or viscous flow) in the quasi-equilibrium approximation. In this approximation, the particle distribution function is assumed to be in local thermodynamic equilibrium, smoothly varying in space and in time following smooth variations of the fluid macroscopic parameters (e. g., the temperature, pressure, concentration, and velocity). In the case of the mass transfer problem (i. e., the diffusion equation), the varying macroscopic parameter is the number concentration of particles, $n(\mathbf{r}, t)$.

Regarding $n(\mathbf{r}, t)$ as a macroscopic value (i. e., assuming its thermodynamic fluctuations to be small in comparison with its value, $\sqrt{\langle(\delta n)^2\rangle} \ll n$) is valid

only if the size of the elementary volume $\delta\tilde{V} = L^3$ with respect to which $n(\mathbf{r})$ is defined is large enough in comparison with the local interparticle distance, $L \gg n^{-1/3}(\mathbf{r})$, which in turn must exceed the minimum interparticle distance equal to the particle size, $n^{-1/3}(\mathbf{r}) \gg 2R$. For this reason, only heterogeneities of the particle spatial distribution on the length scale of $l \gg L \gg n^{-1/3} \gg R$ can be adequately considered in the continuous diffusion approach, under the additional condition $a \ll l$ for the elementary drift distance (see, e. g., [19–21]).

In the case where identical particles (e. g., of type A with a radius R_A) are randomly distributed throughout a medium of infinite extent with the mean bulk concentration n_A that obeys the dilution condition $n_A R_A^3 \ll 1$, the particles can be considered as point objects ($R_A \ll \bar{r}_A$, where $\bar{r}_A \approx n_A^{-1/3}$ is the mean interparticle distance), which, in accordance with the diffusion equation for an ensemble of point-like particles, tend to relax with time to a homogeneous spatial distribution.

The situation changes critically in the case where a group of B-type traps with a relatively large “influence-sphere”, or the reaction radius $R_{AB} \gg R_A$ (with A-particles) and the concentration n_B (obeying $n_B R_{AB}^3 \ll 1$) appears in the ensemble of A-particles. B-type traps cannot be treated as point-like objects if $n_A R_{AB}^3 \gg 1$. In this case, traps should be considered macroscopic with respect to A-particles, because the reaction radius R_{AB} is much larger than the mean interparticle distance $\bar{r}_A \approx n_A^{-1/3}$, and just for this reason additional (absorbing) boundary conditions for diffusion of A-particles emerges on traps surfaces. The heterogeneities in the spatial distribution of A-particles induced by these boundary conditions do not tend to disappear with time, as they do in the previous case (without traps), and the steady-state concentration profiles of A-particles around macroscopic trap centers

$$n_A(r) = n_A(R_{AB}) + (\bar{n}_A - n_A(R_{AB})) \left(1 - \frac{R_{AB}}{r}\right)$$

are attained at $t \gg R_{AB}^2/\pi D_A$ [22]. The diffusion flux of A-particles in this concentration profile calculated at the reaction radius is

$$J_{dif} = 4\pi D_A R_{AB} (\bar{n}_A - n_A(R_{AB})) \approx 4\pi D_A R_{AB} n_A$$

if $n_A(R_{AB}) \ll \bar{n}_A \approx n_A$; it determines the accumulation rate of A-particles in a B-trap, and, in accordance with [10, 22], the collision frequency function between A and B particles, taking migration of traps with the diffusivity D_B into consideration, eventually takes the form

$$K_{AB}^{(dif)} = 4\pi D_{AB} R_{AB}, \tag{3}$$

where $D_{AB} = D_A + D_B$.

To establish the applicability range of this result, we note that the characteristic size l of the zone around a large trap in which the A-particle concentration varies from a value $n_A(R_{AB}) \ll n_A$ near the reaction surface to the value of the same order of magnitude as the mean value n_A attained at large distances from the center is comparable with R_{AB} , i. e., $l \approx R_{AB}$. This size l must naturally exceed the mean distance $n_A^{-1/3}(R_{AB})$ between small A-particles in the vicinity of a B-trap surface,

$$R_{AB} \approx l \gg n_A^{-1/3}(R_{AB}) \gg n_A^{-1/3}$$

(in order to maintain the concentration profile of small particles around the trap), or $n_A R_{AB}^3 \gg 1$. This condition logically coincides with the general requirement for the applicability of the diffusion approximation mentioned above, $l \gg n_A^{-1/3}$.

This condition can be confirmed more rigorously taking into consideration that the diffusion flux at the reaction surface

$$J_{dif} \propto \left. \frac{\partial n_A}{\partial r} \right|_{r=R_{AB}} \approx \frac{n_A(R_{AB} + \Delta r) - n_A(R_{AB})}{\Delta r}$$

can be properly calculated only under the assumption that $\Delta r \ll R_{AB}$. In the vicinity of the surface,

$$n_A(R_{AB} + \Delta r) \ll n_A(2R_{AB}) \approx \bar{n}_A/2,$$

and therefore the mean interparticle distance in this zone can be evaluated as

$$\bar{r} \approx n_A^{-1/3}(R_{AB} + \Delta r) \gg n_A^{-1/3}(2R_{AB}) = (\bar{n}_A/2)^{-1/3}.$$

On the other hand, it should be small enough to maintain the concentration profile in this spatial range (where the diffusion flux is calculated), $\bar{r} \ll \Delta r \ll R_{AB}$, or $n_A^{1/3} R_{AB} \gg 1$.

The same conclusion can also be derived in the Fokker–Planck approach based on the analysis of the probability density of migrating Brownian particles (see the Appendix).

Therefore, the traditional diffusion approach, which stipulates that the local reaction rate is equal to the diffusive current of A-particles into the traps (see, e. g., [16]), is valid only for reactions with the large reaction radius $R_{AB} \gg \bar{r}_A \approx n_A^{-1/3}$.

It follows from this analysis that the intrinsic reason for steady-state heterogeneities in the spatial distribution of small particles is connected to the additional boundary conditions (for the diffusion equation

for these particles) induced by macroscopic (i. e., large scale, $R_{AB} \gg \bar{r}_A$) traps. These macroscopic boundary conditions vanish as soon as the reaction radius becomes small in comparison with the mean interparticle distance ($R_{AB} \approx R_A \ll \bar{r}_A$), eliminating the driving force for the emergence of steady-state spatial heterogeneities.

Indeed, in the opposite case $R_{AB} \ll \bar{r}_A, \bar{r}_B$, the limit of point-like particles is restored, which is characterized by the tendency of the system of two-type particles toward a homogeneous spatial distribution (or mixing) owing to their diffusion migration (in the absence of macroscopic boundaries).

2.2. Diffusion mixing condition

Reactions between point-like particles induce local heterogeneities in the particle spatial distribution on the length scale of their mean interparticle distance, which is evaluated as $\bar{r} \approx n^{-1/3}$ if $n_A = n_B = n$. But such small-scale heterogeneities quickly disappear owing to rapid diffusion relaxation of particles on the length scale of their mean interparticle distance \bar{r} with the characteristic time $\tau_d \approx \bar{r}^2/6D$ (under the simplifying assumption that $D_A \approx D_B = D$), which is generally much shorter than the characteristic time $\tau_c \approx (K_{AB}n)^{-1}$ of the mean concentration variation, $\tau_d \ll \tau_c$, as we explicitly show below in both three-dimensional and two-dimensional cases (in Sec. 3 and 5). This allows considering a random distribution of particles attained in the time step $\tau_d \ll \delta t \ll \tau_c$ chosen for calculation of the reaction rate in Eq. (2).

In this case (corresponding to the kinetic regime), the spatial distributions of the particle centers $n_{A,B}(\mathbf{r}, t)$ can be considered homogeneous functions characterized by their mean concentrations $n_{AB}(t)$, i. e., $n_{A,B}(\mathbf{r}, t) = n_{A,B}(t)$, slowly varying with time owing to particle collisions (reactions). Accordingly, the collision probability is also a spatially uniform function.

In the case $n_A > n_B$, which at large times ($t \gg \gg [K_{AB}(n_A(0) - n_B(0))]^{-1}$) inevitably turns into $n_A(t) \gg n_B(t)$, or $\bar{r}_A(t) \ll \bar{r}_B(t)$, each particle B can be surrounded by a sphere (or a circle in two dimensions) of a radius \tilde{r} obeying $\bar{r}_A(t) \ll \tilde{r} \ll \bar{r}_B(t)$, where a collision of this particle B with one of the surrounding particles A (with a given concentration $n_A(t)$) occurs. Because $\tilde{r} \ll \bar{r}_B(t)$, no other particles B can be considered in this sphere, and therefore homogenization of the reaction system in δt (after reactions in the previous time step) is determined by the relaxation (or diffusion mixing) of particles A (inside this sphere) on the length

scale of their mean interparticle distance $\bar{r}_A \approx n_A^{-1/3}$, i. e., by the diffusion time $\tau_d \approx \bar{r}_A^2/6D$.

Apparently, this conclusion is not violated in the case $D_A \gg D_B$, but it becomes invalid in the opposite case $D_A \ll D_B$. In this last case, mixing of particles A is incomplete and hence the accuracy of the model predictions decreases. But because of the stochastic character of particle movement and collisions, local heterogeneities (“missing particles”) induced by reactions between particles A and B are randomly distributed in space, and therefore the mean collision frequency can still be considered a spatially uniform function, but averaged over a larger scale. This implies that at least in the mean-field approximation (i. e., in the large-scale limit), the current approach can be applied with reasonable accuracy. In what follows, the condition $D_A \approx D_B = D$ is nevertheless assumed for simplicity and for a possible generalization of the theory to the case of concentration fluctuations (see Sec. 2.3).

The characteristic times of particle concentration variation are different for particles A and B, $\tau_c^{(A,B)} \approx (K_{AB}n_{A,B})^{-1}$, and hence the smaller one must be chosen in evaluating the time step,

$$\delta t \ll \tau_c \approx \min[\tau_c^{(A)}, \tau_c^{(B)}] \approx K_{AB}^{-1}n_A^{-1} \text{ (if } n_A > n_B \text{)}.$$

Therefore, assuming that $n_A \geq n_B$ for definiteness (and also that $D_A \approx D_B = D$) in what follows, we can generally represent the mixing condition in the form

$$\tau_d \approx \bar{r}_A^2/6D \ll \delta t \ll \tau_c \approx K_{AB}^{-1}n_A^{-1}.$$

2.3. Applicability of the reaction rate equation

As explained above, the reaction constant K_{AB} is defined as the collision frequency of two point-like particles ($R_{AB} \ll \bar{r}_A, \bar{r}_B$) of different types (A and B) randomly located in the unit volume. This implies that the size of the unit volume $\delta\tilde{V} = L^3$ with respect to which K_{AB} is defined is large in comparison with the minimum distance between particles of different types, $L \gg R_{AB}$. In this case, if there are n_A particles of type A and n_B particles of type B randomly distributed through a sample of the unit volume, the number of collisions between A and B particles per unit time (the number that defines the reaction rate) is given by $K_{AB}n_A n_B$.

This definition of the reaction rate can be apparently extended to the case of spatial heterogeneities (of size l) in the distribution of A and B particles if these heterogeneities are smooth on the length scale of the (appropriately defined) unit volume, $l \gg L \gg R_{AB}$. In this case, the number of collisions in dt between A

and B particles located in the unit volume is calculated as $K_{AB}n_A(\mathbf{r}, t)n_B(\mathbf{r}, t) dt$, resulting in the local balance equations for the particle numbers:

$$\dot{n}_A(\mathbf{r}, t) = \dot{n}_B(\mathbf{r}, t) = -K_{AB}n_A(\mathbf{r}, t)n_B(\mathbf{r}, t), \quad (4)$$

where K_{AB} is calculated in the kinetic regime, i. e., under the assumption of a (locally) homogeneous spatial distribution of particles. For instance, in the continuum limit in three dimensions, the reaction constant in Eq. (4) is calculated as $K_{AB} = 4\pi D_{AB}R_{AB}$ (or $K'_{AB} = 4\pi D_{AB}R_{AB}P_{AB}$ if the sticking probability P_{AB} is smaller than unity; see Eqs. (6) and (6a) below).

Relaxation of spatial fluctuations in the particle distribution can be taken into consideration by the additional diffusion term in the right-hand side of Eq. (4),

$$\dot{n}_i(\mathbf{r}, t) = D_i \Delta n_i(\mathbf{r}, t) - K_{AB}n_A(\mathbf{r}, t)n_B(\mathbf{r}, t), \quad (5)$$

$$i = A, B,$$

under the condition $l \gg n^{-1/3} \gg R_i$ corresponding to the diffusion term definition (as explained above) consistent with the local collision rate definition $l \gg R_{AB} \geq R_i$.

This allows extending the applicability of the reaction rate theory beyond the mean-field approximation, Eq. (2), but only for fluctuations with long wavelengths, $l \gg R_{AB}$ and $l \gg n^{-1/3}$. The results of the analysis of Eq. (5) available in the literature [12–14], where an independent “intrinsic” (or “microscopic”) rate constant k (entering the radiative boundary condition for the diffusion flux $J_{dif}^{(A,B)} = kn_{A,B}|_{r=R_{AB}}$ in the traditional approach [8, 9]) is used instead of K_{AB} , demonstrate that the effect of the renormalization of k by concentration fluctuations, resulting in the effective rate constant

$$K_{eff} = \frac{4\pi D_{AB}R_{AB}k}{4\pi D_{AB}R_{AB} + k}$$

(which reduces to $K_{eff} = 4\pi D_{AB}R_{AB}$ in the limit of high-rate boundary kinetics, $k \rightarrow \infty$, corresponding to complete trapping, $n_{A,B}|_{r=R_{AB}} \rightarrow 0$), occurs on the length scale of the reaction radius, $l \approx R_{AB}$, i. e., beyond the cut-off limit of Eq. (5) for comparable-size (or point-like) particles, $l \gg n^{-1/3} \gg R_{AB}$. This additionally confirms the above conclusion that the results of the traditional approach are grounded only in the case of reactions with a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$, when short-wavelength fluctuations with $\bar{r}_A \ll l \leq R_{AB}$ in the spatial distribution of A particles around B particles can be adequately described by Eq. (5). However, in the opposite case $\bar{r}_A, \bar{r}_B \gg R_{AB}$, such short-wavelength fluctuations are

beyond the cut-off limit of the theory, and therefore predictions of the diffusion approach [12–14] fail.

Therefore, the mean-field approach based on Eq. (2) (with the reaction constant K_{AB} calculated in the kinetic approach) can be generally used as a first-order approximation. In the next-order approximation, taking long-wavelength fluctuations $l \gg n^{-1/3} \gg R_{AB}$ into consideration in Eq. (5), predictions of the mean-field approach may be violated at large times in the particular case of equal initial concentrations, $n_A(0) = n_B(0)$. In that case, the asymptotic ($t \rightarrow \infty$) decay $n_{A,B} \propto (Dt)^{-d/4}$ (where $d < 4$ is the dimension of space) [24, 25] becomes slower compared with predictions of the mean-field theory, valid for intermediate times ($n_{A,B} \propto (4\pi RDt)^{-1}$ in the three-dimensional case and $n_{A,B} \propto \ln(4Dt/R^2)/4\pi Dt$ in the two-dimensional case; see below).

The “crossover” time from the mean field behavior to the fluctuation-induced asymptotic regimes can be estimated from comparison of decay laws in these two approximations as $t^* \propto R^2/D\varepsilon^2$, $\varepsilon = n_{A,B}(0)R^3 \ll 1$, i. e., it is inversely proportional to the square of the initial volume fraction ε of reactants, and can therefore be very large in diluted systems [26]. At this time, the concentration becomes very small, $n_{A,B}(t^*)/n_{A,B}(0) \propto \varepsilon$, i. e., the mean-field approach correctly describes the reaction kinetics during a large time domain and only a very small number of active particles decay via the fluctuation-induced law. In two-dimensional systems, the crossover time is shorter and the number of particles surviving until this time is greater than in three dimensions. For this reason, the crossover from the dependences predicted by the mean-field approximation to the fluctuation-induced asymptotic regimes has been observed in two-dimensional numerical simulations [25] and in experiment [27].

Therefore, the reaction kinetics in this case can be calculated by additional consideration of long-wavelength fluctuations in Eq. (5), e. g., by mapping to a field theory [28, 29] and using the renormalization group methods [30, 31]. But the reaction rate constant in the master equation of field theory can be correctly calculated only in the kinetic regime (e. g., $K_{AB} = 4\pi D_{AB}R_{AB}P_{AB}$ in the continuum mode in three dimensions or by more sophisticated expressions in other cases; see Secs. 3–5), rather than taken as a microscopic (intrinsic) rate constant k (cf. [30]). This might be especially important in the case of complete trapping, when the microscopic rate constant k tends to ∞ , whereas $K_{AB} = 4\pi D_{AB}R_{AB}$ calculated in the current approach is finite.

3. REACTION RATE IN THE THREE-DIMENSIONAL CASE

As explained in Sec. 2.2, in order to calculate the reaction constant in the kinetic regime, a time step δt relatively large in comparison with the diffusion relaxation (or mixing) time should be chosen, $\delta t \gg \tau_d \approx n^{-2/3}/6D$, in order to satisfy the main condition of the kinetic regime for a random (homogeneous) distribution of reacting particles (where it is assumed that $n = n_A \geq n_B$ and $D_A \approx D_B = D$; cf. Sec. 2.2). On the other hand, the time step should be small in comparison with $\tau_c \approx (K_{AB}n)^{-1}$, i. e., $\delta t \ll \tau_c$, which allows neglecting variation of the mean concentrations n_A and n_B in δt . Besides, some additional condition for the time step should be valid, $\delta t \gg \tilde{\tau}$, in order to attain a steady-state value of $K_{AB}(\delta t) \approx \text{const} = K_{AB}$, where $\tilde{\tau}$ is to be evaluated below.

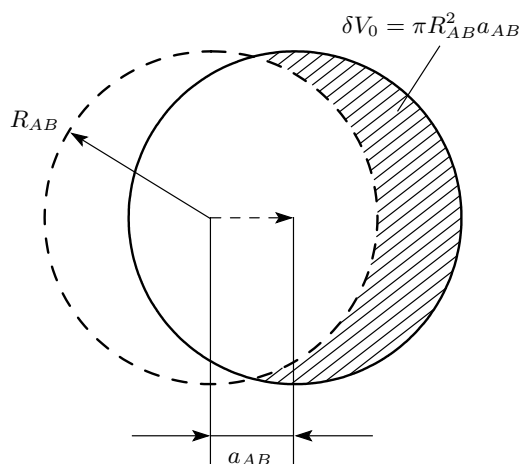
We consider two particles of types A and B located at random in a sample of unit volume. The first (“parent”) particle of type A can be surrounded by a sphere with the reaction radius R_{AB} . If the second particle center is located in this exclusion zone, the reaction occurs.

As shown in [10, 22], the relative displacements between two particles describing diffusion motions independently of each other and with the diffusion coefficients D_A and D_B also follow the law of diffusion motion with the diffusion coefficient $D_A + D_B$. Therefore, to calculate the probability of collisions between the two particles, we can equivalently consider the second particle immobile and the first one migrating with the effective diffusion coefficient $D_{AB} = D_A + D_B \approx 2D$.

In this approximation, it is assumed that the effective (mobile) particle jumps over an elementary distance a_{AB} in random directions with the frequency $\nu_{AB} = \tau_0^{-1}$, obeying the relations for particle diffusivity from the random walk theory, $D_{AB} = a_{AB}^2/6\tau_0$.

As a result of a jump, the exclusion zone also relocates to the distance a_{AB} ; this opens the possibility that the second (immobile) particle with its center located in a zone of the volume $\delta V_0 = \pi R_{AB}^2 a_{AB}$ may be swept out by the mobile particle, as is shown in the Figure (cf. [19–21]).

Depending on the ratio between R_{AB} and a_{AB} , particle migration can be considered in the continuum mode if $R_{AB} \gg a_{AB}$ or in the free molecular mode if $R_{AB} \ll a_{AB}$, with different results for the collision rate (cf. [19–21]).



Schematic representation of the swept zone

3.1. Continuum mode, $a_A, a_B \ll R_{AB} \ll \bar{r}_A, \bar{r}_B$

During the time step $\delta t \gg \tau_0$, the mobile particle makes many jumps, $k = \delta t/\tau_0 \gg 1$, in random directions, but the total swept zone volume δV , which determines the probability of a two-particle collision in δt , is smaller than $k\delta V_0 = \delta V_0\delta t/\tau_0$, owing to a significant overlap of the swept zone segments for $a_{AB} \ll R_{AB}$. This limit corresponds to the continuum mode of the kinetic regime, characterized by a random spatial distribution of particles (quickly reinstated during the time step). Under this basic condition, the probability to sweep a B particle in the unit time is $(\delta V/\delta t)n_B$ if there are n_B randomly distributed B particles per unit volume. Therefore, if there are n_A A particles randomly distributed per unit volume, then the number of collisions $(\delta V/\delta t)n_A n_B$ between A and B particles in the unit time is smaller than $\delta V_0 n_A n_B / \tau_0$.

To calculate the volume δV swept in time δt , we uniformly (randomly) fill the space with auxiliary (fictitious) point-like immobile particles (“markers”) of radius $R_* \rightarrow 0$ with a relatively high concentration $n_* \gg \gg R_{AB}^{-3}$. To facilitate adequate resolution of a fine structure of the swept zone (with the characteristic length $a_{AB} \ll R_{AB}$), the marker concentration n_* must additionally obey the condition that the number $\delta N_*^{(0)}$ of markers swept during one jump is large, $\delta N_*^{(0)} = \pi R_{AB}^2 a_{AB} n_* \gg 1$, or $n_* \ll (\pi R_{AB}^2 a_{AB})^{-1}$. In this case, the swept volume can be calculated as the total number δN_* of the swept markers divided by their concentration, $\delta V = \delta N_*/n_*$.

For the same reasons concerning relative displacements of diffusing particles, the calculation of the sweeping rate of randomly distributed immobile mark-

ers by a large particle of a radius R_{AB} migrating with the diffusivity D_{AB} is equivalent to the calculation of the condensation rate of mobile markers migrating with the diffusivity D_{AB} in an immobile trap of the radius R_{AB} (see the Appendix).

Because $n_*R_{AB}^3 \gg 1$, this problem of condensation of point-like markers in a large (macroscopic) trap can be adequately solved in the continuum approach in [10,22], as explained in Sec. 2.1. In this approach, the total number of markers swept in time δt is equal to [11]

$$\delta N_* = 4\pi D_{AB} R_{AB} n_* \delta t \left(1 + \frac{4R_{AB}}{\sqrt{\delta t \pi D_{AB}}} \right),$$

and the volume swept in unit time is

$$\frac{\delta V}{\delta t} = n_*^{-1} \frac{\delta N_*}{\delta t} = 4\pi D_{AB} R_{AB},$$

if the time step is sufficiently large, $\delta t \gg \tilde{\tau} \approx 16R_{AB}^2/\pi D_{AB}$. The spatial variation of the marker concentration occurs on the length scale l that is comparable with R_{AB} (see Sec. 2.1), i. e., $l \approx R_{AB}$. In accordance with the additional condition of the diffusion equation applicability, $a_{AB} \ll l$, this result is valid only in the case $a_{AB} \ll R_{AB}$ considered here. In this case, the number of collisions $(\delta V/\delta t)n_A n_B$ between A and B particles in unit time becomes equal to $4\pi(D_A + D_B)R_{AB}n_A n_B$, which yields

$$K_{AB} = 4\pi D_{AB} R_{AB}. \tag{6}$$

It is straightforward to see that the first restriction on the time step, $\tau_c \gg \delta t \gg \tau_d \approx n^{-2/3}/6D$, can be applied if the mixing condition $\tau_c \gg \tau_d$, or

$$n^{1/3} R_{AB} \ll \frac{3}{2\pi} \frac{D}{D_{AB}} \approx \frac{3}{4\pi},$$

is valid, which is in agreement with $n^{1/3} R_{AB} \ll 1$.

The second restriction $\delta t \gg \tilde{\tau} \approx 16R_{AB}^2/\pi D_{AB}$ can be applied because $\tau_c \gg \tilde{\tau}$, or $n^{1/3} R_{AB} \ll 1/4$, which is practically indistinguishable from the basic condition $n^{1/3} R_{AB} \ll 1$, within the accuracy of the characteristic time evaluation.

Therefore, the correct expression for the reaction rate in Eq. (6), derived in the kinetic regime (by considering uniform (random) spatial distribution of reacting particles) in the case of a relatively small reaction radius $R_{AB} \ll \bar{r}_A, \bar{r}_B$, coincides with the traditional expression derived in the diffusion regime (by considering concentration profiles and diffusive currents of particles), which is valid in the case of a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$. But this coincidence is accidental and probably reflects some internal symmetry

in the considered system of migrating particles in three dimensions.

This coincidence is violated in the more general case where the sticking probability for A and B particle collisions is smaller than unity, $P_{AB} \leq 1$; in calculating the reaction rate constant, the collision frequency $K_{AB} = 4\pi D_{AB} R_{AB}$ is then multiplied by the probability P_{AB} of the reaction complex formation

$$K'_{AB} = 4\pi D_{AB} P_{AB} R_{AB}. \tag{6a}$$

Again, this result is formally similar to predictions of the traditional approach (which is relevant only in the particular case of reactions with a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$) using the radiative boundary condition for the diffusion flux,

$$J_{dif}^{(i)} = kn_i|_{r=R_{AB}}, \quad i = A, B,$$

in the case of incomplete trapping [8,9], with k being the “intrinsic” (or “microscopic”) rate constant at the boundary, which, by the definition of the boundary kinetics, is independent of the bulk diffusivity D_{AB} and is proportional to the boundary area R_{AB}^2 . Consequently, the reaction rate constant is calculated as [8,9]

$$K''_{AB} = \frac{4\pi D_{AB} R_{AB} k}{4\pi D_{AB} R_{AB} + k}, \tag{6b}$$

which, however, coincides with Eq. (6a) only under the additional assumption that

$$k = \frac{4\pi D_{AB} R_{AB} P_{AB}}{1 - P_{AB}},$$

which is inconsistent with the above definition of the boundary intrinsic rate constant.

3.2. Free molecular mode, $R_{AB} \ll a_A, a_B$

In the opposite case $a_A, a_B \gg R_{AB}$, we can neglect the mean relative volume of the overlaps of swept zone segments (cf. [19–21]). In this approximation, the volume swept per unit time $\delta V/\delta t$ is a constant equal to the ratio of the volume swept per one jump to the jump period, $\delta V_0/\tau_0$, which can be calculated in the free molecular approach. Accordingly, the total swept volume δV (after $k = \delta t/\tau_0 \gg 1$ jumps) is equal to $k\delta V_0 = \delta V_0 \delta t/\tau_0$, and the number of coalescences $(\delta V/\delta t)n_A n_B$ between A and B particles (of masses m_A and m_B) in unit time is equal to

$$\frac{n_A n_B \delta V_0}{\tau_0} = n_A n_B R_{AB}^2 \sqrt{8\pi k T (m_A^{-1} + m_B^{-1})}.$$

Therefore, the kernel $K_{AB}^{(fm)}$ in Eq. (1) is equal to $\delta V_0/\tau_0$, which coincides with the free molecular expression

$$K_{AB}^{(fm)} = \frac{\delta V_0}{\tau_0} = R_{AB}^2 \sqrt{8\pi kT(m_A^{-1} + m_B^{-1})}. \quad (7)$$

This case is applicable for the reaction particles suspended in a fluid, when the parameter R_{AB} is small ($R_{AB} \ll a_A, a_B$) but not negligible in comparison with the mean intermolecular distance of the suspending fluid ($R_{AB} \gg \bar{r}_m \approx n_m^{-1/3}$, where n_m is the fluid molecule concentration). The last value determines the minimum distance $dr \geq n_m^{-1/3}$ between two possible positions of the particle center, \mathbf{r} and $\mathbf{r} + d\mathbf{r}$, and thus allows defining the swept volume (or area) for migrating particles.

In the intermediate range $a_{AB} \approx R_{AB}$ for reaction particles suspended in a fluid, the so-called transition regime is realized that can be described by an interpolation expression derived within the new analytic approach with fitting parameters specified numerically [20, 21].

4. REACTION RATE IN THE TWO-DIMENSIONAL CASE

Similarly to the three-dimensional case, the problem of calculating the area sweeping rate $\delta S/\delta t$ by an effective particle of radius R_{AB} migrating with the diffusivity $D_{AB} = D_A + D_B \approx 2D$ (where $D = D_A \approx D_B$ is assumed; cf. Sec. 2.2) in a plane can be properly reduced to the problem of point markers randomly distributed in the plane with a concentration $n_* \gg (\pi R_{AB})^{-2}$, migrating with the diffusivity D_{AB} into an immobile trap of the radius R_{AB} [1]. The marker condensation rate can be calculated using the well-known analogy with the heat conduction problem in the cylindrical geometry [32]. As a result, the total number of markers swept in time δt is equal to

$$\delta N_* \approx \frac{4\pi D_{AB} n_* \delta t}{\ln(4D_{AB} \delta t / R_{AB}^2)}$$

if

$$\frac{R_{AB}^2}{4D_{AB}} \ll \delta t \ll \tau_c \approx K_{AB}^{-1} \min[n_A^{-1}, n_B^{-1}] \approx K_{AB}^{-1} n_A^{-1}$$

(where $n_A \geq n_B$ is assumed) and δt obeys the diffusion mixing condition $\tau_d \ll \delta t$. In contrast to the three-dimensional case, the sweeping rate $\delta S/\delta t = n_*^{-1}(\delta N_*/\delta t)$ is in this case a function of the time

step even for very large δt , although this dependence is weak and can be neglected with logarithmic accuracy.

Indeed, an expression $\ln(xX)$ can be approximated as

$$\ln(xX) = \ln X + \ln x \approx \ln X$$

if $X \gg x \geq 1$ (and hence $\ln X \gg \ln x \geq 0$). Therefore, choosing the time step as $R_{AB}^2/4D_{AB} \ll \tilde{\tau} \ll \delta t \ll \tau_c$, which under the additional condition

$$\frac{\tilde{\tau}}{R_{AB}^2/4D_{AB}} \gg \frac{\tau_c}{\tilde{\tau}}, \quad (8)$$

can also be represented in the form

$$0 < \ln \frac{\delta t}{\tilde{\tau}} \ll \ln \frac{\tau_c}{\tilde{\tau}} \ll \ln \frac{4D_{AB}\tilde{\tau}}{R_{AB}^2},$$

we obtain

$$\ln \frac{4D_{AB}\delta t}{R_{AB}^2} = \ln \frac{4D_{AB}\tilde{\tau}}{R_{AB}^2} + \ln \frac{\delta t}{\tilde{\tau}} \approx \ln \frac{4D_{AB}\tilde{\tau}}{R_{AB}^2}.$$

In this approximation, the sweeping rate can be calculated as

$$\frac{\delta S}{\delta t} = \frac{1}{n_*} \frac{\delta N_*}{\delta t} \approx \frac{4\pi D_{AB}}{\ln(4D_{AB}\tilde{\tau}/R_{AB}^2)}.$$

The number of collisions $(\delta S/\delta t)n_A n_B$ between A and B particles in unit time becomes

$$\left(\frac{\partial S}{\partial t}\right)_{n_A n_B} \approx \frac{4\pi D_{AB} n_A n_B}{\ln(4D_{AB}\tilde{\tau}/R_{AB}^2)},$$

which corresponds to

$$K_{AB} \approx \frac{4\pi D_{AB}}{\ln(4D_{AB}\tilde{\tau}/R_{AB}^2)}$$

and hence

$$\tau_c \approx K_{AB}^{-1} n_A^{-1} \approx \frac{\ln(4D_{AB}\tilde{\tau}/R_{AB}^2)}{4\pi D_{AB} n_A}$$

(if $n_A \geq n_B$ is specified).

Substituting this expression for τ_c in Eq. (8), we obtain

$$\tilde{\tau} \gg \left(\ln \frac{4D_{AB}\tilde{\tau}}{R_{AB}^2}\right)^{1/2} \frac{R_{AB}\bar{r}_A}{4D_{AB}},$$

where $\bar{r}_A \approx (\pi n_A)^{-1/2}$; this allows specifying $\tilde{\tau} \approx \bar{r}_A^2/4D_{AB}$ (owing to $(\bar{r}_A/R_{AB})^2 \gg \ln(\bar{r}_A/R_{AB})^2$ if $\bar{r}_A/R_{AB} \gg 1$), which apparently obeys the necessary condition $R_{AB}^2/4D_{AB} \ll \tilde{\tau} \ll \tau_c$. Eventually, we obtain the reaction rate in the mean-field approximation as

$$K_{AB} \approx \frac{4\pi D_{AB}}{\ln(\bar{r}_A^2/R_{AB}^2)}, \quad (9)$$

which depends on time implicitly (via $\bar{r}_A \approx (\pi n_A(t))^{-1/2}$), rather than explicitly as in the traditional approach.

In the particular case where $n_A = n_B = n$ (or $\bar{r}_A = \bar{r}_B = \bar{r}$), \tilde{r} practically coincides with $\tau_d \approx \bar{r}^2/4D_{AB}$, and hence δt self-consistently obeys the necessary condition $\tau_d \approx \tilde{r} \ll \delta t$. In this case, the reaction rate reduces to

$$K_{AB} \approx \frac{4\pi D_{AB}}{\ln(\bar{r}^2/R_{AB}^2)} \approx -\frac{4\pi D_{AB}}{\ln(nR_{AB}^2)}$$

(rather than $K_{AB} = 4\pi D_{AB}/\ln(4D_{AB}t/R_{AB}^2)$ in the traditional approach) and eventually results in the solution of the reaction rate equation

$$\frac{1 + \ln(nR_{AB}^2)}{n} \approx 4\pi D_{AB}t, \quad (10)$$

which at large times $t \gg R_{AB}^2/4\pi D_{AB}$ (before crossover to the asymptotic behavior as $t \rightarrow \infty$, discussed in Sec. 2.3), is close to the traditional solution

$$n \approx \frac{\ln(4D_{AB}t/R_{AB}^2)}{4\pi D_{AB}t}.$$

But in the case $n_A > n_B$, the situation changes critically. In this case, the initial relation $n_A(0) > n_B(0)$ unavoidably becomes $n_A(t) \gg n_B(t)$, or $\bar{r}_A(t) \ll \bar{r}_B(t)$ at large times, and the solution of the reaction rate equation (at $t \gg [K_{AB}(n_A(0) - n_B(0))]^{-1}$) results in an exponential decrease in the concentration,

$$n_B(t) \propto \exp(-Ct), \quad (11)$$

where

$$C \approx \frac{2\pi D_{AB}(n_A(0) - n_B(0))}{\ln(\tilde{r}_A/R_{AB})}$$

and \tilde{r}_A is the final value of $\bar{r}_A(t)$, whose variation $\Delta\bar{r}_A(t) = \tilde{r}_A - \bar{r}_A(t)$ at large times, when $\Delta\bar{r}_A(t) \ll \tilde{r}_A$, is neglected in the expression for C in Eq. (11) with the chosen logarithmic accuracy,

$$\begin{aligned} \ln \bar{r}_A &= \ln(\tilde{r}_A + \Delta\bar{r}_A) \approx \ln \tilde{r}_A + \\ &+ \ln(1 + \Delta\bar{r}_A/\tilde{r}_A) \approx \ln \tilde{r}_A. \end{aligned}$$

The obtained solution in Eq. (11) is much steeper in comparison with that in the traditional approach $n_B(t) \propto \exp(-C_1 t/\ln t)$ (see, e. g., [33–35]), and hence the concentration decay rate \dot{n}_B is strongly underestimated at large times in the traditional approach.

This additionally confirms the importance of the new approach to the calculation of the reaction rate in two dimensions.

5. REACTIONS ON A DISCRETE LATTICE

Particle migrations via random walk over discrete cubic lattice sites can be considered in two limits, $R_{AB} \gg a$ and $R_{AB} < a$. In the case of a large reaction radius $R_{AB} \gg a$, the problem is properly reduced to the continuum medium limit considered in Sec. 3.1. In the opposite case, the reaction radius R_{AB} is assumed to be small in comparison with the lattice spacing (corresponding to the elementary jump distance, $a = a_A = a_B$), and reactions occur when two particles occupy the same site (see, e. g., [23]). In this case, R_{AB} is the minimum length scale in the problem and can be excluded from consideration. This situation is qualitatively different from the free molecular regime (for reaction particles suspended in a fluid) considered in Sec. 3.2, where R_{AB} was also a small ($R_{AB} \ll a_A, a_B$) but nonnegligible parameter ($R_{AB} \gg \bar{r}_m \approx n_m^{-1/3}$, where n_m is the fluid molecule concentration), which allowed calculating the swept volume for migrating particles.

We start at $t = 0$ with randomly distributed A and B particles on discrete cubic lattice sites, with mean concentrations n_A and n_B ; $n_{A,B}a^3 \ll 1$. Each particle moves by jumps to nearest-neighbor sites with the jump frequencies τ_A^{-1} and τ_B^{-1} ; thus all particles perform independent random walks, with the associated diffusion coefficients $D_{A,B} = a^2/6\tau_{A,B}$. Again, we assume that $n = n_A \geq n_B$ and $D_A \approx D_B = D$ (cf. Sec. 2.2).

Similarly to the continuum limit considered above, reactions between A and B particles induce local heterogeneities in the particle spatial distribution on the length scale of the mean interparticle distance $\bar{r}_A \approx n^{-1/3} \gg a$. But such heterogeneities quickly disappear owing to rapid diffusion mixing of particles on the length scale of their mean interparticle distance \bar{r}_A with the characteristic time $\tau_d \approx \bar{r}_A^2/6D$, which is generally much shorter than the characteristic time $\tau_c \approx (K_{AB}n)^{-1}$ of the particle concentration variation, $\tau_d \ll \tau_c$. With a time step $\tau_d \ll \delta t \ll \tau_c$ chosen for the calculation of the reaction rate, this allows considering a random distribution of particles attained in δt (owing to $\tau_d \ll \delta t$) and neglecting variation of the mean concentrations n_A and n_B in δt (owing to $\delta t \ll \tau_c = \min[\tau_c^{(A)}, \tau_c^{(B)}]$).

In this case (corresponding to the kinetic regime), the spatial distributions of the particle centers $n_{A,B}(\mathbf{r}, t)$ can be considered homogeneous functions characterized by their mean concentrations $n_{A,B}(t)$, i. e., $n_{A,B}(\mathbf{r}, \mathbf{t}) = n_{A,B}(t)$, slowly varying with time owing to particle collisions (reactions). Accordingly,

the collision probability is also a spatially uniform function.

This problem can be readily reduced to the calculation of the collision probability between two particles randomly located in the unit volume, one of which is immobile (say, particle B) and the other (particle A) is mobile, migrating with the effective diffusivity $D_{AB} = D_A + D_B$.

This approach can be further extended to include spatial heterogeneities in the ensemble of A and B particles if these heterogeneities are smooth on the length scale of the diffusion equation applicability, $l \gg n_{A,B}^{-1/3} \gg R_{AB}$, with the reaction constant calculated in the kinetic regime, similarly to the continuum medium consideration.

But there is also an important difference from the continuum limit. Indeed, in that limit, the probability of the two-particle collision in δt was calculated as the mean volume swept by the mobile particle (of the radius R_{AB} and diffusivity D_{AB}). Instead, in the discrete lattice limit, the collision probability in δt_k is determined by the mean number of distinct sites visited by a k -step random walk of the mobile particle (the so-called random walk range S_k), where

$$k = \frac{\delta t_k}{\tau_{AB}} = \delta t_k \frac{6D_{AB}}{a^2} \gg 1.$$

5.1. Reaction rate on a three-dimensional discrete lattice

In the case of a simple three-dimensional cubic lattice, the mean value of S_k can be calculated as [36–38]

$$\bar{S}_k \approx 0.718 \left[k + 0.729k^{1/2} + O(1) \right], \quad (12)$$

which for the chosen time step

$$\frac{a^2}{6D_{AB}} \ll \frac{\bar{r}^2}{6D_{AB}} \approx \tau_d \ll \delta t_k \ll \tau_c,$$

which corresponds to $k \gg 1$, can be reduced to

$$\bar{S}_k \approx 0.718k, \quad (12a)$$

and results in

$$K_{AB} = a^3 \bar{S}_k / \delta t_k \approx 4.3 D_{AB} a. \quad (13)$$

In the case of incomplete sticking of reactant particles, $P_{AB} \leq 1$, the reaction constant reduces to

$$K'_{AB} = K_{AB} P_{AB} \approx 4.3 D_{AB} a P_{AB}. \quad (13a)$$

A result formally similar to Eq. (13) was obtained in [16] (following [23]). In that approach, the problem

was also reduced to the analysis of collisions between two particles A and B on discrete lattice sites, but was based on additional (unjustified) assumptions. Namely, instead of consideration of the rapid diffusion mixing of particles (as proposed in the current approach), which allows rigorous reduction of the multiparticle problem to two-particle collisions and direct calculation of the reaction rate constant, an additional ansatz for the reaction rate constant in the multiparticle system was used in [16], which eventually resulted in a different (apparently erroneous) numerical factor in Eq. (13).

Therefore, we can conclude that the currently developed approach can be generalized to the reaction kinetics on a three-dimensional lattice, resulting in the new relation for the reaction rate constant, Eq. (13).

5.2. Reaction rate on a two-dimensional discrete lattice

The reaction rate for particles A and B migrating via random walks over discrete square lattice sites ($a^{-2} \gg n = n_A \geq n_B$), when the reaction radius is small in comparison with the lattice spacing, $R_{AB} < a$, can be calculated in a way similar to the three-dimensional approach in Sec. 5.1 using the logarithmic approximation described in Sec. 4. As a result, an equation (corresponding to Eq. (13) in the three-dimensional case) for the reaction rate constant takes the form

$$K_{AB} = a^2 \bar{S}_k / \delta t_k, \quad (14)$$

where

$$\bar{S}_k = \frac{\pi k}{\log k} + O\left(\frac{k}{\log^2 k}\right)$$

is the mean number of distinct square lattice sites visited by a k -step random walk [36–38], $k = \delta t_k / \tau_{AB} = \delta t_k 4D_{AB} / a^2$ and, to provide diffusion mixing in time δt_k , the calculation time step is chosen as

$$\frac{a^2}{4D_{AB}} \ll \frac{n^{-2}}{4D_{AB}} \ll \delta t_k \ll \tau_c \approx K_{AB}^{-1} n^{-1}.$$

With logarithmic accuracy, we obtain

$$K_{AB} \approx \frac{4\pi D_{AB}}{\log(1/na^2)}, \quad (15)$$

which depends on time implicitly (via $n(t)$).

At large times in the case $n_A > n_B$, this time dependence is weak and can be neglected with the chosen logarithmic accuracy

$$K_{AB} \approx \frac{4\pi D_{AB}}{\log(1/\tilde{n}a^2)}, \quad (16)$$

where \tilde{n} is the final value of $n(t)$, whose variation is small, $\Delta n(t) = n(t) - \tilde{n} \ll \tilde{n}$, and hence

$$\begin{aligned} \frac{1}{\log n(t)a^2} &= \frac{1}{\log(\tilde{n} + \Delta n)a^2} \approx \\ &\approx \frac{1}{\log \tilde{n}a^2} - \log\left(1 + \frac{\Delta n}{\tilde{n}}\right) \approx \frac{1}{\log \tilde{n}a^2} \end{aligned}$$

because

$$\log(\tilde{n}a^2)^{-1} \gg 1 \gg \log(1 + \Delta n/\tilde{n}).$$

Similarly to the continuum limit in two dimensions (considered in Sec. 4), the reaction rate constant depends on time implicitly and differs from that calculated in the traditional approach (with $\log(D_{AB}t/a^2)$ instead of $\log(1/\tilde{n}t/a^2)$ in the denominator of Eq. (16)) and therefore predicts a much higher decay rate $\dot{n}_{A,B}$ at large times in comparison with the traditional approach [16, 23].

5.3. Catalytically activated reactions

The new approach can be extended to the kinetics of bimolecular, catalytically activated reactions in two or three dimensions. The elementary reaction act between reactants takes place only when these meet on a catalytic site (CS); such sites are assumed to be immobile and randomly distributed in space with a mean concentration n_C .

We start at $t = 0$ with randomly distributed reactant particles A and B with mean concentrations n_A and n_B . Each A (B) particle migrates by jumps to nearest-neighbor sites with the associated diffusivity D_A (D_B). Whenever an A particle lands on a catalytic site that is already occupied by a particle B, the two particles react with a sticking probability $P_{AB} \leq 1$. Reacting particles are immediately removed from the system, whereas the corresponding CS remains unaffected. On the other hand, particles never react at noncatalytic sites.

In this case, the effective reaction constant reduces to

$$K_{ABC} = K'_{AB}n_C = K_{AB}P_{AB}n_C, \quad (17)$$

where K'_{AB} is derived in Eq. (13a) and n_C is the probability that a collision occurs on a CS (owing to the random distribution of CSs in space).

This expression is obtained in the kinetic approach and essentially differs from the one obtained in [39] in the traditional diffusion approach, where (following [12–14]) short-wavelength fluctuations (on the length scale of the reaction radius, $l \approx R_{AB}$), which are beyond the cut-off limit of the theory (Eq. (5)),

$l \gg n^{-1/3} \gg R_{AB}$ (cf. Sec. 2.3), are erroneously taken into account.

6. CONCLUSIONS

The new approach to the diffusion-limited reaction rate theory [1], based on a similar approach to Brownian coagulation proposed in our papers [19–21], is refined and developed further. The traditional diffusion approach to irreversible reactions $A+B \rightarrow C$ that stipulates that the local reaction rate should be equal to the diffusive current of particles is critically analyzed. In particular, it is shown that the diffusion approach is applicable only in the special case of reactions with a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$ (where $\bar{r}_A \approx n_A^{-1/3}$ and $\bar{r}_B \approx n_B^{-1/3}$ are the mean interparticle distances), corresponding to small A particles and large B traps, and becomes inapplicable in calculating the reaction rate in the case $R_{AB} \ll \bar{r}_A, \bar{r}_B$ most important for reaction kinetics and particularly corresponding to comparable-size (or point-like) particles A and B. Indeed, point-like particles tend to a homogeneous (random) spatial distribution owing to their migration and mixing on the scale of the mean interparticle distance, $l \approx \bar{r}$, with the characteristic diffusion time that is small in comparison with the characteristic reaction time, $\tau_d \ll \tau_c$. This implies that particle collisions occur in the kinetic regime with the reaction rate calculated as the collision frequency of two particles (A and B) randomly located in the unit volume.

This approach can be further extended to the analysis of spatial heterogeneities in the ensemble of comparable-size A and B particles if these heterogeneities are smooth on the length scale of the diffusion equation applicability (for the ensemble of point-like particles) $l \gg n_{A,B}^{-1/3} \gg R_{AB}$, but with the reaction constant calculated in the kinetic regime.

In the continuum mode of the kinetic regime corresponding to $a_A, a_B \ll R_{AB}$, where a_A, a_B are the elementary drift distances of particles migrating via random walks, the calculated reaction rate in three dimensions formally (and, in fact, accidentally) coincides with the expression derived in the traditional approach (which is relevant only in the particular case of reactions with a large reaction radius, $\bar{r}_A \ll R_{AB} \ll \bar{r}_B$). This formal coincidence apparently explains a reasonable agreement of the predictions of the kinetic equation derived in the traditional approach with experimental measurements for three-dimensional reaction systems.

But in the two-dimensional geometry corresponding to the reactant particle migration constrained to

a plane, the reaction rate calculated in the traditional approach as the diffusive current of A particles into B traps naturally predicts an explicit time dependence of the reaction rate. On the contrary, in the new approach, the original multiparticle problem is reduced (under the mixing condition) to calculation of the area sweeping rate by migrating particles (of the radius R_{AB} and diffusivity D_{AB}), which depends on time implicitly, via $n_A(t)$ (in the base case $R_{AB} \ll \bar{r}_A, \bar{r}_B$). As a result, in the case $n_A \neq n_B$, the traditional approach notably underestimates the concentration decay rate $\dot{n}_{A,B}$ at large times in comparison with predictions of the new approach.

In the opposite case $a_A, a_B \gg R_{AB}$ (for reacting particles suspended in a fluid), the reaction rate can be calculated in the free molecular approach, also in direct analogy with the Brownian particle coagulation.

The new approach is further generalized to reaction kinetics for particles migrating via random walks over discrete lattice sites (with the lattice spacing a). Because the case of a large reaction radius $R_{AB} \gg a$ properly reduces to the continuum-medium limit, the opposite case $R_{AB} < a$, with reactions occurring when two particles occupy the same site, was additionally studied. In the new approach, the original multiparticle problem is reduced (under the mixing condition) to the calculation of the mean number of distinct sites visited by a k -step random walk of the mobile particle, which for simple three-dimensional and two-dimensional lattices was evaluated in the literature. As a result, new relations for bimolecular reaction rate constants are derived for three-dimensional or two-dimensional lattices, whereas the traditional approach preserves the main deficiencies of the continuum-medium approach (also in application to catalytically activated reactions).

APPENDIX

We show here that calculating the sweeping rate of randomly distributed immobile point-like particles (markers) by a large particle of radius R_{AB} migrating with a diffusivity D_{AB} is equivalent to calculating the condensation rate of the mobile markers migrating with the diffusivity D_{AB} in the immobile trap of the radius R_{AB} . This assertion is important for the derivation of the collision frequency function in the continuum mode of the kinetic regime (Sec. 3). Simultaneously, the applicability limit of the diffusion approach to the calculation of the reaction rate in Sec. 2.1 is additionally confirmed.

We consider an ensemble of $N \rightarrow \infty$ point-like particles randomly distributed in a sample of volume

$V \rightarrow \infty$ with the mean number concentration $n = N/V$ and migrating with the diffusivity D into an immobile trap particle of radius R . The probability for a point particle from this ensemble located at $t = 0$ at a distance \mathbf{r} from the trap particle to reach the trap in time t is denoted by $w(\mathbf{r}, t)$. The integral of this probability over all point-like particles determines the total number of point-like particles trapped in the time interval between 0 to t ,

$$\Phi_n(t) = \int n w(\mathbf{r}, t) d^3 r = 4\pi n \int_R^\infty w(r, t) r^2 dr, \quad (\text{A.1})$$

in accordance with the Fokker–Planck approach to particle migration ([40], see also [11]).

Correspondingly, the number of point particles trapped in the time interval between t and $t + \delta t$ is equal to

$$\frac{d\Phi_n}{dt} \delta t = 4\pi n \delta t \int_R^\infty \frac{\partial w(r, t)}{\partial t} r^2 dr,$$

which determines the condensation rate of point particles in the trap

$$\nu_n = \frac{d\Phi_n}{dt} \delta t = 4\pi n \delta t \int_R^\infty \frac{\partial w(r, t)}{\partial t} r^2 dr. \quad (\text{A.2})$$

It is important that Eq. (A.1) was derived under an implicit assumption that the number of particles in the volume $4\pi r^2 dr$ is large, i. e., $N_r = n \cdot 4\pi r^2 dr \gg 1$, or $n \cdot 4\pi r^3 (dr/r) \gg 1$; only in this case we can neglect fluctuations of the number of particles in this volume, $\sqrt{\langle (\delta N_r)^2 \rangle} \ll N_r$, which allows the subsequent calculation of the total number of trapped particles [11]. In particular, this inequality should be valid at $r = R$, which gives $n \cdot 4\pi R^3 (dr/R) \gg 1$, whereas $dr/R \ll 1$ (in order to correctly perform the integration), or $4\pi dr/R \leq 1$. Therefore, the necessary condition for the correct calculation of the particle condensation rate is $nR^3 \gg 1$, which coincides with the condition of the diffusion approach applicability derived in Sec. 2.1. This implies that these calculations, being applicable to the condensation of small particles in a large trap, become invalid in the case of a small trap (comparable with the size of the particles).

If there is only one point-like particle randomly located in the sample (of volume $V \rightarrow \infty$), it can be found with the probability $V^{-1} d^3 r$ in the elementary volume $d^3 r$ at each point \mathbf{r} , and therefore the probability for this particle to reach the trap in time t can be calculated as

$$\Phi_0(t) = \int_R^\infty V^{-1} w(r, t) 4\pi r^2 dr. \quad (\text{A.3})$$

The probability to reach the trap in δt is therefore equal to

$$\frac{d\Phi_0}{dt} \delta t = \frac{4\pi}{V} \delta t \frac{\partial}{\partial t} \int_R^\infty w(r, t) r^2 dr, \quad (\text{A.4})$$

or, from comparison of Eq. (A.4) with Eq. (A.2),

$$\frac{d\Phi_0}{dt} \delta t = \frac{1}{nV} \frac{d\Phi_n}{dt} \delta t. \quad (\text{A.5})$$

On the other hand, this last probability is equal to the probability for a sole immobile point particle randomly located in the sample to be swept in time δt by the trap particle migrating with the diffusivity D . Indeed, as explained in Sec. 3, the relative displacements between two particles describing diffusion motions independently of each other and with the diffusion coefficients D_1 and D_2 also follow the law of diffusion motion with the diffusion coefficient $D_1 + D_2$ [10, 22]. In this approximation, the probability of sweeping the sole point particle in time δt by the trap particle migrating with the diffusivity D is equal to $V^{-1}\delta V$, where δV is the volume swept in δt . Equating this probability to Eq. (A.5), we obtain

$$\delta V/\delta t = n^{-1} d\Phi_n/dt. \quad (\text{A.6})$$

If there are $N = nV$ immobile point-like particles randomly distributed in the sample, then the total number of particles swept in δt is

$$n\delta V/\delta t = d\Phi_n/dt = \nu_n, \quad (\text{A.7})$$

with ν_n from Eq. (A.2).

Therefore, the condensation rate ν_n of point-like particles migrating with a diffusivity D in the immobile trap particle of radius R is equal to the rate of sweeping of immobile point-like particles by the trap particle migrating with the diffusivity D .

The author thanks V. V. Lebedev (Landau Institute for Theoretical Physics, Moscow) for the valuable discussion of the obtained results. L. A. Bolshov (IBRAE) is acknowledged for his interest in and support of this work.

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