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Quantum Field Methods in the Theory of Diffusion-Controlled Reactions

A. S. Mikhailov[1] **and V. V. Yashin**[1]

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The diagrammatic perturbation technique for the kinetic theory of classical reacting systems with diffusion is developed. It is further applied to investigation of recombination-type reactions in media of one, two, and three dimensions. The effective rates of this reaction are calculated, covering the whole range from the slow to the fast (diffusion-controlled) regimes.

KEY WORDS: Diffusion; reaction; kinetics; master equation; perturbation methods.

1. INTRODUCTION

There are striking similarities in cooperative behavior of physical, chemical, and biological systems far from thermal equilibrium. Investigations of general models of such behavior are the subject of *synergetics*, the new field of interdisciplinary research.(1) Particularity, there is a wide class of abstract models related to the problem of random diffusional wandering of classical particles with irreversible reactions between them, treated as a Markovian discrete random process. The examples are numerous and include exciton–exciton or defect–defect annihilation in solids, chemical reactions in dilute solutions, predator–prey interactions in natural ecosystems, etc. The problem was first adressed in 1917 by M. Smoluchowski(2) in his studies of coagulation phenomena. Recently, considerable progress was made when M. Doi(3) and Ya. B. Zeldovich and A. A. Ovchinnikov(4) had proposed a "quantum field" reformulation of this purely classical problem.

The "quantum field" representation of a master equation for such discrete Markovian processes opens new ways of application of the advanced

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[1] Department of Physics, Moscow State University, Moscow 117234 USSR.

methods of quantum field theory that have turned out to be extremely fruitful in problems of phase transitions or solid state theory. For instance, it gives the possibility to constract the formal solution of a master equation in terms of path integrals and discuss its properties in the WKB approximation (see Ref. 5). Such formal solution can be used further to construct the diagrammatic perturbation technique(6) that largely resembles the Belyaev diagramms(7) for quantum nonideal Bose gases with condensate.

The aim of the present paper is twofold. First, we further develop the diagrammatic technique, proposed in Ref. 6, and describe another way of construction of infinite diagrammatic expansions. Second, we consider the particular problem of two-particle annihilation reactions and calculate the effective rate of such reaction in media of one, two, and three dimensions.

2. FORMULATION OF THE PROBLEM

We assume that some classical particles X perform random wandering with the diffusion constant D in a continuous medium of d dimensions. When two particles X come sufficiently close one to another they can react (annihilate or recombinate) and form the new particle R that does not participate further in the reaction. The inverse reaction of decay of R into two particles X is assumed to be forbidden. The probability per unit time of an elementary act of reaction $X+X \rightarrow R$ between two particles X separated by a distance r is given by the function $W(r)$. This function is sometimes approximated as $W(r)=w_0 \theta(r_0-r)$, i.e., $W(r)$ is constant and equal to w_0 when r is smaller than the "radius of reaction" r_0, and vanishes for $r>r_0$.

With respect to this situation two questions are significant. First, what would be the effective rate of extinction of particles X in the long time limit when their loss due to reaction is not compensated? Second, what steady population density of particles X would be established in presence of some mechanism of uniform generation of these particles X?

Two qualitatively different regimes can be distinguished depending on the value of the parameter $\lambda^2=w_0 r_0^2/D$. When $\lambda^2 \ll 1$ the reaction is called *slow*. Since $\tau_{\text{coll}}=r_0^2/D$ gives the duration of an elementary diffusional collision of two particles, this condition can be written as $w_0 \tau_{\text{coll}} \ll 1$. We see that in this regime only the tiny fraction of all collisions result in reactions between the colliding particles. Hence, diffusion is "more effective" than the reaction: it permanently restores the homogeneous Poissonian distribution of particles X.

When $\lambda^2 \gg 1$, i.e., $w_0 \tau_{\text{coll}} \gg 1$, the reaction is called *fast*. In such regime almost every collision between particles leads to recombination and diffusion is not able to wash off correlations resulting from the reaction. For small population densities, when the average distance between the particles largely exceeds the reaction radius r_0, the effective rate of reaction is limited by diffusion. In order to react any two particles X should come sufficiently close one to another in the process of diffusional wandering. It is said that in this case the reaction is *diffusion-controlled.*

The first theory of diffusion-controlled reactions was given by M. Smoluchowski$^{(2)}$ in connection with his studies of coagulation of colloidal particles in a solution. The effective rate of coagulation had been calculated in Ref. 20 by imposing the absorbing boundary condition for diffusing particles on the surface of the sphere with the radius r_0 for the one-particle Fokker–Planck equation. Later this approach was applied to studies of diffusion-controlled recombination in presence of potential interactions between particles$^{(8)}$ and other problems. Although the method remains popular, it possesses some essential deficiencies. The most important among them is that such theory cannot take into account cooperative effects. Disappearance of two given particles X should influence the probability of reaction for the neighboring particles X, but this is not reflected in such approach. Most clearly this deficiency is revealed in one or two dimensions where an attempt to apply the Smoluchowski theory in the situation with the uniform generation of particles leads to unsatisfactory results (see Ref. 9).

The more consistent way of construction the theory is to start from the hierarchy of equations for the m-particle distribution functions and truncate the chain of equations by some approximate procedures. This way was first followed in Ref. 10 and later developed in Refs. 9 and 11 where the Kirkwood truncation scheme was applied. In these papers the reaction was again taken into account by imposition of absorbing or partially absorbing boundary conditions. It was still unclear what are the conditions of applicability of such truncation scheme and to what extent partially absorbing boundary conditions can describe regimes with $\lambda^2 = w_0 \tau_{\text{coll}} \sim 1$, that are intermediate between fast and slow reactions.

Complete theoretical description of the system of classical reacting particles is provided by the master equation for the set of the probability functions $\{P_N\}$, which elements[2] $P_N = P_N(\mathbf{r}_1,..., \mathbf{r}_N; t)$ give the probability to find at the moment t in the medium N particles X located at points $\mathbf{r}_1,..., \mathbf{r}_N$. Since all reacting particles are identical, functions P_N are symmetrical under permutations. The master equation mixes the functions P_N corresponding to different total numbers N of particles X because the number of particles is not conserved in the process of the reaction.

It was noted in Refs. 3 and 4 that there exists a profound analogy between this master equation, describing the classical probability problem,

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[2] They should not be confused with the m-particle distribution functions that were discussed above.

and the Schrödinger equation for quantum systems of identical Bose particles with reactions that do not conserve the number of these particles. Indeed, in the latter case the system is described by a set of wave functions $\{\Psi_N\}$ symmetrical under permutations, and the Schrödinger equation mixes the components Ψ_N with different numbers N. It is well known that the best way to deal with a quantum many-body problem is to use the second quantized representation, introducing the creation and annihilation Bose operators. Why could we not apply the same procedure to a classical master equation?

The formal "second quantization" of the master equation has been realized by M. Doi⁽³⁾ and independently by Ya. B. Zeldovich and A. A. Ovchinnikov.⁽⁴⁾ In the new representation this equation is written

$$\frac{\partial}{\partial t}|\phi\rangle = \hat{H}|\phi\rangle \tag{1}$$

where $\hat{H}$ is the linear kinetic operator, expressed in terms of creation and annihilation operators a_k^+ and a_k. For the recombination reaction $X + X \to R$ it has the form⁽³⁾

$$\begin{aligned} H = &-\sum_k Dk^2 a_k^+ a_k + 1/V \sum_k W(k)\, a_k a_{-k} \\ &- 1/V \sum_{k,k_1,k_2} W(k)\, a_{k_1+k}^+ a_{k_2-k}^+ a_{k_1} a_{k_2} + VS(a_0^+ - 1) \end{aligned} \tag{2}$$

Here D is the diffusion constant, $W(k)$ is the Fourier transform of the function $W(r)$, V is the volume of the medium. The uniform generation of particles X at the rate S particles per unit time per unit volume is assumed; a_k^+ and a_k are the usual Bose operators with the commutation rule $[a_k, a_{k'}^+] = \Delta(\mathbf{k} - \mathbf{k}')$.

The "state vector" $|\phi\rangle$ is constructed in the following way. Let us first assume that the medium is divided into a system of cells and every cell can be characterized by indication of its center point $\mathbf{r}_m$. Then we can define the distribution function $P(\{n(\mathbf{r}_m)\}, t)$ that gives the joint probability to find $n(\mathbf{r}_m)$ particles within a cell located at a point $\mathbf{r}_m$. The state vector $|\phi\rangle$ is defined as

$$|\phi\rangle = \sum_{\{n(\mathbf{r}_m)\}} P(\{n(\mathbf{r}_m)\}, t) \prod_m (\psi^+(\mathbf{r}_m))^{n(\mathbf{r}_m)} |0\rangle \tag{3}$$

where summation over all possible occupation numbers $\{n(\mathbf{r}_m)\}$ of the cells is performed; $\psi^+(\mathbf{r}_m)$ is the creation operator,

$$[\psi(\mathbf{r}_m), \psi^+(\mathbf{r}_{m'})] = \Delta_{mm'} \tag{4}$$

The vacuum vector $|0\rangle$ satisfies the equation $\psi(\mathbf{r}_m)|0\rangle = 0$ for every m.

After the definition of the state vector the size of the cells can be taken arbitrarily small, thus realizing the transition to the continuous medium.

In the "second quantized" form the master equation (1) looks like the Schrödinger equation with imaginary time and the non-Hermitian Hamiltonian. There is, however, an additional difference in the procedure for finding the average values.

The normalization relation for the distribution $P(\{n(\mathbf{r}_m)\}, t)$ is

$$\sum_{\{n(\mathbf{r}_m)\}} P(\{n(\mathbf{r}_m)\}, t) = 1 \tag{5}$$

In terms of the state vector it can be written as

$$\langle\bar{\phi}|\,\phi\rangle = 1 \tag{6}$$

where $|\bar{\phi}\rangle$ is the fixed normalization vector, defined by the relations

$$a_k\,|\bar{\phi}\rangle = \Delta(\mathbf{k})\,|\bar{\phi}\rangle \tag{7}$$

Every observable property A is associated with a certain Hermitian operator $\hat{A}$ and the average value of A is found as

$$\bar{A} = \langle\bar{\phi}|\,\hat{A}\,|\phi\rangle \tag{8}$$

For example, the total number of particles in the medium corresponds to an operator

$$\hat{N} = \sum_k a_k^+ a_k \tag{9}$$

The average total number of particles is [cf. (7)]

$$\bar{N} = \langle\bar{\phi}|\,a_0\,|\phi\rangle \equiv \langle a_0\rangle \tag{10}$$

3. THE DIAGRAMMATIC PERTURBATION TECHNIQUE

The "second quantized" representation of the master equation can be used to develop the diagrammatic perturbation methods, analogous to that of the quantum field theory.$^{(6)}$

According to (1), (2), and (10), the temporal evolution of the average population density $\bar{n} = \bar{N}/V$ is determined by the equation

$$\dot{\bar{n}} = 1/V\langle a_0 H\rangle \tag{11}$$

or

$$\dot{\bar{n}} = -(2/V^2)\sum_k W(k)\,\langle a_k a_{-k}\rangle + S \tag{12}$$

Next we introduce the interaction representation. The kinetic operator H can be split as $H = H_0 + H_{\text{int}}$, where $H_0 = -\sum_k Dk^2 a_k^+ a_k$ describes free diffusion and H_{int} includes all the terms related to reactions. In the new representation we have

$$\tilde{a}_k(t) = e^{H_0 t} a_k e^{-H_0 t} \tag{13}$$

$$\frac{\partial}{\partial t} |\tilde{\phi}(t)\rangle = \tilde{H}_{\text{int}}(t)\, |\tilde{\phi}(t)\rangle \tag{14}$$

where $\tilde{H}_{\text{int}}(t) = \exp(H_0 t)\, H_{\text{int}} \exp(-H_0 t)$.

Equation (14) can be formally solved as

$$|\tilde{\phi}(t)\rangle = U(t, t_0)\, |\tilde{\phi}(t_0)\rangle \tag{15}$$

with the evolution operator

$$U(t, t_0) = \hat{T} \exp\left[\int_{t_0}^{t} \tilde{H}_{\text{int}}(t')\, dt'\right] \tag{16}$$

where $\hat{T}$ is the symbol of chronological ordering.

We assume that in the limit $t_0 \to -\infty$ the reaction and generation of particles are adiabatically eliminated so that the initial state $|\tilde{\phi}(-\infty)\rangle$ corresponds to N_0 particles *independently* distributed in the volume V. When the reaction and generation are then slowly switched on, in the limit $t \to \infty$ the steady state $|\tilde{\phi}(+\infty)\rangle$ would be reached that would be characterized by a certain average total number $\bar{N}$ of reacting particles, $\bar{N} = \bar{n}V$. Note that the procedure of slow switching on of the reaction and generation can always be carried out in such a way that the average total number of particles would remain constant. Particularily we are justified to assume that the initial number of particles N_0 was the same as the average number of particles $\bar{N}$ in the final steady state for which $\dot{\bar{n}} = 0$ in Eq. (12).

By using the interaction representation we can write

$$\begin{aligned} \langle \bar{\phi} |\, a_k a_{-k}\, | \phi \rangle &= \langle \bar{\phi} |\, \tilde{a}_k(t)\, \tilde{a}_{-k}(t)\, U(t, -\infty)\, | \tilde{\phi}(-\infty) \rangle \\ &\equiv \langle \tilde{a}_k(t)\, \tilde{a}_{-k}(t)\, U(t, -\infty) \rangle_0 \end{aligned} \tag{17}$$

By expanding $U(t, -\infty)$ into the infinite series the problem of calculation of this expression is reduced to summation of the terms that are the averaged multitime products of the operators $\tilde{a}_k^+(t)$ and $\tilde{a}_k(t)$ over the initial state $|\tilde{\phi}(-\infty)\rangle$ where the correlations between particles are absent.

Note that the operators $\tilde{a}_0^+(t)$ and $\tilde{a}_0(t)$ in the interaction representation coinside with the operators a_0^+ and a_0 [cf. (13)] and do not depend on time.

Moreover, in the large volume limit, when $\bar{N} \to \infty$ and $V \to \infty$ but $\bar{n} = \bar{N}/V = \text{const}$, we have, for instance,

$$\langle \bar{\phi} |\, a_0 a_0^+ \,|\tilde{\phi}(-\infty)\rangle = \langle \bar{\phi} |\, a_0^+ a_0 \,|\tilde{\phi}(-\infty)\rangle + \langle \bar{\phi} |\, \tilde{\phi}(-\infty)\rangle = \bar{N} + 1 \qquad (18)$$

and

$$\langle \bar{\phi} |\, a_0 \,|\tilde{\phi}(-\infty)\rangle = \bar{N}, \qquad \langle \bar{\phi} |\, a_0^+ \,|\tilde{\phi}(-\infty)\rangle = 1 \qquad (19)$$

Hence, in this limit the operators a_0^+ and a_0 can be treated as c-numbers, by substituting $a_0 \to \bar{n} = \bar{N}/V$ and $a_0^+ \to 1$. Such substitution means that we neglect the fluctuations of the *total* number of molecules X in the volume V. This procedure resembles separation of the condensate part in the quantum theory of nonideal Bose gases (see Ref. 12).

It can be easily seen that the multitime averages of the operators $\tilde{a}_k^+(t)$ and $\tilde{a}_k(t)$ with $\mathbf{k} \neq 0$, taken over the uncorrelated initial state $|\tilde{\phi}(-\infty)\rangle$, factorize into the sum of all possible products of pair correlators, given by the relations

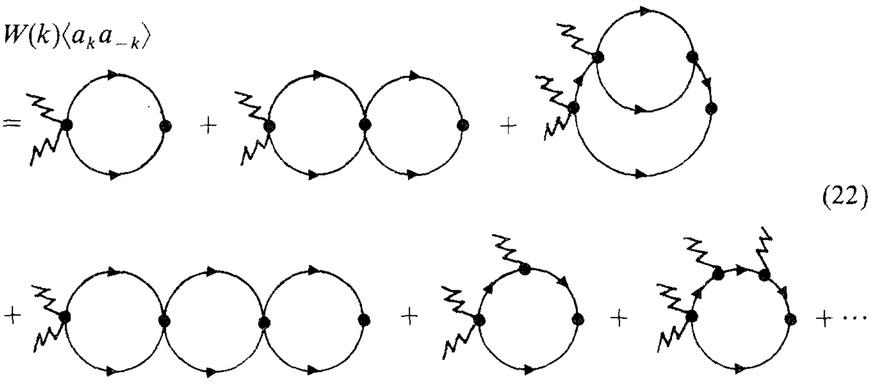
$$\begin{aligned} &\langle \tilde{a}_k(t)\, \tilde{a}_{k'}(t')\rangle_0 = 0 \\ &\langle \hat{T} \tilde{a}_k(t)\, \tilde{a}_{k'}^+(t')\rangle_0 = \Delta(\mathbf{k} - \mathbf{k}')\, G_k^0(t - t') \end{aligned} \qquad (20)$$

Here G_k^0 is the Green's function of free diffusional propagation

$$G_k^0 = \exp(-Dk^2\tau), \qquad \tau > 0; \qquad G_k^0(\tau) = 0, \qquad \tau \leqslant 0 \qquad (21)$$

By introducing the graphic notations, we are able then to represent $\langle a_k a_{-k}\rangle$ as a sum of the infinite diagrammatic series

$W(k)\langle a_k a_{-k}\rangle$

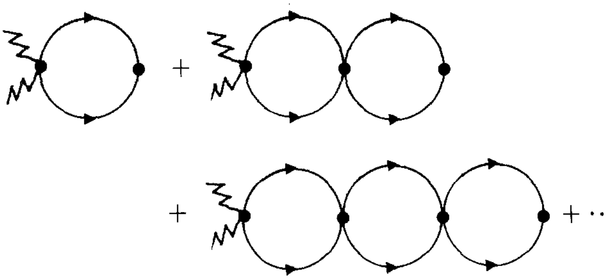


(22)

Here solid lines denote the functions $G_k^0(\tau)$, zigzag lines correspond to the "condensate" $\bar{n}$, and dots indicate the quantity $W(k)$.

Since we are interested in investigation of the limit of small population densities $\bar{n}$, we can omit in (22) all contributions with three or more zigzag lines. The remaining diagramms are of the ladder type,

$W(k)\langle a_k a_{-k} \rangle =$



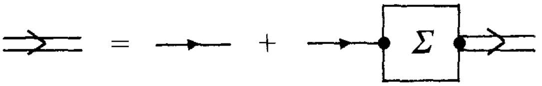
(23)

and can be easily summed.

In the medium of three dimensions this leads to a satisfactory result (see Ref. 6 and discussion below), but in one- or two-dimensional media there would be divergencies at $k \to 0$. More close analysis shows that such divergencies arise because the Laplace transform of the free propagation Green's function $G_k^0(z) = (z + Dk^2)^{-1}$ has singularity at $z \to 0, k \to 0$. In an attempt to eliminate these divergencies we can replace all free propagation Green's functions in (22) by the real propagation Green's functions that are defined as

$$G_k(\tau) = \langle \hat{T} a_k(t+\tau)\, a_k^+(t) \rangle = \langle \hat{T} \tilde{a}_k(t+\tau)\, \tilde{a}_k^+(t)\, U(\infty, -\infty) \rangle_0 \tag{24}$$

After summation of all weakly connected diagrams in the series for G_k we come to the Dyson equation:



(25)

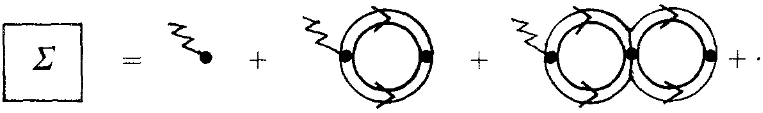
or, in the explicite form,

$$G_k(z) = [z + Dk^2 - \Sigma_k(z)]^{-1} \tag{26}$$

The quantity $\Sigma_k(z)$ is small since it is proportional to the average population density of particles $\bar{n}$. Therefore the difference between $G_k(z)$ and $G_k^0(z)$ is significant only where $G_k^0(z)$ has a singularity, i.e., at $z = 0$ and $k = 0$. Hence we can choose $G_k(z)$ in the approximate form as

$$G_k(z) \cong [z + Dk^2 - \Sigma_0(0)]^{-1} \tag{27}$$

In the diagrammatic series for $\Sigma_0(0)$ we again keep only the terms of the lowest (linear) order in $\bar{n}$ and obtain



(28)

This infinite diagrammatic series is easily summed. As a result we find that

$$\Sigma_0(0) = -4\bar{n}\Gamma_0 \tag{29}$$

where Γ_0 is the value at $k = 0$ of the function Γ_k that satisfies the integral equation

$$\Gamma_k = W(k) - \frac{1}{(2\pi)^d} \int W(\mathbf{k} - \mathbf{k}')\, \Gamma_{k'} \frac{\mathbf{dk}'}{Dk'^2 + |\Sigma_0(0)|} \tag{30}$$

Taken together, Eqs. (29) and (30) determine the quantity $\Sigma_0(0)$.

4. THE EFFECTIVE RATE OF THE REACTION

When the result of summation of the infinite series (23) with real propagation Green's functions is substituted into (12) we find

$$\dot{\bar{n}} = -K_{\text{eff}}\bar{n}^2 + S = 0 \tag{31}$$

where K_{eff} is the *effective rate* of this reaction and is given by the expression

$$K_{\text{eff}} = 2\Gamma_0 \tag{32}$$

Hence, the problem of calculation of the effective rate of the reaction is reduced to solving Eqs. (29) and (30).

Generally this is rather difficult task. However, the situation is simplified if we assume the particular form of the function $W(r)$, i.e., $W(r) = w_0\theta(r_0 - r)$.

After the inverse Fourier transform Eq. (30) can be written

$$\Gamma(r) = W(r) - D^{-1}W(r)\,Z(r) \tag{33}$$

where a new function $Z(r)$, defined as

$$Z(r) = \int \frac{\mathbf{dk}}{(2\pi)^d} \frac{\Gamma_k}{k^2 + \sigma_0^2} e^{i\mathbf{kr}} \tag{34}$$

satisfies the differential equation

$$(\Delta - \sigma_0^2)\, Z(r) = W(r)[D^{-1}Z(r) - 1] \tag{35}$$

We have introduced here the notation $\sigma_0^2 = |\Sigma_0(0)|/D$.

First we consider the one-dimensional case where the solution to (35) is given by

$$Z(x) = A_1 \cosh \mu x + (w_0/\mu^2) \tag{36}$$

with $\mu^2 = \sigma_0^2 + w_0/D$. Therefore the Fourier transform of $\Gamma(x)$ [cf. (33)] is

$$\Gamma_k = 2\sigma_0^2 \mu^{-2} w_0 r_0 \frac{\sin kr_0}{kr_0} - w_0 D^{-1} A_1 \int_{-r_0}^{r_0} \cosh \mu x e^{-ikx}\, dx \tag{37}$$

To find the unknown coefficient A_1 we substitute (37) into (34) and obtain an algebraic equation for A_1. Its solution is

$$A_1 = -\frac{\lambda^2}{(\mu r_0)^2} \frac{D\sigma_0 r_0}{\mu r_0 \sinh \mu r_0 + \sigma_0 r_0 \cosh \mu r_0} \tag{38}$$

where $\lambda^2 = w_0 r_0^2/D$. By using (29) it can be shown that $(\sigma_0 r_0)^2 \leqslant 8\bar{n} r_0 \lambda^2$. Hence, at small densities, such that $(\sigma_0 r_0)^2 \ll \lambda^2$, we have

$$\Gamma_0 = \frac{2w_0 \tanh \lambda}{\lambda} \frac{\sigma_0 r_0}{\sigma_0 r_0 + \lambda \tanh \lambda} \tag{39}$$

The quantity σ_0 is determined from Eq. (29) that can be written

$$(\sigma_0 r_0)^2 = 4\bar{n} r_0^2 D^{-1} \Gamma_0 \tag{40}$$

Solution of (39) and (40) gives the expression for the effective rate

$$K_{\text{eff}} = 4w_0 r_0 \frac{(\lambda^2 \tanh^2 \lambda + 32\bar{n} r_0 \lambda \tanh \lambda)^{1/2} - \lambda \tanh \lambda}{(\lambda^2 \tanh^2 \lambda + 32\bar{n} r_0 \lambda \tanh \lambda)^{1/2} + \lambda \tanh \lambda} \tag{41}$$

At the values of the parameter λ that correspond to the fast or intermediate reactions ($\lambda \gtrsim 1$)

$$K_{\text{eff}} = 32 D\bar{n} \tag{42}$$

In this case the reaction is diffusion-controlled. In the opposite situation of slow reaction ($\lambda \ll 1$) the expression (42) still holds if $\bar{n} r_0 \ll \lambda^2 \ll 1$, while under the condition $\lambda^2 \ll \bar{n} r_0 \ll 1$ the classical result

$$K_{\text{eff}} = 4 w_0 r_0$$

of the "chemically controlled" effective rate is reproduced.

Consider next the two-dimensional system. Here the solution of Eq. (53) for $r < r_0$ should be sought in the form

$$Z(r) = A_2 I_0(\mu r) + (w_0/\mu^2) \tag{43}$$

where $I_0(x)$ is the modified first-order Bessel function.

By following the same line of arguments as in the one-dimensional case, we find

$$\Gamma_k = (2\pi w_0 r_0^2 \sigma_0^2/\mu^2)[J_1(kr_0)/kr_0] - 2\pi(w_0 A_2/D) \int_0^{r_0} r I_0(\mu r)\, J_0(kr)\, dr \tag{44}$$

Here $J_0(x)$ and $J_1(x)$ are the Bessel functions and

$$\begin{aligned} A_2 = {} & -\frac{w_0(\sigma_0 r_0)^2}{\mu^2\lambda^2}\,\frac{\mu r_0 I_1(\sigma_0 r_0)}{\sigma_0 r_0 I_1(\mu r_0)} \left\{ (1 + (\sigma_0 r_0)^2 \lambda^{-2}) \right. \\ & \times \left[I_0(\sigma_0 r_0) + I_1(\sigma_0 r_0) \frac{K_0(\sigma_0 r_0)}{K_1(\sigma_0 r_0)} \right. \\ & \left. - \frac{\mu r_0}{I_1(\mu r_0)} \int_0^1 I_0(\mu r_0 x)\, I_0(\sigma_0 r_0 x) x\, dx \right\}^{-1} \end{aligned} \tag{45}$$

$K_0(x)$ and $K_1(x)$ are the modified second-order Bessel functions. In the limit of small densities, such that $\sigma_0 r_0 \ll 1$ and $\mu r_0 \approx \lambda$, we have

$$A_2 \cong -\frac{D}{\lambda I_1(\lambda)\, |\ln(\sigma_0 r_0)|} \tag{46}$$

By substituting (46) into (44) and using (32) we find that in this limit in two-dimensional systems the effective rate of reaction is

$$K_{\text{eff}} = \frac{4\pi D}{|\ln(\sigma_0 r_0)|} \tag{47}$$

where σ_0 satisfies the transcendental equation

$$\sigma_0^2 = \frac{8\pi \bar{n}}{|\ln(\sigma_0 r_0)|} \tag{48}$$

Finally we turn to investigation of the reaction in three-dimensional media. Simple analysis of Eq. (30) reveals that in this case the long-wave divergencies are absent and the correction term $|\Sigma_0(0)|$ in the denominator of

(30) can be neglected, which corresponds to putting $\sigma_0 = 0$ in Eq. (35). Then the function $Z(r)$ can be sought in the form

$$Z(r) = A_3 \sinh(\lambda r/r_0)/r + D \tag{49}$$

so that

$$\Gamma_k = -4\pi(w_0/D) A_3 \int_0^{r_0} [\sin(kr_0)/k] \sinh[(w_0/D)^{1/2} r] \, dr \tag{50}$$

Substitution of (50) into (34) gives

$$A_3 = -[Dr_0/\lambda \cosh \lambda] \tag{51}$$

Hence, the effective rate of the reaction in three-dimensional systems is

$$K_{\text{eff}} = 8\pi Dr_0[1 - (\tanh \lambda)/\lambda] \tag{52}$$

Note that our derivation has not used any assumptions about the value of λ. In the limit of fast reactions ($\lambda \gg 1$) Eq. (52) reduces to the well-known result of Smoluchowski,

$$K_{\text{eff}} = 8\pi Dr_0 \tag{53}$$

while for the slow reactions ($\lambda \ll 1$) we reproduce the classical result of chemical kinetics

$$K_{\text{eff}} = (8\pi/3) w_0 r_0^3$$

which corresponds to the "chemically controlled" process of reaction.

5. DISCUSSION

In accordance with Refs. 3 and 6 our results show that the Smoluchowski theory gives correst predictions for the three-dimensional media in the limit of extremely fast reactions. For intermediate reactions Eq. (52) for K_{eff} differs from the expression, obtained in Ref. 10 by application of the partially absorbing boundary condition. This difference has clear interpretation. According to the boundary condition used in Ref. 10 a particle cannot penetrate into the reaction sphere (where $|\mathbf{r}| < r_0$)—it is either absorbed by this sphere or reflected. On the contrary, in the model with $W(r) = w_0\theta(r_0 - r)$, that was assumed in the present paper, a particle can penetrate into such sphere and, moreover, the probability of the reaction per unit time remains constant everywhere inside the reaction sphere. Evidently, these two situations are different.

In one- and two-dimensional media in the limit of extremely fast reactions our results [Eqs. (42) and (47), (48)] agree with the predictions of the theories based on the Kirkwood truncation scheme (see Refs. 9 and 11), thus validating such semiphenomenological approximation.

The results [Eqs. (41) and (47), (48)] for the intermidiate and slow reactions in one or two dimensions might seem surprising. We have found that at sufficiently small concentrations, such that $\bar{n}r_0 \ll \lambda^2$ in one dimension, any reaction (slow or intermediate) is effectively controlled by diffusion, owing to a contribution from very slow long-wave fluctuations of density. However, this result is partially supported by the conclusions reached in Ref. 4 where it was shown that in the final stage of *reversible* bimolecular reactions relaxation to thermal equilibrium is, in such situation, diffusionally controlled. In our case the reaction is assumed to be irreversible, but a steady state is still established with time owing to the uniform generation of particles. Note that K_{eff} was defined above as the rate of relaxation to such steady state.

In conclusion we would like to emphasize that the diagrammatic technique, developed in the present paper, can have wide applications in other problems of physics, chemistry, or mathematical biology where the discrete Markovian processes with infinite numbers of states are involved.

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