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1976 J. Phys. A: Math. Gen. 9 1479

(http://iopscience.iop.org/0305-4470/9/9/009)

J. Phys. A: Math. Gen., Vol. 9, No. 9, 1976. Printed in Great Britain.

Stochastic theory of diffusion-controlled reaction

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Received 31 March 1976

Abstract. A stochastic theory of diffusion-controlled reaction is developed with the emphasis on the many-body aspects which rigorous stochastic theories inevitably encounter. The field operator method developed in our previous paper is extensively used in the analysis. The classical Smoluchowski theory is shown to be strictly valid in the long-time scale, and its relation to the Boltzmann equation is discussed.

1. Introduction

Although the theory of diffusion-controlled reaction has been developed by a number of authors, there still remains a fundamental problem open to question (Noyes 1961, Wilemski and Fixman 1973).

To clarify the point, let us consider a simple reaction system

$$A + A \rightarrow B.$$

We assume that all A molecules have Brownian motion independently of each other with diffusion constant D, and that the reaction takes place immediately when a pair of A molecules come within a distance σ. For this system our basic problem is to determine the time evolution of the concentration $\rho(t)$ of A molecules.

The conventional theory, whose original form was given by Smoluchowski (1917) long ago (see also Chandrasekhar 1943, Noyes 1961), solves this problem as follows. In the first step of the theory, attention is focused on a certain A molecule, which we call the test molecule, and the diffusion equation is solved for the concentration $w(\boldsymbol{r}, t)$ of the surrounding A molecules at a point $\boldsymbol{r}$ relative to the test molecule:

$$\frac{\partial w}{\partial t} = D_r \nabla^2 w, \tag{1}$$

under the condition

$$w(\boldsymbol{r}, t = 0) = \rho_0 \tag{2}$$

$$w(\boldsymbol{r}, t) = 0 \qquad \text{at } |\boldsymbol{r}| = \sigma, \tag{3}$$

where $D_r = 2D$ is the relative diffusion constant, and ρ_0 is the initial concentration of the surrounding A molecules which are assumed to be uniformly distributed. The condition (3) means that A molecules cannot be found inside the distance σ because they

immediately react with the test molecule. From the solution of this equation, it follows that the flux of A molecules arriving at the reaction surface $|r| = \sigma$ is given by

$$J(t) = -D_r \int_{|r|=\sigma} \nabla w \cdot d\boldsymbol{S} = \mu\rho_0\left(1 + \frac{\sigma}{(\pi D_r t)^{1/2}}\right), \tag{4}$$

and

$$\mu = 4\pi D_r \sigma. \tag{5}$$

This flux approaches a constant value $\mu\rho_0$ for $t \gg \sigma^2/D$. Then, as the second step, the conventional theory assumes that the mean number of reactions taking place in a unit volume and unit time interval is equal to $\mu\rho_0^2$ if the concentration of A molecules is ρ_0. This assumption leads to the equation for $\rho(t)$:

$$\partial\rho(t)/\partial t = -\mu\rho(t)^2 \qquad (t \gg \sigma^2/D). \tag{6}$$

This equation has the same form as the kinetic equation for the second-order reaction, i.e. the law of mass action. Thus μ is regarded as the second-order reaction rate constant.

Although the above theory may seem plausible, a critical consideration raises many questions. First, in the analysis of $w(r, t)$, the reaction between the test molecule and the surrounding molecules is taken into account by equation (3), but reactions among the surrounding molecules themselves are not taken into account. Thus $w(r, t)$ cannot be the density correlation function, and consequently the meaning of $J(t)$ is not very clear. (In some specific situations, $w(r, t)$ has clear meaning (Steinberg and Kachalski 1968), but the discussion cannot be applied to our pertinent system.) Second, in the actual system, once the test molecule reacts with the surrounding molecules, the test molecule itself disappears from the system. Is this fact taken into account in the above theory? Finally, in the derivation of equation (6), the initial concentration ρ_0 is replaced by $\rho(t)$, the concentration at time t. This is, at least apparently, a curious assumption.

These are not trivial questions. In fact they suggest a basic difficulty in the Smoluchowski theory. The difficulty comes from the following fact: once a pair of reactant molecules react, they cannot react with other molecules, and consequently the histories of the reactant molecules cannot be independent of each other. Therefore the bimolecular reaction problem is essentially a many-body problem even if the molecular motion is assumed to be independent. Clearly, in the Smoluchowski theory, such many-body aspects are hidden behind the probability argument.

The many-body aspects of the bimolecular reaction have been pointed out by several authors. Monchick *et al* (1957) and Waite (1957) derived a hierarchy of equations for the pair distribution functions and showed that a certain decoupling approximation leads to Smoluchowski's result. Teramoto and Shigesada (1967) and Teramoto *et al* (1971) discussed the many-body effect in a more sophisticated manner. Using the binary collision expansion method, they calculated the probability that N particles, initially distributed uniformly, remain unreacted until time t; however, to obtain the time evolution of $\rho(t)$, they had to make the assumption that once any pair of molecules reacts, the remaining molecules are re-arranged so as to be uniformly distributed.

Thus all previous work has included, more or less, some assumptions which, although they may seem plausible, leave us a question in a critical sense.

In this paper we develop a rigorous theory of the diffusion-controlled bimolecular reaction.

Our starting point is the general master equation

$$\frac{\partial}{\partial t}F(x,t) = -\sum_{x'}\lambda(x\to x')F(x,t)+\sum_{x'}\lambda(x'\to x)F(x',t). \tag{7}$$

Here $F(x, t)$ is the probability that the system is in a state specified by a parameter x, and $\lambda(x\to x')$ is the transition rate from the state x to x'.

The master equation has been applied to reaction kinetics by many authors (for a general reference see McQuarrie 1967), but their treatments have been limited to the case where the state of the system is specified only by the number of the reactant molecules included in the system. Such treatment is allowed if the intrinsic reaction rate is slow enough so that the system is assumed to be in spatial equilibrium, but it certainly becomes inappropriate for the diffusion-controlled reaction. In the diffusion-controlled reaction, the spatial gradient for the pair correlation function is essential for the reaction. Thus, in order to apply the master equation to the diffusion-controlled reaction system, we must include the positions of the molecules $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ with the parameter x. In principle there is no conceptual difficulty in such a generalization, but the resulting form of the master equation is very complicated. In the previous paper (Doi 1976, to be referred to as I), we have shown that this difficulty is removed by the field operator representation. The following analysis is extensively based on this representation.

Our master equation includes the most detailed information available for our problem. Any probability or mean values are derived from the fundamental probability $F(x, t)$. Therefore the master equation plays the role of the Liouville equation in the usual dynamical system. Following this analogy, Smoluchowski's kinetic equation corresponds to the Boltzmann equation. In this sense, our problem is to construct the kinetic theory for the diffusion-controlled reaction.

2. Field operator representation

For convenience in the later analysis, we adopt a reaction model proposed by Teramoto and Shigesada (1967), which is more general than that employed in the Smoluchowski theory. In this model, the reaction is assumed to take place between proximate pairs inside a distance σ with a certain intrinsic rate constant λ; $\lambda\,\mathrm{d}t$ is the probability that the proximate pair react in a time interval $\mathrm{d}t$. For this model, the reaction function $R(\boldsymbol{r}, \boldsymbol{r}')$ introduced in I is written as

$$R(\boldsymbol{r},\boldsymbol{r}') = \lambda S(\boldsymbol{r}-\boldsymbol{r}'), \tag{8}$$

where

$$S(\boldsymbol{r}-\boldsymbol{r}') = \begin{cases} 1 & |\boldsymbol{r}-\boldsymbol{r}'|\leqslant\sigma \\ 0 & |\boldsymbol{r}-\boldsymbol{r}'|>\sigma. \end{cases}$$

If λ is very small, the reactants collide many times before reaction, and the system may be assumed to be in spatial equilibrium. On the other hand, if $\lambda\to\infty$, the reaction occurs instantaneously when a pair of reactants come to the distance σ, and the Smoluchowski case is recovered.

According to I, the time evolution operator for this system is written as

$$\mathscr{G} = \mathscr{G}_0 + \mathscr{G}_r \tag{9}$$

$$\mathscr{G}_0 = -D \int d\boldsymbol{r}\, \psi^\dagger(\boldsymbol{r}) \nabla^2 \psi(\boldsymbol{r}) \tag{10}$$

$$\mathscr{G}_r = \tfrac{1}{2}\lambda \int d\boldsymbol{r}\, d\boldsymbol{r}'\, S(\boldsymbol{r}-\boldsymbol{r}')\{\psi^\dagger(\boldsymbol{r})\psi^\dagger(\boldsymbol{r}')\psi(\boldsymbol{r})\psi(\boldsymbol{r}') - \psi(\boldsymbol{r})\psi(\boldsymbol{r}')\}. \tag{11}$$

Here $\psi^\dagger(\boldsymbol{r})$ and $\psi(\boldsymbol{r})$ are the creation and annihilation operators satisfying the commutation relations for Bose particles:

$$[\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r})] = \delta(\boldsymbol{r}-\boldsymbol{r}'), \qquad [\psi^\dagger(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r}')] = [\psi(\boldsymbol{r}), \psi(\boldsymbol{r}')] = 0. \tag{12}$$

Let $P_N(t)$ be the probability that the system includes N A molecules and let $P(\alpha, t)$ be the moment generating function:

$$P(\alpha, t) = \sum_{N=0}^{\infty} \alpha^N P_N(t). \tag{13}$$

In I it was shown that $P(\alpha, t)$ is written in a simple form:

$$P(\alpha, t) = e^{-cV} \langle \alpha | \exp(-\mathscr{G}t) | c \rangle \tag{14}$$

with

$$\langle \alpha | = \langle 0 | \exp\Big(\alpha \int d\boldsymbol{r}\, \psi(\boldsymbol{r})\Big), \qquad |c\rangle = \exp\Big(c \int d\boldsymbol{r}\, \psi^\dagger(\boldsymbol{r})\Big)|0\rangle. \tag{15}$$

Here V is the system volume, c is the initial concentration of A molecules and $|0\rangle$ is the vacuum state:

$$\psi(\boldsymbol{r})|0\rangle = 0, \qquad \langle 0|\psi^\dagger(\boldsymbol{r}) = 0. \tag{16}$$

In equation (14) it is assumed that at $t = 0$ the A molecules are uniformly distributed with concentration c, and that the number of A molecules obeys the Poisson distribution with mean value cV. In fact by using the relation

$$\begin{aligned}\langle \alpha | c \rangle &= \sum_{n,m=0}^{\infty} \frac{c^n \alpha^m}{n!m!} \left\langle 0 \left| \left(\int \psi(\boldsymbol{r})\, d\boldsymbol{r} \right)^m \left(\int \psi^\dagger(\boldsymbol{r}')\, d\boldsymbol{r}' \right)^n \right| 0 \right\rangle \\ &= \sum_{n=0}^{\infty} \frac{c^n \alpha^n}{n!} \left(\int d\boldsymbol{r}\, d\boldsymbol{r}'\, \delta(\boldsymbol{r}-\boldsymbol{r}') \right)^n \\ &= \sum_{n=0}^{\infty} \frac{(c\alpha V)^n}{n!} = e^{c\alpha V}\end{aligned} \tag{17}$$

we have

$$P(\alpha, t=0) = \exp(c\alpha V - cV). \tag{18}$$

This is the moment generating function for the Poisson distribution.

If the initial number of A molecules is fixed at N_0, the moment generating function is written as

$$P_{N_0}(\alpha, t) = \left\langle \alpha \left| \exp(-\mathscr{G}t) \left(V^{-1} \int d\boldsymbol{r}\, \psi^\dagger(\boldsymbol{r}) \right)^{N_0} \right| 0 \right\rangle \tag{19}$$

whose initial value is

$$P_{N_0} = \alpha^{N_0}. \tag{20}$$

The difference in the initial condition will not be important in the limit of $V\to\infty$. Throughout this paper we deal with $P(\alpha, t)$. If necessary, $P_{N_0}(\alpha, t)$ is easily obtained from $P(\alpha, t)$ by the equation

$$P_{N_0}(\alpha, t)=\frac{1}{2\pi i}\frac{N_0!}{V^{N_0}}\oint\frac{dc}{c^{N_0+1}}P(\alpha, t)\,e^{cV}. \tag{21}$$

3. Hierarchy of equations

To show the many-body aspects explicitly, we first derive the hierarchy of equations for the mean density $\rho_1(\boldsymbol{r}; t)$ and the density correlation function $\rho_2(\boldsymbol{r}, \boldsymbol{r}'; t)$ of A molecules defined by;

$$\rho_1(\boldsymbol{r}; t)=\left\langle\sum_{i=1}^{N(t)}\delta(\boldsymbol{r}-\boldsymbol{r}_i(t))\right\rangle,$$

$$\rho_2(\boldsymbol{r}, \boldsymbol{r}'; t)=\left\langle\sum_{i,j=1, i\neq j}^{N(t)}\delta(\boldsymbol{r}-\boldsymbol{r}_i(t))\delta(\boldsymbol{r}'-\boldsymbol{r}_j(t))\right\rangle. \tag{22}$$

Note that in these equations the average $\langle\cdots\rangle$ must be taken not only over the position of A molecules $\boldsymbol{r}_1(t), \boldsymbol{r}_2(t), \ldots$ but also over the number $N(t)$ of A molecules included in the system.

In I, we have shown that these quantities are written as

$$\rho_1(\boldsymbol{r}, t)=\langle\alpha=1|\psi^\dagger(\boldsymbol{r})\psi(\boldsymbol{r})\exp(-\mathscr{G}t)|c\rangle\,e^{-cV}, \tag{23}$$

$$\rho_2(\boldsymbol{r}, \boldsymbol{r}'; t)=\langle\alpha=1|\psi^\dagger(\boldsymbol{r})\psi^\dagger(\boldsymbol{r}')\psi(\boldsymbol{r})\psi(\boldsymbol{r}')\exp(-\mathscr{G}t)|c\rangle\,e^{-cV}. \tag{24}$$

In order to derive the hierarchy of equations, we differentiate equation (23) with respect to t and use the relations

$$\langle\alpha=1|\psi^\dagger(\boldsymbol{r})=\langle\alpha=1|$$

$$[\psi(\boldsymbol{r}), \mathscr{G}]=-D\nabla^2\psi(\boldsymbol{r})+\lambda\int d\boldsymbol{r}'\,S(\boldsymbol{r}-\boldsymbol{r}')\psi^\dagger(\boldsymbol{r}')\psi(\boldsymbol{r})\psi(\boldsymbol{r}')$$

(these relations are obtained from the commutation relation (12) and the definition of the vacuum state (16)), then we have

$$\frac{\partial\rho_1(\boldsymbol{r}; t)}{\partial t}=D\nabla^2\rho_1(\boldsymbol{r}; t)-\lambda\int d\boldsymbol{r}'\,S(\boldsymbol{r}-\boldsymbol{r}')\rho_2(\boldsymbol{r}, \boldsymbol{r}', t). \tag{25}$$

Similarly,

$$\frac{\partial}{\partial t}\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; t)=D(\nabla_1^2+\nabla_2^2)\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; t)-\lambda S(\boldsymbol{r}_1-\boldsymbol{r}_2)\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$$

$$-\lambda\int d\boldsymbol{r}_3(S(\boldsymbol{r}_1-\boldsymbol{r}_3)+S(\boldsymbol{r}_2-\boldsymbol{r}_3))\rho_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3; t). \tag{26}$$

These equations are analogous to the BBKGY equation for the usual many-particle systems.

The above equations have very clear physical meanings, and can be directly derived by a probability argument. However, they have not been presented previously. The

previous hierarchy was concerned with probability densities (Monchick *et al* 1957, Wilemski and Fixman 1973), not mean number densities, and their forms are more complicated than the above equations.

Equation (25) should be compared with equation (6) in the Smoluchowski theory. Since we are considering the homogeneous system, $\rho_1(\boldsymbol{r}; t)$ and $\rho_2(\boldsymbol{r}, \boldsymbol{r}'; t)$ are respectively written as $\rho_1(t)$ ($\equiv\rho(t)$) and $\rho_2(\boldsymbol{r}-\boldsymbol{r}'; t)$. Then equation (25) indicates that equation (6) is a result of the approximation

$$\lambda \int d\boldsymbol{r}'\, S(\boldsymbol{r}-\boldsymbol{r}')\rho_2(\boldsymbol{r}-\boldsymbol{r}'; t) = 4\pi D_r \sigma \rho_1(t)^2 \qquad \text{as } \lambda \to \infty. \tag{27}$$

The validity of such an approximation is not obvious. It is just this point which we wish to clarify in the following sections.

4. Diagrammatic representation

To calculate $P(\alpha, t)$ we make use of the diagram technique. Since the method is now a familiar one in both classical and quantum systems (Resibois 1967, Abrikosov *et al* 1963) we shall give only the outline of the method.

First we introduce the field operator in momentum space:

$$a_{\boldsymbol{k}} = \frac{1}{\sqrt{V}} \int d\boldsymbol{r}\, \psi(\boldsymbol{r})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}; \qquad a_{\boldsymbol{k}}^\dagger = \frac{1}{\sqrt{V}} \int d\boldsymbol{r}\, \psi^\dagger(\boldsymbol{r})\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \tag{28}$$

then equations (9)–(12) are rewritten as

$$\mathcal{G}_0 = D \sum_{\boldsymbol{k}} \boldsymbol{k}^2 a_{\boldsymbol{k}}^\dagger a_{\boldsymbol{k}}$$

$$\mathcal{G}_r = \frac{\lambda}{2V} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} S(\boldsymbol{q}) a_{\boldsymbol{k}+\boldsymbol{q}}^\dagger a_{\boldsymbol{k}'-\boldsymbol{q}}^\dagger a_{\boldsymbol{k}} a_{\boldsymbol{k}'} - \frac{\lambda}{2} \sum_{\boldsymbol{q}} S(\boldsymbol{q}) a_{\boldsymbol{q}} a_{-\boldsymbol{q}} \tag{29}$$

$$|c\rangle = \exp(cV^{1/2} a_0^\dagger)|0\rangle; \qquad \langle\alpha| = \langle 0| \exp(\alpha V^{1/2} a_0) \tag{30}$$

$$[a_{\boldsymbol{k}}, a_{\boldsymbol{k}'}^\dagger] = \delta_{\boldsymbol{k}\boldsymbol{k}'}; \qquad [a_{\boldsymbol{k}}, a_{\boldsymbol{k}'}] = [a_{\boldsymbol{k}}^\dagger, a_{\boldsymbol{k}'}^\dagger] = 0, \tag{31}$$

where

$$S(\boldsymbol{q}) = \int d\boldsymbol{r}\, S(\boldsymbol{r})\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}}. \tag{32}$$

The interaction representation of an operator A is defined by

$$A(t) = \exp(\mathcal{G}_0 t) A \exp(-\mathcal{G}_0 t). \tag{33}$$

In this representation, $P(\alpha, t)$ is written as

$$P(\alpha, t) = e^{-cV} \left\langle \alpha \middle| T \exp\left(-\int_0^t dt'\, \mathcal{G}_r(t') \right) \middle| c \right\rangle$$

$$= e^{-cV} \left\langle 0 \middle| T \exp(cV^{1/2} a_0(t)) \exp\left(-\int_0^t dt'\, \mathcal{G}_r(t') \right) \exp(cV^{1/2} a_0^\dagger(0)) \middle| 0 \right\rangle \tag{34}$$

where T is the chronological operator which arranges the operators $a_{\boldsymbol{k}}(t)$ and

$a^\dagger_{k'}(t')$, . . . , in the order from right to left according to the increase of the time argument. In deriving these equations, we have used the relation $a_0(t) = a_0$ and $a^\dagger_0(t) = a^\dagger_0$.

To calculate equation (34), we expand the exponentials and use Wick's theorem:

$$\langle 0|Ta_{k_1}(t_1)a_{k_2}(t_2)\ldots a_{k_n}(t_n)a^\dagger_{k'_1}(t'_1)\ldots a^\dagger_{k'_m}(t'_m)|0\rangle$$

$$= \delta_{nm} \sum_{\substack{\text{all} \\ \text{permutations}}} \langle 0|Ta_{k_1}(t_1)a^\dagger_{k'_i}(t'_i)|0\rangle\langle 0|Ta_{k_2}(t_2)a^\dagger_{k'_j}(t'_j)|0\rangle$$

$$\times \ldots \langle 0|Ta_{k_n}(t_n)a^\dagger_{k'_p}(t'_p)|0\rangle, \tag{35}$$

where $(i, j, \ldots, p)$ are the permutations of $(1, 2, \ldots, m)$, the summation must be taken over all possible permutations, and

$$\langle 0|Ta_{\boldsymbol{k}}(t)a^\dagger_{\boldsymbol{k}'}(t')|0\rangle = \delta_{\boldsymbol{k}\boldsymbol{k}'}G_{\boldsymbol{k}}(t-t'),$$

$$G_{\boldsymbol{k}}(t) = \begin{cases} \exp(-D\boldsymbol{k}^2 t) & t \geqslant 0 \\ 0 & t < 0. \end{cases} \tag{36}$$

Equation (35) is proved by use of the relations

$$a_{\boldsymbol{k}}(t) = \exp(-D\boldsymbol{k}^2 t)a_{\boldsymbol{k}}, \qquad a^\dagger_{\boldsymbol{k}}(t) = \exp(D\boldsymbol{k}^2 t)a^\dagger_{\boldsymbol{k}},$$

together with equations (16) and (31).

Each term in the expansion of equation (34) is represented by a diagram. The correspondence rule is listed in table 1.

Table 1. Correspondence rule for the evaluation $Q(\alpha, t)$.

Element of a diagram	Factor in $Q(\alpha, t)$	Reference name
$t \quad \boldsymbol{k} \quad t'$	$G_{\boldsymbol{k}}(t-t')$	$G_{\boldsymbol{k}}$ line†
$\boldsymbol{q}$	$-\frac{\lambda}{V}S(\boldsymbol{q})$	$S_1(\boldsymbol{q})$ line†‡
$\boldsymbol{q}$	$\lambda S(\boldsymbol{q})$	$S_2(\boldsymbol{q})$ line†‡

† If momentum is not specified, it is often suppressed, e.g. the $G_{\boldsymbol{k}}$ line is called simply the G line.

‡ S_1 and S_2 lines are both called S lines.

As in the usual many-body problems, $P(\alpha, t)$ can be expressed only by connected diagrams. By use of the first Mayer theorem (Uhlenbeck and Ford 1963), we can show the identity

$$\frac{\langle\alpha|T\exp(-\int_0^t \mathrm{d}t'\ \mathscr{G}_{\mathrm{r}}(t'))|c\rangle}{\langle\alpha|c\rangle} = \exp\left[\left\langle\alpha\left|T\exp\left(-\int_0^t \mathrm{d}t'\ \mathscr{G}_{\mathrm{r}}(t')\right)\right|c\right\rangle_{\mathrm{c}}\right]. \tag{37}$$

Here $\langle\alpha|\ldots|c\rangle_{\mathrm{c}}$ denotes the sum of the connected diagrams which include at least one S line. From equations (34), (37) and (17), we have

$$P(\alpha, t) = \exp(cV(\alpha - 1) + Q(\alpha, t)) \tag{38}$$

with

$$Q(\alpha, t)=\left\langle \alpha \middle| T\exp\left(-\int_0^t \mathscr{G}_r(t')\,dt'\right)\middle| c\right\rangle_c. \tag{39}$$

In figure 1, the diagrams are shown up to the second order in λ.

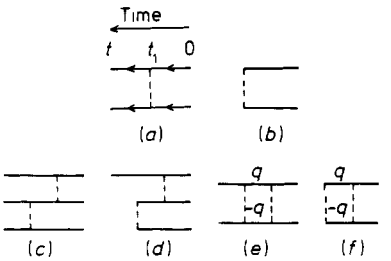

Figure 1. Diagrams for $Q(\alpha, t)$.

The general structure of the diagram is as follows. At time $t=0$, G_0 lines start. They interact through S_1 lines and exchange momenta. The G_k lines terminate either at the ends of $S_2(k)$ lines, or at the final time $t=t$. In the latter case, G_k must be G_0.

We call the starting point at $t=0$ the c-point, and the ending point at $t=t$ the α-point. Then the diagram including n c-points, m α-points, p_1 S_1 lines and p_2 S_2 lines is evaluated as

$$\frac{c^n\alpha^m}{s}V^{(n+m)/2}\left(-\frac{\lambda}{V}\right)^{p_1}\lambda^{p_2}\sum_{q_1,q_2,\ldots}\int_0^t dt_1\ldots\int_0^{t_{p-1}} dt_p \text{ product of } G_k \text{ and } S(q), \tag{40}$$

where $p=p_1+p_2$ is the number of S lines, and the factor s is the so called symmetric number (Uhlenbeck and Ford 1963, chap 2). For example, figure 1(e) is evaluated as

$$\tfrac{1}{2}\lambda^2\alpha^2c^2\sum_q\int_0^t dt_1\int_0^{t_1} dt_2\, S(q)^2G_q(t_1-t_2)G_{-q}(t_1-t_2). \tag{41}$$

5. Spatial equilibrium case

Before proceeding to the analysis of the general case, we first discuss the simple case of $\lambda\to 0$. In this case, as was mentioned in § 2, the system may be assumed to be in spatial equilibrium. This case has been treated by previous stochastic theories (McQuarrie *et al* 1964, Ishida 1964, McQuarrie 1967). Here we discuss it in connection with our diagram technique developed in § 4. The result of this section will be utilized in the discussion of the general case.

Since no interaction potential is assumed in our model, the spatial equilibrium state corresponds to the state where all A molecules are uniformly distributed independently of each other. Therefore we may neglect a_k and $a_k^\dagger$ except for a_0 and $a_0^\dagger$ in $\mathscr{G}$. Thus,

abbreviating a_0 and $a_0^\dagger$ as a and $a^\dagger$ respectively, we may write equations (34) and (39) as

$$P(\alpha, t) = \mathrm{e}^{-cV}\left\langle \alpha \left| \exp\left[-\frac{\mu_0 t}{2}\left(\frac{a^{\dagger 2}a^2}{V} - a^2 \right) \right] \right| c \right\rangle, \tag{42}$$

$$Q(\alpha, t) = \left\langle \alpha \left| \exp\left[-\frac{\mu_0 t}{2}\left(\frac{a^{\dagger 2}a^2}{V} - a^2 \right) \right] \right| c \right\rangle_{\mathrm{c}}, \tag{43}$$

with

$$\mu_0 = \lambda S(\boldsymbol{q} = 0) = \tfrac{4}{3}\pi\sigma^3\lambda. \tag{44}$$

Equation (42) leads to the master equation employed in previous stochastic theories. Differentiating equation (42) with respect to t and using the property,

$$\langle \alpha | a^\dagger = \alpha V^{1/2}\langle \alpha |,$$

we have

$$\begin{aligned} \frac{\partial}{\partial t}P(\alpha, t) &= -\frac{\mu_0}{2}(\alpha^2 - 1)\langle 0 | \exp(\alpha V^{1/2}a)a^2 \exp(-\mathscr{G}t)|c\rangle \mathrm{e}^{cV} \\ &= -\frac{\mu_0}{2V}(\alpha^2 - 1)\frac{\partial^2}{\partial \alpha^2}P(\alpha, t). \end{aligned} \tag{45}$$

From equations (13) and (45), we have the familiar master equation

$$\frac{\partial}{\partial t}P_N(t) = -\frac{\mu_0}{2V}N(N-1)P_N(t) + \frac{\mu_0}{2V}(N+2)(N+1)P_{N+2}(t). \tag{46}$$

The rigorous solution of the above equation is known (McQuarrie *et al* 1964, Ishida 1964), but it is very complicated. We therefore investigate the asymptotic behaviour of the solution as $V \to \infty$.

We first show that in the limit of $V \to \infty$ $P(\alpha, t)$ has the following asymptotic form:

$$P(\alpha, t) = \exp\{V[\chi(\alpha, t) + \mathrm{O}(1/V)]\}. \tag{47}$$

Here the function $\chi(\alpha, t)$ does not depend on V. To prove this, we investigate the V dependence of the general term of equation (43). From equation (40), the diagram including n c-points, m α-points, $p_1 S_1$ lines and $p_2 S_2$ lines is proportional to $V^{(n+m)/2-p_1}$. Since one S_2 line destroys two G lines, the following equality must hold:

$$n - 2p_2 = m. \tag{48}$$

Furthermore, from the condition that the diagram must be connected, we have

$$n \leq p_1 + p_2 + 1. \tag{49}$$

because one S line connects at most two c-points. From equations (48) and (49), the dominant terms in V are found to be proportional to V, and equation (47) is established.

The above discussion indicates the structure of the diagrams contributing to $\chi(\alpha, t)$. In order to satisfy the equality in equation (49), the diagram including n c-points must contain $n-1$ S lines. In figure 2, these diagrams are shown up to order μ_0^3. We call these diagrams open diagrams, and the other diagrams closed diagrams because the latter include at least one closed loop consisting of G and S lines.

The function $\chi(\alpha, t)$ is, of course, directly evaluated from these open diagrams, but the calculation becomes very complicated. A more convenient way is as follows.

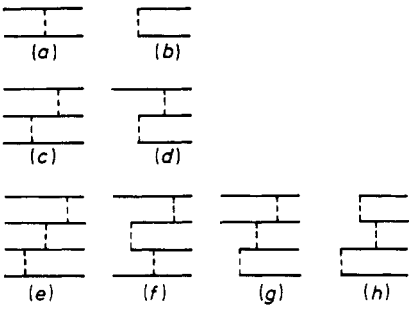

Figure 2. Open diagrams up to the order of μ_0^3.

We substitute equation (47) into equation (45) and retain only the dominant term in V. The result is

$$\frac{\partial \chi}{\partial t} = -\frac{\mu_0}{2}(\alpha^2 - 1)\left(\frac{\partial \chi}{\partial \alpha}\right)^2. \tag{50}$$

This equation is still difficult to solve; however, quantities of our interest can be calculated easily. From equations (13) and (47), we have

$$\langle N(t)\rangle = \sum_{N=0}^{\infty} NP_N(t) = [\partial P(\alpha, t)/\partial \alpha]_{\alpha=1} = V[\partial \chi/\partial \alpha]_{\alpha=1} + O(V^0). \tag{51}$$

Similarly

$$\langle \Delta N^2(t)\rangle = \langle N^2(t)\rangle - \langle N(t)\rangle^2 = V\left[\frac{\partial}{\partial \alpha}\alpha\frac{\partial \chi}{\partial \alpha}\right]_{\alpha=1} + O(V^0). \tag{52}$$

Let us expand $\chi(\alpha, t)$ into a power series of $(\alpha - 1)$:

$$\chi(\alpha, t) = \chi_0(t) + \chi_1(t)(\alpha - 1) + \chi_2(t)(\alpha - 1)^2 + \ldots. \tag{53}$$

Then

$$\langle N\rangle = V\chi_1 \qquad \text{and} \qquad \langle \Delta N^2\rangle = (2\chi_2 + \chi_1)V. \tag{54}$$

Now if we substitute equation (53) into (50) and equate the coefficient of the same power in $(\alpha - 1)$, we have

$$d\chi_0/dt = 0, \qquad d\chi_1/dt = -\mu_0\chi_1^2, \qquad d\chi_2/dt = -\tfrac{1}{2}\mu_0\chi_1^2 - 4\mu_0\chi_1\chi_2, \ldots \tag{55}$$

In terms of $\langle N\rangle$ and $\langle \Delta N^2\rangle$, equation (55) is rewritten as

$$\frac{d}{dt}\langle N\rangle = -\frac{\mu_0}{V}\langle N\rangle^2, \tag{56}$$

$$\frac{d}{dt}\langle \Delta N^2\rangle = -\frac{2\mu_0}{V}(2\langle N\rangle\langle \Delta N^2\rangle - \langle N\rangle^2). \tag{57}$$

Equation (56) is just the law of mass action (6). Thus we obtain an important conclusion: the sum of open diagrams yields the kinetic equation (6).

Note that the above equations are not trivial results. In fact if we start from equation (46), we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle N\rangle = -\frac{\mu_0}{V}\langle N(N-1)\rangle,$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \Delta N^2\rangle = -\frac{2\mu_0}{V}(\langle N(N-1)^2\rangle - \langle N(N-1)\rangle\langle N\rangle). \tag{58}$$

Thus the equations for $\langle N\rangle$ and $\langle \Delta N^2\rangle$ are not closed. In order to obtain a closed equation, we must assume $V\to\infty$.

In previous theories, equation (58) has been analysed by some decoupling approximation. A successful decoupling method was proposed by Teramoto and Shigesada (1967). They assumed that $P_N(t)$ has a Gaussian form

$$P_N(t) = (2\pi\langle \Delta N^2\rangle)^{-1/2}\exp\left(-\frac{(N-\langle N\rangle)^2}{2\langle \Delta N^2\rangle}\right), \tag{59}$$

then

$$\langle N^3\rangle = \langle N\rangle(\langle N\rangle^2 + 3\langle \Delta N^2\rangle). \tag{60}$$

Furthermore, they assumed the specific V dependence of $\langle N\rangle$ and $\langle \Delta N^2\rangle$:

$$\langle N\rangle \propto V \qquad \langle \Delta N^2\rangle \propto V. \tag{61}$$

With these assumptions, equation (58) reduces to equations (56) and (57). Teramoto *et al* had not shown the validity of these assumptions, but their validity is recently established, under a quite general condition, by Kubo *et al* (1973).

If we solve equations (56) and (57) under the initial condition $\langle N(t=0)\rangle = N_0$ and $\langle \Delta N^2\rangle = 0$, we have

$$\langle N(t)\rangle/N_0 = 1/(1+\tau),$$

$$\frac{\langle \Delta N^2\rangle}{N_0} = \frac{2}{3}\left(\frac{1}{1+\tau} - \frac{1}{(1+\tau)^4}\right), \tag{62}$$

where

$$\tau = (\mu N_0/V)t. \tag{63}$$

Table 2. Mean number of reactants and its variation calculated from the exact and asymptotic equations.

τ	$\langle N\rangle/N_0$			$\langle \Delta N^2\rangle/N_0$		
	$N_0=10$	$N_0=50$	asymptotic	$N_0=10$	$N_0=50$	asymptotic
0·25	0·815	0·803	0·800	0·253	0·259	0·262
0·50	0·686	0·671	0·667	0·314	0·313	0·313
0·75	0·593	0·576	0·571	0·317	0·311	0·310
1·00	0·522	0·504	0·500	0·301	0·294	0·292
1·50	0·421	0·404	0·400	0·261	0·252	0·250

In table 2, these results are compared with the values obtained from the rigorous solution of equation (46). The agreement is very good even for the case of $N_0 = 50$.

6. Diffusion-controlled case

Let us consider another limiting case, $\lambda \to \infty$. This is the case discussed in the Smoluchowski theory. To treat this case, we must return to the expression (29) of $\mathcal{G}$. We shall show that even in this case, the open diagrams become dominant and the kinetic equation (6) is justified provided $t \gg \sigma^2/D$.

In the limit of $\lambda \to \infty$, the value of each diagram diverges. To remove this difficulty, we introduce the t matrix, which is defined diagrammatically by figure 3 or explicitly by

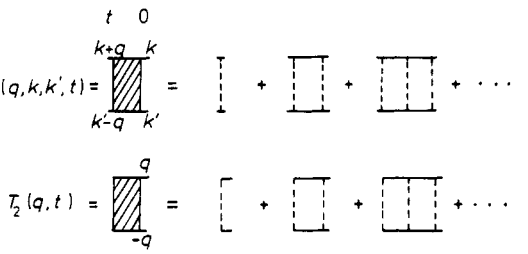

Figure 3. Definition of t matrices.

the equation

$$T_1(\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{k}'; t) = -(\lambda/V)S(\boldsymbol{q})\,\delta(t) + \langle 0|a_{\boldsymbol{k}+\boldsymbol{q}}a_{\boldsymbol{k}'-\boldsymbol{q}}\mathcal{G}_{r1}\exp[-(\mathcal{G}_0+\mathcal{G}_{r1})t]\mathcal{G}_{r1}a^\dagger_{\boldsymbol{k}}a^\dagger_{\boldsymbol{k}'}|0\rangle, \quad (64)$$

$$T_2(\boldsymbol{q}; t) = \lambda S(\boldsymbol{q})\,\delta(t) - \langle 0|\mathcal{G}_{r2}\exp[-(\mathcal{G}_0+\mathcal{G}_{r1})t]\mathcal{G}_{r1}a^\dagger_{\boldsymbol{q}}a^\dagger_{-\boldsymbol{q}}|0\rangle, \quad (65)$$

where

$$\mathcal{G}_{r1} = (\lambda/2V)\sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} S(\boldsymbol{q})a^\dagger_{\boldsymbol{k}+\boldsymbol{q}}a^\dagger_{\boldsymbol{k}'-\boldsymbol{q}}a_{\boldsymbol{k}}a_{\boldsymbol{k}'}; \qquad \mathcal{G}_{r2} = -\tfrac{1}{2}\lambda\sum_{\boldsymbol{q}} S(\boldsymbol{q})a_{\boldsymbol{q}}a_{-\boldsymbol{q}}. \quad (66)$$

These t matrices can be calculated from the solution of the two-body problem. Their explicit expression is complicated, but if we restrict our discussion to the long-time scale, $t \gg \sigma^2/D$, and to small momenta $|\boldsymbol{q}|, |\boldsymbol{k}|, |\boldsymbol{k}'| \ll 1/\sigma$, they can be simplified as

$$T_1(\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{k}'; t) = -(\mu/V)\,\delta(t), \quad (67)$$

$$T_2(\boldsymbol{q}; t) = \mu\,\delta(t). \quad (68)$$

Here $\mu = 4\pi D_r\sigma$ is the second-order reaction rate predicted by the Smoluchowski theory. The derivation of equations (67) and (68) is given in the appendix.

In terms of the t matrices, the diagrams are written as in figure 4. It is readily noted that figures 4(a), (b), (c) and (d) have the same diagrammatic structure as the open diagrams of § 5. Since these diagrams include only G_0 lines, equations (67) and (68) are used in their evaluation. Then the sum of these open diagrams is equal to $Q(\alpha, t)$ in the § 5, where μ_0 must be replaced by μ. Therefore if the other closed diagrams such as figures 4(e) and (f) are neglected, equations (56) and (57) are reproduced, and the Smoluchowski theory is justified.

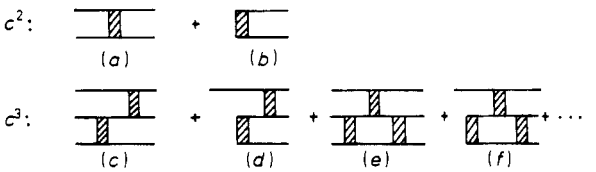

Figure 4. Diagrams for $Q(\alpha, t)$ expressed in terms of the t matrices. The first row is proportional to c^2, and the second to c^3.

We now show that the contribution of the closed diagrams is actually small. We shall show that the sum of the diagrams including n c-points is written as

$$Q^{(n)}(\alpha, t) = cV(c\mu t)^{n-1} q(\alpha)[1 + O(\sigma/(Dt)^{1/2})] \qquad (t \gg \sigma^2/D) \tag{69}$$

where $q(\alpha)$ is a polynomial in α. It is readily verified that sum of the open diagrams has the form of $cV(c\mu t)^{n-1} q(\alpha)$. Thus our task is to show that the value of the closed diagram is smaller than that of the open diagram by a factor $\sigma/(Dt)^{1/2}$.

As an example, let us consider the diagram of figure 4(e). Let $t_1, t_1', \ldots, t_3'$ be defined in such a way as in figure 5. Then figure 4(e) is evaluated as being given approximately by

$$\begin{aligned} c^3\alpha^3 V^3 \sum_{\boldsymbol{k}} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_1' \ldots \int_0^{t_3} \mathrm{d}t_3' \{ & T_1(\boldsymbol{k}, \boldsymbol{k}, -\boldsymbol{k}; t_1 - t_1') \\ & \times T_1(\boldsymbol{k}, \boldsymbol{k}, 0; t_2 - t_2') T_1(\boldsymbol{k}, 0, 0; t_3 - t_3') \\ & \times \exp[-2D\boldsymbol{k}^2(t_1' - t_2)] \exp[-D\boldsymbol{k}^2(t_2 - t_2')] \exp[-2D\boldsymbol{k}^2(t_2' - t_3)]\}. \end{aligned}$$

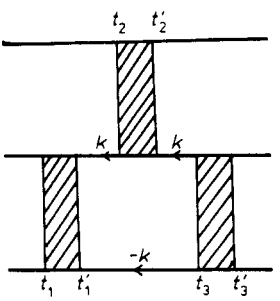

Figure 5.

We estimate this integral in the limit of $t \to \infty$. It is found that dominant divergence of figure 4(e) comes from the contribution from $|t_1' - t_2| \sim t$ and $|t_2' - t_3| \sim t$. Then the momentum k must be small owing to the exponential factor. Therefore T_1 may be approximated by equation (67). Furthermore we may replace the sum over $\boldsymbol{k}$ by the integral assuming $V \to \infty$:

$$\sum_{\boldsymbol{k}} = \frac{V}{(2\pi)^3} \int \mathrm{d}\boldsymbol{k}.$$

Then the integral (figure 4(*e*)) is estimated as

$$c^3\alpha^3 V\mu^3 \int \mathrm{d}\boldsymbol{k} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 \exp[-2D\boldsymbol{k}^2(t_1-t_3)]$$
$$\simeq c^3\alpha^3 V\mu^3 \int \mathrm{d}\boldsymbol{k}\, t^3 \exp(-2D\boldsymbol{k}^2 t) \simeq c^3\alpha^3 V\mu^3 t^3 \int_{|\boldsymbol{k}|<1/(Dt)^{1/2}} \mathrm{d}\boldsymbol{k}$$
$$\simeq \frac{c^3\alpha^3 V\mu^3 t^3}{(Dt)^{3/2}}. \tag{70}$$

On the other hand figure 4(*c*) is estimated approximately as

$$c^3\alpha^3\mu^2 t^2 V. \tag{71}$$

Thus the ratio of figure 4(*e*) to figure 4(*c*) is approximately

$$\mu/D^{3/2}t^{1/2} \approx \sigma/\sqrt{(Dt)}. \tag{72}$$

Therefore figure 4(*e*) is neglected compared to figure 4(*c*) in the limit of $t \gg \sigma^2/D$.

In general, we can obtain a closed diagram by adding a T_1 line to the open diagram. The evaluation of this closed diagram includes an integral over $\boldsymbol{k}$ and t'. Since $\boldsymbol{k}$ is limited to the range $|\boldsymbol{k}| \lesssim k_c \approx (Dt)^{-1/2}$, the diagram value of the closed diagram is smaller than the original open diagram by a factor $\mu t k_c^3 \simeq \sigma/(Dt)^{1/2}$. Thus equation (69) is established.

Therefore even in the diffusion-controlled case, equation (56) and (57) is verified.

7. Conclusion

We have shown that the classical Smoluchowski theory is justified under the condition

$$t \gg \sigma^2/D; \qquad V \to \infty. \tag{73}$$

Let us discuss this condition in comparison to the Boltzmann theory. In the Boltzmann theory, three time scales are important: (i) the time for collision $\tau_c \approx \sigma/\bar{u}$ ($\bar{u}$ is a mean velocity and σ should be understood as the potential range); (ii) the mean free time $\tau_f \approx 1/c\sigma^2\bar{u}$; and (iii) the macroscopic time $\tau_m \approx L/\bar{u}$ (L is a macroscopic length). The Boltzmann equation holds under the condition

$$\tau_c \ll \tau_f \ll \tau_m. \tag{74}$$

The first inequality is equivalent to $c\sigma^3 \ll 1$, i.e. the condition that the gas must be dilute. On the other hand in the Smoluchowski theory, these times correspond to $\tau_c \approx \sigma^2/D$, $\tau_f \approx 1/\rho D\sigma$ and $\tau_m \approx L^2/D$ respectively. Then equation (74) corresponds to

$$\sigma^2 \ll 1/\rho(t)\sigma \ll L^2. \tag{75}$$

Since $\rho(t) = c/(1+8\pi D\sigma ct)$, the first condition is equivalent to $t \gg \sigma^2/D$. Thus the Smoluchowski theory is understood quite analogously to the Boltzmann theory.

With this analogy in mind, we should like to make several remarks on the generalization of our conclusion.

(i) Usually, Smoluchowski's equation (1) is solved under a more realistic condition, considering the effect of partial reflection upon collision and the molecular potential. Clearly such a generalization is allowed provided the 'collision time' τ_c remains finite, independent of $\rho(t)$.

(ii) If the system is inhomogeneous, the diffusion term in equation (25) must be retained, and the kinetic equation is generalized as

$$\partial\rho(\boldsymbol{r}, t)/\partial t = D\nabla^2\rho(\boldsymbol{r}, t) - \mu\rho(\boldsymbol{r}, t)^2. \tag{76}$$

This generalization is allowed if the wavelength λ of the spatial inhomogeneity is longer than the 'mean free path' $(D\tau_f)^{1/2} \approx (\rho\sigma)^{-1/2}$.

(iii) In one- or two-dimensional systems, the flux $J(t)$ does not approach a finite constant value. Thus τ_c becomes infinite. Therefore a direct generalization of the Smoluchowski theory to the lower-dimensional system is dubious. In other words, the many-body effect becomes important in one- or two-dimensional systems.

Appendix

Since the difference between T_1 and T_2 exists only in the factor at the final time t, the equality,

$$T_2(\boldsymbol{q}; t) = -VT_1(\boldsymbol{q}, \boldsymbol{q}, -\boldsymbol{q}; t), \tag{A.1}$$

is evident. Thus we may consider only T_1.

From the diagram of figure 3, T_1 is found to satisfy the integral equation

$$T_1(\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{k}'; t) = -\frac{\lambda}{V}S(\boldsymbol{q})\,\delta(t) + \frac{\lambda}{(2\pi)^3}\int_0^t \mathrm{d}t_1 \int \mathrm{d}\boldsymbol{q}_1 S(\boldsymbol{q}-\boldsymbol{q}_1)$$
$$\times \exp\{-D(t-t_1)[(\boldsymbol{k}+\boldsymbol{q}_1)^2 + (\boldsymbol{k}'-\boldsymbol{q}_1)^2]\}T_1(\boldsymbol{q}_1, \boldsymbol{k}, \boldsymbol{k}'; t_1). \tag{A.2}$$

The solution of this equation is written as

$$T_1(\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{k}'; t) = \exp[-\tfrac{1}{2}D(\boldsymbol{k}+\boldsymbol{k}')^2 t] f(\boldsymbol{k}_r', \boldsymbol{k}_r; t), \tag{A.3}$$

where $\boldsymbol{k}_r = \boldsymbol{k} - \boldsymbol{k}'$ and $\boldsymbol{k}_r' = \boldsymbol{k} - \boldsymbol{k}' + 2\boldsymbol{q}$ are the relative momenta, and $f(\boldsymbol{k}_r', \boldsymbol{k}_r; t)$ is the solution of the equation

$$f(\boldsymbol{k}_r', \boldsymbol{k}_r; t) = -\frac{\lambda}{V}S\left(\frac{\boldsymbol{k}_r' - \boldsymbol{k}_r}{2}\right)\delta(t) + \int_0^t \mathrm{d}t_1 \int \frac{\lambda\,\mathrm{d}\boldsymbol{k}_r''}{(2\pi)^3} S\left(\frac{\boldsymbol{k}_r' - \boldsymbol{k}_r''}{2}\right)$$
$$\times \exp\left(-\frac{D}{2}\boldsymbol{k}_r''^2(t-t_1)\right) f(\boldsymbol{k}_r'', \boldsymbol{k}_r; t_1). \tag{A.4}$$

Note that $S(\boldsymbol{q})$ is almost independent of $\boldsymbol{q}$ for $|\boldsymbol{q}| \ll 1/\sigma$ because

$$S(\boldsymbol{q}) = \int \mathrm{d}\boldsymbol{r} S(\boldsymbol{r})\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} = \int_{|\boldsymbol{r}|<\sigma} \mathrm{d}\boldsymbol{r}(1 + \mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r} + \ldots) = \tfrac{4}{3}\pi\sigma^3 + \mathrm{O}(|\boldsymbol{q}|\sigma). \tag{A.5}$$

From equations (A.4) and (A.5), $f(\boldsymbol{k}_r', \boldsymbol{k}_r; t)$ is found to be almost independent of $\boldsymbol{k}_r'$ provided $|\boldsymbol{k}_r'| \ll 1/\sigma$ because if $|\boldsymbol{k}_r''| \gg |\boldsymbol{k}_r'|$, $S(\frac{1}{2}(\boldsymbol{k}_r' - \boldsymbol{k}_r''))$ may be replaced by $S(-\frac{1}{2}\boldsymbol{k}_r'')$ and if $|\boldsymbol{k}_r''| \lesssim |\boldsymbol{k}_r'|$, $S(\frac{1}{2}(\boldsymbol{k}_r' - \boldsymbol{k}_r''))$ may be replaced by $S(0)$. In a similar manner, starting from the equation

$$f(\boldsymbol{k}_r', \boldsymbol{k}_r; t) = -\frac{\lambda}{V}S\left(\frac{\boldsymbol{k}_r' - \boldsymbol{k}_r}{2}\right)\delta(t) + \int_0^t \mathrm{d}t_1 \int \frac{\lambda\,\mathrm{d}\boldsymbol{k}_r''}{(2\pi)^3} f(\boldsymbol{k}_r', \boldsymbol{k}_r''; t - t_1)$$
$$\times \exp\left(-\frac{D}{2}\boldsymbol{k}_r''^2 t_1\right) S\left(\frac{\boldsymbol{k}_r'' - \boldsymbol{k}_r}{2}\right), \tag{A.6}$$

we can show that $f(\boldsymbol{k}_r', \boldsymbol{k}_r; t)$ does not depend on $\boldsymbol{k}_r$ for $|\boldsymbol{k}_r| \ll 1/\sigma$. Thus we have

$$T_1(\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{k}'; t) = \exp[-\tfrac{1}{2}D(\boldsymbol{k}+\boldsymbol{k}')^2 t] f(t) \qquad (|\boldsymbol{q}|, |\boldsymbol{k}|, |\boldsymbol{k}'| \ll 1/\sigma), \quad \text{(A.7)}$$

where

$$f(t) \equiv f(0, 0; t).$$

To obtain $f(t)$, we consider

$$\phi(t) = \langle 0 | a_0^2 \exp[-(\mathcal{G}_0 + \mathcal{G}_{r1})t] a_0^{\dagger 2} | 0 \rangle. \quad \text{(A.8)}$$

From the diagrammatic representation of $\phi(t)$, we find

$$\begin{aligned} \phi(t) &= 2G_0(t)^2 + 2\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 G_0(t-t_1)^2 T_1(0, 0, 0; t) G_0(t_2)^2 \\ &= 2 + 2\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 f(t_1 - t_2). \end{aligned} \quad \text{(A.9)}$$

On the other hand, by use of equation (28), $\phi(t)$ is written as

$$\phi(t) = V^{-1} \int \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, W(\boldsymbol{r}_1, \boldsymbol{r}_2; t), \quad \text{(A.10)}$$

with

$$W(\boldsymbol{r}_1, \boldsymbol{r}_2; t) = \langle 0 | \psi(\boldsymbol{r}_1) \psi(\boldsymbol{r}_2) \exp\{-(\mathcal{G}_0 + \mathcal{G}_{r1})t\} a_0^{\dagger 2} | 0 \rangle, \quad \text{(A.11)}$$

or

$$\phi(t) = \int \mathrm{d}\boldsymbol{r} \, W(\boldsymbol{r}, t) \quad \text{(A.12)}$$

with

$$W(\boldsymbol{r}, t) = \langle 0 | \psi(\boldsymbol{r}) \psi(0) \exp[-(\mathcal{G}_0 + \mathcal{G}_{r1})t] a_0^{\dagger 2} | 0 \rangle. \quad \text{(A.13)}$$

because of the spatial homogeneity.

It is easy to show that $W(\boldsymbol{r}, t)$ satisfies the diffusion equation

$$\partial W(\boldsymbol{r}, t)/\partial t = D_r \nabla^2 W(\boldsymbol{r}, t) - \lambda S(\boldsymbol{r}) W(\boldsymbol{r}; t) \quad \text{(A.14)}$$

together with the initial condition

$$W(\boldsymbol{r}; 0) = 2/V. \quad \text{(A.15)}$$

In the limit of $\lambda \to \infty$, equation (A.14) becomes equivalent to Smoluchowski's equations (1) and (3). Utilizing equation (4), we have

$$\frac{\partial \phi}{\partial t} = D \int_{|\boldsymbol{r}|=\sigma} \nabla W \cdot \mathrm{d}\boldsymbol{S} = -\frac{2}{V}\mu\left(1 + \frac{\sigma}{(\pi D_r t)^{1/2}}\right). \quad \text{(A.16)}$$

From equations (A.9) and (A.16), it follows that

$$\int_0^t \mathrm{d}t' \, f(t-t') = -\frac{\mu}{V}\left(1 + \frac{\sigma}{\sqrt{(\pi D_r t)}}\right). \quad \text{(A.17)}$$

This integral equation is solved by use of Laplace transforms. As a result we have

$$f(t) = -(\mu/V)\,\delta(t) \qquad (t \gg \sigma^2/D). \quad \text{(A.18)}$$

Therefore

$$T_1(\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{k}'; t) = \exp\left(-\frac{D}{2}(\boldsymbol{k}+\boldsymbol{k}')^2 t\right)\left(-\frac{\mu}{V}\right)\delta(t) = -\frac{\mu}{V}\delta(t). \tag{A.19}$$

Thus equation (67) is established. From equations (67) and (A.1), equation (68) is justified.

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