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General theory of diffusion-controlled reactions* †

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A formal mathematical description of diffusion-controlled bimolecular reactions is presented. The theory is completely general with respect to the kinds of reaction processes that may be considered. Besides the presentation of the general formalism, the paper also contains several examples illustrating the application of the theory to a simple many-particle system for simple catalytic bimolecular reactions, including fluorescence quenching. The manner in which approximate solutions may be obtained is also outlined.

I. INTRODUCTION

Despite the interest shown by many authors¹⁻¹³ in the theory of diffusion-controlled reactions, a general theory of these processes which is free of unphysical assumptions and applicable to a broad range of experimental situations has not yet been presented. This paper represents an attempt to formulate a theory which satisfies both of these requirements.

The focal point of our approach is the use of a many-particle distribution function in the coordinate space of the N molecule system under consideration. We show that if one is able to obtain the kinetic equation which prescribes the time evolution of the distribution function in a nonreacting system, then this equation can be modified in a physically appealing way to account for reactions. Various modifications are considered which cover essentially all varieties of bimolecular and unimolecular rate processes. The applications of the theory which are then presented are intended primarily as illustrations of the kind of results which may be achieved with this formalism, and, as such, are restricted to the simplest bimolecular processes and to fluorescence quenching. An approximation scheme is suggested which, it is hoped, will prove useful in obtaining explicit solutions. Finally, the relation of this theory to its predecessors is discussed.

Several authors^{2,6-8} have taken approaches which are similar to ours in various respects. However, these theories are either too restrictive or too complicated to be usefully applied to any but the simplest many-particle systems. It is hoped that the present approach will be a rigorous compromise between these two extremes and will afford the possibility for a systematic mathematical treatment of many-particle systems using methods developed in other branches of physics and chemistry.

The present work actually developed out of attempts to obtain a tractable formalism which would describe diffusion-controlled relaxation processes in polymeric systems. This latter work will be published in a subsequent paper as a detailed example of the application of the formal theory to a complex many-particle system.

II. BACKGROUND

A. The Physical Problem

The following rate processes are considered. Two species of molecules, A and B, are allowed to react in either of the following two ways:



In (i) only the A molecule changes because of the reaction; the B molecule acts essentially as a catalyst. In (ii) both the A and B molecules are changed in the reaction. Fluorescence quenching is an example of a type (i) reaction, while colloidal coagulation and recombination reactions are examples of type (ii). Colloidal coagulation could also be approximately considered as a type (i) process if the size of the newly formed particle differed only slightly from one of the original particles, $D \approx B$ or A.

Since all of the reactions under consideration here take place intrinsically fast, the net rate of the process will presumably be limited by the frequency with which these particles meet each other. The theoretical problem is to predict the rates of these reactions by utilizing a theory of molecular motions which accounts for the finite encounter frequencies.

B. Survey of Existing Theories

An article by Noyes¹ in 1961 critically reviewed the deficiencies of the most commonly used theories. One general approach, based on concentration gradients, remains popular, but although several authors²⁻⁶ have tried to provide it with a sounder basis it still remains subject to some undesirable limitations. The chief limitations are worth listing. (1) The usual choice of coordinate system is one in which a reactive molecule is fixed at the origin. The diffusive motion of the remaining molecules is then assumed to be random with respect to the fixed molecule. As pointed out by Noyes,¹ this assumption is not self-evidently valid. (2) The reaction process is treated as the continuous diffusion of one species, say B, into the fixed A molecule (the stationary

sink) which is then allowed to react indefinitely. The diffusion equations are then solved with either of the following boundary conditions which are designed to account for the reaction: (a) The concentration of particles at the sink boundary is zero (Smoluchowski boundary condition), or (b) the concentration of particles at the sink boundary is proportional to the concentration gradient at the boundary ("radiation" boundary condition). (3) There are limitations on the concentrations of the different species. One limitation arises from the use of a diffusion equation valid for low concentrations. An additional limitation arises from the method of describing the reaction process in which it is assumed that the distribution of unreacted molecules about the sink is unperturbed by competitive reactions with other sinks. For a type (ii) reaction, this implies that at least one of the species must be present in very low concentration so that the molecules of that species may react independently. For a type (i) reaction with a B chosen as the sink, the distribution of active A's can be affected by additional B's, so, as above, the B concentration should be very low. Alternatively, if an A was chosen as the sink, the B distribution about it would not be affected by reaction with a different A since the B's are indestructible, and the only concentration limitations are those implied by use of the diffusion equation. Thus, the choice of sink may dictate the physical conditions for which the results of the mathematical analysis are expected to be valid. (4) The presence of sources of reactive molecules, e.g., the re-excitation of a previously deactivated molecule capable of undergoing fluorescence, has been handled using the implicit assumption that the newly reactivated A molecules are surrounded by an equilibrium distribution of B molecules. This cannot be the case if the reaction is really diffusion controlled.

More general formalisms than the above have been presented. In several recent papers by Teramoto, Shigesada, Nakajima, and Sato⁶ a theory of diffusion-controlled reactions is extensively developed for a many-particle system in which interparticle forces are neglected and for which a uniform initial distribution pertains. The theory is incorporated in a general stochastic theory of reaction kinetics. However, in order to actually calculate experimentally observable quantities, these authors must assume that after each pair of particles reacts the remaining unreacted particles are also uniformly distributed. This assumption cannot be valid for a diffusion-controlled reaction except at very short times.

The much earlier work of Monchick, Magee, and Samuel⁷ and of Waite⁸ actually contains many elements that must be included in any formally correct theory. These formulations are restricted by their mode of description of the reaction process and by their neglect of interparticle forces. The specific relationship of these theories to ours will be detailed in Sec. V.D.

The most recent work on diffusion-controlled reac-

tions is that of Abell, Mozumder, and Magee.⁹ These authors consider cases for which the reaction process is well described by the reaction of isolated pairs of particles. Other work, not specifically mentioned here, is treated in several review articles.^{1,10} The material discussed in those articles falls into the broad categories sketched above, or into an additional category, the molecular pair development of Noyes,¹ which is generically different from the others and is not considered here.

III. FUNDAMENTAL CONCEPTS

A. Kinetic Equations

The N particle system is defined to consist of n A's, m B's, and z I's, $n+m+z=N$. The I species is included for generality. Whether or not it is specifically needed will depend on the many-particle system under consideration. For example, the I's would probably represent the majority of chain segments in applications dealing with macromolecules.

The system will be described by a configurational distribution function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)$ which is a function of time and of the positions of the N particles. For any initial distribution of the positions of the N particles, ψ will describe the time development of the system in its approach to equilibrium in the absence of any chemical reaction. The kinetic equation which determines ψ will have the form

$$\partial\psi/\partial t + \mathcal{G}\psi = 0, \quad (1)$$

where \mathcal{G} is some type of generalized diffusion operator which includes as much detailed information regarding intermolecular forces between A's, B's, I's, and solvent molecules as is desired or possible. In principle, such an operator can be derived from the Liouville Equation.¹⁴ In practice, the construction of such operators is often intuitive and is based upon analogies with macroscopic diffusion, hydrodynamics, etc.

No matter how simplified or complex the operator is chosen to be, the key point in its construction and use is this: At least initially, the positions of all the particles must be referred to a fixed external coordinate system, often a Cartesian system. In this manner all of the particles' motions are treated on an equal basis and limitation (1) of Sec. II.B is avoided. Coordinate transformations may be made which facilitate the solution of the equation, but any mathematically valid transformation will preserve the physical equivalence of the particles' motions.

There are a few phenomena for which violation of this requirement would possibly not be too serious. Two which immediately come to mind are enzyme catalysis¹¹ and the growth of colloid or aerosol particles¹² (if the particles are large). In both of these cases, the reaction sites could be much more massive than the other components of the solution. The motion of the site would then be much slower than that of the small molecules

and to a good approximation it could be neglected. A third situation also arises where this requirement can be rigorously circumvented. If only isolated pairs of molecules are interacting with no possible competition between members of different pairs, then only the relative diffusion of the two molecules is required.⁹

There is another advantage to using a distribution function which is a function of the positions of all N particles. By so doing, limitations on the relative concentrations of the different species are automatically superseded, at least in principle. The practical difficulty then becomes the construction of the operator \mathcal{G} which is valid in the appropriate concentration range.

B. Modification of Equations by Reaction

1. General Considerations

In the system of molecules under consideration, certain molecules will be undergoing changes because of reaction. Consequently, the composition of the system will also be changing. The development of a systematic method of accounting for these changes is obviously a necessity. This section and the several succeeding ones will be concerned with this problem.

Strictly speaking, reactions are not describable within the framework of a classical theory, so some sort of mathematical trick must be employed in order to circumvent this difficulty. This naturally introduces a certain degree of arbitrariness regarding the choice to be made. One suitable choice is to require that the distribution function be continuously altered in a manner which reflects the changing composition of the system. The meaning of this statement will become clearer as we proceed.

Since the distribution function describes the average behavior of an ensemble of systems, our only concern is with average changes in the system composition. Specifically, we will be interested in the probability that a certain molecule A_i has not yet reacted at time t . This probability will be dependent solely on the average distribution of unreacted B molecules about A_i as a function of time (in the absence of competing unimolecular processes in which A_i can engage). This average distribution will in turn be determined by the diffusive response of the system to the reaction taking place. This response has been discussed by other authors;^{1,2,4} however, the key points will be repeated for emphasis. These remarks strictly apply only to an ensemble of systems with an initial equilibrium distribution in coordinate phase space, but they can easily be extended to cover arbitrary initial conditions. They are also restricted to systems with only one active A molecule. This latter condition does not inherently limit the kinds of physical systems to which the theory can be applied. It only allows the remarks to be greatly simplified.

While it may be true that a particular molecule can react only once, it is not true that this molecule will

react at the same time in all systems of the ensemble. Reaction will occur much more quickly in systems where the initial separations of the A_i and B molecules are small than in those where they are large. Now, as time progresses the distribution of B molecules about A_i in unreacted systems may deviate from equilibrium. This deviation will depend on (1) the rate of reaction for proximate particles, the "intrinsic rate," and on (2) the facility with which the particles are able to diffuse.

The reaction acts as a time dependent perturbation on the equilibrium molecular distribution by preferentially removing from the ensemble systems in which pairs of reactive particles are in close proximity. The remaining unreacted systems are characterized by a deficit in the number of reactive pairs which are close together, so that the average interparticle spacing for reactive pairs is larger than at equilibrium. That is, a nonequilibrium distribution will pertain for unreacted systems at time $t > 0$. This will happen when the diffusive relaxation of the system is not fast enough to offset the perturbative effect of the reaction. If the diffusive relaxation is fast, then the distribution of reactive pairs will not deviate markedly from equilibrium, and the reaction rate will not be diffusion controlled.

Let ψ now stand for the distribution function of a system in which, depending on the mode of description of the reaction, either a particular molecule or a particular pair of molecules is still unreacted at time t . That is, $\psi d\mathbf{r}_1, \dots, d\mathbf{r}_N$ is the probability that the configuration of the N particles is specified by $\mathbf{r}_1, \dots, \mathbf{r}_N$ and that the particular molecule or pair has not yet reacted at time t . Thus, if ψ is integrated over the coordinates of all of the particles, the probability $\phi(t)$ that the molecule or pair is still active at time t is obtained:

$$\phi(t) = \int \psi d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (2)$$

While ψ , and hence ϕ , have been defined in terms of the activity of a single molecule or a single molecular pair, we will show in Sec. IV how to account for the total activity of systems in which there are many reactive molecules or pairs. This can be simply done in terms of the single molecule and single pair activities.

The generalized diffusion equation which was discussed in Sec. III.A is a conservative equation. That is, the total time rate of change of the distribution function in the coordinate phase space is zero. Since the probability that the molecule or molecular pair is active changes in time because of reaction and could go to zero, the generalized diffusion equation must be converted into a nonconservative equation. This requirement of nonconservativity can be enforced either by making ψ satisfy a set of boundary conditions which account for reaction or by adding additional terms to the equation which are designed to represent the rate of change of the distribution function because of reac-

tion. There are no valid *a priori* reasons for using one approach rather than the other. However, significant practical advantages accrue with the use of the latter, generalized sink terms approach.

2. Comparison of Boundary Conditions with Sink Terms

Suppose first that the distribution function ψ which satisfies Eq. (1) is additionally required to satisfy a set of boundary conditions which describe the reaction process. In principle, any boundary value problem may be solved by first obtaining the Green's function of the differential equation which satisfies either homogeneous Dirichlet or Neumann conditions on the boundary, followed by utilizing Green's theorem in the appropriate way.¹⁵ The advantage of this method is that very complicated boundary conditions can be treated, provided the correct Green's function is known. This method will not be of much use in solving the generalized diffusion equation however, because even if boundary conditions appropriate for the reaction process are known it will be virtually impossible to obtain the correct Green's function. The method also presupposes that all reaction processes can be adequately described by boundary conditions.

Now consider the following equation which is supposed to represent a simple model of a system in which a diffusion-controlled reaction is taking place:

$$(\partial c/\partial t) - D\nabla^2 c = -(k/4\pi R^2)\delta(r-R)c. \quad (3)$$

Here $c(\mathbf{r}, t)$ is the concentration at \mathbf{r} , D is the diffusion coefficient, R is the radius of the reaction sink, k is a second order rate constant, and $\delta(x)$ is the Dirac delta function. Spherical symmetry is assumed. Integrating Eq. (3) over the entire volume one obtains

$$dn/dt = -kc(R, t), \quad (4)$$

where n is the total number of unreacted particles at time t , and the gradient of c has been required to vanish on the surface of the container. Integrating Eq. (3) again, but with $r \geq R + \epsilon$ one obtains

$$dm/dt = -4\pi(R+\epsilon)^2(\partial c/\partial r)_{r=R+\epsilon}, \quad (5)$$

where m is the number of unreacted particles exterior to a sphere of radius $R + \epsilon$ centered at the origin. The "radiation" boundary condition $kc(R, t) = 4\pi R^2 D(\partial c/\partial r)_{r=R}$ may be recovered by requiring that the time derivatives of Eqs. (4) and (5) become equal as $\epsilon \rightarrow 0$. This is the standard assumption made in deriving this boundary condition.²

This suggests that an appropriate solution of Eq. (3) could automatically satisfy the radiation boundary condition. Such a solution can be obtained by using the Green's function which satisfies the homogeneous Neumann condition on the surface at $r=R$ and by ignoring the surface integrals which arise when using Green's theorem. That is, one pretends that the surface at R is absent and that the Green's function is defined for use on the entire volume (which it is not),

and instead lets the delta function in the inhomogeneous term take care of these problems automatically (which it does). The initial condition on c would be arbitrary except for $r < R$ where c would have to be zero. This is certainly not a very rigorous way to solve Eq. (3), nor has it reduced the amount of effort involved, but it does illustrate what is involved in obtaining the solution to Eq. (3) which satisfies the radiation boundary condition.

However, an alternative point of view is available. There is no special reason why c should be required to satisfy a boundary condition other than that this is one way to describe the reaction. In fact, the boundary condition may, and perhaps should, be considered only a consequence of the particular choice of sink term appearing in Eq. (3) in conjunction with the reasoning associated with Eqs. (4) and (5). Accepting this premise, one can devise other sink terms which are likely to provide a better description of the reaction than do the boundary conditions. For example, if the reaction can take place over a range of interparticle separations the radiation boundary condition is clearly inadequate, but a sink term can easily be constructed which conveys precisely the necessary information.

The use of sink terms is important in another respect. Since the configuration space is no longer necessarily demarcated by a set of reaction surfaces, Green's functions which are defined on the full configuration space may be employed in solving the generalized diffusion-reaction equations. This is of great practical significance because these functions are much more readily available than their counterparts which satisfy boundary conditions.

In determining how Eq. (1) is to be modified it should be noted that particle configurations in which reactive particles are "far" from each other will contribute nothing to $\partial\psi/\partial t$ and that the effect of nonzero contributions will be directly proportional to the probability of the configurations involved. This means that the following considerations must go into the construction of the sink terms:

(1) The rate of change of the distribution function receives contributions from the reaction only in a restricted part of the configuration space.

(2) The rate of change will be proportional to the distribution function itself.

(3) The proportionality constant must be chosen so that the rate equations agree with those of equilibrium theory in the limit of fast diffusive response.

The sink terms will have the structure $-kS\psi$. The second order rate constant k is that which would govern the rate if the equilibrium distribution function pertained for all time. The "function" S , e.g., a normalized Heaviside step function, limits the region of configuration space where the sink term is effective. The number and type of such terms to be used clearly depends on the nature of the rate process under study.

The remainder of this article should provide the reader with sufficient example of their use.

IV. SPECIFIC TYPES OF RATE PROCESSES

In this section the concepts developed so far will be applied to bimolecular reactions of types (i) and (ii). The effect of competing unimolecular reactions will also be discussed, and a rigorous procedure for the introduction of source terms will be presented. The process of obtaining the generalized diffusion-reaction equations can be thought of as an attempt to effect a rigorous mathematical decoupling of the total activity of a system composed of many active (unreacted) single molecules or pairs of molecules into a sum of independent single molecule or pair activities.

A. Type (i) Reaction

The system contains n A's, m B's, and z I's, with $n+m+z=N$. Let $\phi_i(t)$ be the probability that the i th A molecule is still active at time t . Because the B's are unchanged by the reaction, the probability that a particular A is active is independent of the probability that any other A is active. The average number of A's which are active is then given by

$$N_A(t) = \sum_{i=1}^n \phi_i(t). \quad (6)$$

The ϕ_i are related to the corresponding ψ_i by Eq. (2). The various ψ_i must be obtained by solving the set of n equations, each of the form

$$\frac{\partial \psi_i}{\partial t} + \mathcal{G}\psi_i = -k \sum_{j=1}^m S(A_i, B_j)\psi_i. \quad (7)$$

The function $S(A_i, B_j)$ depends on the positions of both the A_i and B_j molecules, and it restricts the relative range of values that these positions may have in order for a reaction to take place. The sink term consists of m terms because A_i can react with any of the m B's. The activities of different A's can vary because of differences in the initial distribution of the B's about each A. A physical system which can obviously manifest these inequivalent initial distributions is a polymer chain for which the N particles constitute the chain segments.

B. Type (ii) Reaction

The same N particle system is considered, but now the activity of a particular A is influenced by an additional factor. Since the B's are now modified by the reaction, their activities are no longer fixed at unity. The A is now reacting in a field of B's whose activities are decreasing in time. One formulation of this problem is that of Waite.⁸

If $\phi_{ij}(t)$ is the activity of the pair A_iB_j , then the number of active pairs $N_{AB}(t)$ at time t is given by

$$N_{AB}(t) = N_A(t)N_B(t) = \sum_{i,j} \phi_{ij}(t), \quad (8)$$

where $N_A(t)$ and $N_B(t)$ are the average numbers of A and B particles expected to be active at time t . The distribution function ψ_{ij} which gives ϕ_{ij} via Eq. (2) is the probability density for finding configurations in which both the A_i and B_j particles are active. The generalized diffusion-reaction equation must include all possible ways of losing the designated pair. Besides the direct reaction of A_i with B_j , the activity of the pair can be lost if either A_i or B_j reacts with another active B or A, respectively. The equation to be solved reads

$$\begin{aligned} (\partial \psi_{ij}/\partial t) + \mathcal{G}\psi_{ij} = & -kS(A_i, B_j)\psi_{ij} \\ & -k \sum_{k \neq j}^m S(A_i, B_k)\psi_{ijk} - k \sum_{k \neq i}^n S(A_k, B_j)\psi_{ijk}. \end{aligned} \quad (9)$$

The distribution function ψ_{ijk} is the probability density for configurations in which A_i , B_j , and a third particle are all active. Whether the third particle is A_k or B_k is indicated clearly by the argument of the S function associated with ψ in Eq. (9). The equation is not closed with respect to the order of activity of the distribution function. A hierarchy of equations can be generated which is similar to, but more general than, that of Monchick, Magee, and Samuel.⁷

An alternative formulation can be made in terms of the lowest order equation of the hierarchy. The total activity of the A's or B's would still be given by Eq. (6), but the single particle activities would have to be obtained from the solutions to equations such as

$$\frac{\partial \psi_i}{\partial t} + \mathcal{G}\psi_i = -k \sum_{j=1}^m S(A_i, B_j)\psi_{ij}. \quad (10)$$

The relationship of these equations to those of other theories will be discussed in Sec. V.

C. Competing Unimolecular Processes

The inclusion of the effects of unimolecular processes is done straightforwardly. The addition of terms of the form $\gamma\psi$ to the diffusion-reaction equations is all that is necessary. The constant γ is the reciprocal time constant for the spontaneous decay or excitation process which is competing with the bimolecular reaction.

D. Source Terms

The usual method of treating this problem is subject to limitations which are generally left unstated. In the employment of this method, an expression for the diffusion-controlled rate of loss of active molecules is obtained. The possibility of re-excitation of any previously deactivated molecules is ignored in this expression. The decay law, which results upon integration of the rate expression, is, of course, valid only for the particular initial conditions for which the rate expression was obtained. The initial distribution is usually chosen to be the equilibrium distribution. The total response of the system is then obtained by taking the convolution integral of the decay law with the time dependent source.¹³ (We have in mind the specific

example of re-excitation by a light source. The decay law would then include both spontaneous emission and quenching.) If $I(t)$, $F(t)$, and $D(t)$ are, respectively, the number of excited molecules at time t , the source intensity, and the decay law, the above statement has the mathematical form

$$I(t) = \int_0^t F(\tau) D(t-\tau) d\tau.$$

This formulation of the problem implies that each newly re-excited molecule is surrounded by an equilibrium distribution (initial condition) of active molecules with which it can react. A consideration of the microscopic details of the reaction will show why this cannot be true. It will also be apparent that rates for the bimolecular process predicted on the basis of re-excitation in an equilibrium distribution will be too high.

As discussed in Sec. III.B.1, the reaction may act as a perturbation on the molecular distribution function for systems which still contain an active molecule. This implies that the distribution function for reacted systems will also be modified in a way which is complementary to that for unreacted systems. To see this more clearly consider the following argument.

The effect of the reaction is to divide the ensemble of systems into two disjoint sets. One set contains only unreacted systems; the other contains only reacted systems. Now, the evolution of the ensemble of systems in the absence of reaction will be described by a distribution function $\psi^\circ(t)$ which depends on the initial conditions and satisfies Eq. (1). Assume next that the reaction does not significantly alter the physical characteristics of the reacted molecule (diffusion coefficients, intermolecular potentials, etc.) but only "labels" molecules as reacted. Under this assumption ψ° will also describe the evolution of the ensemble in which reaction is taking place if we choose to disregard the labels.

Because the sets are disjoint the following statements must be true: (1) The total probability that any system is in a particular configuration at time t must be the sum of the probabilities of finding such a configuration in the active and reacted sets. (2) The sum of the fractions of systems in the active and reacted sets must be unity for all time. The first statement leads to the identity

$$\psi^\circ(t) = \psi_a(t) + \psi_r(t). \quad (11)$$

The distribution functions ψ_r and ψ_a describe, respectively, systems in which the particle of interest has or has not reacted. Integrating Eq. (11) over all configurations leads to the second statement.

It is obvious that re-excitation can take place only in the set of reacted systems. Hence, the probability for re-excitation will be proportional to ψ_r . By Eq. (11), ψ_r clearly deviates from ψ° . If the initial distribution is chosen to be in equilibrium, ψ° will remain in equilibrium. Then ψ_r deviates from equilibrium in the manner

$\psi_r(t) = \psi_{eq} - \psi_a(t)$. Here ψ_{eq} is the equilibrium distribution function. If the reaction is not diffusion controlled, then $\psi_a = \phi(t)\psi_{eq}$, where $\phi(t)$ is, in general, a time dependent fraction. If $\phi(t)$ is small, then ψ_r approaches ψ_{eq} . If the reaction is diffusion controlled, then ψ_r can only approximate ψ_{eq} if the re-excitation process is slow compared with the reaction (de-excitation) processes taking place.

As a specific example consider fluorescence quenching with the allowance of re-excitation by a light source. The source term is given by

$$F(t)[\psi^\circ(t) - \psi(t)],$$

where $F(t)$ is the number of molecules/sec which the light source is capable of exciting, and ψ is the distribution function for systems containing an excited molecule capable of fluorescing. This term must be added to the diffusion-reaction equation which already contains terms for bimolecular quenching with "intrinsic" rate constant k and for fluorescent emission with specific inverse time constant γ . If the quenching reaction is considered to be a type (i) process, the resulting equation is

$$\partial\psi/\partial t + \mathcal{G}\psi = -kS\psi - \gamma\psi + F(t)[\psi^\circ(t) - \psi], \quad (12)$$

where S is an obvious abbreviation for the corresponding term of Eq. (7).

Notice that the combination of terms $(\gamma + F)\psi$ appears. If $F(t) \ll \gamma$ then the probability for re-excitation will be approximately $F(t)\psi^\circ(t)$. If ψ° is the equilibrium distribution function, then the above restriction on source intensity appears to be a necessary condition for agreement between the correct way of handling re-excitation and the procedure described at the beginning of this section.

Another easily handled case (but perhaps an unphysical one) is a reversible type (i) reaction, where the reverse reaction is characterized by an intrinsic second order rate constant k_r . Contributions to the production of new A molecules will come only from regions of configuration space where previously reacted A molecules are in proximity with B molecules. This means that the source term must include the same S function as was found in the reaction term. The complete diffusion-reaction equation for this process is

$$\partial\psi/\partial t + \mathcal{G}\psi = -kS\psi + k_r S[\psi^\circ(t) - \psi]. \quad (13)$$

The source term for a reversible type (ii) reaction is found in a completely analogous fashion. Of course, in this case notice must be taken of the necessity for accounting for the production of both the particular A molecule and B molecule which comprise the pair whose activity is being computed, and the resulting equations will be considerably more complicated.

Other types of re-excitation processes can presumably be thought of. Source terms for these processes should be obtainable by using the above methods as long as there are no drastic physical modifications to

the molecules because of reaction. If the latter circumstance pertains, the problem then becomes somewhat more difficult.¹⁶

V. MATHEMATICAL DEVELOPMENT

A. General Considerations

Neglecting source terms, the basic equation of interest is of the form

$$\partial\psi/\partial t + \mathcal{G}\psi = -kS\psi \quad (14)$$

for a type (i) reaction. If Eq. (14) is now integrated over the entire configuration space, the result is

$$d\phi/dt = -kv(t). \quad (15)$$

As usual, Eq. (1) defines ϕ , the single particle activity. The joint probability density $v(t)$ that the A molecule is active and is "near" any B molecule is defined as

$$v(t) = \int S\psi d\mathbf{r}_1 \cdots d\mathbf{r}_N. \quad (16)$$

Notice that $v(t)$ is an unconditional probability density. If $\eta(t)$ is the conditional probability density for finding a B molecule near the A, given that the A is active,

$$\eta(t) = v(t)/\phi(t), \quad (17)$$

then Eq. (15) can be rewritten in the form of a second order rate equation as

$$d\phi/dt = -k\eta(t)\phi(t). \quad (18)$$

If the reaction is not diffusion controlled and the initial distribution is chosen to be in equilibrium, then η will always be the equilibrium probability density. In this case the solution to Eq. (18) or, equivalently, Eq. (15) is trivial.

The same kind of analysis can be made for a type (ii) reaction, but with a corresponding shift in the interpretation of the various probabilities. The mathematics is formally the same as above. The difference is that ψ in Eq. (16) is replaced by ψ_{ij} as can be seen by referring to Eq. (10). With this replacement, $v(t)$ is now interpreted as the joint probability density for the particular molecule to be active and be near any *active* molecule of the other species; η is the corresponding conditional probability density. There is no longer an equivalence between these probability densities and those for finding the molecule of interest near *any* molecule of the other species as there would be for the type (i) reaction for which any B's activity is perpetually unity.

The quantities of greatest physical interest are the average numbers of unreacted particles and the rate of reaction. The former are obtained by summing the appropriate single particle or pair probabilities as discussed in Sec. IV, for Eqs. (6) and (8). The rate may be obtained by taking the time derivative of the expressions given by Eqs. (6) or (8). With regard to the use of Eq. (8) it is also useful to note that $dN_A/dt =$

dN_B/dt and $N_B(t) = m - n + N_A(t)$. The rate may also be obtained by directly summing Eqs. (15) or (18) or their analogues for a type (ii) reaction. Solving a generalized diffusion-reaction equation for ψ will, in general, be nontrivial. This obviates any direct calculation of the physically interesting quantities. It is possible, though, to manipulate the equation into a form which allows the removal of at least part of the coordinate dependence (sometimes exactly) either by direct integration or by formation of the average of ψ with S , as in Eq. (16), which then leaves an integral or differential equation for either $v(t)$ or reduced distribution functions.

B. Type (i) Reaction

The problem of solving Eqs. (15) and (16) for a particular system is now considered. Let the N particle system be the simplest imaginable, i.e., the particles have no internal structure, and there are no interparticle forces. The generalized diffusion equation may be obtained by employing the continuity equation

$$\frac{\partial\psi}{\partial t} + \sum_{i=1}^N \nabla_i \cdot \mathbf{j}_i = 0. \quad (19)$$

The probability current \mathbf{j}_i for this system is given by

$$\mathbf{j}_i = -D_i \nabla_i \psi, \quad (20)$$

where D_i is the diffusion constant for the i th particle. The particles have been labeled so that the first m are B's, the next n are A's, and the last z are I's. With this choice of operator, Eq. (14) now reads

$$\frac{\partial\psi}{\partial t} - \sum_i^N D_i \nabla_i^2 \psi = -kS\psi. \quad (21)$$

Since the only couplings that exist are between one particular A and the B's, the coordinate dependence of the remaining A's and of the I's may be removed by direct integration of Eq. (21). Let the reduced distribution function still be designated by ψ , for simplicity of notation. Then the equation to be solved is

$$\partial\psi/\partial t - D_A \nabla_A^2 \psi - D_B \sum_i \nabla_i^2 \psi = -kS\psi, \quad (22)$$

where D_A and D_B are the diffusion constants for A and B particles. Using a Green's function¹⁵ and treating the sink term as an inhomogeneity, the formal solution is found to be

$$\psi(\{\mathbf{r}\}, t) = \psi_{\text{eq}} - k \int_0^t dt^\circ \int d\{\mathbf{r}^\circ\} G(\{\mathbf{r}\}, t; \{\mathbf{r}^\circ\}, t^\circ) \times S(\{\mathbf{r}^\circ\}) \psi(\{\mathbf{r}^\circ\}, t^\circ) \quad (23)$$

where $\{\mathbf{r}^\circ\}$ stands for $\mathbf{r}_A^\circ, \mathbf{r}_1^\circ, \dots, \mathbf{r}_m^\circ$ and $d\{\mathbf{r}^\circ\}$ stands for $d\mathbf{r}_A^\circ, d\mathbf{r}_1^\circ, \dots, d\mathbf{r}_m^\circ$. Here the initial distribution is chosen to be in equilibrium and for the present system is given by

$$\psi_{\text{eq}} = V^{-(m+1)} \quad (24)$$

where V is the volume. The Green's function

$$G(\{\mathbf{r}\}, t; \{\mathbf{r}^0\}, t^0) = [4\pi D_A(t-t^0)]^{-3/2} \times \exp\left(\frac{-|\mathbf{r}_A - \mathbf{r}_A^0|^2}{4\pi D_A(t-t^0)}\right) \prod_{j=1}^m [4\pi D_B(t-t^0)]^{-3/2} \times \exp\left(\frac{-|\mathbf{r}_j - \mathbf{r}_j^0|^2}{4\pi D_B(t-t^0)}\right) \quad (25)$$

is defined for use in an unbounded volume. To be fully rigorous, the Green's function should vanish at the boundary of the volume and be defined for use only within it. This latter Green's function reduces to that given by Eq. (25) in the limit of infinite V . Since V is actually very large compared to molecular dimensions, the use of Eq. (25) can be regarded as a very suitable approximation which helps to simplify the following calculations.¹⁷

Multiplying Eq. (23) by S and integrating over $\{\mathbf{r}\}$ gives

$$v(t) = v_{\text{eq}} - k \int_0^t dt' \int d\{\mathbf{r}\} \int d\{\mathbf{r}^0\} S(\{\mathbf{r}\}) \times G(\{\mathbf{r}\}, t; \{\mathbf{r}^0\}, t') S(\{\mathbf{r}^0\}) \psi(\{\mathbf{r}^0\}, t'), \quad (26)$$

where

$$v_{\text{eq}} = m/V = \int d\{\mathbf{r}\} S(\{\mathbf{r}\}) \psi_{\text{eq}}, \quad (27)$$

and $v(t)$ is defined by Eq. (16). To proceed any further a specific choice for S must be made. One simple choice for S is

$$S(\{\mathbf{r}\}) = (4\pi R^3/3)^{-1} \sum_{i=1}^m H(R - |\mathbf{r}_A - \mathbf{r}_i|). \quad (28)$$

The Heaviside step function $H(x)$ is equal to unity when $x \geq 0$ and is zero otherwise. It has the following useful representation in terms of the delta function:

$$H(R - |\mathbf{r}_A - \mathbf{r}_i|) = \int_0^R d\rho \rho^2 \int d\Omega_\rho \delta[\rho - (R - |\mathbf{r}_A - \mathbf{r}_i|)], \quad (29)$$

where $d\Omega_\rho$ indicates an integration over the solid angle of $\boldsymbol{\rho}$. This choice has the effect of giving the reaction a uniform probability of occurrence whenever the distance separating the A from any B becomes less than or equal to R .

With this choice of sink the remaining integrations over $\{\mathbf{r}\}$ may be carried out explicitly. Equation (26) then becomes

$$v(t) = v_{\text{eq}} - k \sum_{i=1}^m \int_0^t dt' \int_0^R d\rho \rho^2 \int d\Omega_\rho \int d\{\mathbf{r}^0\} \times P_i(\tau) S(\{\mathbf{r}^0\}) \psi(\{\mathbf{r}^0\}, t'), \quad (30)$$

where

$$P_i(\tau) = (4\pi D\tau)^{-3/2} \exp[-|\boldsymbol{\rho} - (\mathbf{r}_A^0 - \mathbf{r}_i^0)|^2/4D\tau].$$

The relative diffusion constant D equals $D_A + D_B$ and $\tau = t - t^0$. To obtain a closed equation for $v(t)$, ψ is approximated as the equilibrium distribution multiplied by a time dependent factor which is determined

by forcing the average of ψ with S to be given correctly by the approximation

$$\psi \approx \psi_{\text{eq}} v(t), \quad (31a)$$

$$\int d\{\mathbf{r}\} S\psi = v(t) \int d\{\mathbf{r}\} S\psi_{\text{eq}}. \quad (31b)$$

Upon solving Eq. (31b) for $v(t)$ and making use of Eqs. (16) and (27), the approximate ψ is seen to have the form $\psi_{\text{eq}} v(t)/v_{\text{eq}}$. Substituting this into Eq. (30) and performing the integrals over $\{\mathbf{r}^0\}$ gives¹⁸

$$v(t) = v_{\text{eq}} - k v_{\text{eq}} \int_0^t dt' v(t') - k \int_0^t dt' K(\tau) v(t'). \quad (32)$$

The kernel $K(t)$ is given by

$$K(t) = (4\pi R^3/3)^{-2} \int_0^R d\rho \rho^2 \int d\Omega_\rho \int_0^R d\mathbf{u} \mathbf{u}^2 \int d\Omega_u \times (4\pi Dt)^{-3/2} \exp\left(\frac{-|\boldsymbol{\rho} - \mathbf{u}|^2}{4Dt}\right). \quad (33)$$

In the limit of large D , the solution to Eq. (32) is trivial, and it agrees with the prediction of equilibrium rate theory. It is just

$$v(t) = v_{\text{eq}} \exp(-k v_{\text{eq}} t),$$

and from Eq. (15)

$$\phi(t) = \exp(-k v_{\text{eq}} t).$$

Under these circumstances the substitution indicated by Eq. (31) is exact. For smaller D or larger k , its reliability is uncertain. It will probably be inadequate for the fastest reactions, except for short times. For longer times, appreciable distortion in the distribution function may occur. This might invalidate the use of ψ_{eq} to describe the coordinate dependence, although the factor $v(t)/v_{\text{eq}}$ would also be small for long times so the quantitative difference between ψ and the approximate $\psi_{\text{eq}} v(t)/v_{\text{eq}}$ might not be large. Higher order solutions can be generated by using Eqs. (23) and (30) in an iterative fashion, treating Eq. (31) and the solution to Eq. (32) as zeroth order approximations.

Equation (32) is an inhomogeneous Volterra equation of the second type whose form is amenable to solution with the use of Laplace transforms. The Laplace transform \hat{g} of a function $g(t)$ is defined as

$$\hat{g}(s) = \int_0^\infty g(t) \exp(-st) dt.$$

Taking the transform of Eq. (32) gives

$$\hat{v}(s) = v_{\text{eq}} s^{-1} - k [v_{\text{eq}} s^{-1} + \hat{K}(s)] \hat{v}(s) \quad (34)$$

which may be easily solved for \hat{v} :

$$\hat{v}(s) = v_{\text{eq}} [s + k v_{\text{eq}} + s k \hat{K}(s)]^{-1}. \quad (35)$$

The transform of the kernel K can be calculated. It is

found to be

$$\hat{K}(s) = (4\pi R^3/3)^{-2} (2\pi/D) p^{-3/2} [2R^3 p^{1/2}/3 - R^2 + p^{-1} - (R^2 + 2R p^{-1/2} + p^{-1}) \exp(-2R p^{1/2})];$$

$$p \equiv s/D. \quad (36)$$

Equation (15) may also be Laplace transformed with the result that the transform of the single particle activity is given in terms of \hat{v} :

$$\hat{\phi}(s) = s^{-1} [1 - k\hat{v}(s)]. \quad (37)$$

Using Eq. (35), Eq. (37) becomes

$$\hat{\phi}(s) = [1 + k\hat{K}(s)] [s + kv_{\text{eq}} + s\hat{K}(s)]^{-1}. \quad (38)$$

In lieu of attempting a complete inversion of Eq. (35) or Eq. (38), it may be anticipated that the long time behavior of $v(t)$ and $\phi(t)$ will be exponential.¹⁹ Accordingly, the lowest lying pole on the negative real axis could be searched for. This analysis will not be carried out here, instead a simpler, but physically satisfactory, result will be demonstrated.

The relation²⁰

$$\lim_{t \rightarrow \infty} g(t) = \lim_{s \rightarrow 0} s\hat{g}(s) \quad (39)$$

enables the limiting value of a function to be obtained through knowledge of its transform. Since it can be shown that

$$\hat{K}(0) = 3/10\pi DR, \quad (40)$$

it follows that for long time both $\phi(t)$ and $v(t)$ become zero. This is in accord with the realization that in a finite volume the particle must eventually react.

One other interesting limit is that of an infinitely large "intrinsic" rate constant $k \rightarrow \infty$. Taking this limit in Eqs. (35) and (38) it is seen that

$$\hat{v}(s) \rightarrow 0, \quad (41)$$

and

$$\hat{\phi}(s) \rightarrow \hat{K}(s) [v_{\text{eq}} + s\hat{K}(s)]^{-1}. \quad (42)$$

Equation (41) is the analog of the Smoluchowski boundary condition.^{1,2} The corresponding equation for the Laplace transform of the rate [Eq. (15)] may be obtained by taking the limit of $k\hat{v}(s)$. All of these expressions are independent of the specific value of k , provided k is large. This is reasonable because it is the diffusive response of the system which ultimately limits the reaction rate. Eventually a point will be reached beyond which further increases in k will have no significant effect on the reaction rate.

C. Fluorescence Quenching

One possible mechanism for fluorescence quenching involves treating the bimolecular reaction as essentially a type (i) process.²¹ The solution to Eq. (12) is then required. For illustrative purposes the source intensity is chosen to be constant, $F(t) = F$. The same generalized

diffusion operator, Green's function, and sink function are employed as in the preceding section. The initial condition is chosen to be the state of equilibrium for a system containing only unexcited particles, that is, $\psi(\{\mathbf{r}\}, t=0) = 0$, but $\psi^{\circ}(t) = \psi_{\text{eq}}$. Having made these choices, the mathematics is virtually the same as above. The integral equation for $v(t)$ reads

$$v(t) = Fv_{\text{eq}} \int_0^t dt^{\circ} \exp[-(\gamma + F)\tau]$$

$$- kv_{\text{eq}} \int_0^t dt^{\circ} \exp[-(\gamma + F)\tau] v(t^{\circ})$$

$$- k \int_0^t dt^{\circ} \exp[-(\gamma + F)\tau] K(\tau) v(t^{\circ}), \quad (43)$$

where the same closure approximation implied by Eq. (31) has been used. Taking the Laplace transform of this equation gives

$$\hat{v}(s) = [Fv_{\text{eq}}/s(s + \gamma + F)]$$

$$\times \{1 + [kv_{\text{eq}}/(s + \gamma + F)] + k\hat{K}(s + \gamma + F)\}^{-1}. \quad (44)$$

Now, if Eq. (12) is integrated over $\{\mathbf{r}\}$, the result is

$$d\phi/dt = -kv(t) - \gamma\phi(t) + F[1 - \phi(t)], \quad (45)$$

and, again, taking the Laplace transform of Eq. (45) leads to

$$\hat{\phi}(s) = [s(s + \gamma + F)]^{-1} [F - s\hat{v}(s)]. \quad (46)$$

Finally, Eqs. (44) and (45) enable $\hat{\phi}$ to be expressed as

$$\hat{\phi}(s) = F[1 + k\hat{K}(s + \gamma + F)] \{s(s + \gamma + F)$$

$$\times [1 + (s + \gamma + F)^{-1} kv_{\text{eq}} + k\hat{K}(s + \gamma + F)]\}^{-1}. \quad (47)$$

Equation (39) allows the calculation of the steady state probability ϕ_{ss} , since

$$\phi_{\text{ss}} = \lim_{t \rightarrow \infty} \phi(t).$$

The result is

$$\phi_{\text{ss}} = \frac{F[1 + k\hat{K}(\gamma + F)]}{(\gamma + F)[1 + k\hat{K}(\gamma + F)] + (\gamma + F)^{-1} kv_{\text{eq}}}. \quad (48)$$

Since the random initial distribution was specified, ϕ_{ss} can also be regarded as the fraction of all the A's which are excited in the steady state. Several limiting forms of Eq. (48) are immediately apparent. If the illumination is very intense, $F \rightarrow \infty$, then $\phi_{\text{ss}} = 1$. It is reasonable to suppose that nearly all the molecules will be in an excited state under these conditions. Alternatively, if $F = 0$ then no molecules are excited. If the spontaneous emission process is very fast relative to the quenching reaction, then

$$k\hat{K}(\gamma + F) \ll 1,$$

$$kv_{\text{eq}}(\gamma + F)^{-1} \ll 1,$$

and ϕ_{ss} approaches $F(\gamma+F)^{-1}$, its value in the complete absence of quenching ($k=0$). Finally, if the quenching reaction is extremely efficient so that $k \rightarrow \infty$, ϕ_{ss} attains the following limit which is independent of k :

$$\phi_{ss} \rightarrow F\hat{K}(\gamma+F)/(\gamma+F)[\hat{K}(\gamma+F)+v_{eq}(\gamma+F)^{-1}].$$

The explanation for this is identical to that given at the end of the preceding section, namely that the diffusive response is the ultimate limiting factor. A similar analysis can be made for v_{ss} with physically consistent results.

The closure approximation which led to Eq. (43) [and to Eq. (32)] is expected to be better for fluorescence quenching than for a simple type (i) process. Since the emission process is generally more efficient than the quenching reaction, at least at low quencher concentrations, and also samples equally all regions of configuration space where active particles are to be found, the total de-excitation process can take place faster and with less distortion of the distribution function. Also, the factorization of ψ into a coordinate dependent part and a time dependent part is partially rigorous since $\exp(-\gamma t)$ always appears as a factor in the solution. Additional evidence for this point of view is rendered by the limit of ϕ_{ss} for large γ which, as was seen above, tended to minimize the effect of the quenching reaction.

D. Relation to Earlier Theories

The hierarchy of equations mentioned in Sec. IV.B is a direct generalization of the hierarchy of Monchick, Magee, and Samuel⁷ (referred to as MMS throughout this section) with one qualification. The formulation of those authors allows for the possible reaction of a given particle with any other active particle, whereas our formulation separates the reactive molecules into the two classes A and B. This restriction can easily be overcome simply by imitating the earlier work, but it serves no useful purpose to do so now. Instead of presenting a complicated set of general relations, with superabundant use of superscripts and subscripts, only the first two equations, Eqs. (9) and (10), of the present hierarchy will be considered. The connection between the two formulations will be evident.

If Eq. (10) is integrated over all coordinates except those of the i th particle, the result is

$$\frac{\partial \psi_i^{(1)}}{\partial t} + \int d\{\mathbf{r}\}_i \mathfrak{G}\psi_i = -k \sum_{j=1}^m \int d\mathbf{r}_j S(A_i, B_j) \psi_{ij}^{(2)}. \quad (49)$$

The reduced distribution functions are defined by

$$\psi_i^{(1)}(\mathbf{r}_i, t) = \int \psi_i d\{\mathbf{r}\}_i \quad (50)$$

and

$$\psi_{ij}^{(2)}(\mathbf{r}_i, \mathbf{r}_j, t) = \int \psi_{ij} d\{\mathbf{r}\}_{ij}, \quad (51)$$

where $d\{\mathbf{r}\}_i$ and $d\{\mathbf{r}\}_{ij}$ indicate, respectively, that the integrations over \mathbf{r}_i and over \mathbf{r}_i and \mathbf{r}_j are to be omitted. Equation (49) can be reduced to its counterpart in

MMS by specializing \mathfrak{G} to be that of Eq. (21) and choosing for $S(A_i, B_j)$ the special form

$$S(A_i, B_j) = (4\pi R^2)^{-1} \delta(|\mathbf{r}_i - \mathbf{r}_j| - R). \quad (52)$$

Similarly, if Eq. (9) is integrated over all coordinates except those of \mathbf{r}_i and \mathbf{r}_j , the reduced equation reads

$$\begin{aligned} \frac{\partial \psi_{ij}^{(2)}}{\partial t} + \int \mathfrak{G}\psi_{ij} d\{\mathbf{r}\}_{ij} = & -k S(A_i, B_j) \psi_{ij}^{(2)} \\ & -k \sum_{k \neq j}^m \int S(A_i, B_k) \psi_{ijk}^{(3)} d\mathbf{r}_k \\ & -k \sum_{k \neq i}^n \int S(A_k, B_j) \psi_{ijk}^{(3)} d\mathbf{r}_k. \end{aligned} \quad (53)$$

The triplet distribution function $\psi_{ijk}^{(3)}$ is defined by analogy with Eqs. (50) and (51). With the same special choices for \mathfrak{G} and $S(A_k, B_j)$, Eq. (53) is almost reduced to the corresponding equation in MMS. The difference is that in MMS the reaction of the i th and j th particles is handled by using the "radiation" boundary condition, whereas in Eq. (53) the sink term accounting for it appears directly. After performing the integration over the remaining coordinate dependence in Eq. (53) (with special S), the resulting equation is identical to the corresponding equation in MMS. This results because, as was seen in Sec. III.B.2, the sink function of Eq. (52) has the effect of reproducing the "radiation" boundary condition. Waite's⁸ equations bear the same relation to Eq. (53) as do those of MMS, but the reaction terms have been approximated to obtain a closed solution.

The generalized diffusion-reaction equation employed by Teramoto, Shigesada, Nakajima, and Sato⁶ corresponds to the highest order equation in the hierarchy discussed here. As mentioned earlier, these authors require a special assumption of uncertain legitimacy to relate the solution of this equation to observable quantities.

The similar treatments of Yguerabide² and Steinberg and Katchalski⁴ are embodied in Eq. (7) for a system consisting of m B's and one A. The usual special choices for \mathfrak{G} and for $S(A, B)$ must be made, and, in addition, the unphysical restriction that $\mathbf{r}_A = 0$ must be used.

VI. DISCUSSION

In presenting this theory of diffusion-controlled reactions our goal has been twofold. First, we wanted a theory which could be applied to any many-particle system regardless of the type of interparticle forces present. Second, we wanted to include sufficient flexibility in the manner of describing the reaction process so that a diverse spectrum of physical and chemical phenomena could be encompassed. Although only a few specific applications were presented, they, in con-

junction with the discussion of the sink terms, should be ample evidence that the latter goal has been substantially achieved. While the former objective has not been explicitly demonstrated, the theory's potential in this regard should be evident. A subsequent paper dealing with linear macromolecules will provide one specific realization of this goal.

In view of the restrictions and difficulties associated with other theories of these processes, further work on the present theory seems warranted. The nature of the approximation scheme could be investigated more fully

with regard to convergence and physical consequences. Other approximations may prove more useful, and for type (ii) processes some alternatives already exist.⁶⁻⁸ Even the simple results presented here may be worth subjecting to numerical study. Though our main numerical effort has been concerned with polymers, the quantity $\phi_{ss}[F/(\gamma+F)]^{-1}$, which is important in fluorescence studies, has been calculated for a typical set of parameters, and a satisfactory result was obtained.²²

At the very least, the present formalism seems to provide a rigorous foundation for future work.

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¹⁹This may not always be true, even for large volumes, and could potentially lead to unphysical results such as non-vanishing reaction rates at very long times. This is not the case in our analysis.

²⁰In the second term on the right hand side v_{eq} has replaced $m - 1/V$ which originally occurred. This is consistent with our usage of G .

²¹This is not obvious from the form of Eqs. (35), (36), and (38), but it implies that η , the conditional probability density, becomes constant for long times. This seems physically reasonable.

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