

## Diffusion-controlled reactions: A revisit of Noyes' theory

H. Van Beijeren

*Institute for Theoretical Physics, Utrecht University, P.O. Box 80006, 3508 TA Utrecht, The Netherlands*

W. Dong<sup>a)</sup>

*Institut de Recherches sur la Catalyse, CNRS, 2, Avenue Albert Einstein, 69626 Villeurbanne, France  
and Laboratoire de Chimie Théorique, École Normale Supérieure de Lyon, 46, Allée d'Italie,  
69364 Lyon Cedex 07, France*

L. Bocquet

*Laboratoire de Physique, École Normale Supérieure de Lyon, 46, Allée d'Italie,  
69364 Lyon Cedex 07, France*

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Noyes' theory of diffusion-controlled reactions is revisited in great details. First, it is shown that this theory provides an interesting alternative approach to perform molecular dynamics simulations for diffusion-controlled reactions. With this approach, reaction rate can be determined from simulations of *nonreactive* equilibrium systems. No annihilation procedure is needed to simulate the reaction event. Provided that encounters with different reactants are strictly uncorrelated, the reaction rate can be determined more directly and accurately than by the methods that compute the survival probability. We describe in detail the method for accurately determining the key quantity in Noyes' theory, i.e., the first recollision probability, from molecular dynamics simulations. It will also be shown that arguments similar to those in Noyes' theory allow us to establish an exact relation (under the same assumptions of absence of correlations) between the distribution function of a reacting system at the encounter distance and that of a nonreactive equilibrium system. This relation can be used to fix the boundary condition at the reaction distance in the approaches based on a diffusion equation. New insights have been gained into the usefulness of the recollision probability. The recollision probability also provides a very useful tool for characterizing quantitatively some dynamic features of the cage effect for reactions in dense liquids. Finally, the method presented here may also be used to calculate reaction rates for diffusion-controlled reactions in systems where the dynamics cannot be described by a diffusion equation. © 2001 American Institute of Physics.  
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### I. INTRODUCTION

The study of diffusion-controlled reactions has already a long history. More than 80 years ago, Smoluchowski formulated the first theoretical approach.<sup>1</sup> In this now classic theory, the relative motion of reactants is described by a diffusion equation. The disappearance of reactants is accounted for by an absorbing boundary condition at an encounter distance. Almost all the subsequent developments followed the same line of thought. Various improvements and refinements have been made. Debye was the first to consider the effect of long-range Coulomb forces between reactants on the reaction rate of diffusion-controlled reactions.<sup>2</sup> Collins and Kimball introduced the radiation boundary condition to describe the chemical reaction at the encounter distance in a more satisfactory way.<sup>3</sup> Hydrodynamic interaction has been considered by introducing distance-dependent relative diffusion coefficient.<sup>4</sup> The study of diffusion-controlled reactions has also been extended to reversible reactions.<sup>5–10</sup> In more recent investigations,<sup>11–15</sup> a variety of approaches (truncated hierarchy for nonequilibrium reduced distribution functions, memory function formalism, etc.) is applied to

obtain macroscopic kinetic equations. Nevertheless, the underlying dynamics is nearly always described by a diffusion equation.

Although the approach based on the diffusion equation started by Smoluchowski has constituted an overwhelming mainstream in the study of diffusion-controlled reactions (see Refs. 16–19 for reviews), exceptions do exist. In 1954, Noyes proposed a theory based on a quite different perspective.<sup>20</sup> Noyes' theory is based on a collision picture. In the formulation of his theory, Noyes introduced an imaginary counterpart system, which is identical to the reacting system under consideration in all the aspects except that the reactants are deprived of their reactivity. So, they can recollide again and again without ever reacting. Although this idea may appear surprising at first sight, Noyes showed that the recollision probability in the counterpart system can serve as a key ingredient in formulating a quite general theory for reaction kinetics. Unfortunately, this recollision probability is not readily accessible to direct experimental measurements. Noyes tried to determine it by resorting to a diffusion equation, thereby restricting himself to only those cases where the relative motion of reactants may be described by a diffusion equation. In this way, he obtained only the long-time asymptotic behavior of this function and recovered the result of Smoluchowski at long times. During

<sup>a)</sup>Electronic mail: dong@catalyse.univ-lyon1.fr

the past 46 years, to our knowledge, nobody has made further attempts to determine the recollision probability in the whole time range. Nowadays, such a task becomes a quite feasible one by using computer simulations. One purpose of the present work is to accomplish this, so that a quantitative assessment can be made for Noyes' theory.

In the present work, by revisiting Noyes' theory, we gained some new insights into the usefulness of the recollision probability. We realized that this quantity also provides a very useful tool for characterizing some dynamic features of the cage effect, which is one of the most helpful concepts for understanding the dynamics of chemical reactions in solution. Although the local structure revealed in the potential of mean force between reactants may be considered as evidence for the existence of a solvent cage, the cage effect itself is intrinsically of a dynamic nature. The recollisions of two reactants at short times are some of the most direct manifestations of the cage effect. Despite its importance and the huge amount of literature on reactions in solution appealing to the concept of the cage effect, a precise dynamic characterization of this effect is still lacking. In this paper, we will show that the recollision probability can be used to make such a characterization.

The paper is arranged as follows. Noyes' theory is recalled in the next section. We also present a derivation of the kinetic equation for the survival probability. This derivation allows one to clearly see the fundamental assumptions and restrictions on which the theoretical framework is based. Section III contains a brief treatment of the long-time limit of reaction rate. Although the description is based on a diffusion equation, new insights are gained, especially into the choice of boundary conditions by applying the ideas in Noyes' theory so as to obtain a sensible expression for the contact value of the distribution function. In Sec. IV, we discuss how to determine the recollision probability by different methods from molecular dynamics (MD) simulations. Section V is devoted to the cage effect, relating its dynamic features to recollisions. Our simulation results are presented and discussed in Sec. VI. Conclusions are summarized in Sec. VII.

## II. A NEW PERSPECTIVE ON NOYES' THEORY

Here, we consider irreversible reactions of the generic type



In a dilute gas, the rate of such a reaction can be expressed as  $k = P_{\text{react}} \nu_{AB}$  with  $\nu_{AB}$  being the collision frequency of an  $A$  molecule with  $B$  molecules in the nonreactive counterpart system and  $P_{\text{react}}$  the probability of reaction in a collision between  $A$  and  $B$ . The collision frequency is an equilibrium property that does not depend on transport coefficients. In such a case, the reaction is usually qualified as an activation-limited one. For a dense system with a large value of  $P_{\text{react}}$ , the situation is radically different. A pair of molecules entering a collision can recollide a large number of times in a dense system if the reaction probability,  $P_{\text{react}}$ , is small. If  $P_{\text{react}}$  is not too small, the pair of reactants will react almost certainly once it starts a collision sequence. Let  $N_{AB}$  denote

the average number of collisions in a recollision sequence between two nonreactive molecules.  $N_{AB}$  is finite for three-dimensional systems and diverges for one- and two-dimensional systems since the recollision probability of a pair is equal to 1 for 1D and 2D systems. Thus, in a 3D system the collision frequency of a given molecule,  $A$ , with new  $B$  molecules, i.e., molecules it has never encountered before, is given by  $\nu_{\text{new}} = \nu_{AB}/N_{AB}$  after a transient initial stage. For values of  $P_{\text{react}}$  such that  $P_{\text{react}} N_{AB} \gg 1$ , the reaction rate for  $A$  is simply  $\nu_{\text{new}}$ .

In some sense, Noyes' theory<sup>20</sup> is a generalization of the above idea which takes into account the time dependence of recollision probability. The conventional approach usually starts with the following kinetic equation for the survival probability of a molecule  $A$ ,  $S_A(t)$ :

$$\frac{dS_A(t)}{dt} = -k(t)S_A(t), \quad (2)$$

where  $k(t)$  is the time-dependent reaction rate. Nevertheless, the status of this equation is scarcely discussed in any depth. In order to see more clearly the assumptions behind the basic kinetic equation, we have chosen a different approach by starting from a formally exact expression for  $S_A(t)$

$$S_A(t) = \sum_{N=0}^{\infty} P_{nr}(N,t)P(N,t), \quad (3)$$

where  $P(N,t)$  is the probability that  $N$  collisions take place in the time interval  $[0,t]$  and  $P_{nr}(N,t)$  is the probability that none of the  $N$  collisions is a reactive one. Although Eq. (3) is an exact expression, it is of little practical use. Now, we will show under what further assumptions Eq. (3) can be reduced to Eq. (2). Here, we are considering the cases in which the reaction rate is time dependent. The time dependence can be easily understood with the help of the nonreacting counterpart system introduced by Noyes.<sup>20</sup> Since the reaction rate is equal to the collision frequency of the  $A$  molecule with new  $B$  molecules in the nonreacting counterpart system, and this frequency decreases with time, it is obvious that the reaction rate must also decrease with time. Now, the probability for a collision in the time interval  $[0,t]$  being a reactive one can be expressed as

$$P_{\text{react}}(t) = \frac{\int_0^t dt' k(t')}{\nu t}, \quad (4)$$

where  $\nu$  is the total collision frequency of the  $A$  molecule in the nonreacting counterpart system with any other molecules (either a solvent or a  $B$  molecule regardless of it being a new one or a recollided one, so  $\nu = \nu_{AS} + \nu_{AB}$ ,  $\nu_{AB}$ : collision frequency of  $A$  with  $B$ s and  $\nu_{AS}$ : collision frequency of  $A$  with solvent molecules). If the correlation between the collisions can be neglected,  $P_{nr}(N,t)$  is given simply by  $(1 - P_{\text{react}}(t))^N$  and  $P(N,t)$  can be described by Poisson distribution, i.e.,

$$P(N,t) = \frac{(\nu t)^N}{N!} e^{-\nu t}. \quad (5)$$

With the above expression of  $P_{nr}(N,t)$  and  $P(N,t)$ , the summation in Eq. (3) can be easily carried out, which leads to the following compact form:

$$S_A(t) = \exp\left(-\int_0^t dt' k(t')\right). \quad (6)$$

This is simply the solution of Eq. (2).

The basic kinetic equation, i.e., Eq. (2), was used intuitively by Noyes and many others without any discussion of its status. Now, the above derivation shows very clearly the basic assumption behind it. Its solution, i.e., Eq. (6), is nothing else but a generalized Poisson distribution for the case where the reactive collisions are not uniformly distributed over time (or, in other terms, for the cases with a time-dependent reaction rate). Moreover, in the above description, the reaction between a pair of reactants is treated as an event independent of the reactions between other pairs. So, the framework described above is rigorously valid only at low concentrations of reactants.

Now, we introduce, following Noyes,<sup>20</sup> the probability density  $f(t)$  for a first recollision between an  $A$  and a  $B$  molecule at time  $t$  after a preceding collision at time 0. Here, we make a further simplifying assumption that  $f(t)$  will be independent of the preceding number of collisions between the  $AB$  pair. For systems at low density or with a rapidly changing local structure, this will be a good assumption, but for systems in which the local surrounding of the pair changes only slowly in time, this assumption may cause deviations when  $P_{\text{react}} < 1$ . Nevertheless, this assumption is not involved in the case of  $P_{\text{react}} = 1$  and has negligible effect in the case of  $P_{\text{react}} \ll 1$ , where the time-dependent part no longer plays any role. So, it can be expected that this approximation most affects the results in the cases of  $P_{\text{react}}$  with intermediate values. With the above assumption, the time-dependent reaction rate, in the case of a general  $P_{\text{react}}$ , can be expressed as

$$\begin{aligned} k(t) = & \nu_{AB} P_{\text{react}} \left[ 1 - P_{\text{react}} \int_0^t dt_1 f(t_1) \right. \\ & - P_{\text{react}} (1 - P_{\text{react}}) \int_0^t dt_2 \int_0^{t_2} dt_1 f(t_2 - t_1) f(t_1) \\ & - P_{\text{react}} (1 - P_{\text{react}})^2 \int_0^t dt_3 \int_0^{t_3} dt_2 f(t_3 - t_2) \\ & \left. \times \int_0^{t_2} dt_1 f(t_2 - t_1) f(t_1) - \dots \right]. \quad (7) \end{aligned}$$

This equation can be understood intuitively by noting that in the counterpart system the probability density for an  $AB$  collision giving rise to a reaction is just  $\nu_{AB} P_{\text{react}}$ . But, this could be counted as a true reaction in the reacting system only if there were no reactive collisions between the same pair before. The probability for such an event is expressed precisely by the subtracted terms. In deriving Eq. (7), it is assumed that the recollisions subsequent to the first one are uncorrelated.

As already pointed out by Noyes himself, the function  $f(t)$  is not accessible to direct experimental measurements. If

no prescription is provided for the practical determination of  $f(t)$ , the above theory remains a very formal one. Noyes attempted to calculate  $f(t)$  from a diffusion equation. This provided only the asymptotic estimation of  $f(t)$  at long times. To our knowledge, no investigation has been made to determine this function over the whole time range. Our task in Sec. IV will be to make such a determination under the simplifying assumptions specified above.

### III. DESCRIPTION BY DIFFUSION EQUATION

After the description based on a collision picture given in the last section, a brief recall of the approach based on a diffusion equation is given below. Our special emphasis here is on discussing some relationships between these two types of approaches. In particular, we will show how the results obtained from the collision picture can help to determine the proper boundary conditions in the approach based on diffusion equation.

In a liquid phase, the relative motion of two particles can be described quite well by a diffusion equation in a potential of mean force,<sup>21</sup>  $\Phi(r)$ , related to the pair correlation function,  $g(r)$ , by

$$g(r) = e^{-\Phi(r)/k_B T}, \quad (8)$$

where  $k_B$  is Boltzmann's constant and  $T$  the absolute temperature. For the sake of simplicity, we consider only spherical molecules without internal degrees of freedom. Otherwise, one has to consider diffusion in an extended configuration space including the internal degrees of freedom of the two reactants. The diffusion coefficient in general depends on the intermolecular distance due to hydrodynamic interactions.<sup>4</sup> At large distances, it approaches the sum of the self-diffusion coefficients of the two reactants. For a spherical distribution of  $B$  molecules around a given  $A$  molecule, the diffusion equation takes the form

$$\begin{aligned} \frac{\partial \rho_{AB}(r,t)}{\partial t} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 e^{-\Phi(r)/k_B T} D(r) \frac{\partial}{\partial r} (e^{\Phi(r)/k_B T} \rho_{AB}(r,t)) \right]. \quad (9) \end{aligned}$$

As pointed out first by Smoluchowski,<sup>1</sup> the reaction rate (or the asymptotic rate at which an  $A$  molecule encounters new  $B$  molecules) can be equated to the rate at which  $B$  molecules are transported to the  $A$  molecule by diffusion from a source which is homogeneous at infinity with density,  $\rho_B$ . As a generalization of this, the time-dependent reaction rate discussed before can be estimated from the time-dependent solution of this diffusion problem with a homogeneous initial density of  $B$  molecules. The boundary conditions can be written in general as

$$4\pi\sigma^2 D(\sigma) g(\sigma) \left[ \frac{\partial}{\partial r} (e^{\Phi(r)/k_B T} \rho_{AB}(r,t)) \right]_{r=\sigma} = \kappa \rho_{AB}(\sigma,t), \quad (10)$$

$$\rho_{AB}(r \rightarrow \infty, t) = \rho_B. \quad (11)$$

Smoluchowski used the absorbing boundary condition, i.e.,  $\rho_{AB}(\sigma, t) = 0$ , which corresponds to the limit  $\kappa \rightarrow \infty$ . Collins and Kimball<sup>3</sup> pointed out that a finite value for  $\kappa$  should be used in order to remove the unphysical singularity of the reaction rate at  $t=0$  in Smoluchowski theory. Nevertheless, the meaning and the value that one should give to  $\kappa$  do not appear clear in the original paper of Collins and Kimball and many subsequent developments. A few years ago, Zhou and Szabo proposed a choice of  $\kappa$  from an intuitive basis.<sup>22</sup> They chose  $\kappa$  in such a way that the initial reaction rate,  $k(t=0)$ , is given exactly, i.e., it is equated to  $\nu_{AB}P_{\text{react}}$  (in fact, Zhou and Szabo considered only the case  $P_{\text{react}}=1$ ). We will show below that  $\kappa$  can also be fixed by an exact relation which should be satisfied by  $\rho_{AB}(\sigma, \infty)$  and which is completely equivalent to the requirement imposed by Zhou and Szabo in the case of  $P_{\text{react}}=1$  but accounts for also the general cases of  $0 < P_{\text{react}} < 1$ .

The stationary solution of Eq. (9) with the boundary conditions, Eqs. (10) and (11), leads to an expression of  $k(\infty)$  of the form

$$k(\infty) = \kappa \rho_{AB}(\sigma, \infty) = \frac{\kappa g(\sigma) \rho_B}{1 + \kappa g(\sigma) \int_{\sigma}^{\infty} \frac{dr}{4\pi r^2 g(r) D(r)}}. \quad (12)$$

So far,  $\kappa$  may still be considered as an undetermined parameter of the theory. Now, we will describe a method for determining the value of  $\kappa$  in an unambiguous way. For simplicity, we first consider the case that  $P_{\text{react}}=1$ . We can apply a reasoning similar to that of Noyes to establish a relation between the distribution of  $A$  and  $B$  at the collision distance,  $\sigma$ , in a reacting system and that in the nonreactive counterpart system. Let us start from the stationary state and turn off the reactivity at, say,  $t+0$ . The  $B$  molecules are now allowed to recollide with the central  $A$  molecule and on average will do so  $1/(1-P_{\text{recoil}})$  times [see Eq. (15) for the definition of  $P_{\text{recoil}}$ ]. Therefore, if again we may ignore correlations between  $B$  molecules, the resulting density of  $B$  molecules at the encounter distance,  $\sigma$ , from the  $A$  molecule will build up to  $\rho_{AB}(\sigma, \infty)/(1-P_{\text{recoil}})$  as soon as the system relaxes to equilibrium. Obviously, this is nothing else but the equilibrium density of  $B$  molecules, i.e.,  $\rho_B g(\sigma)$ , in the nonreacting counterpart system

$$\frac{\rho_{AB}(\sigma, \infty)}{1 - P_{\text{recoil}}} = \rho_B g(\sigma). \quad (13)$$

From Eq. (7), in the case of  $P_{\text{react}}=1$ , one has

$$k(\infty) = \nu_{AB}(1 - P_{\text{recoil}}), \quad (14)$$

where  $P_{\text{recoil}}$  is the recollision probability given by

$$P_{\text{recoil}} = \int_0^{\infty} dt f(t). \quad (15)$$

Now, Eqs. (14), (13), and the first equation in Eq. (12) leads to

$$\kappa = \nu_{AB} / (g(\sigma) \rho_B). \quad (16)$$

This is identical to the choice proposed by Zhou and Szabo.<sup>22</sup> The fitting of  $\kappa$  given by Zhou and Szabo was made

to obtain the exact initial reaction rate,  $k(0)$ . Our fitting just described above aims at  $k(\infty)$ . But, both approaches boil down to the requirement that the initial rate and the stationary one should be proportional to the local density of  $B$  molecules in the immediate neighborhood to the  $A$  molecule with the same proportionality constant and therefore they lead to the same result.

Substituting  $\kappa$  given in Eq. (16) into Eq. (12), one obtains

$$k(\infty) = \frac{k^{\text{abs}}(\infty) \nu_{AB}}{k^{\text{abs}}(\infty) + \nu_{AB}}, \quad (17)$$

where

$$k^{\text{abs}}(\infty) = \left[ \int_{\sigma}^{\infty} dr \frac{1}{4\pi r^2 \rho_B g(r) D(r)} \right]^{-1}, \quad (18)$$

and  $k^{\text{abs}}(\infty)$  is the asymptotic value of the reaction rate obtained by using the absorbing boundary condition, i.e.,  $\rho_{AB}(\sigma, t) = 0$ . In the case of  $P_{\text{react}} < 1$ , we can proceed in a similar way. In this case, Eq. (7) gives the following result for the long-time limit of the reaction rate:

$$k(\infty) = \frac{\nu_{AB} P_{\text{react}} (1 - P_{\text{recoil}})}{1 - (1 - P_{\text{react}}) P_{\text{recoil}}}. \quad (19)$$

Now, the contact value of the steady-state distribution function,  $\rho_{AB}(\sigma, \infty)$ , is related to the equilibrium distribution function,  $g(\sigma)$ , of a nonreacting fluid through the equation

$$\rho_{AB}(\sigma, \infty) \frac{1 - (1 - P_{\text{react}}) P_{\text{recoil}}}{1 - P_{\text{recoil}}} = \rho_B g(\sigma). \quad (20)$$

For  $P_{\text{react}}=1$ , Eq. (20) reduces simply to Eq. (13). For activation-limited reaction, i.e.,  $P_{\text{react}} \ll 1$ , we see clearly, from Eq. (20), that the reactants are distributed as in a nonreacting equilibrium system. Equations (19), (20) and the first equality in Eq. (12) yield the following value for  $\kappa$ :

$$\kappa = \frac{P_{\text{react}} \nu_{AB}}{g(\sigma) \rho_B}. \quad (21)$$

Substituting Eq. (21) into Eq. (12), we obtain

$$k(\infty) = \frac{k^{\text{abs}}(\infty) \nu_{AB} P_{\text{react}}}{k^{\text{abs}}(\infty) + \nu_{AB} P_{\text{react}}}. \quad (22)$$

Equations (21) and (22) are the extension of Eqs. (16) and (17) for the cases in which a collision between reactants does not necessarily lead to a chemical reaction. Now, the physical meaning of the parameter  $\kappa$  is shown very clearly by Eqs. (16) and (21). In the literature, there was a widely spread misinterpretation of  $\kappa$ . It is often stated that the absorbing boundary condition (i.e.,  $\kappa \rightarrow \infty$ ) describes the situation that every collision leads to a reaction (i.e.,  $P_{\text{react}}=1$ ) and the radiation boundary condition (finite  $\kappa$ ) accounts for the circumstances that the reaction takes place with a probability,  $P_{\text{react}} < 1$ , at each collision. To our knowledge, Zhou and Szabo<sup>22</sup> were the first to point out that the radiation boundary condition should be used even in the case of  $P_{\text{react}}=1$ . The results presented above [Eq. (16) in particular] confirm this from a different approach and generalize it to the case with a reaction probability smaller than 1.

## IV. MOLECULAR DYNAMICS SIMULATIONS

### A. Model

Dong, Baros, and André proposed, in 1989, a very simple model for the prototype reaction described by Eq. (1) and carried out the first molecular dynamics simulation for diffusion-controlled reactions.<sup>23</sup> In that paper, all the reactants and solvent molecules are described by hard spheres of the same size and mass. The only difference between reactants and solvent molecules is that a collision between a molecule *A* and a molecule *B* leads immediately to a reaction, i.e., the case  $P_{\text{react}} = 1$ . The survival probability of the *A* molecule is determined in a way very similar to that used in a real experiment. In the present work, we adopt the same model as that used in Ref. 23 for describing diffusion-controlled reactions. In this case, the nonreacting counterpart system is simply a fluid of hard spheres with the total density  $\rho = \rho_A + \rho_B + \rho_S$  ( $\rho_A$ ,  $\rho_B$ , and  $\rho_S$  are, respectively, the densities of *A*, *B*, and solvent species). As in Ref. 23, we will restrict ourselves to the case with the species *A* at infinite dilution.

### B. Calculation of first recollision probability

In Sec. II, it is shown that the key quantity in Noyes' theory is the first recollision probability,  $f(t)$ . We describe now the different methods we developed to determine this function. First, we should recall that the first recollision probability,  $f(t)$ , as defined by Noyes is not a normalized probability density. The integral of  $f(t)$  is equal to the probability that a pair of molecules will recollide after their first collision [see Eq. (15) and Ref. 20]. The normalized function,  $F(t) = f(t)/P_{\text{recoll}}$ , describes the distribution of the length of time intervals between two successive collisions undergone by the same pair of molecules. This distribution function can be readily measured from a molecular dynamics simulation. However, the function  $F(t)$  contains less information than the function  $f(t)$ . Hence, the determination of  $F(t)$  is not sufficient to obtain  $f(t)$ . One also needs to determine the recollision probability,  $P_{\text{recoll}}$ , in some way.

The recollision probability considered here is closely related to the return probability extensively investigated in the studies of random walks on lattices.<sup>24</sup> From the famous work of Polya,<sup>25</sup> we know that the return probability is equal to 1 for random walks in 1D and 2D systems. In 3D systems,  $P_{\text{recoll}} < 1$  and different values have been found depending on the lattice structures on which random walks are considered.<sup>24</sup> To our knowledge, no study has been reported on the recollision probability for off-lattice models. In principle, the recollision probability can also be measured directly from a molecular dynamics simulation. The fate of a colliding pair is either to recollide or to separate forever. Hence, a straightforward way to calculate  $P_{\text{recoll}}$  is to find out from all the collided pairs how many have made subsequent recollisions. Nevertheless, this simple and direct method suffers from two complications directly related to the finite size of the simulation system and the finite length of simulation runs. To determine  $P_{\text{recoll}}$  in a finite length run, a long but finite observation time,  $t_{\text{max}}$ , is prescribed. If a pair of molecules colliding at  $t = 0$  does not recollide up to  $t = t_{\text{max}}$ , they

are considered to escape each other forever. For real macroscopic systems,  $t_{\text{max}} \rightarrow \infty$ . For a finite system used in simulations, reliable results for  $P_{\text{recoll}}$  can be obtained only if  $t_{\text{max}}$  can be chosen in such a way that the results for  $P_{\text{recoll}}$  do not depend on the choice of  $t_{\text{max}}$ . We will come back to discuss this point in Sec. VI when the simulation results are presented. The second complication is that  $t_{\text{max}}$  cannot be increased to an arbitrary large value for a finite system, since all the colliding pairs are bound to recollide after a certain time (estimated to be that needed for a particle to diffuse across the system) because of the use of periodic boundary conditions in a molecular dynamics simulation. The presence of such artificial recollisions plagues the accurate determination of  $P_{\text{recoll}}$ . So, special attention must be paid to eliminate the contribution of the artificial recollisions in the calculation of  $P_{\text{recoll}}$ . First, one needs to distinguish the artificial recollisions from the real ones. For this, the particle positions are followed in two distinct ways. While the position vectors are updated as usual using periodic boundary conditions, a monitoring array is used at the same time to record the distances of all pairs since their first collision. This array is updated without applying the periodic boundary conditions. At each real recollision, the distance recorded in the monitoring array must be equal to the collision distance, i.e.,  $\sigma$  (hard sphere diameter). An artificial recollision takes place between one collided particle and the image of its partner. For such a recollision, the distance recorded in the monitoring array does not equal  $\sigma$ . In fact, this corresponds to the situation in which the considered pair is continuing to move away from each other after their previous collision. So, in the calculation of  $P_{\text{recoll}}$ , one can plausibly view this situation as an event in which the two considered particles escape from each other forever.

The recollisions after long times are essentially determined by the diffusion process. Hence, the long-time asymptotic behavior of the recollision probability,  $f(t)$ , can be expected to be well described by the diffusion equation. In three dimensions, this leads to a decay of  $f(t)$  as  $t^{-3/2}$  at long times. This slow decay complicates a very accurate determination of  $P_{\text{recoll}}$  from simulations of finite length. The drawback of the method which determines the recollision probability by  $f(t) = P_{\text{recoll}} F(t)$  is that the inaccuracy in  $P_{\text{recoll}}$  will spread over the whole time range for  $f(t)$ . However, there does exist an alternative which allows us to extract  $P_{\text{recoll}}$  from other quantities closely related to the recollision probability. One such quantity is the probability of the *A* molecule colliding with new particles (the meaning of the term "new particle" is the same as that explained in Sec. II). The definition and the relation of this probability to  $f(t)$  is

$$P_{\text{new}}(t) = \left\langle \frac{\Delta N_{\text{new}}(t)}{\Delta N_T(t)} \right\rangle = 1 - \int_0^t dt' f(t'), \quad (23)$$

where  $\Delta N_T(t)$  is the total number of collisions undergone by a given molecule in the time interval  $[t, t + \Delta t]$  and  $\Delta N_{\text{new}}(t)$  the number of collisions with a new particle in the same time interval. The average denoted by the angled bracket is an average over all different particles and over many time origins in order to obtain good statistical accuracy. Now, the asymptotic value  $P_{\text{new}}(\infty)$  provides another way to deter-

mine  $P_{\text{recoil}}$  since  $P_{\text{new}}(\infty) = 1 - P_{\text{recoil}}$ . From the long-time behavior of  $f(t)$ , it follows that the deviation of  $P_{\text{new}}(t)$  from its asymptotic value approaches zero as  $t^{-1/2}$ . Therefore, a very accurate determination of  $P_{\text{recoil}}$  can be obtained by simulating over a long time and extrapolating the simulation results of  $P_{\text{new}}(t)$  to  $t \rightarrow \infty$ . This will be discussed in more detail in Sec. VI.

## V. RECOLLISION PROBABILITY AND THE CAGE EFFECT

In this section, we will show that the first recollision probability,  $f(t)$ , is not only the key ingredient of Noyes' theory but also contains information about the cage effect in the liquid phase. Up to now, the cage effect has been a roughly defined qualitative concept. However, some of its dynamic features can be characterized quantitatively by the recollision probability,  $f(t)$ .

The first thing we would like to know is how the cage effect shows up in the system properties considered here. If cages do exist, the recollisions must take place in a quite characteristic way, i.e., occurring in clusters in time. In each cluster, the recollisions are separated by short time intervals characteristic for the shuttling around of a pair within a cage. Then, one should see a longer period during which there is no recollision. This corresponds to the escape from the cage. If eventually the two molecules meet again, one will see another sequence of recollisions with short time intervals and so on. In Fig. 1, a few recollision sequences are shown. One can see that the recollisions indeed take place in such a way. This leads to a natural splitting of  $f(t)$  into two parts,

$$f(t) = f^s(t) + f^l(t), \quad (24)$$

where  $f^s(t)$  is the short-time part describing the recollisions due to the cage effect and  $f^l(t)$  the long-time part accounting

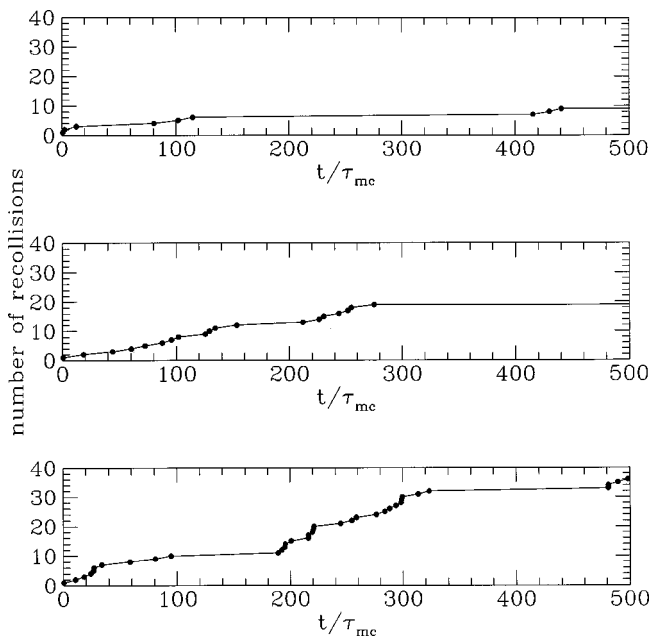


FIG. 1. Some examples of recollision sequences between two given particles for a high density ( $\eta=0.41$ ) hard sphere fluid ( $\tau_{\text{mc}}$ : mean collision time).

for the re-encounters after escaping from the cage. Now, let us define more precisely  $f^s(t)$  and  $f^l(t)$  in Eq. (24). For this, the cage size needs to be prescribed first. The radial distribution function clearly shows the shell structure of neighbors around a given particle in a liquid phase. A plausible choice for the cage size is the radius of the first-neighbor shell.<sup>4</sup> So, the cage radius,  $R_{\text{cage}}$ , is taken to be the position of the first minimum in the radial distribution function or equivalently the position of the barrier to enter into the first-neighbor shell in the potential of mean force. For hard spheres at liquid densities, this radius is found near  $1.5\sigma$ . Then,  $f^s(t)$  is defined as the contribution to  $f(t)$  from all the recollisions taking place before leaving the cage defined above while the recollisions, after escaping from the cage, contribute to  $f^l(t)$ . Hence, the determination of  $f^s(t)$  and  $f^l(t)$  by molecular dynamics simulations necessitates the monitoring of the distance between the colliding pair. Since the recollisions after long times result from diffusive motion,  $f^l(t)$  decays slowly as  $t^{-3/2}$ , as already pointed out in the last section.  $f^s(t)$  describes the distribution of recollisions due to the cage effect and dies away very quickly. Useful characteristics of the cage effect can be obtained from  $f^s(t)$  and the decomposition made in Eq. (24). First, the probability that a recollision is induced by the cage effect can be obtained straightforwardly from

$$\chi_{\text{recoil}}^s = \frac{\int_0^\infty dt f^s(t)}{\int_0^\infty dt f(t)}. \quad (25)$$

In a similar way, the probability of a recollision taking place after escaping the cage is

$$\chi_{\text{recoil}}^l = \frac{\int_0^\infty dt f^l(t)}{\int_0^\infty dt f(t)}. \quad (26)$$

The average time between the recollisions due to the cage effect is given by

$$\tau_{\text{recoil}}^s = \frac{\int_0^\infty dt t f^s(t)}{\int_0^\infty dt f^s(t)}. \quad (27)$$

As a rough estimate, the time needed for a molecule just undergoing a collision to go to the cage boundary is equal to  $\tau_{\text{recoil}}^s/2$ . The pictorial presentation of a recollision sequence given in Fig. 2 can help to show this.

Now, we will see how the characteristic behaviors of  $f^s(t)$  and  $f^l(t)$  enter into the kinetic description of  $S_A(t)$ . In the case of  $P_{\text{react}} = 1$ , the reaction rate given by Eq. (7) becomes

$$k(t) = \nu_{AB} \left( 1 - \int_0^t dt_1 f(t_1) \right). \quad (28)$$

When Eq. (28) is substituted into Eq. (6), one obtains

$$S_A(t) = \exp \left\{ -\nu_{AB} t \left[ 1 - \int_0^t dt_1 f(t_1) \right] - \nu_{AB} \int_0^t dt_1 t_1 f(t_1) \right\}. \quad (29)$$

As pointed above,  $f^l(t)$  decays as

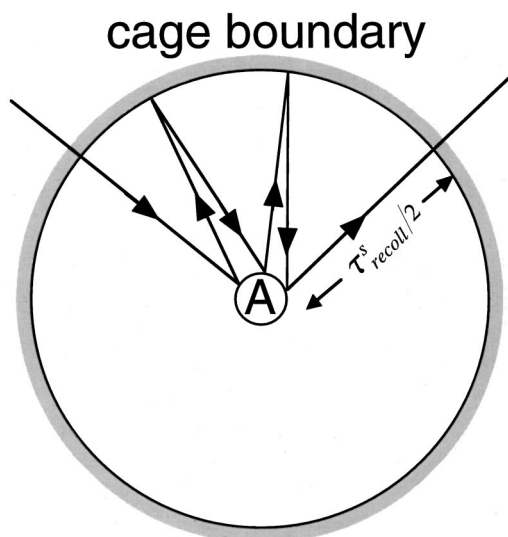


FIG. 2. Schematic presentation of recollisions inside a cage.

$$f^l(t) = \frac{\alpha}{t^{3/2}} \quad t \rightarrow \infty. \quad (30)$$

The determination of  $\alpha$  from molecular dynamics simulations will be described in Sec. VI. Furthermore, one would expect that  $f^s(t)$  dies away quickly. These observations lead to an asymptotic behavior for the survival probability of the form

$$-\ln S_A(t) = k(\infty) \left[ t + \frac{4\alpha}{1-P_{\text{recoll}}} \sqrt{t} + \frac{\delta}{1-P_{\text{recoll}}} \right] \quad t \rightarrow \infty, \quad (31)$$

with

$$\delta = \int_0^\infty dt t f^s(t) + \int_0^\infty dt t \left[ f^l(t) - \frac{\alpha}{t^{3/2}} \right]. \quad (32)$$

From the approaches based on a diffusion equation, an expression similar to Eq. (31) can be obtained for  $S_A(t)$  (see, e.g., Refs. 16 and 18). However, they contain only the first two terms (proportional to  $t$  and  $\sqrt{t}$ ) but not the constant term,  $\delta/(1-P_{\text{recoll}})$ . It was observed a long time ago<sup>26</sup> that the experimental results for  $\ln S_A(t)$  can often be fitted more satisfactorily by a second-order polynomial of  $\sqrt{t}$  with a constant term. In the approach proposed by André *et al.*,<sup>26</sup> a constant term is introduced from the outside. The above derivation of Eq. (31) shows clearly that such a constant term arises naturally in the theory based on the recollision probability. The first term in  $\delta$  is related to the mean recollision time due to the cage effect [see Eq. (27)].

## VI. NUMERICAL RESULTS AND DISCUSSIONS

Our model for the reaction system has been described in Sec IV A. For this model, the nonreacting counterpart system introduced in Noyes' theory is simply a fluid of hard spheres. All the results to be presented below are obtained from molecular dynamics simulations with 2048 hard spheres. A range of densities from  $\eta=0.15$ – $0.48$  is considered ( $\eta = \pi\rho\sigma^3/6$ ,  $\rho$ : number density;  $\sigma$ : hard-sphere diam-

TABLE I. Simulation results for collision frequency  $\nu$ , diffusion coefficient  $D_{AB}$ , recollision probability  $P_{\text{recoll}}$ , coefficient  $\alpha$  in the long-time tail of  $f^l(t)$  [see Eq. (30)].

$\eta$	$\nu^a$	$D_{AB}^b$	$P_{\text{recoll}}$	$\alpha^c$
0.15	3.07	1.126	0.350	0.19
0.30	10.11	0.362	0.781	0.32
0.41	21.61	0.142	0.941	0.21
0.48	35.17	0.0579	0.984	0.14

Units:

<sup>a</sup> $\nu: \sqrt{k_B T/m\sigma^2}$  ( $k_B$ : Boltzmann constant,  $T$ : absolute temperature,  $m$ : mass of a particle).

<sup>b</sup> $D_{AB}(D_A+D_B): \sqrt{\sigma^2 k_B T/m}$ .

<sup>c</sup> $\alpha: \sqrt{\tau_{\text{mc}}}$  (mean collision time,  $\tau_{\text{mc}} = 1/\nu$ ).

eter). The simulation results of the collision frequency and the diffusion coefficient at these densities are summarized in Table I.

### A. First recollision probability

In Fig. 3, the probability for first recollision,  $f(t)$ , is presented for different densities. At short times,  $f(t)$  increases quickly when the density is increased. This reflects directly the enhancement of the cage effect at higher densities leading to a larger number of recollisions.

In order to characterize the cage effect more quantitatively, we proposed in Sec. V to split the recollision probability into a short-time part,  $f^s(t)$ , and a long-time part,  $f^l(t)$ . The results of this decomposition at a low density ( $\eta=0.15$ ) and a high density ( $\eta=0.41$ ) are presented in Fig. 4. In both cases,  $f^s(t)$  is a fast decaying function. We will show shortly that it decays exponentially at long times.  $f^l(t)$  has quite different behaviors when the density is changed. At moderate densities, the amplitude of  $f^l(t)$  relative to  $f^s(t)$  is much larger than at high densities. This reflects directly the enhancement of the cage effect at increased densities. At high densities, all the recollisions at short times take place inside a cage, as shown by the fact that  $f^l(t)=0$  in the initial region [see Fig. 4(b)]. The results in Fig. 4 also show that  $f^l(t)$  has a long time tail and spreads over a large time range. This accounts for the fact that the recollision times after cage escape can vary from a few mean collision times to  $\infty$ . As pointed out earlier, one can show by using a diffusion equation that the recollision probability has a long time tail pro-

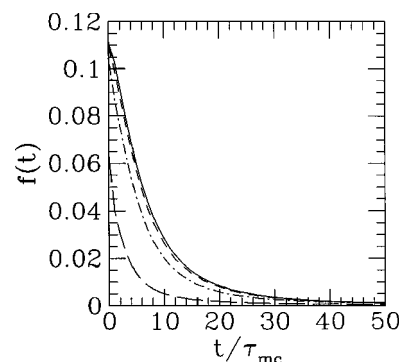


FIG. 3. First recollision probability,  $f(t)$ , of a hard sphere fluid at various densities. (a)  $\eta=0.15$  (long dash); (b)  $\eta=0.3$  (dot-short dash); (c)  $\eta=0.41$  (short dash); (d)  $\eta=0.48$  (full).

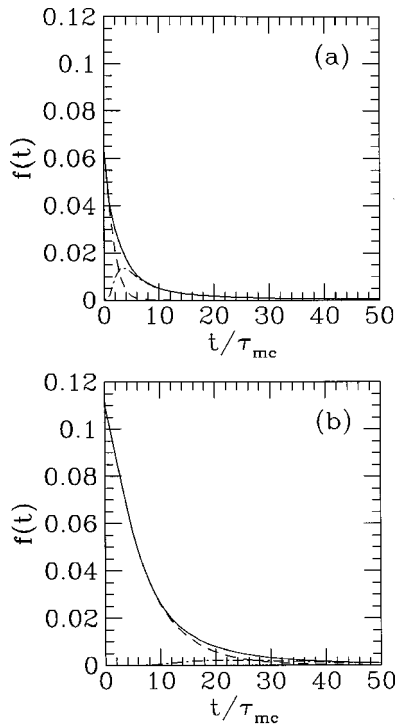


FIG. 4. Decomposition of the first recollision probability,  $f(t)$  (full), into the short-time part,  $f^s(t)$  (dash), and long-time part,  $f^l(t)$  (dot-dash). (a)  $\eta=0.15$  and (b)  $\eta=0.41$ .

portional to  $t^{-3/2}$ . This asymptotic behavior is confirmed by our simulations. In the next subsection, we will discuss its consequence on the asymptotic decay of the time-dependent reaction rate.

In Fig. 5,  $f^s(t)$  at  $\eta=0.41$  is plotted along with an exponential fitting function,  $f^s(t)=f_0^s \exp(t/\tau_{\text{recoil}}^s)$ . In fact, only the value of  $f_0^s$  is fitted to the simulation result for  $f^s(0)$ .  $\tau_{\text{recoil}}^s$  is taken to be the simulation result of the mean recollision time inside a cage. From Fig. 5, one can see that  $f^s(t)$  decays exponentially for  $t > 20\tau_{mc}$  (with  $\tau_{mc}$  the mean collision time). At shorter times, its decay is slightly slower than an exponential function. This implies that at very short times, the instants of recollisions do not occur completely at random. Nevertheless, the exponential function is a quite satisfactory approximation over the whole time range.

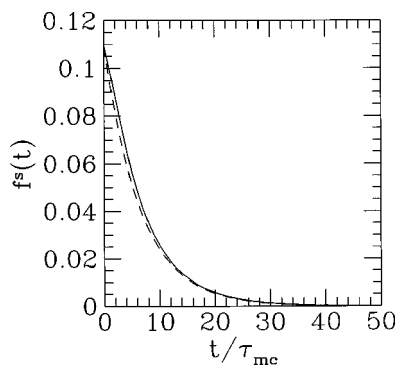


FIG. 5. Exponential decay of the short-time part of the first recollision probability,  $f^s(t)$ , at  $\eta=0.41$ . (a) simulation result (full); (b) fitting (dash) with  $f_0^s \exp(t/\tau_{\text{recoil}}^s)$  ( $f_0^s=0.109$  and  $\tau_{\text{recoil}}^s=6.60\tau_{mc}$ ).

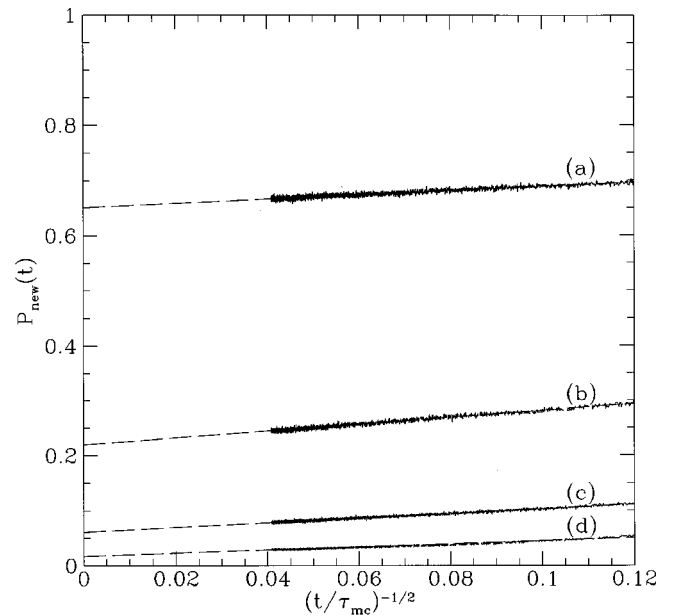


FIG. 6. Asymptotic behavior of the probability for a given particle colliding with a new particle (one which has not collided with the given particle),  $P_{\text{new}}(t)$ . The dashed line extrapolates each asymptote to  $t \rightarrow \infty$ . (a)  $\eta=0.15$ ; (b)  $\eta=0.3$ ; (c)  $\eta=0.41$ ; (d)  $\eta=0.48$ .

## B. Reaction rate

As discussed in Secs. II and IV [see in particular Eqs. (7) and (23)], the reaction rate is given by

$$k(t) = \nu_{AB} P_{\text{new}}(t), \quad (33)$$

for the case that  $P_{\text{react}}=1$ . As pointed out in Sec. IV B,  $P_{\text{new}}(t)$  can be measured directly in MD simulations by counting the collisions with new particles.  $k(\infty)$  and  $P_{\text{recoil}}$  can be obtained from  $P_{\text{new}}(\infty)$ . With the asymptotic behavior of  $f(t)$  given in Eq. (30),  $P_{\text{new}}(t)$  has the following asymptote:

$$P_{\text{new}}(t) = 1 - P_{\text{recoil}} + \frac{2\alpha}{\sqrt{t}} \quad t \rightarrow \infty. \quad (34)$$

At long times, the plot of  $P_{\text{new}}(t)$  versus  $t^{-1/2}$  is a straight line if Eq. (34) holds. The slope and the intercept of this straight line allow us to determine  $\alpha$  and  $P_{\text{recoil}}$ . The asymptotic plot of  $P_{\text{new}}(t)$  versus  $t^{-1/2}$  is presented in Fig. 6. The asymptotic form given in Eq. (34) is perfectly confirmed by the simulation results. It holds for all the densities considered here. The results for  $P_{\text{recoil}}$  and  $\alpha$  obtained in this way are presented in Table I. As one can expect, the recollision probability,  $P_{\text{recoil}}$ , increases with density. The return probability of a random walk has been determined on various lattices.<sup>24</sup> It depends on the topology of the lattice and decreases with the number of the nearest neighbors. Its value ranges from 0.442 for a diamond lattice (4 nearest neighbors) to 0.256 for face-centered-cubic (fcc) lattice (12 nearest neighbors).<sup>24</sup> Nevertheless, it is not straightforward to compare the recollision probability obtained here for a continuum model with the return probability of random walks on lattices. From the results obtained here, we see that the recollision probability can reach much higher values (especially at



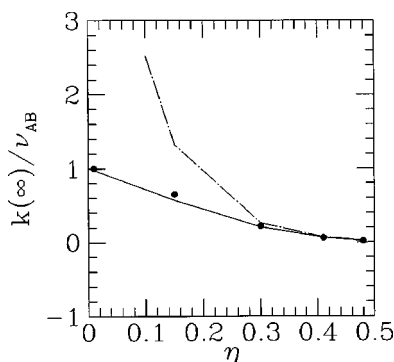


FIG. 7. Steady-state reaction rate,  $k(\infty)$  (measured with respect to the collision frequency  $\nu_{AB}$ ). MD simulation results (dots); results obtained from Eq. (17) with  $g(r)=1$  and  $D_{AB}(r)=D_A+D_B$  (full line); classic Smoluchowski theory (dot-dash line).

high densities) in the case of off-lattice models. Obviously, this enhancement is due to the cage effect of the solvent, which is not taken into account in the study of random walks on lattices. Although high-density liquids exhibit an fcc-like local structure, diffusing particles primarily move around in the cages formed by their neighbors rather than jumping from lattice site to lattice site. In the former process, as one might expect intuitively, the recollision probability can reach much higher values than in a random walk with isotropic jump distribution (but one could mimic the cage effect in a random walk model by introducing a high probability for back jumps).

For the model considered here, Noyes' expression for the reaction rate,  $k(t)$ , is exact provided that  $f(t)$  is known exactly, the concentration of  $B$  molecules is low, and the correlations between subsequent recollision times can be neglected in the case that  $P_{\text{react}} < 1$ . Then, with the  $P_{\text{recoil}}$  determined by the extrapolation method just described, one can readily calculate the steady-state reaction rate, i.e.,  $k(\infty) = \nu_{AB}(1 - P_{\text{recoil}})$ . It is to be noted that  $k(\infty)$  cannot be determined accurately by using the simulation method proposed in Ref. 23. By that method,  $k(t)$  is determined indirectly through the differentiation of the survival probability, which leads to quite noisy results at long times and makes the extrapolation for  $t \rightarrow \infty$  hard. In Sec. III, a quite general expression of  $k(\infty)$ , i.e., Eq. (22), is derived from a diffusion equation with the Collins–Kimball boundary condition. It is interesting to see how accurate the steady-state reaction rate is given by Eq. (22) over a wide density range. In Fig. 7,  $k(\infty)$  as given by Eq. (17) [i.e., the particular case of Eq. (22) with  $P_{\text{react}} = 1$ ] is compared to the predicted value of  $k(\infty) = \nu_{AB}(1 - P_{\text{recoil}})$ . For this comparison, further approximations have been made, i.e.,  $g(r)=1$  and  $D(r) = D_{AB} = D_A + D_B$ . With these approximations,  $k^{\text{abs}}(\infty)$  reduces to the result of the classic Smoluchowski theory,  $k^S(\infty) = 4\pi\sigma D_{AB}\rho_B$ , which is also plotted in Fig. 7. One sees that Eq. (17), even with the above approximations, gives results in remarkably good agreement with the simulation results over the whole density range. The classic Smoluchowski theory gives accurate results only for systems with a density higher than  $\eta=0.3$ . At low densities,  $k^S(\infty)$  is not even bounded by the collision frequency, while  $k(\infty)$

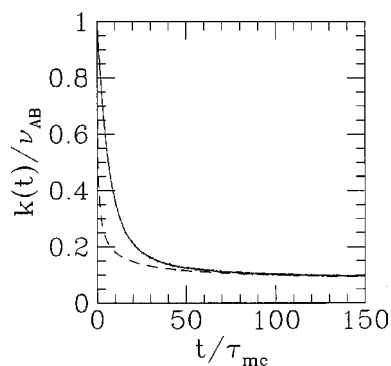


FIG. 8. Time-dependent reaction rate,  $k(t)$  (measured with respect to  $\nu_{AB}$ ) at  $\eta=0.41$ : Simulation result (full line); Collins–Kimball theory with the intrinsic rate given by Eq. (16) (dashed line).

given by Eq. (17) always satisfies the physical requirement that  $k(\infty) \leq \nu_{AB}$  [also true for Eq. (22)]. It is worthwhile noting that the failure of Smoluchowski theory to produce accurate results for  $k(\infty)$  at low densities results mainly from the inappropriateness of the boundary condition at  $r = \sigma$ . But, this failure is not really related to the diffusion equation itself since the same diffusion equation is used to obtain Eq. (17).

Since Fig. 7 shows such a good agreement between the simulation and the diffusion equation under the approximations  $g(r)=1$  and  $D(r)=D_A+D_B$ , it is tempting to see how good a similar approximation is for the time-dependent reaction rate,  $k(t)$ . In the framework of these approximations,  $k(t)$  is given analytically by the expression of Collins–Kimball theory for the time-dependent reaction rate, using the value of  $\kappa$  given by Eq. (16) [ $g(\sigma)$  is set to 1] for the intrinsic reaction rate. Figure 8 shows the comparison of the results obtained from this approximation and simulations for  $\eta=0.41$ . At long times ( $t > 60\tau_{\text{mc}}$ ), there is a very good agreement between the theoretical approach and the simulations. By construction (see Zhou and Szabo<sup>22</sup>), the approach also gives the exact result for  $k(0)$ . In the intermediate time range ( $0^+, 60\tau_{\text{mc}}$ ), the reaction rate is quite underestimated by the above theoretical approach. This may be due in part to the simplification made by neglecting the spatial variation of the diffusion coefficient and the potential of mean force. It might also be possible that the short-time recollision probability is overestimated by the diffusion equation even with the radiation boundary condition.

## VII. CONCLUSIONS

In the present work, a derivation of the kinetic equation of the survival probability is presented for reacting systems with a time-dependent reaction rate. From this derivation, the basic assumptions behind the kinetic equation, mostly about the absence of various types of correlations, become very clear. In the absence of correlations, the reaction rate is closely related to the first recollision probability,  $f(t)$ , in a nonreacting counterpart system. Molecular dynamics simulations have been carried out to determine this quantity. With the simulation results for  $f(t)$ , various features of Noyes' theory are investigated in a thorough way. For the simple reaction model considered in this work, Noyes' theory gives

the exact expression for the reaction rate in the limit of dilute reactants. Using the recollision probability, we find a relation between the contact value of the reactant–reactant distribution function in a stationary reactive system and that of the equilibrium distribution function in the corresponding nonreacting equilibrium system. This relation allows us to establish unambiguously a general boundary condition at the collision distance,  $\sigma$ , for totally diffusion-controlled ( $P_{\text{react}}=1$ ) as well as partially diffusion-controlled ( $P_{\text{react}}<1$ ) reactions. Using this boundary condition in a diffusion equation, one obtains a fairly elaborate expression for the steady-state reaction rate [Eq. (22)]. Remarkably good results are obtained from such an approach for  $k(\infty)$  over the whole density range under the approximation that  $g(r)=1$  and  $D(r)=D_A+D_B$ . However, the same approach underestimates the reaction rate,  $k(t)$ , in the intermediate time range.

Up to now, all the simulations of diffusion-controlled reactions employed an annihilation procedure to account for the disappearance of reactants due to chemical reaction.<sup>22,23,27</sup> We demonstrated here that Noyes' formalism provides a very interesting as well as highly efficient alternative to the previous simulation method. For obtaining the reaction rate in a system with dilute reactants, one needs to carry out only simulations on an equilibrium *nonreactive* system. This is quite reminiscent of the method for determining transport coefficients by equilibrium molecular dynamics simulations with the help of Green–Kubo formulas instead of nonequilibrium MD simulations. Here, Noyes' expression of the reaction rate in terms of the recollision probability of a nonreactive equilibrium system plays a role similar to the Green–Kubo formulas. So far, Noyes' theory has not been exploited in depth in the literature. Further investigations in this direction might lead to new insights and approaches.

A further strength of Noyes' theory is that it is not restricted to systems that are strictly described by a diffusion equation, as in the case of Smoluchowski theory and its extensions. A first example could be fluids at moderate densities, in which the recollision probability is large enough to make the reaction rate (in the case  $P_{\text{react}}=1$ ) notably different from the collision frequency, but the two-particle dynamics from which the recollision time is to be calculated is not of diffusive type, especially at short times. Other examples include dilute or moderately dense systems with a small reaction distance and a long-range attractive force between the reactants which may strongly enhance the recollision probability, diffusion in solid-state materials where the recollision probability is determined by a hopping process rather than a continuum diffusion equation, or motion through porous media where recollisions may be enhanced at long times due to confinement to a single pore for extended times. In all these cases, computer simulations of the probability density of first recollision may be done in principle without any great problems, even though analytical approaches would be highly problematic or at least different from Smoluchowski theory.

In Noyes' theory, correlation effects due to the first recollisions of the same pair of particles are taken fully into account regardless of the type of dynamics. Nevertheless,

correlations due to competition with other reactive pairs are ignored completely (both *A* and *B* particles are assumed to be very dilute). In other modern approaches,<sup>11–15</sup> the latter type of correlation is taken into account (often by quite refined techniques), but most of them assume simple diffusive dynamics. In this respect, the above two types of approaches are complementary. In addition, Noyes' theory ignores correlations between the recollisions after the first one. When all the particles are very mobile, this should be an excellent approximation. But when cage configurations start to change very slowly (e.g., close to a glassy state), this type of correlation may become quite important.

The clustering of recollisions found in the present work reveals unambiguously the characteristic two-particle dynamics due to the cage effect. We show that the first recollision probability not only plays an important role in determining the reaction rate, but also provides a very helpful tool for characterizing some quantitative features of the cage effect. In view of its usefulness in the study of these important subjects, we believe that the recollision probability deserves more investigation. For example, it is highly desirable to have tractable kinetic theory expressions for this quantity.

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