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# Quantum statistical theory of chemical reactions

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# Quantum statistical theory of chemical reactions II. Treatment of reactions in dense systems—the chemical version of the Enskog dense-gas theory

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Starting from the exact rate equations for chemical reactions derived in a previous paper [1], approximate rate equations are derived by considering a convenient class of diagrams containing both two-body dynamics and quasistatic two-body correlations. Thus, in the markovian limit, the rate constants are formulated in terms of the T-matrix elements of two-molecule reactive scattering theory and of pair distribution functions describing the correlations of the molecules of the different species in thermal, but not chemical, equilibrium. The pair correlation functions depend in a complicated way on the concentrations of the different species, which leads to a concentration dependence of the rate constants. Physically, our expressions for the rate constants are closely related to the usual expressions for the transport coefficients of the Enskog dense-gas theory of non-reactive fluids.

## 1. INTRODUCTION

In a previous paper [1], we formulated a quantum-statistical theory of chemical reactions based on exact rate equations, i.e. equations of motion for the concentrations of the different species, and then used diagram perturbation theory to expand the integral kernels occurring in these equations of motion. In [1], by considering the diagrams of lowest order, we obtained rate equations which are valid for dilute systems and reduce to the usual collision theory results after suitable approximations have been made.

In the present paper, we intend to treat denser systems by considering higher approximations. The starting point is again the short-memory version equation (I 15)<sup>†</sup>, of the exact rate equation (I 9). This is correct [2, 3] provided that the set of parameters (the concentrations  $c_X(t)$  and the deviations  $\Delta\beta_X(t)$ of the kinetic temperatures of the different species X) chosen in [1] is complete,

 $<sup>\</sup>dagger$  Equation (I x) means equation (x) of paper I [1].

thus allowing a macroscopic (chemical) description of the system. This is fulfilled for most chemical reactions of practical interest, and in dense systems we may even set  $\Delta\beta_X(t)=0$ , which means that thermalization is a much faster process than chemical relaxation. We are thus left with equation (I 15), the set  $O_n(t)$  being just  $c_X(t)$ , X=A, B, C, D.

In equation (I 15), the only diagrams that contribute are those rapidly decaying in time. The lowest-order diagrams to fulfil this condition were considered in [1]. As a guide for selecting the appropriate higher-order diagrams, we can use the theory of kinetic equations for non-reactive fluids [3, 4], in which it was found that the diagrams we have to consider are those which contain both two-particle dynamics and quasi-static pair correlations in the non-equilibrium ensemble  $\sigma(t)$ . The contribution of these diagrams yields kinetic equations which, in the appropriate limits, reduce to the well-known Enskog equation which describes to a very good approximation the behaviour of dense gases, and is even a good approximation in simple liquids [5, 6].

The diagrams to be considered in this paper (see figures 1 and 2) are topologically the same as those taken into account in the non-reactive case, but the two-body dynamics is now given by reactive molecular collisions. Nevertheless, the physical interpretation of the equations obtained is essentially the same as in the case of non-reactive fluids (see for example [5]).

The Enskog dense-gas theory was originally formulated for classical hardsphere gases, but in recent years several papers concerned with the extension of the theory to realistic potentials have appeared [7]. An application to reactive fluids, however, has not yet been attempted, which, in view of the good results achieved with the Enskog theory in calculating transport coefficients, is rather surprising. The reason probably lies in the fact that the usual procedures for deriving the Enskog theory proceed via the BBGKY hierarchy, and the inclusion of reactive collisions in the theory poses a serious problem which, it seems, cannot be resolved at present.

For the sake of simplicity, we begin in the following section with the derivation of the desired rate equation by considering those diagrams which contain the full quasi-static pair correlations, but treat the two-body dynamics in the weak-coupling limit. The renormalization of the interaction is carried out in  $\S2.2$  by summing the appropriate ladder diagrams. In  $\S3$ , the markovian limit of the rate equations thus obtained is expressed in more familiar terms by the use of scattering theory. In this way the rate constants are expressed in terms of the off-shell T-matrix elements of molecular scattering theory and the pair distribution functions which describe the quasi-static correlations of the molecules in the ensemble  $\sigma(t)$ . This ensemble describes a system which is in thermal, but not chemical, equilibrium. All quantities calculated in this ensemble thus depend on the actual concentrations of the different species at time t. These points are discussed in §4. Finally, in §5, we discuss our results and attempt to outline some possible implications of the present theory on both the theory of reactive molecular collisions and the theory of chemical reactions in general. In concluding this introduction, we would like to mention, that the approximate rate equation (10) could be obtained directly from our general rate equation (I 15) by some kind of cluster expansion, in the Maxwell-Boltzmann limit at least. Any reader who is not interested in the details of the diagram expansion could therefore start directly from equation (10).

#### 2. Consideration of pair correlations in rate equations

The diagrams we wish to consider in this paper are shown in figures 1 and 2. These diagrams contain the correlated part  $F_2^{c}(t)$  of the two-particle density operator  $F_2(t)$  defined by

$$\langle Ii, Kk | F_{2}^{\circ}(t) | Ll, Mm \rangle = \operatorname{Tr} \{ a_{L, l}^{+} a_{M, m}^{+} a_{I, i} a_{K, k}^{-} \sigma(t) \}$$
$$- \{ (1 - \kappa \delta_{I, K}) \delta_{I, L} \delta_{i, l} \delta_{K, M} \delta_{k, m}^{-} + \kappa \delta_{I, K} \delta_{I, M} \delta_{i, m}^{-} \delta_{K, L} \delta_{k, l} \}$$
$$\times G_{l}^{<}(l, L) G_{l}^{<}(m, M).$$
(1)

The first term on the right-hand side of equation (1) corresponds to the twoparticle Green function  $G^{(2)}$  for a special ordering of the creation and annihilation operators. The diagram expansion of  $F_2^{\circ}$  is given in figure 3. In equation (1),  $G_t^{<}$  is the one-particle Green function of equation (I 18), and  $\kappa = +1$  for bosons and -1 for fermions. By the choice of observables discussed in [1],  $\sigma(t)$  is now given by

$$\sigma(t) = \exp\left\{-\lambda_0(t) - \beta(t)[H - \sum_X \mu_X(t)N_X]\right\},\tag{2}$$

which may be considered as a Gibbs grand canonical ensemble with given concentrations of the different species. These concentrations may deviate arbitrarily far from the concentrations in chemical equilibrium. A more detailed description of the above function will be given in § 4.



Figure 1. The diagrams of lowest order considered in this paper. These diagrams are in the weak-coupling limit with respect to the dynamical part, but contain the full quasistatic correlations represented by the box  $F_2^{\circ}$ . The box is explained in figure 3. The labelling is chosen so that only reactive contributions are retained. Two further diagrams are obtained by reversing all the arrow directions. All propagator lines are to be understood as double lines representing exact Green functions.



Figure 2. The renormalized diagrams. The shaded and the open box contain twoparticle ladders and are explained in I. As to labelling, arrow directions and propagator lines see figure 1.



Figure 3. The definition of the correlated part of the two-particle Green function.

#### 2.1. The weak-coupling limit

Let us now consider figure 1. This diagram is obtained from figure 1 in [1] by introducing, either between its particle or hole lines, all possible wavy-line diagram parts, the sum of which is just the matrix element of  $F_2^{\circ}$  given in equation (1). (We shall denote the lines running to the right (left) as particle (hole) lines. Of course, this is rather arbitrary; for more details see the discussion in [3].)

The analytic expression of figure 1 in terms of  $F_2^{c}$  is obtained by separating the box from the remainder of the diagram in the same way as was demonstrated for the general case [2] (see figure 1), and by using the sign rule [1 (vi)] and the equivalent-pair-of-lines rule [1 (iv)]. It is easily verified that we obtain the correct factors if, with respect to rule (iv), we treat the box in the same way as an interaction line, and with respect to rule (vi), we assume the lines to run straight through the box without crossing. The sign factors in figure 2 are then obtained by applying the usual rule [8]. Proceeding in this way, and using the diagram rules given in [1], we find that the sum of the diagrams of figure 1 is

$$\frac{1}{\hbar^{2}} \sum_{\substack{a, b, i, k, l, m \\ I, K, L, M=A, B, C, D}} \exp\left(\frac{i}{\hbar} \left[\mathscr{E}_{A}(a) + \mathscr{E}_{B}(b) - \mathscr{E}_{I}(i) - \mathscr{E}_{K}(k)\right]\vartheta\right) \\
\times \left\{\langle Aa, Bb | W | Ii, Kk \rangle \langle Ii, Kk | PW | Ll, Mm \rangle \\
\times \left\langle Ll, Mm | F_{2}^{c} | Aa, Bb \rangle + \langle Aa, Bb | W | Ii, Kk \rangle \\
\times \left\langle Ii, Kk | F_{2}^{c} | Ll, Mm \rangle \langle Ll, Mm | PW | Aa, Bb \rangle \right\} + \text{c.c.,} \quad (3)$$

where c.c. is the corresponding complex conjugate expression, and P is the operator introduced in [1]. In labelling the propagator lines of the diagrams, it was taken into account that purely elastic processes do not contribute to  $\overline{N}_A$ . It should be clear that in this case there occur no factors of  $\frac{1}{2}$ . The two diagrams which are obtained from those drawn explicitly in figure 1 by reversing all the arrow directions yield the complex conjugate of the above expression (3). This is easily verified by applying the diagram rules and the fact that  $F_2^c$ , as defined by equation (1), is a hermitian operator.

Using the decomposition of the unit operator in two-particle space

$$1 = \sum_{\substack{I,i\\K,k}} |Ii, Kk\rangle \langle Ii, Kk|, \qquad (4)$$

expression (3) is obtained in a more compact form,

$$\sum_{a,b} \langle Aa, Bb | L_1^{(2)}(\vartheta) \mathscr{L}_1 F_2^{c} | Aa, Bb \rangle,$$
(5)

where

$$L_1^{(2)}(\vartheta)A = \frac{1}{\hbar} [W(\vartheta), A].$$
(6)

The matrix elements of  $W(\vartheta)$  are given by

$$\langle Ii, Kk | W(\vartheta) | Ll, Mm \rangle = \exp \{ i / \hbar [\mathscr{E}_{I}(i) + \mathscr{E}_{K}(k) - \mathscr{E}_{L}(l) - \mathscr{E}_{M}(m)] \vartheta \}$$

$$\times \{ \langle Ii, Kk | W | Ll, Mm \rangle + \kappa \delta_{I,K} \langle Ii, Kk | W | Mm, Ll \rangle \}$$
(7)

and

$$\mathscr{L}_1 A = \frac{1}{\hbar} \left[ PWA - AWP \right].$$

The rate equation obtained from expression (5) will be discussed below.

# 2.2. Strong interactions

In the above expressions the dynamics of the two-body system is treated in the limit of weak coupling, corresponding to treating the binary collision in the Born approximation, which is well known from scattering theory. This is, of course, unsatisfying, since in real systems the short-range part of the interaction is in general very strong.

This difficulty is overcome, as it is in [1], by summing the appropriate ladder diagrams. The corresponding diagrams are shown in figure 2, and it is easily concluded that they represent all possible diagrams which can be obtained by introducing additional dashed lines between the particle or hole lines of the diagrams of figure 1.

The corresponding analytical contribution is

$$-\frac{1}{\hbar^{2}}\sum_{a,b}\left\{\left\langle Aa, Bb \middle| \mathscr{V}(\vartheta, 0)F_{2}^{c}(t-\vartheta)\mathscr{U}^{+}(\vartheta, 0)\middle| Aa, Bb\right\rangle + \left\langle Aa, Bb \middle| W(\vartheta)\mathscr{U}(\vartheta, 0)F_{2}^{c}(t-\vartheta)W(0)P\mathscr{U}^{+}(\vartheta, 0)\middle| Aa, Bb\right\rangle \right\} + \text{c.c.}, \quad (8)$$

where equation (I 42) is used. This can be expressed more compactly as

$$\sum_{b} \langle Aa, Bb | L_1^{(2)}(\vartheta) \mathcal{U}(\vartheta, 0) [ \mathcal{L}_1 F_2^{c}(t-\vartheta)] \mathcal{U}^+(\vartheta, 0) | Aa, Bb \rangle.$$
(9)

In labelling the diagrams, it was again taken into account that purely elastic processes do not contribute to  $N_A$ . Expression (9) can be combined with equation (I 41), producing the rate equation

$$\dot{N}_{A}(t) = -\int_{0}^{t} d\vartheta \sum_{a,b} \langle Aa, Bb | L_{1}^{(2)}(\vartheta) \mathcal{U}(\vartheta, 0) [\mathcal{L}_{1}F_{2}(t-\vartheta)] \mathcal{U}^{+}(\vartheta, 0) | Aa, Bb \rangle,$$
(10)

where

$$F_2(t) = F_2^{(0)}(t) + F_2^{c}(t).$$
<sup>(11)</sup>

Equation (10) is the rate equation which is expected to describe chemical reactions in dense fluids.

The right-hand side of equation (10) depends, via  $F_2(t-\vartheta)$ , on the inverse temperature  $\beta(t)$ , which may vary in time, since we are considering a closed system. To determine  $\beta(t)$  we use the condition from equation (I 7),

$$\langle H \rangle_t = \operatorname{Tr} \{H\sigma(t)\} = \operatorname{const.}$$

Using the diagram expansion together with figure 3, we find, after some manipulations, that

$$\langle H \rangle_t = \frac{3}{2} k T(t) \overline{N}(t) + \sum_X \overline{N}_X(t) \mathscr{E}_X' + \sum_{\substack{i,k,l,m \\ I,K,L,M=A,B,C,D}} \langle Ii, Kk | W | Ll, Mm \rangle \langle Ll, Mm | F_2(t) | Ii, Kk \rangle.$$
(12)

This equation supplements equation (10), and thus we have a closed system of equations of motion.

Equation (10) contains memory effects, and takes full account of the fact that the binary collision is affected by the other particles of the system by exchange effects. The most important feature of this equation, however, is the appearance of  $F_2^{c}$ , which describes the two-particle correlations in the ensemble  $\sigma(t)$ . The matrix elements of  $F_2^{c}$  depend in a very complicated way on the concentrations of the different species, and thus it is to be expected that the rate constants in equation (I 44) also depend on the concentrations in a complicated way. A more detailed discussion will be attempted in § 4.

For most chemical reactions the memory effects are very small, so we can take the markovian limit of the rate equations. In §3 we shall study the resulting equations somewhat more closely and derive explicit expressions for the rate constants. Actually, these expressions could be obtained by considerations analogous to those of paper [1]. Since the situation is now rather more complicated, we prefer, however, to carry out the theoretical scattering considerations with greater rigour. Because of the fact that the field operators of the different species commute, the usual non-orthogonality problem of rearrangement scattering theory does not occur in this case.

### 3. The markovian rate equations

The markovian limit of equation (10) is obtained by setting

$$F_2^{\rm c}(t-\vartheta) = F_2^{\rm c}(t).$$

As in [1], we will now introduce the transition operator of scattering theory. To simplify the derivations, we shall assume that we can neglect exchange effects due to the presence of the other particles in the system.<sup>†</sup>

In this limit, we set  $\kappa = 0$ , from which it follows that P = 1. Using the relations

$$\frac{\partial}{\partial t} \mathscr{U}(t, 0) = -\frac{i}{\hbar} W(t) \mathscr{U}(t, 0),$$

<sup>†</sup> For a mono-component fluid, it is shown in [4] how the general case is treated. These ideas can also be applied to the present situation.

and

$$\frac{\partial}{\partial t} \mathscr{U}^{+}(t, 0) = \frac{i}{\hbar} \mathscr{U}^{+}(t, 0) W(t),$$

Where the matrix elements of W are given by equation (I 4) with  $\kappa = 0$ , it is easily recognized that the integrand in equation (10) is equal to

$$i\sum_{a,b} \{\langle Aa, Bb | \mathcal{U}(t,0)[L_1^{(2)} F_2(t)] \mathcal{U}^+(t,0) | Aa, Bb \rangle \\ - \langle Aa, Bb | L_1^{(2)} F_2(t) | Aa, Bb \rangle \}.$$
(13)

Since *U* may be written as

$$\mathscr{U}(t, 0) = \exp\left[(i/\hbar)H_0^{(2)}t\right] \exp\left[(i/\hbar)H^{(2)}t\right],$$
(14)

Where  $H_0^{(2)}$  and  $H^{(2)}$  are the free and full hamiltonians of the two-molecule system respectively, we have, for an infinite system, that

$$\lim_{t \to \infty} P_{I,K} \mathscr{U}(t,0) = \Omega_{I,K}^{(-)+},$$
(15)

where  $\Omega_{I,K}^{(-)+}$  is the Møller wave operator [9] for the scattering of molecules I and K. The projection operator  $P_{I,K}$  is defined as

$$P_{I,K} = \sum_{i,k} |Ii, Kk\rangle \langle Ii, Kk|.$$

Provided that the system is finite, it is more convenient to work with a modified version of the Møller wave operator [10],

$$\Omega_{I,K}^{(-)}(\epsilon) = \left\{ 1 + \frac{i}{\hbar} \int_{0}^{\infty} dt \exp\left(-\epsilon t/\hbar\right) \exp\left(iH^{(2)} t/\hbar\right) W \\ \times \exp\left(-iH_{0}^{(2)} t/\hbar\right) \right\} P_{I,K}, \quad (16)$$

where in an infinite system, for  $\epsilon \rightarrow 0$ ,  $\Omega(\epsilon)$  converges strongly to  $\Omega$ . From the properties of the above limits, it is concluded that the integrand (13) may be written as

$$i\sum_{a,b} \{\langle Aa, Bb | \Omega_{A,B}^{(-)+}(\epsilon) [L_1^{(2)} F_2] \Omega_{A,B}^{(-)}(\epsilon) | Aa, Bb \rangle - \langle Aa, Bb | L_1^{(2)} F_2 | Aa, Bb \rangle \}.$$
(17)

To introduce the transition operator T, we define an operator  $T(\epsilon)$  such that

$$T_{I,K}^{*}(\epsilon) = W\Omega_{I,K}^{(-)}(\epsilon), \quad T^{*}(\epsilon) = T(-\epsilon),$$
(18)

where the asterisk denotes the complex conjugate. T is then obtained from the relation

$$\lim_{\epsilon \to 0} T(\epsilon) = T$$

Now, we note that, by virtue of equation (16),

$$\Omega_{I,K}^{(-)}(\epsilon)|Ii, Kk\rangle = (1 + G^{(-)}(E_{I,K})W)|Ii, Kk\rangle,$$
(19)

where

$$\mathscr{G}^{(-)}(E) = \frac{1}{E - H - i\epsilon}$$

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and

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$$E_{I,K} = \mathscr{E}_{I}(i) + \mathscr{E}_{K}(k).$$
<sup>(20)</sup>

The Green function is written in terms of the scattering states

$$\Psi_{L,M}^{(-)}(l,m) = \Omega_{L,M}^{(-)}|Ll,Mm\rangle$$
(21)

as

$$G^{(-)}(E_{I,K}) = \sum_{\substack{L,M \\ l,m}} |\Psi_{L,M}^{(-)}(l,m)\rangle \frac{1}{E_{I,K} - E_{L,M} - i\epsilon} \langle \Psi_{L,M}^{(-)}(l,m)|, \quad (22)$$

where it is assumed that the interaction of equation (I 4) does not support bound states between different molecules, and where the sum over L and M is carried out in such a way that there appear only those elastic and reactive scattering processes allowed by equation (I 4).

Using equations (18), (19) and the relation

$$\mathscr{G}^{(-)}(E) = G^{(-)}(E) + G^{(-)}(E)W\mathscr{G}^{(-)}(E),$$
(23)

where

$$G^{(-)}(E) = \frac{1}{E - H_0 - i\epsilon},$$

we obtain

$$\Omega_{\mathcal{A},B}^{(-)}(\epsilon)|Aa,Bb\rangle = (1 + G^{(-)}(E_{\mathcal{A},B})T_{\mathcal{A},B}(-\epsilon))|Aa,Bb\rangle; \qquad (24)$$

from this and equation (18),

$$\langle Aa, Bb | \Omega_{A,B}^{(-)+}(\epsilon) [L_1^{(2)} F_2^{c}] \Omega_{A,B}^{(-)}(\epsilon) | Aa, Bb \rangle$$

$$= \frac{1}{\hbar} \langle Aa, Bb | T_{A,B}^{+}(-\epsilon) F_2^{c} [1 + G^{(-)}(E_{A,B}) T_{A,B}^{-}(-\epsilon)]$$

$$- [1 + G^{(-)}(E_{A,B}) T_{A,B}^{-}(-\epsilon)]^+ F_2^{c} T_{A,B}^{-}(-\epsilon) | Aa, Bb \rangle.$$
(25)

Now consider the equation

$$\langle Aa, Bb | T_{A,B}^{+}(-\epsilon)F_{2}^{c}-F_{2}^{c} T_{A,B}(-\epsilon) | Aa, Bb \rangle$$

$$= \hbar \langle Aa, Bb | L_{1}^{(2)}F_{2}^{c} | Aa, Bb \rangle + \langle Aa, Bb | W \mathscr{G}^{(-)+}(E_{A,B})$$

$$\times WF_{2}^{c}-F_{2}^{c} W \mathscr{G}^{(-)}(E_{A,B})W | Aa, Bb \rangle.$$
(26)

Using equations (18), (19), (21) and (22), this becomes

$$\hbar \langle Aa, Bb | L_{1}^{(2)} F_{2}^{c} | Aa, Bb \rangle + 2i \operatorname{Im} \sum_{\substack{i, k, l, m \\ I, K, L, M}} \left\{ \langle Aa, Bb | T_{I,K}(-\epsilon) | Ii, Kk \rangle \right. \\ \left. \times \frac{1}{E_{A,B} - E_{I,K} + i\epsilon} \langle Ii, Kk | T_{I,K}^{+}(-\epsilon) | Ll, Mm \rangle \right. \\ \left. \times \langle Ll, Mm | F_{2}^{c} | Aa, Bb \rangle \right\}.$$
(27)

Applying the above result, the integrand (17) becomes

$$-\frac{2}{\hbar} \operatorname{Im} \sum \left\{ \langle Aa, Bb | T_{A,B}^{+}(-\epsilon) | Ii, Kk \rangle \langle Ii, Kk | F_{2}(t) | Ll, Mm \rangle \right. \\ \left. \times \frac{1}{E_{A,B}^{-} - E_{L,M}^{-} i\epsilon} \left\langle Ll, Mm | T_{A,B}(-\epsilon) | Aa, Bb \rangle \right. \\ \left. + \left\langle Aa, Bb | T_{I,K}(-\epsilon) | Ii, Kk \right\rangle \frac{1}{E_{A,B}^{-} - E_{I,K}^{-} + i\epsilon} \right. \\ \left. \times \left\langle Ii, Kk | T_{I,K}^{+}(-\epsilon) | Ll, Mm \rangle \langle Ll, Mm | F_{2}(t) | Aa, Bb \rangle \right\}.$$
(28)

To obtain the above expression in the form of a rate equation, we define

$$\langle Ii, Kk | F_{2}(t) | Ll, Mm \rangle = \frac{1}{2} \{ n_{I}(i, t) n_{K}(k, t) + n_{L}(l, t) n_{M}(m, t) \} \\ \times g_{IK, LM}(i, k, l, m; t) \delta(\mathbf{p}_{I} + \mathbf{p}_{K} - \mathbf{p}_{L} - \mathbf{p}_{M}), \quad (29)$$

where

$$g_{IK,LM}(i, k, l, m; t) = g_{LM,IK}(l, m, i, k; t),$$
  

$$g_{LM,LM}(l, m, l', m'; t) = g_{LM}(l, m, l', m'; t),$$

the  $\delta$  function expressing the conservation of total momentum is displayed explicitly, and the momentum distribution  $n_X(x, t)$  is given by equation (I 45). The functions  $g_{IK,LM}$  and  $g_{LM}$  are connected with the Fourier transforms of the pair distribution functions in configuration space, and will be discussed in more detail in § 4.

Incorporating the results of [1], the rate equations are now

$$\dot{c}_{A}(t) = -k_{f}c_{A}(t)c_{B}(t) + k_{b}c_{c}(t)c_{D}(t), \qquad (30)$$

where

$$k_f = k_f^{(\mathrm{B})} + k_f^{(\mathrm{E})},$$

 $k_{j}^{(B)}$  being the expression on the Boltzmann level [1]. Either from there or from the above considerations with  $F_2$  replaced by  $F_2^{(0)}$ , and using

$$\frac{1}{x+i\epsilon} = \mathscr{P}\left(\frac{1}{x}\right) - i\pi\delta(x),$$

where  $\mathcal{P}$  means principal part, we find that

$$k_{f}^{(B)} = \frac{2\pi}{\hbar V} \sum_{a, b, c, d} |\langle Aa, Bb | T_{A,B}(-\epsilon) | Cc, Dd \rangle|^{2} \delta[\mathscr{E}_{A}(a) + \mathscr{E}_{B}(b) - \mathscr{E}_{C}(c) - \mathscr{E}_{D}(d)]_{cA}(a, t)_{cB}(b, t), \quad (31)$$

V being the volume of the system.

The expression for  $k_f^{(E)}$ , which is the corrective term calculated at the Enskog level, is immediately obtained from equations (28) and (29) as

$$k_{f}^{(\mathrm{E})} = k_{f,1}^{(\mathrm{E})} + k_{f,2}^{(\mathrm{E})},$$

where

$$k_{f,1}^{(E)} = \frac{2}{\hbar V} \operatorname{Im} \sum_{a, b, c, d, a', b'} \langle Aa, Bb | T_{A,B}(-\epsilon) | Cc, Dd \rangle \frac{1}{E_{A,B} - E_{C,D} + i\epsilon} \\ \times \langle Cc, Dd | T_{A,B}^{+}(-\epsilon) | Aa', Bb' \rangle f_{A}(a', t) f_{B}(b', t) h_{AB}(a, b, a', b'; t), \quad (32)$$
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and

$$h_{IK,LM}(i, k, l, m; t) = -\delta_{I,L}\delta_{L,M}\delta_{i,l}\delta_{k,m} + g_{IK,LM}(i, k, l, m; t)$$

where

$$h_{IK,IK} = h_{IK},$$

so that h=0 in very dilute systems, i.e. in the Boltzmann case.  $k_{f,2}^{(E)}$  then contains the remaining terms and it is easily seen that  $k_{f,2}^{(E)}$  is proportional to the 'reactive' correlation function  $h_{AB,CD}$ . We do not think it necessary to give the explicit expression for  $k_{f,2}^{(E)}$  since its structure is easily ascertained from the above formulae, and, as argued below, the most important contribution is contained in  $k_{f,1}^{(E)}$ .

Analogously we obtain

$$k_{b} = k_{b}^{(\mathrm{B})} + k_{b}^{(\mathrm{E})} = k_{b}^{(\mathrm{B})} + k_{b,1}^{(\mathrm{E})} + k_{b,2}^{(\mathrm{E})},$$
(33)

 $k_b^{(B)}$  being given by equation (I 48), and

$$k_{b,1}^{(E)} = \frac{2}{\hbar V} \operatorname{Im} \sum_{a, b, c, d, c', d'} \langle Aa, Bb | T_{A,B}^{+}(-\epsilon) | Cc, Dd \rangle f_{C}(c, t) f_{D}(d, t) \\ \times h_{CD}(c, d, c', d'; t) \frac{1}{E_{A,B} - E_{C,D} - i\epsilon} \langle Cc', Dd' | T_{A,B}(-\epsilon) | Aa, Bb \rangle, \quad (34)$$

and in the same way as above we find that  $k_{b,2}^{(E)}$  is again proportional to  $h_{AB,CD}$ .

#### 4. The pair distribution function

Because of the choice of the ensemble  $\sigma(t)$  in equation (2), the two-particle distribution functions  $F_2(t)$  depend implicitly on the concentrations of all species in the system. To get an idea of this concentration dependence we assume for the time being that the number of elastic collisions is much greater than the number of reactive collisions, which is the case in dense systems; we can then neglect the reactive collisions in the perturbation expansions of  $h_{IK}$ . For simplicity, we also neglect quantum corrections to the momentum distributions [11] and to  $h_{IK}$ .

We express the matrix elements in terms of Wigner functions, as in [12]. Using the fact that in the classical limit the momentum dependence can be factorized, we can express equation (29) as

$$\lim_{\hbar \to 0} \langle \mathbf{p}_I + \mathbf{k}, \, \mathbf{p}_K - \mathbf{k} | F_2(t) | \mathbf{p}_I - \mathbf{k}, \, \mathbf{p}_K + \mathbf{k} \rangle = n_I(\mathbf{p}_I, \, t) n_K(\mathbf{p}_K, \, t) \\ \times g_{IK}(\mathbf{k}, \, -\mathbf{k}, \, -\mathbf{k}, \, \mathbf{k} \, ; \, t), \quad (35)$$

or

$$\lim_{\hbar\to 0} \langle \mathbf{p}_I + \mathbf{k}, \, \mathbf{p}_K + \mathbf{k} \big| F_2(t) \big| \mathbf{p}_I - \mathbf{k}, \, \mathbf{p}_K - \mathbf{k} \rangle = n_I(\mathbf{p}_I, \, t) n_K(\mathbf{p}_K, \, t) g_{IK}(\mathbf{k}, \, t),$$

where

$$g_{IK}(\mathbf{k}, t) = \int \exp{(i\mathbf{k} \cdot \mathbf{q})} g_{IK}(|\mathbf{q}|, t) d\mathbf{q}, \qquad (36)$$

 $g_{IK}(|\mathbf{q}|, t)$  being the usual radial pair distribution function. After introducing the fugacities  $z_{X}(t)$  and the thermal de Broglie wavelength

$$\Lambda_X(t) = \frac{\sqrt{(2\pi)\hbar}}{\sqrt{(m_X k T(t))}},\tag{37}$$

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equation (35) becomes

$$z_{I}(t)z_{K}(t)\Lambda_{I}^{3}(t)\Lambda_{K}^{3}(t)\exp(-\beta(t)[p_{I}^{2}/2m_{I}+p_{K}^{2}/2m_{K}])g_{IK}(\mathbf{k},t)$$

The fugacities are normalized as

$$\lim_{c_X \to 0} \frac{z_X}{c_X} = 1. \tag{38}$$

Since a generalized grand canonical ensemble is used in the averaging procedure in equation (1),  $h_{IK}(|\mathbf{q}|, t) = g_{IK}(|\mathbf{q}|, t) - 1$  can be represented in the classical limit for short-ranged interactions in known manner in an expansion in powers of the fugacities [13] if we extend the results of Smith [14] to the case of many-component systems :

$$h_{IK}(|\mathbf{q}_{I} - \mathbf{q}_{K}|) = \exp(-\beta W_{IK}) \times \{1 + \sum_{X=A, B, C, D} z_{X} \int d\mathbf{q}_{X}[\exp(-\beta (W_{IX} + W_{XK})) - 1] + O(z^{2})\} - 1, \quad (39)$$

where  $W_{IK}$  is the elastic part of the interaction in equation (I 2). A typical diagram from figure 3 that contributes, in the classical limit, a term of the order  $z_I z_K z_X$ , is



Using the known relation between the concentrations and fugacities

$$c_{I} = \sum_{n \ge 1} n_{I} b_{n} \mathbf{z}^{n}$$
  
=  $z_{I} + 2b_{II} z_{I}^{2} + \sum_{I \ne K} b_{IK} z_{I} z_{K} + 3b_{III} z_{I}^{3} + \sum_{I \ne K} 2b_{IIK} z_{I}^{2} z_{K}$   
+  $\sum_{\substack{K \ge L \\ K \ne I}} \sum_{L \ne I} b_{IKL} z_{I} z_{K} z_{L} + \dots,$  (40)

where  $b_n$  are the reducible cluster integrals [13, 15, 16, 17], we obtain the expansion of z in powers of c, and for  $h_{IK}$  (see for example [17]),

$$z_{I}z_{K}h_{IK}(|\mathbf{q}_{1}-\mathbf{q}_{K}|) = c_{I}c_{K}\{\exp(-\beta W_{IK})[1 + \sum_{X=A, B, C, D} c_{X}\int d\mathbf{q}_{X} \\ \times (\exp(-\beta W_{IX}) - 1)(\exp(-\beta W_{XK}) - 1) + O(c^{2})]^{-1}\} \\ = c_{I}c_{K}\tilde{h}_{IK}(|\mathbf{q}_{I}-\mathbf{q}_{K}|).$$
(41)

Therefore, we finally obtain explicit concentration-dependent expressions for  $k_f^{(E)}$  and  $k_b^{(E)}$  in the rate equation

$$\dot{c}_{A}(t) = -k_{f}^{(B)}(T)c_{A}(t)c_{B}(t) - k_{f}^{(E)}(c, T)c_{A}(t)c_{B}(t) + k_{b}^{(B)}(T)c_{C}(t)c_{D}(t) + k_{b}^{(E)}(c, T)c_{C}(t)c_{D}(t), \quad (42)$$
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where  $k_t^{(E)}$  is given, under the above assumptions, by

$$k_{f}^{(\mathrm{E})} = \frac{2}{\hbar} \frac{1}{(2\pi\hbar)^{15}} \operatorname{Im} \left\{ \int d\mathbf{p}_{A} d\mathbf{p}_{B} d\mathbf{p}_{C} d\mathbf{p}_{D} d\bar{\mathbf{p}}_{A} d\bar{\mathbf{p}}_{B} \langle \mathbf{p}_{A}, \mathbf{p}_{B} | T_{A,B} | \mathbf{p}_{C}, \mathbf{p}_{D} \rangle \right.$$

$$\times \frac{1}{E_{A,B} - E_{C,D} + i\epsilon} \left\langle \mathbf{p}_{C}, \mathbf{p}_{D} | T^{+} | \bar{\mathbf{p}}_{A}, \bar{\mathbf{p}}_{B} \rangle \delta(\mathbf{p}_{A} + \mathbf{p}_{B} - \bar{\mathbf{p}}_{A} - \bar{\mathbf{p}}_{B}) \right.$$

$$\times \Lambda_{A}^{3}(t) \Lambda_{B}^{3}(t) \exp\left(-\beta(t)[\bar{\mathscr{E}}_{A} + \bar{\mathscr{E}}_{B}]\right) \check{h}(\bar{\mathbf{p}}_{A}, \bar{\mathbf{p}}_{B}; t), \quad (43)$$

 $\tilde{h}(\mathbf{p}_I, \mathbf{p}_K; t)$  being the Fourier transform of  $\tilde{h}(\mathbf{q}_I, \mathbf{q}_K; t)$ . There exists an analogous expression for  $k_b^{(E)}(c, T)$ .

# 5. DISCUSSION

The corrective terms  $k_f^{(E)}$  and  $k_b^{(E)}$  derived in § 3 are the main result of the present paper. These terms are derived from our model hamiltonian, equation (I 2), but they no longer contain the model interaction W. Instead, they are formulated entirely in terms of *T*-matrix elements and pair distribution functions. This is a desirable feature, since a serious disadvantage of our hamiltonian consists in the fact that the connection of the phenomenological interaction W with the realistic intermolecular forces (or the quantum chemical potential surfaces) is not known. At the present level of approximation this drawback is easily overcome by assuming that W is chosen such that the *T*matrix elements defined above are just the realistic *T*-matrix elements which, in principle, can be either measured by two-particle scattering experiments in free space, or calculated by the usual theory of molecular scattering which starts from the quantum chemical potential surfaces.

Similar considerations apply to the pair distribution functions introduced in From equations (29) and (1) it is easily seen that the definition equation (29). of  $g_{IK,LM}$  is independent of any particular choice of the representation of the hamiltonian. Thus we may use in equation (1) the realistic hamiltonian which is formulated in terms of atoms; the g functions are then the realistic ones. From these considerations we conclude that by means of this reinterpretation we obtain a theory which is valid in rather dense systems, although our hamiltonian is valid only for dilute systems. Of course, this approach has to be verified in a more fundamental theory which starts from the realistic hamiltonian formulated in terms of atoms rather than molecules. After suitable partial summations, and on a certain level of approximation, such a theory would again be formulated in terms of just the T-matrix elements and pair distribution functions introduced above. From the reinterpretation scheme it seems at least highly probable that expressions obtained for the rate constants in the more fundamental theory should coincide with those derived in the present paper.

The physical interpretation of these expressions for the rate constants is different for the different parts  $k_{f,1}^{(E)}$  and  $k_{b,1}^{(E)}$ , and  $k_{f,2}^{(E)}$  and  $k_{b,2}^{(E)}$ . The former terms contain the pair distribution functions  $g_{AB}$  or  $g_{CD}$  which describe the static correlations between molecules A and B, or C and D respectively. As with the corresponding Boltzmann terms equations (I 48) and (31), the expressions contain the reactive T-matrix elements only. Thus, one might say that the terms considered take into account that in a dense system the frequency of the collisions which lead to reactive transitions is no longer given—as in the Boltzmann case—by the velocity distribution functions  $f_X(x)$  alone, but instead depends sensitively on the structure of the fluid which is expressed by the pair distribution functions  $g_{AB}$  and  $g_{CD}$ . From this point of view, it is not at all surprising that the *T*-matrix elements occurring in the above expressions are in general off the energy shell. In the Boltzmann case, the appearance of the energy-conserving  $\delta$  function may be attributed to the fact that the time of free flight between collisions is large compared with the duration of a collision. Thus, only the asymptotic behaviour of the molecule–molecule collisions, i.e. the cross-sections, enter into the theory. In dense systems, the duration of the collision is of the same order of magnitude as the inverse of the collision frequency, so that effects due to the finite duration of the collisions are important. Therefore, with respect to the two-body dynamics, and after a suitable expansion, the corrective terms  $k_{f,1}^{(E)}$  and  $k_{b,1}^{(E)}$  could be expressed in terms of the crosssection in first order, the lifetime matrix [18] in second order, and so on.

The interpretation of the terms  $k_{f,2}^{(E)}$  and  $k_{b,2}^{(E)}$  is more difficult. These terms contain both elastic and reactive *T*-matrix elements, together with the 'reactive' pair distribution function  $g_{AB,CD}$ . This pair distribution function represents some kinds of chemical correlations in the system which are absent in non-reactive systems.

From these facts it follows that the corrective terms  $k_{f,2}^{(E)}$  and  $k_{b,2}^{(E)}$  can by no means be expressed in terms of physical quantities such as cross-sections, the lifetime matrix or collision frequencies. The appearance of the 'reactive' pair distribution function seems to take account of the fact that, in dense systems, there is always a macroscopic number of molecules which are just undergoing a reactive collision so that the different species are not identifiable. These molecules do not therefore fit into the above scheme, which involves the collision frequency, but instead they should make a more complicated contribution to the chemical change, this contribution being given by  $k_{f,2}^{(E)}$  and  $k_{b,2}^{(E)}$ . If the system is not too dense, and if the number of elastic collisions is much greater than the number of reactive collisions, these terms should be small. Of course, this conclusion and the above tentative interpretation need numerical verification, but this is outside the scope of the present paper.

Let us now return to the off-shell contribution of the *T*-matrix. From the point of view of scattering theory, the appearance of these contributions complicates the evaluation of the rate constants for realistic potentials. With our present knowledge of molecular scattering theory, even the calculation of the quantum cross-section is possible only for very simple molecules. The offshell matrix elements, however, contain much more information concerning the details of the scattering process and the potential surface, and are thus more difficult to calculate. Nevertheless, for the physical reasons given above, this difficulty can never be circumvented if denser systems are to be considered. Thus, the treatment of such systems poses a serious challenge to reactive molecular scattering theory.

On the other hand, the fact that  $k_j^{(E)}$  and  $k_b^{(E)}$  are much more sensitive than  $k_j^{(B)}$  and  $k_b^{(B)}$  to the details of the potential surface could be used as a more detailed check of the calculated potential surfaces. In the same sense, a comparison of the calculated values of  $k_j^{(E)}$  and  $k_b^{(E)}$  with the experimental ones would lead to more detailed conclusions about the progress of the molecule-molecule scattering process, provided that the pair distribution function is known.

The calculation of the pair distribution function is a problem of equilibrium statistical mechanics, and many methods are available for deriving approximate expressions for g. A diagram method has been described in [2].

Some approximate expressions were obtained in § 4. There, we displayed the explicit concentration dependence of g, and thus of the rate constants. This concentration dependence has important consequences for chemical kinetics. While the reaction (I 1) considered in this paper is a reaction of second order [19] in the gas phase, in denser systems there occur higher powers of the concentrations of the different species. Therefore it is not possible to determine the reaction order in an unambiguous way. The importance of the concentration dependence of the rate constants has already been emphasized [20].

At present we cannot give a reliable assessment of the validity of the present theory. However, we know that the usual Enskog dense-gas theory for nonreactive fluids [5, 6] is a good approximation for dense gases, and even for simple liquids. The deviation of the Enskog theory from the Boltzmann results may amount to an order of magnitude. From the great physical similarity of the present theory to the usual Enskog dense-gas theory, it is to be expected that similar conclusions also hold for chemically reacting systems.

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