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Quantum statistical theory of chemical reactions

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Quantum statistical theory of chemical reactions
I. General formulation and lowest-order results

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Exact rate equations for chemical reactions taking place in a closed homogeneous system arbitrarily far from equilibrium are derived by use of a recently developed method. The possibly different kinetic temperatures of the species are taken into account. The diagram expansion of the integral kernels of the rate equations is given and the renormalization of the interaction carried out. In lowest order non-linear non-markovian equations are obtained which reduce after suitable approximations to the usual collision theory results.

1. INTRODUCTION

The microscopic derivation of rate equations for chemically reacting systems usually starts either from the appropriate Boltzmann equation [1–6] or from the linear response theory [7–9]. The theory of real-time Green functions has been used, too [10, 11]. In chemically reacting systems of practical interest the chemical degrees of freedom are often very far away from their equilibrium values. Although the Boltzmann equation is able to tackle such situations, its region of validity is restricted to the dilute gas, and the applicability of the linear response theory as well as of the Green function method is restricted to the vicinity of the equilibrium. Thus, in more dense gases or in liquids a great number of phenomena, like the dependence of the rate constants on the concentrations of the different species, cannot be treated by either of these methods.

In a recent paper [12] there was derived a set of macroscopic equations of motion describing the time evolution of the system which may be arbitrarily far from equilibrium. To evaluate the integral kernels appearing in these equations a diagram expansion method was developed by using field-theoretical methods. In this first paper of an intended series we want to apply this method to derive rate equations for chemically reacting systems.

In § 2 we specify the general equations of motion for the treatment of bimolecular chemical reactions in a closed homogeneous system without external forces.

For the sake of generality we include systems with different kinetic temperatures of the species, too. To make contact with the usual linear theory [7–9], we

rewrite these equations in terms of non-equilibrium correlation functions and consider then the near-equilibrium limit.

In § 3 the rate equations corresponding to the diagram of lowest order are written down both in the limit of weak coupling and in the renormalized form for the case of strong interactions.

2. THE EQUATIONS OF MOTION

Let us consider a gas consisting of molecules A, B, C, D without internal degrees of freedom in which a bimolecular chemical reaction of the type

$$A + B \rightleftarrows C + D \tag{1}$$

takes place.

The hamiltonian is given in the Schrödinger representation by

$$
\begin{aligned}
H = &\sum_{X=A,B,C,D} H_{0X} + W \\
= &\sum_{\substack{i \\ X=A,B,C,D}} \mathscr{E}_X(i) a_{X,i}{}^+ a_{X,i} + \tfrac{1}{2} \sum_{\substack{i,k,l,m \\ I,K,L,M=A,B,C,D}} (1 - \tfrac{1}{2}\delta_{I,K}) \\
&\times \langle Ii, Kk | W | Ll, Mm \rangle a_{I,i}{}^+ a_{K,k}{}^+ a_{M,m} a_{L,l},
\end{aligned} \tag{2}
$$

where $a_{J,j}{}^+(a_{J,j})$ creates (annihilates) a particle of species J with momentum $p_j = m_J d\mathbf{q}_J/dt$, and

$$\mathscr{E}_X(i) = \frac{p_i{}^2}{2m_X} + \mathscr{E}_X{}', \tag{3}$$

$\mathscr{E}_x{}'$ being the internal energy of the ground state of the molecule X. The matrix elements of the interaction part of the hamiltonian are given by

$$
\begin{aligned}
\langle Ii, Kk | W | Ll, Mm \rangle = &\int \phi_{I,i}{}^*(\mathbf{q}_I) \phi_{K,k}{}^*(\mathbf{q}_K') W(\mathbf{q}_I, \mathbf{q}_K', \bar{\mathbf{q}}_L, \bar{\mathbf{q}}_M') \\
&\times [\phi_{L,l}(\bar{\mathbf{q}}_L)\phi_{M,m}(\bar{\mathbf{q}}_M') + \kappa \delta_{L,M}\delta_{I,K}\phi_{L,l}(\bar{\mathbf{q}}_M')\phi_{M,m}(\bar{\mathbf{q}}_L)] \\
&\times d\mathbf{q}_I d\mathbf{q}_K' d\bar{\mathbf{q}}_L d\bar{\mathbf{q}}_M',
\end{aligned} \tag{4}
$$

with $\phi_{J,j}(\mathbf{q}_J) = \langle \mathbf{q}_J | a_{J,j}{}^+ | 0 \rangle$.

In (4) the function W is chosen such that the matrix elements in (2) are proportional to the delta function $\delta(\mathbf{p}_i + \mathbf{p}_k - \mathbf{p}_l - \mathbf{p}_m)$ which expresses the conservation of total momentum. $\delta_{R,S}$ is a Kronecker delta, being equal to 1 if R, S denote the same species and $\kappa = +1(-1)$ if L, M are bosons (fermions). Thus, for the case of elastic scattering of identical particles exchange is taken into account explicitly. Note, that the hamiltonian (2) includes only elastic scattering and reactive scattering according to (1), so that quite a number of matrix elements of (4) are equal to zero.

The hamiltonian (2) has to be considered as a model hamiltonian, since the connection with the quantum-mechanical potential surface is not immediately obvious. This connection would have to be established in a more fundamental theory which starts from the atoms as 'elementary particles' if the Born–Oppenheimer approximation is valid. Into this theory the molecules enter as bound states of the atoms and as usual [13, 14] these are considered as new elementary particles. The operator W in (2) describes the interaction between

just these new elementary particles and is thus valid as long as the macroscopic behaviour of the system is determined by binary collisions only.

2.1. *Derivation of the equations of motion*

To apply the method of [12, 15], as a first step we have to choose the relevant set F of observables of the system. As discussed in more detail in [16], for the short-memory approximation to be strictly valid we have to include into F all operators, the expectation values of which are slowly varying with time. In the present case these are the number operators N_X of the different species and the hamiltonian H. As shown in [17–19], under certain conditions the different species X in a chemically reacting system might have different kinetic temperatures T_X which relax slowly to the mean value of the temperature. For this reason we shall include into F the operators of the kinetic energy H_{0X} of the species X.

From these considerations we obtain the following form of the representative ensemble $\sigma(t)$ introduced in [12, 15]:

$$\sigma(t) = \exp\left\{-\lambda_0(t) - \beta(t)[H - \sum_X \mu_X(t)N_X] - \sum_X \Delta\beta_X(t)H_{0X}\right\}, \qquad (5)$$

where

$$N_X = \sum_i N_{X,i} = \sum_i a_{X,i}^{+} a_{X,i}. \qquad (6)$$

The lagrangian parameters $\lambda_0(t)$, $\beta(t)$, $\mu_X(t)$, $\Delta\beta_X(t)$ are determined from

$$\left.\begin{array}{l} \langle N_X \rangle_t \equiv \bar{N}_X(t) = \text{Tr}\,[N_X\sigma(t)], \\[2mm] \langle H \rangle_t \equiv \bar{H}(t) = \text{Tr}\,[H\sigma(t)] = \text{const.}, \\[2mm] \langle H_{0X} \rangle_t \equiv \bar{H}_{0X}(t) = \text{Tr}\,[H_{0X}\sigma(t)], \\[2mm] \text{Tr}\,\sigma(t) = 1, \end{array}\right\} \qquad (7)$$

where $\bar{O}(t) = \text{Tr}\,[O\rho(t)]$, and $\rho(t)$ is the solution of the Liouville equation.

As usual, we choose the initial condition

$$\sigma(0) = \rho(0). \qquad (8)$$

The condition (8) implies that at $t = 0$ the system is in a state of restricted equilibrium, $\beta(0)$ being the reciprocal temperature of the system and $\mu_X(0)$ the chemical potential of species X. In the limit of vanishing interaction, $\Delta\beta_X$ is the deviation of the reciprocal kinetic temperature from β.

The exact closed integro-differential equations governing the time evolution of the $\bar{N}_X(t)$ and $\bar{H}_{0X}(t)$ are written here as

$$\dot{\bar{O}}_n(t) = \frac{d}{dt}\,\bar{O}_n(t) = \langle \dot{O}_n(0) \rangle_t + \int_0^t dt' \left[\langle \dot{O}_n(t-t') \rangle_{t'} \right.$$
$$\left. - \sum_m \dot{\bar{O}}_m(t') \frac{\partial}{\partial\bar{O}_m(t')} \langle \dot{O}_n(t-t') \rangle_{t'} \right], \qquad (9)$$

where $\langle \ldots \rangle_t = \text{Tr}\,[\ldots\sigma(t)]$.

$\{O_n(t)\}$ is the set of the operators $N_A(t), \ldots, N_D(t)$; $H_{OA}(t), \ldots, H_{OD}(t)$ in the Heisenberg representation, and

$$\dot{O}(t) = \frac{i}{\hbar} [H, O(t)] = iLO(t). \tag{10}$$

It can easily be shown that the first term on the right-hand side of (9) vanishes for a homogeneous system. To compare with expressions in the literature obtained for the vicinity of the equilibrium [7, 9], we rewrite (9) in terms of non-equilibrium correlation functions.

Using the relation [15]

$$L\sigma(t) = \sum_n \int_0^1 dz \, \sigma^z [LO_n] \sigma^{1-z} \, \alpha_n(t), \tag{11}$$

we obtain

$$L\sigma(t) = -i \sum_n \alpha_n(t) \tilde{O}_{n, t} \sigma(t), \tag{12}$$

where

$$\tilde{O}_t = \int_0^1 dz \, \sigma(t)^z \, O\sigma(t)^{-z}, \tag{13}$$

and $\dot{O} = iLO$.

$\{\alpha_n(t)\}$ is the set of lagrangian parameters $\beta(t)\mu_A(t), \ldots, \beta(t)\mu_D(t)$; $-\Delta\beta_A(t)$, $\ldots, -\Delta\beta_D(t)$.

From this and $\dot{\sigma}(t) = \sum_n \dot{\alpha}_n(t) \tilde{O}_{n, t} \sigma(t)$ we obtain the equations of motion

$$\dot{\tilde{O}}_n(t) = - \sum_m \int_0^t dt' [\langle \dot{O}_n(t-t') \tilde{O}_{m, t'} \rangle_{t'} \alpha_m(t')$$

$$+ \langle \dot{O}_n(t-t') \tilde{O}_{m, t'} \rangle_{t'} \dot{\alpha}_m(t')] + \int_0^t dt' \langle \dot{O}_n(t-t') \tilde{H}_{t'} \rangle_{t'} \dot{\beta}(t'). \tag{14}$$

As discussed in more detail in [12] the equations of motion (9) and (14) simplify considerably if the short-memory approximation is valid. Similarly as in [16] this approximation is formulated as

$$\dot{\tilde{O}}_n(t) = - \int_0^t dt' \langle O_n L_1 \exp[-iL(t-t')] L_1 \rangle_{t'}^{\text{RD}}, \tag{15}$$

where

$$L_1 \ldots = \frac{1}{\hbar} [W, \ldots]. \tag{16}$$

RD means that in the trace that part is retained that is rapidly decaying with time. In the following we shall assume the validity of the short-memory approximation. Therefore equation (15) forms the starting-point for the diagram expansion given below. Our diagram expansion is however not restricted to the simplified equation (15) only, but could instead also be used for the treatment of the general equation (9).

The rules for constructing and using the diagrams are given in the Appendix. It proves useful to sum in all of the diagrams the wavy-line self-energy insertions, this leading to the introduction of heavy lines which correspond to exact Green

functions. For the lines connecting dashed interaction lines this means

$$= - \mathrm{Tr}\, [a_{\mathbf{p},X} a_{\mathbf{p},X}^{+} \, \sigma(t)] = G_t^{>}(\mathbf{p}, X). \tag{17}$$

Analogously we have

$$= - \kappa \, \mathrm{Tr}\, [a_{\mathbf{p},X}^{+} a_{\mathbf{p},X} \sigma(t)] = G_t^{<}(\mathbf{p}, X). \tag{18}$$

Note, that the expansion (18) together with (2) and (6) allows the calculation of the traces (7) and thus establishes the connection between the $\{\alpha_n(t)\}$ and the expectation values $\{\bar{O}_n(t)\}$. To calculate $\beta(t)$ we must take into account the two-particle Green function which is given by the corresponding diagram expansion [20].

In the following we shall always assume that the above summation has been carried out, so that all propagator lines connecting two dashed lines correspond to exact Green functions.

2.2. *Linear theory*

To get the expressions of the linear theory we introduce the chemical affinity [21]

$$A(t) = \sum_X \nu_X \mu_X(t), \tag{19}$$

where ν_X is the stoichiometric coefficient of species X. In our case we have

$$- \nu_A = - \nu_B = \nu_C = \nu_D = 1. \tag{20}$$

Introducing the formal operator ΔN,

$$\Delta N = \frac{N_X - \langle N_X \rangle_0 I}{\nu_X}, \tag{21}$$

the expectation value of which is the progress variable $\xi(t)$ [21], the ensemble $\sigma(t)$ is written as

$$\sigma(t) = \exp \left\{ - \lambda_0(t) - \beta(t)[H - A(t)\Delta N - \sum_X \mu_X N_X] - \sum_X \Delta\beta_X(t) H_{0X} \right\}. \tag{22}$$

In (21) $\langle \dots \rangle_0$ means $\mathrm{Tr}\, [\dots \sigma_0]$, where

$$\sigma_0 = \frac{\exp \beta(\sum_X \mu_X N_X - H)}{\mathrm{Tr} \exp \beta(\sum_X \mu_X N_X - H)} \tag{23}$$

is the well-known grand canonical density operator. Here, β is the reciprocal temperature of the system and μ_X the chemical potential of the species X in equilibrium.

Now we introduce the new set of operators

$$\{R_n\} = \{\Delta N, H_{O\!A}, ..., H_{OD}\}$$

and the corresponding lagrangian parameters

$$\{\zeta_n(t)\} = \{\beta(t)A(t), -\Delta\beta_A(t), ..., -\Delta\beta_D(t)\}.$$

Using the linearized form of σ [15] we obtain the linearized version of (14) :

$$\dot{\bar{R}}_n(t) = -\sum_m \int_0^t dt' \{K_{nm}(t-t')\zeta_m(t') + K_{nm}{'}(t-t')\dot{\zeta}_m(t')\}, \qquad (24)$$

with

$$K_{nm}(t-t') = \langle \dot{R}_n \exp[-iL(t-t')]\tilde{R}_m\rangle_0 \qquad (25)$$

and

$$K_{nm}{'}(t-t') = \langle \dot{R}_n \exp[-iL(t-t')]\tilde{R}_m\rangle_0, \qquad (26)$$

where the Kubo transform $\tilde{R}$ is now defined with respect to σ_0.

Except for the term involving K' the equations of motion (24) are exactly the expressions one would obtain from the linear response theory. Putting $\Delta\beta_X = 0$ in (24) the linear rate equation of Yamamoto [7] results. In the Kubo theory the non-mechanical perturbation is considered as a fictive external force which acts independently of the response of the system. In (24) or in (14) this response is taken into account by the second term in (24), which depends on the rate of change of the relaxation and thus represents a kind of feedback effect.

It is instructive to rewrite equation (24) in terms of the memory function. For this, the relation between the $\{\bar{R}_n(t)\}$ and the $\{\zeta_n(t)\}$ is needed. Using the matrix notation of Robertson [15] we can write the linear approximation as

$$\Delta\bar{R}(t) = \bar{R} - \langle R\rangle_0 = \langle R\tilde{R}\rangle_0\zeta(t). \qquad (27)$$

By Laplace transforming (24) and using the convolution theorem and the relation (27) we can solve (24) for $\Delta\dot{\bar{R}}$ and obtain after retransformation

$$\Delta\dot{\bar{R}}(t) = \int_0^t dt' \, M(t-t')\Delta\bar{R}(t'), \qquad (28)$$

where $M(t-t')$ is given by its Laplace transform :

$$\hat{M}(z) = -[1 + \hat{K}'(z)\langle R\tilde{R}\rangle_0^{-1}]^{-1} \hat{K}(z)\langle R\tilde{R}\rangle_0^{-1}. \qquad (29)$$

By means of the projection operator P

$$PB = \tilde{R}\sigma_0\langle R\tilde{R}\rangle_0^{-1} \mathrm{Tr}\{RB\}, \qquad (30)$$

the memory function can also be written as

$$M(t-t') = \langle \dot{R} \exp[-i(t-t')(1-P)L]\tilde{\dot{R}}\rangle_0\langle R\tilde{R}\rangle_0^{-1}. \qquad (31)$$

This is the well-known expression for the memory function [22], and as a result we find that in the vicinity of the equilibrium the relaxation of the system is governed by the memory function and not by the correlation function, as is implied by the Kubo theory.

3. Diagrams of lowest order

3.1. *Weak-coupling approximation*

Let us now study the diagrams of lowest order contributing to (15). For the sake of simplicity we begin with the case of weak interaction and later on re-normalize the interaction.

Figure 1. The diagram of lowest order leading to the expressions (32) and (33). Note that we always draw just a single diagram from each exchange group. A second diagram is obtained by reversing the direction of all of the arrows.

The most simple diagram contributing to (14) is given in figure 1, since the corresponding Hartree–Fock terms are secular divergent and thus cancel with certain expressions in the third term of the right-hand side of (9) [16]. Taking into account that only reactive collisions can contribute to $\dot{\bar{N}}_A$ we obtain the following equations of motion:

$$
\begin{aligned}
\dot{\bar{N}}_A(t) &= - \int_0^t dt' \sum_{a,\,b,\,c,\,d} \mathscr{F}_{Aa,Bb,Cc,Dd}(t,\,t') \\
&= -\frac{2}{\hbar^2} \int_0^t dt' \sum_{a,\,b,\,c,\,d} |\langle Aa,\,Bb|W|Cc,\,Dd\rangle|^2 \\
&\times \cos\{\hbar^{-1}[\mathscr{E}_A(a)+\mathscr{E}_B(b)-\mathscr{E}_C(c)-\mathscr{E}_D(d)](t-t')\}\{n_A(a,\,t')n_B(b,\,t') \\
&\times [1+\kappa(n_C(c,\,t')+n_D(d,\,t'))] - n_C(c,\,t')n_D(d,\,t') \\
&\times [1+\kappa(n_A(a,\,t')+n_B(b,\,t'))]\}, \\
&\times \dot{\bar{N}}_A(t) = \dot{\bar{N}}_B(t) = -\dot{\bar{N}}_C(t) = -\dot{\bar{N}}_D(t),
\end{aligned} \qquad (32)
$$

$$
\dot{\bar{H}}_{0I}(t) = - \int_0^t dt' \sum_{\substack{i,\,x,\,y,\,z \\ X,\,Y,\,Z}} \frac{p_{I,i}^2}{2m_I} \mathscr{F}_{Ii,Xx,Yy,Zz}(t,\,t') + \mathscr{E}_I' \dot{\bar{N}}_I(t). \qquad (33)
$$

The $n_X(X,\,t)$ are connected with the expectation values of $N_{X,i}$ via the relation

$$
n_X(i,\,t) = -\kappa G_i^<(\mathbf{p}_i,\,X). \qquad (34)
$$

The system of equations of motion for $\bar{N}_A(t),\,\ldots,\,\bar{N}_D(t)$; $\bar{H}_{0A}(t),\,\ldots,\,\bar{H}_{0D}(t)$ describes in a closed form the variation of the number densities by reactive scattering and implicitly the relaxation to the equilibrium temperature by elastic and reactive scattering between the particles. In the Boltzmann limit the terms containing κ in (32) and (33) have to be neglected. In this limit the momentum

distribution function is a generalized Maxwell–Boltzmann distribution function. Using (5) and (7) we find in the thermodynamic limit

$$n_X(i,\,t) = c_X(t)\lambda_X{}^3(t)\,\exp\{[-\beta(t)-\Delta\beta_X(t)]\mathscr{E}_X(i)\}, \qquad (35)$$

where $c_X(t)$ is the concentration of the species X and $\lambda_X(t)$ the 'thermal de Broglie wavelength':

$$\lambda_X(t) = \frac{h}{\sqrt{(2\pi m_X[\beta(t)+\Delta\beta_X(t)]^{-1})}}.$$

Using the ansatz for the matrix elements (4) given in [10], it is easy to show that the expression (32) is for the isothermal case and in Maxwell–Boltzmann limit identical to the corresponding expression derived in [10], if the backward reaction and the internal energy are dropped.

3.2. *Renormalization of the interaction*

To carry out the renormalization of the interaction in the above expressions we have to sum as usual the appropriate two-particle ladders. This is achieved automatically by using the diagram elements given in the Appendix. For the case of a monocomponent fluid the relevant expressions P, $F_2{}^{(0)}$, $\mathscr{U}$, $\mathscr{V}$, $\mathscr{A}$ have been given in [23]. These expressions are easily reformulated for the present case as follows. The time development operator in two-particle space $\mathscr{U}$ is obtained from

$$= \delta_{i\,i'}\,\delta_{k,k'} + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t<}^{t>} dt_1 \dots \int_{t<}^{t_{n-1}} dt_n$$

$$\times \langle Ii,\,Kk\,|\,\mathscr{W}(t_1)\dots\mathscr{W}(t_n)\,|\,Ii',\,Kk'\rangle$$

$$= \langle Ii,\,Kk\,|\,\mathscr{U}(t^>,\,t^<)\,|\,Ii',\,Kk'\rangle,$$

where $t^>(t^<)$ is the earlier (later) of the times of the vertices, the propagator lines running to the left (right) are connected with. The two-particle operator $\mathscr{W}(t_i)$ is given by

$$\mathscr{W}(t_i) = P(t')W(t_i) = P(t')\exp\left(\frac{i}{\hbar}H_0 t_i\right) W \exp\left(-\frac{i}{\hbar}H_0 t_i\right),$$

where $P(t')$ is defined by its matrix elements

$$\langle Ii,\ Kk|P(t')|Ll,\ Mm\rangle = \delta_{I,L}\delta_{i,l}\delta_{K,M}\delta_{k,m}[1 + \kappa(n_I(i,\ t') + n_K(k,\ t'))]. \quad (37)$$

In terms of these quantities the operators $\mathscr{V}$, $\mathscr{A}$ are in the same way as in [23] given by

$$\mathscr{V}(t_1,\ t_2) = W(t_1)\delta(t_1 - t_2) - \frac{i}{\hbar}\ W(t_1)\mathscr{U}(t_1,\ t_2)\mathscr{W}(t_2), \quad (38)$$

$$\mathscr{A}(t_1,\ t_2) = \mathscr{U}(t_1,\ t_2)F_2^{(0)}(t')W(t_2), \quad (39)$$

where

$$\langle Ii,\ Kk|F_2^{(0)}(t')|Ll,\ Mm\rangle = \delta_{I,L}\delta_{i,l}\delta_{K,M}\delta_{k,m}n_I(i,\ t')n_K(k,\ t'). \quad (40)$$
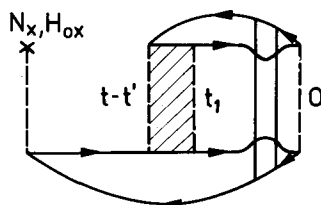
Figure 2. The renormalized diagram corresponding to the diagram in figure 1.

Observing rule (A 10) the renormalized diagram contributing in lowest order to (9), (15) is the one given in figure 2. The corresponding algebraic expression is easily obtained by use of the diagram rules given in the Appendix. Since in almost all chemical reactions the temperature is sufficiently high, so that the particles obey the Boltzmann statistics, we will restrict ourself to this case. Then, the rate equations read

$$\dot{N}_A(t) = -\frac{1}{\hbar^2}\int_0^t d\vartheta \sum_{a,\ b,\ c,\ d,\ a',\ b'} \langle Aa,\ Bb|W(\vartheta)\mathscr{U}(\vartheta,\ 0)|Cc,\ Dd\rangle$$

$$\times \langle Cc,\ Dd|W|Aa',\ Bb'\rangle\langle Aa',\ Bb'|\mathscr{U}(\vartheta,\ 0)^+|Aa,\ Bb\rangle$$

$$\times [n_A(a',\ t-\vartheta)n_B(b',\ t-\vartheta) - n_C(c,\ t-\vartheta)n_D(d,\ t-\vartheta)] + \text{c.c.} \quad (41)$$

where $\mathscr{U}^+$ is the hermitian conjugate of $\mathscr{U}$ and c.c. means the corresponding complex conjugate expression. To get (41) the relation

$$\int_0^\vartheta \mathscr{V}(\vartheta,\ t_1)\ dt_1 = W(\vartheta)\mathscr{U}(\vartheta,\ 0) \quad (42)$$

was used. Similarly we obtain

$$\dot{H}_{0I}(t) = -\int_0^t d\vartheta \sum_{\substack{i,\ x,\ y,\ z,\ i',\ x' \\ X,\ Y,\ Z}} \frac{p_{I,i}^2}{2m_I} \langle Ii,\ Xx|W(\vartheta)\mathscr{U}(\vartheta,\ 0)|Yy,\ Zz\rangle$$

$$\times \langle Yy,\ Zz|W|Ii',\ Xx'\rangle\langle Ii',\ Xx'|\mathscr{U}(\vartheta,\ 0)^+|Ii,\ Xx\rangle$$

$$\times [n_I(i',\ t-\vartheta)n_X(x',\ t-\vartheta) - n_Y(y,\ t-\vartheta)n_Z(z,\ t-\vartheta)]$$

$$+ \text{c.c.} + \mathscr{E}_I'\ \dot{N}_I(t). \quad (43)$$

As in the weak-coupling limit the above equations are non-markovian and thus contain the effects due to the finite duration of the collisions. Thus the rate constants are time dependent, i.e., the usual rate equations read now

$$\dot{c}_A(t) = - \int_0^t dt'[k_f(t, t')c_A(t')c_B(t') - k_b(t, t')c_C(t')c_D(t')], \qquad (44)$$

where because of (35) the k_f, k_b depend on t' and t. To get the usual collision theory expression for k_f, k_b we have to take the markovian limit of (44). This is justified if the variation of the $c_X(t)$ and $\bar{H}_{0I}(t)$ is slow as compared with the duration of a collision. Furthermore, we have to put $\Delta\beta(t) = 0$ in (35). Then,

$$n_X(i, t) = c_X(t) \left(\frac{h^2 \beta(t)}{2\pi m_X}\right)^{3/2} \exp[-\beta(t)\mathscr{E}_X(i)] = c_X(t)f_X(i, t). \qquad (45)$$

In this limit k_b is given as

$$k_b = \frac{1}{\hbar^2} \int_0^t d\vartheta \sum_{a, b, c, d} \langle Aa, Bb | W(\vartheta)\mathscr{U}(\vartheta, 0)|Cc, Dd\rangle$$

$$\times \langle Cc, Dd | W_r \mathscr{U}(\vartheta, 0)^+|Aa, Bb\rangle f_C(c, t)f_D(d, t) + \text{c.c.} \qquad (46)$$

W_r being the reactive part of W. Since [24]

$$\lim_{t\to\infty} W_r \mathscr{U}(t, 0)^+ = W_r \Omega^{(-)} = (W_r \Omega^{(+)})^* = T^*, \qquad (47)$$

where Ω is the Møller wave operator and T the usual T-matrix describing two-particle scattering, and since the limit (47) is reached after some average collision times, we may consider the corresponding matrix elements as constant factors in (46). After introducing the usual damping factor we may replace the upper limit of integration in (46) by ∞. Thus, we have to consider the expression

$$\int_0^\infty \exp(-\epsilon t)W(t)\mathscr{U}(t, 0) \, dt = -i + i\epsilon \int_0^\infty \exp(-\epsilon t]\mathscr{U}(t, 0) \, dt$$

$$= -i(1 - \Omega^{(-)+}).$$

Using

$$\Omega^{(-)}|E\rangle = (1 + G^{(-)}(E)T^*(E))|E\rangle,$$

where $|E\rangle$ is a free two-particle state and

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

we obtain

$$k_b = \frac{2\pi}{\hbar} \sum_{a, b, c, d} |\langle Aa, Bb | T_{AB,CD}|Cc, Dd\rangle|^2 f_C(c, t)f_D(d, t)$$

$$\times \delta[\mathscr{E}_A(a) + \mathscr{E}_B(b) - \mathscr{E}_C(C) - \mathscr{E}_D(d)]. \qquad (48)$$

The analogous expression for k_f is obtained by similar manipulations. Because of the time dependence of f_C, f_D, these expressions depend on time t. This is a consequence of the fact that we consider a closed system and that the ground-state energies of the different species are different. The usual collision theory expressions are obtained by replacing $\beta(t)$ in (45) with its equilibrium value β.

4. CONCLUDING REMARKS

The equations of motion (32), (33) and the renormalized versions (41) and (43) were obtained as lowest-order results of the general equation of motion (9), (15). None of the usual assumptions like molecular chaos, factorization of Green functions [10, 11], or synchronization [25] were necessary. Since the equations are non-markovian they contain the memory effects due to the finite duration of collisions. However, the equations are valid only in dilute systems.

To treat dense systems we must take into account diagrams of higher order. As in the case of general kinetic equations of one-component fluids [16] these diagrams contain two-body dynamics combined with the pair-correlation function. Thus, equations are obtained which are closely related to the Enskog dense gas theory [26]. This theory is well known to describe the behaviour of dense gases and approximately even of liquids [27]. In a following paper of the authors these ideas shall be applied to chemical reacting systems.

The authors are indebted to Dr. W. Stiller for helpful discussions.

APPENDIX

The Diagram Rules

For the case of general kinetic equations the diagram rules for two-particle interactions were given in [16] both in their original and in the renormalized form. The rules applicable to chemical reactions are obtained by some obvious modifications. Thus we formulate them without further proof below.

To get any diagram occurring in the expansion of $\Omega_n^{(1)}(t, t') = - \langle \ddot{O}_n(t - t') \rangle_{t'}$ draw at time $\vartheta = t - t'$ a vertex corresponding to N_X or H_0, an arbitrary number $n \geqslant 2$ of the basic diagram elements given below, and a number $m \geqslant 0$ of wavy lines corresponding to the interaction W and the corresponding propagator lines. Connect the long line ends with the short ones in an arbitrary manner, observing however the direction of the lines. Note that from each exchange group [16] just a single diagram has to be considered. Label the left-most dashed line with time ϑ, the right-most one with time zero, and all the other dashed lines with times ϑ_i. Label the wavy lines with imaginary times τ, and all propagator lines with momenta $\mathbf{p}_X$ and species X.

The algebraic expression associated with such a diagram is then obtained from the following rules :

(i) For each of the basic diagram elements occurring in the diagram include the corresponding factor given by the expression below.

(ii) With each wavy interaction line associate a factor according to

$$\text{(diagram)} \qquad = -\frac{i}{\hbar} \langle Ii, Kk | W | Ll, Mm \rangle,$$

the matrix element being given by (4).

(iii) With each propagator line which is connected with at least one wavy line associate a free Green function according to

$$\tau_i \xrightarrow{\;\;\mathbf{p},X\;\;} \tau_k \;\; = G(\mathbf{p}, X \;;\; \tau_i - \tau_k) = - \operatorname{Tr}\{T_\tau[a_{X,\,\mathbf{p}}(\tau_i)a_{X,\,\mathbf{p}}{}^+(\tau_K)]\sigma_0(t')\},$$

where $A(\tau) = \sigma_0(t')^{-\tau/\hbar\,\cdot\,\beta} A\sigma_0(t')^{\tau/\hbar\,\cdot\,\beta}$, and $\sigma_0(t')$ is obtained from $\sigma(t')$ by putting $W = 0$.
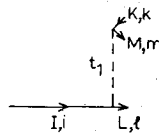
(iv) Include a factor of $\frac{1}{2}$ for each equivalent pair of lines, i.e. for each equally directed pair of two propagator lines of the same species which connect any two (dashed or wavy) interaction lines.

(v) Associate a stepfunction $\Theta(t_i - t_k)$ with each propagator line connecting two dashed lines i, k, i.e.

$$t_i \;\underline{}\; t_k \;\; = \Theta(t_i - t_k)$$
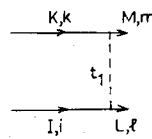
independently on the direction of the line.

(vi) Integrate all real times ϑ_i from 0 to $t - t'$, all imaginary times from 0 to $\beta(t')$ and sum over all momenta and all species labels. The resulting expression is multiplied by $(-1)^L$ where L is the number of closed fermion loops.
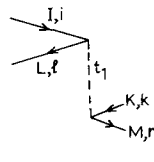
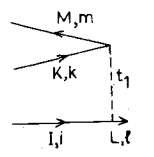The basic diagram elements for the unrenormalized diagrams and the corresponding analytic expressions are

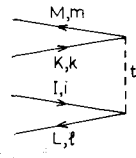$$=\frac{i}{\hbar}\,\langle Ii,\,Kk|W(t_1)|Ll,\,Mm\rangle, \tag{A 1}$$

$$=-\frac{i}{\hbar}\,\langle Ii,\,Kk|PW(t_1)|Ll,\,Mm\rangle, \tag{A 2}$$

$$=-\frac{i}{\hbar}\,\kappa[n_L(l,\,t') - n_I(i,\,t')]$$
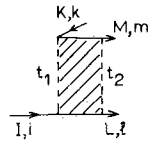$$\times \langle Ii,\,Kk|W(t_1)|Ll,\,Mm\rangle, \tag{A 3}$$

$$=\frac{i}{\hbar}\,\kappa[\langle Ii,\,Kk|PW(t_1)|Ll,\,Mm\rangle n_M(m,\,t')$$
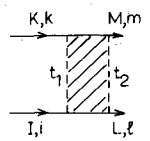$$-\kappa\langle Ii,\,Kk|F_2^{(0)}W(t_1)|Ll,\,Mm\rangle], \tag{A 4}$$

$$= -\frac{i}{\hbar} \langle Ii, \, Kk | (PW(t_1)F_2^{(0)} - F_2^{(0)}W(t_1)P) | Ll, \, Mm \rangle, \quad \text{(A 5)}$$

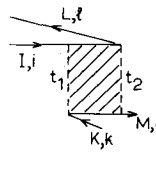where $P = P(t')$, $F_2^{(0)} = F_2^{(0)}(t')$.
The corresponding expressions for renormalized diagrams read

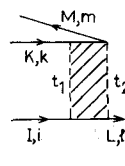$$= \frac{i}{\hbar} \langle Ii, \, Kk | \mathcal{V}(t_1, \, t_2) | Ll, \, Mm \rangle, \quad \text{(A 6)}$$

$$= -\frac{i}{\hbar} \langle Ii, \, Kk | P\mathcal{V}(t_1, \, t_2) | Ll, \, Mm \rangle, \quad \text{(A 7)}$$

$$= -\frac{i}{\hbar} \kappa \langle Ii, \, Kk | \mathcal{V}(t_1, \, t_2) | Ll, \, Mm \rangle n_L(l, \, t')$$

$$+ \frac{1}{\hbar^2} \langle Ii, \, Kk | \mathcal{A}(t_I, \, t_2) | Ll, \, Mm \rangle. \quad \text{(A 8)}$$
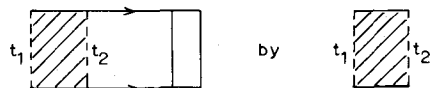
t_I being the time of the dashed line, the propagator line labelled I, i is connected with ;

$$= \frac{i}{\hbar} \kappa [\langle Ii, \, Kk | P\mathcal{V}(t_1, \, t_2) | Ll, \, Mm \rangle n_M(m, \, t')$$

$$- \kappa \langle Ii, \, Kk | \mathcal{A}(t_{I,K}^<, \, t_2) | Ll, \, Mm \rangle], \quad \text{(A 9)}$$
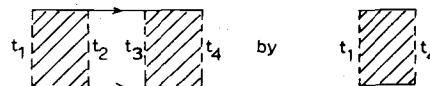
where $t_{I,K}^<$ is the earlier of the times of the vertices, the propagator lines I, K are connected with.

The interaction line (A 5) is renormalized by introducing the open box defined in (36). In working with these diagram elements one has to observe that one has always to replace

$$\text{by} \quad \quad \text{(A 10)}$$

and

$$\text{by} \quad \quad \text{(A 11)}$$

thus avoiding the problem of over-generation of diagrams. Note that reversing all of the line directions in a given diagram element is equivalent to taking the complex conjugate of the corresponding analytic expression. As discussed in more detail in [16, 23] the Maxwell–Boltzmann limit of the above expressions is obtained by putting $P = 1$, $\mathscr{A} = 0$ and neglecting the term containing $F_2^{(0)}$ in (A 4).

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