A quantum kinetic equation for nonideal gases in the three-particle collision approximation

A quantum kinetic equation for non-ideal gases in the three-particle collision approximation

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Abstract. A quantum mechanical version of a kinetic equation is derived which accounts for three-particle collisions. It is shown that the total energy is conserved in the binary collision approximation.

1. Introduction

The main problem of kinetic theory is the determination of the single-particle distribution function. With its help it is possible to calculate, e.g., the transport properties of a many-particle system.

The single-particle distribution function may be determined from the Boltzmann equation. The latter was formulated more than a hundred years ago. Since that time there have been many attempts to provide rigorous statistical foundations and generalisations of the Boltzmann equation.

The generalisations were developed in different directions. One direction was to include higher-order collisions in classical statistics in order to describe denser systems and to account for the formation of 'complexes' (Cohen 1968, Dorfman and Cohen 1972). Another direction was to formulate in a similar way a kinetic equation for quantum systems (Paltsev 1977). One of the most powerful directions seemed to be the attempt to formulate kinetic equations with the help of Green functions (Martin and Schwinger 1959, Keldysh 1964, Kadanoff and Baym 1962, Kremp *et al* 1985).

In this paper, we wish to discuss quantum statistical generalisations of kinetic equations of Cohen type and to consider the consequences.

The state of a quantum mechanical many-particle system is described by the density operator ρ_N, the normalisation of which is given by

$$\text{Tr } \rho_N = 1. \tag{1}$$

For practical applications it is sufficient to consider reduced density operators only, namely

$$F_s = \frac{1}{V^s} \underset{s+1\ldots N}{\text{Tr}} \rho_N \qquad \underset{1\ldots s}{\text{Tr}} F_s = V^s. \tag{2}$$

Moreover, it is necessary to use certain restrictions, e.g. in the homogeneous case the momentum representation for the single-particle density operator is

$$\langle p_1 | F_1 | p_1' \rangle = \delta(p_1 - p_1') F(p_1).$$ (3)

Here $F(p_1)$ is the (momentum) distribution function.

Mean values of additive and binary operators, respectively, are given by

$$\langle A_1 \rangle = n \operatorname*{Tr}_1 (A_1 F_1)$$ (4)

and

$$\langle A_{12} \rangle = \tfrac{1}{2} n^2 \operatorname*{Tr}_{12} (A_{12} F_{12}).$$

Here $n = N/V$ is the number density. The equation of motion for F_s follows from the von Neumann equation and reads

$$i\hbar \frac{\partial}{\partial t} F_s + [H_s, F_s] = n \operatorname*{Tr}_{s+1} \sum_{i=1}^{s} [V_{i,s+1}, F_{s+1}].$$ (5)

H_s is the Hamiltonian of the s-particle subsystem:

$$H_s = H_s^0 + \sum_{i<j}^{s} V_{ij}$$ (6)

with H_s^0 being the single-particle contribution of the s particles; in the ideal system without external forces we have $H_s^0 = \Sigma_{i=1}^{s} p_i^2 / 2 m_i$. V_{ij} is the two-particle interaction.

In the kinetic theory, the equation of motion for the single-particle density operator plays, of course, a special role. However, as usual, equation (5) has the shape of a hierarchy. In order to get a closed equation for the determination of F_1, i.e. a *kinetic equation*, we must apply certain approximations for F_{12} occurring in this equation. To this end we write the formal solution of equation (5):

$$F_s(t) = \exp[-iH_s(t-t_0)/\hbar] F_s(t_0) \exp[iH_s(t-t_0)/\hbar]$$

$$+ \frac{n}{i\hbar} \int_0^{t-t_0} dt' \exp(-iH_s t'/\hbar) \operatorname*{Tr}_{s+1} \sum_{i=1}^{s}$$

$$\times [V_{i,s+1}, F_{s+1}(t-t')] \exp(iH_s t'/\hbar).$$ (7)

$F_s(t_0)$ is the value of $F_s(t)$ at time t_0. So far, t_0 is an arbitrary time.

In order to specify (7), it is necessary to choose an initial condition in agreement with the physical situation. It is possible to get a closed kinetic equation if we apply the principle of the total weakening of the initial correlation. According to Bogolyubov (1946) we write in this case

$$\lim_{t_0 \to -\infty} F_s(t_0) = \lim_{t_0 \to -\infty} \prod_{i=1}^{s} F_i(t_0).$$ (8)

It is possible to write an equality of type (8) if we neglect the initial correlations, for which the correlation time τ_{corr} is much smaller than the relaxation time τ_{rel} of F_1. Thus we neglect the correlations for which

$$\tau_{\mathrm{corr}} \ll \tau_{\mathrm{rel}}.$$ (9)

Therefore the condition of the complete weakening of initial correlations corresponds to the assumption that long living correlations (with $\tau_{\mathrm{corr}} \gtrsim \tau_{\mathrm{rel}}$) do not play an essential role.

In other words, assumption (9) means that we exclude bound states and long living (large scale) fluctuations. If, however, the formation of bound states is possible, condition (8) must be replaced by another condition which accounts for the fact that bound states exist as asymptotic states (Schlanges 1985).

The usual Boltzmann equation may be derived in the frame of the binary collision approximation if the condition of the complete weakening of initial correlations is applied and if retardation effects are neglected. The properties of such an equation are, of course, well known, e.g. it conserves the kinetic energy (only). In this sense the Boltzmann equation is referred to as a kinetic equation for ideal gases.

The layout of this paper is as follows. After a brief derivation of the Boltzmann equation for ideal gases, the kinetic equation will be generalised to the case of three-particle collisions. In § 3 we will show that the kinetic equation derived represents a kinetic equation for non-ideal gases which conserves the total (kinetic and potential) energy in the binary collision approximation (approximation of the second virial coefficient). Thus a generalisation of the classical kinetic equation derived by Cohen will be given. Quantum mechanical kinetic equations of such a type were given first by Paltsev (1972), Klimontovich and Kremp (1981), McLennan (1982) and Lagan and McLennan (1984). In the later papers, especially, the aspect of bound states was mainly stressed, while we will focus our attention on the problem of non-ideality.

2. Kinetic equation for ideal gases: Boltzmann equation

We start from the equation for F_1:

$$i\hbar \frac{\partial F_1}{\partial t} + [H_1, F_1] = n \, \underset{2}{\mathrm{Tr}} \, [V_{12}, F_{12}]. \tag{10}$$

From equation (7) we obtain, in the binary collision approximation,

$$F_{12}(t) = \exp[-iH_{12}(t-t_0)/\hbar] F_{12}(t_0) \exp[iH_{12}(t-t_0)/\hbar]. \tag{11}$$

In such an approximation higher-order collisions (e.g. of three particles) are totally neglected. The Bogolyubov condition of the weakening of the initial correlation with (8) becomes

$$\lim_{t \to -\infty} \| \exp[-iH_{12}(t-t_0)/\hbar] F_{12}(t_0) \exp[iH_{12}(t-t_0)/\hbar]$$

$$- \exp[-iH_{12}^{(0)}(t-t_0)/\hbar] F_1(t_0) F_2(t_0) \exp[iH_{12}^{(0)}(t-t_0)/\hbar] \| = 0. \tag{12}$$

From (12) we get for any t_0

$$F_{12}(t_0) = \Omega_{12} F_1(t_0) F_2(t_0) \Omega_{12}^+. \tag{13}$$

Here we use Møller operators according to Taylor (1975):

$$\Omega_{12} = \lim_{t \to -\infty} \exp(-iH_{12}t/\hbar) \exp(iH_{12}^{(0)}t/\hbar). \tag{14}$$

The Møller operator has the property

$$\Omega_{12}^+ \Omega_{12} = 1 \tag{15}$$

and for potentials which do not support bound states we have

$$\Omega_{12} \Omega_{12}^+ = 1. \tag{16}$$

An essential property is the intertwining relation

$$\Omega_{12} H_{12}^{(0)} = H_{12} \Omega_{12}. \tag{17}$$

Now we eliminate the quantities $F_1(t_0)$. From (11) we get with (13)

$$F_{12}(t) = \exp[-iH_{12}(t-t_0)/\hbar]\Omega_{12} F_1(t_0) F_2(t_0)\Omega_{12}^{+} \exp[iH_{12}(t-t_0)/\hbar]. \tag{18}$$

The single-particle density operator obeys the equation

$$F_1(t) = \exp[-iH_1(t-t_0)/\hbar] F_1(t_0) \exp[iH_1(t-t_0)/\hbar] + O(n). \tag{19}$$

With (19) we get from (18) up to higher orders in the density:

$$F_{12}(t) = \Omega_{12} F_1(t) F_2(t)\Omega_{12}^{+} + O(n). \tag{20}$$

Thus we have shown that F_{12} may be represented (approximately) as a functional of the single-particle density operator:

$$F_{12}(t) = \mathscr{F}(F_1(t) F_2(t)) \tag{21}$$

and consequently we get a closed kinetic equation for the determination of $F_1(t)$. The 'operator version' of the Boltzmann equation is

$$i\hbar \frac{\partial}{\partial t} F_1 - [H_1, F_1] = n \, \underset{2}{\mathrm{Tr}} \, [V_{12}, \Omega_{12} F_1(t) F_2(t)\Omega_{12}^{+}]. \tag{22}$$

The usual shape of the Boltzmann equation may be achieved if we use scattering quantities and especially scattering cross sections.

According to Taylor (1975) we may introduce the scattering operator T (the matrix elements are the T matrix):

$$T_{12} = V_{12}\Omega_{12} \tag{23}$$

and with the propagator G^0 we write

$$\Omega_{12} = 1 + G_{12}^0 T_{12}. \tag{24}$$

Furthermore we have to apply the optical theorem which reads

$$T_{12} - T_{12}^{+} = -T_{12}(G_{12}^0 - G_{12}^{0+}) T_{12}^{+}. \tag{25}$$

With equations (3) and (22)–(25), we obtain in the momentum representation and the homogeneous case the usual shape of the quantum Boltzmann equation:

$$\frac{\partial}{\partial t} F_1(p_1 t) = I(p_1 t)$$

$$I(p_1 t) = \frac{N(2\pi\hbar)^3}{\hbar} \int dp_2 \, d\bar{p}_1 \, d\bar{p}_2 |\langle p_1 p_2 | T_{12} | \bar{p}_2 \bar{p}_1 \rangle|^2$$

$$\times 2\pi\delta(E_{p_1 p_2} - E_{\bar{p}_1 \bar{p}_2})[F_1(\bar{p}_1 t) F_2(\bar{p}_2 t) - F_1(p_1 t) F_2(p_2 t)]. \tag{26}$$

Besides particle number and momentum, equation (26) conserves the kinetic energy:

$$\frac{d}{dt} \langle p_1^2/2m_1 \rangle = 0. \tag{27}$$

The kinetic equation (26) (quantum Boltzmann equation) is valid for ideal systems only, as can be seen from equation (27). In particular, the T matrix involved does not contain many-body effects and the phase space occupation (Pauli blocking) is not accounted for. This would lead, e.g., to additional factors $1 - nF_1(p)$ in the square brackets of equation (26).

In order to include many-body effects in a consistent manner it would be appropriate to use the technique of Green functions as carried out by Martin and Schwinger (1959), Keldysh (1964), Kadanoff and Baym (1962) and Kremp *et al* (1985).

In particular, we did not include bound states; for this purpose see Klimontovich and Kremp (1981), McLennan (1982) and Lagan and McLennan (1984).

In the next section we shall deal with non-ideality effects, and in particular we will show that the total energy is conserved by the kinetic equation to be derived (see also Klimontovich 1975).

3. Kinetic equation for non-ideal gases: energy conservation

We will now construct kinetic equations which account for higher-order collisions. In particular, we will expand the binary density operator into a cluster series; such an expansion seems to be a very general method to derive kinetic equations for non-ideal systems.

The investigations by Bogolyubov (1946, 1971), Bogolyubov and Gurov (1947), Cohen (1968), Dorfman and Cohen (1972) and Weinstock (1963) showed that in this connection divergent terms appear. In simple cases these terms may be eliminated by a corresponding elimination of the initial time t_0 in a consistent manner.

We will consider now the cluster expansion of F_{12} in the triple collision approximation. In this approximation, the first three equations of the hierarchy of density operators are, in the spatially homogeneous case,

$$\frac{\hbar}{i}\frac{\partial}{\partial t}F_1 = n \operatorname{Tr}_2 [V_{12}, F_{12}] \tag{28}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial t}F_{12} + [H_{12}, F_{12}] = n \operatorname{Tr}_3 [V_{13} + V_{23}, F_{123}] \tag{29}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial t}F_{123} + [H_{123}, F_{123}] = 0. \tag{30}$$

Using the condition of the total weakening of the initial correlations we get from the formal solution of (30)

$$F_{123}(t) = \exp[-iH_{123}(t-t_0)/\hbar]F_{123}(t_0)\exp[iH_{123}(t-t_0)/\hbar] \tag{31}$$

and with the application of Møller operators

$$F_{123}(t_0) = \Omega_{123}F_1(t_0)F_2(t_0)F_3(t_0)\Omega_{123}^+. \tag{32}$$

The formal solution of (29) for F_{12} is

$$F_{12}(t) = \exp[-iH_{12}(t-t_0)/\hbar]F_{12}(t_0)\exp[iH_{12}(t-t_0)/\hbar]$$
$$+\frac{n}{i\hbar}\int_0^{t-t_0} dt' \exp(-iH_{12}t'/\hbar)$$
$$\times \operatorname{Tr}_3 [V_{13} + V_{32}, F_{123}(t-t')]\exp(iH_{12}t'/\hbar). \tag{33}$$

In our approximation, we will discuss (33) in the case where three-particle collisions are taken into account.

Using the identity

$$V_{13} + V_{23} = H_{123} - H_{12} - H_1 \tag{34}$$

and the homogeneity of the system, we carry out the integration over t' in (33). Replacing $F_{12}(t_0)$ in the first RHS term of (33), according to equation (13), we obtain

$$F_{12}(t) = \exp[-iH_{12}(t-t_0)/\hbar]\Omega_{12}F_1(t_0)F_2(t_0)\Omega_{12}^+ \exp[iH_{12}(t-t_0)/\hbar]$$
$$+ n \underset{3}{\mathrm{Tr}} \{F_{123}(t) - \exp[-iH_{12}(t-t_0)/\hbar]F_{123}(t_0)\exp[iH_{12}(t-t_0)/\hbar]\}.$$
$$(35)$$

Two problems occur in connection with equation (35). The first one is that of secular divergences. This means that there are terms which grow with $\tau/\tau_{\mathrm{coll}}$ as $\tau \to \infty$. The physical origin of such terms are successive binary collisions (Cohen 1968, Dorfman and Cohen 1972). The second problem is that of the retardation, i.e. $F_{12}(t)$ is given in terms of $F_1(t_0)$. Both these problems are closely connected with each other.

Let us consider, for this reason, the formal solution of equation (28). Using the binary collision approximation for F_{12}, the t' integration may be carried out as before. The result is

$$F_1(t) = \exp[-iH_1(t-t_0)/\hbar]F_1(t_0)\exp[iH_1(t-t_0)/\hbar]$$
$$+ n \underset{2}{\mathrm{Tr}} \{\exp[-iH_{12}(t-t_0)/\hbar]F_{12}(t_0)\exp[iH_{12}(t-t_0)/\hbar]$$
$$- \exp[-iH_1(t-t_0)/\hbar]F_{12}(t_0)\exp[iH_1(t-t_0)/\hbar]\}.$$
$$(36)$$

Neglecting the retardation in the second RHS term of (36), we obtain

$$F_1(t) = \exp[-iH_1(t-t_0)/\hbar]F_1(t_0)\exp[iH_1(t-t_0)/\hbar]$$
$$+ n \underset{2}{\mathrm{Tr}} [\Omega_{12}F_1(t)F_2(t)\Omega_{12}^+ - F_1(t)F_2(t)].$$
$$(37)$$

From (37) we see that the difference between $F_1(t)$ and $F_1(t_0)$ is of the order of n. Therefore we may conclude that retardation effects are of the same density order as three-particle collisions, and thus in the two-particle density operator such effects must be retained.

Consequently we get from (35), on elimination of $F_1(t_0)$ (Paltsev 1972, Klimontovich and Kremp 1981, McLennan 1982)

$$F_{12}(t) = \Omega_{12}F_1(t)F_2(t)\Omega_{12}^+ + n$$
$$\times \underset{3}{\mathrm{Tr}} [\Omega_{123}F_1(t)F_2(t)F_3(t)\Omega_{123}^+ - \Omega_{12}F_1(t)F_2(t)F_3(t)\Omega_{12}^+]$$
$$- n \underset{3}{\mathrm{Tr}} [\Omega_{12}(\Omega_{13}F_1(t)F_2(t_2)F_3(t)\Omega_{13}^+)\Omega_{12}^+$$
$$+ \Omega_{12}(\Omega_{23}F_1(t)F_2(t)F_3(t)\Omega_{23}^+)\Omega_{12}^+].$$
$$(38)$$

The first RHS term of (38) leads, as we have shown, to the usual Boltzmann collision integral. Among the terms of order n, the first one describes three-particle collisions and has the same structure as the Boltzmann collision term. The second term of order n arises from the elimination of the retardation. It describes two successive binary collisions of three particles. By this term the secular divergences are avoided. As we will now show, this term in particular provides for the conservation of the potential energy.

With equation (38), we get from (28) the following kinetic equation:

$$\frac{\partial}{\partial t} F_1(p_1 t) = I(p_1 t) \equiv I_{(p_1 t)}^{(2)} + I_{(p_1 t)}^{(3)} + I_{(p_1 t)}^{(R)}.$$
$$(39)$$

Here $I^{(2)}_{(p_1 t)}$ is the usual Boltzmann collision integral. The contribution $I^{(3)}_{(p_1 t)}$ represents the three-particle collision and may be written as

$$I^{(3)}_{(p_1 t)} = n^2 (2\pi\hbar)^3 \frac{1}{2\hbar} \int dp_2\, dp_3\, d\bar{p}_1\, d\bar{p}_2\, d\bar{p}_3$$
$$\times |\langle p_1 p_2 p_3 | T(E + i\varepsilon) | \bar{p}_3 \bar{p}_2 \bar{p}_1 \rangle|^2 2\pi\delta(E_{123} - \bar{E}_{123})$$
$$\times [F_1(\bar{p}_1 t) F_2(\bar{p}_2 t) F_3(\bar{p}_3 t)$$
$$- F_1(p_1 t) F_2(p_2 t) F_3(p_3 t)] - \tfrac{1}{2} n I^{(2)}_{(p_1 t)}. \tag{40}$$

The retardation term $I^{(R)}_{(p_1 t)}$ is

$$I^{(R)}_{(p_1 t)} = \frac{i}{\hbar} n \operatorname*{Tr}_{2} [V_{12}, F^{(R)}_{12}] \tag{41}$$

where $F^{(R)}_{12}$ is given by the expression

$$F^{(R)}_{12}(t) = -n \operatorname*{Tr}_{3} [\Omega_{12}(\Omega_{13} F_1 F_2 F_3 \Omega^+_{13}) \Omega^+_{12} + \Omega_{12}(\Omega_{23} F_1 F_2 F_3 \Omega^+_{23}) \Omega^+_{12}]$$

according to (38).

Equation (39) is the quantum version of the Choh–Uhlenbeck kinetic equation, derived by Paltsev (1972), Klimontovich and Kremp (1981) and McLennan (1982).

Let us now consider the question of energy conservation. We start from the expression for the time derivative of the mean value of the kinetic energy (Klimontovich 1975, Klimontovich and Ebeling 1972):

$$\frac{\partial}{\partial t} \langle T \rangle = \frac{\partial}{\partial t} n \operatorname*{Tr}_{1} \left(F_1 \frac{p_1^2}{2m} \right) \equiv \dot{E}_{\text{kin}}. \tag{42}$$

According to (28) we get

$$\dot{E}_{\text{kin}} = \frac{1}{i\hbar} n^2 \operatorname*{Tr}_{12} \left(\frac{p_1^2}{2m} [V_{12}, F_{12}(t)] \right). \tag{43}$$

For $F_{12}(t)$ we use (38), which consists of five contributions. According to these five contributions we write

$$\dot{E}_{\text{kin}} = \sum_{i=1}^{5} \dot{E}^i_{\text{kin}}. \tag{44}$$

$\dot{E}^1_{\text{kin}}$ corresponds to the level of the Boltzmann equation and is equal to zero. In the third term, the trace Tr may be carried out, and we have the Boltzmann case, giving $\dot{E}^3_{\text{kin}} = 0$. The second term gives

$$\dot{E}^2_{\text{kin}} = \frac{1}{i\hbar} n^3 \operatorname*{Tr}_{123} \left(\frac{p_1^2}{2m} [V_{12}, \Omega_{123} F_1(t) F_2(t) F_3(t) \Omega^+_{123}] \right)$$
$$= \frac{1}{i\hbar} \frac{n^3}{2} \operatorname*{Tr}_{123} \left(\frac{p_1^2 + p_2^2 + p_3^2}{2m} [V_{12}, \Omega_{123} F_1(t) F_2(t) F_3(t) \Omega^+_{123}] \right).$$

Here we have taken into account the fact that the addition of p_3^2 yields zero (cyclic invariance) while the addition of p_2^2 produces the factor $\tfrac{1}{2}$. Furthermore, we use the fact that V_{12} produces the same result as V_{13} and V_{23}. Thus we may write

$$\dot{E}^2_{\text{kin}} = \frac{1}{i\hbar} \frac{n^3}{6} \operatorname*{Tr}_{123} \{ H^0_{123} [V_{123}, \Omega_{123} F_1(t) F_2(t) F_3(t) \Omega^+_{123}] \}. \tag{45}$$

Here we have used

$$H^0_{123} = \frac{p^2_1}{2m} + \frac{p^2_2}{2m} + \frac{p^2_3}{2m}$$

$$V_{123} = V_{12} + V_{23} + V_{13} \qquad H_{123} = H^0_{123} + V_{123}.$$

Replacing V_{123} in (45) by H_{123} is possible because

$$\mathrm{Tr}\{A[A, B]\} = 0.$$

Taking into account the intertwining relation

$$H_{123}\Omega_{123} = \Omega_{123}H^0_{123} \tag{46}$$

and the adjoint formula

$$\Omega^+_{123}H_{123} = H^0_{123}\Omega^+_{123} \tag{47}$$

we obtain, instead of (45),

$$\dot{E}^2_{\mathrm{kin}} = \frac{1}{i\hbar} \frac{n^3}{6} \mathop{\mathrm{Tr}}_{123} \{H^0_{123}\Omega_{123}[H^0_{123}, F_1(t)F_2(t)F_3(t)]\Omega^+_{123}\}. \tag{48}$$

The commutator vanishes, and thus

$$\dot{E}^2_{\mathrm{kin}} = 0.$$

For the remaining contributions of (44) it is necessary to have commutation rules for Hamiltonians and products of two-particle Møller operators. From

$$H_{12}\Omega_{12} = \Omega_{12}H^0_{12} \quad \text{and} \quad [H^0_3, \Omega_{12}] = 0$$

follows

$$\Omega_{12}H^0_{123} - H^0_{123}\Omega_{12} = V_{12}\Omega_{12} \tag{49}$$

and

$$\Omega_{12}\Omega_{13}H^0_{123} - H^0_{123}\Omega_{12}\Omega_{13} = \Omega_{12}V_{13}\Omega_{13} + V_{12}\Omega_{12}\Omega_{13}. \tag{50}$$

The adjoint equation is

$$H^0_{123}\Omega^+_{13}\Omega^+_{12} - \Omega^+_{13}\Omega^+_{12}H^0_{123} = \Omega^+_{13}V_{13}\Omega^+_{12} + \Omega^+_{13}\Omega^+_{12}V_{12}. \tag{51}$$

In a similar way to before we have for the fourth and the fifth terms of (44)

$$\dot{E}^{4+5}_{\mathrm{kin}} = -\frac{1}{i\hbar} n^3 \mathop{\mathrm{Tr}}_{123} \left(\frac{p^2_1}{2m} [V_{12}, \Omega_{12}\Omega_{13}F_1(t)F_2(t)F_3(t)\Omega^+_{13}\Omega^+_{12} \right.$$

$$\left. + \Omega_{12}\Omega_{23}F_1(t)F_2(t)F_3(t)\Omega^+_{23}\Omega^+_{12}] \right)$$

$$= \frac{1}{i\hbar} \frac{n^3}{2} \mathop{\mathrm{Tr}}_{123} \{ V_{12}[H^0_{123}, \Omega_{12}\Omega_{13}F_1(t)F_2(t)F_3(t)\Omega^+_{13}\Omega^+_{12}$$

$$+ \Omega_{12}\Omega_{23}F_1(t)F_2(t)F_3(t)\Omega^+_{23}\Omega^+_{12}] \}. \tag{52}$$

The application of (50) and (51) to (52) gives the result

$$\dot{E}^{4+5}_{\mathrm{kin}} = -\frac{1}{i\hbar} \frac{n^3}{2} \mathop{\mathrm{Tr}}_{123} (V_{12}\Omega_{12}\{ [V_{13}, \Omega_{13}F_1(t)F_2(t)F_3(t)\Omega^+_{13}]$$

$$+ [V_{23}, \Omega_{23}F_1(t)F_2(t)F_3(t)\Omega^+_{23}]\}\Omega^+_{12}). \tag{53}$$

Here we have again applied $\mathrm{Tr}\{A[A, B]\} = 0$ and $[H^0_{123}, F_1(t)F_2(t)F_3(t)] = 0$.

According to equation (20) we have

$$F_{13}(t) = \Omega_{13}F_1(t)F_3(t)\Omega_{13}^+ + O(n). \tag{54}$$

Taking into account

$$[V_{13}, F_2] = 0$$

and

$$\frac{\partial}{\partial t} F_1 = \frac{1}{i\hbar} n \operatorname*{Tr}_3 [V_{13}, F_{13}]$$

we have

$$\dot{E}_{kin}^{4+5} = -\frac{n^2}{2} \operatorname*{Tr}_{12} [V_{12}\Omega_{12}\partial[(F_1(t)F_2(t))\Omega_{12}^+]/\partial t]$$

$$= -\frac{\partial}{\partial t} \frac{n^2}{2} \operatorname*{Tr}_{12} [V_{12}F_{12}(t)] + O(n^3). \tag{55}$$

Equation (55) represents the negative time derivative of the mean value of the potential energy in the approximation of the second virial coefficient (binary collision approximation). Therefore we have from (42) and (55)

$$\frac{\partial}{\partial t} \langle T \rangle = -\frac{\partial}{\partial t} \langle V \rangle. \tag{56}$$

The potential energy contribution comes from the retardation correction and corresponds to self-energy correlations.

4. Concluding remarks

The aim of our paper was to discuss the influence of higher-order collisions on the structure of the equation of motion for the single-particle distribution function, i.e. of the kinetic equation. Thus we derived additional collision integrals, which go beyond that of the usual Boltzmann equation. While the latter equation conserves the kinetic energy only, we accounted in our paper for non-ideality (strong coupling) effects, which exist if the mean value of the potential energy is of the same order as that of the kinetic energy.

Non-ideality effects are not only of relevance for the determination of transport properties, but also for the kinetics of chemically reacting systems. Here, of course, bound states must be included additionally (McLennan 1982).

In particular, the theoretical approach to chemical equilibrium is qualitatively changed by the inclusion of non-ideality effects. The problem of non-ideality in connection with equilibrium and transport properties was discussed in Ebeling *et al* (1976, 1984) and Kraeft *et al* (1986). The kinetic equation described in our paper accounts for non-ideality effects (in contrast to the usual Boltzmann equation) on the level of the second virial coefficient.

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