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Kinetic Equations Without "Memory" for the Time-Displaced Correlation Functions

A. R. Altenberger[1] and J. Stecki[1]

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The relations between the kinetic equations with and without convolution in time are discussed on the basis of the kinetic equation for the Van Hove self-correlation function. Formal equivalence of both the equations is shown, and approximate scattering operators for the dilute-gas case and for the Brownian particle are considered.

KEY WORDS: Time correlation function; non-Markovian kinetic equation; distribution function; collision integral; memory function; projection operator.

1. INTRODUCTION

During the last ten years, a great deal of progress has been made in the field of irreversible statistical mechanics. In particular, the general theory of the kinetic equations has been developed. Two main approaches to the derivation of the kinetic equations have been formulated. The first, due to Cohen, Ernst, Haines, and Dorfman,[1-4] is based on the resummation of the cluster expansion of the reduced distribution functions and leads to a scattering operator which is a function of the same time as the time argument of the distribution function. Usullay, the authors use only an asymptotic, long-time form of the scattering operator, in agreement with the earlier ideas of Bogoliubov, but the extension to the full time scale is straightforward and

[1] Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland.

can be obtained readily.[2,3] The second approach, developed by Prigogine's group,[5–7] gives the kinetic equations with convolution in time. This non-Markovian form, being related to the finite duration of collision processes, is frequently called "the memory" effect. For the derivation of this convolution equation, the Zwanzig[8] projection operator technique has been frequently applied.

Some time ago, Fuliński[9] suggested that the Markovian kinetic equations with the time-dependent scattering operator could be derived from the formal solution of the Liouville equation by the projection operator technique or from the familiar Zwanzig[8] equation by the use of the Taylor expansion method in principle analogous to the method in the Prigogine monograph.[6] Later, Fuliński and Kramarczyk[10] and Kramarczyk and Voss[11] proposed a short and unconventional method of the derivation of the Markovian kinetic equations directly from the Liouville equation by the application of a projection operator technique which is different from the Zwanzig method.

In the present paper, we discuss the relations between the kinetic equations with and without convolution in time. As the basis for comparison, we chose the kinetic equation for the Van Hove self-correlation function. The Van Hove correlation function has been studied by several authors[12–15] using different methods, but all of the equations which have been obtained belong to the convolution formalism. In the next section, we present a more conventional derivation of the Markovian kinetic equation of Kramarczyk and Voss which exhibits the difference with the familiar Zwanzig technique. We also show the new method of derivation of the Markovian equation by the direct resummation of the Zwanzig formulas. In the same section, we derive the general form of the Markovian scattering operator and prove that for a certain projection operator, the Kramarczyk–Voss technique is equivalent to the resummed cluster expansion method of Ernst *et al.*[3] In Section 3, the low activity limit of the scattering operator is discussed, and in Section 4, the appropriate scattering operator for the Brownian motion problem is considered. The two problems allow us to show more directly the relations between the kinetic equations in both formalisms.

2. GENERAL KINETIC EQUATION

We restrict ourselves to a system with binary interactions only. The Liouville operator of such a system is given by

$$K_N = K_N{}^0 + \delta K_N \tag{1}$$

where

$$K_N{}^0 = \sum_{i=1}^{N} \mathbf{v}_i \cdot \partial/\partial \mathbf{r}_i$$

$$K_N = \sum_{i<j}^{N} \Theta_{ij}$$

$$\Theta_{ij} = \partial U(|\,\mathbf{r}_i - \mathbf{r}_j\,|)/\partial \mathbf{r}_j \cdot [(\partial/\partial \mathbf{v}_i) - (\partial/\partial \mathbf{v}_j)]$$

and $\mathbf{r}_i$ and $\mathbf{v}_i$ denote, respectively, the position and velocity of the ith particle.

Let us now define the Van Hove self-correlation function $G(\mathbf{R}, t)$ and the intermediate scattering function $I(\mathbf{k}, t)$. Using the grand canonical ensemble, we obtain

$$G(\mathbf{R}, t) = (\Omega/\bar{N}\Xi) \sum_{N\geqslant 1} (\alpha^N/N!) \int d\mathbf{r} \int d\mathbf{r}^N \, d\mathbf{v}^N \sum_{i=1}^{N} \delta(\mathbf{R} + \mathbf{r} - \mathbf{r}_i)$$
$$\times \, \delta[\mathbf{r}_i(-t) - \mathbf{r}] \prod_{i=1}^{N} \varphi(\mathbf{v}_i) \, e^{-\beta U_N} \tag{2}$$

and

$$I(\mathbf{k}, t) = (1/\bar{N}\Xi) \sum_{N\geqslant 1} [\alpha^N/(N-1)!] \int d\mathbf{r}^N \, d\mathbf{v}^N (\exp -i\mathbf{k} \cdot \mathbf{r}_1)$$
$$\times \prod_{i=1}^{N} \varphi(\mathbf{v}_i)(\exp -\beta U_N) \exp i\mathbf{k} \cdot \mathbf{r}_1(-t); \qquad \beta = 1/k_B T \tag{3}$$

where Ω is the volume of the system; N is the mean number of molecules in the volume; α is the activity; Ξ is the grand canonical partition function; $\varphi(\mathbf{v})$ is the normalized Maxwellian velocity distribution function; and U_N is the total potential energy of the N-particle system. We also define the initial N-particle distribution function $F(\mathbf{k}, \mathbf{r}^N, \mathbf{v}^N)$ given by

$$F(\mathbf{k}, \mathbf{r}^N, \mathbf{v}^N) = (\exp i\mathbf{k} \cdot \mathbf{r}_1) \prod_{i=1}^{N} \varphi(\mathbf{v}_i) \exp(-\beta U_N) \tag{4}$$

and the auxiliary one-particle distribution function $f(\mathbf{k}, \mathbf{v}_1, t)$ by

$$f(\mathbf{k}, \mathbf{v}_1, t) = \sum_{N\geqslant 1} (1/\bar{N}\Xi)[\alpha^N/(N-1)!]$$
$$\times \int d\mathbf{v}_{\neq 1}^{N-1} \int d\mathbf{r}^N (\exp -i\mathbf{k} \cdot \mathbf{r}_1) \, F(\mathbf{k}, \mathbf{r}^N, \mathbf{v}^N, t) \tag{5}$$

The function $F(\mathbf{k}, \mathbf{r}^N, \mathbf{v}^N, t)$ is the solution of the Liouville equation for the initial distribution given by Eq. (4), i.e.,

$$F(\mathbf{k}, \mathbf{r}^N, \mathbf{v}^N, t) = e^{-tK_N} F(\mathbf{k}, \mathbf{r}^N, \mathbf{v}^N) \tag{6}$$

If we now use the projection operator $P = ><$, where

$$> = (\exp i\mathbf{k}\cdot\mathbf{r}_1)(\exp -\beta U_N)\prod_{i=2}^{N}\varphi(\mathbf{v}_i) \tag{7}$$

and

$$< = \sum_{N\geqslant 1}(1/\bar{N}\Xi)[\alpha^N/(N-1)!]\int d\mathbf{v}_{\neq 1}^{N-1}\int d\mathbf{r}^N \exp(-i\mathbf{k}\cdot\mathbf{r}_1) \tag{8}$$

which is the generalized version of the projection operator of Stecki and Wojnar,[13] we have

$$\begin{aligned} f(\mathbf{k},\mathbf{v}_1,t) &= \langle F(\mathbf{k},\mathbf{r}^N,\mathbf{v}^N,t) \\ f(\mathbf{k},\mathbf{v}_1,0) &= \varphi(\mathbf{v}_1) \end{aligned} \tag{9}$$

and

$$(1-P)\,F(\mathbf{k},\mathbf{r}^N,\mathbf{v}^N) = 0 \tag{10}$$

In addition, the intermediate scattering function $I(\mathbf{k}, t)$ can be expressed as

$$I(\mathbf{k},t) = \int d\mathbf{v}_1 f(\mathbf{k},\mathbf{v}_1,t) \tag{11}$$

The general form of the "Markovian" kinetic equation for our problem is

$$-\partial_t f(\mathbf{k},\mathbf{v}_1,t) = i\mathbf{k}\cdot\mathbf{v}_1 f(\mathbf{k},\mathbf{v}_1,t) + M(t)f(\mathbf{k},\mathbf{v}_1,t) \tag{12}$$

where the scattering operator $M(\mathbf{k}, \mathbf{v}_1, t)$ and the distribution function have the same time argument.

An explicit form of the Markovian scattering operator can be obtained directly from the expression given by Kramarczyk and Voss;[11] however, it seems instructive to discuss the derivation of the Markovian kinetic equations in detail. In the original paper, Kramarczyk and Voss used a very compact method of deriving the Markovian equation. We present here another derivation of this equation which explains its difference with the more familiar Zwanzig method.

We start from the Liouville equation in the differential and integral forms

$$-\partial_t F_N(t) = K_N(P+Q)\,F_N(t) \tag{13}$$

$$F_N(t) = F_N(0) - \int_0^t dt'\,K_N F_N(t') \tag{14}$$

Here, $F_N(t)$ is an N-particle distribution function. Using the abbreviation $Q = 1 - P$, we decompose the first equation by splitting $F_N(t)$ function into two parts,

$$F_N(t) = PF_N(t) + QF_N(t)$$

All that we need do in order to obtain the closed kinetic equation for $PF_N(t)$ is to express the function $QF_N(t)$ as a functional of $PF_N(t)$. This can be done by means of the equation

$$QF_N(t) = QF_N(0) - \int_0^t dt'\, QK_N F_N(t') \tag{15}$$

which follows directly from (14). The difference between the Zwanzig and Kramarczyk–Voss methods lies in dealing with the integrand. Zwanzig rewrites Eq. (15) in the form

$$QF_N(t) = QF_N(0) - \int_0^t dt'\, QK_N[PF_N(t') + QF_N(t')]$$

and by iteration obtains

$$QF_N(t) = [\exp(-tQK_N)]\, QF_N(0) - \int_0^t dt'\, [\exp(-t'QK_N)]\, QK_N PF_N(t-t') \tag{16}$$

Inserting this expression in Eq. (13), one obtains the convolution kinetic equation of Zwanzig:

$$\begin{aligned} -\partial_t PF_N(t) = {} & PK_N PF_N(t) - \int_0^t dt'\, PK_N[\exp(-t'QK_N)]\, QK_N PF_N(t-t') \\ & + PK_N[\exp(-tQK_N)]\, QF_N(0) \end{aligned} \tag{17}$$

In order to obtain the Markovian kinetic equation, we should use the relation

$$QF_N(t) = QF_N(0) - \int_0^t dt'\, QK_N \exp[-(t'-t)\, K_N][PF_N(t) + QF_N(t)] \tag{18}$$

which also follows from (15). The time integration can be formally performed to obtain

$$QF_N(t) = QF_N(0) + Q(1 - e^{tK_N})\, PF_N(t) + Q(1 - e^{tK_N})\, QF_N(t)$$

and by iteration we have

$$\begin{aligned} QF_N(t) = {} & [1 - Q(1 - e^{tK_N})]^{-1}\, Q(1 - e^{tK_N})\, PF_N(t) \\ & + [1 - Q(1 - e^{tK_N})]^{-1}\, QF_N(0) \end{aligned} \tag{19}$$

After simple rearrangement, the Kramarczyk–Voss kinetic equation[11] follows:

$$\begin{aligned} -\partial_t PF_N(t) = {} & PK_N e^{-tK_N}[1 + P(e^{-tK_N} - 1)]^{-1}\, PF_N(t) \\ & + PK_N e^{-tK_N}[1 + P(e^{-tK_N} - 1)]^{-1}\, QF_N(0) \end{aligned} \tag{20}$$

By $(1 - x)^{-1}$, we mean $\sum_{n=0}^{\infty} x^n$. In addition, if we have

$$PK_N{}^0 Q = 0, \qquad PQ = QP = 0$$

Eq. (20) can be transformed to the form

$$-\partial_t PF_N(t) = PK_N{}^0\, PF_N(t) + P\delta K_N e^{-tK_N}[1 + P(e^{-tK_N} - 1)]^{-1}\, PF_N(t) + PK_N\, e^{-tK_N}[1 + P(e^{-tK_N} - 1)]^{-1}\, QF_N(0) \qquad (21)$$

and we take the Markovian scattering operator to be equal to

$$M(t, \mathbf{k}, \mathbf{v}_1) = P\delta K_N e^{-tK_N}[1 + P(e^{-tK_N} - 1)]^{-1} \qquad (22)$$

Equations (20) and (21) represent the exact Markovian form of the generalized master equation valid for all times. Another form of the Markovian kinetic equation can be easily obtained by the resummation of the convolution kinetic equation of Zwanzig [given by the Eq. (17)]. We put in Eq. (16)

$$[PF_N(t - t') = P \exp(t'K_N)(P + Q)\, F_N(t)$$

and perform the resummation to obtain

$$QF_N(t) = \mathscr{L}(t)\, e^{-tQK_N}\, QF_N(0) + \mathscr{L}(t)Z(t)\, PF_N(t)$$

where $\mathscr{L}(t)$ is the iteration solution of the equation

$$\mathscr{L}(t) = 1 + Z(t)\, \mathscr{L}(t)$$

and $Z(t)$ is given by

$$Z(t) = -\int_0^t dt' \exp(-t'QK_N)QK_NP \exp(t'K_N)$$

Using above expressions, we obtain the Markovian kinetic equation in the form

$$-\partial_t PF_N(t) = PK_N PF_N(t) + PK_N\mathscr{L}(t)\, Z(t)\, PF_N(t) + PK_N\mathscr{L}(t)\, QF_N(0) \qquad (23)$$

which is especially convenient when the long-time limit ($t \to \infty$) is taken.

For our particular problem, all the terms containing the $QF_N(0)$ function vanish and we obtain the kinetic equation for the $f(\mathbf{k}, \mathbf{v}_1, t)$ function in the form

$$-\partial_t f(\mathbf{k}, \mathbf{v}_1, t) - i\mathbf{k} \cdot \mathbf{v}_1 f(\mathbf{k}, \mathbf{v}_1, t) = M(\mathbf{k}, \mathbf{v}_1, t) f(\mathbf{k}, \mathbf{v}_1, t) \qquad (24)$$

where $M(\mathbf{k}, \mathbf{v}_1, t)$ can be expressed as

$$M(\mathbf{k}, \mathbf{v}_1, t) = \langle \delta K_N \exp(-tK_N)\rangle[1 - \langle 1 - \exp(-tK_N)\rangle]^{-1}$$

or

$$M(\mathbf{k}, \mathbf{v}_1, t) = \langle \delta K_N \exp(-\, tK_N)\rangle[1 - \int_0^t dt'\, \langle \exp(t'K_N)\rangle \times \langle \delta K_N \exp(-\, t'K_N)\rangle]^{-1}\langle \exp(tK_N{}^0)\rangle \qquad (25)$$

It can be easily shown that the last form of this operator is identical to that obtained by the application of the resummed t-method of Ernst *et al.*[3] Indeed, using this method, we have for the auxiliary function $f(\mathbf{k}, \mathbf{v}_1, t)$ and for its time derivative the following expressions:

$$f(\mathbf{k}, \mathbf{v}_1, t) = \langle \exp -tK_N{}^0 \rangle [1 - \int_0^t dt' \langle \exp t'K_N{}^0 \rangle \times \langle \delta K_N \exp -t'K_N \rangle] \, \varphi(\mathbf{v}_1)$$

$$\partial_t f(\mathbf{k}, \mathbf{v}_1, t) = -\langle K_N{}^0 \rangle f(\mathbf{k}, \mathbf{v}_1, t) - \langle \delta K_N \exp -tK_N \rangle \, \varphi(\mathbf{v}_1)$$

Then, we invert the last expression to obtain

$$\varphi(\mathbf{v}_1) = [1 - \int_0^t dt' \langle \exp t'K_N{}^0 \rangle \langle \delta K_N \exp -t'K_N \rangle]^{-1} \langle \exp tK_N{}^0 \rangle f(\mathbf{k}, \mathbf{v}_1, t)$$

and insert it in the place of $\varphi(\mathbf{v}_1)$ in Eq. (22). In this way, we obtain exactly the same form of the scattering operator as the second one given by (25). It It should be noted that the analogous relations exist within the convolution formalism between the resummed ϵ-method,[2,3] the method of inverse operators of Blum and Lebowitz,[14] and the Zwanzig projection operator technique[8] [so far as $QF_N(0) = 0$].

We can also find an exact relation between the scattering operator $M(\mathbf{k}, \mathbf{v}_1, t)$ and the appropriate scattering operator in the convolution formalism, which is given by [12]

$$G(t) = \langle K_N \exp(-t'QK_N) \, QK_N \rangle$$

From the relation

$$M(t, \mathbf{k}, \mathbf{v}_1) \langle \exp -tK_N \rangle = \langle \delta K_N \exp -tK_N \rangle$$

we obtain, by the application of the Laplace transform, the following relation between the operators:

$$(2\pi i)^{-1} \int_{s-i\infty}^{s+i\infty} dq \, \tilde{M}(\mathbf{k}, \mathbf{v}_1, z - q)[q + i\mathbf{k} \cdot \mathbf{v} + \tilde{G}(\mathbf{k}, \mathbf{v}_1, q)]^{-1}$$
$$= \tilde{G}(\mathbf{k}, \mathbf{v}_1, z)[z + i\mathbf{k} \cdot \mathbf{v}_1 + \tilde{G}(\mathbf{k}, \mathbf{v}_1, z)]^{-1} \tag{26}$$

where $\tilde{G}(\mathbf{k}, \mathbf{v}_1, z)$ is the Laplace transform of the scattering operator $G(t, \mathbf{k}, \mathbf{v}_1)$, which is given by

$$G(\mathbf{k}, \mathbf{v}_1, z) = \langle K_N R_N(z) \rangle \sum_{n=0}^{\infty} [\langle \delta K_N \, R_N(z) \rangle]^n \, [\langle R_N{}^0 \rangle]^{-1}$$

and $R_N(z)$ and $R_N{}^0(z)$ are given by

$$R_N(z) = 1/(z + K_N), \qquad R_N{}^0(z) = 1/(z + K_N{}^0)$$

respectively. The complicated relation between M and G simplifies greatly if any particular expansion of the scattering operator is applied. We return to this problem in the next two sections.

3. SCATTERING OPERATOR FOR DILUTE GASES

The scattering operator that depends on the dynamics of only two particles is of central interest in the whole theory of nonequilibrium phenomena. It is for this case that the equations of motion can be solved, so that the scattering equation can be found explicitly. For our problem, the two-body scattering operator can be easily obtained by the application of the activity expansion of the operator given by Eq. (25). For the lowest-order term of the expansion, we have

$$M^{(1)}(\mathbf{k}, \mathbf{v}_1, t) = (\alpha/\Omega) \int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{v}_2 [\exp(-i\mathbf{k}\cdot\mathbf{r}_1)] \delta K_2 \exp(-tK_2) \times [\exp i\mathbf{k}\cdot(\mathbf{r}_1 + \mathbf{v}_1 t)][\exp -\beta U(|\mathbf{r}_1 - \mathbf{r}_2|)]\, \varphi(\mathbf{v}_2) \tag{27}$$

or, equivalently,

$$M^{(1)}(\mathbf{k}, \mathbf{v}_1, t) = -(\alpha/\Omega) \int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{r}_2 \int_0^t dt' \delta K_2 [\exp -t'(K_2 + i\mathbf{k}\cdot\mathbf{v}_1)] \times K_2 (\exp i\mathbf{k}\cdot\mathbf{v}_1 t')\, \varphi(\mathbf{v}_2) \exp[-\beta U(|\mathbf{r}_1 - \mathbf{r}_2|)] \tag{28}$$

It should be noted that the application of the grand canonical ensemble in the definition of the projection operator greatly simplifies the problem of the determination of the particular terms of the activity (or density) expansion of the scattering operator.

The kinetic equation for the dilute-gas, binary collision case is given by

$$-\partial_t f(\mathbf{k}, \mathbf{v}_1, t) - i\mathbf{k}\cdot\mathbf{v}_1 f(\mathbf{k}, \mathbf{v}_1, t) = (\alpha/\Omega) \int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{r}_2\, \delta K_2\, [\exp -t(K_2 + i\mathbf{k}\cdot\mathbf{v}_1)](\exp i\mathbf{k}\cdot\mathbf{v}_1 t) [\exp -\beta U(|\mathbf{r}_1 - \mathbf{r}_2|)]\, \varphi(\mathbf{v}_2) f(\mathbf{k}, \mathbf{v}_2, t) \tag{29}$$

or in position space by

$$-\partial_t f(\mathbf{R}, \mathbf{v}_1, t) - \mathbf{v}_1\cdot\nabla_R f(\mathbf{R}, \mathbf{v}_1, t) = (\alpha/\Omega) \int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{r}_2 \int d\mathbf{r}\, \delta(\mathbf{R} - \mathbf{r}_1 - \mathbf{r})\, \delta K_2\, (\exp -tK_2)\, \varphi(\mathbf{v}_2) \times [\exp -\beta U(|\mathbf{r}_1 - \mathbf{r}_2|)](\exp tK_2{}^0) f(\mathbf{r}_1 + \mathbf{r}, \mathbf{v}_1, t) \tag{30}$$

For the short-time limit, we obtain immediately

$$\lim_{t\to 0} M^{(1)}(\mathbf{k}, \mathbf{v}_1, t) = 0 \tag{31}$$

If we restrict our considerations to times of order of the mean free time of the particle motion, we obtain the so-called linear trajectory approximation

$$M_{\mathrm{LT}}^{(1)}(\mathbf{k}, \mathbf{v}_1, t) = -(\alpha/\Omega)\, \bar{\mathbf{F}} \cdot \partial/\partial \mathbf{v}_1 \tag{32}$$

with the mean force $\bar{\mathbf{F}}$ given by

$$\bar{\mathbf{F}}(\mathbf{v}_1, t) = -\int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{r}_2\, \varphi(\mathbf{v}_2)[\exp -\beta U(|\, \mathbf{r}_1 - \mathbf{r}_2 + (\mathbf{v}_1 - \mathbf{v}_2)t \,|)]$$
$$\times (\partial/\partial \mathbf{r}_2)\, U(|\, \mathbf{r}_1 - \mathbf{r}_2 \,|)$$

The long-time limit of the scattering operator can be obtained by the application of the limit theorem for the Laplace transform. We use the relation

$$\lim_{t\to\infty} M^{(1)}(\mathbf{k}, \mathbf{v}_2, t) = \lim_{s\to 0} M^{(1)}(\mathbf{k}, \mathbf{v}_1, s)$$
$$= \int_0^\infty dt\, \partial_t M^{(1)}(\mathbf{k}, \mathbf{v}_1, t) - M^{(1)}(\mathbf{k}, \mathbf{v}_1, t = 0)$$

and obtain the asymptotic form of the scattering operator by

$$\lim_{t\to\infty} M^{(1)}(\mathbf{k}, \mathbf{v}_1, t)$$
$$= -(\alpha/\Omega) \int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{r}_2 \int_0^\infty dt' \delta K_2\, [\exp -t'(K_2 + i\mathbf{k} \cdot \mathbf{v}_1)]$$
$$\times K_2 \varphi(\mathbf{v}_2)[\exp -\beta U(|\, \mathbf{r}_1 - \mathbf{r}_2 \,|)] \exp i\mathbf{k} \cdot \mathbf{v}_1 t' \tag{33}$$

It is interesting to compare the above results with the analogous equations of the convolution formalism. In the same low-activity limit, we obtain the convolution equation

$$\partial_t f(\mathbf{k}, \mathbf{v}_1, t) + i\mathbf{k} \cdot \mathbf{v}_1 f(\mathbf{k}, \mathbf{v}_1, t) = (\alpha/\Omega) \int d\mathbf{v}_2 \int d\mathbf{r}_1\, d\mathbf{r}_2 \int_0^t dt' \delta K_2$$
$$\times (\exp -tK_2)\, K_2 (\exp i\mathbf{k} \cdot \mathbf{r}_1)\, \varphi(\mathbf{v}_2)[\exp -\beta U(|\, \mathbf{r}_1 - \mathbf{r}_2 \,|)] f(\mathbf{k}, \mathbf{v}_1, t) \tag{34}$$

This equation was derived by Stecki and Wojnar[13] by the application of the Zwanzig projection operator technique. In the original equation,[13] the α factor is replaced by the density. The convolution scattering operator vanishes in the short-time limit. The long-time asymptotic form of the equation is given, following Balescu,[7] by

$$\partial_t f(\mathbf{k}, \mathbf{v}_1, t) + i\mathbf{k} \cdot \mathbf{v}_1 f(\mathbf{k}, \mathbf{v}_1, t) = (\alpha/\Omega) \int d\mathbf{r}_2\, d\mathbf{r}_1\, d\mathbf{v}_2 \int_0^\infty dt'$$
$$\times (\exp -i\mathbf{k} \cdot \mathbf{r}_1)\, \delta K_2\, (\exp -tK_2)\, K_2 (\exp i\mathbf{k} \cdot \mathbf{r}_1)\, \varphi(\mathbf{v}_2)$$
$$\times [\exp -\beta U(|\, \mathbf{r}_1 - \mathbf{r}_2 \,|)] f(\mathbf{k}, \mathbf{v}_1, t - t') \tag{35}$$

It is interesting to discuss how the non-Markovian kinetic equation can be reduced to the Markovian one. The general procedure presented in the Balescu paper[7] gives the long-time version at once, and here we use the method used in the Prigogine book,[6] which consists in the application of the Taylor expansion of the function $f(\mathbf{k}, \mathbf{v}_1, t - t')$. We have

$$f(\mathbf{k}, \mathbf{v}_1, t - \tau) = (\exp i\mathbf{k} \cdot \mathbf{v}_1\tau) f(t, \mathbf{k}, \mathbf{v}_1) - (\exp i\mathbf{k} \cdot \mathbf{v}_1\tau) \int_0^t dt'\, G(\mathbf{k}, \mathbf{v}_1, t') f(\mathbf{k}, \mathbf{v}_1, t) + \cdots \tag{36}$$

It should be stressed that every appearance of the scattering operator or its time derivatives in the right-hand side of the expansion (36) introduces one more α factor. If we strictly treat this parameter as the small one, we should retain in the resummed expression only the first term of the expansion (36), which is independent on α. Doing so, we obtain as the Markovian, low-activity limit of the convolution scattering operator the expression identical with that previously derived for $M^{(1)}(\mathbf{k}, \mathbf{v}_1, t)$ operator. Certainly we obtain the same result using the general relation (26). It follows from the above considerations that the right-hand side of the Markovian kinetic equation (29) is [apart from the α dependence of the function $f(\mathbf{k}, \mathbf{v}_1, t)$] linear with respect to the activity, whereas for the convolution kinetic equation (34) we also have an implicit α dependence due to (36).

4. THE BROWNIAN MOTION PROBLEM

Another problem which seems instructive to discuss is the equation for the distribution function of a heavy particle moving in a fluid of light particles. It is an essentially Brownian motion problem, which has been studied recently by several authors.[16–18] Nevertheless, they applied the convolution formalism (see especially the paper of Lebowitz and Rubin,[16] where the derivation of the nonstationary Fokker–Planck equation is given) so that the classical Fokker–Planck equation can be obtained only when a certain limit involving the size of the fluid and the time scale were taken. We shall show that using the Markovian scattering operator (22), we can obtain the classical form of the Fokker–Planck equation with the time-dependent diffusion coefficient as the first (different from zero) term of the expansion of the scattering operator in powers of the γ parameter equal to $(m/M)^{1/2}$. We have only to modify our definition of the projection operator in order to include the fact that the heavy particle is different from the fluid particles and cannot leave the system.

In the previous section, we assumed that the particles are of the same mass so that there was no necessity to distinguish between the velocities and moments of the particles. Here, we have the heavy particle with mass M and light particles of mass m. The Hamiltonian of the system is then

$$H(\mathbf{P}, \mathbf{R}, \mathbf{p}^N, \mathbf{r}^N) = (\mathbf{P}^2/2M) + U_B + U_f + \sum_{i=1}^{N} (\mathbf{p}_i^2/2m)$$

where

$$U_B = \sum_{i=1}^{N} U(|\,\mathbf{R} - \mathbf{r}_i\,|); \qquad U_f = \sum_{i<j} U(|\,\mathbf{r}_i - \mathbf{r}_j\,|)$$

We choose the initial distribution function as

$$F_N(\mathbf{k}, \mathbf{P}, \mathbf{R}, \mathbf{p}^N, \mathbf{r}^N) = (1/\Xi)(\alpha_N/N!) \times \prod_{i=1}^{N} \varphi(\mathbf{p}_i)(\exp -\beta[U_B + U_f])\, \varphi(\mathbf{P}) \exp i\mathbf{k} \cdot \mathbf{R} \tag{37}$$

The distribution function of the heavy particle is given by

$$f(\mathbf{k}, \mathbf{P}, t) = \sum_{N\geqslant 0} \int d\mathbf{R} \int d\mathbf{r}^N\, d\mathbf{p}^N\, (\exp -i\mathbf{k} \cdot \mathbf{R}) \times (\exp -tK_N)\, F_N(\mathbf{k}, \mathbf{R}, \mathbf{P}, \mathbf{p}^N, \mathbf{r}^N) \tag{38}$$

where

$$\Xi = \sum_{N\geqslant 0} (\alpha^N/N!) \int d\mathbf{R} \int d\mathbf{r}^N \exp -\beta[U_B + U_f]$$

We apply the projection operator defined analogically to (7) and (8),

$$P = \,>\!< \,= \prod_{i=1}^{N} \varphi(\mathbf{p}_i)(\exp -\beta[U_B + U_f])(\exp i\mathbf{k} \cdot \mathbf{R}) \times \sum_{N\geqslant 0} (1/\Xi)(\alpha^N/N!) \int d\mathbf{R} \int d\mathbf{r}^N\, d\mathbf{p}^N \exp -i\mathbf{k} \cdot \mathbf{R} \tag{39}$$

and we denote here

$$> \,= \prod_{i=1}^{N} \varphi(\mathbf{p}_i)(\exp -\beta[U_B + U_f]) \exp i\mathbf{k} \cdot \mathbf{R} \tag{40}$$

Following the paper of Résibois and Davis,[17] we express the Liouville operator in the form

$$K_N = K_N^{0f} + \delta K_N^f + \gamma K^{0B} = K_N^{0f} + \gamma K_B^{0} + \delta K_N$$

where

$$K_f^0 = \sum_{i=1}^{N} \mathbf{p}_i \cdot \partial/\partial \mathbf{r}_i; \qquad K_B = (\mathbf{P}/M) \cdot \partial/\partial \mathbf{R}$$

$$\gamma\, \delta K_N{}^B = \sum_{i=1}^{N} - \frac{\partial U(|\mathbf{R} - \mathbf{r}_i|)}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{P}} = \mathbf{F}(\{\mathbf{R} - \mathbf{r}_i\}) \cdot \frac{\partial}{\partial \mathbf{P}}$$

$$K_N{}^f = - \sum_{i<j}^{N} \frac{U(|\mathbf{r}_i - \mathbf{r}_i|)}{\partial \mathbf{r}_i} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_i} \right) - \sum_{i=1}^{N} \frac{\partial U(|\mathbf{R} - \mathbf{r}_i|)}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_j} \tag{41}$$

The Markovian scattering operator can be obtained from the operator equation

$$\begin{aligned} M(t, \mathbf{k}, \mathbf{P}) = {} & \langle \delta K_N \exp - tK_N \rangle \exp[i\mathbf{k} \cdot (\mathbf{P}/M)t] \\ & + M(\mathbf{k}, \mathbf{P}, t) \int_0^t dt' \exp[-i\mathbf{k} \cdot (\mathbf{P}/M)(t - t')] \\ & \times \langle \delta K_N \exp - t'K_N \rangle \exp [i\mathbf{k} \cdot (\mathbf{P}/M)t] \end{aligned} \tag{42}$$

If we expand the operator $\langle \delta K_N\, e^{-tK_N} \rangle$ in powers of $\gamma = (m/M)^{1/2}$, we can show that the first-order term vanishes and the second-order term of the expansion gives the classical Fokker–Planck operator with the time-dependent diffusion tensor.[19] We obtain

$$\begin{aligned} M^{(2)}(t, \mathbf{k}, \mathbf{P}) &= - \gamma^2 \langle \delta K_N{}^B \int_0^t dt' (\exp - t'K_N{}^f)(K_B{}^0 + \delta K_N{}^B) \rangle \\ &= - D(t)(\partial/\partial \mathbf{P}) \cdot [(\mathbf{P}/M) + \beta^{-1}(\partial/\partial \mathbf{P})] \end{aligned} \tag{43}$$

where the diffusion tensor is given by

$$\begin{aligned} D(t) = {} & \tfrac{1}{3}\beta \sum_{N\geqslant 0} \int_0^t dt' \int d\mathbf{R} \int d\mathbf{r}^N\, d\mathbf{p}^N \\ & \times (\alpha^N/N!\Xi) \prod_{i=1}^{N} \varphi(p_i) \exp - \beta[U_B + U_f] \\ & \times \mathbf{F}(\{\mathbf{R} - \mathbf{r}_i\}) \cdot \mathbf{F}(\{\mathbf{R} - \mathbf{r}_i(-t')\}) \end{aligned} \tag{44}$$

and by $\mathbf{F}(\{\mathbf{R} - \mathbf{r}_i(-t'\})$ we denote

$$\mathbf{F}(\{\mathbf{R} - \mathbf{r}_i(-t)\}) = -[\exp - t(K_N^{0f} + \delta K_N{}^f)] \sum_{i=1}^{N} \partial U(|\mathbf{R} - \mathbf{r}_i|)/\partial \mathbf{r}_i$$

If we take the long-time limit, i.e., if we put

$$\lim_{t\to\infty} D(t) = D(\infty)$$

we obtain the scattering operator of Résibois and Davis.[17]

The appropriate kinetic equation in the convolution formalism has been derived recently by Stecki and Narbutowicz,[20] who obtain

$$\partial_t f(\mathbf{k}, \mathbf{P}, t) + i\mathbf{k} \cdot (\mathbf{P}/M) f(\mathbf{k}, \mathbf{P}, t)$$
$$= \int_0^t dt' \, \eta(t')(\partial/\partial\mathbf{P}) \cdot [(\mathbf{P}/M) + \beta^{-1}(\partial/\partial\mathbf{P})] f(\mathbf{k}, \mathbf{P}, t - t') \qquad (45)$$

where

$$\eta(t) = \tfrac{1}{3}\beta\langle \mathbf{F}(\{\mathbf{R} - \mathbf{r}_i\}) \cdot \mathbf{F}(\{\mathbf{R} - \mathbf{r}_i(-t)\})\rangle$$

and

$$\int_0^t dt' \, \eta(t') = D(t)$$

The trivial difference with respect to Ref. 20 follows from the application of the grand canonical ensemble in the present paper. Equation (45) can be transformed to the Markovian form by the method analogous to that used in Section 3. The resummed scattering operator contains terms proportional to all powers of the γ parameter. The first term of the expansion, which is proportional to γ^2, is identical with the $M^{(2)}(\mathbf{k}, \mathbf{P}, t)$ operator.

5. SUMMARY OF RESULTS

The aim of the present paper has been to discuss and to clarify the relations between the two formalisms of the kinetic theory. We have shown how the familiar method of the Zwanzig derivation of the kinetic equation may be modified so as to obtain the kinetic equation without convolution. We have also presented a new method of the derivation of such an equation by the resummation of the Zwanzig formulas. We have discussed the relations between the formalism of Fuliński, Kramarczyk, and Voss and the earlier results of the Cohen *et al.* It has also been shown that for projection operators such that $(1 - P) F_N(0) = 0$, the Kramarczyk–Voss equation and the resummed t-method of Ernst and Cohen give identical results. In general, the Kramarczyk–Voss formalism of projection operators is in the same relation to the Cohen–Ernst method as the Zwanzig projection operator technique is to the method of inverse operators (or, as is called by Ernst *et al.*,[3] to the resummed ϵ-method). From the discussion given in Section 2, it follows that the kinetic equations with and without convolution in time are fully equivalent and equally general.

The usual interpretation of the scattering operator $G(t)$ assumes that it is short-ranged in time, i.e., $G(t)$ approaches zero rapidly as t grows on the molecular (collision-time) scale. It also represents a "single event" whose unending repetition produces $f(t)$ from $f(0)$. The asymptotic (e.g., Boltzmann) scattering operator is obtained as $\tilde{G}(z = 0)$ or $\int_0^\infty dt\, G(t)$. On the other hand, $M(t)$ depends on the macroscopic time t and for this reason, it may be thought, contains fast, high-frequency events mixed together with slow, low-frequency processes. There is no indication of separation of time scales. However, repeated action of $M(t)$ on $f(0)$ also produces $f(t)$. The asymptotes at long times are obtained by the limit $t \to \infty$ in $M(t)$. The results were correct in the cases we examined.

We have also discussed the case of dilute gases and the case of the motion of a heavy particle in a fluid of light particles. On the basis of these two examples, we have displayed rather explicitly that, although the general forms forms of the Markovian and convolution equations are equivalent, this is no longer so when a certain approximation scheme is applied to the scattering operator. The convolution of the kinetic equation in the lowest-order approximation exhibits a more complicated dependence with respect to the expansion parameter than the Markovian kinetic equation in the same order of approximation. The last equation can be obtained from the former one if the "Markovianization" procedure is applied (for example, by the use of the Taylor expansion method) and only the lowest-order term with respect to the expansion parameter is retained.

The Markovian form of the kinetic equation is without doubt more closely related to the old kinetic equations, as for example, the Boltzmann or Fokker–Planck equation, and gives them in the lowest order of the appropriate approximation scheme, but, in general, it is not yet known which formalism will be more useful in the theory of transport processes.

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