QUANTUM-STATISTICAL EQUATION OF MOTION FOR NON-EQUILIBRIUM PROCESSES

R. DER and R. HABERLANDT

Zentralinstitut für Isotopen- und Strahlenforschung der AdW, 705 Leipzig, Permoserstr. 15, GDR

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We propose a new simple method to derive exact equations of motion for non-equilibrium processes which does not need projection operators. The connection with the formalism of Robertson is established.

In several papers it is shown that exact solutions of the Liouville equation can be constructed in such a manner that their time dependence is entirely determined by the expectation values $\langle F_n(\kappa)\rangle_t$ of a set of observables $F_n(\kappa)$ characterising the macroscopic state of the system at time t [1, 2]. Here we propose another method to derive exact equations of motion for the $\langle F_n(\kappa)\rangle_t$ which does not need projection operators.

As a starting point we use the formal solution of the Liouville equation

$$\rho(t) = U(t,0)\rho(0) \tag{1}$$

where $U(t,t')$ is the usual time development operator

$$\frac{\mathrm{d}}{\mathrm{d}t}U(t,t') = -\mathrm{i}L(t)U(t,t'), \qquad \frac{\mathrm{d}}{\mathrm{d}t'}U(t,t') = \mathrm{i}U(t,t')L(t') \tag{2}$$

and L is the Liouville operator $L(t)\ldots = \hbar^{-1}[H(t), \ldots]$.

We introduce a formal operator $\eta(t)$ fulfilling the following two conditions:
(i) $\eta(t)$ depends on time only implicitly through the set of $\langle F_n(\kappa)\rangle_t$, i.e., $\eta(t) = \eta\{\langle F_n(\cdot)\rangle_t\}$;
(ii) At time $t = 0$ η has to represent the desired initial density distribution, i.e., $\rho(0) = \eta(0)$.
Otherwise $\eta(t)$ can be chosen arbitrarily.

Now we use the identity

$$\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = -\mathrm{i}L(t)U(t,0)\eta(0) = -\mathrm{i}L(t)\eta(t) + \mathrm{i}L(t)\int_0^t \mathrm{d}t'\left[\frac{\mathrm{d}}{\mathrm{d}t'}U(t,t')\eta(t')\right] \tag{3}$$

and carry out the time derivation by means of (2) and

$$\frac{\mathrm{d}}{\mathrm{d}t}\eta(t) = \sum_n \int \mathrm{d}^3\kappa \frac{\delta}{\delta\langle F_n(\kappa)\rangle_t}\eta(t)\langle F_n(\kappa)\rangle_t^{\cdot} \tag{4}$$

where $\langle\ \rangle_t^{\cdot} = (\mathrm{d}/\mathrm{d}t)\langle\ \rangle$.

Multiplying both sides of (3) by $F_n(\kappa)$ and taking the trace we finally get

$$\begin{aligned}\langle F_n(\kappa)\rangle_t^{\cdot} = &-\mathrm{i}\,\mathrm{Tr}\{F_n(\kappa)L(t)\eta(t)\} - \int_0^t \mathrm{d}t'\,\mathrm{Tr}\{F_n(\kappa)L(t)U(t,t')L(t')\eta(t')\} \\ &+\mathrm{i}\int_0^t \mathrm{d}t' \sum_m \int \mathrm{d}^3\kappa'\,\mathrm{Tr}\{F_n(\kappa)L(t)U(t,t')\eta(t')\}\frac{\overleftarrow{\delta}}{\delta\langle F_m(\kappa')\rangle_{t'}}\langle F_m(\kappa')\rangle_{t'}^{\cdot}.\end{aligned} \tag{5}$$

Since $\eta(t)$ depends on the $\langle F_n(\kappa)\rangle_t$, (5) can be considered as the desired exact equations of motion. If wanted,

the time derivative on the r.h.s. can be eliminated by iteration or by formally considering (5) to be a system of linear Volterra equations of the second kind for the $\langle F_n(\kappa)\rangle_t^{\cdot}$ as the unknown functions.

As a special case $\eta(t)$ can be taken to be the information-theoretical ensemble $\sigma(t)$ used e.g. by Robertson. Then, from (5) we can obtain Robertson's equations of motion [2, eq. (29)]. This is achieved by observing that his time development operator $T(t, t')$ obeys the following integral equation

$$T(t, t') = U(t, t') + \mathrm{i}\int_{t'}^{t} \mathrm{d}t'' U(t, t'')P(t'')L(t'')T(t'', t') \tag{6}$$

where $P(t)$ is the projection operator.

Since (5) does not contain any projection operator we can calculate the kernels – choosing $\eta(t)$ as an information-theoretical ensemble – by use of Wick's theorem and perturbation theory. Thus we obtained a diagram expansion of these kernels, consisting of linked diagrams only.

As a first application we have derived a kinetic equation for the matrix elements of the single-particle density operator of an inhomogeneous gas interacting via two-body forces. In the momentum representation the matrix elements of $\rho^{(1)}(t)$ are given by

$$\langle p_1|\rho^{(1)}(t)|p_2\rangle = \mathrm{Tr}\,[a^{+}_{p_1} a_{p_2}\rho(t)] = f(p_1, p_2; t)$$

where a^{+}_{p} (a_p) creates (annihilates) a particle having momentum p. Thus the convenient observables of the system are given by the products $a^{+}_{p_1'} a_{p_2}$ and the ensemble $\eta(t)$ by

$$\eta(t) = \exp\{-\lambda_0(t) - \sum_{i,k} \lambda_{i,k} a^{+}_{p_i} a_{p_k}\}$$

the $\lambda_{i,k}$ being parameters which are eliminated afterwards by summing certain self energy structures in the diagram expansion.

From the renormalized diagram of lowest order the following kinetic equation is obtained

$$\begin{aligned}\frac{\partial}{\partial t} f(p_1, p_2; t) = &-\frac{\mathrm{i}}{2m}(p_1^2 - p_2^2) - \int_0^t \mathrm{d}t' \sum_{p_3 \cdots p_7} \langle p_1 p_5|V(t)K(t, t')|p_3 p_4\rangle\langle p_6 p_7|V(t')K(t', t)|p_2 p_5\rangle \\ &+ \langle p_1 p_5|K(t, t')V(t')|p_3 p_4\rangle\langle p_6 p_7|K(t', t)V(t)|p_2 p_5\rangle - \langle p_1 p_5|V(t)K(t, t')V(t')|p_3 p_4\rangle\langle p_6 p_7|K(t, t')|p_2 p_5\rangle \\ &- \langle p_1 p_5|K(t, t')|p_3 p_4\rangle\langle p_6 p_7|V(t')K(t', t)V(t)|p_2 p_5\rangle \cdot f(p_3, p_6; t')f(p_4, p_7; t')\end{aligned} \tag{7}$$

where m is the mass of one particle, $V(t)$ the interaction and $K(t, t')$ is the time development operator describing the scattering of two particles in free space. Both operators are written in interaction representation.

Because of the time integration (7) is a non-Markowian equation. After introducing Wigner functions one observes that this equation is also non-local. Neglecting the memory effects and the nonlocalities the classical Boltzmann equation is obtained from (7) by taking the limit $\hbar \to 0$.

As further applications we derived rate equations for chemical reactions and equations of motion for an oscillator in a bath. It should be mentioned that in the applications considered so far higher order terms containing secular divergencies cancel each other exactly or at least in a good approximation. This seems to be a general property of this expansion. More detailed information concerning the diagram expansion and its application will be given elsewhere.

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[1] E.g., D.N. Zubarev, Fortschr. d. Physik 18 (1970) 125, and references therein.
[2] B. Robertson, Phys. Rev. 144 (1966) 151.