PROJECTION-OPERATOR DETERMINATION OF KINETIC EQUATIONS FOR A SYSTEM OF MANY PARTICLES

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The projection-operator method worked out in general form by Nakajima and Zwanzig is used to construct the kinetic equations describing real physical systems. The method is generalized to the case of time-dependent projection operators which perform a nonlinear projection in functional phase space. The projection-operator method is used to develop a common method for finding collision operators in a system of particles characterized by different correlation properties. In examples, this common method is used to find modified microscopic Fokker–Planck, Vlasov, Boltzmann, and Landau collision operators.

1. Introduction

In this paper we will derive the kinetic equation for a many-particle medium by the projection-operator method. In other derivations of the kinetic equations, by Landau [1], Bogolyubov [2, 3], Kirkwood and Rice [4], Prigogine [5], and Balescu [6] among others, various assumptions about the properties of the systems were made at the outset, and a wide variety of approximations was used to take into account interactions in the medium. Typical approximations are an account of only binary collisions, a correlation-weakening condition, series expansion in terms of the density or a weak interaction, etc.

Because of these restrictions, a sufficiently general method which would satisfactorily describe condensed media (e.g., liquids) at all stages in the dyanmics of the motion and interaction of particles has not been derived. Accordingly, one of the problems of the statistical theory of irreversible processes is to find a common approach to studying the dynamic processes in multiparticle media.

A method which seems promising in this regard is the projection-operator method developed by Nakajima [7] and Zwanzig [8]. This method is based on an exact functional analysis of the kinetics of elements of the phase space, which govern the complete dynamics of the system. Although the equations obtained in the initial step of the theory seem at first blush slightly formal, the projection-operator method can be used for a quite rigorous and accurate description of interactions in the medium. The projection-operator method has the undisputed advantages of taking into account non-Markovian and Markovian temporal processes and of being compact, exceptionally simple, and mathematically elegant.

Among the disadvantages of this method, which are apparently only temporary, is the lack of specific results for real systems which could be used as building blocks. Below we attempt to fill this void, using the projection-operator method as a common method for finding kinetic equations for systems of many particles. In this manner more general results can be found; in particular, it will be possible to take into account in more detail than was previously possible equilibrium structural and dynamic temporal correlations in a medium.

2. Basic Kinetic Equation

We start from the classical Liouville equation* for N particles:

$$\frac{\partial f_N}{\partial t} = \hat{L}_N f_N, \quad \hat{L}_N = \sum_{j=1}^{N} -\frac{1}{m_j} \mathbf{p}_j \vec{\nabla}_j + \nabla_j U \cdot \vec{\nabla}_{p_j}, \tag{1}$$

* There is no particular difficulty in transforming to the quantum-mechanical case [9, 10]. This method is widely used, e.g., in the theory of spin-relaxation phenomena in NMR [11].

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$$U = \frac{1}{2}\sum_{i \neq j=1}^{N} \Psi(|r_i - r_j|). \tag{2}$$

Here r_i and p_i are the radius vector and momentum of particle i, U is the total potential energy for the N particles of the system; $\hat{L}_N$ is the Liouville operator; Γ_N is a phase point; and

$$f_N = f_N(\Gamma_N, t), \quad \Gamma_N = \{r_1, p_1; r_2, p_2; \ldots r_N, p_N\}.$$

The single-particle distribution function $f_1(q_1)$ and the kinetic equation for it can be found by the projection operation [12] (s = 1, 2, . . . , N – 1)

$$\begin{gathered} f_1 = \int d\Gamma_{N-1} \cdot f_N(\Gamma_N, t), \\ f_1 \sim \hat{\Pi}_1 f_N, \quad \hat{\Pi}_s = \hat{R}_s \hat{T}_s, \quad \hat{T}_s f_N(\Gamma_N, t) = \int d\Gamma_{N-s} f_N(\Gamma_N, t), \end{gathered} \tag{3}$$

where the integration is carried out over the phase space of N – s particles. Projection operator $\hat{\Pi}_S$ is generally a nonlinear operator [12]:

$$\hat{\Pi}_s f_N = (\hat{R}_s \hat{T}_s) f_N = \int d\Gamma_s f_N(\Gamma_N, t) \cdot \int d\Gamma_{N-s} f_N(\Gamma_N, t). \tag{4}$$

We can transform to a linear projection using

$$\hat{R}_s = \hat{R}_{s0} = f_{N-1}(\Gamma_{N-1}, 0) = f_{N-1}^{(0)} = \frac{f_N^{(0)}(\Gamma_N)}{f_1^{(0)}(\Gamma_1)}, \tag{5}$$

where the right side gives the initial values of the distribution functions. Since deviations from equilibrium are usually slight, we can write the initial conditions for any classical system on the basis of a canonical Gibbs ensemble:

$$f_n^{(0)}(\Gamma_n) = Z_N \int d\Gamma_{N-n} \exp\{-H_N / K_B T\}, \quad Z_N = \int d\Gamma_N \cdot e^{-H_N / K_B T}, \tag{6}$$

where H_N is the total Hamiltonian of the system.

Generally speaking, the choice of a particular operator $\hat{\Pi}_S$ depends on the particular problem. The general conditions are that [8, 12] this operator must be an idempotent operator and must leave the initial conditions invariant:

$$\hat{\Pi}_s^2 = \hat{\Pi}_s \text{ и } \hat{\Pi}_s f_N(\Gamma_N, 0) = f_N(\Gamma_N, 0). \tag{7}$$

Using Eqs. (1)-(7), we find the basic kinetic equation for $f_S = f_S(\Gamma_S, t)$ in general form:

$$\frac{\partial f_s}{\partial t} = \hat{A}_s(t) f_s(t) + \int_0^t \hat{\Gamma}_s(t, \tau) \cdot f_s(\tau) d\tau, \tag{8}$$

where $\hat{A}_S(t)$ is the Markovian collision integral and $\hat{\Gamma}_S(t, \tau)$ is the non-Markovian collision integral,

$$\begin{gathered} \hat{A}_s(t) = \hat{T}_s \hat{L}_N \hat{R}_s(t), \quad \hat{\Gamma}_s(t, \tau) = \hat{T}_s \hat{L}_N \hat{N}_s(t) \exp\left\{\int_\tau^t d\tau' \cdot \hat{N}_s(\tau')\right\} \hat{R}_s(\tau), \\ \hat{N}_s(t) = [1 - \hat{\Pi}_s(t)] \hat{L}_N - \frac{\partial \hat{\Pi}_s(t)}{\partial t}. \end{gathered} \tag{9}$$

No specific physical properties of the system have been stated up to this point. Equation (8) is a general equation, and by making specific assumptions we can work from it to obtain kinetic equations having various structures.

3. Derivation of the Fokker – Planck Equation for a Liquid

This particle system is characterized by strong correlations in the equilibrium state. It is convenient to choose a linear operator $\hat{\Pi}_S$:

$$\hat{\Pi}_s = \hat{\Pi}_s(0), \quad \hat{\Pi}_s f_N(t) = \frac{f_N^{(0)}(\Gamma_N)}{f_s^{(0)}(\Gamma_s) \cdot f_{N-s}^{(0)}(\Gamma_{N-s})} \cdot f_s(t). \tag{10}$$

For a spatially uniform liquid, we use Eqs. (1)-(10) to find the collision integrals for the single-particle problem:

$$A_1(t) = -\frac{1}{m}\boldsymbol{p}_1\nabla_1, \quad \hat{\Gamma}_1(0,0) = \gamma\vec{\nabla}_{p_1}(\boldsymbol{p}_1 + mK_BT\cdot\vec{\nabla}_{p_1}), \tag{11}$$

$$\gamma = \frac{1}{3m}(N/V)\int d\bar{r}\cdot g(\bar{r})\,\nabla_r^2\Psi(\bar{r}), \tag{12}$$

where we have introduced the radial distribution function g(r) for the particles in the liquid. Because of (11) and (12), we can write the equation in two forms; we find the first form by completely neglecting the time dependence of the non-Markovian collision integral at t

$$\frac{\partial f_1}{\partial t} + \frac{\boldsymbol{p}_1\vec{\nabla}_1}{m}f_1 = \gamma\int_0^t \vec{\nabla}_{p_1}(\boldsymbol{p}_1 + mK_BT\cdot\vec{\nabla}_{p_1})f_1(\boldsymbol{r}_1, \boldsymbol{p}_1; t-\tau)\,d\tau. \tag{13}$$

The other form for writing this equation is related to the fact that "Fokker–Planck collisions" are effective only over a time interval τ_r (where τ_r is the corresponding relaxation time), which characterizes the deviation of the system from an equilibrium Maxwell distribution. It is thus sufficient to take these collisions into account. In this case, for sufficiently long time intervals, the equation requires the usual Markovian form ($t \gg \tau_r$):

$$\frac{\partial f_1}{\partial t} + \frac{\boldsymbol{p}_1\nabla_1}{m}f_1 = \gamma\tau_r\vec{\nabla}_{p_1}(\boldsymbol{p}_1 + mK_BT\cdot\vec{\nabla}_{p_1})f_1. \tag{14}$$

4. The Self-Consistent Vlasov Field

The projection operator is assigned a nonlinear property which follows from the conditions of the problem:

$$\hat{\Pi}f_N(t) = f_{N-1}(t)\cdot\Gamma(N-1,1)f_1(t) = \left\{\int d\Gamma_1\cdot f_N(\Gamma_N, t)\right\}\Gamma(N-1,1)\left\{\int d\Gamma_{N-1}\cdot f_N(\Gamma_N, t)\right\}. \tag{15}$$

The structure factor $\Gamma(N-1, 1)$ is introduced to take approximate account of the correlation effects in the medium. For a rarefied gas, we have $\Gamma(N-1, 1) = 1$, while for a liquid we assume (if the first particle is fixed)

$$\Gamma(N-1, 1) = \prod_{j>1}^{N} g(|\boldsymbol{r}_1 - \boldsymbol{r}_j|). \tag{16}$$

For an equilibrium distribution we would use the approximation*

$$f_N^{(0)}(\Gamma_N) = f_{N-1}^{(0)}(\Gamma_{N-1})\Gamma(N-1,1)f_1^{(0)}(\Gamma_1). \tag{17}$$

Taking Eqs. (15)-(17) into account, we find an operator describing the self-consistent Vlasov field from Markovian collision integral (9) [14]; this operator differs from the ordinary operator in that the initial equilibrium correlations are taken into account:

$$\frac{\partial f_1}{\partial t} + \frac{1}{m}\boldsymbol{p}_1\vec{\nabla}_1 f_1 = (N-1)\int d\boldsymbol{r}_2 d\boldsymbol{p}_2 f_1(\boldsymbol{r}_2, \boldsymbol{p}_2; t)\cdot g(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$$
$$\nabla_1\Psi(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\,\nabla_{p_1}f_1(\boldsymbol{r}_1, \boldsymbol{p}_1; t) + \text{(the Fokker – Planck collision operator)}. \tag{18}$$

5. The Boltzmann Equation

This equation is found by a nonlinear projection in (15) from Markovian operator $\hat{A}_1(t)$ in Eq. (8) with the structure factor $\Gamma(N-1, 1) = 1$. Using the general commutation property for the operators in (3),

$$\hat{T}_s\hat{L}_N = \hat{L}_N\hat{T}_s + (N-s)\hat{\Phi}_s\hat{T}_{s+1},$$
$$\hat{\Phi}_s = \int d\boldsymbol{r}_{s+1}d\boldsymbol{p}_{s+1}\sum_{j=1}^{s}\nabla_j\Psi(|\boldsymbol{r}_j - \boldsymbol{r}_{s+1}|)\vec{\nabla}_{p_j}, \tag{19}$$

*Along with (16), this relation is equivalent to the ordinary superposition approximation [13], extended to the case of more than three particles.

we find

$$\hat{T}_1\hat{L}_N = -\frac{1}{m}\vec{p}_1\vec{\nabla}_1\hat{T}_1 + (N-1)\int dq_2\{\nabla_1\Psi(|r_1-r_2|)\nabla_{p_1} + \nabla_2\Psi(|r_1-r_2|)\nabla_{p_2}\}\hat{T}_2. \quad (20)$$

As in the Bogolyubov method [2, 3], we consider the particular case of the motion of only two objects, interacting by means of binary potential $\Psi(r_{12})$. Here we have the condition $\Gamma(N-1, 1) = 1$ for an arbitrary time t (including t = 0), by analogy with the two simultaneous Bogolyubov conditions [2]: the correlation-weakening and synchronization conditions. We can therefore write

$$\nabla_1\Psi(1, 2)\vec{\nabla}_{p_1} + \nabla_2\Psi(1, 2)\vec{\nabla}_{p_2} = \frac{1}{m}(p_{1\alpha}\vec{\nabla}_{1\alpha} + p_{2\alpha}\vec{\nabla}_{2\alpha}), \quad (21)$$

where α indicates that only binary collisions are taken into account here. The complete collision integral is

$$-\frac{1}{m}\vec{p}_1\vec{\nabla}_1 + (N-1)\int dr_{2\alpha}dp_{2\alpha}\left(\frac{p_{2\alpha}-p_{1\alpha}}{m}\right)\vec{\nabla}_{r_{2\alpha}}\{f_1(r_1, p_1; t)\, f_1(r_2, p_2; t)\}. \quad (22)$$

Transforming to a cylindrical coordinate system for the variables (x_2, y_2, z_2) in which the z axis is parallel to the momentum $p_2 - p_1$, and assuming the first particle to be incident on the second, we find the ordinary Boltzmann collision ($t \to \infty$, so we have $t \gg \tau_{coll}$):

$$\frac{\partial f_1}{\partial t} = (N-1)\int_0^\infty d\rho\cdot\rho\int_0^{2\pi} d\varphi\int dp_2\cdot\left|\frac{p_2-p_1}{m}\right|\{f_1(p_1', t)\, f_1(p_2', t) - f_1(p_1, t)\, f_1(p_2, t)\}, \quad (23)$$

where ρ is the impact parameter; φ is the scattering angle, the primed momenta correspond to the situation before the collision, and the unprimed momenta correspond to the situation after the collision. On the right side is a spatially homogeneous distribution; there is no particular difficulty in generalizing to the inhomogeneous case.

6. Modified Landau Collision Integral in a Liquid

Let us consider the evolution operator in non-Markovian integral (8). Using (9) and (19), and making use of the fact that the spatial distribution is assumed homogeneous and that the structure factor $\Gamma(N-1, 1)$ satisfies property (16), we find the last term in (8) to be

$$\hat{I}_1 = \int_0^t d\tau\hat{T}_1\hat{L}_N\exp\left\{\int_\tau^t d\tau'\hat{N}_1(\tau')\right\}\hat{N}_1(\tau)f_{N-1}(\tau)\Gamma(N-1, 1)f_1(\tau). \quad (24)$$

The subsequent calculation of the "effective" single-particle Liouville operator $\hat{N}_1(\tau)$ with (19) leads to

$$\hat{N}_1(\tau)f_{N-1}(\tau)\Gamma(N-1, 1)f_1(\tau) = \{\hat{L}_N - \hat{R}_{1\tau}[\hat{L}_1\hat{T}_1 + (N-1)\hat{\Phi}_1\hat{T}_2] - [[\hat{T}_{N-1}\cdot\hat{L}_N f_N(\tau)]]\,\hat{T}_1\}\hat{R}_{1\tau}. \quad (25)$$

where $\hat{R}_{1\tau} = f_{N-1}(\tau)\Gamma(N-1, 1)$. Here the double brackets limit the range of the Liouville operator $\hat{L}_N$; because of the spatial homogeneity, all terms contained in the operators $\hat{L}_1\hat{T}_1$ subsequently drop out. We then find

$$(25) = (\hat{L}_N - \hat{L}_{N-1})f_{N-1}(\tau)\Gamma(N-1, 1)f_1(\tau) - (N-1)f_{N-1}(\tau)\Gamma(N-1, 1)$$
$$\times\int dr_2dp_2\cdot\nabla_1\Psi(1, 2)\nabla_{p_1}f_1(1, \tau)\, g(1, 2)\, f_1(2, \tau). \quad (26)$$

The second term in (26) vanishes, since we have the following for a spatially homogeneous distribution:

$$\int dq_2\cdot\nabla_1\Psi(1, 2)f_1(1)\, g(1, 2)\, f_1(2) = 0. \quad (27)$$

Since the exponential evolution operator in (24) is complex, we will take into account in it only those operators which lead to free inertial motion of particles; i.e., we assume

$$\hat{N}_1(\tau) = -\sum_{j=1}^{N}\frac{1}{m_j}(\vec{p}_1\vec{\nabla}_1 + \vec{p}_2\vec{\nabla}_2). \quad (28)$$

Using (20) and (26)-(28) for sufficiently long time intervals ($t \to \infty$), we find

$$\hat{I}_1 = (N-1)\int dq_2 \cdot \nabla_1 \Psi(1,2)\nabla_{p_1}\int_0^t d\tau \cdot \exp\left[-\frac{\tau}{m}(p_1\vec{\nabla}_1 + p_2\vec{\nabla}_2)\right]$$

$$\times \nabla_1 \Psi(1,2)\, g(1,2)(\vec{\nabla}_{p_1} - \vec{\nabla}_{p_2}) f_1(1, t-\tau) f_1(2, t-\tau). \tag{29}$$

Since the exponential operator in (29) is a functional operator of a displaced argument, of the form

$$\exp(a\,\partial/\partial x) f(x) = f(x+a), \tag{30}$$

the general form of the collision integral is

$$\hat{I}_1 = (N-1)\int_0^\infty d\tau \int dr_2 dp_2 [\nabla_1 \Psi(1,2)\cdot\vec{\nabla}_{p_1}]\left[\nabla_1 \Psi\left(\left|r_{12} - \frac{\tau}{m} p_{12}\right|\right) g\left(\left|r_{12} - \frac{\tau}{m} p_{12}\right|\right)(\vec{\nabla}_{p_1} - \vec{\nabla}_{p_2})\right] f_1(1,t) f_1(2,t). \tag{31}$$

After carrying out all the averaging and introducing the binary-collision mechanism for the momentum distribution $\varphi(p_1, t)[f_1(1, t) = V^{-1}\varphi(p_1, t)]$, we find the Landau kinetic equation with a modified collision integral:

$$\frac{\partial \varphi(1,t)}{\partial t} = \frac{\partial}{\partial p_{1,\alpha}} \int dp_2 \cdot S_{\alpha,\beta}(p_1 - p_2)\left\{\frac{\partial \varphi(1,t)}{\partial p_{1\beta}} \cdot \varphi(2,t) - \varphi(1,t)\cdot\frac{\partial \varphi(2,t)}{\partial p_{2\beta}}\right\}, \tag{32}$$

$$S_{\alpha,\beta}(p) = \frac{\pi m}{2(V/N)} \cdot \frac{p^2 \cdot \delta_{\alpha\beta} - p_\alpha \cdot p_\beta}{p^3} \cdot \int_0^\infty d\rho \cdot \rho^3 \Phi(\rho),$$

$$\Phi(\rho) = \int_{-\infty}^{+\infty} \frac{\Psi'(\sqrt{\rho^2 + x^2})}{\sqrt{\rho^2 + x^2}}\, dx \cdot \int_{-\infty}^{+\infty} \frac{\Psi'(\sqrt{\rho^2 + z^2})}{\sqrt{\rho^2 + z^2}}\, g(\sqrt{\rho^2 + z^2})\, dz, \tag{33}$$

where x is the impact parameter. In the case of liquids the integration over the impact parameter is only over the interval (a, ∞), where a is the distance of closest approach. We can therefore qualitatively explain the elimination of the divergence at small distances which is typical of the Landau collision integral in the case of neutral gases and plasmas: it is due to the appearance of the radial distribution function g(r), which takes the liquid structure into account.

7. Conclusions

We have shown that the projection-operator method can be used as a common method for deriving the kinetic equations with modified Fokker–Planck, Vlasov, Boltzmann, and Landau collision integrals. These equations are microscopic equations and do not contain any phenomenological parameters. Interestingly, these equations are not only Markovian: they may also contain dynamic memory effects typical of non-Markovian processes. We should emphasize that the structure of a general non-Markovian collision operator is apparently such that in the case of a liquid the familiar Fokker–Planck operator is apparently only a "zeroth" approximation for a more complicated operator, which has not yet been determined in modern statistical theory. We can draw an analogy with the situation in rarefied gases: use of the projection-operator method shows that, e.g., the modified Landau collision integral serves as a "zeroth approximation" for the Lennard–Balescu collision integral [3, 5, 6]. In this case the approximation consists of neglecting the interaction of particles in the evolution operator for the system.

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