On the Kinetic Equation Nonlocal in Time
for the Generalized Self-Diffusion Process*

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The dynamical structure of equilibrium fluids is conveniently described by the van Hove functions $G(r, t)$ and $G_s(r, t)$. The Fourier transforms $S(k, \omega)$ and $S_s(k, \omega)$ are known experimentally in quite a few instances. For small k and ω, $S(k, \omega)$ approaches its hydrodynamic form reflecting the long-time behaviour of $G(r, t)$. The short-time behaviour of $G(r, t)$ is closely related to the sum rules for $S(k, \omega)$, often used in assesment and correlation of experimental results. In this paper we discuss an exact kinetic equation valid on any time scale, directly related to the function

$$I_s(k, t) = \int dr \, e^{ikr} G_s(r, t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} S_s(k, \omega), \tag{1}$$

$$I_s(k, t) = \overline{e^{-ikr_1(t)} e^{ikr_1(0)}}, \tag{2}$$

where the bar stands for the average in the canonical ensemble.

It was Nelkin and his coworkers [1] who first introduced an auxiliary distribution function $f_s(\mathbf{k}, \mathbf{v}, t)$, a function of the velocity $\mathbf{v}$, so defined that

$$I_s(k, t) = \int d\mathbf{v} \, f_s(\mathbf{k}, \mathbf{v}, t). \tag{3}$$

As noted in a preliminary report [2], it is possible to construct a kinetic equation of a general form

$$\left(\frac{\partial}{\partial t} + i\mathbf{k}\mathbf{v} \right) f_s(\mathbf{k}, \mathbf{v}, t) = \int_0^t d\tau \, G(\mathbf{k}, \mathbf{v}, \tau) f_s(\mathbf{k}, \mathbf{v}, t - \tau) \tag{4}$$

with a time-dependent kernel $G(\mathbf{k}, \mathbf{v}, t)$. General kinetic equations with convolution time integral (thus nonlocal in time) were first derived and discussed by Prigogine

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and his coworkers [3]. For the particular case considered here, the kernel G is *"dressed"* and not *"bare"*, as it contains also the statistical averages with full intermolecular potential. The kinetic equation is linear and no additional linearization is necessary. No additional terms corresponding to the Prigogine–Résibois "destruction term" make their appearance. Finally, the sum rules for $S_s(k, \omega)$ corresponding I_s to the short-time behaviour of F_s and of f_s, are verified exactly.

The derivation of the kinetic Eq. (4) is made possible by our ability to guess the appropriate projection operator. The canonical-ensemble definition of f_s is

$$f_s(\mathbf{k}, \mathbf{v}, t) = \int d\mathbf{r}^N \, e^{-i\mathbf{k}\mathbf{r}_1} \int dv_{\neq 1}^{N-1} F_N(t), \tag{5}$$

where $F_N(t)$ verifies the Liouville equation

$$F_N(t) = e^{tK_N} F_N(0), \tag{6}$$

with

$$F_N(0) = e^{ikr_1} f_N(0) \tag{7}$$

and $f_N^{(0)}$ is the full N-particle equilibrium canonical distribution function.

Here

$$K_N = \sum_{i=1}^{N} \left(\mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \frac{\partial}{\partial \mathbf{p}_i} \right), \qquad \mathbf{v}_i = m^{-1}\mathbf{p}_i, \tag{8}$$

$\mathbf{v}_i$, $\mathbf{r}_i$ are the velocity and position of Particle i of mass m, and $\mathbf{F}_i$ is the force due to all other particles. At $t = 0$,

$$f_s(\mathbf{k}, \mathbf{v}, 0) = \varphi_M(v) \equiv \sqrt{\frac{\beta m}{2\pi}} \, e^{-\beta \frac{1}{2}mv^2}, \tag{9}$$

$$f_s(\mathbf{r}, \mathbf{v}, 0) = \delta(\mathbf{r} - \mathbf{r}^0) \, \varphi_M(v). \tag{10}$$

Thus the generalized diffusion described by f_s and I_s can also be viewed as a relaxation from an initial state in which Particle 1 is fixed at $\mathbf{r}^0$ and the $N-1$ particles are canonically distributed. The projection operator we use [2] is

$$P = ><, \tag{11}$$

$$> = e^{ikr_1} f_N^0 / \varphi_M(\mathbf{v}_1), \tag{12}$$

$$< = \int d\mathbf{r}^N \, e^{-i\mathbf{k}\mathbf{r}_1} \int dv_{\neq 1}^{N-1}, \tag{13}$$

$$PP = P \qquad PF_N(t) = > f_s(k, v, t). \tag{14}$$

In addition,

$$QF_N(0) = 0, \qquad Q = 1 - P, \tag{15}$$

which secures the absence of a "destruction-type" term. As Zwanzig [4] has shown, the convolution type kinetic equation can be readily obtained by applying to the Lionville equation the operators P and Q. Introducing the Laplace transforms by

$$\tilde{X}(z) = \int_0^\infty dt \, e^{izt} X(t), \qquad \text{Im } z > 0, \tag{16}$$

we have

$$(-iz + K_N) \tilde{F}_N = F_N(0) \tag{17}$$

$$izP\tilde{F}_N - PF_N(0) = PK_N P\tilde{F}_N + PK_N Q\tilde{F}_N \tag{18}$$

$$izQ\tilde{F}_N - QF_N(0) = QK_N P\tilde{F}_N + QK_N Q\tilde{F}. \tag{19}$$

Eliminating $Q\tilde{F}_N$, we find

$$-izP\tilde{F}_N - PF_N(0) - PK_N P\tilde{F}_N = PK_N Q \frac{1}{-iz + QK_N Q} QK_N P\tilde{F}_N, \tag{20}$$

which is the desired kinetic equation. This derivation is in fact well known for the case of a decay of a prepared state [5]. In our case,

$$PK_N P\tilde{F}_N = > i\mathbf{k}\mathbf{v}_1 \tilde{f}_s(\mathbf{v}_1) \tag{21}$$

and the kinetic equation takes the form

$$(-iz + i\mathbf{k}\mathbf{v}_1) f_s(\mathbf{k}, \mathbf{v}_1, z) - f_s(t = 0) = \left\langle K_N Q \frac{1}{-iz + QK_N Q} QK_N \right\rangle f_s(\mathbf{k}, \mathbf{v}_1, z) \tag{22}$$

The first desirable feature is the trivial ease with which the case of noninteracting particles is obtained; the r.h. s is equal to zero, and

$$(-iz + i\mathbf{k}\mathbf{v}_1) f_s(\mathbf{v}_1) - f_s(t = 0) = 0. \tag{23}$$

This is to be contrasted with the so-called memory functions, which were introduced to simulate the convolution integral on the r.h.s of (4), avoiding simultaneously the velocity-dependence of f_s. One writes (for our case of I_s)

$$\frac{\partial}{\partial t} I_s(k, t) = \int_0^t d\tau \, K(\tau) I_s(t - \tau), \tag{24}$$

hoping that $K(t)$ would show a simpler structure than I_s [6]. Unfortunately, already for the case of ideal noninteracting gas, where $I_s(k, t)$ is a known (gaussian) function, the apparent simplicity of (24) breaks down, because $K(t)$ cannot be expressed in terms of elementary functions and no interpretation of it has ever been suggested.

The second desirable feature of (4) is that the short-time behaviour of f_s is reproduced exactly. This is to be contrasted with the Résibois kinetic equations which for our case take the form, also exact at all times,

$$\left(\frac{\partial}{\partial t} + i\mathbf{kv}\right) f_s(t) = \int_0^t d\tau\, \psi(\tau) f_s(t - \tau) + \mathscr{D}(t). \tag{25}$$

The operators ψ and D are, however, so defined that at short times both diverge for ordinary intermolecular potentials. This happens when one attempts a power series development $\psi(\tau) = \psi(0) + \tau\psi' + (\tau^2/2!)\,\psi'' + \cdots$ and $\mathscr{D}(t) = D_0 + tD_1 + (t^2/2)\,D_2 + \cdots$; all coefficients $\psi^{(n)}$ and D_n diverge for the simple reason that the r-integrals in the position space are not "protected" by any $\exp(-\beta u_{ij})$ factors. Thus, integrals

$$\frac{1}{V^N} \int d\mathbf{r}^N\, e^{-i\Sigma \mathbf{k}_j \mathbf{r}_j} \mathbf{F}_{1j}\mathbf{F}_{1l} \cdots e^{i\Sigma \mathbf{k}_j{'} \mathbf{r}_j} \frac{\partial}{\partial \mathbf{p}_j} \frac{\partial}{\partial \mathbf{p}_l} \cdots$$

will not be finite for intermolecular potentials which do not have Fourier transforms. No resummation (similar to the one that is performed to obtain the Boltzmann equation) is possible since $\psi(0)$ contains two vertices (two forces $\mathbf{F}_{ij}\mathbf{F}'_{ij}$) and no more, $\psi''(0)$ contains four forces $\mathbf{F}_{ij}$, etc.

When the r.h.s of (25) is combined together to yield (4), no divergent terms appear, as will be shown below. Therefore, at least in some cases, the division of r.h.s. into a diagonal operator (ψ) + destruction term ($\mathscr{D}$) may be undesirable. The immediate cause of these short-time divergencies is remedied by the introduction of dressed operators like G, instead of bare operators such as ψ. Inverting the Laplace transforms in (22), we find Eq. (4) with

$$G(\tau) = \langle K_N Q\, e^{-\tau Q K_N Q}\, Q K_N \rangle \tag{26}$$

For time $t = 0$,

$$G(0) = \langle K_N Q K_N \rangle = \langle K_N K_N \rangle - \langle K_N \rangle\langle K_N \rangle \tag{27}$$

The meaning of $\rangle$ and $\langle$ is given by Eqs. (12) and (13). Thus,

$$G(0) = \int d\mathbf{r}^N\, e^{-i\mathbf{kr}_1} \int d\mathbf{v}_{\neq 1}^{N-1} [K_N K_N - (i\mathbf{kv}_1)^2]\, e^{i\mathbf{kr}_1} f_N{}^0/\varphi_M(v_1)$$

$$= \overline{\mathbf{F}_1\mathbf{F}_1} : \frac{\partial}{\partial \mathbf{p}_1}\left(\beta\mathbf{v}_1 + \frac{\partial}{\partial \mathbf{p}_1}\right). \tag{28}$$

It is remarkable that the exact $G(0)$ is identical with the Fokker–Planck operator with a friction coefficient expressed by the canonical average of $\mathbf{F}_1(t = 0) \mathbf{F}_1(t = 0)$. It is therefore tempting to approximate $G(\tau)$ by

$$G^{FP}(\tau) = \xi(\tau, \mathbf{p}_1) : \frac{\partial}{\partial \mathbf{p}_1} \left(\beta \mathbf{v}_1 + \frac{\partial}{\partial \mathbf{p}_1} \right) \tag{29}$$

with

$$\xi(\tau, \mathbf{p}_1) = \int d\mathbf{r}^N \, d\mathbf{v}^{N-1} \, \mathbf{F}_1(\tau) \, \mathbf{F}_1(0) \, f_N{}^0 / \varphi(v_1).$$

This would, however, hardly represent a good approximation at long times for a Particle 1 identical to the fluid particles. Similar approximation was used by Akcasu et al. [7] who introduced a velocity-dependent time-independent friction coefficient. From the general form of $G(t)$ it is clear that a time-dependent ξ would represent a superior approximation.

The general structure of $G(\tau)$ can be analysed along the following lines:
The coefficients G_n in the power series

$$G(\tau) = \sum_{n=0}^{\infty} \frac{(-\tau)^n}{n!} \, G_n \tag{30}$$

can be expressed as

$$G_n = \sum_{\{P\}} (-)^P \prod A_j , \tag{31}$$

where the sum is over all partitions of the number $n + 2$ into a set of integers $\{j\}$, P is the number of partitions made. Thus,

$$
\begin{aligned}
G_1 &= A_3 - A_2 A_1 - A_1 A_2 + A_1 A_1 A_1 , \\
G_2 &= A_4 - A_3 A_1 - A_1 A_3 - A_2 A_2 + A_2 A_1 A_1 + A_1 A_2 A_1 + A_1 A_1 A_2 - A_1{}^4 ,
\end{aligned}
\tag{32}
$$

etc. The operators A_j do not commute, $A_1 = i\mathbf{k}\mathbf{v}_1$, and

$$A_j = \langle K_N{}^j \rangle. \tag{33}$$

Several terms besides G_0 have been calculated by R. Wojnar [8]. For example,

$$G'(0) = G_1 = \overline{\mathbf{F}_1\mathbf{F}_1} : \frac{\partial}{\partial \mathbf{p}} (i\mathbf{k}\mathbf{v}) \left(\beta \mathbf{v} + \frac{\partial}{\partial \mathbf{p}} \right). \tag{34}$$

The expressions for $G^{II}(0)$, $G^{III}(0)$ and $G^{IV}(0)$ are already quite complex. Another representation of the operator $G(\tau)$ is the following

$$G(\tau) = \langle K_N \exp - \tau [K_N - \langle K_N \rangle] (K_N - \langle K_N \rangle) \rangle. \tag{35}$$

In our case, $\langle K_N \rangle = i\mathbf{k}\mathbf{v}_1$, and

$$G(\tau) = \langle K_N e^{-\tau(K_N - i\mathbf{k}\mathbf{v}_1)}(K_N - i\mathbf{k}\mathbf{v}_1)\rangle. \tag{36}$$

Now, however, the factor $\exp(i\mathbf{k}\mathbf{r}_1)$ contained in $\rangle$ can be commuted with $K_N - i\mathbf{k}\mathbf{v}_1$, as

$$(K_N - i\mathbf{k}\mathbf{v}_1)\, e^{i\mathbf{k}\mathbf{r}_1} = e^{i\mathbf{k}\mathbf{r}_1} K_N \tag{37}$$

and hence

$$G(\tau) = \int d\mathbf{r}^N\, d\mathbf{v}_{\neq1}^{N-1}(K_N - i\mathbf{k}\mathbf{v}_1)\, e^{-\tau K_N} K_N\, \frac{f_N^{\,0}}{\varphi_M(v_1)} \tag{38}$$

or

$$G(\tau) = \int d\mathbf{r}^N\, d\mathbf{v}_{\neq1}^{N-1}\, \frac{f_N^{\,0}}{\varphi_M(\mathbf{v}_1)}\, (K_{N}{}' - i\mathbf{k}\mathbf{v}_1)\, e^{-\tau K_{N}{}'} K_{N}{}', \tag{39}$$

with

$$K_{N}{}' = K_N - \mathbf{F}_1 \cdot \beta \mathbf{v}_1\,.$$

As a first step towards the examination of dense systems, we are currently investigating the binary collision limit, for which

$$G_{\text{Binary}}(\tau) = \iiint d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_2\, e^{-i\mathbf{k}\mathbf{r}_1} K_2 e^{-\tau(K_2 - i\mathbf{k}\mathbf{v}_1)}(K_2 - i\mathbf{k}\mathbf{v}_1)\, e^{i\mathbf{k}\mathbf{r}_1} g_2(r_{12})\, \varphi_M(\mathbf{v}_2),$$

where $g_2(r)$ is the equilibrium radial distribution function equal to $\exp -\beta u(r)$ in the low density limit. The particular case of the Lorentz gas (light Particle 1, infinitely heavy scatterers) is amenable to numerical computations. For the
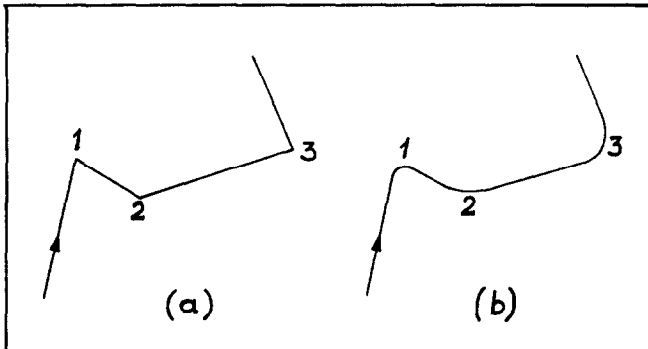

FIGURE 1

hard-sphere potential $u(r_{12})$, it can be shown by a direct calculation that $\tilde{G}_{\text{Binary}}(z)$ reduces to the ordinary Boltzmann (linearized) operator, no matter what values are taken by k and z (Im $z > 0$). For this case and for the Lorentz gas, the kinetic equation can be solved explicitly. When we superimpose on the hard core an attractive potential, the trajectory of 1 is modified (see Fig. 1), and it will be instructive to see the k and z dependence of $\tilde{G}$ for such a particularly simple case, as well as the modification of k and z dependence of $\tilde{f}_s(\mathbf{k}, \mathbf{v}, z)$, thus introduced.

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