

# KINETIC EQUATION FOR THE DILUTE BOLTZMANN GAS IN AN EXTERNAL FIELD\*

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(Received May 7, 2018)

We report a kinetic equation for an auxiliary distribution function  $f(\mathbf{k}, \mathbf{v}_1, t)$  which yields the intermediate scattering function  $I_s(\mathbf{k}, t)$ . To this end, the projection operator proposed by Stecki was applied. The scattering operator was given in explicit form in the limit of low density gas. The general kinetic equation was next specialized for the case of Lorentz gas.

DOI:10.5506/APhysPolB.49.905

## 1. Introduction

Marian Smoluchowski has described and discussed a diffusion process evolving in an external field of forces [1–3]. The problem belongs to the non-equilibrium statistical mechanics and can be studied by two different methods: numerical calculations and theory of kinetic equations.

The first method was substantially developed by Rahman, who applied numerical integration of Newtonian equations of motion to simulate the classical dynamics of a liquid system with arbitrary continuous interatomic potentials [4]. Rahman calculated the diffusion coefficient in a system of argon atoms interacting through a Lennard–Jones potential. This was a groundbreaking paper as it showed that the diffusion and structural evolution of small molecules takes place by a series of small, highly coordinated motions of neighbouring molecules, *cf.* also [5]. A discussion of Rahman’s motivations, the depth of his investigation, and the legacy that both the methodology and the style of investigation is given in [6].

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\* Presented at the XXX Marian Smoluchowski Symposium on Statistical Physics, Kraków, Poland, September 3–8, 2017.

This paper deals with the second method. A general kinetic equation for the time evolution of a marked particle in a fluid has been derived in several ways. The derivations lead to equations which are non-local in time according to the discussion developed by Kubo [7–11]. It is generally accepted that the Fourier transform of the one particle distribution function  $f(\mathbf{r}_1, \mathbf{v}_1, t)$  denoted by  $\tilde{f}(\mathbf{k}, \mathbf{v}_1, t)$  satisfies the following linear kinetic equation:

$$\left( \frac{\partial}{\partial t} + i\mathbf{k}\mathbf{v}_1 \right) f(\mathbf{k}, \mathbf{v}_1, t) = \int_0^t d\tau \mathcal{G}(\mathbf{k}_1, \tau) f(\mathbf{k}, \mathbf{v}_1, t - \tau), \quad (1)$$

where

$$F_N(t) = e^{-tK_N} F_N(0) \quad \text{and} \quad F_N(0) = e^{i\mathbf{k}\mathbf{r}_1} \varphi_M(v_1) \dots \varphi_M(v_N) \frac{e^{-\beta U}}{Q}, \quad (2)$$

and  $\varphi_M(v_i)$  is the Maxwell distribution function for the velocity  $v_i$ .

$$\varphi_M(v_i) = \left( \frac{\beta m_i}{2\pi} \right)^{3/2} e^{-\beta m_i v_i^2 / 2}, \quad (3)$$

$\beta^{-1} = k_B T$ , with  $k_B \approx 1.3806 \times 10^{-23} \text{ J/K}$ ,  $T$  being the equilibrium absolute temperature, while

$$U = \sum_{j=i+1}^N \sum_{i=1}^{N-1} u(|\mathbf{r}_i - \mathbf{r}_j|) \equiv \sum_{i<j} u_{ij}, \quad (4)$$

where  $u_{ij}$  is the interaction potential between particles No.  $i$  and No.  $j$ . Moreover,  $Q$  is the configurational sum of states

$$Q = \int e^{-\beta U} d\mathbf{r}^N. \quad (5)$$

The vectors  $\mathbf{r}_i$  and  $\mathbf{v}_i$ ,  $i = 1, 2, \dots, N$  denote the position and velocity of the particle No.  $i$ . The integration is performed over the whole configurational space, we write  $d\mathbf{r}^N = d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$ .

For the brevity sake, in Eq. (1) and further, the tilde sign above the letter  $f$  is omitted. The function  $f(\mathbf{k}, \mathbf{v}_1, t)$  satisfies the initial condition

$$f(\mathbf{k}, \mathbf{v}_1, 0) = \varphi_M(v_1) \quad (6)$$

and has been so constructed as to yield the intermediate self-scattering function  $I_s(\mathbf{k}, t)$ , cf. [12].

The scattering operator  $\mathcal{G}(\mathbf{k}_1, t)$  is expressed by the  $N$ -particle Liouville operator

$$K_N \equiv \sum_{i=1}^N \left( \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} \frac{1}{m_i} \frac{\partial}{\partial \mathbf{v}_i} \right). \quad (7)$$

A kinetic equation of the form of (1) was derived by Stecki using a projection operator method [13]. A binary collision operator has also been derived by Altenberger [14, 15]. It was shown by Narbutowicz that this equation reduces to the Fokker–Planck-type equation as a particular case [16]. The projection operator method was applied also by Chong *et al.* to derive an equation for the time-dependent pair distribution function [17]. These all calculations were performed under assumption of the linear response theory of Kubo.

The projection operator method was initiated by Zwanzig to derive a master equation, [18, 19], and has found a wide applications. The Zwanzig projection operates in the linear space of phase-space functions and projects onto the linear subspace of *slow* phase-space functions.

One can add that the terminology Liouville’s operator or Liouville’s equation is a customary only. Although the equation is usually referred to as the “Liouville’s equation”, it was Gibbs who was the first to recognize the importance of this equation as the fundamental equation of statistical mechanics [20, 21]. It is referred to as the Liouville equation because its derivation for non-canonical systems uses an identity first derived by Liouville in 1838 [22].

Liouville’s operator was introduced in reality by Koopman in 1931 [23]. In mathematics, and in particular functional analysis, the shift operator also known as translation operator is an operator that takes a function  $f(x)$  to its translation  $f(x + a)$ . In time series analysis, the shift operator is called the lag operator.

The integro-differential equation (1) can be simplified in two limit cases: the Lorentz gas, in which only one particle has finite mass  $m$  and all remaining in number  $N - 1$  particles are immobile, and the gas of Brownian movement, in which the mass of a Brownian particle is much greater than the masses of remaining  $N - 1$  particles. The first case is treated in this contribution, in which the influence of the exterior potential  $U^{\text{ext}}$  on the gas behaviour is investigated.

## 2. The system and Liouville’s operator

### *The system*

Consider a fluid of  $N$  particles, numbered by  $i = 1, 2, \dots, N$ , and closed in the volume  $\Omega$  with the boundary  $\partial\Omega$ . The mass of the particle  $i$  is  $m_i$ ,

the velocity  $\mathbf{v}_i$ , the momentum  $\mathbf{p}_i = m_i \mathbf{v}_i$ . The quantities  $\mathbf{r}_i$  and  $\mathbf{p}_i$ ,  $i = 1, 2, \dots, N$  denote the position and momentum of the  $i^{\text{th}}$  particle

$$\mathbf{r}_i = (r_{i1}, r_{i2}, r_{i3}) \equiv (r_{i\alpha}) \quad \text{and} \quad \mathbf{p}_i = (p_{i1}, p_{i2}, p_{i3}) \equiv (p_{i\alpha}), \quad \alpha = 1, 2, 3.$$

The particles are interacting by the radially symmetric potential  $u_{ij}(r_{ij})$ , with  $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ , subdued to the external potential  $U^{\text{ext}}$ . The Hamiltonian of the system

$$H = H^0 + U \quad \text{with} \quad U \equiv U^{\text{fl}} + U^{\text{ext}},$$

$$H^0 = \sum_{i=1}^N \frac{1}{2} m_i v_i^2, \quad U^{\text{fl}} = \sum_{i=2}^{N-1} \sum_{j=i+1}^N u_{ij}(r_{ij}) \quad \text{and} \quad U^{\text{ext}} = \sum_{n=1}^N U_n(\mathbf{r}_i), \quad (8)$$

where  $H^0$  is the kinetic energy,  $U^{\text{fl}}$  is the potential of binary interactions of the fluid particles, and  $U^{\text{ext}}$  represents an external potential, the term absent in potential (4). For simplicity of boundary conditions, we assume that  $U^{\text{fl}} = 0$  on the boundary  $\partial\Omega$  of the volume  $\Omega$ . Then, by Gauss' theorem

$$\int_{\Omega} e^{-\beta U} \frac{\partial U}{\partial \mathbf{r}_1} d\mathbf{r}_1 = -\frac{1}{\beta} \int_{\Omega} \frac{\partial}{\partial \mathbf{r}_1} (e^{-\beta U}) d\mathbf{r}_1 = -\frac{1}{\beta} \int_{\partial\Omega} e^{-\beta U^{\text{ext}}} \mathbf{n} dS \quad (9)$$

or, by the same theorem

$$\int_{\Omega} e^{-\beta U} \frac{\partial U}{\partial \mathbf{r}_1} d\mathbf{r}_1 = \int_{\Omega} e^{-\beta U^{\text{ext}}} \frac{\partial U^{\text{ext}}}{\partial \mathbf{r}_1} d\mathbf{r}_1 \quad (10)$$

what means that the average force acting on the particle No. 1 comes from the external potential only.

The function  $f_N^0$  is the full equilibrium (canonical) distribution function

$$f_N^0 = f_N^0(\mathbf{v}^N, \mathbf{r}^N) \equiv \prod_{i=1}^N \varphi_M(v_i) \frac{e^{-\beta U}}{Q}, \quad (11)$$

where  $\mathbf{v}^N = (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_N)$ ,  $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ .

We admit that the function  $f_N^0$  describes the distribution of  $N$  particles in the phase space at the time instant  $t = 0$ .

### *Liouville's operator*

We introduce Liouville's operator

$$K_N \equiv \sum_{i=1}^N \left( \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} \frac{1}{m_i} \frac{\partial}{\partial \mathbf{v}_i} \right) \quad (12)$$

and specify the potential  $U$  according to Hamiltonian (8)

$$K_N \equiv K_N^0 - \sum_{i < j} \theta_{ij} - \sum_i \frac{\partial U_i(\mathbf{r}_i)}{\partial \mathbf{r}_i} \frac{1}{m_i} \frac{\partial}{\partial \mathbf{v}_i} \tag{13}$$

with

$$K_N^0 \equiv \sum_{i=1}^N \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} \quad \text{and} \quad \theta_{ij} \equiv \frac{\partial u_{ij}}{\partial \mathbf{r}_i} \left( \frac{1}{m_i} \frac{\partial}{\partial \mathbf{v}_i} - \frac{1}{m_j} \frac{\partial}{\partial \mathbf{v}_j} \right). \tag{14}$$

We easily verify that  $K_N f_N^0 = 0$  and

$$K_N f_N^0(\dots) = f_N^0 K_N(\dots) \tag{15}$$

what means that the operator  $K_N$  is commuting with the equilibrium distribution  $f_N^0$ .

### 3. Stecki's projection operator

The evolution of  $N$ -particle system is described by Liouville's equation for the probability density function  $f_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N, t)$  in  $6N$ -dimensional phase space. Namely, Liouville's equation describes the time evolution of the phase-space distribution function

$$\frac{\partial f_N}{\partial t} = -K_N f_N.$$

Applying Koopman's shift operator, after [13], the function

$$F_N(t) = e^{-tK_N} F_N(0) \tag{16}$$

is defined, where

$$F_N(0) = e^{i\mathbf{k}_1 \mathbf{r}_1} f_N^0. \tag{17}$$

Then Fourier's transform of the one-particle distribution function is

$$f(\mathbf{k}, \mathbf{v}_1, t) = \int_{\Omega} d\mathbf{r}_1 e^{-i\mathbf{k}\mathbf{r}_1} \int_{\Omega^{N-1} \times \mathbb{R}^{3(N-1)}} d\mathbf{v}^{N-1} d\mathbf{r}^{N-1} F_N(t). \tag{18}$$

In relation (18) and below, integrating  $d\mathbf{r}_1$ , also  $d\mathbf{r}_i, i = 2, \dots, N$ , is performed over the volume  $\Omega$ , while integrating  $d\mathbf{v}_1$ , also  $d\mathbf{v}_i, i = 2, \dots, N$ , is performed over the whole space  $\mathbb{R}^3$ .

The function  $f(\mathbf{k}, \mathbf{v}_1, t)$  satisfies the initial condition

$$f(\mathbf{k}_1, \mathbf{v}_1, 0) = \varphi_M(v_1). \tag{19}$$

In definition (16), the potential  $U$  is given by the sum of  $U^{\text{fl}}$  and  $U^{\text{ext}}$ , cf. relation (6). Now, Stecki's projection operator reads, cf. [13],

$$\mathcal{P} \equiv e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1}, \tag{20}$$

where  $\mathbf{v}^N \equiv (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_N)$ , and  $\mathbf{r}^N \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ . Moreover,  $d\mathbf{v}^{N-1} \equiv d\mathbf{v}_2 d\mathbf{v}_3 \dots d\mathbf{v}_N$  and  $d\mathbf{r}^N \equiv d\mathbf{r}_1 d\mathbf{r}_1 \dots d\mathbf{r}_N$ . We observe that

$$\begin{aligned} \mathcal{P}F_N(t) &= e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} F_N(t) \\ &= e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, t), \end{aligned} \tag{21}$$

where definition (18) was exploited. In particular, for  $t = 0$ ,

$$\mathcal{P}F_N(0) = e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, 0) = F_N(0) \tag{22}$$

by condition (19) and definition (17). Hence,  $(1 - \mathcal{P})F_N(0) = 0$ . Moreover,

$$\begin{aligned} \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} \mathcal{P}F_N(t) &= \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} \\ \times e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, t) &= f(\mathbf{k}, \mathbf{v}_1, t) \end{aligned} \tag{23}$$

because

$$\int d\mathbf{v}^{N-1} d\mathbf{r}^N \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} = 1. \tag{24}$$

We write Liouville's equation for the function  $F_N(t)$

$$\frac{\partial F_N(t)}{\partial t} = -K_N F_N(t)$$

in the form of

$$\begin{aligned} \frac{\partial}{\partial t} [\mathcal{P}F_N(t)] &= -\mathcal{P}K_N \mathcal{P}F_N(t) - \mathcal{P}K_N (1 - \mathcal{P})F_N(t), \\ \frac{\partial}{\partial t} [(1 - \mathcal{P})F_N(t)] &= -(1 - \mathcal{P})K_N \mathcal{P}F_N(t) - (1 - \mathcal{P})K_N (1 - \mathcal{P})F_N(t). \end{aligned}$$

Hence,

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{P}F_N(t) &= -\mathcal{P}K_N \mathcal{P}F_N(t) \\ &+ \mathcal{P}K_N \int_0^t d\tau e^{-\tau(1-\mathcal{P})K_N} (1 - \mathcal{P})K_N \mathcal{P}F_N(t - \tau). \end{aligned} \tag{25}$$

Substitute  $\mathcal{P}F_N(t)$  by Eq. (21), multiply both sides by  $\exp(-i\mathbf{k}\mathbf{r}_1)$  and integrate over the whole phase space, with except of velocity  $\mathbf{v}_1$ . We have

$$\int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} \frac{\partial}{\partial t} \mathcal{P} F_N(t) = \frac{\partial}{\partial t} f(\mathbf{k}, \mathbf{v}_1, t)$$

as the  $\mathcal{P}$  does neither depend on the time  $t$  nor on the velocity  $\mathbf{v}_1$ , and

$$\begin{aligned} & \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} \mathcal{P} K_N \mathcal{P} F_N(t) \\ &= i\mathbf{k}v_1 f(\mathbf{k}, \mathbf{v}_1, t) + \mathbf{F}_1^{\text{ext}} \left( \beta\mathbf{v}_1 + \frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \right) f(\mathbf{k}_1, \mathbf{v}_1, t), \end{aligned}$$

where, cf. Eq. (10),

$$\mathbf{F}_1^{\text{ext}} = -\frac{1}{Q} \int d\mathbf{r}^N \frac{\partial U^{\text{ext}}}{\partial \mathbf{r}_1} e^{-\beta U^{\text{ext}}} \quad (26)$$

represents an external force, which as an averaged quantity is independent of the position. As a result, Eq. (25) takes the form of

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + i\mathbf{k}v_1 \right) f(\mathbf{k}, \mathbf{v}_1, t) + \mathbf{F}_1^{\text{ext}} \left( \beta\mathbf{v}_1 + \frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \right) f(\mathbf{k}_1, \mathbf{v}_1, t) \\ &= \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} \mathcal{P} K_N \\ & \times \int_0^t d\tau e^{-\tau(1-\mathcal{P})K_N} e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, t - \tau). \end{aligned} \quad (27)$$

Notice also that

$$\int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} \mathcal{P} K_N (\dots) = \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} K_N (\dots).$$

Thus, the kinetic equation (27) for the one-particle function  $f(\mathbf{k}, \mathbf{v}_1, t)$  reads

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + i\mathbf{k}v_1 \right) f(\mathbf{k}, \mathbf{v}_1, t) + \mathbf{F}_1^{\text{ext}} \left( \beta\mathbf{v}_1 + \frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \right) f(\mathbf{k}, \mathbf{v}_1, t) \\ &= \int_0^t d\tau \mathcal{G}(\mathbf{k}, \tau) f(\mathbf{k}, \mathbf{v}_1, t - \tau) \end{aligned} \quad (28)$$

with

$$\mathcal{G}(\mathbf{k}, \tau) \equiv \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} K_N e^{-\tau(1-\mathcal{P})K_N} e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v_1)} \quad (29)$$

which is the scattering operator for the problem.

After expanding  $\exp[-\tau(1-\mathcal{P})K_N]$  in the scattering operator, the right-hand side of Eq. (28) takes the form of

$$\int_0^t d\tau \mathcal{G}(\mathbf{k}, \tau) f(\mathbf{k}, \mathbf{v}, t - \tau) \equiv \int_0^t d\tau \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} f_N^0(\mathbf{v}^N, \mathbf{r}^N) K_N \times \sum_{n=1}^{\infty} \frac{(-\tau)^n}{n!} (K_N - \mathcal{P}K_N)^n (K_N - \mathcal{P}K_N) e^{i\mathbf{k}\mathbf{r}_1} \frac{f(\mathbf{k}, \mathbf{v}, t - \tau)}{\varphi_M(v)}, \quad (30)$$

where the commutation rule (15) was applied to translate the  $f_N^0(\mathbf{v}^N, \mathbf{r}^N)$  to the left.

### 4. Low density kinetic equation

We write the scattering operator in expression (30) in the form of

$$\mathcal{G}(\mathbf{k}, \tau) = \sum_{n=1}^{\infty} \frac{(-\tau)^n}{n!} \mathcal{G}^{(n)}(\mathbf{k}, 0) \quad (31)$$

and extract the term proportional to the density

$$\rho = \frac{N}{\Omega} \quad (32)$$

from the function

$$\mathcal{G}^{(n)}(\mathbf{k}, 0) f(\mathbf{v}_1) = \int d\mathbf{v}^{N-1} d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} K_N \times (K_N - \mathcal{P}K_N)^n e^{i\mathbf{k}\mathbf{r}_1} K_N \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v)} f(\mathbf{v}_1), \quad (33)$$

where  $f(\mathbf{v}_1)$  is an arbitrary function of  $\mathbf{v}_1$ . We calculate

$$\begin{aligned} & (K_N - \mathcal{P}K_N)^n e^{i\mathbf{k}\mathbf{r}_1} f_N^0(\dots) \\ &= (K_N - \mathcal{P}K_N)^{n-1} (K_N - \mathcal{P}K_N) e^{i\mathbf{k}\mathbf{r}_1} f_N^0(\dots) \\ &= (K_N - \mathcal{P}K_N)^{n-1} f_N^0 e^{i\mathbf{k}\mathbf{r}_1} \\ &\times \left( i\mathbf{k}\mathbf{v}_1 + K_N - \frac{1}{\varphi_M(v_1)} \int d\mathbf{v}'^{N-1} d\mathbf{r}'^N (i\mathbf{k}\mathbf{v}_1 + K'_N) \right) (\dots). \end{aligned} \quad (34)$$

After introducing the operator

$$\mathcal{P}^0(\dots) = \int d\mathbf{v}^{N-1} d\mathbf{r}^N \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(v)} (\dots), \quad (35)$$



we write expression (33) in the form of

$$\mathcal{G}^{(n)}(\mathbf{k}, 0) f(\mathbf{v}_1) = \int d\mathbf{v}^{N-1} d\mathbf{r}^N f_N^0(i\mathbf{k}\mathbf{v}_1 + K_N) \times [(i\mathbf{k}\mathbf{v}_1 + K_N - \mathcal{P}^0(i\mathbf{k}\mathbf{v}_1 + K_N))^n \chi(\mathbf{r}^N, \mathbf{v}_1)] , \quad (36)$$

where

$$\chi(\mathbf{r}^N, \mathbf{v}_1) \equiv \frac{\partial U}{\partial \mathbf{r}_1} \frac{(-1)}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \frac{f(\mathbf{v}_1)}{\varphi_M(v)} . \quad (37)$$

We observe that the operator  $\mathcal{P}^0$  rises the order of the density  $\rho$  by 1. After rejecting the components of the evidently higher order than 1, we keep only

$$\mathcal{G}^{(n)}(\mathbf{k}, 0) f(\mathbf{v}_1) = \int d\mathbf{v}^{N-1} d\mathbf{r}^N f_N^0(\mathbf{v}^N, \mathbf{r}^N) K_N (i\mathbf{k}\mathbf{v}_1 + K_N)^n \chi(\mathbf{r}^N, \mathbf{v}_1) . \quad (38)$$

However,

$$(i\mathbf{k}\mathbf{v}_1 + K_N)^n \chi(\mathbf{r}^N, \mathbf{v}_1) = \sum_{j=2}^N [i\mathbf{k}\mathbf{v}_1 + K_2(1, j)]^n \chi(\mathbf{r}^N, \mathbf{v}_1) , \quad (39)$$

where

$$K_2(1, j) \equiv \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{F}_{1j} \frac{\partial}{\partial \mathbf{v}_1} + \mathbf{F}_1^{\text{ext}} \frac{\partial}{\partial \mathbf{v}_1} \quad (40)$$

with

$$\mathbf{F}_{1j} \equiv -\frac{\partial u_{1j}}{\partial \mathbf{r}_i} \quad \text{and} \quad \mathbf{F}_1^{\text{ext}} \equiv -\frac{\partial U^{\text{ext}}}{\partial \mathbf{r}_i} . \quad (41)$$

We remind that, *cf.* for example [1],

$$\begin{aligned} & \sum_{j=2}^N \int d\mathbf{r}_1 \dots d\mathbf{r}_j \dots d\mathbf{r}_N F_2(\mathbf{r}_1, \mathbf{r}_j) \frac{1}{Q} e^{-\beta U} \\ &= (N - 1) \int d\mathbf{r}_1 d\mathbf{r}_2 F_2(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{Q} e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N \\ &= \frac{N}{\Omega^2} \int d\mathbf{r}_1 d\mathbf{r}_2 F_2(\mathbf{r}_1, \mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2) , \end{aligned} \quad (42)$$

where  $F_2(\mathbf{r}_1, \mathbf{r}_2)$  is an arbitrary function of given arguments and  $g(\mathbf{r}_1, \mathbf{r}_2)$  is the second order correlation function

$$g(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{1}{\Omega^2} \frac{\int d\mathbf{r}_3 \dots d\mathbf{r}_N e^{-\beta U}}{\int d\mathbf{r}^N e^{-\beta U}} \approx e^{-\beta[u_{12}(\mathbf{r}_1, \mathbf{r}_2) + U^{\text{ext}}(\mathbf{r}_1) + U^{\text{ext}}(\mathbf{r}_2)]} . \quad (43)$$

Therefore, we write

$$\mathcal{G}^{(n)}(\mathbf{k}, 0) f(\mathbf{k}_1, \mathbf{v}_1, t) = \sum_{j=2}^N \int d\mathbf{v}^{N-1} d\mathbf{r}^N f_N^0(\mathbf{v}^N, \mathbf{r}^N) K_{1j} \times (i\mathbf{k}\mathbf{v}_1 + K_{1j})^n (F_{1j} + F_1^{\text{ext}}) \frac{\partial}{\partial \mathbf{v}_1} \frac{f(\mathbf{k}_1, \mathbf{v}_1, t)}{\varphi_M(v_1)}. \tag{44}$$

Again, after extracting the lowest terms in the density  $\rho = N/\Omega$ , we obtain

$$\mathcal{G}^{(n)}(\mathbf{k}, 0) f(\mathbf{k}_1, \mathbf{v}_1, t) = \frac{N}{\Omega} \int d\mathbf{v}_2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\Omega} g(\mathbf{r}_1, \mathbf{r}_2) \varphi_M(v_1) \varphi_M(v_2) \times K_{12} (i\mathbf{k}\mathbf{v}_1 + K_{12})^n \frac{\partial}{\partial \mathbf{v}_1} \frac{f(\mathbf{k}_1, \mathbf{v}_1, t)}{\varphi_M(v_1)}. \tag{45}$$

As a result,

$$\begin{aligned} \mathcal{G}_{12}(\mathbf{k}, \tau) &= \sum_{j=2}^N \frac{(-\tau)^n}{n!} \mathcal{G}_{12}^{(n)}(\mathbf{k}, 0) \\ &= \frac{N}{\Omega} \int d\mathbf{v}_2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\Omega} g(\mathbf{r}_1, \mathbf{r}_2) \varphi_M(v_1) \varphi_M(v_2) K_{12} \\ &\quad \times e^{-i\mathbf{k}\mathbf{r}_1} e^{-\tau K_{12}} e^{i\mathbf{k}\mathbf{r}_1} K_{12} \frac{1}{\varphi_M(v_1)}. \end{aligned} \tag{46}$$

Let us perform the Laplace transform of the  $\mathcal{G}_{12}(\mathbf{k}, \tau)$

$$\bar{\mathcal{G}}_{12}(\mathbf{k}, z) \equiv \int_0^\infty dt e^{izt} \mathcal{G}_{12}(\mathbf{k}, \tau) \quad \text{with} \quad \Im z > 0.$$

We have

$$\begin{aligned} \bar{\mathcal{G}}_{12}(\mathbf{k}, z) &= \frac{N}{\Omega} \int d\mathbf{v}_2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\Omega} g(\mathbf{r}_1, \mathbf{r}_2) \varphi_M(v_1) \varphi_M(v_2) K_{12} \\ &\quad \times e^{-i\mathbf{k}\mathbf{r}_1} \frac{1}{-iz + K_{12}} e^{i\mathbf{k}\mathbf{r}_1} K_{12} \frac{1}{\varphi_M(v_1)} \end{aligned} \tag{47}$$

or

$$\begin{aligned} \bar{\mathcal{G}}_{12}(\mathbf{k}, z) &= \frac{N}{\Omega} \int d\mathbf{v}_2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\Omega} g(\mathbf{r}_1, \mathbf{r}_2) \varphi_M(v_1) \varphi_M(v_2) e^{-i\mathbf{k}\mathbf{r}_1} \\ &\quad \times (K_{12} - i\mathbf{k}\mathbf{v}_1) \frac{1}{-iz + K_{12}} (K_{12} - i\mathbf{k}\mathbf{v}_1) e^{i\mathbf{k}\mathbf{r}_1} K_{12} \frac{1}{\varphi_M(v_1)}. \end{aligned} \tag{48}$$

Since

$$(iz - K_{12} + K_{12} - i\mathbf{k}\mathbf{v}_1) \left( \frac{1}{-iz + K_{12}} (K_{12} - i\mathbf{k}\mathbf{v}_1) - 1 + 1 \right) \\ = (-iz + i\mathbf{k}\mathbf{v}_1) \left( \frac{1}{-iz + K_{12}} (-iz + i\mathbf{k}\mathbf{v}_1) - \frac{1}{-iz + i\mathbf{k}\mathbf{v}_1} (-iz + i\mathbf{k}\mathbf{v}_1) \right)$$

and

$$\frac{1}{-iz + i\mathbf{k}\mathbf{v}_1} e^{i\mathbf{k}\mathbf{r}_1} f(\mathbf{v}_1) = \frac{1}{-iz + K_{12}^0} e^{i\mathbf{k}\mathbf{r}_1} f(\mathbf{v}_1)$$

therefore,

$$\bar{\mathcal{G}}_{12}(\mathbf{k}, z) = \frac{N}{\Omega} \int d\mathbf{v}_2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\Omega} g(\mathbf{r}_1, \mathbf{r}_2) \varphi_M(v_1) \varphi_M(v_2) e^{-i\mathbf{k}\mathbf{r}_1} \\ \times \left( \frac{1}{-iz + K_{12}} - \frac{1}{-iz + K_{12}^0} \right) e^{i\mathbf{k}\mathbf{r}_1} (-iz + i\mathbf{k}\mathbf{v}_1) \frac{1}{\varphi_M(v_1)} \quad (49)$$

or, equivalently,

$$\bar{\mathcal{G}}_{12}(\mathbf{k}, z) = \frac{N}{\Omega} \int d\mathbf{v}_2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\Omega} g(\mathbf{r}_1, \mathbf{r}_2) \varphi_M(v_1) \varphi_M(v_2) e^{-i\mathbf{k}\mathbf{r}_1} \\ \times \int_0^\infty d\tau e^{iz\tau} \left( e^{-\tau K_{12}} - e^{-\tau K_{12}^0} \right) e^{i\mathbf{k}\mathbf{r}_1} (-iz + i\mathbf{k}\mathbf{v}_1) \frac{1}{\varphi_M(v_1)}. \quad (50)$$

This form is similar to the difference form of Boltzmann's equation.

### Moments of scattering law

Moment of  $n^{\text{th}}$  order of the intermediate scattering function  $I_s(\mathbf{k}, t)$  is given by

$$(-i)^n I_s^{(n)} = \int_{-\infty}^\infty f^{(n)}(\mathbf{k}, \mathbf{v}_1, 0) d\mathbf{v}_1.$$

Kinetic equation (28) describes the behaviour of the function  $f(\mathbf{k}, \mathbf{v}_1, t)$  for all times, in particular for very short. It can be applied to find from it the moments of scattering law. To this end, we write Eq. (28) in the form of

$$\left( \frac{\partial}{\partial t} + i\mathbf{k}\mathbf{v}_1 \right) f(\mathbf{k}, \mathbf{v}_1, t) + \mathbf{F}_1^{\text{ext}} \left( \beta\mathbf{v}_1 + \frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \right) f(\mathbf{k}, \mathbf{v}_1, t) = \mathcal{J}(t),$$

where

$$\mathcal{J}(t) \equiv \int_0^t d\tau \mathcal{G}(\mathbf{k}, \tau) f(\mathbf{k}, \mathbf{v}_1, t - \tau).$$

Differentiating with respect to time both sides of this equation, at the instant  $t = 0$ , we get

$$\begin{aligned} f'(0) &= - \left\{ i \mathbf{k} v_1 + \mathbf{F}_1^{\text{ext}} \left( \beta \mathbf{v}_1 + \frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \right) \right\} f(0), \\ f''(0) &= - \left\{ i \mathbf{k} v_1 + \mathbf{F}_1^{\text{ext}} \left( \beta \mathbf{v}_1 + \frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}_1} \right) \right\} f'(0) + \mathcal{J}'(0), \end{aligned}$$

and so on. We have omitted arguments  $\mathbf{k}$  and  $\mathbf{v}_1$  and write simply  $f(0)$  instead of  $f(\mathbf{k}, \mathbf{v}_1, 0)$ ; similarly abbreviate the arguments of derivatives. Here,

$$\begin{aligned} \mathcal{J}(0) &= 0, & \mathcal{J}'(0) &= \mathcal{G}(0)f(0), \\ \mathcal{J}''(0) &= \mathcal{G}(0)f'(0) + \mathcal{G}'(0)f(0), \end{aligned}$$

an so on.

## 5. Lorentz' gas

The kinetic theory of the Lorentz gas has been studied in the past extensively, *cf.* [27, 28]. This system consists of  $N - 1$  fixed scatterers and one particle moving between them. Such a system is known also as Ehrenfest's wind-tree model or Sinai's billiard, *cf.* [29, 30] and [31–33], respectively. The model was exploited by Lebowitz and Spohn to investigate the stationary equilibrium and to derive Fourier's law of heat conduction [34]. Piasecki applied the Lorentz gas to study the flow of charged particles in a constant and uniform electric field through the medium of immobile, randomly distributed scatterers [36, 37], while in the paper with Wajnryb to model propagation of neutrinos in a medium composed of nuclei [38].

Therefore, in the Lorentzian gas, a classical particle moves in an infinite random array of stationary spherical scatterers, what means that the mass of a selected particle No. 1 is small in comparison with the masses of remaining particles, *cf.* [35, 39]

$$m_1 \equiv m \quad \text{and} \quad m_2 = m_3 = \dots = m_N \equiv M \rightarrow \infty.$$

Thus,  $m \ll M$  and  $v_i \rightarrow 0$ ,  $i \geq 2$ . Hence,

$$\int d\mathbf{v}_i \varphi_M(v_i) = 1 \quad \text{for} \quad i = 2, 3, \dots, N.$$

We have only one moving particle now, and we omit the index 1 at the velocity of the particle No. 1

$$\mathbf{v}_1 \equiv \mathbf{v}.$$

This means also that the kinetic energy of the light particle is a constant of motion. Liouville's operator (12) is now written in the form of

$$K_N = \mathbf{v} \frac{\partial}{\partial \mathbf{r}_1} - \sum_{j=2}^N \frac{\partial u_{1j}}{\partial \mathbf{r}_1} \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} - \frac{\partial U_1(\mathbf{r}_1)}{\partial \mathbf{r}_1} \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} \quad (51)$$

and Stecki's operator (20) takes the form

$$\mathcal{P} \equiv e^{i\mathbf{k}\mathbf{r}_1} \frac{e^{-\beta U}}{Q} \int d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1}. \quad (52)$$

With these definitions of the  $K_N$  and  $\mathcal{P}$ , we expand the  $\exp[-\tau(1-\mathcal{P})K_N]$  in the right-hand side of Eq. (28) and get

$$\begin{aligned} & \int_0^t d\tau \mathcal{G}(\mathbf{k}, \tau) f(\mathbf{k}, \mathbf{v}, t - \tau) \equiv \int_0^t d\tau \int d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} K_N \\ & \times \sum_{\ell=1}^{\infty} \frac{(-\tau)^\ell}{\ell!} [(1-\mathcal{P})K_N]^\ell e^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0(\mathbf{v}^N, \mathbf{r}^N)}{\varphi_M(\mathbf{v})} f(\mathbf{k}, \mathbf{v}, t - \tau). \end{aligned} \quad (53)$$

Then the kinetic equation (28) reads

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + i\mathbf{k}\mathbf{v} + \mathbf{F}_1^{\text{ext}} \left( \beta\mathbf{v} + \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} \right) \right\} f(\mathbf{k}, \mathbf{v}, t) \\ & = \int_0^t d\tau \sum_{\ell=1}^{\infty} \frac{(-\tau)^\ell}{\ell!} G^{(\ell)}(\mathbf{k}) f(\mathbf{k}, \mathbf{v}, t - \tau), \end{aligned} \quad (54)$$

where

$$G^{(\ell)}(\mathbf{k}) \equiv \int d\mathbf{r}^N e^{-i\mathbf{k}\mathbf{r}_1} K_N [(1-\mathcal{P})K_N]^\ell e^{i\mathbf{k}\mathbf{r}_1} \frac{e^{-\beta U}}{Q}. \quad (55)$$

We find

$$\begin{aligned} & K_N e^{i\mathbf{k}\mathbf{r}_1} \frac{e^{-\beta U}}{Q} f(\mathbf{k}, \mathbf{v}, t) \\ & = \varphi_M(\mathbf{v}) \frac{e^{-\beta U}}{Q} e^{i\mathbf{k}\mathbf{r}_1} \left( i\mathbf{k}\mathbf{v} - \frac{\partial U_1(\mathbf{r}_1)}{\partial \mathbf{r}_1} \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} \right) \frac{f(\mathbf{k}, \mathbf{v}, t)}{\varphi_M(\mathbf{v})} \end{aligned} \quad (56)$$

and, cf. definition (26) of the force vector  $\mathbf{F}_1^{\text{ext}}$ ,

$$\begin{aligned} & \mathcal{P} K_N e^{i\mathbf{k}\mathbf{r}_1} \frac{e^{-\beta U}}{Q} f(\mathbf{k}, \mathbf{v}, t) \\ & = \varphi_M(\mathbf{v}) \frac{e^{-\beta U}}{Q} e^{i\mathbf{k}\mathbf{r}_1} \left( i\mathbf{k}\mathbf{v} + \mathbf{F}_1^{\text{ext}} \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} \right) \frac{f(\mathbf{k}, \mathbf{v}, t)}{\varphi_M(\mathbf{v})}. \end{aligned} \quad (57)$$

Hence,

$$\begin{aligned}
 & (1 - \mathcal{P})K_N e^{i\mathbf{k}\mathbf{r}_1} \frac{e^{-\beta U}}{Q} f(\mathbf{k}, \mathbf{v}, t) \\
 &= \frac{e^{-\beta U}}{Q} e^{i\mathbf{k}\mathbf{r}_1} (-\mathbf{F}_1^{\text{ext}}) \left( \beta \mathbf{v}_1 + \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} \right) f(\mathbf{k}, \mathbf{v}, t). \tag{58}
 \end{aligned}$$

In the absence of the exterior field, the last expression vanishes.

*Low density kinetic equation for the Lorentz gas*

Recalling definition (51) of  $K_N$ , we see that it contains a summation over all scattering centers. The only term giving rise to a single factor  $N$  after averaging is the one in which none of these summations is allowed to introduce additional  $N$  factors. Hence, operator (55) reads

$$G_2^{(\ell)}(\mathbf{k})f \equiv \int d\mathbf{r}^N \frac{e^{-\beta U}}{Q} \varphi_M(v_1) e^{-i\mathbf{k}\mathbf{r}_1} K_2 (i\mathbf{k}\mathbf{v} + K_2)^\ell K_2 \frac{f}{\varphi_M(v_1)}, \tag{59}$$

where

$$K_2 = \mathbf{v} \frac{\partial}{\partial \mathbf{r}_1} - \frac{\partial[u_{12} + U_1(\mathbf{r}_1)]}{\partial \mathbf{r}_1} \frac{1}{m} \frac{\partial}{\partial \mathbf{v}}$$

and the arguments of the function  $f(\mathbf{k}, \mathbf{v}_1, t)$  were omitted. Hence, after resummation, we can write the kinetic equation (28) in the form of

$$\begin{aligned}
 & \left\{ \frac{\partial}{\partial t} + i\mathbf{k}\mathbf{v} + \mathbf{F}_1^{\text{ext}} \left( \beta \mathbf{v} + \frac{1}{m} \frac{\partial}{\partial \mathbf{v}} \right) \right\} f(\mathbf{k}, \mathbf{v}, t) \\
 &= \int_0^t d\tau \int d\mathbf{r}^N \frac{e^{-\beta U}}{Q} \varphi_M(v_1) e^{-i\mathbf{k}\mathbf{r}_1} K_2 e^{-\tau(i\mathbf{k}\mathbf{v} + K_2)} \frac{f(\mathbf{k}, \mathbf{v}, t - \tau)}{\varphi_M(v_1)}. \tag{60}
 \end{aligned}$$

Comparing with Eq. (3.30), derived in [40] for the dilute Lorentz gas in the absence of the external potential, we find that at the left-hand side a new term appears containing the force  $\mathbf{F}_1^{\text{ext}}$ , while the right-hand side is similar to that in Eq. (3.30) from [40], but with the different operator  $K_2$ , comprising the external field.

### 6. Conclusions

We have found a general kinetic equation for the classical gas of particles with short-range attraction valid within the framework of classical statistical mechanics and its alternative Fourier transform for a system of binary interacting particles in the external potential. We have applied to this problem the technique of projection operators. The kinetic equation for the dilute Lorentz gas of interacting particles in an external potential was derived.

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