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Kinetic equation for a gas with attractive forces as a functional equation

Abstract. Diffusion problems studied in the time scale comparable with time of particles collision lead to kinetic equations which for step-wise potentials are functional equations in the velocity space. After a survey of derivation of kinetic equations by projective operator method, an attention is paid to the Lorentz gas with step potential. The gas is composed of N particles: $N-1$ of which are immovable; between those $N-1$ immovable particles – scatterers, particle number 1 is moving, and we describe its movement by means of one-particle distribution function satisfying a kinetic equation. Solutions of the kinetic equation for some simple potentials are given. We derive also a kinetic equation for one-dimensional Lorentz gas, which is a functional equation.

1. Introduction

General kinetic equations with convolution time integral (hence nonlocal in time and non-markovian) were first derived and discussed by the Brussels group, headed by Ilya Prigogine, [1]. Different correlation functions used to describe non-equilibrium processes satisfy such equations, [2] − [7].

A comparison of the theory of the Brussels group, with the Bogolyubov theory, then being developed by the Uhlenbeck group was given in a paper by Stecki and Taylor, [8]. These results were next extended and ordered by the Brussels group, [9].

Robert Zwanzig, [4, 10] described a new method of derivation of kinetic equations. The main tool of this derivation is the use of projection operators in the Hilbert space of Gibbsian ensemble densities. It was noted by Nelkin and Ghatak that the Van Hove self-correlation function $G_s(r, t)$ for a dilute fluid is determined by a linearized Boltzmann equation identical to that occuring in the theory of neutron diffusion, [11].

The kinetic equation (KE) describing diffusion in time scale comparable with time of the particles collision, is also a time convolution kinetic equation, which for

a step-wise interaction potential takes form of a functional equation in the velocity space.

We work in the framework of kinetic theory of a Boltzmann gas, with use of statistical mechanics methods. The gas is composed of N particles, and the problem discussed concerns the diffusion of a marked particle (number 1) amid $(N-1)$ other classical dilute gas particles.

Applying to the Liouville equation the proper projection operator, a kinetic equation for one-particle distribution function $f(\mathbf{k}, \mathbf{v}_1, t)$ is derived. Here $\mathbf{k}$ denotes the Fourier vector variable (wave vector) after transformation of spacial coordinate $\mathbf{r}_1$, which denotes the position of particle number 1. The vector $\mathbf{v}_1$ is the velocity of this particle, while t is a time. Function $f(\mathbf{k}, \mathbf{v}_1, t)$ is Fourier transform of one-particle distribution function $f_s(\mathbf{r}, \mathbf{v}_1, t)$, which represents the probability of finding a particle at time t at $\mathbf{r}$ with velocity $\mathbf{v}_1$, if the same particle was at time $t = 0$ at $\mathbf{r} = \mathbf{0}$ with the given distribution of velocity $\mathbf{v}_1$, e.g. the Maxwellian.

Right-hand side of KE has a form of time convolution of a scattering operator $\mathcal{G} = \mathcal{G}(\mathbf{k}, t)$ and function $f = f(\mathbf{k}, \mathbf{v}_1, t)$. It is valid not only for long times (in comparison with time of collision, as it is in case of the Boltzmann equation and in Brownian movement theory) but also for short times.

KE considered here was found previously by Jan Stecki, [12], cf. also [13, 14]. This is a time convolution equation for a gas which particles interact by attractive-repelling potential with step dependence on distance. In such a case the phase space consists of distincly separated regions and the kinetic equations is transformed from a convolutive one into a functional equation.

1.1.   Notation

The gas occupies volume V and consists of N particles, numbered by indices $i = 1, \ldots, N$, and m_i, $\mathbf{v}_i$ and $\mathbf{r}_i$ are the mass, velocity and position of particle number i, respectively. Cartesian coordinates of vector $\mathbf{v}_i$ are denoted by v_{ix}, v_{iy}, v_{iz} and those of $\mathbf{r}_i$ by x_i, y_i, z_i.

The Maxwell distribution function of the velocity is denoted by

$$\varphi_M(v_i) = \sqrt{\left(\beta \frac{m}{2\pi}\right)^3} \exp\left(-\beta m \frac{v_i^2}{2}\right).$$

Here the velocity modulus $v_i = |\mathbf{v}_i|$ is used and $v_i^2 = v_{ix}^2 + v_{iy}^2 + v_{iz}^2$, while $\beta^{-1} = k_{\mathrm{B}}T$ with the Boltzmann constant k_{B} and absolute temperature T.

The temperature of an ideal gas is related to its average kinetic energy *per* particle by the relation

$$\bar{E}_{\mathrm{kin}} = \frac{3}{2}k_{\mathrm{B}}T = \frac{3}{2\beta}.$$

The second law of thermodynamics states that any two interacting systems will reach the same average energy *per* particle and hence the same temperature. In equilibrium, the probability of finding a particle with velocity $\mathbf{v}_i$ in the infinitesimal element $d\mathbf{v}_i = [dv_{ix}, dv_{iy}, dv_{iz}]$ about velocity $\mathbf{v}_i = [v_{ix}, v_{iy}, v_{iz}]$ is $\varphi_M(v_i)dv_{ix}dv_{iy}dv_{iz}$ or $\varphi_M(v_i)d\mathbf{v}_i$.

The interaction potential u_{ij} between particles number i and number j depends on distance between these particles only:

$$u_{ij} = u_{ij}(|\mathbf{r}_i - \mathbf{r}_j|).$$

Hence the total potential energy of the system

$$U = \sum_{i<j}^{N} u(|r_i - r_j|) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u_{ij}(r_{ij}) = \sum_{i<j} u_{ij},$$

where $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$.

1.2.   Physical meaning

The function $f = f(\mathbf{k}, \mathbf{v}_1, t)$ is related to scattering phenomena. Essential for interpretation of incoherent scattering experiments is the Van Hove function

$$G_s(|\mathbf{r} - \mathbf{r}_0|, t) = \left\langle \frac{V}{N} \sum_{i=1}^{N} \delta(\mathbf{r}_i(0) - \mathbf{r}_0) \delta(\mathbf{r}_i(t) - \mathbf{r}) \right\rangle \tag{1}$$

where

$$\langle (\dots) \rangle = \int \frac{1}{Z_N} e^{-\beta H} (\dots) \, d\mathbf{v}^N d\mathbf{r}^N \quad \text{with} \quad Z_N = \int e^{-\beta H} \, d\mathbf{v}^N d\mathbf{r}^N$$

denotes the canonical average.

The function $G_s(\mathbf{r}, t)$ represents the probability of finding a particle at $\mathbf{r}$ at time t if the same particle was at $\mathbf{r} = 0$ at time $t = 0$.

Van Hove law for incoherent scattering reads

$$S_s(\mathbf{k}, \omega) = \frac{1}{2\pi} \int \exp[i(\mathbf{kr} - \omega t)] G_s(\mathbf{r}, t) \, d\mathbf{r}dt = \frac{1}{2\pi} \int \exp(-i\omega t) I_s(\mathbf{k}, t) \, dt,$$

where

$$I_s(\mathbf{k}, t) = \int \exp(i\mathbf{kr}) G_s(\mathbf{r}, t) \, d\mathbf{r}$$

cf. $[15] - [19]$. On the other hand, we have

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

and $I_s(\mathbf{k}, t)$ is the Fourier transform of $G_s(\mathbf{r}, t)$ and function $f(\mathbf{k}, \mathbf{v}_1, t)$ can be found by kinetic theory. Namely, it satisfies the following linear KE

$$\left(\frac{\partial}{\partial t} + i\mathbf{kv}_1\right) f(\mathbf{k}, \mathbf{v}_1, t) = \int_0^t \mathcal{G}(\mathbf{k}, \tau) f(\mathbf{k}, \mathbf{v}_1, t - \tau) \, d\tau \tag{2}$$

where

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

and

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

with

$$F_N(0) = \mathrm{e}^{i\mathbf{kr}_1} \varphi_M(v_1) \cdot \ldots \cdot \varphi_M(v_N) \frac{\mathrm{e}^{-\beta U}}{Q} \tag{3}$$

Here $U = \sum_{i<j} u_{ij}$ and

$$K_N = \sum_{i=1}^{N} v_i \frac{\partial}{\partial \mathbf{r}_i} - \sum_{i<j} \frac{\partial U}{\partial \mathbf{r}_i} \frac{1}{m_i} \frac{\partial}{\partial \mathbf{v}_i} \tag{4}$$

is the N-particle Liouville operator.

Normalization factor in (3)

$$Q = \int_V \mathrm{e}^{-\beta U} \, d\mathbf{r}^N, \quad \text{where } d\mathbf{r}^N = d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

is known as the partition function or sum-over-states.

The partition function Q is related to thermodynamical properties of the system, cf. [20], [21], [22]. With a model of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamical properties of the system.

Research in the prediction of binding affinities has been a continuing effort for more than half a century, [23, 24]. An important application of the configuration integral lies in the development of computational models for the ligand-receptor binding affinities. Their study constitutes the most important problem in computational biochemistry. Especialy, the prediction of absolute ligand-receptor binding affinities is essential in a wide range of biophysical questions, from the study of protein-protein interactions to structure-based drug design.

In a ligand-receptor binding, a ligand is in general any molecule that binds to another molecule; the receiving molecule is called a receptor, which is a protein on the cell membrane or within the cell cytoplasm. Such binding can be represented by the chemical reaction describing noncovalent molecular association $A + B \leftrightarrow AB$, where A represents the protein (receptor), B the ligand molecule, and AB the protein-ligand complex. The change in the Gibbs free energy can be expressed as a ratio of configuration integrals, [25].

An alternative form of the kinetic equation (2) is

$$(-iz + i\mathbf{k}\mathbf{v}_1)f(\mathbf{k}, \mathbf{v}_1, z) - f(\mathbf{k}, \mathbf{v}_1, t = 0) = G(\mathbf{k}, z)f(\mathbf{k}, \mathbf{v}_1, z) \tag{5}$$

where $f(\mathbf{k}, \mathbf{v}_1, z)$ is the Laplace transform of $f(\mathbf{k}, \mathbf{v}_1, t)$ defined as $f(z) = \int_0^\infty \mathrm{e}^{izt} f(t) \, dt$. We use the same letter for a function and its Laplace transform, but it does not lead to confusion, because all arguments are explicitly written.

If $m_1 \gg m_i$, $i = 2, 3, \ldots, N$ we have the Brownian diffusion of particle number 1. If $m_1 \ll m_i$, $i = 2, 3, \ldots, N$ - the Lorentz gas is dealt with, cf. also [26, 27].

1.3. Diffusion in biology

For big times and for isotropic medium the Van Hove function $G_s = G_s(r,t)$ is given by a solution of the classical Fick's equation, namely,

$$G_s(r,t)_{t\to\infty} = \frac{1}{8(\pi Dt)^{\frac{3}{2}}}\mathrm{e}^{\frac{-r^2}{4Dt}},$$

where D denotes the (macroscopic) diffusion coefficient. After tranformations we get $I_s(k,t)_{t\to\infty} = \exp(-k^2 Dt)$ and

$$S_s(k,\omega) = \frac{1}{\pi}\frac{Dk^2}{\omega^2 + (Dk^2)^2}.$$

Hence

$$D = \lim_{\omega\to 0}\lim_{k\to 0}\pi\frac{\omega^2 S_s(k,\omega)}{k^2}.$$

We have also

$$D = -\lim_{t\to\infty}\frac{1}{6t}\frac{\partial^2 I_s(k,t)}{\partial k^2}.$$

In spite of passing to the limit, residual information about the dynamics of system is still contained in the diffusion coefficient D. For example, in the random walk diffusion the coefficient $D = \frac{h^2}{2\tau}$, with h and τ being the length and duration of one step in the walk, respectively.

The laws of diffusion (in which coefficient D is used) were discovered in 1855 by physician and physiologist Adolf Eugen Fick, [28] − [30].

At the beginning of the 20th century, Einstein and Smoluchowski, independently, have found relation between macroscopic diffusion coefficient D and the Brownian movement phenomenon, explaining it in microscopic, molecular terms, cf. [31, 32]. The phenomenon was first explicitly described in 1828 by the physician and botanist Robert Brown, who observed in aqueous suspensions of pollen grains from *Clarkia pulchella* a rapid, continuous, short-range motion of small included particles that "arose neither from currents in the fluid nor from its gradual evaporation, but belonged to the particle itself", [33, 34].

After discovery of Fick's laws, in physiology dominated the opinion that diffusion laws should explain all problems of metabolism. It was widely believed in XIX century that diffusion is responsible for such organic processes as gas exchange in the leaves of plants, gas exchange in the lungs of animals, the uptake of the products of digestion from the gut.

However, the development of knowledge on the cell structure has permitted to gather an abundant evidence on inadequacy of diffusion theory for explaining much of the movements of substances in organisms, studied in biology and medicine. The Fick diffusion alone could described physiological processes only in dead tissues.

In 1912 medical doctor and physiologist, Otto Heinrich Warburg published a discovery: oxygen utilization requires structural elements in the cell − a solid phase. These structures, now recognized as mitochondria, had been described by light microscopists two decades before Warburg's publication, and 80 years later were found to be places where Brownian motors work, [35].

The assumptions of the Einstein–Smoluchowski model are not even approximately met *in vivo*. The cell contains a highly concentrated and heterogeneous assembly of deformable, interacting and inelastically colliding particles; much of the solvent (water) is bound to solid structures which, although not necessarily long-living, have huge surface areas; and in any case the conditions only tend to thermodynamic equilibrium after death. The model representing the "microscopic" aspect of diffusion theory assumes a dilute, homogeneous suspension of rigid, non-interacting and elastically colliding particles, a monophasic system with the solvent (largely) unbound, and a tendency towards equilibrium. Also, the model assumes that there are no net solvent movements, and this is undoubtedly relevant in intracellular transport, [36, 37], also [38].

After the idea arose that the cell internum does, at least in part, behave as a gel, the diffusion through gels became an important subject of study. Investigations of diffusion in gels put a question on applicability of Fick's laws in the field.

Bigwood has shown in 1930 that not only is diffusion in gels highly dependent on the absolute concentration of diffusing substance (in contrast to the classical linear Fick's theory that diffusion rates depend only on concentration gradients), but that it is both slow and unpredictable, particularly when the gel is made of protein, as the gel state of the cell internum should be, cf. [39, 40]. It became clear then that in description of biological cell extreme order has to be reconciled with a fluid anatomy. Two kinds of intracellular transport are possible: one, which accounts for the movements of macromolecules and assemblies; and second, which will account for the movements of small molecules and ions, [41].

In 1949 Hans Ussing conducted investigations with use of radioactive tracers and gave the systematic molecular level account of a "secretion" process in biology, as an opposite to the "diffusion" description. Ussing defined the term "active transport", which means the creation of a genuinely "uphill" concentration gradient, cf. [42, 43]. Active transport is now an accepted part of biological knowledge, and individual active transport mechanisms are frequently objects of research.

In 1950 BBC lecture J.Z. Young concluded: the more we come to know of the flux of chemical changes in the body, the more one great weakness of the machine analogy stands out. The concept of a dynamic organization, such as that of a whirlpool, demands a consideration of time – of before and after and of gradual development and change of pattern, but the machine models of physiology allow no place for this element. In the tissue spaces, as well as inside the cell, there is fluid circulation among solid-state elements, [44].

The diffusion concepts persisted for a long time in description of respiratory processes. Until now, the method of "diffusion capacity" is practised as a measurement of the lungs ability to transfer gases. Oxygen absorption may be limited by diffusion in circumstances of low ambient oxygen or high pulmonary blood flow. Carbon dioxide is not limited by diffusion under most circumstances. The "diffusion capacity" is part of comprehensive test series of lung function called pulmonary function testing. It is known, however, diffusivity estimates are seriously problematic even with modern equipment. Longmuir wrote: "If simple diffusion is the sole mechanism of tissue oxygen transport as proposed by Krogh (1919), it is difficult to see how acclimatization could occur without a reduction in the

diffusion coefficient. The kinetics of oxygen transport cannot be explained by passive diffusion alone; the search for other mechanisms led to the observation that all kinetic data could be explained by channels in cells along which the oxygen diffuses faster than in water, [45, 46]."

The cell internum is far more complex organised right down to the molecular level than was hitherto appreciated, to the point where ideas of a relatively solid-state chemistry model have occoured. The flow theory of enzyme kinetics — a role of solid geometry in the control reaction velocity in live animals. This contrasts sharply with the former concept that diffusion is the way by which molecules interact within an aqueous solution of the cell internum, [47] − [52].

In living systems, most molecules do not generally move, but are moved, when we consider what would happen if everything depended upon Brownian motion and the law of mass action. R.P.C. Johnson in 1983 recognised a grey area at the molecular level when considering the movement of molecules within living cells: "This is the region of scale where flow and diffusion are not clearly separated; where the concepts of temperature and molecular movement overlap; where it is not clear whether molecules move or are moved; where the ideas of active and passive lose their meaning", [53, 48], also [54] and [55].

Until now, biologists use the term "diffusion" in a twofold meaning. One is Fick's diffusion, and the second one is vernacular, for spreading process, when "diffusion" is not adhered to a specific, defined scientific term. For an active transport the term active diffusion is sometimes used, as an opposite to passive (i.e. Fickian) diffusion.

The complication in the description of biological processes may be found in application of the Smoluchowski diffusion with drift equation. In this equation an aleatory aspect is coupled with deterministic. The drift force controls diffusion and diffusion reflects the influence of thermal vibrations of the evironment on the process.

All phenomena, biological also, are developing in given thermal conditions, and the application of thermodynamics is inevitable. The "microscopic" aspect of diffusion theory, is that random thermal motions of molecules in liquids are responsible for return of diffusion, particularly Brownian movement theories, into contemporary biophysics.

Brownian or molecular motors are biological "nanomachinees" and are the essential agents of movement in living organisms. A motor is regarded as a device that consumes energy and converts it into motion or mechanical power. Adenosine triphosphate (ATP) is the fuel for the molecular motors action. Many protein-based molecular motors convert the chemical energy present in ATP into mechanical energy. The ATPase molecular motors are found in the membranes of mitochondria, the microscopic bodies in the cells of nearly all living organisms, as well as in chloroplasts of plant cells, where the enzyme is responsible for converting food to usable energy, [56] and [57].

It was shown by Streater that the Smoluchowski equation for a Brownian particle potentially can be supplemented by an equation for the dynamics of the temperature, so that the first and the second laws of thermodynamics are obeyed. He considered also a model studied by David Smith, known as the dumbbell model,

in which the Brownian particle is a two-level atom, and had shown that under isothermal conditions, the free energy can be given a natural definition out of equilibrium, and is a decreasing function of time, [58], also [59]. Smith has applied his model to describe a myosin molecule, [60, 61], also [62] and [63].

Macromolecular particles playing a role in protein motors are heavy (Brownian) in comparison with solvent (water) molecules, but are light (Lorentzian) in comparison with mass of substratum (mitochondrium).

Another biological example in which the passive diffusion plays a role is provided by alimentation processes in cartilage, tissue which supplies smooth surfaces for the movement of articulating bones. The cartilage is built of cells, called chondrocytes, producing a large amount of extracellular matrix composed of collagen fibers, abundant ground substance rich in proteoglycan, and elastin fibers. Unlike other connective tissues, cartilage does not contain blood vessels. The chondrocytes are fed by diffusion, helped by the pumping action generated by compression of the articular cartilage or flexion of the elastic cartilage. Thus, compared to other connective tissues, cartilage grows and repairs more slowly, [64].

The diffusion process appears in biology also as the property of homeostasis in organisms.

Homeostasis (from Greek: hómos, "equal"; and istemi, "to stand" lit. "to stand equally"; coined by Walter Bradford Cannon) is the property of either an open system or a closed system, especially a living organism, that regulates its internal environment so as to maintain a stable, constant condition. Multiple dynamic equilibrium adjustment and regulation mechanisms make homeostasis possible. The concept came from that of milieu interieur that was created by Claude Bernard, often considered as the father of physiology, and published in 1865.

With respect to any given life system parameter, an organism may be a conformer or a regulator. Regulators try to maintain the parameter at a constant level over possibly wide ambient environmental variations. On the other hand, conformers allow the environment to determine the parameter. For instance, endothermic animals maintain a constant body temperature, while exothermic animals exhibit wide body temperature variation. Examples of endothermic animals include mammals and birds, examples of exothermic animals include reptiles and some sea animals.

Most homeostatic regulation is controlled by the release of hormones into the bloodstream. However other regulatory processes rely on simple diffusion to maintain a balance.

Homeostatic regulation extends far beyond the control of temperature. All animals also regulate their blood glucose, as well as the concentration of their blood. Mammals regulate their blood glucose with insulin and glucagon. These hormones are released by the pancreas, the inadequate production of the two for any reason, would result in diabetes. The kidneys are used to remove excess water and ions from the blood. These are then expelled as urine. The kidneys perform a vital role in homeostatic regulation in mammals, removing excess water, salt, and urea from the blood. These are the body's main waste products, [65].

2. Projective operator method

The projection operator is introduced, [66],

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

where

$$f_N^0 = \prod_{i=1}^{N} \varphi_M(v_i) \frac{1}{Q} \mathrm{e}^{-\beta U}$$

is the equilibrium distribution function. We observe

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

In particular

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

and

$$(1 - \mathcal{P}) F_N(0) = 0.$$

Also

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

The Liouville equation

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

with K_N given by (4), is now rewritten in the form

$$\frac{\partial}{\partial t} [\mathcal{P} F_N(t)] = -\mathcal{P} K_N \mathcal{P} F_N(t) - \mathcal{P} K_N (1 - \mathcal{P}) F_N(t)$$

and

$$\frac{\partial}{\partial t} [(1 - \mathcal{P}) F_N(t)] = -(1 - \mathcal{P}) K_N \mathcal{P} F_N(t) - (1 - \mathcal{P}) K_N (1 - \mathcal{P}) F_N(t).$$

Hence

$$\frac{\partial}{\partial t} [\mathcal{P} F_N(t)]$$

$$= -\mathcal{P} K_N \mathcal{P} F_N(t) + \mathcal{P} K_N \int_0^t \mathrm{e}^{-\tau(1-\mathcal{P})K_N} (1 - \mathcal{P}) K_N \mathcal{P} F_N(t - \tau) \, d\tau$$

and finally

$$\left(\frac{\partial}{\partial t} + i\mathbf{k}\mathbf{v}_1\right) f(\mathbf{k}, \mathbf{v}_1, t)$$

$$= \int d\mathbf{v}^{N-1} dr^N \, \mathrm{e}^{-i\mathbf{kr}_1} \mathcal{P} K_N \int\limits_0^t \mathrm{e}^{-\tau(1-\mathcal{P})K_N} \mathrm{e}^{i\mathbf{kr}_1} \frac{f_N^0}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, t - \tau) \, d\tau$$

it is a general form of KE, correct also for small times, compared to the time of collision.

3.   Density expansion

An alternative form of the kinetic equation (2) is

$$(-iz + i\mathbf{k}\mathbf{v}_1) f(k, v_1, z) = G(k, z) f(\mathbf{k}, \mathbf{v}_1, z) + f(\mathbf{k}, \mathbf{v}_1, t = 0),$$

where

$$f(t = 0) = \varphi_M(v_1) = \left(\frac{2\pi}{\beta m}\right)^{-\frac{3}{2}} \mathrm{e}^{-\frac{1}{2}\beta v_1^2}$$

with $f(\mathbf{k}, \mathbf{v}_1, z)$ being Laplace transform of $f(\mathbf{k}, \mathbf{v}_1, t)$

$$f(z) = \int\limits_0^\infty \mathrm{e}^{izt} f(t) \, dt.$$

The scattering operator in (2)

$$G(\tau) = \int dr^N d\mathbf{v}^{N-1} \, \mathrm{e}^{-i\mathbf{kr}_1} K_N \mathrm{e}^{-\tau(1-\mathcal{P})K_N} (1-\mathcal{P}) K_N \mathrm{e}^{i\mathbf{kr}_1} f_N^0 \frac{1}{\varphi_M(v_1)}.$$

After Laplace transformation we get the equation

$$(-iz + i\mathbf{k}\mathbf{v}_1) f(\mathbf{k}, \mathbf{v}_1, z) - \varphi_M(v_1)$$

$$= \int d\mathbf{v}^{N-1} dr^N \, \mathrm{e}^{-i\mathbf{kr}_1} \mathcal{P} K_N \frac{1}{-iz + (1-\mathcal{P})K_N}$$

$$\times (1-\mathcal{P}) K_N \mathrm{e}^{i\mathbf{kr}_1} \frac{f_N^0}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, z)$$

which right-hand side can be written as

$$G(\mathbf{k}, z) f(\mathbf{k}, \mathbf{v}_1, z) = \int d\mathbf{v}^{N-1} dr^N \, \mathrm{e}^{-i\mathbf{kr}_1} K_N \frac{1}{-iz} \frac{1}{1 - \frac{1}{iz}(1-\mathcal{P})K_N}$$

$$\times (1-\mathcal{P}) K_N \mathrm{e}^{i\mathbf{kr}_1} \frac{f_N^0}{\varphi_M(v_1)} f(\mathbf{k}, \mathbf{v}_1, z).$$

The first terms of the expansion are

$$G(\mathbf{k}, z) = \int d\mathbf{v}^{N-1} d\mathbf{r}^N \, \mathrm{e}^{-i\mathbf{k}\mathbf{r}_1} \Big[\frac{1}{iz} (K_N K_N - K_N \mathcal{P} K_N)$$
$$+ \Big(\frac{1}{iz} \Big)^2 (K_N K_N K_N - K_N K_N \mathcal{P} K_N - K_N \mathcal{P} K_N K_N + K_N \mathcal{P} K_N \mathcal{P} K_N)$$
$$+ \Big(\frac{1}{iz} \Big)^3 (\ldots) + \ldots \Big] \mathrm{e}^{i\mathbf{k}\mathbf{r}_1} \frac{f_N^0}{\varphi_M(v_1)}.$$

In the dilute gas approximation only linear terms with respect to $\rho = \frac{N}{V}$ are kept, and the following form of binary scattering operator is obtained

$$G_{12}(\mathbf{k}, z) = \frac{N-1}{V^2} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_2 \, (-iz + i\mathbf{k}\mathbf{v}_1) \mathrm{e}^{-i\mathbf{k}\mathbf{r}_1}$$
$$\times \int_0^\infty dt \, \mathrm{e}^{izt} \big(\mathrm{e}^{-tK_2} - \mathrm{e}^{-tK_2^0} \big) (-iz + i\mathbf{k}\mathbf{v}_1) \mathrm{e}^{i\mathbf{k}\mathbf{r}_1} \mathrm{e}^{-\beta u} \varphi_M(v_2).$$

For $\mathbf{k} = \mathbf{0}$ and $z = 0$ the scattering operator reduces to the Boltzmann scattering operator. It also takes the Boltzmann form for $\mathbf{k} = \mathbf{0}$, arbitrary z and sufficiently high velocity v_1.

4. Lorentz gas

The Lorentz gas corresponds to the case $m_2 \to \infty$, $v_2 \to 0$ and $\varphi_M(v_2) \to \delta(v_2)$. Only the velocity of particle 1 remains and is denoted by $\mathbf{v}_1 = \mathbf{v}$. The Lorentz model is widely studied as a simple model of a crystal, cf. for example [67] − [78].
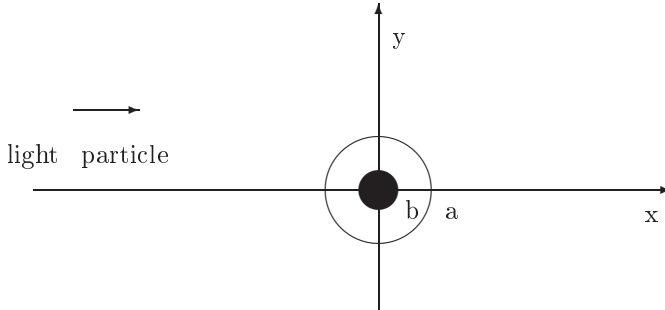

Figure 1. Spherical potential: hard core of radius b (black circle) and well (white ring) with internal radius b and external radius a

The Lorentz gas was examined in [66] for the following case of repulsive − attractive potential, see Figure 1,

$$u(r) = \infty \quad \text{if } r < b, \qquad u(r) = -u_0 < 0 \quad \text{if } b < r < a, \qquad u(r) = 0 \quad \text{if } r > a,$$

where r is the radius in polar coordinates. Thus, the potential possesses spherical rigid repulsive core of radius b surrounded by a well ($b < r < a$) of depth $-u_0$,

$u_0 > 0$. Scattering operator for this potential, for the dilute Lorentz gas has the following form

$$G_{12} f(\mathbf{k}, z, \mathbf{v}) = i(-z + \mathbf{k}\mathbf{v}) \frac{N}{V} \int d\mathbf{r}\, e^{-\beta u} \varphi_M(v) e^{-i\mathbf{k}\mathbf{r}}$$

$$\times \int_{t_1}^{\infty} dt\, e^{izt} \left(e^{-tK_2} - e^{-tK_2^0} \right) e^{i\mathbf{k}\mathbf{r}} i(-z + \mathbf{k}\mathbf{v}) \frac{f(\mathbf{k}, z, \mathbf{v})}{\varphi_M(v)}.$$

The KE for three-dimensional Lorentz gas of $N - 1$ fixed rigid spheres with the square-well attractive potential was given also in [66]. It is an integral (in configurational space) and functional (in velocity space) equation for the unknown distribution function $\psi(v)$ which links the values of $\psi(v)$ at 8 different values of argument v.

5. Lorentz gas of rigid spheres with finite time of collision τ^*

The potential of rigid sphere with rectangular well changes the time of interaction of the light particle with scatterer, is contrast to the zero time of interaction with the rigid sphere potential alone. To avoid additional consideration of scattering trajectory we accept the rigid sphere potential ($R_1 = R_2$), in which, however, the interacting particles remain connected for a certain time τ^*. This time of collision is negative in case of the potential well. In this case

$$G_{12} f(\mathbf{k}, z, \mathbf{v}) = v \varphi_M(v) \frac{N}{V} \frac{a^2}{4} \int d\Omega \left[\Psi(\mathbf{k}, z, \mathbf{v}') e^{iz\tau^*} - \Psi(\mathbf{k}, z, \mathbf{v}) + 1 - e^{iz\tau^*} \right],$$

where integration is performed over the full solid angle and

$$\Psi(\mathbf{k}, z, \mathbf{v}) \equiv \frac{f(\mathbf{k}, z, \mathbf{v})}{\varphi_M(v)}.$$

We introduce the following notation

$$\pi a^2 v \frac{N}{V} = \varepsilon_0^{-1}, \qquad \frac{1}{4\pi} \int d\Omega = \hat{P}.$$

Kinetic equation takes the form

$$(-iz + i\mathbf{k}\mathbf{v} + \varepsilon_0^{-1}) \Psi - h = \varepsilon_0^{-1} e^{iz\tau^*} (\hat{P}\Psi) + 1 - e^{iz\tau^*}.$$

Here $h = \delta(v - v')$ is the initial condition. Hence

$$\Psi = \frac{\varepsilon_0^{-1} e^{iz\tau^*}}{-iz + i\mathbf{k}\mathbf{v} + \varepsilon_0^{-1}} \hat{P}\Psi + \frac{h + 1 - e^{iz\tau^*}}{-iz + i\mathbf{k}\mathbf{v} + \varepsilon_0^{-1}}.$$

Therefore the solution reads

$$\Psi = \frac{\varepsilon_0^{-1} e^{iz\tau^*}}{-iz + i\mathbf{k}\mathbf{v} + \varepsilon_0^{-1}} \left(1 - \frac{e^{iz\tau^*}}{\mathbf{k}v\varepsilon_0} \arctan \frac{\mathbf{k}v\varepsilon_0}{1 - i\varepsilon_0 z} \right)^{-1}$$

$$\times \hat{P} \frac{h + 1 - e^{iz\tau^*}}{-iz + i\mathbf{k}\mathbf{v} + \varepsilon_0^{-1}} + \frac{h + 1 - e^{iz\tau^*}}{-iz + i\mathbf{k}\mathbf{v} + \varepsilon_0^{-1}}.$$

For the hydrodynamic pole we have

$$-iz = \varepsilon_0^{-1} + \mathbf{kv}\cot[(\cos z\tau^* - i\sin z\tau^*)\mathbf{kv}\varepsilon_0].$$

If the time of collision $\tau^* = 0$, KE equation becomes

$$(-iz + i\mathbf{kv} + \varepsilon_0^{-1})\Psi - h = v\varphi_M(v)\frac{N}{V}\frac{a^2}{4}\int d\Omega.$$

This is the classical Boltzmann equation for the Lorentz gas. Its solution has the form discussed by Hauge in [78].

6. One-dimensional KE

The 3 dimensional dynamics, even for the Lorentz gas, is still too complicated to be effectively solved and for this reason we limit ourselves to 1-dimensional model. It posseses some important features of 3-dimensional case, but mechanics of the light particle motion is more simple. It may be expected that the obtained results will have a more general meaning. Such procedure is often used, see [79] − [82].

The one-dimensional considerations permitted Fermi, Pasta, Ulam and Mary Tsingou to find that the behaviour of a 32-atom chain is quite different from intuitive expectation. Instead of thermalisation, a complicated quasi-periodic behaviour of the system was observed, [83], also [84].

Morita and Fukui considered the heat transfer in one-dimensional gas, [85], while Kac [86] − [89] and McKean [90] considered one-dimensional analogues of the linear Boltzmann equation.
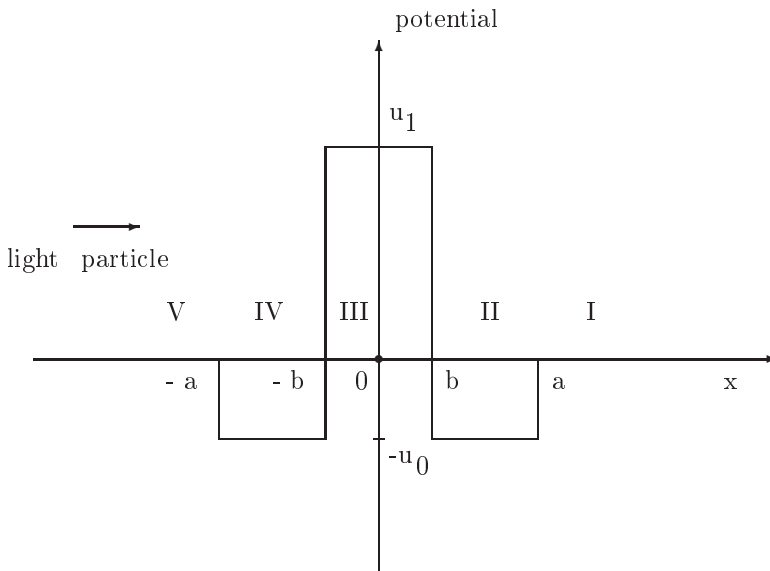

Figure 2. Configurational space of one-dimensional model. Light particle moves in potential of a well of depth $-u_0 < 0$ and a repulsive core of hight $u_1 > 0$

The Lorentz gas is examined here in one dimension, for the case of attractive – repulsive potential

$$u(x) = \begin{cases} u_1, & |x| < b, \\ -u_0 < 0, & b < |x| < a, \\ 0, & |x| > a. \end{cases}$$

The quantity $-u_0$, with $u_0 > 0$ is the depth of the potential well, while $u_1 > 0$ denotes the height of the potential barrier, see Figure 2.

6.1.   Kinetic equation in 1 dimension

The KE has still structure of (5) but vectors are now one-dimensional

$$(-iz + ikv)f(k, v, z) - f(k, v, t = 0) = G(k, z)f(k, v, z).$$

Scattering operator for the dilute Lorentz gas of N particles in one-dimensional segment L, $(-\frac{L}{2} < x < \frac{L}{2})$, has the following form

$$G(k,z)f(k,v,z) = i(-z + kv)\frac{N}{L}\int dx\, e^{-\beta u}\varphi_M(v)e^{-ikx}$$
$$\times \int\limits_{t_1}^{\infty} dt\, e^{izt}\left(e^{-tK_2} - e^{-tK_2^0}\right)e^{ikx}i(-z + kv)\frac{f(k,z,v)}{\varphi_M(v)} \qquad (6)$$

Here K_2 is the two particle Liouville operator, see (4), for $N = 2$. In calculations $L \to \infty$ but $\frac{N}{L}$ is kept constant. Such procedure is known as the thermodynamic limit (one increases the volume together with the particle number so that the average particle number density remains constant). Thus, integration with respect to x extends from minus to plus infinity. Below we put

$$\Psi(v) = \frac{f(k,z,v)}{\varphi_M(v)}.$$

The phase space is now two-dimensional only: one-dimension for positions and another for velocities of the light particle. The position space is divided into 5 regions, from I to V, see Figure 2, while the velocity space in each of these regions is divided, in dependence of kinetic energy of the particle (whether it permits for bounded or unbounded motion of the particle).

6.2.   Bounded motions

The bounded motion of particle occurs in regions of the potential well, II and IV, only, if simultaneously the particle kinetic energy is less than the depth of the well u_0.

Regions $b \leq x \leq a$ and $-a \leq x \leq -b$

Let us consider bounded motion of our particle in segment $b \leq x \leq a$ with velocity $v < \sqrt{\frac{2}{m} u_0}$. The position of particle along its trajectory is given by relation

$$
\begin{aligned}
e^{-tK_2} x &= x(-t) \\
&= x - vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)\eta(t_2 - t) \\
&\quad - [vt_1 + v'(t_2 - t_1) + v''(t - t_2)]\eta(t - t_2)\eta(t_3 - t) \\
&\quad - [vt_1 + v'(t_2 - t_1) + v''(t_3 - t_2) + v'''(t - t_3)]\eta(t - \tau_3)\eta(t_4 - t) \\
&\quad - \ldots - [vt_1 + v'(t_2 - t_1) + v''(t_3 - t_2) + v'''(t_4 - t_3) + v''''(t_5 - t_4) \\
&\quad + \ldots + v^{(2n)}(t_{2n+1} - t_{2n}) + v^{(2n+1)}(t - t_{2n+1})]\eta(t - \tau_{2n+1}).
\end{aligned}
$$

Similarly, the velocity is given by

$$
\begin{aligned}
e^{-tK_2} v &= v(-t) \\
&= v\eta(t_1 - t) + v'(t - t_1)\eta(t_2 - t) + v'(t - t_1)\eta(t_2 - t) \\
&\quad + v''\eta(t - t_2)\eta(t_3 - t) + v'''\eta(t - t_3)\eta(t_4 - t) \\
&\quad + \ldots + v^{(2n-1)}\eta(t - t_{2n-1})\eta(t_{2n} - t) \\
&\quad + v^{(2n)}\eta(t - t_{2n})\eta(t_{2n+1} - t) + v^{(2n+1)}\eta(t - t_{2n+1}).
\end{aligned}
$$

In the equation above we have

$$
v' = -v, \quad v'' = v, \ldots, v^{(2n-1)} = -v, \quad v^{(2n)} = v
$$

and $2n$ denotes the number of full periods performed by the particle in the time t. Moreover, t_m, $m = 1, 2, \ldots$ denotes the moment of bouncing from the wall of the well. The instant of the first collision of the particle with wall is given by

$$
t_1 = \frac{x - b}{|v|} \tag{7}
$$

and the next instants satisfy relations

$$
t_2 - t_1 = t_3 - t_2 = \ldots = t_m - t_{m-1} = \tau = \frac{a - b}{|v|}.
$$

Differences between the subsequent moments are identical and equal τ. Therefore the period of bouncing is 2τ.

For the time being we replace the infinity in the upper limit of time integral in (6) by T, and next extend $T \to \infty$ and $n \to \infty$.

$$
(G(k, z) f(k, v, z))_{IIA}
$$

$$
= i(-z + kv) \frac{N}{L} e^{\beta u_0} \varphi_M(v) \int_b^a dx\, e^{-ikx} \left\{ \int_{t_1}^{t_2} dt\, e^{i(z+kv)t} e^{-ik2vt_1} i(-z - kv) t \Psi(-v) \right.
$$

$$+ \int\limits_{t_2}^{t_3} dt \, e^{i(z-kv)t} e^{-ik[vt_1 - v(t_2 - t_1) - vt_2]} i(-z + kv) t \Psi(v)$$

$$+ \int\limits_{t_3}^{t_4} dt \, e^{i(z+kv)t} e^{-ik[vt_1 + vt_3]} i(-z - kv) t \Psi(-v)$$

$$+ \int\limits_{t_4}^{t_5} dt \, e^{i(z-kv)t} e^{-ik[vt_1 - v(t_4 - t_3) - vt_4]} i(-z + kv) t \Psi(v)$$

$$+ \ldots + \int\limits_{t_{2n-1}}^{t_{2n}} dt \, e^{i(z+kv)t} e^{-ik[vt_1 + vt_{2n-1}]} i(-z - kv) t \Psi(-v)$$

$$+ \int\limits_{t_{2n}}^{t_{2n+1}} dt \, e^{i(z-kv)t} e^{-ik[vt_1 - v(t_{2n} - t_{2n-1}) - vt_{2n}]} i(-z + kv) t \Psi(v)$$

$$+ \int\limits_{t_{2n+1}}^{T} dt \, e^{i(z+kv)t} e^{-ik[vt_1 + vt_{2n+1}]} i(-z - kv) t \Psi(-v)$$

$$- \int\limits_{t_1}^{T} dt \, e^{i(z-kv)t} i(-z + kv) t \Psi(v) \bigg\}.$$

We take n so large that

$$T - t_{2n+1} < \tau.$$

We integrate at first with respect to t, and next with respect to x. Variable x is found only in time of the first collision $t_1 = \frac{x-b}{v}$, cf. (7). After integration and passing with n to infinity, there appear series ot type

$$1 + e^{iz2\tau} + e^{iz4\tau} + \ldots + e^{iz2n\tau} + \ldots = \frac{1}{1 - e^{iz2\tau}} \qquad \text{for } n \to \infty.$$

Finally we find the following KE

$$(-iz + ikv)\Psi(v) - h(v) = C[\Psi(-v) - \Psi(v)]$$

with

$$h(v) = \frac{f(k, v, t = 0)}{\varphi_M(v)} \quad \text{and} \quad C = \frac{N}{L} |v| \frac{1 - 2e^{iz\tau} \cos(kv\tau) + e^{iz\tau}}{1 - e^{iz\tau}} e^{\beta u_0}.$$

Remark that C is even in v. The solution of KE reads

$$\Psi(v) = \frac{(-iz - ikv + C)h(v) + Ch(-v)}{-z^2 - 2izC + k^2 v^2}.$$

Identical relation describes the bound motion in segment $-a \leq x \leq -b$, with velocity $v < \sqrt{\frac{2}{m} u_0}$.

6.3. Unbounded motions

The phase subspaces of bounded and unbounded one-dimensional motions of the particle are separated by the value of its kinetic energy, in the dilute gas approximation. The particle once trapped in bounded motion, persists in it forever, and a particle in the phase subspace where unbounded motion occurs can never become bounded.

6.3.1. Region I: $(a < x < \infty)$

The particle which is at the time $t = 0$ in this region is subject to 3 accelerations if its kinetic energy is less then the height of the potential barrier u_1 (Case IA) or 4 accelerations if it is higher (Case IB).

Case IA: if $0 < v < \sqrt{\frac{2}{m}u_1}$ we have

$$
\begin{aligned}
x(-t) = x &- vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)\eta(t_2 - t) \\
&- [vt_1 + v'(t_2 - t_1) + v''(t - t_2)]\eta(t - t_2)\eta(t_3 - t) \\
&- [vt_1 + v'(t_2 - t_1) + v''(t_3 - t_2) + v'''(t - t_3)]\eta(t - t_3)
\end{aligned}
$$

and

$$
v(-t) = v\eta(t_1 - t) + v'\eta(t_2 - t)\eta(t - t_1) + v''\eta(t_3 - t)\eta(t - t_2) + v'''\eta(t - t_3)
$$

with

$$
v' = \frac{v}{|v|}\sqrt{v^2 + \frac{2}{m}u_0}, \quad v'' = -v', \quad v''' = -v \tag{8}
$$

and

$$
t_1 = \frac{x - a}{|v|}, \quad t_2 = t_1 + \frac{a - b}{|v'|}, \quad t_3 = t_2 + \frac{a - b}{|v'|} = t_1 + 2\frac{a - b}{|v'|}
$$

denote the moments of subsequent collisions. As before (Section 6.2), the position variable x is hidden in t_1.

After straightforward calculations we get the part of right hand side of (6) linked to this subregion

$$
\begin{aligned}
Gf_{(IA)} = \frac{N}{L}|v|\varphi_M(v) &\left\{ \left[1 - e^{i(z - kv')\frac{a-b}{|v'|}} \right] \Psi(v') \right. \\
&\left. + \left[1 - e^{i(z + kv')\frac{a-b}{|v'|}} \right] e^{i(z - kv')\frac{a-b}{|v'|}} \Psi(-v') + e^{iz2\frac{a-b}{|v'|}}\Psi(-v) - \Psi(v) \right\}
\end{aligned}
$$

Case IB: if $v > \sqrt{\frac{2}{m}u_1}$ we have

$$
\begin{aligned}
x(-t) = x &- vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)\eta(t_2 - t) \\
&- [vt_1 + v'(t_2 - t_1) + v''(t - t_2)]\eta(t - t_2)\eta(t_3 - t) \\
&- [vt_1 + v'(t_2 - t_1) + v''(t_3 - t_2) + v'''(t - t_3)]\eta(t - \tau_3)\eta(t_4 - t) \\
&- [vt_1 + v'(t_2 - t_1) + v''(t_3 - t_2) + v'''(t_4 - t_3) + v''''(t - t_4)]\eta(t - t_4)
\end{aligned}
$$

and

$$v(-t) = v\eta(t_1 - t) + v'\eta(t_2 - t)\eta(t - t_1) + v''\eta(t_3 - t)\eta(t - t_2)$$
$$+ v'''\eta(t_4 - t)\eta(t - t_3) + v''''\eta(t - t_4)$$

with

$$v' = \frac{v}{|v|}\sqrt{v^2 + \frac{2}{m}u_0}, \quad v'' = \frac{v}{|v|}\sqrt{v^2 - \frac{2}{m}u_1}, \quad v''' = v', \quad v'''' = v \qquad (9)$$

and

$$t_1 = \frac{x - a}{v}, \quad t_2 = t_1 + \frac{a - b}{v'}, \quad t_3 = t_2 + \frac{2b}{v''} \quad t_4 = t_3 + \frac{a - b}{v'}.$$

In this subregion

$$Gf_{(IB)} = \frac{N}{L}|v|\varphi_M(v)\left\{\left[1 - e^{i(z-kv')\frac{a-b}{|v'|}}\right]\left[1 + e^{i(z-kv'')\frac{2b}{|v''|}}e^{i(z-kv')\frac{a-b}{|v'|}}\right]\Psi(v')\right.$$
$$+ \left[1 - e^{i(z+kv'')\frac{2b}{|v''|}}\right]e^{i(z-kv')\frac{a-b}{|v'|}}\Psi(v'')$$
$$\left. - \left[1 - e^{i(z-kv')2\frac{a-b}{|v'|}}e^{i(z-kv'')\frac{2b}{|v''|}}\right]\Psi(v)\right\}.$$

6.3.2. Region II: $b < x < a$

The bounded motion in this region was described in Section 6.2.

The particle which is at the time $t = 0$ in this region and has kinetic energy higher than the depth of the well u_0, is in an unbounded motion and has undergone 2 accelerations if its kinetic energy is lower than the hight of potential barrier u_1 (Case IIA) or 3 accelerations if its kinetic energy is higher than the barrier (Case IIB).

Case IIA: if $\sqrt{\frac{2}{m}u_1} > v > \sqrt{\frac{2}{m}u_0}$ we have

$$x(-t) = x - vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)\eta(t_2 - t)$$
$$- [vt_1 + v'(t_2 - t_1) + v''(t - t_2)]\eta(t - t_2)$$

and

$$v(-t) = v\eta(t_1 - t) + v'\eta(t_2 - t)\eta(t - t_1) + v''\eta(t - t_2)$$

with

$$v' = -v, \quad v'' = -\frac{v}{|v|}\sqrt{v^2 - \frac{2}{m}u_0} \quad \text{and} \quad t_1 = \frac{x - b}{|v|}, \quad t_2 = t_1 + \frac{a - b}{|v|}.$$

Now

$$Gf_{(IIA)} = \frac{N}{L}|v|e^{\beta u_0}\varphi_M(v)\left[1 - e^{-i(z+kv)\frac{a-b}{|v|}}\right]$$
$$\left\{\left[1 - e^{i(z+kv)\frac{a-b}{|v|}}\right]\Psi(-v) + e^{i(z+kv)\frac{a-b}{|v|}}\Psi(v'')) - \Psi(v)\right\}.$$

Case IIB: if $v > \sqrt{\frac{2}{m}u_1}$ we have

$$x(-t) = x - vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)\eta(t_2 - t)$$
$$- [vt_1 + v'(t_2 - t_1) + v''(t - t_2)]\eta(t - t_2)\eta(t_3 - t)$$
$$- [vt_1 + v'(t_2 - t_1) + v''(t_3 - t_2) + v'''(t - t_3)]\eta(t - \tau_3)$$

and

$$v(-t) = v\eta(t_1 - t) + v'\eta(t_2 - t)\eta(t - t_1) + v''\eta(t - t_2)\eta(t_3 - t) + v'''\eta(t - t_3)$$

with

$$v' = \frac{v}{|v|}\sqrt{v^2 - \frac{2}{m}(u_0 + u_1)}, \quad v'' = v, \quad v''' = \frac{v}{|v|}\sqrt{v^2 - \frac{2}{m}u_0} \qquad (10)$$

and

$$t_1 = \frac{x - b}{v}, \quad t_2 = t_1 + \frac{2b}{|v'|} \quad t_3 = t_2 + \frac{a - b}{|v|}.$$

Now

$$Gf_{(IIB)} = \frac{N}{L}|v|\, e^{\beta u_0}\varphi_M(v)\left[1 - e^{i(z-kv)\frac{a-b}{|v|}}\right]$$
$$\times \left\{\left[1 - e^{i(z-kv')\frac{2b}{|v'|}}\right]\Psi(v') + e^{i(z-kv')\frac{2b}{|v'|}}e^{i(z-kv)\frac{a-b}{|v|}}\Psi(v''')\right.$$
$$\left. + \left(\left[1 - e^{i(z-kv)\frac{a-b}{|v|}}\right]e^{i(z-kv')\frac{2b}{|v'|}} - 1\right)\Psi(v)\right\}.$$

6.3.3. Region III: $-b < x < b$

The particle being at $t = 0$ in this region, has undergone 2 accelerations. The time dependence of its position and velocity is the following

$$x(-t) = x - vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)\eta(t_2 - t)$$
$$- [vt_1 + v'(t_2 - t_1) + v''(t - t_2)]\eta(t - t_2)$$

and

$$v(-t) = v\eta(t_1 - t) + v'\eta(t_2 - t)\eta(t - t_1) + v''\eta(t - t_2)$$

with

$$v' = \frac{v}{|v|}\sqrt{v^2 + \frac{2}{m}(u_0 + u_1)}, \quad v'' = \frac{v}{|v|}\sqrt{v^2 + \frac{2}{m}u_1} \qquad (11)$$

and

$$t_1 = \frac{x + b}{|v|}, \quad t_2 = t_1 + \frac{a - b}{|v'|}.$$

Now

$$Gf_{(III)} = \frac{N}{L}e^{-\beta u_1}|v|\varphi_M(v)\left[1 - e^{i(z-kv)\frac{2b}{|v|}}\right]$$
$$\times \left\{e^{i(z-kv')\frac{a-b}{|v'|}}\Psi(v'') + \left[1 - e^{i(z-kv')\frac{a-b}{|v'|}}\right]\Psi(v') - \Psi(v)\right\}.$$

6.3.4.   Region IV: $-a < x < -b$

The particle which is at the time $t = 0$ in this region and has kinetic energy less than the depth of the well, is in the bounded motion (see section 6.2). In the opposite case, the particle has undergone 1 acceleration.

If $v > \sqrt{\frac{2}{m}u_0}$ we have

$$x(-t) = x - vt\eta(t_1 - t) - [vt_1 + v'(t - t_1)]\eta(t - t_1)$$

and

$$v(-t) = v\eta(t_1 - t) + v'\eta(t - t_1)$$

with

$$v' = \frac{v}{|v|}\sqrt{v2 - \frac{2}{m}u_0} \qquad \text{and} \qquad t_1 = \frac{x + a}{|v|}.$$

Then

$$Gf_{(IV)} = \frac{N}{L}e^{\beta u_0}|v|\varphi_M(v)\left[1 - e^{i(z-kv)\frac{a-b}{v}}\right][\Psi(v') - \Psi(v)].$$

6.3.5.   Region V: $-\infty < x < -a$

In this region the potential vanishes and operators $\exp(-tK_2)$ and $\exp(-tK_2)$ are identical, and contribution of this region to the integral operator G is zero.

7.   Kinetic equation in 1 dimension

We gather all contributions to the scattering operator found in the previous section to get KE for unbounded motions $(v^2 > \frac{2}{m}u_0)$. At first we introduce common definitions of velocities appearing in the equation. These are

$$v_1 = \frac{v}{|v|}\sqrt{v2 - \frac{2}{m}(u_0 + u_1)} \qquad \text{for } v^2 \geq \frac{2}{m}(u_0 + u_1) \quad \text{cf. } (10)_1$$

$$v_2 = \frac{v}{|v|}\sqrt{v2 - \frac{2}{m}u_1} \qquad \text{for } v^2 \geq \frac{2}{m}u_1 \qquad \text{cf. } (9)_2$$

$$v_3 = \frac{v}{|v|}\sqrt{v2 - \frac{2}{m}u_0} \qquad \text{for } v^2 \geq \frac{2}{m}u_0 \qquad \text{cf. } (10)_3$$

$$v_4 = \frac{v}{|v|}\sqrt{v2 + \frac{2}{m}u_0} \qquad\qquad\qquad\qquad \text{cf. } (8)_1$$

$$v_5 = \frac{v}{|v|}\sqrt{v2 + \frac{2}{m}u_1} \qquad\qquad\qquad\qquad \text{cf. } (11)_2$$

$$v_6 = \frac{v}{|v|}\sqrt{v2 + \frac{2}{m}(u_0 + u_1)} \qquad\qquad\qquad \text{cf. } (11)_1$$

in the form

$$(-iz + ikv)\Psi(v) - h(v) = \mathcal{G}\Psi(v)$$

with

$$h(v) = \frac{f(k, v, t = 0)}{\varphi_M(v)}$$

and

$$\mathcal{G}\Psi(v)$$
$$= \frac{N}{L}|v|\frac{1}{\varphi_M(v)}\Big[Gf_{(III)} + Gf_{(IV)}$$
$$+ \eta(v^2 < \frac{2}{m}u_1)\left(Gf_{(IA)} + Gf_{(IIA)}\right) + \eta(v^2 > \frac{2}{m}u_1)\left(Gf_{(IB)} + Gf_{(IIB)}\right)\Big]$$

or

$$\mathcal{G}\Psi(v)$$
$$= \frac{N}{L}|v|\Big[\mathrm{e}^{-\beta u_1}\left(1 - \mathrm{e}^{i(z-kv)\frac{2b}{|v|}}\right)\Big\{\mathrm{e}^{i(z-kv_6)\frac{a-b}{|v_6|}}\Psi(v_5)$$
$$+ \Big[1 - \mathrm{e}^{i(z-kv_6)\frac{a-b}{|v_6|}}\Big]\Psi(v_6) - \Psi(v)\Big\} + \mathrm{e}^{\beta u_0}\Big[1 - \mathrm{e}^{i(z-kv)\frac{a-b}{v}}\Big][\Psi(v_3) - \Psi(v)]$$
$$+ \eta\big(\frac{2}{m}u_1 - v^2\big)\Big\{\Big[1 - \mathrm{e}^{i(z-kv_4)\frac{a-b}{|v_4|}}\Big]\Psi(v_4)$$
$$+ \Big[1 - \mathrm{e}^{i(z+kv_4)\frac{a-b}{|v_4|}}\Big]\mathrm{e}^{i(z-kv_4)\frac{a-b}{|v_4|}}\Psi(-v_4) + \mathrm{e}^{iz2\frac{a-b}{|v_4|}}\Psi(-v) - \Psi(v)\Big\}$$
$$+ \mathrm{e}^{\beta u_0}\Big[1 - \mathrm{e}^{-i(z+kv)\frac{a-b}{|v|}}\Big]$$
$$\times \Big\{\Big[1 - \mathrm{e}^{i(z+kv)\frac{a-b}{|v|}}\Big]\Psi(-v) + \mathrm{e}^{i(z+kv)\frac{a-b}{|v|}}\Psi(-v_3) - \Psi(v)\Big\}$$
$$+ \eta\big(v^2 - \frac{2}{m}u_1\big)\Big\{\Big[1 - \mathrm{e}^{i(z-kv_4)\frac{a-b}{|v_4|}}\Big]\Big[1 + \mathrm{e}^{i(z-kv_2)\frac{2b}{|v_2|}}\mathrm{e}^{i(z-kv_4)\frac{a-b}{|v_4|}}\Big]\Psi(v_4)$$
$$+ \Big[1 - \mathrm{e}^{i(z+kv_2)\frac{2b}{|v_2|}}\Big]\mathrm{e}^{i(z-kv_4)\frac{a-b}{|v_4|}}\Psi(v_4)$$
$$- \Big[1 - \mathrm{e}^{i(z-kv_4)2\frac{a-b}{|v_4|}}\mathrm{e}^{i(z-kv_2)\frac{2b}{|v_2|}}\Big]\Psi(v)\Big\}$$
$$+ \mathrm{e}^{\beta u_0}\Big[1 - \mathrm{e}^{i(z-kv)\frac{a-b}{|v|}}\Big]\Big\{\Big[1 - \mathrm{e}^{i(z-kv_1)\frac{2b}{|v_1|}}\Big]\Psi(v_1)$$
$$+ \mathrm{e}^{i(z-kv_1)\frac{2b}{|v_1|}}\mathrm{e}^{i(z-kv)\frac{a-b}{|v|}}\Psi(v_3)$$
$$+ \Big(\Big[1 - \mathrm{e}^{i(z-kv)\frac{a-b}{|v|}}\Big]\mathrm{e}^{i(z-kv_1)\frac{2b}{|v_1|}} - 1\Big)\Psi(v)\Big\}\Big]$$

For $k, z \to 0$, it is for the long waves and low frequencies, the scattering operator of our KE changes to the Boltzmann operator

$$G\Psi((v) = \frac{N}{L}|v|\ [\Psi(-v) - \Psi(v)]\,. \tag{12}$$

Our scattering operator takes also the form of the Boltzmann operator for sufficiently high velocity v, if the time of collision of light partile with heavy particle of crystal can be neglected.

From mathematical point of view, we see that our KE generates an infinite sequence of functional equations. Its solution is a problem for the next publication.

8.   Conclusions

We have analyzed KE valid for a dilute Lorentz gas with short range attraction potential and have given the explicit forms of the scattering operator for different forms of potential, for which some exact solutions can be found. For $k = 0$ and $z = 0$ operator reduces to the Boltzmann scattering operator. Thus our approach enlarges the possibility of description of diffusion for the case when time of particle collisions is not negligeable. The KE for light particle diffusion in one-dimensional Lorentz gas was also derived. The solution of this KE will be discussed later.

The common feature of the obtained kinetic equations is that they link the values of the probability density Fourier-Laplace transform in different points of the velocity axis. Therefore these equations are the functional equations, [91, 92].

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