

# Boltzmann Kinetics and Mathematical Modeling in Nanotechnology

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**Abstract.** . We investigate some properties of discrete velocity models and their generalizations. We discuss perspectives of their applications in chemical and nanotechnologies.

**Keywords:** Boltzmann equation, discrete velocity models, chemical kinetics, nanotechnology.

**PACS:** 51.10.+y, 05.20.Dd, 87.15.Rn

Discrete Velocity Models are now flourished and widely used now for simulation in hydro- and gas dynamics and Chemical Kinetics. [1,2] The following questions are discussed.

- (1) Boltzmann equation, first discrete models and Nanotechnology projects.
- (2) First models for mixtures. Conservational laws and spurious invariants [3,4].
- (3) Generalizations for chemical kinetics. H-theorem [1],[5].
- (4) Motion of a large particle in chemically active gaz. [6].

1. What is Nanotechnology? Nano is a prefix that means  $10^{-9}$  (milly, micro, nano, pico, femto...). When they say about nanotechnology, they mean technology at the scale of nanometer. Why this scale is so important? We discuss it as it was explained in the Report “Nanotechnology Development Directions” of Interagency Working Group on Nanoscience, Engineering and Technology of National science and Technology Council of USA. In the chapter 2 (Investigative tools: theory, modeling, experiment) of this Report we read “The growing speed of computers allows us to find numerical solutions, including Shockley equation for semiconductors, Maxwell equations , Boltzmann equation, Shrodinger equation – all with real boundary conditions in three dimensional cases.” So the first scientists in nanotechnology are the creators of molecular kinetic theory Maxwell, Boltzmann... History of Boltzmann equation is nontrivial and interesting..

2. It is very important to write correct discrete models. One of the properties is correct number of conservational laws for discrete models: conservational laws have to be the same as in the original equation. In the case of Boltzmann equation for mixtures we have to keep exactly  $r+d+1$  (r for number of particles for every specie, d components for moments in d-dimensional case, and one for energy). First models for mixtures were created recently and classification was proposed by Cercigniani, Cornile, Bobylev, Vinerean, Vedenyapin, Amossov [3,4,10]. The only model in onedimentional case without spurious invariants was constructed : this was possible to do only for the rtatio of masses  $M/m=3$  (Amossov, Vedenyapin). Approximation theorem was proved for the Boltzmann equation by discrete models for  $d = 3$  (Bobylev, Paltchevskii, Shnider) and for  $d = 1$  (Adjiev, Amossov, Vedenyapin).

Estimates for number of particles for given ratio of masses  $M/m$  is proposed. If we try to construct a symmetrical cubic model with the origin as the center of the cube and the side parallel to the axis, then we see that the side grows with the ratio of masses. What is the speed of this grow? The simplest estimate is the following. The half of the length of the side  $S_d$  of the cube satisfies the following inequality :  $S_d(M/m) \geq \sqrt{M / md}$  .

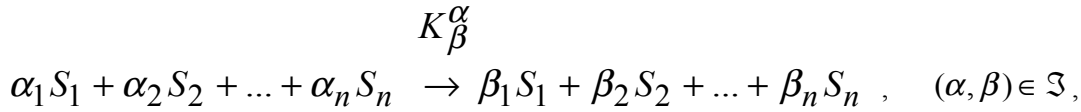
3. Generalized H-theorem.

For the case of chemically reacting gas one can write generalized version of discrete velocity model. We investigated conditions for cross sections for which H-theorem could be proved [5].

In general case equations for complex chemical reactions are written as follows [1]:

$$\frac{df_i}{dt} = \sum_{(\alpha, \beta) \in \mathfrak{S}} (\beta_i - \alpha_i) K_{\beta}^{\alpha} f^{\alpha}, \quad i=1, \dots, n. \quad (1)$$

Here  $f^{\alpha}$  is a product  $f^{\alpha} = f_1^{\alpha_1} f_2^{\alpha_2} \dots f_n^{\alpha_n}$ , summation is over a finite set  $\mathfrak{S}$  of multiindexicies  $(\alpha, \beta)$ , where  $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_n)$  и  $\beta = (\beta_1, \beta_2, \dots, \beta_n)$  are vectors with integer nonnegative components. An item  $(\alpha, \beta)$  corresponds to an elementary reaction



$S_i$  — are chemical symbols of reacting substances,  $K_{\beta}^{\alpha}$  are coefficients of speeds of reactions.  $\alpha_i, \beta_i$  are called stoichiometric coefficients. We can consider the set  $\mathfrak{S}$  symmetrical over transposition of  $\alpha$  and  $\beta$ .

When the system (1) has  $H$ -function — a functional of entropy type, decreasing on the solutions of the system (1)?

The simplest case, when  $H = \sum f_i (\ln f_i - 1)$  decreases for the system (1) — is *symmetrical* case (

$K_{\beta}^{\alpha} = K_{\alpha}^{\beta}$  for all reactions  $(\alpha, \beta) \in \mathfrak{S}$ ). The set of such systems denote as  $S$  (symmetrical).

One more important case are systems for which detailed balance is possible, i.e. there exists at least one solution of the system of  $m$  equations ( $m$  is a number of elementary reactions).

$$K_{\beta}^{\alpha} f^{\alpha} = K_{\alpha}^{\beta} f^{\beta}. \quad (2)$$

this equation can be written in the form

$$f_1^{\alpha_1 - \beta_1} f_2^{\alpha_2 - \beta_2} \dots f_n^{\alpha_n - \beta_n} = \frac{K_{\alpha}^{\beta}}{K_{\beta}^{\alpha}}. \quad (3)$$

Taking the logarithm we obtain the system of linear equations for  $\ln f_i$  ( $i=1, \dots, n$ ).

The set of systems that possess such solution denote by  $D$  (*detailed balanced systems*). H-theorem now can be proved for modified H-function

$$H = \sum f_i \left( \ln \frac{f_i}{\xi_i} - 1 \right), \quad (4)$$

where  $\xi$  — is one of positive solutions of system (2).

Consider more general condition with the function (4) decreasing for system (1) *Condition of dynamical balance*. Let there exist at least one solution of the system

$$\sum_{\beta} K_{\beta}^{\alpha} \xi^{\alpha} = \sum_{\beta} K_{\alpha}^{\beta} \xi^{\beta}, \quad (5)$$

here  $\alpha$  are such that  $(\alpha, \beta) \in J$  for some  $\beta$ . Summation is going only over those  $\beta$ , for which  $K_{\beta}^{\alpha} \neq 0$  or  $K_{\alpha}^{\beta} \neq 0$ . Those systems we shall call of class  $E$  (dynamical balanced).

*Theorem 1.* Let for the system (1) coefficients  $K_{\beta}^{\alpha}$  are such that there exists at least one solution  $\xi$  of the system of equations (5).

Then:

a)  $H$ -function (4) does not increase on the solutions of the system (1):  $\frac{dH}{dt} \leq 0$ . All the stationary solutions of the system (1) satisfy (5);

б) system (1) have  $n-r$  linear conservational laws  $\sum \mu_i^k f_i(t) = A^k = \text{const} \quad (k=1, \dots, n-r)$ , where  $r$  is the dimension of linear hull of vectors  $\alpha - \beta$ , and vectors  $\mu^k$  are orthogonal to all  $\alpha - \beta$ :  $\sum \mu_i^k (\alpha_i - \beta_i) = 0$ . Stationary solution of system (6.1) is unique, if we fix all the constants  $A^k$  of those conservational laws, and those stationary solutions can be found by the following formula

$$f_{0i} = \xi_i \exp \left( \sum_k \mu_i^k \lambda^k \right), \quad (6)$$

where  $\lambda^k$  can be find by  $A^k$  uniquely;

в) this stationary solution exists, if  $A^k$  can be found by the initial data  $f(0)$ ,  $A^k = \sum \mu_i^k f_i(0)$ . The solution  $f(t)$  with this initial data exists for all  $t > 0$ , unique and tends to (6) as  $t$  tends to infinity.[1,5].

Let show that the situation also can be generalized for continuity equation for an arbitrary dynamical system  $dx/dt=v(x)$ :

$$\frac{\partial f}{\partial t} + \left( v(x), \frac{\partial f}{\partial x} \right) + f \text{div} v(x) = 0. \quad (7)$$

This equation can be written as a partial case of the following

$$\frac{\partial f}{\partial t} = \int [K(w, v) f(w) dw - K(v, w) f(v, t)] dw = L(f) \quad (8)$$

we get equation (7) from (8), if we take

$$K(x, y) = (v(x), \nabla \delta(x-y)). \quad (9)$$

For (8) H-theorem can be proved for the following H-function:

$$H(f) = \int f \ln[f(v)/\xi(v)] dv.$$

Here  $\xi(v)$  is some positive solution of stationary equation (8).

Another direction of generalizations is connected with more serious changing of H-functions and includes quantum versions [1,7].

Let  $H(n)$  — is some arbitrary function and  $h_i = \exp(\partial H / \partial n_i)$ . Let  $B_{\beta}^{\alpha}(n)$  — is a set of positive functions, symmetrical over transposition of  $\alpha$  and  $\beta$ . Consider a system of differential equations:

$$\frac{dn_i}{dt} = \sum_{(\alpha, \beta)} (\alpha_i - \beta_i) B_{\beta}^{\alpha} (h^{\beta} - h^{\alpha}). \quad (10)$$

It also has a set of conservational laws  $\sum \mu_i n_i$ , where  $(\mu, \beta - \alpha) = 0$ .

Functional  $H$  decreases for (10):

$$dH/dt = - \sum_{(\alpha, \beta)} B_{\beta}^{\alpha} (\nabla H, \alpha - \beta) (\exp(\nabla H, \alpha) - \exp(\nabla H, \beta)) \leq 0.$$

We get quantum versions of (2.5) if we take H-function in the following form

$$H = \sum_j H_{\theta_j}(f_j), \text{ for } H_{\theta}(f) = f \ln f - \theta^{-1} (1 + \theta f) \ln(1 + \theta f),$$

with  $\theta = +1$  for bosons,  $\theta = -1$  for fermions and  $\theta = 0$  for Boltzmann statistics. The simplest case of those quantum discrete velocity models was considered in [2], where in particular global existence theorem was proved for fermions.

It would be perspective to prove theorem 1 for nonstandard H-function with nonsymmetrical coefficients

$B_{\beta}^{\alpha}$  and to construct simple spatially non-homogeneous models for mixtures in the sense of point 2 but with

chemical reactions. But the reality is much more difficult and interesting as big particles can interact with molecules with reactive forces. In the following point we shall describe this situation.

4. The case of a big particle, moving in chemically reacting gas, was considered. It was called chemo-jet motion and was found experimentally by chemists. A model of a chemical reaction on the surface of a body was created and a system of equations of motion was written and investigated. We got an ideal cylindrical spiral trajectory in asymptotic when time tends to infinity. This justified qualitatively the result of experiment of European Cosmic Agency and of a group of scientists from Chemical faculty of Moscow State University. A step and a diameter of those cone were calculated in exact form [6].

A model can be described as follows. A particle is considered as a ball which is determined by coordinates of center of mass  $R$ , momentum  $Q$ , angular momentum  $K$ , and the unit vector  $S$  directed from a center of mass to the center of active zone. We assume that some molecules are elastically reflected from the surface of the particle and some of them adheres (the adherence models chemical interaction). We assume that the fraction of adhering particles

at a point of the ball with the internal normal  $n$  is  $\beta = \beta(n)$ , and we put  $A = \int_{S_2} n \cdot \beta(n) dn$  and orientation vector

$S = A/|A|$ . Dynamics of this vector is described by the equation  $\frac{dS}{dt} = \frac{1}{J} \cdot [K, S]$ , where  $\bar{J}$  is a moment of inertia.

A system of equation can be written in the form

$$\begin{cases} \frac{dR}{dt} = \frac{Q}{M}, \\ \frac{dQ}{dt} = F_{chem} + F_{elast}, \\ \frac{dK}{dt} = M_{chem}, \\ \frac{dS}{dt} = \frac{1}{J} [K, S]. \end{cases} \quad (11)$$

The first equation is the definition of a velocity, the second is Newton law with two terms. The first one is connected with inelastic collisions and have the form

$$F_{chem} = \rho^2 \iint_{\mathbb{R}^3 \times S^2} \beta(n, S) \{p - 2\mu(u, n)n\} (u, n) \theta((u, n)) f(R - \rho n, p) dn dp. \quad (12)$$

The second is determined by elastic collisions

$$F_{elast} = 2\mu\rho^2 \iint_{\mathbb{R}^3 \times S^2} n(u, n)^2 \theta((u, n)) f(R - \rho n, p) dn dp. \quad (13)$$

The third equation describes changing of a moment  $\frac{dK}{dt}$  and connected only with inelastic collisions (in the case of a ball):

$$M_{chem} = \mu \rho^3 \iint_{\mathbf{R}^3 \times \mathbf{S}^2} \beta(n, S) [u, n] (u, n) \theta((u, n)) f(R - \rho n, p) dn dp. \quad (14)$$

Here  $\mu = \frac{mM}{M+m}$  — is the reduced mass,  $\rho$  is the radius of the ball particle,  $u$  is the relative velocity,  $\theta$  is a Heaviside function,  $f(r, p)$  is a distribution function of molecules.

We take distribution function  $f$  Maxwellian, assume that the ratio of the particle velocity and the mean square velocity of gas molecules is small and the rotation is almost constant. Then we get the following system

$$\begin{cases} \frac{dR}{dt} = \frac{Q}{M}, \\ \frac{dQ}{dt} = (\chi_0 + \chi_1(Q, S))S - \lambda Q, \quad \omega = K/J \approx const. \\ \frac{dS}{dt} = [\omega, S], \end{cases} \quad (15)$$

Integration of this system shows that the trajectory  $R(t)$  tends to cylindrical spiral with a constant step  $L$  and diameter  $D$ :

$$L = \frac{2\pi(P_\infty, \omega)}{M\omega^2}, \quad D = \frac{2\sqrt{P_\infty^2 \omega^2 - (P_\infty, \omega)^2}}{M\omega^2}. \quad (16)$$

The case of general form of a particle was considered by Batisheva [8].

This model was used for explanation of photophoresis. This is a movement of a particle under light and there is direct Photophoresis (from the source of light) and indirect one (towards the source of light) [9].

The further development of the subject is the derivation of Kinetic equation of such particles in order to describe chemical reactions of particles of different sizes. And to construct simple discrete models.

## ACKNOWLEDGMENTS

The author is acknowledged to RFBR-grant № 05-01-00642, programm 3.5 of Mathematical department of RAS, and grant of Russian Science Support Foundation.

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