On Derivation of Kinetic Equations for Granular Media: Brief Survey

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Abstract. A new approach to the rigorous derivation of a priori kinetic equations from the dynamics of inelastically colliding particles, namely, the Enskog-type and Boltzmann-type kinetic equations describing granular media, is reviewed. The problem of potential possibilities inherent in describing the evolution of the states of a system of many hard spheres with inelastic collisions by means of a one-particle distribution function is also considered.

Key words: granular media, inelastic collision, Boltzmann equation, Enskog equation

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Contents

1 Introduction

It is well known, that the properties of granular media (sand, powders, cements, seeds, etc.) have been extensively studied, in the last decades, by means of experiments, computer simulations and analytical methods, and a huge amount of physical literature on this topic has been published (for pointers to physical literature see in [1–6]).

Granular media are systems of many particles that attract considerable interest not only because of their numerous applications, but also as systems whose collective behavior differs from the statistical behavior of ordinary media, i.e. typical macroscopic properties of media, for example, such as gases. In particular, the most spectacular effects include with the phenomena of collapse or cooling effect at the kinetic scale or clustering at the hydrodynamical scale, spontaneous loss of homogeneity, modification of Fourier's law and non-Maxwellian equilibrium kinetic distributions [1–3].

In modern works [4–6], it is assumed that the microscopic dynamics of granular media is dissipative and it is described by a system of many hard spheres with inelastic collisions. The purpose of this survey is to review some advances in the mathematical understanding of kinetic equations of systems with inelastic collisions.

As is known [7], the collective behavior of many-particle systems can be effectively described by means of a one-particle distribution function governed by the kinetic equation derived from underlying dynamics in a suitable scaling limit. At present the considerable advance is observed in a problem of the rigorous derivation of the Boltzmann kinetic equation for a system of hard spheres in the Boltzmann–Grad scaling limit [7–10]. At the same time many recent papers [5], [11] (and see references therein) consider the Boltzmann-type and the Enskog-type kinetic equations for inelastically interacting hard spheres, modelling the behavior of granular gases, as the original evolution equations and the rigorous derivation of such kinetic equations remains still an open problem [12], [13].

Hereinafter, an approach will be formulated, which makes it possible to rigorously justify the kinetic equations previously introduced a priori for the description of granular media, namely, the Enskog-type and Boltzmann-type kinetic equations. In addition, we will consider the problem of potential possibilities inherent in describing the evolution of the states of a system of many hard spheres with inelastic collisions by means of a one-particle distribution function.

2 Dynamics of hard spheres with inelastic collisions

As mentioned above, the microscopic dynamics of granular media is described by a system of many hard spheres with inelastic collisions. We consider a system of a non-fixed, i.e. arbitrary, but finite average number of identical particles of a unit mass with the diameter $\sigma > 0$, interacting as hard spheres with inelastic collisions. Every particle is characterized by the phase coordinates: $(q_i, p_i) \equiv x_i \in \mathbb{R}^3 \times \mathbb{R}^3$, $i \geq 1$.

Let C_γ be the space of sequences $b = (b_0, b_1, \ldots, b_n, \ldots)$ of bounded continuous functions $b_n \in C_n$ defined on the phase space of n hard spheres that are symmetric with respect to the permutations of the arguments $x_1, \ldots, x_n$, equal to zero on the set of forbidden configurations $\mathbb{W}_n \doteq \big\{(q_1, \ldots, q_n) \in \mathbb{R}^{3n} \big| |q_i - q_j| < \sigma$ for at least one pair $(i,j) : i \neq j \in (1, \ldots, n)\big\}$ and equipped with the norm: $\|b\|_{C_\gamma} = \max_{n\geq 0} \frac{\gamma^n}{n!} \|b_n\|_{C_n} = \max_{n\geq 0} \frac{\gamma^n}{n!} \sup_{x_1,\ldots,x_n} |b_n(x_1, \ldots, x_n)|$. We denote the set of continuously differentiable functions with compact supports by $C_{n,0} \subset C_n$.

We introduce the semigroup of operators $S_n(t)$, $t \geq 0$, that describes dynamics of n hard spheres. It is defined by means of the phase trajectories of a hard sphere system with inelastic collisions almost everywhere on the phase space $\mathbb{R}^{3n} \times (\mathbb{R}^{3n} \setminus \mathbb{W}_n)$, namely, outside the set $\mathbb{M}_n^0$ of the zero Lebesgue measure, as follows [14]:

$$
\begin{aligned}
&(S_n(t)b_n)(x_1, \ldots, x_n) \equiv S_n(t, 1, \ldots, n) b_n(x_1, \ldots, x_n) \doteq \\
&\begin{cases} b_n(X_1(t), \ldots, X_n(t)), & \text{if } (x_1, \ldots, x_n) \in (\mathbb{R}^{3n} \setminus \mathbb{W}_n) \times \mathbb{R}^{3n}, \\ 0, & \text{if } (q_1, \ldots, q_n) \in \mathbb{W}_n, \end{cases}
\end{aligned} \tag{1}
$$

where the function $X_i(t) \equiv X_i(t, x_1, \ldots, x_n)$ is a phase trajectory of ith particle constructed in [7] and the set $\mathbb{M}_n^0$ consists from phase space points specified initial data $x_1, \ldots, x_n$ that generate multiple collisions during the evolution.

On the space C_n one-parameter mapping (1) is an bounded $*$-weak continuous semigroup of operators, and $\big\|S_n(t)\big\|_{C_n} < 1$.

The infinitesimal generator $\mathcal{L}_n$ of the semigroup of operators (1) is defined in the sense of a $*$-weak convergence of the space $\mathcal{C}_n$ and it has the structure $\mathcal{L}_n = \sum_{j=1}^n \mathcal{L}(j) + \sum_{j_1<j_2=1}^n \mathcal{L}_{\mathrm{int}}(j_1, j_2)$, and the operators $\mathcal{L}(j)$ and $\mathcal{L}_{\mathrm{int}}(j_1, j_2)$ are defined by formulas:

$$
\mathcal{L}(j) \doteq \langle p_j, \frac{\partial}{\partial q_j} \rangle, \tag{2}
$$

and

$$
\begin{aligned}
&\mathcal{L}_{\mathrm{int}}(j_1, j_2) b_s \doteq \sigma^2 \int_{\mathbb{S}_+^2} d\eta \langle \eta, (p_{j_1} - p_{j_2}) \rangle \big(b_s(x_1, \ldots, x_{j_1}^*, \ldots, x_{j_2}^*, \ldots, x_s) - \\
&b_s(x_1, \ldots, x_s) \big) \delta(q_{j_1} - q_{j_2} + \sigma\eta),
\end{aligned} \tag{3}
$$

respectively. In (2),(3) the following notations are used: $x_j^* \equiv (q_j, p_j^*)$, the symbol $\langle\cdot,\cdot\rangle$ means a scalar product, δ is the Dirac measure, $\mathbb{S}_+^2 \doteq \{\eta \in \mathbb{R}^3 \big| \, |\eta| = 1, \, \langle \eta, (p_{j_1} - p_{j_2})\rangle \geq 0\}$ and the post-collision momenta are determined by the expressions:

$$\begin{aligned} p_{j_1}^* &= p_{j_1} - (1-\varepsilon)\,\eta\langle\eta,(p_{j_1}-p_{j_2})\rangle, \\ p_{j_2}^* &= p_{j_2} + (1-\varepsilon)\,\eta\langle\eta,(p_{j_1}-p_{j_2})\rangle, \end{aligned} \tag{4}$$

where $\varepsilon = \frac{1-e}{2} \in [0, \frac{1}{2})$ and $e \in (0,1]$ is a restitution coefficient [6].

Let $L_\alpha^1 = \oplus_{n=0}^\infty \alpha^n L_n^1$ be the space of sequences $f = (f_0, f_1, \ldots, f_n, \ldots)$ of integrable functions $f_n(x_1, \ldots, x_n)$ defined on the phase space of n hard spheres that are symmetric with respect to the permutations of the arguments $x_1, \ldots, x_n$, equal to zero on the set of forbidden configurations $\mathbb{W}_n$ and equipped with the norm: $\|f\|_{L_\alpha^1} = \sum_{n=0}^\infty \alpha^n \int dx_1 \ldots dx_n |f_n(x_1, \ldots, x_n)|$, where $\alpha > 1$ is a real number. We denote by $L_0^1 \subset L_\alpha^1$ the everywhere dense set in L_α^1 of finite sequences of continuously differentiable functions with compact supports.

On the space of integrable functions it is defined the semigroup of operators $S_n^*(t)$, $t \geq 0$, adjoint to semigroup of operators (1) in the sense of the continuous linear functional (the functional of mean values of observables)

$$\big(b, f\big) = \sum_{n=0}^\infty \frac{1}{n!} \int_{(\mathbb{R}^3 \times \mathbb{R}^3)^n} dx_1 \ldots dx_n \, b_n(x_1, \ldots, x_n) f_n(x_1, \ldots, x_n).$$

The adjoint semigroup of operators is defined by the Duhamel equation

$$\begin{aligned} &S_n^*(t, 1, \ldots, n) = \\ &\prod_{i=1}^n S_1^*(t, i) + \int_0^t d\tau \prod_{i=1}^n S_1^*(t-\tau, i) \sum_{j_1 < j_2 = 1}^n \mathcal{L}_{\mathrm{int}}^*(j_1, j_2) S_n^*(\tau, 1, \ldots, n), \end{aligned} \tag{5}$$

where for $t \geq 0$ the operator $\mathcal{L}_{\mathrm{int}}^*(j_1, j_2)$ is determined by the formula

$$\begin{aligned} \mathcal{L}_{\mathrm{int}}^*(j_1, j_2) f_s \doteq \sigma^2 \int_{\mathbb{S}_+^2} d\eta \langle \eta, (p_{j_1} - p_{j_2})\rangle \big(\frac{1}{(1-2\varepsilon)^2} f_n(x_1, \ldots, x_{j_1}^\diamond, \ldots, \\ x_{j_2}^\diamond, \ldots, x_n) \delta(q_{j_1} - q_{j_2} + \sigma\eta) - f_n(x_1, \ldots, x_n) \delta(q_{j_1} - q_{j_2} - \sigma\eta)\big), \end{aligned} \tag{6}$$

In (6) the notations similar to formula (3) are used, $x_j^\diamond \equiv (q_j, p_j^\diamond)$, and the pre-collision momenta (solutions of equations (4)) are determined as follows:

$$\begin{aligned} p_{j_1}^\diamond &= p_{j_1} - \frac{1-\varepsilon}{1-2\varepsilon}\,\eta\langle\eta,(p_{j_1}-p_{j_2})\rangle, \\ p_{j_2}^\diamond &= p_{j_2} + \frac{1-\varepsilon}{1-2\varepsilon}\,\eta\langle\eta,(p_{j_1}-p_{j_2})\rangle. \end{aligned} \tag{7}$$

Hence an infinitesimal generator of the adjoint semigroup of operators $S_n^*(t)$ is defined on $L_{0,n}^1$ as the operator: $\mathcal{L}_n^* = \sum_{j=1}^n \mathcal{L}^*(j) + \sum_{j_1<j_2=1}^n \mathcal{L}_{\mathrm{int}}^*(j_1, j_2)$, where it was introduced the operator adjoint to free motion operator (2): $\mathcal{L}^*(j) \doteq -\langle p_j, \frac{\partial}{\partial q_j}\rangle$.

On the space L_n^1 the one-parameter mapping defined by equation (5) is an bounded strong continuous semigroup of operators.

3 The dual hierarchy of evolution equations for observables

It is well known [7] that many-particle systems are described by means of states and observables. The functional for mean value of observables determines a duality of states and observables, and, as a consequence, there exist two equivalent approaches to describing the evolution of systems of many particles. Traditionally, the evolution is described in terms of the evolution of states by means of the BBGKY hierarchy for marginal distribution functions. An equivalent approach to describing evolution is based on marginal observables governed by the dual BBGKY hierarchy. In the same framework the evolution of particles with the dissipative interaction, namely hard spheres with inelastic collisions, is described [14].

Within the framework of observables the evolution of a system of hard spheres is described by the sequences $B(t)=(B_0,B_1(t,x_1),\ldots,B_s(t,x_1,\ldots,x_s),\ldots)\in C_\gamma$ of the marginal observables $B_s(t,x_1,\ldots,x_s)$ defined on the phase space of $s\geq 1$ hard spheres that are symmetric with respect to the permutations of the arguments $x_1,\ldots,x_n$, equal to zero on the set $\mathbb{W}_s$ and for $t\geq 0$ they are governed by the Cauchy problem of the weak formulation of the dual BBGKY hierarchy [14]:

$$\frac{\partial}{\partial t}B_s(t,x_1,\ldots,x_s)=\big(\sum_{j=1}^{s}\mathcal{L}(j)B_s(t)+\sum_{j_1<j_2=1}^{s}\mathcal{L}_{\mathrm{int}}(j_1,j_2)B_s(t)\big)(x_1,\ldots,x_s)+ \sum_{j_1\neq j_2=1}^{s}\big(\mathcal{L}_{\mathrm{int}}(j_1,j_2)B_{s-1}(t)\big)(x_1,\ldots,x_{j_1-1},x_{j_1+1},\ldots,x_s), \tag{8}$$

$$B_s(t,x_1,\ldots,x_s)\mid_{t=0}=B_s^0(x_1,\ldots,x_s),\quad s\geq 1, \tag{9}$$

where on the set $C_{s,0}\subset C_s$ the free motion operator $\mathcal{L}(j)$ and the operator of inelastic collisions $\mathcal{L}_{\mathrm{int}}(j_1,j_2)$ are defined by the formulas (2) and (3) respectively. We refer to recurrence evolution equations (8) as the dual BBGKY hierarchy for hard spheres with inelastic collisions.

The solution $B(t)=(B_0,B_1(t,x_1),\ldots,B_s(t,x_1,\ldots,x_s),\ldots)$ of the Cauchy problem (8),(9) is determined by the expansions [10]

$$B_s(t,x_1,\ldots,x_s)=\sum_{n=0}^{s-1}\frac{1}{n!}\sum_{j_1\neq\ldots\neq j_n=1}^{s}\mathfrak{A}_{1+n}\big(t,\{Y\setminus Z\},Z\big)\,B_{s-n}^0(x_1,\ldots, x_{j_1-1},x_{j_1+1},\ldots,x_{j_n-1},x_{j_n+1},\ldots,x_s), \tag{10}$$

where the $(1+n)th$-order cumulant of semigroups of operators (1) of hard spheres with inelastic collisions is defined by the formula

$$\mathfrak{A}_{1+n}(t,\{Y\setminus X\},X)\doteq\sum_{\mathrm{P}:\,(\{Y\setminus X\},\,X)=\bigcup_i X_i}(-1)^{|\mathrm{P}|-1}(|\mathrm{P}|-1)!\prod_{X_i\subset\mathrm{P}}S_{|\theta(X_i)|}(t,\theta(X_i)), \tag{11}$$

and $Y\equiv(1,\ldots,s),Z\equiv(j_1,\ldots,j_n)\subset Y$, $\{Y\setminus Z\}$ is the set consisting of one element $Y\setminus Z=(1,\ldots,j_1-1,j_1+1,\ldots,j_n-1,j_n+1,\ldots,s)$, i.e. this set is a connected subset of the partition

P such that $|\mathrm{P}| = 1$, the mapping $\theta(\cdot)$ is a declusterization operator defined by the formula: $\theta(\{Y \setminus Z\}) = Y \setminus Z$.

We note that one component sequences of marginal observables correspond to observables of certain structure, namely the marginal observable $B^{(1)} = (0, b_1(x_1), 0, \ldots)$ corresponds to the additive-type observable, and the marginal observable $B^{(k)} = (0, \ldots, 0, b_k(x_1, \ldots, x_k), 0, \ldots)$ corresponds to the k-ary-type observable. If as initial data (9) we consider the additive-type marginal observable, then the structure of solution expansion (10) is simplified and attains the form

$$B_s^{(1)}(t, x_1, \ldots, x_s) = \mathfrak{A}_s(t, 1, \ldots, s) \sum_{j=1}^{s} b_1(x_j), \quad s \geq 1.$$

In the case of k-ary-type marginal observables for $s \geq k$ solution expansion (10) takes the form

$$B_s^{(k)}(t, x_1, \ldots, x_s) = \frac{1}{(s-k)!} \sum_{j_1 \neq \ldots \neq j_{s-k}=1}^{s} \mathfrak{A}_{1+s-k}\big(t, \{(1, \ldots, s) \setminus (j_1, \ldots, j_{s-k})\}, \\ j_1, \ldots, j_{s-k}\big)\, b_k(x_1, \ldots, x_{j_1-1}, x_{j_1+1}, \ldots, x_{j_s-k-1}, x_{j_s-k+1}, \ldots, x_s), \quad s \geq k,$$

and, for $1 \leq s < k$ we have $B_s^{(k)}(t) = 0$, respectively.

On the space C_γ for abstract initial-value problem (8),(9) the following statement is true. If $B(0) = (B_0, B_1^0, \ldots, B_s^0, \ldots) \in C_\gamma^0 \subset C_\gamma$ is finite sequence of infinitely differentiable functions with compact supports, then the sequence of functions (10) is a classical solution and for arbitrary initial data $B(0) \in C_\gamma$ it is a generalized solution.

We remark that expansion (10) can be also represented in the form of the weak formulation of the perturbation (iteration) series as a result of applying of analogs of the Duhamel equation to cumulants of semigroups of operators (11).

The mean value of the marginal observable $B(t) = (B_0, B_1(t), \ldots, B_s(t), \ldots) \in \mathcal{C}_\gamma$ in initial state specified by a sequence of marginal distribution functions $F(0) = (1, F_1^0, \ldots, F_s^0, \ldots) \in L_\alpha^1 = \oplus_{s=0}^\infty \alpha^s L_s^1$ is determined by the following functional:

$$\big(B(t), F(0)\big) = \sum_{s=0}^{\infty} \frac{1}{s!} \int_{(\mathbb{R}^3 \times \mathbb{R}^3)^s} dx_1 \ldots dx_s\, B_s(t, x_1, \ldots, x_s) F_s^0(x_1, \ldots, x_s). \tag{12}$$

In particular, functional (12) of mean values of the additive-type marginal observables $B^{(1)}(0) = (0, B_1^{(1)}(0, x_1), 0, \ldots)$ takes the form:

$$\big(B^{(1)}(t), F(0)\big) = \big(B^{(1)}(0), F(t)\big) = \int_{\mathbb{R}^3 \times \mathbb{R}^3} dx_1\, B_1^{(1)}(0, x_1) F_1(t, x_1),$$

where the one-particle marginal distribution function $F_1(t, x_1)$ is determined by the series expansion [10]

$$F_1(t, x_1) = \sum_{n=0}^{\infty} \frac{1}{n!} \int_{(\mathbb{R}^3 \times \mathbb{R}^3)^n} dx_2 \ldots dx_{n+1}\, \mathfrak{A}_{1+n}^*(t) F_{1+n}^0(x_1, \ldots, x_{n+1}),$$

and the generating operator $\mathfrak{A}^*_{1+n}(t)$ of this series is the $(1+n)th$-order cumulant of adjoint semigroups of hard spheres with inelastic collisions. In the general case for mean values of marginal observables the following equality is true:

$$\big(B(t),F(0)\big)=\big(B(0),F(t)\big),$$

where the sequence $F(t)=(1,F_1(t),\ldots,F_s(t),\ldots)$ is a solution of the Cauchy problem of the BBGKY hierarchy of hard spheres with inelastic collisions [14]. The last equality signify the equivalence of two pictures of the description of the evolution of hard spheres by means of the BBGKY hierarchy [7] and the dual BBGKY hierarchy (8).

Hereinafter we consider initial states of hard spheres specified by a one-particle marginal distribution function, namely

$$F_s^{(c)}(x_1,\ldots,x_s)=\prod_{i=1}^{s}F_1^0(x_i)\mathcal{X}_{\mathbb{R}^{3s}\setminus\mathbb{W}_s},\quad s\geq 1, \tag{13}$$

where $\mathcal{X}_{\mathbb{R}^{3s}\setminus\mathbb{W}_s}\equiv\mathcal{X}_s(q_1,\ldots,q_s)$ is a characteristic function of allowed configurations $\mathbb{R}^{3s}\setminus\mathbb{W}_s$ of s hard spheres and $F_1^0\in L^1(\mathbb{R}^3\times\mathbb{R}^3)$. Initial data (13) is intrinsic for the kinetic description of many-particle systems because in this case all possible states are described by means of a one-particle marginal distribution function.

4 The non-Markovian Enskog kinetic equation

In the case of initial states (13) the dual picture of the evolution to the picture of the evolution by means of observables of a system of hard spheres with inelastic collisions governed by the dual BBGKY hierarchy (8) for marginal observables is the evolution of states described by means of the non-Markovian Enskog kinetic equation and a sequence of explicitly defined functionals of a solution of such kinetic equation.

Indeed, in view of the fact that the initial state is completely specified by a one-particle marginal distribution function on allowed configurations (13), for mean value functional (12) the following representation holds [14], [15]:

$$\big(B(t),F^{(c)}\big)=\big(B(0),F(t\mid F_1(t))\big),$$

where $F^{(c)}=(1,F_1^{(c)},\ldots,F_s^{(c)},\ldots)$ is the sequence of initial marginal distribution functions (13), and the sequence $F(t\mid F_1(t))=\big(1,F_1(t),F_2(t\mid F_1(t)),\ldots,F_s(t\mid F_1(t))\big)$ is a sequence of the marginal functionals of the state $F_s(t,x_1,\ldots,x_s\mid F_1(t))$ represented by the series expansions over the products with respect to the one-particle marginal distribution function $F_1(t)$:

$$F_s(t,x_1,\ldots,x_s\mid F_1(t))\doteq \tag{14}$$
$$\sum_{n=0}^{\infty}\frac{1}{n!}\int_{(\mathbb{R}^3\times\mathbb{R}^3)^n}dx_{s+1}\ldots dx_{s+n}\,\mathfrak{V}_{1+n}(t,\{Y\},X\setminus Y)\prod_{i=1}^{s+n}F_1(t,x_i),\quad s\geq 2.$$

In series (14) we used the notations: $Y\equiv(1,\ldots,s),X\equiv(1,\ldots,s+n)$, and the $(n+1)th$-order generating operator $\mathfrak{V}_{1+n}(t)$, $n \geq 0$, is defined as follows [15]:

$$\mathfrak{V}_{1+n}(t,\{Y\},X\setminus Y) \doteq \sum_{k=0}^{n}(-1)^k \sum_{m_1=1}^{n}\ldots \sum_{m_k=1}^{n-m_1-\ldots-m_{k-1}} \frac{n!}{(n-m_1-\ldots-m_k)!}\times$$
$$\widehat{\mathfrak{A}}_{1+n-m_1-\ldots-m_k}(t,\{Y\},s+1,\ldots,s+n-m_1-\ldots-m_k)\prod_{j=1}^{k}\sum_{k_2^j=0}^{m_j}\ldots$$
$$\sum_{k^j_{n-m_1-\ldots-m_j+s}=0}^{k^j_{n-m_1-\ldots-m_j+s-1}} \prod_{i_j=1}^{s+n-m_1-\ldots-m_j} \frac{1}{(k^j_{n-m_1-\ldots-m_j+s+1-i_j}-k^j_{n-m_1-\ldots-m_j+s+2-i_j})!}\times$$
$$\widehat{\mathfrak{A}}_{1+k^j_{n-m_1-\ldots-m_j+s+1-i_j}-k^j_{n-m_1-\ldots-m_j+s+2-i_j}}(t,i_j,s+n-m_1-\ldots-m_j+1+$$
$$k^j_{s+n-m_1-\ldots-m_j+2-i_j},\ldots,s+n-m_1-\ldots-m_j+k^j_{s+n-m_1-\ldots-m_j+1-i_j}),$$

where it means that: $k_1^j\equiv m_j$, $k^j_{n-m_1-\ldots-m_j+s+1}\equiv 0$, and we denote the $(1+n)th$-order scattering cumulant by the operator $\widehat{\mathfrak{A}}_{1+n}(t)$:

$$\widehat{\mathfrak{A}}_{1+n}(t,\{Y\},X\setminus Y) \doteq \mathfrak{A}^*_{1+n}(t,\{Y\},X\setminus Y)\mathcal{X}_{\mathbb{R}^{3(s+n)}\setminus\mathbb{W}_{s+n}}\prod_{i=1}^{s+n}\mathfrak{A}^*_1(t,i)^{-1},$$

and the operator $\mathfrak{A}^*_{1+n}(t)$ is the $(1+n)th$-order cumulant of adjoint semigroups of hard spheres with inelastic collisions.

We emphasize that in fact functionals (14) characterize the correlations generated by dynamics of a hard sphere system with inelastic collisions.

The second element of the sequence $F(t\mid F_1(t))$, i.e. the one-particle marginal distribution function $F_1(t)$, is determined by the following series expansion:

$$F_1(t,x_1)=\sum_{n=0}^{\infty}\frac{1}{n!}\int_{(\mathbb{R}^3\times\mathbb{R}^3)^n}dx_2\ldots dx_{n+1}\,\mathfrak{A}^*_{1+n}(t)\mathcal{X}_{\mathbb{R}^{3(1+n)}\setminus\mathbb{W}_{1+n}}\prod_{i=1}^{n+1}F_1^0(x_i), \tag{15}$$

where the generating operator $\mathfrak{A}^*_{1+n}(t)\equiv\mathfrak{A}^*_{1+n}(t,1,\ldots,n+1)$ is the $(1+n)th$-order cumulant of adjoint semigroups of hard spheres with inelastic collisions.

For $t\geq 0$ the one-particle marginal distribution function (15) is a solution of the following Cauchy problem of the non-Markovian Enskog kinetic equation [14], [15]:

$$\frac{\partial}{\partial t}F_1(t,q_1,p_1)=-\langle p_1,\frac{\partial}{\partial q_1}\rangle F_1(t,q_1,p_1)+ \tag{16}$$
$$+\sigma^2\int_{\mathbb{R}^3\times\mathbb{S}^2_+}dp_2d\eta\langle\eta,(p_1-p_2)\rangle\Big(\frac{1}{(1-2\varepsilon)^2}\,F_2(t,q_1,p_1^\diamond,q_1-\sigma\eta,p_2^\diamond\mid F_1(t))-$$
$$-F_2(t,q_1,p_1,q_1+\sigma\eta,p_2\mid F_1(t))\Big),$$

$$F_1(t)|_{t=0}=F_1^0, \tag{17}$$

where the collision integral is determined by the marginal functional of the state (14) in the case of $s=2$ and the expressions $p_1^\diamond$ and $p_2^\diamond$ are the pre-collision momenta of hard spheres with inelastic collisions (7), i.e. solutions of equations (4).

We note that the structure of collision integral of the non-Markovian Enskog equation for granular gases (16) is such that the first term of its expansion is the collision integral of the Boltzman–Enskog kinetic equation and the next terms describe all possible correlations which are created by hard sphere dynamics with inelastic collisions and by the propagation of initial correlations connected with the forbidden configurations.

We remark also, that based on the non-Markovian Enskog equation (16) we can formulate the Markovian Enskog kinetic equation with inelastic collisions [14].

For the abstract Cauchy problem of the non-Markovian Enskog kinetic equation (16),(17) in the space of integrable functions $L^1(\mathbb{R}^3 \times \mathbb{R}^3)$, the following statement is true [14]. A global in time solution of the Cauchy problem of the non-Markovian Enskog equation (16) is determined by function (15). For small densities and $F_1^0 \in L_0^1(\mathbb{R}^3 \times \mathbb{R}^3)$ function (15) is a strong solution and for an arbitrary initial data $F_1^0 \in L^1(\mathbb{R}^3 \times \mathbb{R}^3)$ it is a weak solution.

Thus, if initial state is specified by a one-particle marginal distribution function on allowed configurations, then the evolution, describing by marginal observables governed by the dual BBGKY hierarchy (8), can be also described by means of the non-Markovian kinetic equation (16) and a sequence of marginal functionals of the state (14). In other words, for mentioned initial states the evolution of all possible states of a hard sphere system with inelastic collisions at arbitrary moment of time can be described by means of a one-particle distribution function without any approximations.

5 The Boltzmann kinetic equation for granular gases

It is known, [7,8], the Boltzmann kinetic equation describes the evolution of many hard spheres in the Boltzmann–Grad (or low-density) approximation. In this section the possible approaches to the rigorous derivation of the Boltzmann kinetic equation from dynamics of hard spheres with inelastic collisions are outlined.

One approach to deriving the Boltzmann kinetic equation for hard spheres with inelastic collisions, which was developed in [10] for a system of hard spheres with elastic collisions, is based on constructing the Boltzmann–Grad asymptotic behavior of marginal observables governed by the dual BBGKY hierarchy (8). A such scaling limit is governed by the set of recurrence evolution equations, namely, by the dual Boltzmann hierarchy for hard spheres with inelastic collisions [14]. Then for initial states specified by a one-particle distribution function (13) the evolution of additive-type marginal observables governed by the dual Boltzmann hierarchy is equivalent to a solution of the Boltzmann kinetic equation for granular gases [12] and the evolution of nonadditive-type marginal observables is equivalent to the property of the propagation of initial chaos for states [10].

One more approach to the description of the kinetic evolution of hard spheres with inelastic collisions is based on the non-Markovian generalization of the Enskog equation (16).

Let the dimensionless one-particle distribution function $F_1^{\epsilon,0}$, specifying initial state (13), satisfies the condition: $|F_1^{\epsilon,0}(x_1)| \leq ce^{-\frac{\beta}{2}p_1^2}$, where is $\epsilon > 0$ is a scaling parameter (the ratio of the diameter $\sigma > 0$ to the mean free path of hard spheres), $\beta > 0$ is a parameter and $c < \infty$

is some constant, and there exists the following its limit in the sense of a weak convergence: $\mathrm{w-}\lim_{\epsilon\rightarrow 0}(\epsilon^2 F_1^{\epsilon,0}(x_1)-f_1^0(x_1))=0$. Then for finite time interval the Boltzmann–Grad limit of dimensionless solution (15) of the Cauchy problem of the non-Markovian Enskog kinetic equation (16),(17) exists in the same sense, namely $\mathrm{w-}\lim_{\epsilon\rightarrow 0}\big(\epsilon^2 F_1(t,x_1)-f_1(t,x_1)\big)=0$, where the limit one-particle distribution function is a weak solution of the Cauchy problem of the Boltzmann kinetic equation for granular gases [6], [12]:

$$\frac{\partial}{\partial t}f_1(t,x_1)=-\langle p_1,\frac{\partial}{\partial q_1}\rangle f_1(t,x_1)+ \tag{18}$$
$$\int_{\mathbb{R}^3\times\mathbb{S}^2_+}dp_2\,d\eta\,\langle\eta,(p_1-p_2)\rangle\big(\frac{1}{(1-2\varepsilon)^2}\,f_1(t,q_1,p_1^\diamond)f_1(t,q_1,p_2^\diamond)-f_1(t,x_1)f_1(t,q_1,p_2)\big),$$

$$f_1(t,x_1)|_{t=0}=f_1^0(x_1), \tag{19}$$

where the momenta $p_1^\diamond$ and $p_2^\diamond$ are pre-collision momenta of hard spheres with inelastic collisions (7).

As noted above, the all possible correlations of a system of hard spheres with inelastic collisions are described by marginal functionals of the state (14). Taking into consideration the fact of the existence of the Boltzmann–Grad scaling limit of a solution of the non-Markovian Enskog kinetic equation (16), for marginal functionals of the state (14) the following statement holds:

$$\mathrm{w-}\lim_{\epsilon\rightarrow 0}\big(\epsilon^{2s}F_s\big(t,x_1,\ldots,x_s\mid F_1(t)\big)-\prod_{j=1}^{s}f_1(t,x_j)\big)=0,$$

where the limit one-particle distribution function $f_1(t)$ is governed by the Boltzmann kinetic equation for granular gases (18). This property of marginal functionals of the state (14) are means the propagation of the initial chaos [7].

It should be emphasized that the Boltzmann–Grad asymptotics of a solution of the non-Markovian Enskog equation (16) in a multidimensional space is analogous of the Boltzmann–Grad asymptotic behavior of a hard sphere system with the elastic collisions [10]. Such asymptotic behavior is governed by the Boltzmann equation for a granular gas (18), and the asymptotics of marginal functionals of the state (14) are the product of its solution (this property is interpreted as the propagation of the initial chaos).

6 One-dimensional granular gases

As is known, the evolution of a one-dimensional system of hard spheres with elastic collisions is trivial (free motion or Knudsen flow) in the Boltzmann-Grad scaling limit [7], but, as it was taken notice in paper [16], in this aproximation the kinetics of inelastically interacting hard spheres (rods) is not trivial and it is governed by the Boltzmann kinetic equation for one-dimensional granular gases [16–19]. Below the approach to the rigorous derivation of Boltzmann-type equation for one-dimensional granular gases will be outlined. It should be emphasized that a system of many hard rods with inelastic collisions displays the basic properties of granular gases inasmuch as under the inelastic collisions only the normal component of relative velocities dissipates in a multidimensional case.

In case of a one-dimensional granular gas for $t \geq 0$ in dimensionless form the Cauchy problem (16),(17) takes the form [20]:

$$\frac{\partial}{\partial t}F_1(t,q_1,p_1) = -p_1\frac{\partial}{\partial q_1}F_1(t,q_1,p_1) + \int_0^\infty dP\,P\big(\frac{1}{(1-2\varepsilon)^2}\,F_2(t,q_1,p_1^\diamond(p_1,P),q_1-\epsilon,p_2^\diamond(p_1,P)\mid F_1(t)) - F_2(t,q_1,p_1,q_1-\epsilon,p_1+P\mid F_1(t))\big) + \int_0^\infty dP\,P\big(\frac{1}{(1-2\varepsilon)^2}\,F_2(t,q_1,\tilde{p}_1^\diamond(p_1,P),q_1+\epsilon,\tilde{p}_2^\diamond(p_1,P)\mid F_1(t)) - F_2(t,q_1,p_1,q_1+\epsilon,p_1-P\mid F_1(t))\big), \tag{20}$$

$$F_1(t)|_{t=0} = F_1^{\epsilon,0}, \tag{21}$$

where $\epsilon > 0$ is a scaling parameter (the ratio of a hard sphere diameter (the length) $\sigma > 0$ to the mean free path), the collision integral is determined by marginal functional (14) of the state $F_1(t)$ in the case of $s = 2$ and the expressions:

$$p_1^\diamond(p_1,P) = p_1 - P + \frac{\varepsilon}{2\varepsilon-1}\,P,$$
$$p_2^\diamond(p_1,P) = p_1 - \frac{\varepsilon}{2\varepsilon-1}\,P$$

and

$$\tilde{p}_1^\diamond(p_1,P) = p_1 + P - \frac{\varepsilon}{2\varepsilon-1}\,P,$$
$$\tilde{p}_2^\diamond(p_1,P) = p_1 + \frac{\varepsilon}{2\varepsilon-1}\,P,$$

are transformed pre-collision momenta in a one-dimensional space.

If initial one-particle marginal distribution functions satisfy the following condition: $|F_1^{\epsilon,0}(x_1)| \leq Ce^{-\frac{\beta}{2}p_1^2}$, where $\beta > 0$ is a parameter, $C < \infty$ is some constant, then every term of the series

$$F_1^\epsilon(t,x_1) = \sum_{n=0}^\infty \frac{1}{n!}\int_{(\mathbb{R}\times\mathbb{R})^n} dx_2\ldots dx_{n+1}\,\mathfrak{A}_{1+n}^*(t)\prod_{i=1}^{n+1}F_1^{\epsilon,0}(x_i)\mathcal{X}_{\mathbb{R}^{(1+n)}\setminus\mathbb{W}_{1+n}}, \tag{22}$$

exists, for finite time interval function (22) is the uniformly convergent series with respect to x_1 from arbitrary compact, and it is determined a weak solution of the Cauchy problem of the non-Markovian Enskog equation (20),(21). Let in the sense of a weak convergence there exists the following limit

$$\mathrm{w-}\lim_{\epsilon\to 0}\big(F_1^{\epsilon,0}(x_1) - f_1^0(x_1)\big) = 0,$$

then for finite time interval there exists the Boltzmann–Grad limit of solution (22) of the Cauchy problem of the non-Markovian Enskog equation for one-dimensional granular gas (20) in the sense of a weak convergence

$$\mathrm{w-}\lim_{\epsilon\to 0}\big(F_1^\epsilon(t,x_1) - f_1(t,x_1)\big) = 0, \tag{23}$$

where the limit one-particle marginal distribution function is defined by uniformly convergent on arbitrary compact set series:

$$f_1(t,x_1)=\sum_{n=0}^{\infty}\frac{1}{n!}\int_{(\mathbb{R}\times\mathbb{R})^n}dx_2\ldots dx_{n+1}\,\mathfrak{A}^0_{1+n}(t)\prod_{i=1}^{n+1}f_1^0(x_i), \tag{24}$$

and the generating operator $\mathfrak{A}^0_{1+n}(t)\equiv\mathfrak{A}^0_{1+n}(t,1,\ldots,n+1)$ is the $(n+1)th$-order cumulant of adjoint semigroups $S^{*,0}_n(t)$ of point particles with inelastic collisions. An infinitesimal generator of the semigroup of operators $S^{*,0}_n(t)$ is defined as the operator:

$$\begin{aligned}&(\mathcal{L}^{*,0}_n f_n)(x_1,\ldots,x_n)=-\sum_{j=1}^{n}p_j\frac{\partial}{\partial q_j}f_n(x_1,\ldots,x_n)+\\&\sum_{j_1<j_2=1}^{n}|p_{j_2}-p_{j_1}|\big(\frac{1}{(1-2\varepsilon)^2}f_n(x_1,\ldots,x^\diamond_{j_1},\ldots,x^\diamond_{j_2},\ldots,x_n)-\\&f_n(x_1,\ldots,x_n)\big)\delta(q_{j_1}-q_{j_2}),\end{aligned}$$

where $x^\diamond_j\equiv(q_j,p^\diamond_j)$ and the pre-collision momenta $p^\diamond_{j_1}$, $p^\diamond_{j_2}$ are determined by the following expressions:

$$\begin{aligned}p^\diamond_{j_1}&=p_{j_2}+\frac{\varepsilon}{2\varepsilon-1}(p_{j_1}-p_{j_2}),\\p^\diamond_{j_2}&=p_{j_1}-\frac{\varepsilon}{2\varepsilon-1}(p_{j_1}-p_{j_2}).\end{aligned}$$

For $t\geq 0$ the limit one-particle distribution function represented by series (24) is a weak solution of the Cauchy problem of the Boltzmann-type kinetic equation of point particles with inelastic collisions [20]

$$\begin{aligned}&\frac{\partial}{\partial t}f_1(t,q,p)=-p\frac{\partial}{\partial q}f_1(t,q,p)+\int_{-\infty}^{+\infty}dp_1\,|p-p_1|\times\\&\big(\frac{1}{(1-2\varepsilon)^2}f_1(t,q,p^\diamond)\,f_1(t,q,p^\diamond_1)-f_1(t,q,p)\,f_1(t,q,p_1)\big)+\sum_{n=1}^{\infty}\mathcal{I}^{(n)}_0.\end{aligned} \tag{25}$$

In kinetic equation (25) the remainder $\sum_{n=1}^{\infty}\mathcal{I}^{(n)}_0$ of the collision integral is determined by the expressions

$$\begin{aligned}&\mathcal{I}^{(n)}_0\equiv\frac{1}{n!}\int_0^\infty dP\,P\int_{(\mathbb{R}\times\mathbb{R})^n}dq_3dp_3\ldots dq_{n+2}dp_{n+2}\mathfrak{V}_{1+n}(t)\big(\frac{1}{(1-2\varepsilon)^2}f_1(t,q,p^\diamond_1(p,P))\times\\&f_1(t,q,p^\diamond_2(p,P))-f_1(t,q,p)f_1(t,q,p+P)\big)\prod_{i=3}^{n+2}f_1(t,q_i,p_i)+\\&\int_0^\infty dP\,P\int_{(\mathbb{R}\times\mathbb{R})^n}dq_3dp_3\ldots dq_{n+2}dp_{n+2}\mathfrak{V}_{1+n}(t)\big(\frac{1}{(1-2\varepsilon)^2}f_1(t,q,\tilde{p}^\diamond_1(p,P))\times\\&f_1(t,q,\tilde{p}^\diamond_2(p,P))-f_1(t,q,p)f_1(t,q,p-P)\big)\prod_{i=3}^{n+2}F_1(t,q_i,p_i),\end{aligned}$$

where the generating operators $\mathfrak{V}_{1+n}(t) \equiv \mathfrak{V}_{1+n}(t,\{1,2\},3,\ldots,n+2)$, $n \geq 0$, are represented by expansions (15) with respect to the cumulants of semigroups of scattering operators of point hard rods with inelastic collisions in a one-dimensional space

$$\widehat{S}^0_n(t,1,\ldots,n) \doteq S^{*,0}_n(t,1,\ldots,s)\prod_{i=1}^{n} S^{*,0}_1(t,i)^{-1}.$$

In fact, the series expansions for the collision integral of the non-Markovian Enskog equation for a granular gas or solution (22) are represented as the power series over the density so that the terms $\mathcal{I}^{(n)}_0$, $n \geq 1$, of the collision integral in kinetic equation (18) are corrections with respect to the density to the Boltzmann collision integral for one-dimensional granular gases stated in [17], [21].

Since the scattering operator of point hard rods is an identity operator in the aproximation of elastic collisions, namely, in the limit $\varepsilon \to 0$, the collision integral of the Boltzmann kinetic equation (25) in a one-dimensional space is identical to zero. In the quasi-elastic limit [21] the limit one-particle distribution function (24)

$$\lim_{\varepsilon\to 0}\varepsilon f_1(t,q,v) = f^0(t,q,v),$$

satisfies the nonlinear friction kinetic equation for granular gases of the following form [16, 21]

$$\frac{\partial}{\partial t}f^0(t,q,v) = -v\frac{\partial}{\partial q}f^0(t,q,v) + \frac{\partial}{\partial v}\int_{-\infty}^{\infty} dv_1\,|v_1-v|\,(v_1-v)\,f^0(t,q,v_1)f^0(t,q,v).$$

Taking into consideration result (23) on the Boltzmann–Grad asymptotic behavior of the non-Markovian Enskog equation (16), for marginal functionals of the state (14) in a one-dimensional space the following statement is true [20]:

$$\mathrm{w-}\lim_{\epsilon\to 0}\big(F_s\big(t,x_1,\ldots,x_s \mid F^{\epsilon}_1(t)\big) - f_s\big(t,x_1,\ldots,x_s \mid f_1(t)\big)\big) = 0, \quad s \geq 2,$$

where the limit marginal functionals $f_s\big(t \mid f_1(t)\big)$, $s \geq 2$, with respect to limit one-particle distribution function (24) are determined by the series expansions with the structure similar to series (14) and the generating operators represented by expansions (15) over the cumulants of semigroups of scattering operators of point hard rods with inelastic collisions in a one-dimensional space.

Note that, as mention above, in the case of a system of hard rods with elastic collisions the limit marginal functionals of the state are the product of the limit one-particle distribution functions, describing the free motion of point hard rods.

Thus, the Boltzmann–Grad asymptotic behavior of solution (22) of the non-Markovian Enskog equation (20) is governed by the Boltzmann kinetic equation for a one-dimensional granular gas (25). We emphasize that the Boltzmann-type equation (25) describes the memory effects in one-dimensional granular gases.

In addition, the limit marginal functionals of the state $f_s\big(t,x_1,\ldots,x_s \mid f_1(t)\big)$, $s \geq 2$, which are defined above, describe the process of the propagation of initial chaos in one-dimensional granular gases, or, in other words, the process of creation correlations in a system of hard rods with inelastic collisions.

7 Conclusion

In the survey the origin of the kinetic description of the evolution of a system of hard spheres with inelastic collisions was considered.

It was established that for initial states (13) specified by a one-particle distribution function, solution (10) of the Cauchy problem of the dual BBGKY hierarchy (8),(9) and a solution of the Cauchy problem of the non-Markovian Enskog equation (16),(17) together with marginal functionals of the state (14) give two equivalent approaches to the description of the evolution of states of a hard sphere system with inelastic collisions. In fact, the rigorous justification of the Enskog kinetic equation for granular gases (16) is a consequence of the validity of equality (14).

We note that the developed approach is also related to the problem of a rigorous derivation of the non-Markovian kinetic-type equations from underlaying many-particle dynamics which make possible to describe the memory effects of granular gases.

One more advantage also is that the considered approach gives the possibility to construct the kinetic equations in scaling limits, involving correlations at initial time which can characterize the condensed states of a hard sphere system with inelastic collisions [10].

Finally, it should be emphasized that the developed approach to the derivation of the Boltzmann equation for granular gases from the dynamics governed by the non-Markovian Enskog kinetic equation (16) also allows us to construct higher-order corrections to the collision integral compared to the Boltzmann-Grad approximation.

References

[1] Cercignani C. The Boltzmann equation approach to the shear flow of a granular material Phil. Trans. R. Soc. Lond. 2002;360(1792):407-414. DOI:10.1098/rsta.2001.0939

[2] Goldhirsch I. Scales and kinetics of granular flows. Chaos. 1999;9:659-672. DOI:10.1063/1.166440

[3] Mehta A. Granular Physics. Cambridge Univ. Press; 2009. 362 p. DOI:10.1017/CBO9780511535314

[4] Pöschel T, Brilliantov NV, editors. Granular Gas Dynamics. (Lecture Notes in Phys. 624) Berlin Heidelberg: Springer-Verlag; 2003. 369 p. ISBN 978-3-540-20110-6

[5] Brilliantov NV, Pöschel T. Kinetic Theory of Granular Gases. Oxford University Press; 2004. 329 p. ISBN-13 978-0199588138

[6] Brey JJ, Dufty JW, Santos A. Dissipative dynamics for hard spheres. J. Stat. Phys. 1997;87(5-6):1051-1066. DOI:10.1007/BF02181270

[7] Cercignani C, Gerasimenko VI, Petrina DYa. Many-Particle Dynamics and Kinetic Equations. The Netherlands: Springer; 2012. 247 p. ISBN 978-94-010-6342-5

[8] Gallagher I, Saint-Raymond L, Texier B. From Newton to Boltzmann: Hard Spheres and Short-range Potentials. EMS Publ.House: Zürich Lectures in Advanced Mathematics, 2014. 146 p. ISBN-10: 3037191295

[9] Pulvirenti M, Simonella S. The Boltzmann–Grad limit of a hard sphere system: analisis of the correlation error. Invent. Math. 2017;207(3):1135-1237. DOI:10.1007/s00222-016-0682-4

[10] Gerasimenko VI, Gapyak IV. Low-density asymptotic behavior of observables of hard sphere fluids. Advances in Math. Phys. 2018;2018:6252919. DOI:10.1155/2018/6252919

[11] Pareschi L, Russo G, Toscani G, editors. Modelling and Numerics of Kinetic Dissipative Systems. N.Y.: Nova Science Publ. Inc.; 2006. 220 p. ISBN-13 978-1594545030

[12] Villani C. Mathematics of granular materials. J. Stat. Phys. 2006;124(2-4):781-822. DOI:10.1007/s10955-006-9038-6

[13] Capriz G, Mariano PM, Giovine P, editors. Mathematical Models of Granular Matter. (Lecture Notes in Math. 1937). Berlin Heidelberg: Springer-Verlag; 2008. 228 p. ISBN 978-3-540-78276-6

[14] Gerasimenko VI, Borovchenkova MS. On the non-Markovian Enskog equation for granular gases. J. Phys. A: Math. Theor. 2014;47(3):035001. DOI:10.1088/1751-8113/47/3/035001

[15] Gerasimenko VI, Gapyak IV. Hard sphere dynamics and the Enskog equation. Kinet. Relat. Models. 2012;5(3):459-484. DOI:10.3934/krm.2012.5.459

[16] Mac Namara S, Young WR. Kinetics of a one-dimensional granular medium in the quasielastic limit Phys. Fluids A. 1993;5(1):34-45. DOI:10.1063/1.858896

[17] Bellomo N, Pulvirenti M, editors. Modeling in Applied Sciences. Modeling and Simulation in Science, Engineering and Technology. Boston: Birkhäuser, 2000. 433 p. ISBN 978-1-4612-6797-3

[18] Williams DRM, MacKintosh FC. Driven granular media in one dimension: Correlations and equation of states. Phys. Rev. E. 1996;54:R9(R). DOI:10.1103/PhysRevE.54.R9

[19] Toscani G. One-dimensional kinetic models with dissipative collisions. Math. Mod. and Num. Anal. 2000;34(6):1277-1291. DOI:10.1051/m2an:2000127

[20] Gerasimenko VI, Borovchenkova MS. The Boltzmann–Grad limit of the Enskog equation of one-dimensional granular gases. Reports of the NAS of Ukraine. 2013;10:11-17.

[21] Toscani G. Kinetic and hydrodynamic models of nearly elastic granular flows. Monatschefte für Mathematik. 2004;142:179-192. DOI:10.1007/s00605-004-0241-8