ON STATUS OF THE BOLTZMANN KINETIC EQUATION IN THE STATISTICAL MECHANICS

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ABSTRACT. It is shown that early suggested derivation of the Boltzmann kinetic equation for dilute hard sphere gas from the time-reversible BBGKY equations is incorrect since in fact a priori substitutes for them definite irreversible equations. Alternative approach to analysis of the hard sphere gas is formulated which conserves the reversibility and makes it clear that at any gas density one can reduce the BBGKY equations to the Boltzmann equation only in case of spatially uniform gas.

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1. The Boltzmann kinetic equation (BE) [1, 2, 3, 4] is one of most beautiful and fruitful models of theoretical physics. However, its status from viewpoint of statistical mechanics still stays under question. By the conventional opinion, solutions of BE coincide with solutions of exact equations of statistical mechanics, i.e. Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) equations (BBGKYE) [5], at least in the low-density gas limit or in the mathematically equivalent Boltzmann-Grad limit (BGL) when $a \rightarrow 0\,,\ \nu \rightarrow \infty\,,\ \mu = a^3\nu \rightarrow 0\,,\ \lambda = (\pi a^2 \nu)^{-1} = \text{const}\,,$ with ν being mean gas density (concentration of gas particles) and a and λ being interaction radius and mean free path of gas particles, respectively [4, 6]. The attempt to prove this assumption by considering the hard (elastic) sphere gas was made by Lanford and is known as "Lanford theorem" [6, 7, 8]. But the Lanford result does not seem to be quite convincing because it was based on the formal series of iterations of BBGKYE which converges for absurdly small evolution times only, $t < \tau$ ($\tau \sim \lambda/\sqrt{T/m}$ is mean free path time). Nevertheless, the "Lanford theorem" hardly is compatible with results of [9] (see also [10, 11, 12, 13, 14]) where for the gas of "soft elastic spheres" it

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was shown that in case of its spatial non-uniformity BE does not follow from BBGKYE even under BGL.

The aim of the present paper is to reveal the origin of this contradiction starting from the "hard sphere BBGKY hierarchy" [2, 6, 8, 15, 16]. We will see that such the method for building solutions to this hierarchy as applied in [6, 7, 8] destroys its symmetry in respect to time inversion and insensibly replaces it by definite kinetic, i.e. irreversible, equations. Therefore the results of [6, 7, 8] can not be qualified as BE derivation from BBGKYE. Besides, we will suggest and discuss a new approach to analysis of true solutions of the hard sphere BBGKY hierarchy.

2. Let us consider the hard sphere gas [8, 15]. There are no rigorous rules for transition to it from gas with smooth inter-particle interaction (thought a non-rigorous procedure was considered e.g. in [16]). But it is possible first to postulate the Liouville equation for the hard sphere system, as combination of Liouville equation for free particles,

$$\partial F/\partial t = -\sum_i \mathbf{v}_i \cdot \nabla_i F \quad \texttt{at} \quad |\mathbf{r}_i - \mathbf{r}_j| > a$$

(where $\mathbf{v}_i = \mathbf{p}_i/m$, $\nabla_i = \partial/\partial\mathbf{r}_i$), and boundary conditions to it,

$$\begin{gathered} F(...\mathbf{p}_i^*...\mathbf{p}_j^*...) = F(...\mathbf{p}_i...\mathbf{p}_j...) \;\; \texttt{at} \;\; \mathbf{r}_j - \mathbf{r}_i = a\Omega \;, \\ \mathbf{p}_{i,j}^* \;=\; \mathbf{p}_{i,j} \,\pm\, \Omega\,(\Omega\cdot(\mathbf{p}_j - \mathbf{p}_i)) \end{gathered} \tag{0.1}$$

(Ω is unit vector), which establishe continuity of (density of) probability measure F along phase trajectories of particles under their collisions. Then, second, from here one can in usual way [5] deduce the desirable BBGKYE:

$$\frac{\partial F_n}{\partial t} = -\sum_{j=1}^{n} \mathbf{v}_j \cdot \nabla_j \, F_n \,+\, \nu \sum_{j=1}^{n} \widehat{\mathbf{I}}_{j,n+1} \, F_{n+1} \;\;, \tag{0.2}$$

where satisfaction of the boundary conditions (0.1) is presumed, and the "collision operators" are defined by

$$\widehat{\mathbf{I}}_{j,k} F = a^2 \int\!\!\int \Omega\cdot(\mathbf{v}_k - \mathbf{v}_j)\, F(\mathbf{r}_k = \mathbf{r}_j + a\Omega)\, d\mathbf{p}_k \, d\Omega \tag{0.3}$$

It should be emphasized that these equations, like BBGKY in general, are time-reversible: if $\{F_n(t,\,\mathbf{r},\mathbf{p})\}$ is some solution to equations (0.1)-(0.3) then $\{F_n(-\,t,\,\mathbf{r},-\,\mathbf{p})\}$ also is their solution.

At this point the serious question does arise: how we have to deal with the conditions (0.1)? For the first look, we can merely use these conditions to express probabilities of post-collision (*out*-) states via probabilities of pre-collision (*in*-) states and after that exclude the conditions from consideration.

Then the collision operators take the form

$$\begin{aligned} \widehat{\mathbf{I}}_{j,k}\,F = a^2 \iint (-\Omega\cdot(\mathbf{v}_k - \mathbf{v}_j))\; \theta(-\Omega\cdot(\mathbf{v}_k - \mathbf{v}_j))\; \times \\ \times\; [\,F(\mathbf{r}_k = \mathbf{r}_j - a\Omega\,,\mathbf{p}_j^*\,,\mathbf{p}_k^*\,)\; - \\ -\,F(\mathbf{r}_k = \mathbf{r}_j + a\Omega\,,\mathbf{p}_j\,,\mathbf{p}_k\,)\,]\; d\mathbf{p}_k\,d\Omega\;\;, \end{aligned} \tag{0.4}$$

where $\theta(\cdot)$ is the Heavyside function indicating that the integration includes *in*-states only.

Just such transformed equations conventionally are assumed as a basis of the theory. All the more, they a priori are well predisposed to the Boltzmann's Stoßzahlansatz [1]. Indeed, if we truncate the transformed hierarchy of equations at $n = s$, neglecting $(s+1)$-particle correlations, then the residuary s equations, - e.g.

$$\begin{aligned} \frac{\partial F_1}{\partial t} = -\mathbf{v}_1\cdot\nabla_1\,F_1 + \nu a^2\!\int\! d\mathbf{p}_2\!\int d\Omega\,(\Omega\cdot\mathbf{v}_{21})\,\theta(\Omega\cdot\mathbf{v}_{21})\,\times \\ \times[F_2(\mathbf{r}_{21}\!= -a\Omega,\mathbf{p}_1^*,\mathbf{p}_2^*) - F_2(\mathbf{r}_{21}\!= a\Omega,\mathbf{p}_1,\mathbf{p}_2)]\;, \\ \frac{\partial F_2}{\partial t} = -\sum_{j=1}^{2}\mathbf{v}_j\cdot\nabla_j\,F_2 + \sum_{j=1}^{2}\nu a^2\int\! d\mathbf{p}_3\!\int d\Omega\,(\Omega\cdot\mathbf{v}_{3j})\,\times \\ \times\,\theta(\Omega\cdot\mathbf{v}_{3j})\,[F_2(\mathbf{p}_j^*)\,F_1(\mathbf{r}_3\!= \mathbf{r}_{21} - a\Omega,\mathbf{p}_3^*)\; - \\ -\,F_2(\mathbf{p}_j)\,F_1(\mathbf{r}_3\!= \mathbf{r}_{21} + a\Omega,\mathbf{p}_3)] \end{aligned} \tag{0.5}$$

at $s = 2$ [1], - under the BGL directly lead to the BE [2],

$$\frac{\partial F_1}{\partial t} = -\mathbf{v}_1 \cdot \nabla_1 F_1 + \nu a^2 \int\int (\Omega \cdot \mathbf{v}_{21})\, \theta(\Omega \cdot \mathbf{v}_{21}) \, \times \tag{0.6}$$
$$\times \, [\, F_1(\mathbf{p}_1^*)\, F_1(\mathbf{p}_2^*) - F_1(\mathbf{p}_1)\, F_1(\mathbf{p}_2)\,]\, d\Omega\, d\mathbf{p}_2$$

(we introduced $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$). This statement is in essence equal to the 'Lanford theorem" [3], because behavior of any term of the iteration series [6, 8] under BGL is determined by a finite number of the transformed equations.

3. Notice, however, that the transformation of Eqs.0.2, by substituting (0.4) for (0.3), takes away from them their aforesaid time-reversibility property: now they are not invariant in respect to the inversion $t \to -t$, $\mathbf{p} \to -\mathbf{p}$. Consequently solutions of the transformed equations in general are not solutions of the initial BBGKYE, and vise versa. In other words, that non-equivalent hierarchies of equations!

Or, to be more precise, probably, we would be able to consider them as equivalent if we were able to deal simultaneously with all possible many-particle correlations (of arbitrary high orders). But they are certainly non-equivalent if we neglect even a part of correlations [4].

Therefore the term by term consideration of iteration series for the transformed equations [6, 8] leads away from a true solution of the initial "hard sphere BBGKY hierarchy" (0.1)-(0.3). Instead it offers solution of another, in essence, postulated kinetic equations. Seemingly, this result sorts with true BBGKY solutions approximately like

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[1] At $s = 1$ that is the Boltzmann-Enskog equation [2, 17].

[2] In more detail, if at $t = 0$ the "mplecular chaos" takes place, $F_n(t = 0, \mathbf{r}, \mathbf{p}) = \prod_{j=1}^{n} F_1^0(\mathbf{r}_j, \mathbf{p}_j)$, then under BGL it propagates to $t > 0$, with $F_1(t)$ satisfying BE.

[3] Formally, it is even stronger than the Lanford theorem since is not restricted in respect to the evolution time.

[4] For example, irreversibility of equations (0.5) is obvious.

complex-energy solutions of the Schrodinger equations [18] (or, in classical statmechanics, solutions of the Liouville equations corresponding to the complex "Ruelle-Pollicott resonances" [19]) sort with their actual solutions [5].

4. Thus, the replacement of (0.3) by (0.4) gives the same effect as the Boltzmann's Stoßzahlansatz. From the physical point of view, this "ansatz" is bad as for it forces us to neglect pre-collision (*in*-) inter-particle correlations and hence neglect fluctuations in "relative frequency", or "frequency ratio" ("chastost"' in Russian [21]) of collisions [9, 10].

Indeed, any collision starts from a pre-collision configuration and finishes with a post-collision configuration, hence, fluctuations in "relative frequency of collisions" equally give rise to both *out*- and *in*-correlations [6].

It is necessary to emphasize that we say about statistical correlations which do not presume presence of some cause-and-consequence relations beyond them [7].

The cause of the "fluctuations in relative frequency of collisions" is mere absence of back reaction to them when they do not disturb the system's state (for instance, when relative frequencies of mutually time-reversed collisions fluctuate with keeping definite proportions between them) [8].

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[5] All these resemble also the "strange" phenomenon of "unitary non-equivalence" of different mathematical descriptions of one and the same physical situation [20].

[6] In addition, since pre-collision configurations arise by time $\sim\tau$ earlier than really collision at distance $\sim\lambda$ from it and post-collision configurations disappear at time $\sim\tau$ after it at distance $\sim\lambda$ from it, then both *out*- and *in*-correlations enclose volumes $\sim\pi a^2\lambda = 1/\nu$ [12, 13, 14].

[7] Mutual independence of colliding particles in the sense of absence of some mutual prehistory generally does not mean statistical independence of the particles in the sense of the probability theory. Citing [21], "*That are prejudices ... that phenomena which are "obviously independent" should possess independent probability distribution laws*", or "*that for any phenomenon one always can point out some definite probability value*" (this is my own translation from Krylov's original Russian text). And more: "*... relative frequencies of one or another phenomenon along phase trajectory, generally speaking, in no way are related to their a priori probabilities*".

[8] Such kind of fluctuations for the first timr were discussed in [22, 23], later in application to fluids in [9, 11, 10] and in application to other systems in in [10, 24, 25], and besides recently in [12, 13, 14]. In [9] it was shown that these fluctuations are indifferent to a degree of smallness of the gas parameter μ. In opposite, just at $\mu\to 0$ (in BGL) the "absence of back reaction" is especially easy understandable.

Clearly, these fluctuations are as well reflected by the distribution functions (DF) $\{F_n(t)\}$ as strong is spatial non-uniformity of the system [9, 10], and therefore they are reflected in the form of correlations between particles' coordinates (while their velocities can be uncorrelated as in the Boltzmann's theory) [9].

These spatial correlations [10], in their turn, do mean that the DF values at collision configurations, e.g. $F_2(\mathbf{r}_2 = \mathbf{r}_1 + a\Omega$, represent independent on $F_1(t)$ and complementary to $F_1(t)$ characteristics of statistical ensemble [11].

5. In view of the aforesaid, we have to come back to the question how we must deal with the conditions (0.1).

Since "contact" DF's values which enter (0.1), first of all $F_2(\mathbf{r}_1 = \mathbf{r}_2 + a\Omega$, play the role of "governing parameters" for BBGKY hierarchy (0.2) as the whole, it is natural to treat them as independent on F_1 characteristics of gas. In more detail, when considering $F_2(\mathbf{r}_1 = \mathbf{r}_2 + a\Omega$, we inevitably come to rest (in the collision integral) against three-particle configurations corresponding to pairs of infinitely close [air collisions. The, considering such configurations, we will come to analogous four-particle ones, and so on. Categorizing all them, one would construct a full (infinite) system of equations for the "contact" Dfs. Such a system, of course, would be time-reversible [12].

There is a key to understanding the 1/f-noise observed in various physical systems [9, 11, 10, 22, 23, 24, 25]. And we can expect that exact time-reversible solutions of BBGKYE contain 1/f fluctuations in kinetic characteristics of the system.

[9] By this reason, a correct derivation of BE from BBGKYE is possible only for uniform gas. This was claimed in [26] on those ground that in non-uniform case the averaging over statistical ensemble can not be replaced by averaging over gas volume.

[10] Or, better saying, configurational correlations, since in general they are dependent on small details of relative particle's dispositions at scales $\lesssim a$.

[11] Already because for ensemble averages generally the inequalities $\langle \widetilde{\nu}^s \rangle \neq \langle \widetilde{\nu} \rangle^s$ take place, where $\widetilde{\nu}$ is local gas density.

[12] Just by this reason it would present true statistical weights of any of kinematically possible scenarios of collisions.
Generally, since irreversibility equally manifests itself in both opposite time directions, its completely adequate description can be done only by reversible equations!

Realization of such a program just would give the answer to the question. On this way, one can easy immediately see a mechanism of generation of the spatial correlations and destroying the Stoßzahlansatz.

Making the first step, let us rewrite the second of BBGKYE in the “pseudo-Liouville” form [8]:

$$\frac{\partial F_2}{\partial t} = a^2 \int (\mathbf{v}_{12} \cdot \Omega)\, \delta(\mathbf{r}_{12} - a\Omega)\, F_2\, d\Omega \; - \\ -\mathbf{v}_{12} \cdot \frac{\partial F_2}{\partial \mathbf{r}_{12}} - \frac{\mathbf{v}_1 + \mathbf{v}_2}{2} \cdot \frac{\partial F_2}{\partial \mathbf{R}} + \nu \sum_{j=1}^{2} \widehat{\mathbf{I}}_{j,3}\, F_3 \tag{0.7}$$

Here, the coordinates $\mathbf{r}_j$ may enter the forbidden region $|\mathbf{r}_1 - \mathbf{r}_2| < a$, where $F_2 \equiv 0$, and the new (first on r.h.s.) term represents a force of repulsion of particles at the border of this region [13]. Besides, we separated the relative displacement of particles, with $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, and motion of their center of mass, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. The first of these two in turn can be divided into norma; and tangential components:

$$-\mathbf{v}_{12} \cdot \frac{\partial F_2}{\partial \mathbf{r}_{12}} = -(\mathbf{v}_{12} \cdot \Omega) \frac{\partial F_2}{\partial \rho_{12}} - \left(\frac{\mathbf{v}_{12}}{\rho_{12}}\, \Lambda(\Omega)\, \frac{\partial F_2}{\partial \Omega} \right), \tag{0.8}$$

where $\Omega = \mathbf{r}_{12}/|\mathbf{r}_{12}|$, $\rho_{12} = |\mathbf{r}_{12}|$ and

$$\Lambda(\Omega)\, \mathbf{f} = \mathbf{f} - \Omega\, (\Omega \cdot \mathbf{f}) = -\, [\Omega \times [\Omega \times \mathbf{f}\,]]$$

Next, consider, with the help of (0.7), the contact DF $F_2(\mathbf{r}_1 = \mathbf{r}_2 + a\Omega) \equiv F_2^{(c)}(t, \mathbf{R}, \Omega, \mathbf{p}_1, \mathbf{p}_2)$, taking in mind that the first term on r.h.s. of (0.7) and the first (normal) component of (0.8) have quite similar, but oppositely signed, singularities which compensate one another. Let us assume that this is exact compensation, that is

$$a^2 \int (\mathbf{v}_{12} \Omega')\, \delta(\rho_{12} \Omega - a\Omega')\, F_2\, d\Omega' - (\mathbf{v}_{12} \Omega) \frac{\partial F_2}{\partial \rho_{12}} = 0 \tag{0.9}$$

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13 In place of $(\nabla_{12} \Phi(\mathbf{r}_{12})) \cdot (\partial F_2 / \partial \mathbf{p}_1 - \partial F_2 / \partial \mathbf{p}_2)$ in case of a smooth interaction potential $\Phi(\rho)$.

Then from (0.7)-(0.9) the necessary autonomous evolution equation for the pair contact DF does follow:

$$\frac{\partial F_2^{(c)}}{\partial t} = -\frac{\mathbf{v}_1+\mathbf{v}_2}{2}\cdot\frac{\partial F_2^{(c)}}{\partial \mathbf{R}} - \\ -\left(\frac{\mathbf{v}_{12}}{a}\,\Lambda(\Omega)\,\frac{\partial F_2^{(c)}}{\partial \Omega}\right) + \nu\sum_{j=1}^{2}\widehat{\mathbf{I}}_{j,3}\;F_3^{(c)}\quad , \tag{0.10}$$

where $F_3^{(c)}$ is the mentioned contact DF for two "bound together" pair collisions.

Notice that formally (0.9) is not assumption but identity. It expresses continuity f probability distribution at breaks of phase trajectories because of collisions, that is the same as the condition (0.1) does express. In essence, this is analogue of equalities (3)-(4) from [9] for a gas with smooth interaction [14].

From the equation (0.10) it it clear that any spatial inhomogeneity, which induces $\partial F_1^{(c)}/\partial \mathbf{r}_1 \neq 0$ and $\partial F_2^{(c)}/\partial \mathbf{R} \neq 0$, automatically excludes possibility of reduction of $F_2^{(c)}$ to F_1 and thus BBGKYE to BE, absolutely independently on value of μ [15].

Notice also that, firstly, the equation (0.10) is reversible and besides invariant in respect to replacing $\mathbf{p}_1, \mathbf{p}_2$ by $\mathbf{p}_1^*, \mathbf{p}_2^*$, as it should be according to (0.1) (thus, the function of (0.1) now is extension of this symmetry property from equations to their solutions).

Secondly, the equality (0.9) says, in particular, that $\partial F_2/\partial \rho_{12} = 0$ at $\rho_{12} = a + 0$ and $(\mathbf{v}_{12}\Omega) \neq 0$. This is natural analogue of behavior of gas density nearby a flipping (in accordance with (0.1)) surface.

[14] Or, to be more concrete, analogue of the equality
$(\nabla_{12}\Phi(\mathbf{r}_{12}))\cdot(\partial F_2/\partial \mathbf{p}_1 - \partial F_2/\partial \mathbf{p}_2) - (\mathbf{v}_{12}\cdot\nabla_{12})\,F_2 \,=\, 0$
which should be satisfied (as identity or as "ansatz") in the space region occupied by collision [9] (for instance, inside the "collision cylinder" [12, 13]), in order to equalize probabilities of mutually corresponding *in*- and *out*-states.

[15] In other words, the inhomogeneity works as a source of pre-collision inter-particle correlations. And this is not surprising: regardless of velocity of a given particle, in its vicinity with linear size $\sim \lambda$ there is always $\sim (\pi a^2/\lambda^2) * *\lambda^3 \nu = 1$ particles forming an *in*-state together with the given one and thus kinematically suitable for pre-collision correlation with it.

6. The contact DF $F_2^{(c)}$ serves as a measure of mean (ensemble averaged) number density of pair collisions. It is clear that it drifts with the center of mass velocity of colliding particles. Similarly, DFs $F_s^{(c)}$ will drift with velocities $(\mathbf{v}_1 + ... + \mathbf{v}_s)/s$. Therefore they are mutually independent. All together they determine statistics of key s-particle configurations which produce all other configurations and eventually evolution of F_1 [16].

7. Formulation of equations for $F_3^{(c)}$, $F_4^{(c)}$, etc. we leave for the future. At present, it is more important to point out existence of alternative, just discussed, treatment of the hard sphere BBGKY hierarchy. This treatment, in contrast with the conventional one, does not ignore the fundamental reversibility property of the BBGKY equations but uses it as basis of definite constructive approach to solutions of these equations. A qualitatively similar approach to a gas of "soft spheres" was tested in citei1,i2,p12. The model of "hard spheres" is of special interest because, expectedly, it can more easily achieve formal quantitative rigor.

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[16] In more detail, on such kind of DFs see [9, 10, 11]. To avoid misunderstandings, it is useful to underline that the smallness of probabilities of contacts of two or more particles in no way means smallness of corresponding contact DFs since the latter (as well as all the DFs under consideration) represent density of probability.

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