Dynamical Virial Relations and Invalidity of the Boltzmann Kinetic Equation

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Abstract

A sequence of exact relations is found which connect one- and many-particle time-dependent distribution functions of non-equilibrium low-density gas with their derivatives in respect to mean density. It is shown that, at least in the context of spatially non-uniform gas evolutions, these relations forbid the "molecular chaos propagation" and imply inapplicability of the Boltzmann kinetic equation even under the Boltzmann-Grad limit and regardless of degree of the non-uniformity. Statistical and physical meaning of this result is explained.

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I. INTRODUCTION

Two main questions under our interest here will be (i) rigorous results about non-equilibrium many-particle systems and (ii) theoretical status of the celebrated L. Boltzmann's kinetic equation [1–6] from viewpoint of such results.

The Boltzmann equation (BE) can be written as

$$\dot{F}(t,r,v) = -v\nabla F(t,r,v) \,+\, n\,\mathbf{C}_2\,F(t,r,v) * F(t,r,w)\ , \tag{1}$$

where $F(t,r,v)$ is one-particle distribution function normalized to volume, n is mean gas density, and $\mathbf{C}_2$ is the Boltzmann's pair collision operator ("collision integral") which acts onto F's velocity argument as

$$\begin{gathered} \mathbf{C}_2\,F(v) * F(w) \,= \int d^3w\,|v-w| \int d^2b \,\times \\ \times\,[F(v^{in}(b,v,w))F(w^{in}(b,v,w)) - F(v)F(w)] \end{gathered} \tag{2}$$

with b being the impact parameter vector (perpendicular to $v-w$) and v^{in} and w^{in} input velocities what lead to the given output ones.

Anybody can agree that today's kinetic theory, as well as 100 years ago, is unthinkable without BE. Nevertheless, nobody have presented a conclusive enough derivation of BE from exact equations of statistical mechanics, e.g. the BBGKY equations (BBGKYE) [2–5].

In general, the BBGKYE can only produce much more complicated equation,

$$\begin{gathered} \dot{F} = -v\nabla F + n\,\mathbf{C}_2\,F*F + n^2\,\mathbf{C}_3\,F*F*F + \\ +\,n^3\,\mathbf{C}_4\,F*F*F*F\,+\dots \end{gathered} \tag{3}$$

(see below), where operator $\mathbf{C}_s$ ($s>2$) represents ring-like connected clusters of s collisions involving s particles (for $s=3$ described e.g. in [4]). Therefore, BE follows from BBGKYE under formal "low-density limit" only, when $n\to 0$ [2–5]. But this is non-physical limit, since it enforces the mean free path of gas atoms, $\lambda\sim 1/\pi a^2 n$, - with a denoting characteristic radius of atom-atom interaction, - to become greater than free flights of atoms, $\sim |v|t$, during any given evolution time t (so that the resulting BE is in fact addressed to collisionless gas).

More physically reasonable idealization, - which allows λ to be less than typical $|v|t$, - is the "Bpltzmann-Grad limit" (BGL) when $n\to\infty$ and simultaneously $a\to 0$, in such way that λ is kept constant. At that, $a^3n\to 0$, i.e. gas becomes "infinitely rare".

This gave rise to hopes that the terms with $\mathbf{C}_3$, $\mathbf{C}_4$, etc., in Eq.3 must vanish under BGL too. Moreover, O. Lanford and others even suggested a proof of this hypothesis for hard-sphere gas [7, 8]. But their interpretation of BBGKYE in this singular case hardly is unconditionally acceptable (in essence, in my opinion, they considered different equations where some of interaction terms were inadvertently rejected while another from the very beginning treated as pair collision integrals) [9].

In any case, contributions with $\mathbf{C}_3$, $\mathbf{C}_4$, etc., in Eq.3 appear due to violation of the Boltzmann's "molecular chaos hypothesis", that is due to statistical correlations between atoms what are in mutually input (**pre-collision**) state (aimed to each other). Naturally, such correlations take place mainly at inter-atom separations comparable with a, but this does not mean that they vanish under BGL (merely they sit just where they are most "harmful").

What is physical meaning of the pre-collision correlations?

Notice that BE (1)-(2) fully corresponds to the "probability-theoretical view" at physical world: it presumes that gas evolution consists of elementary random events (collisions with various input velocities and impact parameters) which occur independently one on another and all possess strictly certain (though may be unknown numerically) *a priori* (conditional) probabilities.

Such the view was originated by J. Bernoully 300 years ago [10]. But in 20-th century N. Krylov [11] showed that assumption that any sort of events can be furnished with certain *a priori* probability, or relative frequency, has no support in rigorous statistical mechanics. In opposite, mechanics allows different relative frequencies on different phase trajectories of a many-particle system. Then, fluctuations of relative frequencies from one phase trajectory (experiment) to another, - being averaged over a statistical ensemble of trajectories' initial conditions , - produce correlations between events and particles even in absence of direct cause-and-consequence connections between them (see item 1 in Sec. "Footnotes" below).

Just such statistical correlations were found and investigated in my works [12] (see also [13]) and [14–20] on spatially inhomogeneous evolutions of fluids and random walks of their particles. And just such correlations determine higher-order terms in Eq.3, impeding reduction of BBGKYE to BE even in spite of BGL.

At that, role of the inhomogeneity is to visualize and magnify effects of the uncertainty of collision probabilities of fluid's particles. In particular experiments the uncertainty manifests itself in the form of scaless (1/f-type) low-frequency fluctuations of both individual particles' mobilities and collective transport characteristics of a fluid.

Here, I suggest new proofs of invalidity of the BE (1). It means that BE is qualitatively defective model, therefore, its quantitatively precise investigation does not garantee full physical correctness of the results even in application to dilute gas.

Starting from general properties and exact density expansions of $F(t, r, v)$ and many-particle distribution functions (DF), we will derive a sequence of exact relations between them and their derivatives in respect to density n, and then, with the help of these relations, demonstrate that the pre-collision inter-particle statistical correlations, - and hence all higher-order terms in Eq.3, - stay finite and significant even under BGL.

II. MANY-PARTICLE STATISTICAL DYNAMICS

Let $N \gg 1$ gas atoms are contained, by means of an auxiliary external potential, in volume $\Omega = N/n$. Let $x_i = \{r_i, v_i\}$ denote variables of i-th, atom,

$F_i(t) \equiv F(t, x_i) \equiv F_1(t, x_i)$, $F_{ij}(t) \equiv F_2(t, x_i, x_j)$, $F_{ijk}(t) \equiv F_3(t, x_i, x_j, x_k)$, ... $F_{1...N}(t) \equiv F_N(t, x_1, x_2, \dots x_N)$ are one-, two-, three-, ... N-particle DFs,

L_i, L_{ij}, L_{ijk}, ... $L_{1...N}$ are one-, two-, three-, ... N-particle Liouville operators (including the auxiliary potential), and

$S_i(t) = \exp(L_i t)$, $S_{ij}(t) = \exp(L_{ij} t)$, ... $S_{1...N}(t) = \exp(L_{1...N} t)$ are corresponding evolution operators.

All these objects are fully symmetric functions of their arguments (indices).

If all DFs are thought normalized to volume and all obey the requirement of mutual consistency, then

$$\frac{1}{\Omega^s} \int_1 \dots \int_s F_{1\dots s}(t) = 1 , \qquad (4)$$

$$F_{1\dots s}(t) = \frac{1}{\Omega} \int_{s+1} F_{1\dots s\, s+1}(t) = \frac{1}{\Omega^{N-s}} \int_{s+1} \dots \int_N F_{1\dots N}(t) ,$$

where $\int_k \dots \equiv \int_\Omega d^3 r_k \int d^3 v_k \dots$. Evolution of all marginal DFs is determined by that of the whole system's DF according to

$$F_{1\dots N}(t) = S_{1\dots N}(t)\, F_{1\dots N}(0) \qquad (5)$$

Since it conserves full phase volume, the equalities (4) will be satisfied at all times if it is so at one, "initial", time moment, e.g. at $t = 0$. But some specific form of DFs can realize at one moment only. For example, we may choose

$$F_{1\,\dots\,s}(0) \;=\; \prod_{j=1}^{s} F_j(0) \;\;, \tag{6}$$

thus assuming ideal "molecular chaos" at the initial time moment.

Further, it is convenient to apply a useful formal trick and introduce operation $\circ$ of "coherent product" of the evolution operators. By definition, for any two non-intersecting sets of indices,

$$S_{i\dots j} \,\circ\, S_{k\dots l} \;=\; S_{i\dots j\,k\dots l} \tag{7}$$

In essence, the left side here is mere equivalent notation for the right-hand side. For intersecting sets, of course, one must take their union. Thus, for instance, $S_{i\dots j} = S_i \circ \dots \circ S_j$, and we can write identities

$$\begin{aligned} S_{1\dots N} \;=\; S_{1\dots s} \prod_{j\,=\,s+1}^{N} \circ S_j \;=\; S_{1\dots s} \prod_{j\,=\,s+1}^{N} \circ[\,1 \,+\, (S_j - 1)\,] \;=\; \\ =\; S_{1\dots s} \,+\, \sum_{j\,=\,s+1}^{N} S_{1\dots s} \circ (S_j - 1) \;+ \\ +\, \sum_{s+1\,\leq j<k\,\leq N} S_{1\dots s} \circ (S_j - 1) \circ (S_k - 1) \;+ \\ +\, \sum_{s+1\,\leq j<k<l\,\leq N} S_{1\dots s} \circ (S_j - 1) \circ (S_k - 1) \circ (S_l - 1) \,+\, \dots \\ \dots + S_{1\dots s} \prod_{i\,=\,s+1}^{N} \circ (S_i - 1) \;=\; \\ =\; S_{1\dots s} \,+\, \sum_{j\,=\,s+1}^{N} [\,S_{1\dots s\,j} - S_{1\dots s}\,] \;+ \\ +\, \sum_{s+1\,\leq j<k\,\leq N} [\,S_{1\dots s\,j\,k} - S_{1\dots s\,j} - S_{1\dots s\,k} + S_{1\dots s}\,] \,+\, \dots \;\;, \end{aligned} \tag{8}$$

where $0 \leq s < N$ (at $s = 0$, of course, both $S_{1\dots s}$ and $F_{1\dots s}$ should be replaced by 1).

Combining these identities with Eqs.4 and 5, after simple algebra one obtains

$$\begin{aligned} F_{1\dots s}(t) \;=\; S_{1\dots s}(t)\, F_{1\dots s}(0) \,+\, \sum_{k\,=\,1}^{N-s} \frac{(N-s)!}{k!\,(N-s-k)!\,\Omega^k} \;\times \\ \times \int_{s+1} \dots \int_{s+k} \{\, S_{1\dots s}(t) \prod_{j=1}^{k} \circ[\,S_{s+j}(t) - 1\,]\,\}\; F_{1\,\dots\,s+k}(0) \end{aligned} \tag{9}$$

Advantage of this representation of the marginal DFs' evolution, in comparison with that given by (4) and (5), is that it can be directly extended to the **thermodynamic limit**, when $N \to \infty$ and $\Omega \to \infty$ (the auxiliary potential removes) at fixed $N/\Omega \to n = \text{const}$.

III. DENSITY EXPANSION

The Eq.9 by itself does prompt conditions of this extension. Namely, a limit form of the initial DFs $F_{1\dots s}(0)$ at $\Omega \to \infty$ should be such that all the integrals in Eq.9 turn to well converging "proper integrals". That is such that, at any s and k,

$$[\, S_{s+1}(t) - 1\,] \circ \dots \circ [\, S_{s+k}(t) - 1\,] \; F_{1\dots s\, s+1 \dots s+k} \;\to\; 0 \qquad \texttt{when} \quad r_{s+1} \dots r_{s+k} \;\to\; \infty \;, \tag{10}$$

in fast enough (integrable) way. This means that "at infinity" (asymptotically) all the initial DFs are invariant in respect to both translations and collisions of atoms. It will be the case if our gas is thermodynamically equilibrium (hence, homogeneous and rest) at infinity, i.e.

$$F_{1\dots s-1\, s} \;\to\; F_{1\dots s-1}\, F^{(eq)}(v_s) \qquad \texttt{at} \quad r_s \;\to\; \infty \;, \tag{11}$$

where $F^{(eq)}(v) = (2\pi T/m)^{-3/2} \exp{(-mv^2/2T)}$ is the Maxwell velocity distribution with some temperature T (m is atomic mass). This agrees with requirements (4) in their limit form, that is, - in the case (6), - with

$$\lim_{\Omega\to\infty} \frac{1}{\Omega} \int_{\Omega} d^3 r_1 \int d^3 v_1 F_1 \;=\; 1 \tag{12}$$

We see that the thermodynamic limit in Eq.9 presumes that our gas (or, generally, fluid) is essentially inhomogeneous (if not equilibrium at all).

Then Eq.9 transforms to infinite series

$$\begin{aligned} F_{1\dots s}(t) \;=\; S_{1\dots s}(t)\, F_{1\dots s}(0) \;+ \\ +\sum_{k=1}^{\infty} \frac{n^k}{k!} \int_{s+1} \dots \int_{s+k} \{\, S_{1\dots s}(t) \prod_{j=1}^{k} \circ [\, S_{s+j}(t) - 1\,]\,\}\; F_{1\dots s+k}(0) \;= \\ =\; S_{1\dots s}(t)\, F_{1\dots s}(0) \;+\; n \int_{s+1} [\, S_{1\dots s\, s+1}(t) - S_{1\dots s}(t)\,]\, F_{1\dots s\, s+1}(0) \;+ \\ +\; \frac{n^2}{2!} \int_{s+1} \int_{s+2} [\, S_{1\dots s\, s+1\, s+2}(t) - S_{1\dots s\, s+1}(t) \;- \\ -\, S_{1\dots s\, s+2}(t) + S_{1\dots s}(t)\,]\, F_{1\dots s\, s+1\, s+2}(0) \;+\; \dots \end{aligned} \tag{13}$$

with initial DFs (and, hence, arbitrary-time DFs) satisfying conditions (10) and (11), and $\int_j \dots = \int d^3r_j \int d^3v_j \dots$.

The Eq.13 represents density expansion of total evolution operator of the infinitely-many-particle system. If its initial state is treated irrespective to n , then Eq.13 becomes density expansion of its time-dependent future (or past) DFs. This formal treatment has literal physical sense at least when Eq.13 applies (as below) to sufficiently rare gas, and especially in the framework of statistical ensemble determined by initial "molecular chaos" (6).

Readers themselves can characterize meaning of any k-th term of Eq.13 and see that it is rougly $\propto (na^2|v|t)^k \propto (|v|t/\lambda)^k$, at that being some functions of $(r_i - r_j)/a$ ($i, j \in 1 \dots s$).

IV. DYNAMICAL VIRIAL RELATIONS

Below, we will confine ourselves by dilute gas, starting from the "molecular chaos" and examining its "propagation" with time.

At $s = 1$ and $s = 2$ Eq.13, as combined with (6), yields

$$F_1(t) = S_1(t)\, F_1(0) + n \int_2 [\, S_{12}(t) - S_1(t)\,]\, F_1(0)\, F_2(0) + \\ + \frac{n^2}{2!} \int_2 \int_3 [\, S_{123}(t) - S_{12}(t) - S_{13}(t) + S_1(t)\,]\, F_1(0)\, F_2(0)\, F_3(0) + \dots , \tag{14}$$

$$\begin{aligned} F_{12}(t) &= S_{12}(t)\, F_1(0)\, F_2(0) + \\ &+ n \int_3 [\, S_{123}(t) - S_{12}(t)\,]\, F_1(0)\, F_2(0)\, F_3(0) + \\ &+ \frac{n^2}{2!} \int_3 \int_4 [\, S_{1234}(t) - S_{123}(t) - S_{124}(t) + \\ &+ S_{12}(t)\,]\, F_1(0)\, F_2(0)\, F_3(0)\, F_4(0) + \dots \end{aligned} \tag{15}$$

There is definite relation between these expressions. To perceive it, let us

(i) introduce functions

$$G_{1\dots s}(t) \equiv \prod_{j=1}^{s} \circ [S_j(t) - 1]\;\, F_{1\dots s}(0) + \\ + \sum_{k=1}^{\infty} \frac{n^k}{k!} \int_{s+1} \dots \int_{s+k} \prod_{j=1}^{s+k} \circ [S_j(t) - 1]\;\, F_{1\dots s+k}(0) \tag{16}$$

(ii) return to Eq.13, expend factors $S_{1\dots s}(t)$ into "coherent product" of $1 + [S_j(t) - 1]$,

(iii) take into account identity

$$0 \,=\, \sum_{k\,=\,1}^{\infty} \frac{n^k}{k!} \int_1 \dots \int_k [\, S_1(t) - 1\,] \circ \, \dots \, \circ [\, S_k(t) - 1\,] \; F_{1\,\dots\,k}(0) \tag{17}$$

what follows from Eqs.9 and 13 at $s = 0$ (and seems trivial in view of general properties of Liouville operators), and

(iv) with the help of (17) rewrite $F_1(t)$ and $F_{12}(t)$ in the form

$$\begin{gathered} F_1(t) \,=\, F_1(0) \,+\, G_1(t) \;\;, \\ F_{12}(t) \,=\, F_{12}(0) \,+\, F_1(0)\, G_2(t) \,+\, F_2(0)\, G_1(t) \,+\, G_{12}(t) \end{gathered} \tag{18}$$

Next, let us apply here the initial "molecular chaos" (6) and take into account that the initial one-particle DF, - since being normalized to volume (according to (12)), - is independent on mean gas density n . Then, considering n dependence of functions (16), we obviously can write exact relations

$$\frac{\partial}{\partial n}\; G_{1\,\dots\,s}(t) \,=\, \int_{s+1} G_{1\,\dots\,s\,s+1}(t) \tag{19}$$

Besides, differentiations of (17) in respect to n produce identities

$$\begin{gathered} \int_1 \dots \int_s G_{1\,\dots\,s}(t) \,=\, 0 \;\;, \\ \int_1 \dots \int_k \{\prod_{j=1}^k \circ[\, S_j(t) - 1\,]\,\} \, \prod_{j=1}^k \, F_j(0) \,=\, 0 \end{gathered} \tag{20}$$

At $s = 1$ equality (19), - together with Eqs.18 and 20, - gives

$$\begin{aligned} \frac{\partial}{\partial n}\; F_1(t) \,=\, & \int_2 [\, F_{12}(t) - F_1(0)G_2(t) - G_1(t)F_2(0) - F_1(0)F_2(0)\,] \,= \\ & \qquad = \int_2 [\, F_{12}(t) + G_1(t)G_2(t) - - F_1(t)F_2(t)\,] \,= \\ & \qquad\qquad = \int_2 [\, F_{12}(t) - F_1(t)F_2(t)\,] \end{aligned} \tag{21}$$

Formulae (19) and (21) are direct analogues of the "virial relations" found and considered in [15–19] as inportant statistical properties of "molecular Brownian motion". Here, I added the word "dynamical" in order to underline their principal difference from the relations known in equilibrium statistical mechanics.

Another forms of the "dynamical virial relations" (DVR) (19) is expounded in Appendix A below. Importantly, they are indifferent to a form of atom-atom interaction (thus enclosing the hard-sphere model) although can depend on statistical ensemble under consideration (thus reflecting predisposition of infinitely-many-particle systems to "non-ergodicity of kinetic behaviour" [17]).

V. SYMBOLIC KINETIC EQUATION

Kinetic equation (KE) is an equation what closely expresses, - like Eqs.1 and 3, - time derivative of the one-particle DF through it itself [2]. To construct a KE, first let us write

$$\begin{gathered} L_{1\dots s} \,=\, L^0_{1\dots s} \,+\, L'_{1\dots s} \;, \\ L^0_{1\dots s} \,=\, \textstyle\sum_{1\leq i\leq s} L^0_i \;, \quad L'_{1\dots s} \,=\, \textstyle\sum_{1\leq i<j\leq s} L'_{ij} \;, \end{gathered} \tag{22}$$

where operators L^0 and and L' represent free motion of atoms and their (pair) interactions, respectively:

$$L^0_i \,=\, -\,v_i\,\nabla_i \;, \quad L'_{ij} \,=\, m^{-1}\,\Phi'(r_i - r_j)\,(\partial/\partial v_i \,-\, \partial/\partial v_j) \;,$$

with $\Phi(\rho)$ being (short-range repulsive) interaction potential and $\Phi'(\rho) = \partial\Phi(\rho)/\partial\rho$. At once, introduce free evolution operators and “scattering operators”:

$$S^0_{1\dots s}(t) \,\equiv\, \exp\,(L^0_{1\dots s}\,t) \;, \quad Z_{1\dots s}(t) \,\equiv\, S_{1\dots s}(t)\,S^0_{1\dots s}(-t) \tag{23}$$

(taking in mind that for any of our evolution operators $S^{-1}(t) = S(-t)$).

Then, perform time differentiation of Eq.13. Using the boundary conditions at infinity, (10) or (11), and the symmetry of DFs, is not too hard to make sure that, naturally, the result is the BBGKYE:

$$\dot F_{1\dots s}(t) \,=\, L_{1\dots s}\,F_{1\dots s}(t) \,+\sum_{j=1}^{s} n\int_{s+1} L'_{j\,s+1}\,F_{1\dots s+1}(t) \tag{24}$$

Hence, we have only to express F_{12} in terms of F_1 .

With this purpose, let us treat Eq.14) as series expansion of $nF_1(t)$ over $nF_1(0)$ and try to invert it:

$$\begin{aligned} F_1(0) \,=\, S_1(-t)\,F_1(t) \,-\, \\ -\,n\,S_1(-t)\int_2 [\,S_{12}(t) - S_1(t)\,]\,S_1(-t)\,S_2(-t)\,F_1(t)\,F_2(t) \,+\, \dots \end{aligned} \tag{25}$$

Inserting this into Eq.15, after a tedious non-commutative algebra, we obtain an infinite series whose first two terms look as follow,

$$\begin{gathered} F_{12}(t) \,=\, \sum_{k=0}^{\infty} n^k\,F^{(k)}_{12}(t) \,=\, Z_{12}(t)\,F_1(t)\,F_2(t) \,+ \\ +\,n\int_3 [\,Z_{123}(t) \,-\, Z_{12}(t)\,Z_{13}(t) \,-\, Z_{12}(t)\,Z_{23}(t) \,+ \\ +\,Z_{12}(t)\,]\,F_1(t)\,F_2(t)\,F_3(t) \,+\, \dots \end{gathered} \tag{26}$$

Here, a term with s-th degree of one-particle DF is of $(s-2)$-th order in respect to density and contains $s-2$ integrations. Insertion of this expansion into Eq.24 at $s=1$ yields the Eq.3 with

$$\mathbf{C}_2\, F*F \;=\; \int_2 L'_{12}\, Z_{12}(t)\, F*F\;\;, \tag{27}$$

$$\begin{aligned}\mathbf{C}_3\, F*F*F \;=\; \int_2\int_3 L'_{12}\,[\, Z_{123}(t) \;-\; Z_{12}(t)\, Z_{13}(t) \;- \\ -\, Z_{12}(t)\, Z_{23}(t) \;+\; Z_{12}(t)\,]\;\; F*F*F\end{aligned} \tag{28}$$

Spending a lot of time, one could continue series in (25) and (26) and find also $F^{(2)}_{12}(t)$ and $\mathbf{C}_4$.

Notice that two written out right-hand terms of Eq.26 confirm the results of semi-heuristic considerations [2, 4, 27], although with essential differences. Namely, in [4] the second term is thought as a small correction to the first one, in the framework of the low-density limit (see Introduction), and time arguments of the "scattering operators" there are not unambiguously defined. In contrast to it, time argument of our operators $Z_{ij}(t)$, $Z_{123}(t)$,etc., is definitely total evolution time, so that they represent the whole pre-history of collisions.

This difference is especially important from viewpoint of higher-order terms of Eq.26 as considered under such more adequate approach as the BGL. Actually, one can see that lower-order terms in Eq.26 and hence in Eq.3 arise fully independently on higher-order terms in Eqs.14, 15 and 25. Therefore, if higher-order terms of Eq.26 and 3 were insignificant then this would mean that arbitrary long evolution of one-particle DF is determined by only a few collisions.

Absurdity of this enforced deduction clearly shows that in fact any of (infinitely many) terms of Eq.26 essentially contributes to Eq.3 even under BGL. Hence, Eq.3 has a symbolic meaning only (though one may try to transform it to Boltzmann-like equation but with collisions' cross-section being a functional of $F(t,r,v)$), while BE (1) is invalid at all.

Next, this logical necessity will be sustained mathematically.

VI. FAILURE OF "MOLECULAR CHAOS PROPAGATION"

The first term of the series Eq.26 practically reproduces the Bogolyubov's formulation [2] of the "molecular chaos" (MC) hypothesis: $F_{12}(t) \Rightarrow F^{(0)}_{12}(t) = Z_{12}(t)\, F_1(t)F_2(t)$. Or, exploiting the pair correlation function, $C_{12}(t) = F_{12}(t) - F_1(t)F_2(t)$ (see Appendix A), $C_{12}(t) \Rightarrow [Z_{12}(t) - 1]\, F_1(t)F_2(t)$ What does it say?

By definition of the scattering operators,

$$Z_{12}(t)\, F(r_1, v_1)\, F(r_2, v_2) \;=\; F(r_1' + v_1' t, v_1')\, F(r_2' + v_2' t, v_2') \;\;, \tag{29}$$

where the primed variables represent such past state, time t ago, which leads to the given current state. Therefore, the MC hypothesis, - i.e. assumption about insignificance of second and higher terms of Eq.26, - impliess that $C_{12}(t)$ differs from zero for two sorts of states. First, for currently interacting atoms, at $|r_2 - r_1| \lesssim a$. Second, for atoms in mutually post-collision (out-) states, at $v_{12} \cdot r_{12} > 0$, $a \lesssim |r_{12}| < |v_{12}| t$ and $|b| \lesssim a$, where $r_{12} = r_2 - r_1$, $v_{12} = v_2 - v_1$, and $b = r_{12} - v_{12}(v_{12} \cdot r_{12})/|v_{12}|^2$ is impact parameter vector (already mentioned in Sec.1).

Thus, under the MC there are no correlations between atoms in mutually pre-collision states, - defined like the post-collision ones but with $v_{12} \cdot r_{12} < 0$, - and no correlations between mere close though non-interacting atoms (for which $|r_{12}|$ is greater than a but comparable with a), but the payment for such pleasure is presence of the unreservedly far propagating post-collision correlations.

If it was really so under BGL, then the exact relation (21), - after its multiplying by n , - would reduce to

$$n \frac{\partial}{\partial n}\; F_1(t) \;=\; n \int_2 [\, Z_{12}(t) - 1\,]\, F_1(t)\, F_2(t) \tag{30}$$

The multiplication ensures finiteness of both sides here under transition to BGL, along with transition from n to physically more meaningful variable like $\kappa = \pi a^2 n = 1/\lambda$, so that $n\, \partial/\partial n \Rightarrow \kappa\, \partial/\partial \kappa$.

In combination with Eq.29 this equality yields-

$$\begin{aligned} n \frac{\partial}{\partial n}\; F_1(t, r_1, v_1) \;=\; n \int_0^t d\tau \int d^3 v_2 \int d^2 b\; |v_1 - v_2| \;\times \\ \times\, [\, F_1(t, r_1 + (v_1' - v_1)\tau, v_1')\, F_1(t, r_1 + (v_2' - v_1)\tau, v_2') \;- \\ -\, F_1(t, r_1, v_1)\, F_1(t, r_1 + (v_2 - v_1)\tau, v_2)\,] \;= \\ = n \int_0^t d\tau\;\, \exp\,(-\tau v_1 \nabla_1)\, \mathbf{C}_2\, F_1(t, r_1 + v_1 \tau, v_1)\, F_1(t, r_1 + v_2 \tau, v_2) \end{aligned} \tag{31}$$

Here $'$ plays the same role as in the BE (1). And, as in (1), transition to BGL allows to neglect F_1 's changes at time and space scales related to a .

Simultaneously, according to the previous section, the same MC assumption, - that $F_{12}(t) = Z_{12}(t)\, F_1(t) F_2(t)$, - produces the BE (1) itself.

Hence, if this is true assumption then Eqs.31 and 1 should be compatible one with another. In fact, however, they can not be satisfied simultaneously, except purely spatially homogeneous case when $\nabla_1 F_1(t) = 0$ (see Footnote 2) ! To become convinced of this fact in detail, one may e.g. consider linearized evolution of small local or periodic perturbations of equilibrium state ($F^{eq}(v_1)$ from above).

Consequently, contribution of the rejected terms of Eq.26 into integral in DVR (21) is on order of its value (see Eq.30) under the MC assumption, and the latter, as applied to spatially inhomogeneous evolutions, is incompatible with the exact relation (21) even in spite of the BGL.

In other words, the "molecular chaos propagation" fails in spatially inhomogeneous case, so that the BE proves to be invalid even under BGL (see Footnotes 3 and 4).

I would like to underline that all the aforesaid equally embrace the hard-sphere interaction.

To finish the paper and exclude hopes to "save" BE, we will supplement just presented proof of its invalidity with short notes on the pre-collision correlations. Additional comments on related many-particle correlations and their influence onto $F_1(t)$'s evolution are placed to Appendix B.

VII. EXCESS AND PRE-COLLISION CORRELATIONS

Let us return to Eq.26 and consider functions

$$\begin{gathered} \Delta F_{12}(t) \,\equiv\, Z_{12}(t)\, \Delta F'_{12}(t) \,\equiv\, F_{12}(t) \,-\, Z_{12}(t)\, F_1(t)\, F_2(t) \;= \\ =\, \sum_{k=1}^{\infty} n^k\, F_{12}^{(k)}(t) \;= \\ =\, n \int_3 [\, Z_{123}(t) \,-\, Z_{12}(t)\, Z_{13}(t) \,-\, Z_{12}(t)\, Z_{23}(t) + \\ +\, Z_{12}(t)\,]\, F_1(t)\, F_2(t)\, F_3(t) \;+\; \dots \end{gathered} \tag{32}$$

They characterize those part of statistical correlations between two atoms what is due to not their interaction between themselves but common pre-history of their interactions (collisions) with the rest of gas. At that, k-th term of the sum represents connected chains (clusters) of at least $k+1$ collisions (actual or virtual ones) conjointly involving $k+2$ atoms. Statistical meaning of such "excess" (or "historical" [17]) correlations was exhaustively explained in [12, 13] (see also Introduction and notes in [9, 14, 18, 28]).

It is clear that, first, if $\Delta F_{12}(t) \neq 0$ somewhere in two-particle phase space, then $\Delta F_{12}(t) \neq 0$ almost everywhere, since anyway there are many various clusters of collisions resulting in given current states of atoms 1 and 2.

Second, $\Delta F_{12}(t) \neq 0$ for post-collision states, since $\Delta F_{12}(t)$ must compensate and stop nonphysical unrestricted propagation of the above mentioned post-collision correlations prescribed by the MC approximation $F_{12}(t) = F_{12}^{(0)}$. Hence, undoubtedly $\Delta F_{12}(t) \neq 0$ almost everywhere, including the pre-collision states.

This reasoning shows that appearance of pre-collision correlations along with other ("non-collision") excess correlations (at states for which $\Delta F_{12}(t) \approx \Delta F'_{12}(t)$ in Eq.32) is quite inevitable from physical point of view.

Third, on the other hand, separation of atoms 1 and 2 must decrease a number of the clusters determining $C_{12}(t)$ nearly proportionally to visual space angle $\o$ of one of the atoms from viewpoint of another, $\o \sim \pi a^2/4\pi |r_{12}|^2$. The matter is that, since $F_{12}^{(k)}(t)$ involves $k+1$ (or more) collisions but contains only k integrations, one (or more) of k integration velocities is restricted in respect to its direction by a space angle $\sim \o$.

By these reasons, we can propose the following qualitative fit of the correlation function:

$$C_{12}(t) \,=\, \frac{a^2}{a^2 + 4|r_2 - r_1|^2}\, C'_{12}(t) \ , \tag{33}$$

where function $C'_{12}(t)$ keeps non-zero under BGL and smmothly depends on $|r_{12}|$ at $|r_{12}| \gtrsim a$.

Then DVR (21) implies (under BGL) that

$$\frac{a^2}{4} \int d\o \int_0^\infty d|r_{12}| \int d^3v_2 \;\; C'_{12}(t) \;=\; \pi\, a^2\, \frac{\partial F_1(t)}{\partial \kappa} \ , \tag{34}$$

where $\o = r_{12}/|r_{12}|$.

We see that at any fixed distance $|r_{12}|$ the excess correlations, - particularly, the pre-collision ones, - turn to zero under BGL. In this sense, the MC really takes place.

But contribution of these correlations to the "triple collision integral" (28), to $\mathbf{C}_4$, ..., and thus to the whole Eq.3 is determined by region $|r_{12}| \sim a$ where all excess (pre-collision) correlations stay finite under BGL (Footnote 5). Hence, in essence MC fails.

And last remarks.

(i) Both the left-hand integral in Eq.34 and right-hand derivative there define some (one and the same) characteristic length. Of course, it must be nothing but the λ (since $C_{12}(t)$ can not be indifferent to λ). At the same time, obviously, any of constituent parts of $C_{12}(t)$, namely, $[Z_{12}(t) - 1]F_1(t)F_2(t)$ and $F_{12}^{(k)}(t)$ ($k = 1, 2, \dots$), extends up to $|r_{12}| \sim v_0 t$, with v_0 being characteristic velocity of gas atoms. Hence, indeed all these parts are required in order to introduce λ in place of $v_0 t$.

(ii) The reasonings and conclusions of this section (as well as that at end of Sec.5 and in Appendix B) in no way rely on some measure of non-uniformity of gas state. Therefore, all they are equally valid, - and thus BE is equally invalid, - for arbitrary weakly non-uniform gas (Footnotes 4 and 6).

VIII. CONCLUSION

Considering spatially inhomogeneous evolution of low-density gas, we introduced a non-standard representation of its time-dependent distribution functions (DF) in the form of their density expansion, and then exploited it to derive original exact "dynamical virial relations" (DVR) connecting DFs with their density derivatives. Then we applied DVR to analysis of behavior of two-particle correlation function under the Boltzmann-Grad limit (BGL), in order to examine validity of the "folklore" opinion that evolution of one-particle DF under BGL exactly obeys the Boltzmann kinetic equation (BE) while many-particle DFs undergo the "molecular chaos propagation".

We showed that the corresponding approximate approaches to gas kinetics [2–5], which seem well grounded in the "low-density limit", at the same time appear non-grounded under BGL, since contradict the DVR and thus fail when applied to spatially non-uniform situations (independently on degree of the non-uniformity).

This fact does not mean, of course, that idea of the Boltzmann collision operator (integral) is defective. This is excellent concept if one applies it to a separate collision. But it by itself is unable to comprise those inter-atom statistical correlations what arise from uniqueness ("non-ergodicity" [17]) of histories of collisions in particular experiments (see Introduction and comments in [12–15, 17–19, 26, 29]).

One of ways to take into account all these correlations is the approach to correct solution of the BBGKY equations (the "collisional approximation") suggested in [12] (see also [13, 14]).

In principle, this approach allows to consider a wide variety of phenomena and problems ("from molecular Brownian motion to shock waves" [29]).

In [12, 14] this approach was used to investigate statistical characteristics of molecular random walks in fluids (in particular, the related 1/f noise). The results then were confirmed from viewpoint of corresponding exact "virial relations" [15, 17, 19]. Thus, some ancient prejudices, pointed out in [11], like "molecular chaos", were overcome with substantial physical profit.

Therefore, it seems reasonable to try to apply the mentioned approach (strengthened with the DVR) to macroscopic gas (fluid) kinetics and hydrodynamics too. All the more so as their difference from Boltzmannian kinetics and classical hydrodynamics may be practically important even for weakly non-equilibrium (non-uniform) processes (see Footnote 7).

Appendix A: Correlation (cumulant) distribution functions and the DVR

Let us introduce irreducible many-particle correlation, or cumulant, functions (CF) by

$$\begin{gathered} F_{12} \,=\, F_1 F_2 + C_{12}\;, \quad F_{123} \,=\, F_1 F_2 F_3 + \\ + C_{12} F_3 + C_{23} F_1 + C_{13} F_2 + C_{123}\;\;, \end{gathered} \tag{A1}$$

and so on. Higher-order CFs can be defined with the help of generating functionals:

$$\begin{gathered} 1 + \sum_{s=1}^{\infty} F_s(t)\, \frac{\psi^s}{s!} \;= \\ =\, \exp\,[\, F_1(0)\, \psi\,]\; \{\, 1 + \sum_{s=1}^{\infty} G_s(t)\, \frac{\psi^s}{s!} \} \;= \\ =\, \exp\,[\, F_1(t)\, \psi \,+ \sum_{s=2}^{\infty} C_s(t)\, \frac{\psi^s}{s!}\,]\;, \end{gathered} \tag{A2}$$

where, of course,

$$F_s(t)\, \psi^s \;=\; \int_1 \dots \int_s F_{1\,\dots\,s}(t)\, \psi(x_1) \dots \psi(x_s)$$

and so on. In these shortened notations, the DVR (19) altogether can be accumulated into single generating DVR

$$\begin{gathered} \frac{\partial}{\partial n}\, \sum_{s=1}^{\infty} G_s(t)\, \frac{\psi^s}{s!} \;\; = \\ = \int dx \frac{\delta}{\delta \psi(x)}\, \sum_{s=1}^{\infty} G_s(t)\, \frac{\psi^s}{s!} \end{gathered} \tag{A3}$$

(to be supplemented with equality (17) and thus also (20)). Obviously, this generating DVR is equivalent to

$$\frac{\partial C_{1\,\dots\,s}(t)}{\partial n} \;=\; \int_{s+1} C_{1\,\dots\,s\,s+1}(t) \quad (s\geq 2)\ , \tag{A4}$$

$$\frac{\partial F_1(t)}{\partial n} \;=\; \int_2 C_{12}(t) \tag{A5}$$

Generalization of these DVR to dense gases (fluids), - when the "initial molecular chaos" (6) is too bad choice for initial DFs (since they must include effects of atom-atom interaction and thus depend on the mean density), - will be considered elsewhere.

Appendix B: Many-particle correlations and falsity of the BE's "derivations"

According to the BBGKY equations (24) or the DVR (19) and/or (A5), the pair pre-collision correlations arise in company with various many-particle ones. Their importance for correct approach to gas (fluid) kinetics was demonstrated already in [12] (see also [13, 14, 17]). For one more demonstration, let us criticize the "derivation" of BE (1) suggested in [5].

Assume, as there, that the irreducible ("pure") three-particle correlations (see Appendix 1), - described by CF $C_{123}(t)$, - can be neglected at $a^3n\ll 1$ and hence under BGL. Then the second of Eqs.24, when written in terms of CFs, reduces to

$$\dot{C}_{12} \;=\; L_{12}\,C_{12} \,+\, L^{\prime}_{12}\,F_1\,F_2 \;=\; L^0_{12}\,C_{12} \,+\, L^{\prime}_{12}\,F_{12} \tag{B1}$$

Solving Eq.B1 (with zero initial condition) and inserting the result, C_{12} , into the first of Eqs.24, one can come (at $a^3n\ll 1$) to the BE [5].

If this is true derivation of BE, then it should be compatible with the DVR, at least, with Eq.21 (i.e. Eq.A5). In fact, however, this is not the case. Indeed, integration of Eq.B1 over x_2 , after multiplying it by n , yields

$$\begin{aligned}\frac{\partial}{\partial t}\,n\int_2 C_{12} \;=\; L^0_1\,n\int_2 C_{12} \,+\, n\int_2 L^{\prime}_{12}\,F_{12} \;=\\ =\; L^0_1\,n\int_2 C_{12} \,+\, \left[\,\frac{\partial}{\partial t} \,-\, L^0_1\right]\,F_1\ \ ,\end{aligned}$$

where we used also the first of the BBGKY equations (24). Combining this equality with the DVR (21), we come to equality

$$[\,\partial/\partial t \,-\, L^0_1\,]\,[\,n\,\partial F_1/\partial n \,-\, F_1\,] \;=\; 0\ \ , \tag{B2}$$

which certainly is wrong.

Hence, the above BF's "derivation", based on approximation (B1), is erroneous. And, in order to get a correct description of F_1's evolution, one should seriously think about role of many-particle correlations.

FOOTNOTES

1. Similar statements were formulated, independently on the Krylov's work, 30 years ago and confirmed at the level of semi-phenomenological statistical theory by the author of this communication together with Prof. G. Bochkov in [21, 22] and [23, 24]), where the idea of realistic "non-ergodic" random walks (of charge carriers), - which have no certain diffusivity and mobility and do not obey Boltzmannian kinetics ("quasi-Gaussian random walks [13]), - was suggested and mathematically designed (about my recent considerations on this subject see [25, 26]). For understanding our principal idea of 1/f-noise, my preprint [13] may be useful and, besides, my recent presentation

`http://yuk-137.narod.ru/What_is_1_by_F_noise.pdf`

2. At that, Eq.31 turns to $n\,\partial F/\partial n \;=\; t\,n\mathbf{C}_2\,F * F$, while Eq.1 can be written as $t\,\partial F/\partial t \;=\; t\,n\mathbf{C}_2\,F * F$, therefore, both they are satisfied by a function depending on time and density via their product $\xi = nt$ and obeying equation $\partial F/\partial\xi \;=\; \mathbf{C}_2\,F * F$.

3. Notice that the modified formulation [4] of the "molecular chaos" hypothesis, like $F_{12}(t) \;=\; Z_{12}(t_0)\,F_1(t)F_2(t)$, - with a fixed t_0 (at $t \,>\, t_0$), - is worse than the above formulation, since appears incompatible with virial relation (21) even in homogeneous case.

4. It is useful to add that the incompatibility of (both hypothetical) equations (30) and (1) is sufficient but not necessary condition for invalidity of one (or both) of them. Therefore, both they can be wrong for homogeneous gas too. This suspicion is confirmed by argumentation presented in Sec.7 (another matter that under our conditions for existence of the thermodynamic limit, - see Sec.3, - homogeneous gas means merely equilibrium gas).

5. Seemingly, possibility of such rather subtle circumstance was not foreseen by the authors of [7, 8], and this oversight caused subtle errors in their formal construction (see notes in [9, 13, 16, 28]).

6. This circumstance highlights that the Boltzmann equation is from mathematical tale but not from real life: it describes ensemble of "dice tosses" ("coin tossings") instead of ensemble of dynamical trajectories (which in fact appears to be irreducible to "dice tosses" [15, 17]).

7. This statement comes from (i) essential difference of our theory of self-diffusion of gas atms [12] from the classical one, and (ii) observation that in case of (infinitesimally) weak non-equilibrium equations of our approach ("collisional approximation") [12] are quite similar to the equations describing the self-diffusion (the only difference is that the place of the Boltzmann-Lorentz operators is occupied by the linearized Boltzmann operators).

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