Hard-Sphere Brownian Motion in Ideal Gas: Inter-Particle Correlations, Boltzmann-Grad Limit, and Destroying the Myth of Molecular Chaos Propagation

Yuriy E. Kuzovlev

Donetsk A.A. Galkin Institute for Physics and Technology of NASU,
ul. R. Luxemburg 72, Donetsk 83114, Ukraine

(Dated: 10 January 2010)

The BBGKY hierarchy of equations for a particle interacting with ideal gas is analyzed in terms of irreducible many-particle correlations between gas atoms and the particle’s motion. The transition to the hard-sphere interaction is formulated from viewpoint of the recently discovered exact relations connecting the correlations with the particle’s probability distribution. Then the Boltzmann-Grad limit is considered and shown not to lead to the Boltzmann hierarchy and the molecular chaos, since correlations of all orders keep significant in this limit, merely taking a singular form.

PACS numbers: 05.20.Jj, 05.40.Fb

I. INTRODUCTION

In the work [1], as well as in its arXive preprints [2] and premising works [3–4], based on principles and methods of rigorous statistical mechanics, - first of all, on the Bogolyubov approach to it [5]. - I proved existence of general exact relations (“virial relations”) connecting (i) probability law of random walk of a test “Brownian” particle (BP) in a fluid and (ii) irreducible many-particle statistical correlations between molecules of the fluid and the BP’s walk (in particular, BP may be merely a marked molecule). I emphasized also that these relations make it clearly visible that all n-particle correlations always are quantitatively significant, even under the low-density (“Boltzmann-Grad”) gas limit. This fact, in turn, implies that the Boltzmannian kinetics is incorrect even in this limit, and true kinetics of fluids, - including low-density gases! - should take into account all the correlations.

The meaning of so universal correlations was explained already in [6] (this article is hardly available on-line, but one can read its own author’s translation [7] from Russian original, or see preprint [8]). It is sufficient to notice that a fluid as the whole (and first of all dilute gas!) is indifferent to a number of past collisions happened to its given particular molecule. Therefore any molecule has no definite (a priori predictable) “time-average” rate of collisions [6, 10]. In other words, actual rate of its collisions undergoes fluctuations which are indifferent to time averaging. Thus that are scaleless fluctuations with 1/f type spectrum [11]. The mentioned statistical correlations directly reflect complicity of particles (via mutual collisions) in these fluctuations and, hence, indirectly describe their statistics (for detail see [6] or [7] or [8]).

As far as I know, first such statements about molecular motion were put forward in works by G.Bochkov and me [12–17] as conjectures about origin and properties of 1/f noise accompanying charge transport (i.e. Brownian motion of charge carriers) and other transport processes (in generalized sense [8]). We demonstrated once again that correct ideology leads to useful results even at phenomenological level. In particular, in [14, 17] it was shown that fluctuations of rate of collisions (or, equivalently, 1/f fluctuations of diffusivity and mobility) possess essentially non-Gaussian statistics gravitating towards power-law probability tails.

The latter circumstance requires, in view of the well known Marcinkiewicz theorem (see e.g. [18]), to deal with whole infinite chain of cumulants of the fluctuations. On the other hand, according to the later works made at the microscopic level, firstly [6] and then its development in [19, 20], n-order cumulant of fluctuations in the rate of collisions associates with specifically (n + 1)-particle correlations (irreducible component of (n + 1)-particle distribution function). That is why one should not truncate the BBGKY hierarchy of equations! Anyway, neglect of three-particle (and thus higher) correlations means rejection of the fluctuations at all (like neglect of two-particle correlations rejects any collisions at all [20]).

The aforesaid was confirmed by exact results of [1–3]. Nevertheless, a specially visual analysis of inter-particle correlations may be useful. This is just one of purposes of the present paper.

With this purpose it is natural to concentrate on the Brownian motion of (molecular-size) particle in ideal gas (see [21] or some of preprints [22] and also [1, 2]), which is most simple “kinetic process” since it produces least amount of inter-particle correlations. Besides, this is good motive to scan the limit transition from smooth interaction (between BP and gas atoms) to singular “hard-sphere” one dividing into momentary “collisions”.

Another our purpose is to perceive falsity of popular treatments of the “hard-sphere BBGKY hierarchy of equations” [22, 23] trying to reduce it, in the Boltzmann-Grad limit, to so-called “Boltzmann hierarchy”.

We will begin in Sec.2 by formulation of the BBGKY hierarchy for our particular problem and corresponding
(above mentioned) exact virial relations \[1\ 2\ 21\ 22\]. After their consideration in Sec.3 we will see for ourselves that collisions constantly give birth to various statistical correlations, and not only post-collision ones but also pre-collision correlations. Then, in Sec.4, discuss and execute the hard-sphere limit of our BBGKY hierarchy, taking in mind that it should stay compatible with the virial relations as they are independent on character of interactions (interaction potentials). The result is (i) modified BBGKY equations combined with (ii) familiar boundary conditions to them at hyper-surfaces (in many-particle phase spaces) corresponding to collisions. The second ingredient allows to transform the first into usual “hard-sphere BBGKY hierarchy” \[24\ 27\ 28\ 29\ 31\] under the Boltzmann-Grad limit. Thus, the correct theory does not present such marvel “chry” \[24, 25, 28, 29, 31\] under the Boltzmann-Grad limit. After their consideration in Sec.3 we will see for our- 

II. BBGKY HIERARCHY, ITS CUMULANT REPRESENTATION, AND VIRIAL RELATIONS

We want to consider random walk \( R(t) \) of a Brownian particle (BP) in thermodynamically equilibrium ideal gas, assuming that at initial time moment \( t = 0 \) BP starts from certainly known position \( R(0) = 0 \). The BBGKY equations for this problem can be either derived \[22\] directly from the Liouville equation, following Bogolyubov \[5\], or extracted \[21\] from general results of \[1\ 3\]. They reads as

\[
\frac{\partial F_k}{\partial t} = [H_k, F_k] + n \frac{\partial}{\partial \Phi} \int_{k+1} \Phi'(R - r_{k+1}) F_{k+1} ,
\]

where \( k = 0, 1, \ldots \), \( H_k \) is Hamiltonian of subsystem “k atoms + BP”, \( \ldots \ldots \) means the Poisson brackets, \( \Phi(r) \) is potential of (short-range repulsive) interaction between BP and atoms, \( \Phi'(r) = \nabla \Phi(r) \), \( n \) is gas density (mean concentration of atoms), \( F_0 = F_0(t, R, P; n) \) is normalized DF of the BP’s coordinate \( R \) and momentum \( P \), \( F_k = F_k(t, R, r_{(k)}, P, p^{(k)}; n) \) are \((k+1)\)-particle DFs for BP and k atoms, \( r_{(k)} \) and \( p^{(k)} \) denote coordinates and momenta of atoms, respectively, \( r_{(k)} = \{r_1, r_k\} \), \( p^{(k)} = \{p_1, \ldots, p_k\} \), and \( j_k = \ldots = j \int dR dp_k \).

Initial conditions to these equations, corresponding to the gas equilibrium, at temperature \( T \), are

\[
F_k|_{t=0} = \delta(R) \exp(-H_k/T) = \delta(R) G_M(P) \prod_{j=1}^{k} E(r_j - R) G_m(p_j),
\]

where \( M \) and \( m \) are masses of BP and atoms, respectively, \( G_m(p) = (2\pi m)^{-3/2} \exp(-p^2/2m) \) is the Maxwell momentum distribution of a particle with mass \( m \), and \( E(r) = \exp(-\Phi(r)/T) \). Besides, existence of the thermodynamical limit presumes the “cluster property” of DFs. that is vanishing of inter-particle correlations under large spatial separation of particles, so that \( F_k \to F_{k-1} G_m(p_s) \) at \( r_s - R \to \infty \), where \( 1 \leq s \leq k \) and \( F_{k-1} \) does not include \( r_s \) and \( p_s \). That are boundary conditions to Eq(1).

In view of these conditions, in order to visually extract inter-particle correlations, it is convenient to make the linear change of variables, from the DFs \( F_k \) to new functions \( C_k \) \[33\] as follow:

\[
F_0(t, R, P; n) = C_0(t, R, P; n),
\]

\[
F_1(t, R, r_1, P, p_1; n) = C_0(t, R, P; n) f(r_1 - R, p_1) + C_1(t, R, r_1, P, p_1; n),
\]

\[
F_2(t, R, r^{(2)}, P, p^{(2)}; n) = C_0(t, R, P; n) f(r_1 - R, p_1) f(r_2 - R, p_2) + C_1(t, R, r_1, P, p_1; n) f(r_2 - R, p_2) + C_1(t, R, r_2, P, p_2; n) f(r_1 - R, p_1) + C_2(t, R, r^{(2)}, P, p^{(2)}; n),
\]

and so on. with \( f(r, p) = E(r) G_m(p) \).

Clearly, such defined \( C_k \) can be named cumulant functions (CF) since represent irreducible correlations between \( k \) gas atoms and total BP’s path \( R \). In their terms the BBGKY hierarchy \[1\] takes the form \[1\ 2\ 22\]

\[
\frac{\partial C_k}{\partial t} = [H_k, C_k] + n \frac{\partial}{\partial P} \int_{k+1} \Phi'(R - r_{k+1}) C_{k+1} +
\]

\[
+ T \sum_{j=1}^{k} G_m(p_j) E'(p_j) \left[ \frac{P}{MT} + \frac{\partial}{\partial P} \right] P_{kj} C_{k-1} ,
\]

where \( E'(r) = \nabla E(r) \), \( p_k = r_k - R \), and \( P_{kj} \) means replacement of pair of arguments \( x_j = \{r_j, p_j\} \) (if it is present) by \( x_k = \{r_k, p_k\} \). The mentioned initial and boundary conditions simplify to

\[
C_0(0, R, P; n) = \delta(R) G_M(P), \quad C_0(0, R, r^{(k)}, P, p^{(k)}; n) = 0 , \quad C_k(t, R, r^{(k)}, P, p^{(k)}; n) \to 0 \quad \text{at} \quad r_j - R \to \infty
\]

\((1 \leq j \leq k)\). A careful enough scanning of these equations results in observation \[22\] that exact relations

\[
\frac{\partial}{\partial t} C_k(t, R, r^{(k)}, P, p^{(k)}; n) =
\]

\[
= \int_{k+1} C_{k+1}(t, R, r^{(k+1)}, P, p^{(k+1)}; n) .
\]

take place. This is particular case of general “virial relations” found in \[1\ 2\ 21\] as exact properties of solutions to BBGKY equations describing molecular Brownian motion in fluids (they can be also deduced \[5\] from the generalized fluctuation-dissipation relations \[33, 34\]).

These relations demonstrate existence and significance of all many-particle correlations. To see straight away that they keep significant in the Boltzmann-Grad limit
(BGL), let us introduce characteristic interaction radius $r_0$ of the potential $\Phi(\rho)$, corresponding free-path length of BP, $\lambda = (\pi r_0^2 n)^{-1}$, and integrated correlations

$$W_k(t, R; \lambda) \equiv n^k \int \left[ \int \cdots \int C_k(t, R, r^{(k)}, P, p^{(k)}; n) \right] dP$$

Thus, $W_0(t, R; \lambda) = \int F_0(t, R, P; 1/\pi r_0^2 \lambda) dP$ is probability distribution of the BP’s path. Then Eqs.6 yield

$$W_k(t, R; \lambda) = \frac{1}{\lambda^k} \left( \frac{\partial}{\partial \lambda} \right)^k W_0(t, R; \lambda) \quad (7)$$

These exact relations hold at any values of $r_0$ and $n$, hence, under BGL ($r_0 \to 0$, $n \to \infty$, $\lambda = \text{const}$) too. They show that anyway by order of magnitude $W_k(t, R; \lambda) \sim W_0(t, R; \lambda)$.

III. PRE-COLLISION CORRELATIONS AND FAILURE OF MOLECULAR CHAOS

Is the Boltzmann’s molecular chaos (“Stoßahlansatz”) compatible with virial relations (8), (7)? May be, correlations there are purely post-collision and therefore do not contradict Boltzmann’s ansatz proclaiming absence of pre-collision correlations?

Unfortunately, this is vain hope, and the answer is no. To make sure of this, let us agree that post-collision (“post-collision correlation”) since it passes to finishing of pair correlation by BP-atom interaction, and the result correlation represented by the $C$.

FIG. 1. A simplest diagram transforming post-collision pair correlation, $C_1^{\text{out}}$, into pre-collision pair correlation, $C_1^{\text{in}}$, through three-particle correlation, $C_1$. The “Brownian particle” is represented by circles and entire arrows while gas atoms by dots, light lines and short arrows.

“Boltzmann-Lorentz” equation for the BP’s distribution $C_0 = F_0$, thus realizing the dream of “molecular chaos”.

However, the last term in Eq.(10) for $C_2$, quite similarly (even under neglect of $C_3$) produces three-particle correlations out of the two-particle one, $C_1^{\text{out}}$. Resulting $C_2$ contributes, via integral in Eq(8), back to evolution of $C_1$, and produces, in particular, pre-collision pair correlations between particles going to meet one another. In such way, $C_1$ acquires pre-collision component $C_1^{\text{in}}$, thus turning the dream into a rough approximation. This is illustrated schematically by Fig. 1.

IV. HARD-SPHERE LIMIT

For further, first notice that Eqs(10) can be written in equivalent form

$$\frac{\partial C_k}{\partial t} = -V \cdot \frac{\partial C_k}{\partial R} - n \frac{\partial}{\partial P} \int_1 \Phi'(\rho_1) C_1 + T G_m(p_1) E'(\rho_1) \left[ \frac{P}{MT} + \frac{\partial}{\partial P} \right] C_0 \quad (9)$$

$$\frac{\partial C_2}{\partial t} = -V \cdot \frac{\partial C_2}{\partial R} + (L_1 + L_2) C_2 - n \frac{\partial}{\partial P} \int_3 \Phi'(\rho_3) C_3 + T (1 + P_{21}) G_m(p_2) E'(\rho_2) \left[ \frac{P}{MT} + \frac{\partial}{\partial P} \right] C_1 \quad (10)$$

Here, we introduced the Liouville operator

$$L_j = (V - v_j) \cdot \frac{\partial}{\partial \rho_j} + \Phi'(\rho_j) \left( \frac{\partial}{\partial p_j} - \frac{\partial}{\partial P} \right)$$

and made use of the relative atoms’ coordinates $\rho_j$.

Evidently, the last term in Eq.(10) represents generation of pair correlation by BP-atom interaction, and the result is “post-collision correlation” since it passes to finishing “out-state” of the particles. If we neglected three-particle correlation represented by CF $C_2$ then solution to Eq(8) would be just this post-collision correlation: $C_1 = C_1^{\text{out}}$. Substitution of this $C_1$ to Eq(8) would yield a closed
In these collision regions, in opposite, \( C_k \) (\( k > 0 \))
become more and more sharp functions of \( \rho_j \), so that \( \partial C_k / \partial \rho_j \sim \delta^{-1} C_k \), similarly to \( \Phi(\rho_j) \sim \delta^{-1} \Phi(\rho_j) \).
Hence, the second and the fourth right-hand terms in Eq. (3), Eq. (10), etc., both are infinitely increasing \( \propto \delta^{-1} \)
in collision regions and, in view of absence of other such terms, should compensate one another. Equivalently, the expressions in square brackets in Eqs. (11) should become eigenfunctions of operators \( L_j \) corresponding to zero eigenvalues, that is
\[
L_j \left[ C_k + G_m(p_j) E(\rho_j) P_{kj} C_{k-1} \right] = 0 \quad (12)
\]
asymptotically, inside the collision regions.
This statement, in its turn, means that expression in the square brackets represents integral of motion, and its values at beginning and at end of the pair collision, are equal. Thus, visualizing only variables what change during collision, we can write
\[
C_k(p^\text{in}, p_j) + G_m(p_j^\text{in}) P_{kj} C_{k-1} = \]
\[
C_k(p^\text{out}, p_j^\text{out}) + G_m(p_j^\text{out}) P_{kj} C_{k-1} \quad (13)
\]
where \( \rho_j = \rho_0 \Omega \), with \( \Omega \) being unit normal vector, and \( \rho_0 \cdot u_j < 0 \) and \( \Omega \cdot u_j > 0 \), respectively, and are connected via the limit collision dynamics (mirror reflection):
\[
P^\text{in} + p_j^\text{in} = P^\text{out} + p_j^\text{out}, \]
\[
\Omega \cdot (v^\text{out}_j - V^\text{out}) = -\Omega \cdot (v^\text{in}_j - V^\text{in}) \quad (14)
\]
\[
(1 - \Omega \otimes \Omega) (v^\text{out}_j - V^\text{out}) = (1 - \Omega \otimes \Omega) (v^\text{in}_j - V^\text{in})
\]
On the other hand, integration of (14) over the collision region, for instance, at \( j = k \), yields
\[
- \frac{\partial}{\partial F} \int_k \Phi(\rho_k) C_k = -\hat{\Gamma} C_k \equiv 0 \quad (15)
\]
Substituting this equality into Eqs. (11) for complement of the now forbidden regions \( |\rho_j| \leq r_0 \) we obtain
\[
\frac{\partial C_k}{\partial t} = -V \cdot \frac{\partial C_k}{\partial R} - \sum_{j=1}^k u_j \cdot \frac{\partial C_k}{\partial \rho_j} - n \hat{\Gamma} C_{k+1} \quad (16)
\]
where \( u_j = v_j - V \). At boundaries of the forbidden regions, i.e. at \( |\rho_j| = r_0 \), these equations should be supplemented with boundary conditions (13)–(14).
Combining Eqs. (16) with (13) and (14) we come to
\[
\frac{\partial C_k}{\partial t} = -V \cdot \frac{\partial C_k}{\partial R} + \sum_{j=1}^k L_j C_k + \]
\[
+ \frac{1}{\pi \lambda} \int dp \int_{(V - v) \cdot \Omega > 0} d\Omega \quad ((V - v) \cdot \Omega) \times \]
\[
\times [G_m(p^*) C_k(p^*) - G_m(p) C_k(P) + C_{k+1}(\rho = \rho_0 \Omega, p^* - C_{k+1}(\rho = \rho_0 \Omega, P, p)]
\]
with \( \rho = \rho_{k+1} \), \( P = p_{k+1} \), \( v = v_{k+1} = p_{k+1}/m \), and momenta \( P^* \), \( p^* \) being related to \( P \), \( p \) in the same way as pre-collision momenta \( P^\text{in} \), \( p^\text{in} \) in (12) are related to post-collision ones, \( P^\text{out} \), \( p^\text{out} \), and the integration involves pre-collision states only.
What is for the operators \( L_j \), in respect to CFs they are defined as \( L_j = -(v_j - V) \cdot \partial / \partial \rho_j \) at \( |\rho_j| > r_0 \) and by boundary conditions (13) at \( |\rho_j| = r_0 \). Thus, importantly, \( L_j \) are not mere translation operators: at collision surfaces \( |\rho_j| = r_0 \) they act as creation operators, creating \((k + 1)\)-order correlations from \( k\)-order ones. Therefore factually \( C_k \) remain coupled with both \( C_{k+1} \) and \( C_{k-1} \), as in basic Eqs. (3). In other words, due to conditions (13), hierarchy (17) keeps characteristic three-diagonal structure of equations for CFs!
Return from CFs back to DFs, according to the CFs definition (3), transforms these equations to
\[
\frac{\partial F_k}{\partial t} = -V \cdot \frac{\partial F_k}{\partial R} - \sum_{j=1}^k u_j \cdot \frac{\partial F_k}{\partial \rho_j} - n \hat{\Gamma} F_{k+1} \quad (18)
\]
and conditions (13) to
\[
F_k(p^\text{in}, p_j^\text{in}) = F_k(p^\text{out}, p_j^\text{out}) \quad (19)
\]
along with (14). Their substitution into the “collision integral” \( \hat{\Gamma} F_{k+1} \) gives, similarly to (17),
\[
\frac{\partial F_k}{\partial t} = -V \cdot \frac{\partial F_k}{\partial R} + \sum_{j=1}^k L_j F_k + \]
\[
+ \frac{1}{\pi \lambda} \int dp \int_{(V - v) \cdot \Omega > 0} d\Omega \quad ((V - v) \cdot \Omega) \times \]
\[
\times [F_{k+1}(\rho = \rho_0 \Omega, p^*, p^*) - F_{k+1}(\rho = \rho_0 \Omega, P, p)]
\]
Here again \( L_j = -(v_j - V) \cdot \partial / \partial \rho_j \) at \( |\rho_j| > r_0 \) but at \( |\rho_j| = r_0 \) action of the operator \( L_j \) onto DFs is defined by boundary conditions (19).

V. THE BOLTZMANN-GRAD LIMIT AND “MATHEMATICAL NON-PHYSICS”

Equations (16) as combined with boundary conditions (13)–(14) at collision surfaces \( |\rho_j| = r_0 \) (and conditions (3) at infinity) or, equivalently, equations (18) combined with (13) and (14) represent direct analogue of so-called “hard-sphere BBGKY hierarchy” (see e.g. Eq.2.2 from [29] or Eq.4.1 from [29]).
Importantly, the term “hard-sphere BBGKY hierarchy” is adequate on the understanding only that when the boundary conditions are substituted into \( F_{k+1} \) inside the “collision integral” in equation for \( F_k \) then simultaneously and necessarily they are satisfied by \( F_{k+1} \) in the next equation for \( F_{k+1} \) itself (i.e. included into definition of the operators \( L_j \) as above). Otherwise one makes some “mathematical non-physics”, since resulting equations will be non-derivable from Liouville equation for an (infinitely) many hard sphere system!
In opposite, fulfilment of the mentioned requirement guarantees observance of the virial relations (see Appendix) and consequently belonging of resulting equations to the class of BBGKY hierarchies (since virial relations do follow already from most general properties of many-particle dynamics and Liouville equations [13]).

In view of these facts, it seems impossible to accept the old idea that under the Boltzmann-Grad limit (BGL) the “hard-sphere BBGKY hierarchy” is equivalent to so-called “hard-sphere Boltzmann hierarchy” (see e.g. [24, 28, 29, 31]).

For our system it looks as

$$\frac{\partial F_k}{\partial t} = -V \cdot \frac{\partial F_k}{\partial \mathbf{R}} - \sum_{j=1}^{k} (\mathbf{v}_j - \mathbf{v}) \cdot \frac{\partial F_k}{\partial \mathbf{p}_j} +$$

$$+ \frac{1}{\pi \lambda} \int d\mathbf{p} \int_{(\mathbf{v} - \mathbf{v}) \cdot \Omega > 0} d\Omega \cdot ((\mathbf{v} - \mathbf{v}) \cdot \Omega) \times \quad (21)$$

$$\times \left[ F_{k+1}(\rho = 0, \mathbf{P}, \mathbf{p}) - F_{k+1}(\rho = 0, \mathbf{P}, \mathbf{p}) \right],$$

where there are no forbidden regions, that is \( \rho_j \) can take arbitrary values from the whole \( \mathbb{R}^3 \), and the boundary conditions [19] at \( |\rho_j| \to r_0 \to 0 \) are thrown, that is operators \( \mathbf{L}_j^0 \) are replaced by trivial translation operators, \(- (\mathbf{v}_j - \mathbf{v}) \cdot \partial / \partial \rho_j \).

This means that in corresponding equations for CFs any \( k \) is now connected to \( C_{k+1} \) only, and not to \( C_{k-1} \). Thus, these equations form two-diagonal hierarchy qualitatively different from the original one!

As the result of such frivolity, these equations allow for factored solution with “propagation of chaos”, when \( F_k = F_0 \prod_{j=1}^{k-1} G_m(\mathbf{p}_j), \quad C_k = 0 \) at \( k > 0 \), and \( F_0 = C_0 \) undergoes the “Boltzmann-Lorentz equation”.

Evidently, this “Boltzmann hierarchy” contraries to the above emphasized requirement: it uses the boundary conditions to write “collision integrals” but neglects the same conditions in higher equations what determines the integrands (as if the latter took particles from a “parallel world!”) ! As the consequence, the Boltzmann hierarchy does not satisfy the virial relations. Its wrong is clear already from observation that it results when one first damages Eqs [23] by replacing \( \mathbf{L}_j^0 \) with \(- (\mathbf{v}_j - \mathbf{v}) \cdot \partial / \partial \rho_j \) and only after that goes to \( r_0 = 0 \) [37]. Therefore, it is not surprising that the famous Lanford’s attempt [24] to prove the mentioned idea was in fact unsuccessful [38].

Possible formal cause of this nonsuccess is very simple: the smaller is \( r_0 \) the less smooth functions of \( \rho_j \) are all the CFs [3, 4], since conditions [19] ensure continuity and smoothness of the probability measures \( F_k \) along phase trajectories only but not in perpendicular dimensions.

Indeed, let \( \mathbf{u}_j, \rho_j > 0 \), that is BP and an atom scatter one from another. If at that \( r_0 \ll |\rho_j| \lesssim \lambda \) and additionally \( |\mathbf{u}_j \times \rho_j| / |\mathbf{u}_j| < r_0 \) (where \( \times \) denotes vector product), i.e. vectors \( \mathbf{u}_j \) and \( \rho_j \) are nearly parallel, then the particles form an out-state which (almost certainly) arise from their recent collision (especially if \( |\rho_j| \ll \lambda \)). According to [19], post-collision correlations of any order between such particles inevitably take place, and by order of magnitude all they are equal to \( C_0 = F_0 \). With time, as was explained in Sec.3, also quite similar pre-collision correlations do arise, at \( |\mathbf{u}_j \times \rho_j| / |\mathbf{u}_j| < r_0 \), since statistical picture acquires more and more time-reversal symmetry.

At the same time, at \( |\mathbf{u}_j \times \rho_j| / |\mathbf{u}_j| > r_0 \) there are almost no reasons for correlations. Hence, in directions perpendicular to \( \mathbf{u}_j \) all CFs become more and more sharp functions of \( \rho_j \). At that, the integral value of correlation per one atom goes to zero \( \propto \pi \rho_j^2 / \lambda = 1/n \). But this has no significance since correlations concentrate just where they are most effective. This is confirmed by the virial relations (7). The latter show also that really significant correlational characteristics are \( n^k C_k \) which turn under BGL into singular generalized functions.

VI. CONCLUSION

We have seen that the Boltzmann-Grad limit does not lead to any essential simplifications (and in this sense it does not exist). In particular, it does not lead to the mythologic Botzmannian kinetics with Boltzmann equation, Boltzmann-Lorentz equation, etc., except noninteresting spatially homogeneous case [39]. Physical and statistical reasons of this pleasant fact already were over and over again explained in [6] and earlier [12–17] and later [1, 3, 4, 19, 22, 40, 41]. The fact is pleasant because it shows once again that real many-particle dynamical chaos does not degenerates into miserable stochastics.

Appendix: Virial relations for hard-sphere system

Integration of \((k+1)\)-th of Eqs [10] over \( \mathbf{p}_{k+1} \) and \( \rho_{k+1} \) at \( |\rho_{k+1}| > r_0 \) yields for \( \bar{C}_k = \int_{r_0}^{\infty} C_{k+1} \), in view of (5), equations

$$\frac{\partial \bar{C}_k}{\partial t} = -V \cdot \frac{\partial \bar{C}_k}{\partial \mathbf{R}} - \sum_{j=1}^{k} \mathbf{u}_j \cdot \frac{\partial \bar{C}_k}{\partial \rho_j} - \hat{\Gamma} C_{k+1} - n \hat{\Gamma} \bar{C}_{k+1}$$

At the same time, differentiation of Eqs [10] in respect to the density produces for \( \bar{C}_k = \partial C_k / \partial \rho \) equations

$$\frac{\partial \bar{C}_k}{\partial t} = -V \cdot \frac{\partial \bar{C}_k}{\partial \mathbf{R}} - \sum_{j=1}^{k} \mathbf{u}_j \cdot \frac{\partial \bar{C}_k}{\partial \rho_j} - \hat{\Gamma} C_{k+1} - n \hat{\Gamma} \bar{C}_{k+1}$$

which are identical to the previous ones. Since, according to (5), initial conditions for \( \bar{C}_k \) and \( \bar{C}_k \) also are identical (all are zeros), we come to equalities \( \bar{C}_k = \bar{C}_k \), that is to the virial relations (6), \( \partial C_k / \partial \rho = \int_{r_0}^{\infty} C_{k+1} \).

Notice that this consideration is valid regardless of concrete form of boundary conditions at \( |\rho_j| = r_0 \). Therefore, virial relations hold under replacement of the hard-sphere “mirror reflection” conditions [19] by some other rule. Correspondingly, equations (10) and (13) can be extended to collision operators \( \hat{\Gamma} \) with other “scattering laws” than (14).
Yu. E. Kuzovlev, “Molecular random walk and a symmetry group of the Bogoliubov equation” Theoretical and Mathematical Physics 160 (3) 1300-1314 (Sep. 2009) {DOI:10.1007/s11232-009-0117-0} [in Russian: Teoreticheskaya i Matematicheskaya Fizika 160 (3) 517-533 (Sep. 2009)].

Yu. E. Kuzovlev, arXiv: 0810.5383, 0908.0274.

Yu. E. Kuzovlev, arXiv: 0705.4580, 0710.3831, 0802.0288, 0803.0301, 0804.2023.

Yu. E. Kuzovlev, arXiv: cond-mat/0903350.

Similarly, in the human life, if somebody is so much free that forgets his past expenses, then he can not plan “mean expenses per unit time”!

In the low-density gas limit these fluctuations become merely they manifest non-ergodicity of kinetic behavior of many-particle dynamical systems [1, 2, 6, 8]. In particular, statistical correlations at low density have little influence on statistical physics. North-Holland, Amsterdam, 1962.

Yu. E. Kuzovlev, Math. Physics Archive [http://www.ma.utexas.edu]: 07-144, 07-309, 08-209, 09-26.

N.N. Bogolyubov. Problems of dynamical theory in statistical physics. North-Holland, Amsterdam, 1962.

Yu. E. Kuzovlev, arXiv: cond-mat/9903350.

“Relative frequencies of some phenomenon along a given phase trajectory, generally speaking, in no way are connected to hypothetica probabilities”, in spite of the mixing of phase trajectories (moreover, in essence, just due to the mixing).

In the low-density gas limit these fluctuations become even more (maximally) pronounced since get rid of damping by collective (hydrodynamical) interactions. As these fluctuations have no specific reasons, one can say that statistical correlations never influence on some real processes, since reside in theory. But there (at arbitrary density!) they are the only representatives of any orocosces including particles’ interactions and collisions.

Yu. E. Kuzovlev, “On Brownian motion in ideal gas and related principles”, arXiv: 0806.4157.

Yu.E.Kuzovlev and G.N.Bochkov, Pis’ma v ZhTF No.3, 228-233 (1983).

Yu. E. Kuzovlev, arXiv: 0907.3475.

Yu. E. Kuzovlev and G.N.Bochkov, “On origin and statistical characteristics of 1/f noise.” Preprint No.157, NIRFI, Gorkii (Nijniy-Novgorod), Russia, 1982.

Yu.E.Kuzovlev and G.N.Bochkov, Sov.Phys.-JETP 72, 574 (2000).