A Truth of Molecular Chaos

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The BBGKY hierarchy of equations for a particle interacting with an ideal gas is investigated. Principal properties of its solutions are disclosed, as exact identities which connect probability distribution of path of the particle, its derivatives in respect to gas density and irreducible many-particle correlations between gas molecules and the path. They show that all the correlations always give equally important contributions to evolution of the path distribution, and therefore the exact theory does not reduce to the classical kinetics even at arbitrary small gas density.

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1. One of creators of the modern probability theory A. Kolmogorov underscored [1] that in it "*the concept of independence of experiments fills most important place*" and "*correspondingly one of most important objectives of philosophy of natural sciences*" is "*clearing-up and refinement of those prerequisites under which one can treat given phenomena as independent*". Recall that in the probability theory some random phenomena or quantities A and B by definition are independent if their probability distributions are independent, that is $P(A,B) = P(A)\,P(B)$ [1]. However, in natural sciences the independence of phenomena A and B is thought as absence of cause-and-effect relations between them, that is an influence of one to another. Whether independence in this usual sense does mean independence in the sense of the probability theory?

From viewpoints of common sense and philosophy, certainly does not mean. Merely because A and B which do not directly influence one on another nevertheless both can be parts of a same another random event and thus turn out to be indirectly related.

From the scientific point of view, it is natural to bring the same question to the statistical mechanics. One of creators of modern theory of dynamical systems and statistical mechanics N. Krylov thoroughly analyzed it [2] and also came to the negative answer: he concluded that opinions that "*phenomena which are "manifestly independent" should have independent probability distributions*", and the like, are nothing but "*prejudices*" [2].

Especially Krylov pointed [2] to firmness of such prejudices [3]. Only it explains why the molecular chaos hypothesis put forward by Boltzmann many years ago [4] until now dominates kinetics although never was logically substantiated [5]. And why N. Bogolyubov, when he obtained [6] an exact hierarchy of evolution equations for s-particle distribution functions, straight away truncated his equations at $s = 2$ thus reducing it to the Boltzmann equation.

Undoubtedly, molecules of sufficiently rarefied gas are independent in usual sense since almost surely have nothing common in the past. Nevertheless they can be essentially dependent in the sense of the probability theory. This is quite understandable [7] (or you may see [8]). The absence of common causes of colliding particles in the past means, for each of them, absence of any back reaction of the gas to its past collisions. Therefore arbitrary long fluctuations in relative frequency of collisions are allowable [9]. These fluctuations just play the role of aforesaid random events producing indirect statistical interdependencies between pairs (or groups) of molecules capable of being participators of one and the same collision (or a cluster of successive collisions).

As the consequence, $P(A,B) \neq P(A)\,P(B)$ where $P(A)$ is probability of finding a molecule at (phase) point A and $P(A,B)$ is probability of finding simultaneously two molecules at points A and B. At that, relaxation of one-particle distribution $P(A)$ is determined by pair correlation $P(A,B) - P(A)\,P(B)$. Relaxation of the latter just similarly always (regardless of the gas rarefaction) is determined by three-particle correlation. And so on up to infinity. Since during time interval t a molecular undergoes $\sim t/\tau$ collisions (with τ being characteristic free-flight time), a correct description of gas evolution over this interval requires taking into account s-particle correlations with at least $s \lesssim t/\tau$. Hence, in practice the whole hierarchy of equations deduced by Bogolyubov [6] is necessary.

In work [7] (and additionally or instead in [8]) and in work [10] approximate solutions to this hierarchy or, in other words, the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) equations [11] were suggested for the problem about random wandering of a test molecule, and explanations were expounded why the Boltzmann's hypothesis is wrong. The aim of the present communication is to prove the statements of preceding paragraph without any approximations. At that we will strengthen the proof and besides simplify it due to replacing the usual gas by ideal gas whose molecules interact with the test molecule only but not with each other.

2. We want to consider thermal random motion of a test molecule (TM) in thermodynamically equilibrium gas, at that specifying its position $\mathbf{R}(t)$ at some initial time moment $t = 0$: $\mathbf{R}(0) = \mathbf{R}_0$.

Let $\mathbf{P}$ and M denote momentum and mass of TM,

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m , $\mathbf{r}_j$ and $\mathbf{p}_j$ ($j=1,2,...$) denote masses, coordinates and momenta of other molecules, $\Phi(\mathbf{r})$ is (short-range repulsive) potential of interaction between any of them and TM, and n is gas density (mean concentration of molecules). At arbitrary time $t\geq 0$, full statistical description of this system is presented by the chain of $(k+1)$-particle distribution functions ($k=0,1,2,...$): $F_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0\,;n\,)$ which is normalized (to unit) density of probability distribution of TM's variables, and $F_k(t,\mathbf{R},\mathbf{r}^{(k)},\mathbf{P},\mathbf{p}^{(k)}|\,\mathbf{R}_0\,;n\,)$ (where $\mathbf{r}^{(k)}=\{\mathbf{r}_1...\mathbf{r}_k\,\}$, $\mathbf{p}^{(k)}=\{\mathbf{p}_1...\mathbf{p}_k\,\}$) which are probability densities of finding TM at point $\mathbf{R}$ with momentum $\mathbf{P}$ and simultaneously finding out some k molecules at points $\mathbf{r}_j$ with momenta $\mathbf{p}_j$. A rigorous definition of such distribution functions (DF) was done in [6]. In respect to the coordinates $\mathbf{r}_j$ they are not normalized, but instead (as in [6]) obey the conditions of weakening of inter-particle correlations under spatial separation of particles. Subject to the symmetry of DF in respect to $x_j=\{\mathbf{r}_j,\mathbf{p}_j\}$ these conditions can be compactly written as follows: $F_k\,\rightarrow\,F_{k-1}\,G_m(\mathbf{p}_k)$ at $\mathbf{r}_k\rightarrow\infty$, where $G_m(\mathbf{p})$ is the Maxwell momentum distribution of a particle with mass m .

The enumerated DF satisfy a standard chain of the Bogolyubov equations [6]:

$$\frac{\partial F_k}{\partial t}=[\,H_k,F_k\,]+n\,\frac{\partial}{\partial \mathbf{P}}\int_{k+1}\Phi\,'(\mathbf{R}-\mathbf{r}_{k+1})\,F_{k+1} \qquad (1)$$

($k=0,1,...$) along with obvious initial conditions

$$\begin{gathered}F_k|_{t=0}\,=\delta(\mathbf{R}-\mathbf{R}_0)\,\exp\left(-H_k/T\,\right)=\\=\delta(\mathbf{R}-\mathbf{R}_0)\,G_M(\mathbf{P})\prod\nolimits_{j=1}^k E(\mathbf{r}_j-\mathbf{R})\,G_m(\mathbf{p}_j)\ ,\end{gathered} \qquad (2)$$

where H_k is Hamiltonian of subsystem "k molecules + TM", $\int_k...\,=\,\int\int...\,d\mathbf{r}_k\,d\mathbf{p}_k$, $[...,...]$ means the Poisson brackets, $\Phi\,'(\mathbf{r})\,=\,\nabla\Phi(\mathbf{r})$, and $E(\mathbf{r})\,=\,\exp\,[-\Phi(\mathbf{r})/T\,]$. Notice that TM can be considered as a molecule of non-uniformly distributed impurity, and equations (1) are identical to the equations of two-component gas [6] in the limit of infinitely rare impurity, when the main component is spatially homogeneous and thermodynamically equilibrium.

Equations (1) together with (2) unambiguously determine evolution of F_0 and eventually probability distribution of TM's displacement $\mathbf{R}-\mathbf{R}_0$. These equations will become more clear if we make a linear change of DF F_k by new functions V_k with the help of recurrent relations as follow:

$$F_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;n)\;=\;V_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;n)\ \ ,$$

$$\begin{gathered}F_1(t,\mathbf{R},\mathbf{r}_1,\mathbf{P},\mathbf{p}_1|\,\mathbf{R}_0;n)\;=\\=\;V_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;n)\,f(\mathbf{r}_1-\mathbf{R},\mathbf{p}_1)\,+\\+\,V_1(t,\mathbf{R},\mathbf{r}_1,\mathbf{P},\mathbf{p}_1|\,\mathbf{R}_0;n)\ \ ,\end{gathered} \qquad (3)$$

where $f(\mathbf{r},\mathbf{p})=E(\mathbf{r})\,G_m(\mathbf{p})$,

$$\begin{gathered}F_2(t,\mathbf{R},\mathbf{r}^{(2)},\mathbf{P},\mathbf{p}^{(2)}|\mathbf{R}_0;n)\;=\\=V_0(t,\mathbf{R},\mathbf{P}|\mathbf{R}_0;n)f(\mathbf{r}_1-\mathbf{R},\mathbf{p}_1)f(\mathbf{r}_2-\mathbf{R},\mathbf{p}_2)\,+\\+\,V_1(t,\mathbf{R},\mathbf{r}_1,\mathbf{P},\mathbf{p}_1|\,\mathbf{R}_0;n)\,f(\mathbf{r}_2-\mathbf{R},\mathbf{p}_2)\,+\\+\,V_1(t,\mathbf{R},\mathbf{r}_2,\mathbf{P},\mathbf{p}_2|\,\mathbf{R}_0;n)\,f(\mathbf{r}_1-\mathbf{R},\mathbf{p}_1)\,+\\+\,V_2(t,\mathbf{R},\mathbf{r}^{(2)},\mathbf{P},\mathbf{p}^{(2)}|\,\mathbf{R}_0;n)\ \ ,\end{gathered}$$

and so on.

Apparently, from viewpoint of the probability theory, V_k represent a kind of cumulants (semi-invariants), or cumulant functions (CF). It is important to notice that zero values of these CF would mean that all conditional DF of gas, F_k/F_0 , are independent on initial position $\mathbf{R}_0$ of TM and thus on its displacement $\mathbf{R}-\mathbf{R}_0$. This fact makes visible an interesting specificity of CF V_k : they are irreducible correlations of not only current dynamic states of TM and k gas molecules but also correlations of all them with total previous TM's displacement.

In terms of the CF the BBGKY hierarchy acquires a more complicated tridiagonal structure (we omit uninteresting algebraic details):

$$\begin{gathered}\frac{\partial V_k}{\partial t}=[H_k,V_k]+n\,\frac{\partial}{\partial \mathbf{P}}\int_{k+1}\Phi'(\mathbf{R}-\mathbf{r}_{k+1})V_{k+1}\,+\\+\,T\sum_{j\,=1}^{k}\,\mathrm{P}_{kj}\,G_m(\mathbf{p}_k)\,E'(\mathbf{r}_k-\mathbf{R})\left[\frac{\mathbf{P}}{MT}+\frac{\partial}{\partial \mathbf{P}}\right]V_{k-1}\end{gathered} \qquad (4)$$

Here $E'(\mathbf{r})=\nabla E(\mathbf{r})$, and P_{kj} symbolizes transposition of the pairs of arguments x_j and x_k . On the other hand, initial conditions (2) and the above-mentioned conditions of weakening of correlations [6] take very simple form:

$$\begin{gathered}V_0(0\,,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;\,n)\;=\delta(\mathbf{R}-\mathbf{R}_0)\,G_M(\mathbf{P})\ ,\\V_k(0\,,\mathbf{R},\mathbf{r}^{(k)},\mathbf{P},\mathbf{p}^{(k)}|\,\mathbf{R}_0;n)=0\ ,\\V_k(t,\mathbf{R},\mathbf{r}^{(k)},\mathbf{P},\mathbf{p}^{(k)}|\mathbf{R}_0;n)\rightarrow 0\quad \mathtt{at}\ \ \mathbf{r}_j\rightarrow\infty\end{gathered} \qquad (5)$$

($1\leq j\leq k$). Thus, as it should be with cumulants, CF V_k disappear under removal of even one of molecules.

From these equations and initial conditions (as well as physical reasonings) it is clear that the reduction to zero in (5) realizes in an integrable way, so that integrals $\overline{V}_k=\int_{k+1}V_{k+1}$ are finite. Let us consider them. By applying the operation $\int_k$ to equations (4) one easy obtains equations

$$\begin{gathered}\frac{\partial \overline{V}_k}{\partial t}=[H_k,\overline{V}_k]+n\,\frac{\partial}{\partial \mathbf{P}}\int_{k+1}\Phi'(\mathbf{R}-\mathbf{r}_{k+1})\,\overline{V}_{k+1}\,+\\+\,\frac{\partial}{\partial \mathbf{P}}\int_{k+1}\Phi'(\mathbf{R}-\mathbf{r}_{k+1})\,V_{k+1}\,+ \qquad (6)\\+\,T\sum_{j\,=1}^{k}\,\mathrm{P}_{kj}\,G_m(\mathbf{p}_k)\,E'(\mathbf{r}_k-\mathbf{R})\left[\frac{\mathbf{P}}{MT}+\frac{\partial}{\partial \mathbf{P}}\right]\overline{V}_{k-1}\end{gathered}$$

(with $k=0,1,...$). Because of (5) initial conditions to these equations are zero: $\overline{V}_k(t=0)=0$ at any k .

Now, in addition to $\overline{V}_k$, let us consider derivatives of CF in respect to the gas density, $V'_k = \partial V_k/\partial n$. It is easy to see that differentiation of (4) in respect to n yields equations for the V'_k which exactly coincide with (6) after changing there $\overline{V}_k$ by V'_k. Besides, in view of (5), initial conditions to these equations again all are zero: $V'_k(t=0) = 0$ at any $k \geq 0$. These observations strictly imply exact equalities $V'_k = \overline{V}_k$, or

$$\frac{\partial}{\partial n} V_k(t, \mathbf{R}, \mathbf{r}^{(k)}, \mathbf{P}, \mathbf{p}^{(k)} | \mathbf{R}_0; n) = \qquad (7)$$
$$= \int_{k+1} V_{k+1}(t, \mathbf{R}, \mathbf{r}^{(k+1)}, \mathbf{P}, \mathbf{p}^{(k+1)} | \mathbf{R}_0; n)$$

This is main formal result of the present paper.

3. The result (7) contains the proof promised in Sec.1. Indeed, equalities (7) show, firstly, that all the many-particle correlations between gas molecules and past displacement of test molecule (TM) really exist, i.e. differ from zero. Secondly, all they have roughly one and the same order of magnitude. For instance, if comparing their integral values, due to (7) we can write, in natural dimensionless units,

$$n^k \int_1 \dots \int_k \int V_k \, d\mathbf{P} \; = \; n^k V_0^{(k)}(t, \Delta; n) \; \sim \; c_k V_0(t, \Delta; n) \; ,$$

where $V_0(t, \Delta; n) = \int V_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; n) \, d\mathbf{P}$ is probability distribution of the TM's displacement $\Delta = \mathbf{R} - \mathbf{R}_0$, $V_0^{(k)}(t, \Delta; n) = \partial^k V_0(t, \Delta; n)/\partial n^k$ are its derivatives in respect to gas density n, and c_k some numeric coefficients. Hence, all the correlations are equally important, and none of them can be neglected if we aim at knowledge about true statistics of TM's random walk.

For more details, let us suppose that $(s+1)$-particle correlation is so insignificant that one can assign $V_s = 0$ in (4). At that, according to (4)-(5), all higher-order correlations also will be rejected. Then, obviously, according to (7), distribution $V_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; n)$ and thus $V_0(t, \Delta; n)$ must depend on n definitely as an $(s-1)$-order polynomial. But, from the other hand, distribution V_0 what follows from the truncated chain of equations (4) certainly is absolutely non-polynomial function of n. With taking into account that equalities (7) do express exact properties of solutions to (4)-(5) we see that very deep contradiction is on hand.

This contradiction clearly prompts us that truncation of the BBGKY hierarchy leads to qualitative losses in its solution.

Some possible losses already were characterized in [7] and [8] (and firstly even much earlier in [12]) and in part filled up in [7, 10]. Therefore here we confine ourselves (continuing 5-th paragraph of Sec.1) by remark that cutting of the $(s+1)$-particle correlation means cutting of s-th and higher statistical moments of fluctuations in relative frequency of TM's collisions with gas molecules (in other words, fluctuations in diffusivity of TM [12]). At $s = 2$ these fluctuations are completely ignored, and such truncated equations (4) yield a closed equation for $V_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; n)$ which is equivalent to the Boltzmann-Lorentz equation [11].

It is necessary to emphasize that above reasonings, as well as the exact relations (7), are indifferent to a degree of the gas rarefaction. Consequently, one can state that the Boltzmann-Lorentz equation (moreover, all the classical kinetics including the Boltzmann equation and its generalizations) does not represent a (low-density) limit of the exact statistical mechanical theory. The conventional kinetics is only (more or less adequate or caricature) probabilistic model of exact theory. Of course, in the latter also molecular chaos does prevail. But here it is much more rich, even if speaking about rarefied gas, and does not keep within naive probabilistic logics.

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[1] A. N. Kolmogorov. Foundations of the theory of probability. Chelsea, New York, 1956.

[2] N. S. Krylov. Works on the foundations of statistical physics. Princeton, 1979.

[3] These prejudices "*are so habitual that even persons who agreed with our argumentation usually automatically go back to them when facing with a new question*" [2].

[4] L. Boltzmann. Vorlesungen uber Gastheorie. Bd. 1-2. Leipzig, 1896-1898.

[5] J. R. Dorfman. An introduction to chaos in nonequilibrium statistical mechanics. Cambridge, 1999.

[6] N. N. Bogolyubov. Problems of dynamical theory in statistical physics. North-Holland, 1962.

[7] Yu. E. Kuzovlev, Sov.Phys.-JETP **67**, No. 12, 2469 (1988).

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

[9] "*... relative frequencies of some phenomenon along a given phase trajectory, generally speaking, in no way are connected to probabilities*" [2].

[10] Yu. E. Kuzovlev, arXiv: cond-mat/0609515, 0612325.

[11] P. Resibois and M. de Leener. Classical kinetic theory of fluids. Wiley, New-York, 1977.

[12] Yu. E. Kuzovlev and G. N. Bochkov, Radiophysics and Quantum Electronics **26**, No. 3, 228 (1983); **27**, No.9 (1984).