

On statistics of molecular chaos

YURIY E. KUZOVLEV

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

PACS 05.20.Dd – Kinetic theory

PACS 05.20.Jj – Statistical mechanics of classical fluids

PACS 05.40.Fb – Random walks and Levy flights

Abstract. - It is shown that the BBGKY equations for a particle interacting with ideal gas imply exact relations between probability distribution of path of the particle, its derivatives in respect to the gas density and irreducible many-particle correlations of gas atoms with the path. These relations visualize that the correlations of any order always significantly contribute to evolution of the path distribution, so that the exact statistical mechanics theory does not reduce to the classical kinetics even in the low-density (or Boltzmann-Grad) limit.

Introduction. – In the seminal book [1] Bogoliubov formulated powerful tools for statistical theory of transport processes and noises in many-particle systems, in particular, the exact hierarchy of evolution equations (now referred to as the Bogolyubov-Born-Green-Kirkwood-Yvon, or BBGKY, hierarchy [2]) for s -particle ($s = 1, 2, \dots$) distribution functions. But in practice the theory was canceled out by common prejudice that it must confirm, at least for dilute gases, the Boltzmann’s “molecular chaos hypothesis”, - the “Stoßzahlansatz” [3], - and thus reduce to the Boltzmann equation. This idea is so much attractive that Bogoliubov introduced own hypotheses which allow to truncate the BBGKY hierarchy at $s = 2$ and perform the desired reduction [1]. In fact, however, until now neither Boltzmann’s nor Bogoliubov’s assumptions have a rigorous substantiation based on the BBGKY hierarchy itself¹, and hence the Boltzmann equation also stays without substantiation².

Here, I suggest a short visual proof of that all this never will be substantiated, even for arbitrary dilute gas (or

Boltzmann-Grad gas). At that, in order to simplify the proof and at once strengthen it, instead of the usual gas I consider a test particle in thermodynamically equilibrium ideal gas whose atoms interact with this particle only but not with each other (thus concentrating on situation least favorable for inter-particle correlations).

Our first step will be representation of the BBGKY hierarchy of equations for this system in terms of irreducible s -particle correlations between the test particle and $s - 1$ gas atoms ($s = 1$ corresponds to probability distribution of variables of the test particle). Then, we discover that these equations produce a set of formally exact relations between any s -particle correlation and derivative of the previous ($s - 1$)-particle one in respect to the gas density. Next, make sure that all the correlations keeps non-zero even under the low-density (or Boltzmann-Grad) limit and, consequently, no truncation of the BBGKY hierarchy can be made without qualitative detriment to its solution. Finally, we touch upon important properties of the correlations.

The BBGKY equations and cumulant distribution functions. – We are interested in random walk $\mathbf{R}(t)$ of a test molecule (TM) which is placed into thermodynamically equilibrium gas and starts at initial time moment $t = 0$ from a specified position $\mathbf{R}(0) = \mathbf{R}_0$.

Let \mathbf{P} and M denote momentum and mass of TM, m , \mathbf{r}_j and \mathbf{p}_j ($j = 1, 2, \dots$) are masses, coordinates and momenta of gas atoms, $\Phi(\mathbf{r})$ is potential of (short-range repulsive) interaction between any of them and TM, and n is gas density (mean concentration of atoms). At arbitrary time $t \geq 0$, full statistical description of this system

¹ We take in mind spatially inhomogeneous gas evolutions, of course, since in respect to strictly homogeneous (translation invariant) dilute gas the Stoßzahlansatz is undoubtedly true.

² The frequently mentioned Lanford theorem [4] about gas of hard spheres under the Boltzmann-Grad limit concerns the so called “hard-sphere BBGKY hierarchy” (about it see also e.g. [2,5]) which is not a true BBGKY hierarchy since represents interactions of the spheres by invented terms like the Boltzmann collision integrals (i.e. postulates what should be proved, if any).

We here consider regular smooth interaction potentials only and thus the true BBGKY equations where the interaction is represented by the forces (potential gradients) like in the parent Liouville equation. But our conclusions naturally extend to the limit of singular “hard-sphere” interaction.

is presented by the chain of $(k + 1)$ -particle distribution functions ($k = 0, 1, 2, \dots$): $F_0(t, \mathbf{R}, \mathbf{P} | \mathbf{R}_0; n)$ 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 $\mathbf{r}^{(k)} = \{\mathbf{r}_1 \dots \mathbf{r}_k\}$, $\mathbf{p}^{(k)} = \{\mathbf{p}_1 \dots \mathbf{p}_k\}$) which are probability densities of finding TM at point \mathbf{R} with momentum \mathbf{P} and simultaneously finding out some k atoms at points \mathbf{r}_j with momenta \mathbf{p}_j . A rigorous definition of such distribution functions (DF) was done in [1]. In respect to the coordinates \mathbf{r}_j they are not normalized, but instead (as in [1]) satisfy the conditions of vanishing of inter-particle correlations under spatial separation of particles (in other words, DF satisfy a cluster property with respect to spacial variables). 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 obey the standard equations [1]:

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

with $k = 0, 1, \dots$ and along with obvious initial conditions

$$\begin{aligned} F_k|_{t=0} &= \delta(\mathbf{R} - \mathbf{R}_0) \exp(-H_k/T) = \\ &= \delta(\mathbf{R} - \mathbf{R}_0) G_M(\mathbf{P}) \prod_{j=1}^k E(\mathbf{r}_j - \mathbf{R}) G_m(\mathbf{p}_j), \end{aligned} \quad (2)$$

where H_k is Hamiltonian of subsystem “ k atoms + TM”, $[\dots, \dots]$ means the Poisson brackets, $\int_k \dots = \int \dots d\mathbf{r}_k d\mathbf{p}_k$, $\Phi'(\mathbf{r}) = \nabla \Phi(\mathbf{r})$, and $E(\mathbf{r}) = \exp[-\Phi(\mathbf{r})/T]$. Notice that one can treat TM as molecule of non-uniformly distributed impurity and (1) as equations of two-component gas [1] in the limit of infinitely rare impurity with main component being in spatially uniform and thermodynamically equilibrium state.

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

$$\begin{aligned} F_0(t, \mathbf{R}, \mathbf{P} | \mathbf{R}_0; n) &= V_0(t, \mathbf{R}, \mathbf{P} | \mathbf{R}_0; n), \\ F_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1 | \mathbf{R}_0; n) &= \\ &= V_0(t, \mathbf{R}, \mathbf{P} | \mathbf{R}_0; n) f(\mathbf{r}_1 - \mathbf{R}, \mathbf{p}_1) + \\ &+ V_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1 | \mathbf{R}_0; n), \end{aligned} \quad (3)$$

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

$$\begin{aligned} F_2(t, \mathbf{R}, \mathbf{r}^{(2)}, \mathbf{P}, \mathbf{p}^{(2)} | \mathbf{R}_0; n) &= \\ &= V_0(t, \mathbf{R}, \mathbf{P} | \mathbf{R}_0; n) f(\rho_1, \mathbf{p}_1) f(\rho_2, \mathbf{p}_2) + \\ &+ V_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1 | \mathbf{R}_0; n) f(\rho_2, \mathbf{p}_2) + \\ &+ V_1(t, \mathbf{R}, \mathbf{r}_2, \mathbf{P}, \mathbf{p}_2 | \mathbf{R}_0; n) f(\rho_1, \mathbf{p}_1) + \\ &+ V_2(t, \mathbf{R}, \mathbf{r}^{(2)}, \mathbf{P}, \mathbf{p}^{(2)} | \mathbf{R}_0; n), \end{aligned}$$

where $\rho_j \equiv \mathbf{r}_j - \mathbf{R}$, and so on.

Apparently, from viewpoint of the probability theory, V_k are a kind of cumulants, or semi-invariants, or cumulant functions (CF). It is important to notice that if all these CF were zeros then all conditional DF of gas, F_k/F_0 , would be independent on initial position \mathbf{R}_0 of TM and thus on its displacement $\mathbf{R} - \mathbf{R}_0$. This fact makes visible very interesting speciality of the CF V_k : they are not mere correlations between instant dynamic states of TM and k gas atoms but simultaneously their irreducible correlations with the total past TM's displacement.

Relation of many-particle correlations to probability law of diffusion of the test particle. – In terms of CF the BBGKY hierarchy acquires tridiagonal structure (we omit uninteresting algebraic details):

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

Here $E'(\mathbf{r}) = \nabla E(\mathbf{r})$, and P_{kj} symbolizes transposition of the pairs of arguments x_j and x_k . At that, initial conditions (2) and the above-mentioned clustering conditions [1] take extremely simple form:

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

($1 \leq j \leq k$). Thus, as it should be with cumulants, V_k ($k > 0$) vanish under removal of already one of atoms.

From equations (4) as combined with the boundary and initial conditions (5) it is clear that passage to the limit in (5) must realize in an integrable way, so that integrals $\tilde{V}_k = \int_{k+1} V_{k+1}$ take finite values. Let us consider them. By applying the operation \int_k to equations (4) one obtains

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

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

Now, in addition to \tilde{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 \tilde{V}_k by V'_k . Besides, in view of (5), initial conditions to these equations again all are equal to zero: $V'_k(t=0) = 0$ at any $k \geq 0$. These observations strictly

imply the equalities $V'_k = \tilde{V}_k$, or

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

This is main, original and formally exact, result of the present paper. Evidently, it confirms the assumed finiteness of integrals $\tilde{V}_k = \int_{k+1} V_{k+1}$. Notice also that it anticipates similar but more complicated general statements of statistical kinetics of fluids.

Discussion and resume. – The equalities (7) contain the proof promised in the beginning of this paper. Indeed, they show, firstly, that all the many-particle correlations between gas atoms and total path, or displacement, of the test molecule (TM) really exist, i.e. differ from zero. Secondly, integral values of all the correlations, represented in the natural dimensionless form, have roughly one and the same order of magnitude. Indeed, multiplying equalities (7) by n^k and integrating them over TM's momentum and all gas variables, we have

$$\begin{aligned} n^k V_k(t, \Delta; n) & \equiv n^k \int_1 \dots \int_k \int V_k d\mathbf{P} = \\ & = n^k \frac{\partial^k V_0(t, \Delta; n)}{\partial n^k} \sim c_k V_0(t, \Delta; n) , \end{aligned}$$

where $V_0(t, \Delta; n) = \int V_0(t, \mathbf{R}, \mathbf{P} | \mathbf{R}_0; n) d\mathbf{P}$ is just the probability density distribution of the TM's displacement, $\Delta = \mathbf{R} - \mathbf{R}_0$, and c_k some numeric coefficients obviously comparable with unit. Equivalently, unifying all CF into one generating function, we can write

$$\begin{aligned} V_0(t, \Delta; n) + \sum_{k=1}^{\infty} \frac{u^k n^k}{k!} V_k(t, \Delta; n) = \\ = V_0(t, \Delta; (1+u)n) . \end{aligned} \quad (8)$$

We see that distribution of total of the TM's random walk "is made of its correlations with gas atoms" like the walk itself is made of collisions with them. Hence, none of the correlations can be neglected if we aim at adequate analysis of solution of the BBGKY equations.

We see also that characteristic spacial volume occupied by the correlations has an order of the specific volume: $(\int_1 \dots \int_k \int V_k d\mathbf{P} | V_0)^{1/k} \sim n^{-1}$. In the Boltzmann-Grad limit, $n \rightarrow \infty$, $r_0 \rightarrow 0$ (r_0 is effective radius of the interaction), $\pi r_0^2 n = 1/\lambda = \text{const}$, this volume becomes vanishingly small as measured by the TM's mean free path λ . But, nevertheless, it remains on order of the effective "volume of collision", $\sim \pi r_0^2 \lambda$. This observation prompts that k -particle correlations are concentrated just at those particular subsets of k -particle phase space which correspond to collisions. Therefore effects of the correlations completely hold under the limit. The same is said by the equality (8) which also holds out. This becomes obvious if we take into account that actually important parameter of

the integrated CF under the Boltzmann-Grad limit must be λ instead of n and rewrite (8) in the form

$$W_0(t, \Delta; \lambda) + \sum_{k=1}^{\infty} \frac{u^k}{k!} W_k(t, \Delta; \lambda) = W_0(t, \Delta; \lambda/(1+u)) ,$$

where $W_k(t, \Delta; \lambda) = \lim n^k V_k(t, \Delta; n)$. Thus, in essence nothing changes under the Boltzmann-Grad limit.

It is necessary to underline that the correlations under our attention are qualitatively different from correlations which appear in standard approximations of the BBGKY hierarchy and connect velocities of particles after collision (see e.g. [6]). In our notations, a pair correlation of such the kind would look nearly as $V_1(t, \mathbf{R}, \mathbf{r}, \mathbf{P}, \mathbf{p}) = F_1(t, \mathbf{R}', \mathbf{r}', \mathbf{P}', \mathbf{p}') - F_1(t, \mathbf{R}, \mathbf{r}, \mathbf{P}, \mathbf{p})$, where the primed variables describe the pre-collision state. Clearly, because of the phase volume conservation during collision, integration of this expression over $\rho = \mathbf{r} - \mathbf{R}$ and the momenta results in zero. This observation shows that correlations under our interest do live not so much in momentum space as in the configuration space. Their salt is that they connect coordinates and walks of particles and may coexist with statistical independence of particles' velocities. By their very nature, they are attributes of spatially inhomogeneous states and evolutions (evolution of $V_0(t, \Delta; n)$ gives an example). More profoundly, statistical and physical meanings of such correlations were discussed already in [7] (so for detail see [7]³).

In view of the aforesaid⁴ we have to conclude that the Boltzmann-Lorentz equation [2, 5] and, moreover, the Boltzmann equation in itself do not represent a (low-density) limit of the exact statistical mechanical theory. The classical kinetics is only its approximate probabilistic model (may be good in one respects but caricature in others). Of course, in the exact theory also molecular chaos does prevail. But here it is much more rich, even (and first of all) in case of dilute gas, and does not keep within naive probabilistic models.

REFERENCES

- [1] BOGOLYUBOV N.N., *Problems of dynamical theory in statistical physics* (North-Holland, Amsterdam) 1962.
- [2] RESIBOIS P. and DE LEENER M., *Classical kinetic theory of fluids* (Wiley, New York) 1977.
- [3] BOLTZMANN L., *Vorlesungen uber Gastheorie* (Leipzig) 1896-1898.
- [4] LANFORD O.E., *Lecture Notes in Physics*, **38** (1974) 1.
- [5] VAN BEIJEREN H., LANFORD O.E., LEBOWITZ J. L. and SPOHN H., *J. Stat. Phys.*, **22** (1979) 237.
- [6] BALESCU R., *Statistical dynamics* (ICP, London) 1997.
- [7] KUZOVLEV YU. E., *Sov. Phys. JETP*, **67** (1988) 2469.

³ Reprint of this article is available from the arXiv: 0907.3475.

⁴ See also [Yu. Kuzovlev, *Theoretical and Mathematical Physics*, 160 (3), 1301 (2009)] and references therein.