Molecular Brownian motion and falsity of the " law of large numbers "

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Real thermal motion of gas particles, free electrons, etc., at long time intervals (much greater than mean free-flight time) possesses, contrary to its popular mathematical models, essentially non-Gaussian statistics, thus implying that chaotic path of a molecular Brownian particle can not be separated into "statistically independent" constituent parts and so the "law of large numbers" is not applicable, even under the Boltzmann-Grad limit. A simple proof of this statement is suggested basing on only the determinism and reversibility of microscopic dynamics and besides incidentally derived virial expansion of the path probability distribution.

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I. INTRODUCTION

1. Thermal chaotic motion of unbound particles of the matter is mechanism of diffusion as well as many other transport processes. It is interesting by itself too, since statistics of random walk of a test or marked "Brownian" particle contains rich information about transport process as a whole including its noise and fluctuations. In spite of this, dynamical theory of molecular Brownian motion remains almost undeveloped. Apparently, the common opinion is that anyway it should confirm the well known beautiful probability-theoretic scheme based on the celebrated Bernoulli's "law of large numbers" [1] which foretells that at sufficiently large spatio-temporal scales probability density of displacement, or path, $\Delta \boldsymbol{R}$, of a Brownian particle (BP) during time t has asymptotically universal form of the Gaussian distribution. For symmetric 3-D random walk that is

$$V_G(t,\Delta \boldsymbol{R}) \,=\, (4\pi Dt)^{-3/2}\, \exp\left(-\Delta \boldsymbol{R}^2/4Dt\right) \;.$$

In fact, it was rigorously proved [2, 3] that such is the asymptotic of chaotic walk of hard ball in so non-random environment as static periodic lattice of elastic scatterers (also hard balls). It might seem that all the more Brownian motion of gas atoms can not display something else. Indeed, the Boltzmann-Lorentz equation [4], which comes from the Boltzmann equation when adapted to self-diffusion of gas atoms, produces the Gaussian asymptotic. Nevertheless, not all is so simple as seems.

2. Recall, firstly, that the Boltzmann equation represents rather rough model resulting from violent truncation of the exact BBGKY hierarchy of equations and its closure with the help of archaic Boltzmann's "molecular chaos" hypothesis [4–6]. However, it was pointed out more than once, e.g. in [4, 7], that Boltzmann's argumentation [8] looks enough convincing only if applied to spatially uniform gas. As to attempts to deduce "molecular chaos" from BBGKY equations themselves, they proved to be unsuccessful [9]. In opposite, it was shown [10] (see also [11, 12]) that reformulation of BBGKY equations in terms of inter-particle "collisions", instead of continuous interactions, leads to such new infinite hierarchy of equations which is evidently incompatible with "molecular chaos" if a gas is spatially non-uniform. The matter is that the very fact of participation of particles in same collision (or connected group of collisions) *at certain place* (distinguishable due to non-uniformity) is sufficient reason for mutual statistical dependence of the particles.

Various (higher-order, time-non-local, etc.) corrections to the Boltzmann equation for comparatively dense gas do not change the matter, since all they eventually exploit the same "molecular chaos" assumption and therefore in strict sense touch uniform gas states only.

At the same time, if wishing to consider displacement of BP (test particle) one has to localize its initial position and thereby disturb uniformity (translational invariance) of infinitely many distribution functions (DF) what describe BP under its interactions with gas. Consequently, after all one inevitably has to deal with infinite chain of equations. Attempts to construct their approximate solutions for comparatively rare, or weakly non-ideal, gas (formally, in the Boltzmann-Grad limit) were made in works [10] (see also [11]) and [12]. Their findings, of course, qualitatively differ from the Gaussian asymptotic (but qualitatively confirm the early phenomenological theory [13–15]).

3. Secondly, Gaussian asymptotic of the ball's walk in static lattice is closely connected with its ergodicity [2, 3, 16]: results of time averaging over $n \to \infty$ fragments of its trajectory (with each fragment consisting of free flight and collision) almost surely are independent on the trajectory. This is possible due to the fact that any trajectory is fully determined by its single fragment (e.g. initial one), and a ratio of number, $d = 5n$, of quantities describing the trajectory to the number, $p = 5$, of its specifying parameters is unrestrictedly large, $d/p \to \infty$. Infinitely many observations per parameter are sufficient to exclude specificity of almost any trajectory.

But a gas is quite another matter. Here any trajectory of Brownian (test) particle is made of $n \approx t/\tau$ similar fragments, with t being observation time and τ mean free flight time, and is exhaustively characterized by $d = 6n$ quantities. However, it is specified by not only initial state of the particle under consideration but

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also initial states of many other particles. It is easy to see [12] that a number m of such particles grows with time by far faster than n, so that $n/m \rightarrow 0$. Thus now the ratio of number of quantities what completely describe all details of a trajectory to number, $p = 6m$, of parameters (initial conditions) what determine these details, tends to zero, $d/p \rightarrow 0$, as contrasted with above case. In my opinion, this big nothing of observations per parameter is insufficient to get rid of specificity of trajectories (though standard "logics" would give rise to exactly opposite conclusion about "stochasticity" and statistical identity of trajectories).

By the above reason, hardly results of time averaging (for instance, such as "particle's diffusivity" or "collision probabilities") will turn out to have "almost surely" same limits for different trajectories. There are no grounds for ergodicity, the "law of large numbers" (which needs in beforehand prescribed "collision probabilities" [1, 11, 17]) and Gaussian asymptotic. Even in finite gas of $N < \infty$ particles (in box or torus) necessary grounds for ergodicity arise not earlier than after time $> N\tau$ [12]. This gives illustration of footnote remark in [16] that a value of ergodicity in physics looks overestimated since limit $N \rightarrow \infty$ is much more important for physics than limit $t \rightarrow \infty$. Besides, in essence, analogous warning was highlighted already by N. Krylov in the forties. See his book [18] where he tried to disclose such prejudices that "some probabilistic law does exist regardless of a theoretical construct and full-scale experiments" or that "obviously independent phenomena should possess independent probability distributions".

4. In principle, similar reasonings [11, 15, 19, 20], as well as equations like the BBGKY hierarchy, are applicable to any realistic many-particle system, and therefore particular case of gas has general physical significance. But BBGKY equations yet are so bad investigated that none supplementary tools would be superfluous. In the present paper, basing in fact on determinism and reversibility of Hamiltonian microscopic dynamics only, we will derive a kind of virial expansion for true probability distribution of the BP's displacement, $V_0(t, \Delta\boldsymbol{R})$. Then connect coefficients of this expansion with joint correlation functions of BP and gas and with usual many-particle DF. To make the consideration purified of non-principal complications, the limit of Boltzmann-Grad gas is convenient. Finally, show that all these taken together imply an interesting differential inequality for $V_0(t, \Delta\boldsymbol{R})$ which definitely forbids Gaussian asymptotic of $V_0(t, \Delta\boldsymbol{R})$. Instead, it points out essentially non-Gaussian asymptotic possessing long (though somehow truncated) power-law tail.

It must be underlined that we will not use the BBGKY or any other differential equations. Thus we may forget all previous "world outlook" text and start afresh, without detriment to our results. Anyway, they will appear in agreement with non-Gaussian distribution of BP's path obtained in [12] from approximative solution of the BBGKY equations. From the other hand, the present paper, along with its short prototype [21], logically continues and improves paper [17] where gas density perturbation was under attention in place of individual test particle. Careful comparison of the one and another will be theme of separate work.

II. MANY-PARTICLE CORRELATIONS AND VIRIAL EXPANSION OF BROWNIAN PATH PROBABILITY DISTRIBUTION

1. Let a gas of $N \gg 1$ atoms in volume Ω contains a "Brownian particle" (BP). Consider, under the thermodynamical limit $N \rightarrow \infty$, $\Omega \rightarrow \infty$, $N/\Omega = \nu_0 =$ const, statistical ensemble of phase trajectories of this system which responds to canonical equilibrium distribution of its initial state at $t = 0$. At that we suppose that at $t > 0$ BP may be subject to constant external force $\boldsymbol{f}$.

The time reversibility of Hamiltonian dynamics and its phase trajectories implies many relations between statistical characteristics of their ensemble [22–24]. In particular, if Hamiltonian of the system is invariant of inversion $\boldsymbol{p} \rightarrow -\boldsymbol{p}$, where $\boldsymbol{p} = \{\boldsymbol{P}, \boldsymbol{p}_1, \dots, \boldsymbol{p}_N\}$ are momentums of BP and atoms, then according to [22] one can write

$$\langle A(\boldsymbol{q}(t)) B(\boldsymbol{q}(0))\, e^{-\,\mathcal{E}(t)/T} \rangle = \langle B(\boldsymbol{q}(t)) A(\boldsymbol{q}(0)) \rangle \qquad (1)$$

Here angle brackets $\langle ... \rangle$ designate the ensemble average, $\boldsymbol{q}(0) = \boldsymbol{q} = \{\boldsymbol{R}, \boldsymbol{r}_1, \dots, \boldsymbol{r}_N\}$ are space coordinates of BP and atoms, $\mathcal{E}(t) = \boldsymbol{f} \cdot [\boldsymbol{R}(t) - \boldsymbol{R}(0)]$ is work made by the external force during time interval t, $A(\boldsymbol{q})$ and $B(\boldsymbol{q})$ are "arbitrary functions", and T is initial temperature of the system. Notice that equality (1) holds also when BP has internal degrees of freedom. In case of no external force, when $\boldsymbol{f} = 0$ and hence $\mathcal{E}(t) = 0$, it looks so obvious that even does not need in derivation or references.

Let $B(\boldsymbol{q}) = \Omega\, \delta(\boldsymbol{R} - \boldsymbol{R}_0) \exp[-\sum_j U(\boldsymbol{r}_j)/T]$ and $A(\boldsymbol{q}) = \delta(\boldsymbol{R} - \boldsymbol{R}')$. Then right-hand side of (1) in the thermodynamical limit takes form

$$\begin{gathered} \langle B(\boldsymbol{q}(t)) A(\boldsymbol{q}) \rangle \rightarrow \\ \rightarrow \mathcal{F}\{t, \boldsymbol{R}_0, \phi | \boldsymbol{R}'\} \equiv V_0(t, \boldsymbol{R}_0 | \boldsymbol{R}') + \\ + \sum_{n=1}^{\infty} (\nu_0^n / n!) \int^n F_n(t, \boldsymbol{R}_0, \boldsymbol{r}_1 \dots \boldsymbol{r}_n | \boldsymbol{R}') \prod_{j=1}^{n} \phi(\boldsymbol{r}_j)\ , \end{gathered}$$

where $\phi(\boldsymbol{r}) = \exp[-U(\boldsymbol{r})/T] - 1$, symbol $\int^n$ means integration over $\boldsymbol{r}_1 \dots \boldsymbol{r}_n$, function $V_0(t, \boldsymbol{R}_0 | \boldsymbol{R}')$ is conditional probability density of finding BP at $t \geq 0$ at point $\boldsymbol{R}_0$ under condition that BP had started at $t = 0$ from point $\boldsymbol{R}'$, and $F_n(t, \boldsymbol{R}_0, \boldsymbol{r}_1 \dots \boldsymbol{r}_n | \boldsymbol{R}')$ is joint conditional probability density of simultaneous finding BP at point $\boldsymbol{R}_0$ and some atoms at points $\boldsymbol{r}_j$ under the same condition.

Notice that the series here converges and the limit functional $\mathcal{F}\{t, \boldsymbol{R}_0, \phi | \boldsymbol{R}'\}$ is well defined at least when $\int |\phi(\boldsymbol{r})|\, d\boldsymbol{r} < \infty$, in analogy with the generating functional originally considered by Bogolyubov [5]. At that, functions F_n are fully analogous to usual non-normalized DF of infinite gas [5, 6]. In particular, in respect to arguments $\boldsymbol{r}_j$ (coordinates of atoms) the role of normalization is played by the "principle of decay of correlations":

$F_n(t,\boldsymbol{R}_0,...\boldsymbol{r}_k...|\boldsymbol{R}')\,\rightarrow\,F_{n-1}(t,\boldsymbol{R}_0,...\boldsymbol{r}_{k-1},\boldsymbol{r}_{k+1}...|\boldsymbol{R}')$ if $\boldsymbol{r}_k\rightarrow\infty$, and $F_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1|\boldsymbol{R}')\rightarrow V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')$ if $\boldsymbol{r}_1\rightarrow\infty$. But, due to the initial localization of BP, in respect to argument $\boldsymbol{R}_0$ all the DF are normalized in literal sense. In particular, $\int V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')\,d\boldsymbol{R}_0=1$.

Ratios $F_n(t,\boldsymbol{R}_0,\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}')/V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')$ represent conditional DF of gas, under condition that both initial and current positions of BP are known.

Correspondingly, $V_0(0,\boldsymbol{R}_0|\boldsymbol{R}')=\delta(\boldsymbol{R}_0-\boldsymbol{R}')$ and

$$\begin{gathered}F_n(0,\boldsymbol{R}_0,\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}')=\delta(\boldsymbol{R}_0-\boldsymbol{R}')\,F_n^{(eq)}(\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}_0)\;,\\ \mathcal{F}\{0,\boldsymbol{R}_0,\phi|\boldsymbol{R}'\}=\delta(\boldsymbol{R}_0-\boldsymbol{R}')\,\mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}\;,\\ \mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}\;\equiv\;1+\\ +\sum_{n=1}^{\infty}(\nu_0^n/n!)\int^n F_n^{(eq)}(\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}_0)\prod_{j=1}^n\phi(\boldsymbol{r}_j)\;,\end{gathered}$$

where $F_n^{(eq)}(\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}_0)$ are conditional equilibrium DF of gas under fixed position of BP and $\mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}$ is their generating functional. And, of course, all DF obey translational invariance: $V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')=V_0(t,\boldsymbol{R}_0-\boldsymbol{R}')$, $F_n(t,\boldsymbol{R}_0,\{\boldsymbol{r}\}|\boldsymbol{R}')=F_n(t,\boldsymbol{R}_0-\boldsymbol{R}',\{\boldsymbol{r}\}-\boldsymbol{R}'|0)$, etc.

2. By definition, $F_n(0,\boldsymbol{R}_0,\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}')$ include all equilibrium correlations between BP and atoms. But any evolution of (ensemble of states of) the system is conjugated with disturbance of detailed balance of collisions and therefore births additional correlations. The latter reflect joint participation of particles in excess collisions or "joint nonparticipation" in missing ones. These correlations might be qualified as non-equilibrium ones, but with those reservation that sometimes they describe evolution of not so much a system on its own as our knowledge about it (indeed, if $\boldsymbol{f}=0$ then the system always remains in equilibrium state and the only thing what is under change is our information about position of BP).

Traditionally, contributions of these correlations to DF are termed "correlation functions" (CF) [4–6, 25]. Let us designate them as $V_n(t,\boldsymbol{R}_0,\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}')$ and pick out them from $F_n(t>0,...)$ by definition as follows:

$$\begin{gathered}\mathcal{F}\{t,\boldsymbol{R}_0,\phi|\boldsymbol{R}'\}\;=\;\mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}\;[\,V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')+\\ +\sum_{n=1}^{\infty}(\nu_0^n/n!)\int^n V_n(t,\boldsymbol{R}_0,\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}')\prod_{j=1}^n\phi(\boldsymbol{r}_j)\,]\end{gathered}$$

Of course, it is not solely possible definition of the "correlation functions" but it is most suitable for our needs below. Importantly, it ensures satisfaction of the necessary requirements that $V_n(0\,,...\,)=0$ at $n\geq 1$ and $V_n(t,\boldsymbol{R}_0,...\boldsymbol{r}_k...|\boldsymbol{R}')\rightarrow 0$ at $\boldsymbol{r}_k\rightarrow\infty$.

Particularly,

$$\begin{gathered}F_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1|\boldsymbol{R}')\;=\\ =V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')F_1^{(eq)}(\boldsymbol{r}_1|\boldsymbol{R}_0)+V_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1|\boldsymbol{R}')\;\;,\end{gathered}$$

where function $V_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1|\boldsymbol{R}')$ represents pair correlations between positions of BP and atoms. This equality can be considered as consequence of similar equality for pair DF and CF defined in the full two-particle phase space:

$$\begin{gathered}F_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1,\boldsymbol{P}_0,\boldsymbol{p}_1|\boldsymbol{R}')\;=\;V_0(t,\boldsymbol{R}_0,\boldsymbol{P}_0|\boldsymbol{R}')\times\\ \times F_1^{(eq)}(\boldsymbol{r}_1,\boldsymbol{p}_1|\boldsymbol{R}_0)+V_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1,\boldsymbol{P}_0,\boldsymbol{p}_1|\boldsymbol{R}')\;\;,\end{gathered}\tag{2}$$

where $F_1^{(eq)}(\boldsymbol{r}_1,\boldsymbol{p}_1|\boldsymbol{R}_0)=F_1^{(eq)}(\boldsymbol{r}_1|\boldsymbol{R}_0)\,G^{(eq)}(\boldsymbol{p}_1)$, with $G^{(eq)}(\boldsymbol{p})$ being the Maxwellian distribution of atomic momentum, and $V_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1,\boldsymbol{P}_0,\boldsymbol{p}_1|\boldsymbol{R}')$ is direct analogue of the usual "pair correlation function" [6, 25]. It produces the above defined pair correlation in configurational space after integration over momentums:

$$V_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1|\boldsymbol{R}')=\int\int V_1(t,\boldsymbol{R}_0,\boldsymbol{r}_1,\boldsymbol{P}_0,\boldsymbol{p}_1|\boldsymbol{R}')\,d\boldsymbol{P}_0\,d\boldsymbol{p}_1\tag{3}$$

3. Next, turn to left side of (1). Multiply and divide it by $\langle B(\boldsymbol{q})\rangle$ and use the fact that any expression $\langle\Phi\,B(\boldsymbol{q})\rangle/\langle B(\boldsymbol{q})\rangle$, with $B(\boldsymbol{q})\geq 0$ and Φ being some functional of system's phase trajectory, in view of determinism of evolution along any concrete trajectory, can be interpreted as Φ's average over new ensemble of trajectories induced by new, non-equilibrium, ensemble of initial coordinates and momentums of the system. Namely, the ensemble determined by probability distribution $\rho(\boldsymbol{q},\boldsymbol{p})=B(\boldsymbol{q})\,\rho_0(\boldsymbol{q},\boldsymbol{p})/\langle B(\boldsymbol{q})\rangle$, where $\rho_0(\boldsymbol{q},\boldsymbol{p})$ denotes original equilibrium distribution, in whose terms $\langle B(\boldsymbol{q})\rangle=\int\int B(\boldsymbol{q})\rho_0(\boldsymbol{q},\boldsymbol{p})\,d\boldsymbol{q}d\boldsymbol{p}$. Noticing also, from the other hand, that $\langle B(\boldsymbol{q})\rangle=\mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}$, we have

$$\begin{gathered}\langle A(\boldsymbol{q}(t))B(\boldsymbol{q}(0))\,e^{-\,\mathcal{E}(t)/T}\,\rangle\rightarrow\\ \rightarrow\,V\{t,\boldsymbol{R}'|\phi,\boldsymbol{R}_0\}\;e^{-\,\boldsymbol{f}\cdot[\,\boldsymbol{R}'-\,\boldsymbol{R}_0]/T}\,\mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}\;\;,\end{gathered}$$

where $V\{t,\boldsymbol{R}'|\phi,\boldsymbol{R}_0\}$ is probability density of finding BP at time t at point $\boldsymbol{R}'$ under conditions that initially it was placed at point $\boldsymbol{R}_0$ while the gas was in such perturbed spatially nonuniform non-equilibrium state which would be equilibrium in presence of external potential $U(\boldsymbol{r})$. Spatial distribution of mean concentration of atoms in such nonuniform state is expressed by

$$\nu\{\boldsymbol{r}|\phi,\boldsymbol{R}_0\}=[1+\phi(\boldsymbol{r})]\,\delta\ln\mathcal{F}^{(eq)}\{\phi|\boldsymbol{R}_0\}/\delta\phi(\boldsymbol{r})$$

Hence, in total, we come to formally exact relation

$$\begin{gathered}V\{t,\boldsymbol{R}'|\phi,\boldsymbol{R}_0\}\;e^{-\,\boldsymbol{f}\cdot[\,\boldsymbol{R}'-\,\boldsymbol{R}_0]/T}\;=\;V_0(t,\boldsymbol{R}_0|\boldsymbol{R}')+\\ +\sum_{n=1}^{\infty}(\nu_0^n/n!)\int^n V_n(t,\boldsymbol{R}_0,\boldsymbol{r}_1...\boldsymbol{r}_n|\boldsymbol{R}')\prod_{j=1}^n\phi(\boldsymbol{r}_j)\end{gathered}\tag{4}$$

which connects, from one (left) hand, probability distribution of BP's path in initially non-equilibrium nonuniform gas and, from the other (right) hand, probability distribution of BP's path, along with generating functional of "non-equilibrium correlations" between this previously accumulated path and current BP's environment, in initially equilibrium uniform gas. In case $\boldsymbol{f}=0$, therefore, right-hand side of (4) represents wholly equilibrium Brownian motion.

It goes without saying that all the DF and CF depend on the mean gas density ν_0 (and on the force $\boldsymbol{f}$ if any) but for brevity in (4), as well as before it and somewhere below, corresponding arguments are omitted.

4. Further, make a special choice of the function $\phi(\boldsymbol{r})$. Let $\phi(\boldsymbol{r})=\phi=$const inside some sphere $|\boldsymbol{r}-\boldsymbol{R}_0|<\xi$ and (fast but smoothly) vanishes outside it. Since $\phi(\boldsymbol{r})$ is absolutely integrable, radius ξ must be finite but can be as large as we want. For example, $\xi=k\,v_s t_0$, where

v_s is speed of sound in our gas, t_0 is maximal duration of watching BP, and $k > 1$. Then, if the external force is not too strong and k is sufficiently large, we can be sure that at $t < t_0$ the Brownian motion mentioned in left part of (4) practically takes place in equilibrium uniform gas with constant mean density $\nu = \text{const}$ what corresponds to $\phi = \text{const}$. More precisely, ν equals to $\nu\{\boldsymbol{r}|\phi, \boldsymbol{R}_0\}$ taken far from BP, at $|\boldsymbol{r}-\boldsymbol{R}_0| \gg r_B$ with r_B being radius of pair interaction between BP and atoms.

Under formulated conditions, clearly, the functional $V\{t, \boldsymbol{R}'|\phi, \boldsymbol{R}_0\}$ simplifies to mere function $V_0(t, \Delta\boldsymbol{R}\,;\, \nu)$, where we introduce $\Delta\boldsymbol{R} = \boldsymbol{R}' - \boldsymbol{R}_0$ and add the density argument ν, taking in mind that it is definite function of ϕ and the seed density, $\nu = \nu(\nu_0\,, \phi)$.

On right-hand side of (4), under the same conditions, *a fortiori* none correlations might propagate out of the sphere $|\boldsymbol{r} - \boldsymbol{R}_0| < \xi$. Therefore in all integrals $\phi(\boldsymbol{r})$ can be replaced by the constant.

As the consequence, relation (4) transforms into

$$V_0(t, \Delta\boldsymbol{R}\,;\, \nu(\nu_0, \phi))\; e^{-\boldsymbol{f}\cdot\Delta\boldsymbol{R}/T} = V_0(t, -\Delta\boldsymbol{R}\,;\, \nu_0) + \\ + \sum_{n=1}^{\infty} \phi^n\, V_n(t, -\Delta\boldsymbol{R}\,;\, \nu_0)/n! \tag{5}$$

with functions V_n, at $n > 0$, defined as

$$V_n(t, \boldsymbol{R}_0 - \boldsymbol{R}'\,;\, \nu_0) = \nu_0^n \int^n V_n(t, \boldsymbol{R}_0, \boldsymbol{r}_1 ... \boldsymbol{r}_n|\boldsymbol{R}') \tag{6}$$

The result (5), together with (6), may be qualified as "virial expansion" of the BP's path probability distribution, $V_0(t, \Delta\boldsymbol{R}\,;\, \nu)$, in gas with given density.

At $n = 1$, in particular, formulas (5) and (6) yield

$$\widetilde{\nu}_0\, \frac{\partial V_0(t, \boldsymbol{R}' - \boldsymbol{R}_0\,;\, \nu_0)}{\partial \nu_0}\; e^{-\boldsymbol{f}\cdot[\boldsymbol{R}'-\boldsymbol{R}_0]/T} = \tag{7}$$

$$= V_1(t, \boldsymbol{R}_0 - \boldsymbol{R}'\,;\, \nu_0) \equiv \nu_0 \int V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1|\boldsymbol{R}')\, d\boldsymbol{r}_1 \;,$$

where, as one can easy verify,

$$\widetilde{\nu}_0 \equiv \left[\frac{\partial \nu(\nu_0, \phi)}{\partial \phi}\right]_{\phi=0} = \nu_0 + \nu_0^2 \int [F_2^{(eq)}(\boldsymbol{r}) - 1]\, d\boldsymbol{r} \;,$$

with $F_2^{(eq)}(\boldsymbol{r})$ being usual (unconditional) pair DF of equilibrium gas with density ν_0. Notice that function $V_1(t, \boldsymbol{R}_0 - \boldsymbol{R}'\,;\, \nu_0)$ can be interpreted as pair correlation of BP with whole gas but counted per (elementary volume ν_0^{-1} what falls at) one gas atom.

III. BOUNDS OF PAIR CORRELATION, RATE OF CHANGE OF THE PATH DISTRIBUTION AND FAILURE OF GAUSSIAN ASYMPTOTIC

1. It is time to make some simplifications. Below we will assume that (i) BP is of molecular size, i.e. $r_B \sim r_A$, where r_A is radius of atom-atom interaction, (ii) all interactions are short-range and repulsive, and (iii) the gas parameter is small, $4\pi r_A^3 \nu_0/3 \ll 1$, i.e. gas is "dilute", or "weakly non-ideal". If necessary it can be turned into "ideal weakly non-ideal gas" under the formal Boltzmann-Grad limit, when $\nu_0 \to \infty$ while $r_B \sim r_A \to 0$ in such way that the gas parameter vanishes but mean free paths of atoms, $\lambda = (\pi r_A^2 \nu_0)^{-1}$, and BP, $\Lambda = (\pi r_B^2 \nu_0)^{-1}$, stay fixed. Besides, below we confine ourselves by the case of no external force, $\boldsymbol{f} = 0$. Then both sides of (5) and (7) describe equilibrium and hence *spherically symmetric* Brownian motion.

It is not hard to show that under the Boltzmann-Grad limit (BGL), in (5) and (7),

$$\nu(\nu_0, \phi)/\nu_0 \to 1 + \phi \;, \quad \widetilde{\nu}_0/\nu_0 \to 1$$

At that, $V_0(t, \Delta\boldsymbol{R}\,;\, \nu)$ must have finite limit, since in fact it depends on not bare density ν itself but on a rate of collisions, $\sim \pi r_B^2 \nu$, or corresponding mean free paths of BP, $\widetilde{\Lambda} = (\pi r_B^2 \nu)^{-1} = \Lambda/(1 + \phi)$, and atoms, $\widetilde{\lambda} = (\pi r_A^2 \nu)^{-1} = \lambda/(1 + \phi)$, which remain constant.

This means that on right-hand side of (5) and (7) all $V_n(t, \boldsymbol{R}_0 - \boldsymbol{R}'\,;\, \nu_0)$ also have finite limits. Moreover, for arbitrary function $\phi(\boldsymbol{r})$, whose spatial scale is fixed in units of λ, the BGL yields $\nu\{\boldsymbol{r}|\phi, \boldsymbol{R}_0\}/\nu_0 \to 1 + \phi(\boldsymbol{r})$, and it follows from (4) that any of the integral quantities $\nu_0^n \int^n V_n(t, \boldsymbol{R}_0, \boldsymbol{r}_1 ... \boldsymbol{r}_n|\boldsymbol{R}') \prod_{j=1}^n \phi(\boldsymbol{r}_j)$ possess finite limit.

Hence, even in arbitrary "dilute", or Boltzmann-Grad, gas *spatial* pair and many-particle correlations keep safe in relative sense, if counted per atom, although they disappear in literal sense: $V_n(t, \boldsymbol{R}_0, \boldsymbol{r}_1 ... \boldsymbol{r}_n|\boldsymbol{R}') \to 0$. To make them clear, consider *full* phase space correlations, firstly recollecting those few things what are known about them from classical books (e.g. [4–6, 25]), especially about the pair CF, $V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')$.

2. According to [4–6, 25], in respect to relative distance between two particles (in our case, BP and an atom), $\boldsymbol{r}_1 - \boldsymbol{R}_0$, the pair CF differs from zero inside a "*collision cylinder*" only which has radius $\approx r_B$ and is directed in parallel to relative velocity of the particles, $\boldsymbol{v}_1 - \boldsymbol{V}_0$. It is known also that characteristic value of the pair CF in this cylinder is comparable with product of one-particle DF, that is first right-hand term in (2). In other words, in arbitrary "dilute" gas the full phase space pair correlation keeps safe in magnitude, although inside more and more narrow (hyper-)cylinder only.

Unfortunately, conventional theory what hopes for the "molecular chaos" can not say anything about length of the collision cylinder, because completely neglects contributions from three-particle correlations and, all the more, higher-order ones. But taking them into account means allowing collisions of the pair with "third particles" (the rest of gas). We can surmise that then significant pair correlations could exist only not too far from the place of possible contact, $|\boldsymbol{r}_1 - \boldsymbol{R}_0| \lesssim r_B$. More concretely, at $|r_\parallel| \lesssim \Lambda'$, where $r_\parallel = (\boldsymbol{v}_1 - \boldsymbol{V}_0) \cdot (\boldsymbol{r}_1 - \boldsymbol{R}_0)|/|\boldsymbol{v}_1 - \boldsymbol{V}_0|$ designates longitudinal internal coordinate in the collision cylinder and Λ' is comparable with Λ (for instance, $\Lambda' = \lambda\Lambda/(\lambda+\Lambda)$). In other words, effectively the collision cylinder has finite length $\Lambda_C \sim 2\Lambda'$. Stronger separated particles hardly are candidates for mutual collision even if they aim exactly one to another.

Corresponding effective volume of the collision cylinder is $\Omega_C \sim \pi r_B^2 \Lambda_C = \Lambda_C/\nu_0\Lambda \sim \nu_0^{-1}$. Hence, in spite of all limitations, totally the pair correlation occupies the whole of volume displayed per one atom.

The same conclusions directly follow from relations (5)-(7) as combined with (3). Indeed, rearranging integrations over $\boldsymbol{r}_1$ and momentums, one can write

$$V_1(t, \boldsymbol{R}_0 - \boldsymbol{R}' \,;\, \nu_0) = \\ = \int\int [\, \nu_0 \int V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')\, d\boldsymbol{r}_1 \,]\, d\boldsymbol{P}_0\, d\boldsymbol{p}_1$$

and then, due to the mentioned knowledge on pair CF,

$$\nu_0 \int V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')\, d\boldsymbol{r}_1 = \\ = \nu_0\, \Omega_C\, \overline{V}_1(t, \boldsymbol{R}_0 - \boldsymbol{R}', \boldsymbol{P}_0, \boldsymbol{p}_1) \;\; ,$$

where Ω_C is volume of those central region of the collision cylinder where the pair CF significantly differs from zero, and $\overline{V}_1(t, \boldsymbol{R}_0 - \boldsymbol{R}', \boldsymbol{P}_0, \boldsymbol{p}_1)$ represents characteristic or mean value of the pair CF inside this region. Then the above underlined finiteness, and invariance, of both sides of (7) under BGL clearly prompts that, firstly, Ω_C is really finite and, secondly, $\Omega_C \sim \nu_0^{-1}$ and $\Lambda_C \sim \Lambda$.

At the same time, integration over momentums in (3), again with applying our knowledge, yields quite another estimate. For $r_B \lesssim |\boldsymbol{r}_1 - \boldsymbol{R}_0| \lesssim \Lambda_C$, simply

$$V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1|\boldsymbol{R}') \sim \\ \sim V_1(t, \boldsymbol{R}_0 - \boldsymbol{R}' \,;\, \nu_0)\, r_B^2/|\boldsymbol{r}_1 - \boldsymbol{R}_0|^2 \sim \\ \sim \nu_0^{-1}\, V_1(t, \boldsymbol{R}_0 - \boldsymbol{R}' \,;\, \nu_0)/(\Lambda|\boldsymbol{r}_1 - \boldsymbol{R}_0|^2)$$

It shows that in literal sense the spatial pair correlation disappears under BGL, because vanishingly small part of differently oriented collision cylinders only covers a given segment $(\boldsymbol{R}_0\, , \boldsymbol{r}_1)$.

3. Of course, neither $\overline{V}_1(t, \Delta\boldsymbol{R}, \boldsymbol{P}_0, \boldsymbol{p}_1)$ nor Ω_C , or Λ_C , above is unambiguously defined if being taken separately. But an arbitrariness is not strong since Λ_C , like generally free paths in gases, should be insensible to momentums. The more so as physically the "third particles" responsible for Λ_C originate from gas background which stays constant (uniform and equilibrium) regardless of BP's walk. Nevertheless, we will try more formal definition of Ω_C and Λ_C .

Let $\Omega = \Omega(\boldsymbol{P}_0, \boldsymbol{p}_1)$ denotes at once a finite (exactly ar nearly) cylindric region in the $\boldsymbol{r}_1$ space and volume of this region, presuming that it is centered at point $\boldsymbol{R}_0$ and elongated in parallel to $\boldsymbol{v}_1 - \boldsymbol{V}_0$. Then introduce $\Omega_C(\delta) = \Omega_C(\delta, \boldsymbol{P}_0, \boldsymbol{p}_1)$ as *minimum* of all those regions Ω what satisfy

$$|\int_\Omega V_1\, d\boldsymbol{r}_1 \,-\, \int V_1\, d\boldsymbol{r}_1| \,<\, \delta\, |\int V_1\, d\boldsymbol{r}_1|$$

with $0 < \delta \ll 1$ and $V_1 = V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')$. Orally, $\Omega_C(\delta)$ is minimal region containing at least $100\,(1-\delta)$ percents of total pair correlation.

From the other hand, let us turn to identity (2) and integrate it over $\boldsymbol{r}_1 \in \Omega_C(\delta)$. It is important, although trivial, that $F_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')$ as well as any distribution function is *a fortiori* non-negative. Therefore the result must be non-negative, and we can write

$$\int_{\Omega_C(\delta)} F_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')\, d\boldsymbol{r}_1 = \\ = (\,1-\epsilon)\, \Omega_C(\delta)\, V_0(t, \boldsymbol{R}_0, \boldsymbol{P}_0|\boldsymbol{R}')\, G^{(eq)}(\boldsymbol{p}_1) + \\ + \int_{\Omega_C(\delta)} V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')\, d\boldsymbol{r}_1 \,\geq\, 0$$

Here $\epsilon \equiv \Omega_C^{-1}(\delta) \int_{\Omega_C(\delta)} [1 - F_1^{(eq)}(\boldsymbol{r}_1|\boldsymbol{R}_0)\,]\, d\boldsymbol{r}_1$. Clearly, for more or less dilute gas ϵ is indifferent to $\Omega_C(\delta)$, positive and small, $\epsilon \sim 4\pi r_B^3 \nu_0/3 \ll 1$.

Further, it is easy to make sure that the two above inequalities together imply a more interesting one:

$$(\,1-\epsilon)\, \Omega_C(\delta)\, V_0(t, \boldsymbol{R}_0, \boldsymbol{P}_0|\boldsymbol{R}')\, G^{(eq)}(\boldsymbol{p}_1) + \\ + (1-\delta\,) \int V_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1|\boldsymbol{R}')\, d\boldsymbol{r}_1 \,\geq\, 0 \qquad (8)$$

Next, let us integrate this inequality over momentums. In view of above remarks on mean free paths, it is natural to expect that momentum dependence of the volume $\Omega_C(\delta) = \Omega_C(\delta, \boldsymbol{P}_0, \boldsymbol{p}_1)$ is negligible. Otherwise, we can replace $\Omega_C(\delta)$ in (8) by the Ω's minimax, i.e. maximum with respect to momentums of the minimums $\Omega_C(\delta, \boldsymbol{P}_0, \boldsymbol{p}_1)$. Or, alternatively, take into account that at $t \gg \tau$, where $\tau = \Lambda/v_T$ is mean free flight time of BP and v_T its thermal velocity, momentum of BP becomes almost uncorrelated with its displacement, $\boldsymbol{R}_0 - \boldsymbol{R}'$, and obeys almost exactly equilibrium Maxwellian probability distribution (see [12] and also [10, 11]). Therefore integration of first term in (8) merely replaces $\Omega_C(\delta)$ by equilibrium average of $\Omega_C(\delta, \boldsymbol{P}_0, \boldsymbol{p}_1)$.

Anyway, integrating (8) and combining it with (3) and first of (6), we come to inequality

$$(\,1-\epsilon)\, \Omega_C(\delta)\, V_0(t, \boldsymbol{R}_0 - \boldsymbol{R}' \,;\, \nu_0) + \\ + (1-\delta\,)\, \nu_0^{-1}\, V_1(t, \boldsymbol{R}_0 - \boldsymbol{R}' \,;\, \nu_0) \,\geq\, 0 \;\; , \qquad (9)$$

where $\Omega_C(\delta)$ represents characteristic volume occupied by ($100\,(1-\delta)$ percents of total) pair correlation of two particles (BP and atom) in the space of their separations. Corresponding effective length of the collisions cylinder, $\Lambda_C = \Omega_C(\delta)/\pi r_B^2$, may be somewhat greater than Λ' (see § 2 in this Sec.). If the correlation exponentially decreases at large separations (at $|r_\parallel| > \Lambda'$) then admittedly $\Lambda_C \approx \Lambda' \ln(1/\delta)$. In fact, however, there is no need in conjectures or speculations. The only principal thing is that $\Omega_C(\delta)$ is finite quantity of order of ν_0^{-1} , i.e. $\nu_0 \Omega_C(\delta) \sim 1$.

4. We have approached to curious conclusions.

Inequalities (8) and (9) say that pair correlation can not be "too negative", while relation (7) shows that sign of the summary pair correlation, $V_1(t, \Delta\boldsymbol{R}\,;\, \nu_0)$, coincides with sign of small change in the BP's path probability density distribution, $V_0(t, \Delta\boldsymbol{R}\,;\, \nu_0)$, under infinitesimally small uniform addition to gas density. Naturally, the latter should squeeze $V_0(t, \Delta\boldsymbol{R}\,;\, \nu_0)$ and thus decrease it at large $|\Delta\boldsymbol{R}|$, at least at $\Delta\boldsymbol{R}^2 \gg 4Dt$, with $D = D(\nu_0)$ being BP's diffusivity. Hence, just there $V_1(t, \Delta\boldsymbol{R}\,;\, \nu_0) < 0$ and the restriction (9) does work.

It is clear also that the faster is decrease of $V_0(t, \Delta\boldsymbol{R};\, \nu_0)$ at $\Delta\boldsymbol{R}^2/4Dt \to \infty$ the stronger is its change there under variation of gas density. Therefore inequality (9) implies some limitations of possible shapes of $V_0(t, \Delta\boldsymbol{R};\, \nu_0)$. To consider them in evident form, let us combine (9) and (7). This yields

$$c_1\, V_0(t, \Delta\boldsymbol{R};\, \nu_0) \,+\, \nu_0\, \frac{\partial V_0(t, \Delta\boldsymbol{R};\, \nu_0)}{\partial \nu_0} \,\geq\, 0 \qquad (10)$$

Here we introduced $c_1 \,\equiv\, (\,1-\epsilon\,)\,\Omega_C(\delta)\,\nu_0^2/(1-\delta\,)\,\widetilde{\nu}_0$. According to above consideration, in more or less dilute gas (or under BGL) $c_1 \,\approx\, \Omega_C(\delta)\,\nu_0 \,\sim\, 1$ independently on the density.

5. Now assume that at $t \gg \tau$, when

$$\langle \Delta\boldsymbol{R}^2 \rangle \,=\, \int \Delta\boldsymbol{R}^2\, V_0(t, \Delta\boldsymbol{R};\, \nu_0)\, d\Delta\boldsymbol{R} \,\approx\, 6Dt \,\gg\, 3\Lambda^2 \;,$$

the BP's path distribution tends to the Gaussian one (see Introduction), $V_0(t, \Delta\boldsymbol{R};\, \nu_0) \to V_G(t, \Delta\boldsymbol{R})$. Then inequality (10) turns into requirement

$$\left[\, c_1 \,+\, \left(\frac{\Delta\boldsymbol{R}^2}{4Dt} - \frac{3}{2}\right) \frac{\partial \ln D}{\partial \ln \nu_0}\,\right] V_G(t, \Delta\boldsymbol{R}) \,\geq\, 0$$

Since diffusivity certainly is a decreasing function of gas density, and $\partial \ln D/\partial \ln \nu_0 \,<\, 0$, this requirement inevitably gets broken at sufficiently large values of $\Delta\boldsymbol{R}^2/4Dt$, while we get contradiction.

Consequently, the theory forbids the Gaussian asymptotic! This statement, or rather its new proof since it itself is not quite novel (see Introduction and resume below), is principal result of the present paper.

6. But what kind of asymptotic is allowed instead of the Gaussian one?

Let $V_0(t, \Delta\boldsymbol{R};\, \nu_0)$ at $t \gg \tau$ is characterized, similarly to $V_G(t, \Delta\boldsymbol{R})$, by a single parameter, that is diffusivity:

$$V_0(t, \Delta\boldsymbol{R};\, \nu_0) \to (4Dt)^{-3/2}\, \Psi(\Delta\boldsymbol{R}^2/4Dt) \;,$$

where $\int \Psi(\boldsymbol{a}^2)\, d\boldsymbol{a} \,=\, 1$ (the normalization condition) and $\int \boldsymbol{a}^2 \Psi(\boldsymbol{a}^2)\, d\boldsymbol{a} \,=\, 3/2$ (that is $\langle \Delta\boldsymbol{R}^2 \rangle = 6Dt$). If take in mind dilute or Boltzmann-Grad gas, where $D \sim \Lambda v_T$ and thus $D \propto \nu_0^{-1}$, then inequality (10) reduces to

$$(c_1 + 3/2)\, \Psi(x) + x\, d\Psi(x)/dx \,\geq\, 0$$

It requires that function $\Psi(x)$ must have power-law long tail: $\Psi(x) \propto x^{-\alpha}$ at $x \to \infty$, where $\alpha \leq c_1 + 3/2$.

But such behavior leads to unboundedness of higher-order statistical moments of BP's path. Recall, however, that we have one more parameter, the thermal velocity v_T (or, equivalently, speed of sound, $v_s \sim v_T$) and therefore possibility at $t \gg \tau$ to write

$$V_0(t, \Delta\boldsymbol{R};\, \nu_0) \to \frac{1}{(4Dt)^{3/2}}\, \Psi\left(\frac{\Delta\boldsymbol{R}^2}{4Dt}\right) \Theta\left(\frac{|\Delta\boldsymbol{R}|}{v_T t}\right) \qquad (11)$$

with a cut off function $\Theta(x)$ which satisfies $\Theta(0) = 1$ and fast enough decreases at infinity. From the point of view of inequality (10) this is also allowed variant. And at $c_1 = 2$, i.e. $\alpha = 7/2$, and $\Psi(x) = \Gamma(\alpha)\, \pi^{-3/2}\, (1+x)^{-\alpha}$ it qualitatively and and in part quantitatively reproduces the asymptotic of distribution of BP's path found in [12] in the frame of the "collisional approximation" of BBGKY equations [10, 11] (there BP was identical to atoms).

IV. DISCUSSION AND RESUME

Why it is so that the Gaussian asymptotic fails (and usual intuition does along with it)? In principle, the answer was provided many years ago, firstly (as far as I know), in general, by Krylov in book [18] (see citation from it in Introduction) and later, in context of Brownian motion of micro-particles and transport processes (particularly, electrons and charge transport), in [14, 15] and then in [10, 11].

Briefly, if a system actually is constantly forgetting history of "Brownian particle" (BP), that is a number of its previous collisions, etc., then such system is physically unable to check a "number of collisions (of this particle) per unit time". Therefore one can not describe BP's walk in terms of *a priori* "probabilities of collisions per unit time" or other beforehand assigned probabilities of "elementary" steps or events. In other words, the walk can not be divided into "statistically independent" pieces, and thus products of "the art of conjecturing" like the "law of large numbers" become out of job. The resulting non-ergodicity of Brownian trajectories may be characterized as "1/f-fluctuations" in "probabilities of collisions" and thus in BP's diffusivity and mobility [10–15, 26].

In present work, the aforesaid is concretized by inequality (10). It shows that hypothetical Gaussian asymptotic has too large relative speed of decrease at infinity: $\partial \ln V_G/\partial \ln \Delta\boldsymbol{R}^2 \,=\, -\Delta\boldsymbol{R}^2/4Dt \,\to\, -\infty$. So much large that the quantity (see § 3 in Sec.III)

$$\overline{F}_1(t, \boldsymbol{R}_0 - \boldsymbol{R}', \boldsymbol{P}_0, \boldsymbol{p}_1) = \int_{\Omega_C} F_1(t, \boldsymbol{R}_0, \boldsymbol{r}_1, \boldsymbol{P}_0, \boldsymbol{p}_1 | \boldsymbol{R}')\, \frac{d\boldsymbol{r}_1}{\Omega_C}$$

(with Ω_C shortening $\Omega_C(\delta, \boldsymbol{P}_0, \boldsymbol{p}_1)$) and even quantity $\overline{W}_1(t, \Delta\boldsymbol{R}) \,=\, \int \overline{F}_1(t, \Delta\boldsymbol{R}, \boldsymbol{P}_0, \boldsymbol{p}_1)\, d\boldsymbol{P}_0\, d\boldsymbol{p}_1$ would become negative. However, in reality this is impossible even under maximally allowable statistical unbalance of mutually antithetic BP's collisions, since $\overline{F}_1(t, \Delta\boldsymbol{R}, \boldsymbol{P}_0, \boldsymbol{p}_1)$, by its probabilistic sense, must be non-negative.

Notice that $\overline{F}_1(t, \Delta\boldsymbol{R}, \boldsymbol{P}_0, \boldsymbol{p}_1)$ and $\overline{W}_1(t, \Delta\boldsymbol{R})$ are direct analogues of function A_2 from [10] (or F_2 from [11]) and W_2 from [12] and represent ensemble averages of number density of those two-particle configurations what match up BP's collisions with atoms.

But where in present consideration one can see "fluctuations in probabilities of collisions"? Notice that ratio $\overline{W}_1(t, \Delta\boldsymbol{R})/V_0(t, \Delta\boldsymbol{R})$ is a measure of conditional probability of BP's collisions. Or, in other words, it represents *a posteriori* probabilities what emerge from factual BP's path. According to §§ 3-4 in Sec.III,

$$\overline{W}_1(t,\Delta\boldsymbol{R}) \approx V_0(t,\Delta\boldsymbol{R}) + c_1^{-1}\, V_1(t,\Delta\boldsymbol{R})$$

(argument ν_0 is omitted). At far tail of the BP's path distribution $V_0(t,\Delta\boldsymbol{R})$, at $x = \Delta\boldsymbol{R}^2/4Dt \to \infty$, it goes to zero much faster than $V_0(t,\Delta\boldsymbol{R})$, so that $\overline{W}_1(t,\Delta\boldsymbol{R})/V_0(t,\Delta\boldsymbol{R}) \propto x^{-1} \to 0$. If $x \ll 1$ then, in opposite, $\overline{W}_1 > V_0$. So substantial changeability of the *a posteriori* probabilities (in contrast with their constancy imposed by the "molecular chaos" in conventional theory) just shows that asymptotic like (11) reflects what can be named long-scale "fluctuations in probabilities of collisions".

Importantly, our consideration has outlined a way to formalizing connections between usual many-particle distribution and correlation functions, on one hand, and specific distribution functions (first introduced in [10]) for two- and many-particle collisional configurations, on the other hand. Their deeper investigation would mean better understanding real statistics of molecular Brownian motion and related noise and might open new applications of the virial expansions (4) and (5).

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[26] The present paper signifies 25 years after first (to the best of my knowledge) work [13], by G. N. Bochkov and me, on the subjects under current consideration.