MOLECULAR BROWNIAN MOTION AND INVARIANCE GROUP OF THE BOGOLYUBOV EQUATION

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Abstract. Statistics of molecular random walks in a fluid is considered with the help of Bogolyubov equation for generating functional of distribution functions. An invariance group of this equation is found. It results in many exact relations between path probability distribution of a test particle and its correlations with the fluid. As the consequence, significant restrictions on possible shape of the path distribution do arise. In particular, the hypothetical Gaussian form of long-range asymptotic proves to be forbidden, even (and first of all) under the Boltzmann-Grad limit. An allowed diffusive asymptotic possesses power-law long tail (cut off by free flight length).

1. Introduction

Random wandering of particles of the matter is mechanism of diffusion and many other transport processes as well as various noises and fluctuations. What can be its statistics? Strangely, this important question never was addressed to rigorous statistical mechanics. At present, seemingly, the answer is obvious without it: since even in the Lorentz gas asymptotic of random walks is Gaussian [1], all the more it must be the same in a usual fluid. However, one can notice that such conclusion is founded on instinctive identifying dynamical independence of events in "real life" (concrete realization of many-particle system) and statistical independence of events in "theory" (statistical ensemble of systems). But already Krylov [2] thoroughly explained that the first does not imply the second [1].

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[1] In the probability theory *by definition* A and B are independent if $\mathcal{P}(A \wedge B) = \mathcal{P}(A)\mathcal{P}(B)$ [3]. Therefore statement "events are independent if they have "nothing to do" with each other" [4] is wrong: such A and B may both depend on common conditions so that $\mathcal{P}(A \wedge B) \neq \mathcal{P}(A)\mathcal{P}(B)$!

This can understood by the example of gas of N hard balls in a box if considering their motion as motion of one ball in $3N$-dimensional billiard [5] which resembles the Lorentz gas. Here as well initially one-dimensional (straight-line) motion becomes multidimensional. However hardly it is possible to speak about ergodicity before all the dimensions and scatteres become apparent, that is before time $\sim \frac{1}{2}N(N-1)/(N/\tau) \sim N\tau \sim \Omega/\pi r_0^2 v_0$ passed after start of observations, with Ω , $\tau \sim (\pi r_0^2 \nu v_0)^{-1}$, r_0 , v_0 and $\nu = N/\Omega$ being volume of the box, typical free path time of gas particles, radius of their interaction (diameter of the balls), their characteristic velocity and mean gas density, respectively. Even for $1\,\mathrm{cm}^3$ of the air this is time greater than 1000 years! Thus, it was true remark [6] that role of ergodicity in physics is strongly exaggerated since in physical reality limit $N \to \infty$ precedes limit $t/\tau \to \infty$.

If it is so then trajectory of test particle in gas of sufficiently many particles (formally, under $N \to \infty$) is non-ergodic: its even very relatively distant fragments (separated by time intervals $\gg \tau$) are statistically dependent one on another although independent in dynamical sense. This means that any concrete realization of random walk of the test particle (corresponding to some concrete phase trajectory of the whole system) possesses its own specific *kinetic characteristics* (diffusivity and mobility, etc.) or, better to say, has no certain kinetic characteristics [7, 8].

Theoretical tools for investigations of such statistics a long time ago were presented by N. Bogolyubov [9] and his followers. That are the BBGKY (Bogolyubov-Born-Green-Kirkwood-Yvon) hierarchy of equations or equivalent Bogolyubov's equation for generating functional of many-particle distribution functions. But, unfortunately, nobody has learned honest use of them without some cutting off the hierarchy and justifying such vivisection by imaginary intuitive "independencies". Therefore complementary tools are not unnecessary.

In the present work we describe an invariance group of the Bogolyubov equation and its solutions. For simplicity, it is formulated directly with reference to the problem about random walk of test particle in thermodynamically equilibrium fluid. We want to demonstrate that exact relations of the group point to essentially non-Gaussian statistical features of long-range asymptotic of the random walk. Importantly, in case of gas these relations and their consequences, along with the mentioned characteristic time scale $\sim N\tau$, are indifferent to gas density, even in the limit of dilute gas (or the Boltzmann-Grad limit).

2. Equations of molecular random walk

Let box with volume Ω contains $N \gg 1$ identical atoms plus one more test particle. Atoms have mass m, coordinates $\mathbf{r}_j$ and momenta $\mathbf{p}_j$ ($j = 1, 2... N$) and interact with each other via potential $\Phi_a(\mathbf{r}_j - \mathbf{r}_k)$. The test particle has mass M, coordinate $\mathbf{R}$, momentum $\mathbf{P}$ and interacts with atoms via potential $\Phi_b(\mathbf{r}_j - \mathbf{R})$. The potentials are spherically symmetric and short-range with impenetrable point core. Because of interactions the test particle is in chaotic motion, therefore let us name it "molecular Brownian particle" (BP).

We are interested in probability distribution of current position of BP, $\mathbf{R}(t)$, under condition that at initial time moment $t = 0$ it was placed at certainly known position: $\mathbf{R}(0) = \mathbf{R}_0$, while personal positions of atoms all the times are unknown. The simplest statistical ensemble what satisfies this requirement is determined by the Liouville equation, $\partial D_N/\partial t = [\, H_N \, , D_N \,]$, for full normalized distribution function of the system, D_N, and initial condition

$$D_N(\, t = 0\,) \,=\, \frac{\delta(\mathbf{R} - \mathbf{R}_0)\; e^{-\,H_N/T}}{\int d\mathbf{R} \int d\mathbf{P} \int_1 ... \int_N \delta(\mathbf{R} - \mathbf{R}_0)\, e^{-\,H_N/T}} \tag{2.1}$$

to it, where H_N is full Hamiltonian of the system (including interactions with the box walls) and $\int_k \dots = \int\int \dots \, d\mathbf{r}_k \, d\mathbf{p}_k$. Evidently, such ensemble differs from the Gibbs canonic ensemble by initial BP's localization only. The latter does not prevent us to introduce particular distribution functions (DF) $F_n(t) = \Omega^n \int_{n+1} \dots \int_N D_N(t)$ and then go to the thermodynamical limit ($N \to \infty$, $\Omega \to \infty$, $\nu = N/\Omega =$ const) just as in [9]. The only, non-principal, difference from [9] is that all n-atom DF under consideration include also BP's variables, i.e. in fact are $(n+1)$-particle DF, therefore their numeration takes beginning at zero, and in respect to BP's variables all they are normalized in usual sense of the probability theory. Writing out complete list of arguments, $F_n(t) = F_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)} | \, \mathbf{R}_0 \, ; \nu \,)$, where $\mathbf{r}^{(n)} = \{\mathbf{r}_1 \dots \mathbf{r}_n \}$, $\mathbf{p}^{(n)} = \{\mathbf{p}_1 \dots \mathbf{p}_n \}$. In particular, $F_0(t, \mathbf{R}, \mathbf{P} | \, \mathbf{R}_0 \, ; \nu \,)$ describes BP itself, and $\int d\mathbf{R} \int d\mathbf{P} \; F_0 = 1$. What is for the atomic coordinates, in respect to them all DF are "normalized to volume", exactly as in [9]. In other words, the "weakening of correlations" between distant particles holds: $F_n \to F_{n-1} \, G_m(\mathbf{p}_k)$, if k-th particle keeps away from others, where $G_m(\mathbf{p}) = (2\pi T m)^{-3/2} \exp{(-\mathbf{p}^2/2Tm)}$ is the Maxwell momentum distribution of a particle with mass m . The full Liouville equation induces the BBGKY equations

$$\frac{\partial F_n}{\partial t} = [\, H_n \, , F_n \,] \, + \, \nu \, \frac{\partial}{\partial \mathbf{P}} \int_{n+1} \Phi_b'(\mathbf{R} - \mathbf{r}_{n+1}) \, F_{n+1} \, + \, \nu \sum_{j=1}^{n} \frac{\partial}{\partial \mathbf{p}_j} \int_{n+1} \Phi_a'(\mathbf{r}_j - \mathbf{r}_{n+1}) \, F_{n+1} \tag{2.2}$$

($n = 0, 1, \dots$) with initial conditions

$$F_n(t=0) \, = \, \delta(\mathbf{R} - \mathbf{R}_0) \, F_n^{(eq)}(\mathbf{r}^{(n)} \, | \mathbf{R}; \nu) \, G_M(\mathbf{P}) \prod_{j=1}^{n} G_m(\mathbf{p}_j) \;\; , \tag{2.3}$$

where H_n is Hamiltonian of subsystem " n atoms plus BP ", $\Phi'_{a,\,b}(\mathbf{r}) = \nabla \Phi_{a,\,b}(\mathbf{r})$, and $F_n^{(eq)}(\mathbf{r}^{(n)} \, | \mathbf{R}; \nu)$ are usual thermodynamically equilibrium DF for n atom in presence of BP occupying point $\mathbf{R}$. In principle, that will do for finding $F_0(t, \mathbf{R}, \mathbf{P} | \, \mathbf{R}_0 \, ; \nu \,)$ and thus probability distribution of BP's path, $\Delta \mathbf{R}(t) = \mathbf{R}(t) - \mathbf{R}_0$, without any additional assumptions.

Following Bogolyubov, let us combine all our DF into generating functional (GF)

$$\mathcal{F}\{t, \mathbf{R}, \mathbf{P}, \psi\,|\mathbf{R}_0; \nu\} \;=\; F_0 \;+ \sum_{n=1}^{\infty} \frac{\nu^n}{n!} \int_1 \dots \int_n F_n \prod_{j=1}^{n} \psi(\mathbf{r}_j, \mathbf{p}_j) \tag{2.4}$$

and equations (2.2) into corresponding "generating equation" for it:

$$\frac{\partial \mathcal{F}}{\partial t} + \frac{\mathbf{P}}{M} \cdot \frac{\partial \mathcal{F}}{\partial \mathbf{R}} = \widehat{\mathcal{L}} \left(\psi, \frac{\delta}{\delta \psi}\right) \mathcal{F} \;\;, \tag{2.5}$$

where operator $\widehat{\mathcal{L}}$ is composed by usual and variational derivatives,

$$\begin{aligned} \widehat{\mathcal{L}} \left(\psi, \frac{\delta}{\delta \psi}\right) \;=\; & -\int_1 \psi(x_1)\, \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} \frac{\delta}{\delta \psi(x_1)} \;+ \\ & + \int_1 [\,1 + \psi(x_1)\,] \left[\, \Phi_b(\mathbf{R} - \mathbf{r}_1)\,, \frac{\delta}{\delta \psi(x_1)} \right] + \\ & + \frac{1}{2} \int_1 \int_2 [\,1 + \psi(x_1)\,] [\,1 + \psi(x_2)\,] \left[\, \Phi_a(\mathbf{r}_1 - \mathbf{r}_2)\,, \frac{\delta^2}{\delta \psi(x_1)\, \delta \psi(x_2)} \right] \;\;, \end{aligned} \tag{2.6}$$

with $x_j \;=\; \{\mathbf{r}_j, \mathbf{p}_j\}$. This is direct analogue of equation (7.9) from [9]. To make it well visible, notice that $\psi(x) = u(x)/\nu$, where $u(x)$ is functional argument used in [9], and factor $[1+\psi(x_1)]\,[1+\psi(x_2)]$ can be replaced by $[\,\psi(x_1) + \psi(x_2) + \psi(x_1)\psi(x_2)\,]$ due to identity $\int_1 \int_2 [\, \Phi_a(\mathbf{r}_1 - \mathbf{r}_2)\,, \dots] = 0$. Initial condition to equation (2.5) is obvious:

$$\begin{aligned} \mathcal{F}\{0,\, \mathbf{R}, \mathbf{P}, \psi\,|\, \mathbf{R}_0; \nu\} \;&=\; \delta(\mathbf{R} - \mathbf{R}_0)\, G_M(\mathbf{P})\, \mathcal{F}^{(eq)}\{\phi|\, \mathbf{R}; \nu\} \;\;, \\ \mathcal{F}^{(eq)}\{\phi|\, \mathbf{R}; \nu\} \;&=\; 1 \;+ \sum_{n=1}^{\infty} \frac{\nu^n}{n!} \int \dots \int F_n^{(eq)}(\mathbf{r}^{(n)}|\, \mathbf{R}; \nu) \prod_{j=1}^{n} \phi(\mathbf{r}_j)\, d\mathbf{r}_j \;\;, \end{aligned} \tag{2.7}$$

where we introduced new functional argument $\phi(\mathbf{r}) \;\equiv\; \int \psi(\mathbf{r}, \mathbf{p})\, G_m(\mathbf{p})\, d\mathbf{p}$ and besides generating functional $\mathcal{F}^{(eq)}$ of equilibrium DF. It is easy to guess that expression $G_M(\mathbf{P})\, \mathcal{F}^{(eq)}$ should bring stationary solution of (2.5):

$$\left[-(\mathbf{P}/M) \cdot \partial/\partial \mathbf{R} + \widehat{\mathcal{L}} \right]\; G_M(\mathbf{P})\, \mathcal{F}^{(eq)}\{\phi|\, \mathbf{R}; \nu\} \;=\; 0$$

From here equation

$$\left[\frac{\partial}{\partial \mathbf{r}} + \frac{\Phi_b'(\mathbf{r} - \mathbf{R})}{T} \right] \frac{\delta \mathcal{F}^{(eq)}}{\delta \phi(\mathbf{r})} \;=\; \frac{1}{T} \int [\,1 + \phi(\mathbf{r}')\,]\, \Phi_a'(\mathbf{r}' - \mathbf{r})\, \frac{\delta^2 \mathcal{F}^{(eq)}}{\delta \phi(\mathbf{r})\, \delta \phi(\mathbf{r}')}\, d\mathbf{r}' \tag{2.8}$$

follows which is analogue of equation (2.14) in [9] and determines equilibrium DF.

Unfortunately, to the best of my knowledge, non-stationary solutions to "generating equations" like (2.5) (or (7.9) from [9]) never were investigated by Bogolyubov or any other authors. However, past experience in the BBGKY equations (see e.g. [10]) points to desirability of a change of variables, i.e. transition from DF to some suitably defined "correlation functions". With this purpose, let us discuss hypothetical equalities

$$F_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)} | \, \mathbf{R}_0; \nu) \overset{?}{=} F_0(t, \mathbf{R}, \mathbf{P} | \, \mathbf{R}_0; \nu) \; F_n^{(eq)}(\mathbf{r}^{(n)} | \, \mathbf{R}; \nu) \prod_{j=1}^n G_m(\mathbf{p}_j)$$

or, equivalently, $\mathcal{F}\{t, \mathbf{R}, \mathbf{P}, \, \psi \, | \, \mathbf{R}_0; \nu\} \overset{?}{=} F_0(t, \mathbf{R}, \mathbf{P} | \, \mathbf{R}_0; \nu) \, \mathcal{F}^{(eq)}\{\phi \, | \, \mathbf{R}; \nu\}$ (recollect that $\phi(\mathbf{r}) = \int \psi(\mathbf{r}, \mathbf{p}) \, G_m(\mathbf{p}) \, d\mathbf{p}$). They state that correlations of atoms with wandering BP always stay the same as with pinned BP. It seems reasonable in view of thermodynamically equilibrium character of the wandering. Nevertheless, it may be true only if all possible BP's positions are statistically equivalent. The latter in our case is not true since translation symmetry is destroyed by information about BP's start point $\mathbf{R}_0$. Correspondingly, above equalities are incompatible with equations (2.2). For example, substitution of equality for F_1 to "collision integral" in equation for F_0 turns it into zero as if BP does not interact with atoms at all.

The aforesaid shows that, first, BP's wandering produces specific non-equilibrium (in statistical sense) "historical" correlations between its total path $\Delta\mathbf{R}(t) = \mathbf{R}(t) - \mathbf{R}_0$ and current state of surrounding medium. Second, we can adequately separate these correlations from equilibrium ones if define them as follows:

$$\begin{aligned} \mathcal{F}\{t, \mathbf{R}, \mathbf{P}, \, \psi \, | \, \mathbf{R}_0; \nu\} \; &= \; \mathcal{V}\{t, \mathbf{R}, \mathbf{P}, \, \psi \, | \, \mathbf{R}_0; \nu\} \; \mathcal{F}^{(eq)}\{\phi \, | \, \mathbf{R}; \nu\} \;\; , \\ \mathcal{V}\{t, \mathbf{R}, \mathbf{P}, \psi \, | \, \mathbf{R}_0; \nu\} \; &= \; V_0 \; + \sum_{n=1}^{\infty} \frac{\nu^n}{n!} \int_1 ... \int_n V_n \prod_{j=1}^n \psi(\mathbf{r}_j, \mathbf{p}_j) \;\; , \end{aligned} \tag{2.9}$$

where $V_n = V_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)} | \, \mathbf{R}_0; \nu)$ are corresponding correlation functions (CF) and $\mathcal{V}$ their GF. In particular, evidently, $V_0(t, \mathbf{R}, \mathbf{P} | \, \mathbf{R}_0; \nu) = F_0(t, \mathbf{R}, \mathbf{P} | \, \mathbf{R}_0; \nu)$ and

$$F_1(t,\mathbf{R},\mathbf{r}_1,\mathbf{P},\mathbf{p}_1|\,\mathbf{R}_0;\nu) \;= \\ = \;F_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;\nu)\,F_1^{(eq)}(\mathbf{r}_1|\mathbf{R};\nu)\,G_m(\mathbf{p}_1)\;+\;V_1(t,\mathbf{R},\mathbf{r}_1,\mathbf{P},\mathbf{p}_1|\,\mathbf{R}_0;\nu) \tag{2.10}$$

In terms of CF the initial conditions (2.3) and "normalization to volume" conditions ("weakening of correlations" at infinity) take very simple form:

$$V_n(t=0)\;=\;\delta_{n,0}\;\delta(\mathbf{R}-\mathbf{R}_0)\;\;,\quad \mathcal{V}\{0,\,\mathbf{R},\mathbf{P},\,\psi|\,\mathbf{R}_0;\nu\}\;=\;\delta(\mathbf{R}-\mathbf{R}_0)\;\;, \tag{2.11}$$

$$V_{n>0}\,(t\,,...\;\mathbf{r}_k\to\infty\;...\,)\;\to\;0 \tag{2.12}$$

Substituting (2.9) into (2.5) one obtains equation for GF of "historical" correlations:

$$\frac{\partial\mathcal{V}}{\partial t}\;+\;\frac{\mathbf{P}}{M}\cdot\frac{\partial\mathcal{V}}{\partial\mathbf{R}}\;=\;\widehat{\mathcal{L}}\left(\psi,\frac{\delta}{\delta\psi}\right)\,\mathcal{V}\;+\;\widehat{\mathcal{L}}\,'\left(\nu,\psi,\frac{\delta}{\delta\psi}\right)\,\mathcal{V}\;\;, \tag{2.13}$$

$$\widehat{\mathcal{L}}\,'\left(\nu,\psi,\frac{\delta}{\delta\psi}\right)\;=\;\left\{\int[\,1\;+\phi(\mathbf{r})\,]\;\Phi_b'(\mathbf{R}-\mathbf{r})\;\nu\,\mathcal{C}\{\mathbf{r},\phi\,|\,\mathbf{R};\,\nu\}\;d\mathbf{r}\right\}\left(\frac{\mathbf{P}}{MT}+\frac{\partial}{\partial\mathbf{P}}\right)\;+ \\ +\;\int_1\!\int_2[\,1+\psi(x_1)\,]\,[\,1+\psi(x_2)\,]\left[\,\Phi_a(\mathbf{r}_1-\mathbf{r}_2)\,,\,\nu\,\mathcal{C}\{\mathbf{r}_2,\phi\,|\,\mathbf{R};\,\nu\}\,G_m(\mathbf{p}_2)\,\frac{\delta}{\delta\psi(x_1)}\,\right]\;\;,$$

where new functional $\mathcal{C}$ is defined as

$$\mathcal{C}\{\mathbf{r},\phi\,|\,\mathbf{R};\,\nu\}\;=\;\frac{\delta\ln\mathcal{F}^{(eq)}\{\phi|\,\mathbf{R};\,\nu\}}{\nu\,\delta\phi(\mathbf{r})}\;= \tag{2.14}$$

$$=\;F_1^{(eq)}(\mathbf{r}|\,\mathbf{R};\nu)+\sum_{n\,=\,1}^{\infty}\frac{\nu^n}{n!}\int\!...\!\int C_{n+1}(\mathbf{r},\mathbf{r}_1...\,\mathbf{r}_n|\,\mathbf{R};\nu)\prod_{j\,=1}^{n}\phi(\mathbf{r}_j)\,d\mathbf{r}_j$$

Complication of equation (2.13) in comparison with (2.5) is pay for simple conditions (2.11)-(2.12). Corresponding equations for CF also are more complicated than (2.2). Therefore here we write out them only for extreme but interesting case of "BP in ideal gas" (when $\Phi_a(\mathbf{r})=0$, i.e. atoms do not interact with themselves):

$$\frac{\partial V_0}{\partial t}\;=\;-\frac{\mathbf{P}}{M}\cdot\frac{\partial V_0}{\partial\mathbf{R}}\;+\;\nu\,\frac{\partial}{\partial\mathbf{P}}\int_1\Phi_b'(\mathbf{R}-\mathbf{r}_1)\,V_1\;\;,$$

$$\frac{\partial V_{n>0}}{\partial t}\;=\;[\,H_n\,,V_n\,]\;+\;\nu\,\frac{\partial}{\partial\mathbf{P}}\int_{n+1}\Phi_b'(\mathbf{R}-\mathbf{r}_{n+1})\,V_{n+1}\;+ \tag{2.15}$$

$$+\;T\sum_{j\,=1}^{n}\mathcal{P}(j,n)\;G_m(\mathbf{p}_n)\,E'(\mathbf{r}_n-\mathbf{R})\left(\frac{\mathbf{P}}{MT}+\frac{\partial}{\partial\mathbf{P}}\right)V_{n-1}\;\;,$$

where $H_n = \mathbf{P}^2/2M + \sum_{j=1}^{n} [\,\mathbf{p}_j^2/2m + \Phi_b(\mathbf{R}-\mathbf{r}_j)\,]$, $E(\mathbf{r}) = \exp[\,-\Phi(\mathbf{r})/T\,]$, $E'(\mathbf{r}) = \nabla E(\mathbf{r}) = -\Phi'(\mathbf{r})E(\mathbf{r})/T$ and $\mathcal{P}(j,n)$ denotes operation of transposition of arguments $x_j = \{\mathbf{r}_j, \mathbf{p}_j\}$ and $x_n = \{\mathbf{r}_n, \mathbf{p}_n\}$. Thus natively bidiagonal BBGKY hierarchy in terms of CF becomes tridiagonal.

3. Invariance group of equilibrium generating functional

Equilibrium CF C_n in (2.14) are determined by first equality in (2.14):

$$\begin{aligned} C_2(\mathbf{r},\mathbf{r}_1|\,\mathbf{R};\nu) \,&=\, F_2^{(eq)}(\mathbf{r},\mathbf{r}_1|\mathbf{R};\nu) - F_1^{(eq)}(\mathbf{r}|\mathbf{R};\nu)\,F_1^{(eq)}(\mathbf{r}_1|\mathbf{R};\nu)\ , \\ C_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2) \,&=\, F_3^{(eq)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2) \,+\, 2\,F_1^{(eq)}(\mathbf{r})\,F_1^{(eq)}(\mathbf{r}_1)\,F_1^{(eq)}(\mathbf{r}_2) - \\ &- F_1^{(eq)}(\mathbf{r})\,F_2^{(eq)}(\mathbf{r}_1,\mathbf{r}_2) \,-\, F_1^{(eq)}(\mathbf{r}_1)\,F_2^{(eq)}(\mathbf{r},\mathbf{r}_2) \,-\, F_1^{(eq)}(\mathbf{r}_2)\,F_2^{(eq)}(\mathbf{r},\mathbf{r}_1)\ , \end{aligned}$$

and so on. In the second of these expressions for brevity we omitted arguments $\mathbf{R}$ and ν . The conditions of normalization to volume, i.e. weakening of correlations at infinity, which in essence establish existence of the thermodynamical limit [9, 11], do mean that all these CF vanish when distance between any two atoms goes to infinity and turn into usual equilibrium CF when BP is moved off to infinity:

$$\begin{aligned} &C_{n+1}(\mathbf{r},\mathbf{r}_1\dots\mathbf{r}_n|\,\mathbf{R};\nu) \,\rightarrow\, 0 \quad \texttt{at} \quad \mathbf{r}_j - \mathbf{r} \rightarrow \infty\ , \\ &C_n(\mathbf{r}_1\dots\mathbf{r}_n|\,\mathbf{R};\nu) \,\rightarrow\, C_n(\mathbf{r}_1\dots\mathbf{r}_n;\,\nu) \quad \texttt{at} \quad \mathbf{R} - \mathbf{r}_j \rightarrow \infty \end{aligned} \tag{3.1}$$

Moreover, under sufficiently short-range interactions all these limits are achieved in a fast (absolutely) integrable way, which will be assumed below.

Next, consider equation (2.8) rewriting it in the form

$$\left[\frac{\partial}{\partial\mathbf{r}} + \frac{\Phi_b'(\mathbf{r}-\mathbf{R})}{T}\right]\mathcal{C}\{\mathbf{r},\phi\,|\mathbf{R};\,\nu\} \,=\, \frac{1}{T}\int [\,1+\phi(\mathbf{r}')\,]\,\Phi_a'(\mathbf{r}'-\mathbf{r})\,\frac{\delta\mathcal{C}\{\mathbf{r}',\phi\,|\mathbf{R};\,\nu\}}{\delta\phi(\mathbf{r})}\,d\mathbf{r}' +$$

$$+\,\mathcal{C}\{\mathbf{r},\phi\,|\mathbf{R};\,\nu\}\,\frac{\nu}{T}\int [\,1+\phi(\mathbf{r}')\,]\,\Phi_a'(\mathbf{r}'-\mathbf{r})\,\mathcal{C}\{\mathbf{r}',\phi\,|\mathbf{R};\,\nu\}\,d\mathbf{r}' \tag{3.2}$$

as equation for the functional $\mathcal{C}$. The latter interests us here only so far as it influences equation (2.13) for GF of "historical correlations". In this respect, we have (perhaps, for the first time) to pay attention to some important properties of this GF. Firstly, due to integrability of the asymptotic (3.1), $\mathcal{C}$ can be extended to bounded functions

$\phi(\mathbf{r})$ which do not turn to zero at infinity, particularly, to constants, and introduce objects as follow:

$$C(\sigma,\nu) = \lim_{\mathbf{R}-\mathbf{r}\to\infty} \mathcal{C}\{\mathbf{r},\sigma|\mathbf{R};\nu\} = 1 + \sum_{n=1}^{\infty} \frac{\nu^n\sigma^n}{n!} \int_1 ... \int_n C_{n+1}(\mathbf{r},\mathbf{r}_1 ... \mathbf{r}_n;\nu) \ , \qquad (3.3)$$

$$\mathcal{C}_\sigma\{\mathbf{r},\phi\,|\mathbf{R};\nu\} \ = \ \frac{\mathcal{C}\{\mathbf{r},\sigma+\phi\,|\mathbf{R};\,\nu\}}{C(\sigma,\nu)} \ , \qquad (3.4)$$

where $\sigma = \text{const}$, $\int_n ... \ = \ \int ... \, d\mathbf{r}_n$, and integrals in (3.3) are factually independent on $\mathbf{r}$. Secondly, replacement $\phi(\mathbf{r}) \ \to \ \sigma + \phi(\mathbf{r})$ in (3.2) and elementary algebraic manipulations transform (3.2) to equation for $\mathcal{C}_\sigma$:

$$\left[\frac{\partial}{\partial\mathbf{r}} + \frac{\Phi_b'(\mathbf{r}-\mathbf{R})}{T}\right]\mathcal{C}_\sigma\{\mathbf{r},\phi\,|\mathbf{R};\nu\} = \frac{1}{T}\int\left[1+\frac{\phi(\mathbf{r}')}{1+\sigma}\right]\Phi_a'(\mathbf{r}'-\mathbf{r})\,\frac{\delta\,\mathcal{C}_\sigma\{\mathbf{r}',\phi\,|\mathbf{R};\nu\}}{\delta\,[\,\phi(\mathbf{r})/(1+\sigma)\,]}\,d\mathbf{r}' +$$

$$+\mathcal{C}_\sigma\{\mathbf{r},\phi\,|\mathbf{R};\nu\}\,\frac{\nu\,C(\sigma,\nu)\,(1+\sigma)}{T}\int\left[1+\frac{\phi(\mathbf{r}')}{1+\sigma}\right]\Phi_a'(\mathbf{r}'-\mathbf{r})\,\mathcal{C}_\sigma\{\mathbf{r}',\phi\,|\mathbf{R};\nu\}\,d\mathbf{r}' \qquad (3.5)$$

It differs from (3.2) only by scale transformation of the functional argument, $\phi(\mathbf{r}) \to \phi(\mathbf{r})/(1+\sigma)$, and replacement of the density ν by

$$\upsilon(\sigma,\nu) \ = \ \nu\,C(\sigma,\nu)\,(1+\sigma) \qquad (3.6)$$

Third, formal solution to (3.2) in the form of series (2.14) is unambiguously determined by the normalization conditions, that is conditions (3.1) plus quite obvious equality $\lim_{\mathbf{R}-\mathbf{r}\to\infty} \mathcal{C}\{\mathbf{r},\phi = 0\,|\mathbf{R};\,\nu\} = 1$ which determines first term of the series. Fourth, functional $\mathcal{C}_\sigma$ defined by (3.3)-(3.4) satisfies same conditions since (3.1) imply

$$\sum_{k=0}^{\infty} \frac{\nu^k\sigma^k}{k!} \int_{n+1} ... \int_{n+k} C_{n+k+1}(\mathbf{r},\mathbf{r}_1 ... \mathbf{r}_{n+k}|\,\mathbf{R};\nu) \ \to \ 0 \quad \texttt{at} \quad \mathbf{r}_j - \mathbf{r} \to \infty \ , \qquad (3.7)$$

at least, if one understands (3.1) in the sense of absolute integrability of CF C_{n+1} and speaks about not too large values of the density [2].

Summarizing all that, we can conclude that solution to equation (3.5) is nothing but $\mathcal{C}_\sigma\{\mathbf{r},\phi\,|\mathbf{R},\nu\} \ = \ \mathcal{C}\{\mathbf{r},\phi/(1+\sigma)\,|\,\mathbf{R};\,\upsilon(\sigma,\nu)\}$. With taking into account (3.4)

[2] An useful information in this respect comes from rigorous consideration of “group properties of correlation functions” [11].

and (3.6) this means that at arbitrary (admissible in definite sense) constant σ and bounded function $\phi = \phi(\mathbf{r})$ equality

$$\nu\,\mathcal{C}\{\mathbf{r},\sigma+\phi\,|\,\mathbf{R};\,\nu\} \;=\; \frac{\upsilon(\sigma,\nu)}{1+\sigma}\;\mathcal{C}\left\{\mathbf{r},\frac{\phi}{1+\sigma}\,|\,\mathbf{R};\,\upsilon(\sigma,\nu)\right\} \tag{3.8}$$

is valid. It can be rewritten also as

$$\widehat{\mathcal{T}}(\sigma)\,\mathcal{C}\{\mathbf{r},\phi\,|\,\mathbf{R};\,\nu\} \;\equiv\; C(\sigma,\nu)\;\mathcal{C}\left\{\mathbf{r},\frac{1+\phi}{1+\sigma}-1\,|\,\mathbf{R};\,\upsilon(\sigma,\nu)\right\} \;=\; \mathcal{C}\{\mathbf{r},\phi\,|\,\mathbf{R};\,\nu\}\;\;, \tag{3.9}$$

where functions $C(\sigma,\nu)$ and $\upsilon(\sigma,\nu)$ are connected by means of (3.6), and the left equality defines one-parameter family of such transformations of arguments of functional $\mathcal{C}\{\mathbf{r},\phi\,|\,\mathbf{R};\,\nu\}$ which do not change its value. It is not hard to verify that this is group described by the composition rules

$$\begin{aligned}
\widehat{\mathcal{T}}(\sigma_2)\,\widehat{\mathcal{T}}(\sigma_1) \;&=\; \widehat{\mathcal{T}}(\sigma_1+\sigma_2+\sigma_1\sigma_2)\;\;,\\
\upsilon(\sigma_2\,,\,\upsilon(\sigma_1\,,\nu)) \;&=\; \upsilon(\sigma_1+\sigma_2+\sigma_1\sigma_2\,,\nu)\;\;,\\
C(\sigma_2\,,\,(1+\sigma_1)\,C(\sigma_1\,,\nu)\,\nu)\,C(\sigma_1\,,\nu) \;&=\; C(\sigma_1+\sigma_2+\sigma_1\sigma_2\,,\nu)
\end{aligned} \tag{3.10}$$

with restrictions $\sigma > -1$, $\phi(\mathbf{r}) > -1$. The latter are clear in the light of that

$$\upsilon\{\mathbf{r}|\,\phi,\mathbf{R};\nu\} \equiv [1+\phi(\mathbf{r})]\,\frac{\delta\ln\mathcal{F}^{(eq)}\{\phi|\,\mathbf{R};\nu\}}{\delta\phi(\mathbf{r})} \;=\; \nu\,[1+\phi(\mathbf{r})]\,\mathcal{C}\{\mathbf{r},\phi\,|\,\mathbf{R};\,\nu\}$$

represents mean concentration of atoms under external potential $U(\mathbf{r})$ which is related to $\phi(\mathbf{r})$ by $\phi(\mathbf{r}) = \exp\,[\,-U(\mathbf{r})/T\,]-1$ (see e.g. [12]). Substitution $\sigma = \exp\,(a)-1$ gives $\widehat{\mathcal{T}}(a_2)\,\widehat{\mathcal{T}}(a_1) = \widehat{\mathcal{T}}(a_1+a_2)$ thus eliminating the restrictions.

Infinitesimal form of (3.8) or (3.9) looks best if written through particular CF:

$$\begin{aligned}
&\left\{\varkappa(\nu)+[\,1+\varkappa(\nu)\,]\,\nu\,\frac{\partial}{\partial\nu}\right\}F_1^{(eq)}(\mathbf{r}|\,\mathbf{R};\nu) \;=\; \nu\int C_2(\mathbf{r},\mathbf{r}'|\mathbf{R};\nu)\,d\mathbf{r}'\;\;,\\
&\left\{n\varkappa(\nu)+[\,1+\varkappa(\nu)\,]\,\nu\,\frac{\partial}{\partial\nu}\right\}C_n(\mathbf{r}_1\ldots\mathbf{r}_n|\,\mathbf{R};\nu) = \nu\int C_{n+1}(\mathbf{r}_1\ldots\mathbf{r}_n,\mathbf{r}'|\mathbf{R};\nu)\,d\mathbf{r}'\;\;,\\
&\varkappa(\nu)\;\equiv\;\left[\frac{\partial C(\sigma,\nu)}{\partial\sigma}\right]_{\sigma=0} \;=\; \nu\int C_2(\mathbf{r},0;\,\nu)\,d\mathbf{r}
\end{aligned} \tag{3.11}$$

The function $\varkappa(\nu)$ is known (see e.g. [13]) to be directly related to a state equation of the system: $1+\varkappa(\nu) = T\,(\partial\nu/\partial\mathcal{P})_T$, where $\mathcal{P}$ denotes the pressure. Notice that in the framework of the grand canonical ensemble substantially similar relations can be easy derived by differentiation of DF in respect to the activity.

4. Invariance group of generating functional of historical correlations

Now, let us show that solution to equation (2.13) has invariance properties quite similar to (3.9). Since initial condition to this equation (see (2.11)) does not depend on variables $\psi = \psi(\mathbf{r},\mathbf{p})$ and ν at all, solution to is is completely determined by structure of operators $\widehat{\mathcal{L}}$ and $\widehat{\mathcal{L}}\,'$ and conditions (2.12). The latter formally allow to extend functional $\mathcal{V}\{t,\mathbf{R},\mathbf{P},\psi\,|\mathbf{R}_0;\nu\}$ (like $\mathcal{C}$ before) to arguments $\sigma+\psi(\mathbf{r},\mathbf{p})$, with $\sigma=\mathrm{const}$, in place of $\psi(\mathbf{r},\mathbf{p})$. The fact that limit in (2.12) is achieved fast enough to indeed ensure this extension can be confirmed afterwards. Besides, thanks to (2.12) variable $\psi(x_1)$ in expression $\widehat{\mathcal{L}}\,\mathcal{V}$ inside (2.13) (see definition (2.6) of the operator $\widehat{\mathcal{L}}$) can be shifted by arbitrary constant:

$$\int_1 \psi(x_1)\,\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{r}_1}\,\frac{\delta\mathcal{V}}{\delta\psi(x_1)} \;=\; \int_1 [\,a+\psi(x_1)\,]\,\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{r}_1}\,\frac{\delta\mathcal{V}}{\delta\psi(x_1)}\;\;,$$

where $a=\mathrm{const}$, for instance, $a=1$. This is important difference of $\widehat{\mathcal{L}}\,\mathcal{V}$ from $\widehat{\mathcal{L}}\,\mathcal{F}$. Consequently, taking in mind action of $\widehat{\mathcal{L}}$ onto $\mathcal{V}$, one can write

$$\widehat{\mathcal{L}}\left(\sigma+\psi\,,\frac{\delta}{\delta\psi}\right) \;=\; \widehat{\mathcal{L}}\left(\frac{\psi}{1+\sigma}\,,\frac{\delta}{\delta\,[\,\psi/(1+\sigma)\,]}\right) \tag{4.1}$$

Further, let us carefully consider operator $\widehat{\mathcal{L}}\,'$ (see also (2.13)). In contrast to $\widehat{\mathcal{L}}$, it depends on the density ν . Nevertheless, with the help of equality (3.8) it is easy to make sure that it obeys the same relation if transformation of argument $\psi(\mathbf{r},\mathbf{p})$ is accompanied by transformation of argument ν in accordance with (3.6) and (3.3):

$$\widehat{\mathcal{L}}\,'\left(\nu\,,\,\sigma+\psi\,,\frac{\delta}{\delta\psi}\right) \;=\; \widehat{\mathcal{L}}\,'\left(\upsilon(\sigma,\nu)\,,\,\frac{\psi}{1+\sigma}\,,\frac{\delta}{\delta\,[\,\psi/(1+\sigma)\,]}\right) \tag{4.2}$$

Formulas (4.1) and (4.2) just imply the noted invariance property of solutions of (2.13):

$$\mathcal{V}\{t,\mathbf{R},\mathbf{P},\,\sigma+\psi\,|\,\mathbf{R}_0;\,\nu\}\,=\,\mathcal{V}\left\{t,\mathbf{R},\mathbf{P},\,\frac{\psi}{1+\sigma}\,|\,\mathbf{R}_0;\,\upsilon(\sigma,\nu)\right\} \tag{4.3}$$

or, equivalently and similarly to (3.9),

$$\widehat{\mathcal{T}}(\sigma)\,\mathcal{V}\{t,\mathbf{R},\mathbf{P},\,\psi\,|\,\mathbf{R}_0;\,\nu\}\,\equiv\,\mathcal{V}\{t,\mathbf{R},\mathbf{P},\,\frac{1+\psi}{1+\sigma}-1\,|\,\mathbf{R}_0;\,\upsilon(\sigma,\nu)\}\,=$$
$$=\,\mathcal{V}\{t,\mathbf{R},\mathbf{P},\,\psi\,|\,\mathbf{R}_0;\,\nu\}\;\;, \tag{4.4}$$

where left inequality together with (3.6) and (3.3) defines action of the above described group onto GF of historical correlations. Expansion of (4.3) into series over ψ yields

$$V_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;\,\upsilon(\sigma,\nu))\,=\,V_0(t,\mathbf{R},\mathbf{P}|\,\mathbf{R}_0;\,\nu)\,+ \tag{4.5}$$
$$+\sum_{n=1}^{\infty}\frac{\nu^n\sigma^n}{n!}\int_1\!\!...\!\int_n V_n(t,\mathbf{R},\mathbf{r}^{(n)},\mathbf{P},\mathbf{p}^{(n)}|\,\mathbf{R}_0;\,\nu)\;\;,$$

$$\left[\frac{\upsilon(\sigma,\nu)}{(1+\sigma)\nu}\right]^k V_k(t,\mathbf{R},\mathbf{r}^{(k)},\mathbf{P},\mathbf{p}^{(k)}|\mathbf{R}_0;\,\upsilon(\sigma,\nu))\,=\,V_k(t,\mathbf{R},\mathbf{r}^{(k)},\mathbf{P},\mathbf{p}^{(k)}|\mathbf{R}_0;\,\nu)\,+$$
$$+\sum_{n=1}^{\infty}\frac{\nu^n\sigma^n}{n!}\int_{k+1}\!\!...\!\int_{k+n} V_{k+n}(t,\mathbf{R},\mathbf{r}^{(k+n)},\mathbf{P},\mathbf{p}^{(k+n)}|\mathbf{R}_0;\,\nu) \tag{4.6}$$

Corresponding infinitesimal (in respect to σ) relations are similar to (3.11):

$$\left\{n\,\varkappa(\nu)\,+\,[\,1+\varkappa(\nu)\,]\,\nu\,\frac{\partial}{\partial\nu}\right\}\,V_n(t,\mathbf{R},\mathbf{r}^{(n)},\mathbf{P},\mathbf{p}^{(n)}|\mathbf{R}_0;\,\nu)\,= \tag{4.7}$$
$$=\,\nu\int_{n+1} V_{n+1}(t,\mathbf{R},\mathbf{r}^{(n+1)},\mathbf{P},\mathbf{p}^{(n+1)}|\mathbf{R}_0;\,\nu)$$

Formulas (4.5)-(4.6) can be interpreted as "virial expansions" of probabilistic law of BP's random wandering and historical correlations between BP and medium, with those difference from usual virial expansions of thermodynamic quantities [13] or kinetic coefficients [14] that here decrements of the density do figure instead of its full value. However, in the limit $\nu\rightarrow 0$, $\sigma\rightarrow\infty$, $\nu\sigma=\text{const}$ these relations take quite usual form. The simplest of them, (4.5), recently was obtained [12, 15, 16] in other way, starting from the "generalized fluctuation-dissipation relations" [17, 18].

As far as I know, exact relations of this kind never before were under consideration. It would be rather hard to extract equalities (4.7) (all the more, (4.5)-(4.6)) directly from the BBGKY equations (2.2). This is possible only in the case of "BP in ideal gas" (the reader can try to see how (4.7) follows directly from equations (2.15) for CF).

5. On principal consequences from the virial relations

All the exact "virial relations" (4.5)-(4.7) are automatically satisfied by exact solution to BBGKY equations. Therefore these relations can be applied to "testing of statistical hypotheses" about the solution or constructing approximations to it. Moreover, in the just mentioned limit $\nu \rightarrow 0$, $\sigma \rightarrow \infty$, $\nu\sigma = \nu' = \text{const}$, with the help of formulas (3.3), (3.4) and (3.6), it is easy to transform equalities (4.5)-(4.6) into explicit formal representation of exact solution of BBGKY hierarchy for $V_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}|\mathbf{R}_0;\, \nu')$ as a power series in respect to ν'.

It should be emphasized that (4.5)-(4.6) connect random walks of BP in two media whose densities may form arbitrary large or arbitrary small ratio, $\upsilon(\sigma, \nu)/\nu$. Therefore, any cutting off the series in (4.5)-(4.6) would present not an approximate but incorrect result. This means that from the viewpoint of exact theory all historical correlations always are equally significant. Even in the "Boltzmann-Grad limit" ("dilute gas limit") when gas parameters tend to zero, $4\pi r_a^3\nu/3 \rightarrow 0$, $4\pi r_b^3\nu/3 \rightarrow 0$ (with $r_{a,b}$ standing for radii of interactions of atoms and BP) while free paths $\Lambda_b = (\pi r_b^2\nu)^{-1}$ and $\Lambda_a = (\pi r_a^2\nu)^{-1}$ stay fixed, or in the limit of ideal gas (where $\Lambda_a = \infty$ but Λ_b is finite). In both cases, formulas (4.5)-(4.7) simplify to

$$\frac{\partial^k V_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}|\, \mathbf{R}_0;\, \nu)}{\partial \nu^k} = \int_{k+1} \dots \int_{k+n} V_{k+n}(t, \mathbf{R}, \mathbf{r}^{(k+n)}, \mathbf{P}, \mathbf{p}^{(k+n)}|\mathbf{R}_0;\, \nu) \quad (5.1)$$

We must conclude that Boltzmann's kinetics which does not know correlations (except may be two-particle one) is not true "zero-order approximation" in respect do density.

As an illustration, let us consider BP in ideal gas and apply relations (5.1) to test "statistical hypothesis" that a correct approximate solution of exact equations (2.15) can be obtained under neglect of three-particle and higher correlations. Such hypothesis always is (directly or indirectly) involved into derivation of kinetic equations for "sufficiently rarefied" gas. Examples can be found e.g. in [9, 10, 14, 19, 20] [3]. Setting $V_2 = 0$ in the second ($n = 1$) of equations (2.15) and then inserting result of its integration to the first one ($n = 0$) we come to closed Boltzmann-Lorentz kinetic equation [19, 20] for $V_0(t, \mathbf{R}, \mathbf{P}|\, \mathbf{R}_0;\, \nu)$. Asymptotic of solution to this equation at $t \gg \tau = \Lambda_b/v_0$ (with $v_0 \sim \sqrt{T/M}$) is wittingly Gaussian:

$$V_0(t, \Delta\mathbf{R}; \nu) \equiv \int V_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; \nu)\, d\mathbf{P} \;\rightarrow\; \frac{\exp\left(-\Delta\mathbf{R}^2/4Dt\right)}{(4\pi Dt)^{\,3/2}} \quad , \tag{5.2}$$

where D is BP's diffusivity, $D = v_0\Lambda_b \propto \nu^{-1}$. Undoubtedly, this is a complicated function of the density ν . At the same time, in the view of exact relations (5.1) the statement $V_2 = 0$ implies that $V_0(t, \Delta\mathbf{R};\, \nu)$ should be purely linear function of ν !

So strong discrepancy prompts that our hypothesis is erroneous, asymptotic (5.2) is doubtful, and thus we should return to BBGKY equations. More correct approach to their approximate solving, with including correlations of any order, was suggested in [8] (or see [22]) and developed in [23]. It confirmed the guess [24] that actual molecular random walk represents a diffusive random process possessing scaleless "flicker" (i.e. with $1/f$ -type spectrum [7]) fluctuations of diffusivity (as well as mobility) of BP. In corresponding asymptotic of $V_0(t, \Delta\mathbf{R};\, \nu)$, in contrary to (5.2), the exponential is replaced by a function with power-law long tails (cut off at distances $\sim v_0 t$) [23]:

$$V_0(t, \Delta\mathbf{R};\, \nu) \;\rightarrow\; \frac{\Gamma(7/2)}{[4\pi D\, t\,]^{\,3/2}} \left[1 + \frac{\Delta\mathbf{R}^2}{4D\, t}\right]^{-7/2} \Theta\left(\frac{|\Delta\mathbf{R}|}{v_0 t}\right) \quad , \tag{5.3}$$

where $\Theta(x) \approx 1$ at $x < 1$ and $\Theta(x) \rightarrow 0$ at $x > 1$ in a very fast way.

[3] The work [20] on gas of hard spheres gave example of illusory discard of correlations, as it is discussed in [21].

Origin of the diffusivity fluctuations is trivial. Heuristically, that is indifference of the system to a number and relative frequency of BP's collisions with atoms (all the more, to distribution of collisions over impact parameter values) [8, 22]. At that, higher historical correlations described by $V_{n>1}$ are caused by complicity of particles in (uncontrolled and therefore scaleless and may be non-ergodic) fluctuations of relative frequency of BP's collisions (see also [12, 16, 21, 23]).

Let us demonstrate that one can come to analogous conclusions without solving BBGKY equations but instead resting upon their invariance group and besides the trivial fact that all the DF F_n always are non-negative.

From non-negativity of F_1 and identity (2.10) we have

$$V_0(t,\Delta\mathbf{R};\,\nu)\int_\Omega F_1^{(eq)}(\mathbf{r}|\mathbf{R};\nu)\,d\mathbf{r}\,+\int_\Omega V_1(t,\mathbf{R},\mathbf{r}|\mathbf{R}_0;\,\nu)\,d\mathbf{r}\,\geq\,0\;\;, \tag{5.4}$$

where $V_1(t,\mathbf{R},\mathbf{r}|\mathbf{R}_0;\,\nu)\,\equiv\,\int\int\,V_1(t,\mathbf{R},\mathbf{r},\mathbf{P},\mathbf{p}|\mathbf{R}_0;\,\nu)\;d\mathbf{p}\,d\mathbf{P}$, and Ω is any region in the space of vectors $\mathbf{r}-\mathbf{R}$. Introduce $\Omega(\delta,t,\Delta\mathbf{R};\nu)\equiv\Omega(\delta)$ to be minimum (in the sense of volume) of all regions Ω what satisfy condition

$$\left|\int_\Omega V_1\,d\mathbf{r}\,-\int V_1\,d\mathbf{r}\right|\,\leq\,\delta\left|\int V_1\,d\mathbf{r}\right|\;\;, \tag{5.5}$$

where $0<\delta<1$. One can easy justify that (5.4) and (5.5) together imply inequality

$$V_0(t,\Delta\mathbf{R};\,\nu)\int_{\Omega(\delta)}F_1^{(eq)}(\mathbf{r}|\mathbf{R};\nu)\,d\mathbf{r}\,+\,(1-\delta)\int V_1(t,\mathbf{R},\mathbf{r}|\mathbf{R}_0;\,\nu)\,d\mathbf{r}\;\geq\;0 \tag{5.6}$$

Combining it with exact virial relation (4.7) for $n\,=\,0$ and taking into account the equality $1+\varkappa(\nu)\,=\,T\,(\partial\nu/\partial\mathcal{P})_T$ (see Section 3) after clear reasonings one obtains

$$T\,\frac{\partial V_0(t,\Delta\mathbf{R};\,\nu)}{\partial\mathcal{P}}\,+\,\overline{\Omega}(t,\Delta\mathbf{R};\,\nu)\;V_0(t,\Delta\mathbf{R};\,\nu)\,\geq\,0\;\;, \tag{5.7}$$

where quantity $\overline{\Omega}(t,\Delta\mathbf{R};\,\nu)$ is defined by

$$\overline{\Omega}(t,\Delta\mathbf{R};\,\nu)\;=\;\min_{0<\delta<1}\,\frac{1}{1-\delta}\int_{\Omega(\delta)}F_1^{(eq)}(\mathbf{r}|\,\mathbf{R};\nu)\,d\mathbf{r}\;\approx\;\min_{0<\delta<1}\frac{\Omega(\delta,t,\Delta\mathbf{R};\nu)}{1-\delta} \tag{5.8}$$

According to the aforesaid, if $V_1(t,\mathbf{R},\mathbf{r}|\mathbf{R}_0;\,\nu)$ as a function of $\mathbf{r}$ (at given other arguments) has constant sign, then $\overline{\Omega}(t,\Delta\mathbf{R};\,\nu)$ represents volume occupied by the pair correlation or, briefly, “pair correlation volume”. Otherwise $\overline{\Omega}(t, \Delta\mathbf{R};\, \nu)$ is something smaller than this volume.

Now discuss hypothetical asymptotic (5.2) from the viewpoint of inequality (5.7). It says that the hypothesis can be true only if

$$\nu\,\overline{\Omega}(t, \Delta\mathbf{R};\, \nu) \,\geq\, -\,\nu T\,\frac{\partial \ln D}{\partial \mathcal{P}}\left(\frac{\Delta\mathbf{R}^2}{4Dt}-\frac{3}{2}\right) \,\rightarrow\, \frac{\Delta\mathbf{R}^2}{4Dt}-\frac{3}{2}\;, \tag{5.9}$$

where last expression concerns dilute gas. In other words, if quantity $\nu\,\overline{\Omega}(t, \Delta\mathbf{R};\, \nu)$, which is the pair correlation volume measured in units of specific volume per one atom, $1/\nu$, is not bounded above. In opposite, if it is bounded above,

$$\nu\,\overline{\Omega}(t, \Delta\mathbf{R};\, \nu) \,\leq\, c_1 \,=\, \text{const}\;, \tag{5.10}$$

then Gaussian asymptotic (5.2) is forbidden. Instead, inequality (5.7) allows for a generalized diffusion law as, for instance,

$$V_0(t, \Delta\mathbf{R};\, \nu) \,\rightarrow\, \frac{1}{(4\pi Dt)^{3/2}}\,\Psi\left(\frac{\Delta\mathbf{R}^2}{4Dt}\right)\,\Theta\left(\frac{|\Delta\mathbf{R}|}{v_0 t}\right)\;, \tag{5.11}$$

where function $\Psi(z)$ should satisfy inequality

$$z\,\frac{d\Psi(z)}{dz} \,+\, \alpha\,\Psi(z) \,\geq\, 0\;,\quad \alpha \,\equiv\, \frac{3}{2} \,+\, c_1\left[-\,\nu T\,\frac{\partial \ln D}{\partial \mathcal{P}}\right]^{-1} \tag{5.12}$$

(supposing that D falls when pressure grows). Consequently, $\Psi(z\rightarrow\infty) \,\propto\, 1/z^{\alpha}$. In the case of gas, $\alpha = 3/2 + c_1$. Formula (5.3) corresponds to $c_1 = \nu\overline{\Omega} = 2$.

Hence, the theory inevitably leads to statistical correlations which have unlimited extension either in space, as under variant (5.9), or in time, as under alternative variant (5.10). It remains to ascertain what of the variants is closer to exact solution of BBGKY equations. From physical point of view, the second one certainly is preferable, at least if speak about gas. Indeed, as it is clear from equations (2.15), a source of correlations between BP and atoms is their collisions. A collision realizes at such disposition of BP and atom when vector $\mathbf{r}-\mathbf{R}$ lies in the “collision cylinder” which is oriented in parallel to the relative velocity $\mathbf{p}/m - \mathbf{P}/M$ and has radius $\approx r_b$. At that distance between colliding particles should not be much greater than $\Lambda = \min\,(\Lambda_a, \Lambda_b)$, since otherwise their collision almost surely will be prevented by an encounter with the rest of atoms. Consequently, at any values of momenta (all the more, at any t and $\Delta\mathbf{R}$) it is natural to estimate the pair correlation volume as $\overline{\Omega} \approx 2\Lambda\,\pi r_b^2$. If BP is mere marked atom [23], then $\Lambda = \Lambda_b$ and $\overline{\Omega} \approx 2\Lambda_b\,\pi r_b^2 = 2/\nu$. As the result, we arrive to (5.10) with $c_1 \approx 2$.

6. Conclusion

Thus, to resume, the problem about thermodynamically equilibrium random walk of a molecular "Brownian" particle (BP) in a fluid was formulated as a problem of classical statistical mechanics of a system of (infinitely) many particles. Corresponding BBGKY equations for distribution functions (DF) and equation for their generating functional were considered in terms of correlation functions (CF) introduced so that they extract statistical correlations between total path of BP during all its observation time and current state of the medium ("historical correlations"). We showed (in case of Gibbs canonical ensemble) that generating functionals of both equilibrium DF and time-dependent CF are invariant in respect to definite continuous group of transformations of their arguments including density of the medium (mean concentration of particles).

The found invariance group produces a sequence of exact "virial relations" which connect full sets of DF or CF taken at different values of the density and therefore can serve as quality test of approximate solutions of the BBGKY equations. In this respect, we demonstrated that conventional "Boltzmannian" approximation to kinetics of BP in dilute gas (or ideal gas) is incorrect. The matter is that it rejects correlations of third and higher orders, while actually correlations of any order are equally important, even (and most of all) under the Boltzmann-Grad limit. The virial relations automatically allow for all the correlations and therefore imply significant restrictions on possible forms of probabilistic distribution of the BP's path. In particular, they rather surely (especially in case of dilute gas) forbid Gaussian asymptotic of this distribution. What is possible instead of it is an automodel diffusive asymptotic possessing power-law long tails (cut off at ballistic flight length). This conclusion well agrees with previous approximate solutions of BBGKY equations [8, 22, 23]. It means that in real gas random BP's trajectories are so much unique that, in contrast to the Lorentz gas, they can not be divided into statistically independent constituent parts. In other words, they can not be imitated by "dice tosses". In this sense actual molecular random walk is non-ergodic [7, 22, 23, 24].

In should be noted that results of this work can be easily extended to thermodynamically non-equilibrium walk under influence of an external force applied to BP from start of its observation (in this respect see [12, 16, 22]). From the other hand, it would be interesting to generalize the mentioned invariance group to more usual problems where not some select particles but hydrodynamic fields are in the centre of attention.

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References

[1] Ya. G. Sinai, Russian Mathematical Surveys, **25**, No.2 (1970).
[2] N. S. Krylov. Works on the foundations of statistical physics. Princeton, 1979 [Russian original: USSR Academy of Sciences Publ., Moscow-Leningrad, 1950].
[3] A. N. Kolmogorov. Fundamental concepts of probability theory. Moscow, 1936 (in Russian) [English transl.: Foundations of the theory of probability. Chelsea, New York, 1956].
[4] David Ruelle. Chance and chaos. Princeton, 1991.
[5] G. A. Galperin, A. N. Zemlyakov. Mathematical billiards. Moscow, Nauka, 1990.
[6] V. I. Arnold and A. Avez. Ergodic problems of classical mechanics. Addison-Wesley, Redwood City, 1989.
[7] G. N. Bochkov and Yu. E. Kuzovlev, Sov.Phys.-Uspekhi **26**, 829 (1983).
[8] Yu. E. Kuzovlev, Sov.Phys.- JETP **67**, No. 12, 2469 (1988).
[9] N. N. Bogolyubov. Problems of dynamical theory in statistical physics. North-Holland, 1962.
[10] V. P. Silin. Introduction to kinetic theory of gases. Moscow, PI RAS, 1998 (in Russian).
[11] D. Ruelle. Statistical mechanics. Rigorous results. Benjamin, New-York-Amsterdam, 1969.
[12] Yu. E. Kuzovlev, Math. Physics Archive (www.ma.utexas.edu) : 07-309 (2007).
[13] L. D. Landau and E. M. Lifshitz. Statistical physics. Part I. Moscow, Nauka, 1976.
[14] E. M. Lifshitz and L. P. Pitaevski. Physical kinetics. Pergamon, 1981.
[15] Yu. E. Kuzovlev, arXiv : 0710. 3831 ; 0803.0301 ; 0804.2023 .
[16] Yu. E. Kuzovlev, arXiv : 0802. 0288 .
[17] G. N. Bochkov and Yu. E. Kuzovlev, Sov.Phys.-JETP **45**, 125 (1977); **49**, 543 (1979); **52**, No. 12 (1980).
[18] G. N. Bochkov and Yu. E. Kuzovlev, Physica **A 106** (1981) 443, 480.
[19] P. Resibois and M. de Leener. Classical kinetic theory of fluids. Wiley, New-York, 1977.
[20] H. van Beijeren, O. E. Lanford III, J. L. Lebowitz, and H. Spohn, J. Stat. Phys. **22**, 237 (1979).
[21] Yu. E. Kuzovlev, arXiv : 0806. 4157 .
[22] Yu. E. Kuzovlev, arXiv : cond-mat/9903350 .
[23] Yu. E. Kuzovlev, arXiv : cond-mat/0609515 .
[24] Yu. E. Kuzovlev and G. N. Bochkov, Radiophysics and Quantum Electronics **26**, No. 3, 228 (1983); **27**, No.9 (1984).

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