Molecular random walks in a fluid and an invariance group of the Bogolyubov generating functional equation

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Abstract

The problem of statistics of molecular random walks in a classical fluid is analyzed by means of the BBGKY hierarchy of equations reformulated in terms of the Bogolyubov evolution equation for generating functional of many-particle distribution functions. A proper equivalent set of correlation functions is introduced so that all they are integrable, vanish in statistical equilibrium, otherwise accumulate statistical information about history of collisions of a “molecular Brownian particle” (test molecule) with other molecules of the fluid. An exact evolution equation for generating functional of such correlation functions is derived. Then it is shown that time-dependent solution to this equation, as well as a properly defined generating functional of static thermodynamically equilibrium correlations, possesses invariance with respect to a definite group of transformations of independent variables of the functional, if density of the fluid (number of molecules per unit volume) is treated as one of the independent variables. Such invariance results in infinitely many exact relations between the correlation functions and probability distribution of path of the molecular Brownian particle. Even simplest of these relations suggest significant restrictions on a profile of the path probability distribution, even without literal solving the BBGKY hierarchy.

Key words: diffusion, molecular random walks, Brownian motion, BBGKY hierarchy, Bogolyubov generating functional, Bogolyubov functional equation, kinetic theory of fluids

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1. Introduction

Everybody knows that all thermodynamic and kinetic properties of a fluid are determined by thermal motion of its atoms or molecules. This motion by its nature is unbound and represents a “random walk” or, in other words, “Brownian motion”. What kind of statistics characterizes it?

Strangely enough, this principally interesting question never was a special issue of those fundamental approach to statistical mechanics of fluids what originated from the Bogolyubov’s book [1] and resulted in the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) infinite hierarchy of equations [12345]. Unfortunately, next work of Bogolyubov and other theorists was concentrated at not conscientious solving these equations but forcible reducing them to a single “kinetic equation” for one-particle distribution function, at that being guided by the old Boltzmann’s “molecular chaos” hypothesis. The latter assumes that two molecules entering into collision are statistically independent one on another, at least in case of dilute gas.
Such hypotheses rise up from naive identifying dynamical independence of particles and statistical one, in spite of that the first concerns individual phase trajectory of a dynamical system while the second statistical ensemble of trajectories corresponding to some ensemble of their initial conditions. But Krylov in his remarkable book [6] (first published in 1950) finally proved that dynamical independence gives no grounds for statistical one. Although, to tell the truth, this is clear as it is. Analogously, in a statistical ensemble of the mankind histories any two contemporaries would have somehow statistically dependent destinies even if they reside in different continents and do not influence one another. All the more if they do. Saying about gases, for example, in [7] (see also [8]) it was shown that in spatially non-uniform statistical ensemble the pair distribution function for atoms in pre-collision states does not reduce to one-particle distribution function, even under the limit of infinitely dilute gas (or so-called Boltzmann-Grad limit).

In fact, fortunately, the BBGKY hierarchy is self-consistent and has no need in extraneous hypotheses. It is quite another matter if a technique of its correct solving is in embryo. In respect to the above formulated question, an approximate approach was suggested in [7] (or see [8]). Its results were principally different from predictions of conventional theory operating with the Boltzmann and Boltzmann-Lorentz or similar equations [2,3,4,5] implied by the “molecular chaos” hypothesis. But since then no response to [7] was noticed. Hence, importance of the question still is not realized. This circumstance stimulated work [9] where due to simplification and improvement of method of [7] a whole probability distribution of Brownian path of a test atom was approximately found (instead of its four lowest statistical moments as in [7]). Recently in [10] and then in [11,12] a new approach to the same problem was developed which exploits the “generalized fluctuation-dissipation relations” [13,14]. A peculiar exact “virial expansion” for the probability distribution of Brownian path was obtained which allows to describe characteristic spatial profile of this distribution without any quantitative approximations at all. At that, results of [9] were confirmed.

Well, clearly, now considerations of the BBGKY hierarchy are next in turn to be improved. With this purpose, in the present paper we make use of the Bogolyubov’s formulation of the BBGKY hierarchy in terms of generating functional of many-particle distribution functions and evolution equation for this functional [1]. Notice that Bogolyubov himself analyzed stationary solution to this equation only, that is mere thermodynamically equilibrium functional, and in fact had not investigated its non-equilibrium time-dependent solutions. Apparently, because of this an interesting property of the generating functional and its evolution equation remained unnoticed, and we had to catch it.

The matter concerns (i) logarithmic variational derivative of the equilibrium functional, (ii) generating functional of properly introduced non-equilibrium $n$-particle “correlation functions” which together represent statistical correlations between a total previous path of the “molecular Brownian particle” (test atom) and current state of the fluid, and (iii) time evolution operator for this new functional. All these three objects turn out to be invariant with respect to definite continuous group of transformations of their independent variables. The latter are (i) arbitrary probe function defined in the 6D $\mu$-space and (ii) density of fluid (number of particles per unit volume).

It will be shown that this invariance property implies an infinite set of exact relations connecting the probability distribution of Brownian path and the correlation functions. A solution to the BBGKY hierarchy automatically satisfy all these relations. One of them coincides with the mentioned “virial expansion”. Therefore they present essential information about solution to the BBGKY hierarchy and even can prescribe it accurate to quantitative details. Let us go to these curious things.

2. Equations of molecular Brownian motion and Bogolyubov’s generating functional

Let a macroscopic box with volume $\Omega$ contains $N \gg 1$ identical atoms plus one more different but similar particle which will be under our special attention. The atoms have mass $m$, coordinates $\mathbf{r}_j$ and momenta $\mathbf{p}_j$ ($j = 1, 2, \ldots, N$) and all interact one with another by means of spherically symmetric potential $\Phi_\alpha(\mathbf{r}_j - \mathbf{r}_k) = \phi_\alpha(|\mathbf{r}_j - \mathbf{r}_k|/r_a)$. The additional particle has mass $M$, coordinate $\mathbf{R}$, momentum $\mathbf{P}$ and interacts with all atoms through spherically symmetric potential $\Phi_\beta(\mathbf{r}_j - \mathbf{R}) = \phi_\beta(|\mathbf{r}_j - \mathbf{R}|/r_b)$. Due to the interactions, this particle undergoes, along with atoms, a chaotic wandering, therefore we can name it “Brownian particle” (BP). We want to consider probability distribution of its position, $\mathbf{R}(t)$, assuming that
at some initial time moment, e.g. \( t = 0 \), it is certainly known: \( \mathbf{R}(t = 0) = \mathbf{R}_0 \).

On the contrary, personal coordinate of any concrete atom all the time is unknown and possesses nearly uniform probability distribution over \( \Omega \). In such situation, normalized particular distribution functions for the BP together with any \( n = 0, 1, 2, \ldots \) atoms, following Bogolyubov [1], can be written as

\[
D_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}) = \Omega^n F_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}|\mathbf{R}_0; \nu_0) ,
\]

where \( \mathbf{r}^{(n)} = \{ \mathbf{r}_1 \ldots \mathbf{r}_n \} \), \( \mathbf{p}^{(n)} = \{ \mathbf{p}_1 \ldots \mathbf{p}_n \} \), and new distribution functions \( F_n \) depend on \( \Omega \) through mean density (number of atoms per unit volume), \( \nu_0 = N/\Omega \), only. Argument \( \mathbf{R}_0 \) is added in order to remind of the mentioned initial condition for BP. At that

\[
F_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}|\mathbf{R}_0; \nu_0) = \Omega^n \int_{n+1} \ldots \int_{N} D_N(t, \mathbf{R}, \mathbf{r}^{(N)}, \mathbf{P}, \mathbf{p}^{(N)})
\]

with \( \int_{k \ldots} = \int \ldots \int d\mathbf{r}_k d\mathbf{p}_k \) and \( D_N \) being normalized probability distribution function of the whole system. This distribution function (DF) is solution to the Liouville equation

\[
\frac{\partial D_N}{\partial t} = [L_N + L_{N}^{\text{box}}] D_N
\]

with initial condition, in the framework of the Gibbs canonical statistical ensemble,

\[
D_N(t = 0, \ldots) = \delta(\mathbf{R} - \mathbf{R}_0) e^{-H_N/T} \left[ \int d\mathbf{R} \int d\mathbf{P} \int_{n+1} \ldots \int_{N} \delta(\mathbf{R} - \mathbf{R}_0) e^{-H_N/T} \right]^{-1}
\]

Symbol \( H_n \) here means Hamiltonian of system “\( n \) atoms plus BP in the box”, \( L_n + L_n^{\text{box}} \) is the Liouville operator corresponding to \( H_n \), and \( L_n \) is its autonomous box-independent part:

\[
\hat{L}_n = -\frac{\mathbf{P}}{M} \cdot \frac{\partial}{\partial \mathbf{R}} - \sum_{j=1}^{n} \frac{\mathbf{p}_j}{m} \cdot \frac{\partial}{\partial \mathbf{r}_j} + \sum_{j=1}^{n} \hat{L}_j^b + \sum_{1 \leq j < k \leq n} \hat{L}_{jk}^a ,
\]

where

\[
\hat{L}_j^b \equiv \nabla \Phi_b(\mathbf{r}_j - \mathbf{r}_j) \cdot \left( \frac{\partial}{\partial \mathbf{P}} - \frac{\partial}{\partial \mathbf{p}_j} \right) , \quad \hat{L}_{jk}^a \equiv \nabla \Phi_a(\mathbf{r}_j - \mathbf{r}_k) \cdot \left( \frac{\partial}{\partial \mathbf{p}_j} - \frac{\partial}{\partial \mathbf{p}_k} \right)
\]

and \( \nabla \Phi(\mathbf{r}) = \partial \Phi(\mathbf{r})/\partial \mathbf{r} \).

Choosing initial distribution in the form [1], we thus confine ourselves by investigation of random walk of the BP in a thermodynamically equilibrium fluid.

Under reasonable interaction potentials \( \phi_{a,b}(x) \) (fast enough tending to infinity at \( x \to 0 \) and to zero at \( x \to \infty \)) the particular DF \( F_n \) have definite “thermodynamical limit” when walls of the box withdraw to infinity, \( N \to \infty \) and \( \Omega \to \infty \) at \( N/\Omega = \nu_0 = \text{const} \). In this limit the Liouville equation produces [1] infinite hierarchy of the BBGKY equations for \( F_n \) [2,3,4,5]. In our case it appears as

\[
\frac{\partial F_0}{\partial t} = -\frac{\mathbf{P}}{M} \cdot \frac{\partial F_0}{\partial \mathbf{R}} + \nu_0 \int_1 \hat{L}_1^b F_1 ,
\]

\[
\frac{\partial F_1}{\partial t} = \hat{L}_1 F_1 + \nu_0 \int_2 \hat{L}_2^b F_2 + \nu_0 \int_2 \hat{L}_{12}^a F_2 ,
\]

\[
\frac{\partial F_n}{\partial t} = \hat{L}_n F_n + \nu_0 \int_{n+1} \hat{L}_{n+1}^b F_{n+1} + \nu_0 \sum_{j=1}^{n} \int_{n+1} \hat{L}_{j,n+1}^a F_{n+1}
\]
The only difference of these equations from routine ones \[1\], \[2\], \[3\], \[4\], \[5\] is presence of a distinct particle, namely, the BP. Integration over its variables eliminates equation \[2\] and turns \[3\]–\[1\] to simplest BBGKY hierarchy for a system of equivalent particles. According to \[1\], initial conditions for our hierarchy are

\[
\begin{align*}
F_0(0, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; \nu_0) &= \delta(\mathbf{R} - \mathbf{R}_0) G_M(\mathbf{P}) , \\
F_n(0, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}|\mathbf{R}_0; \nu_0) &= \delta(\mathbf{R} - \mathbf{R}_0) F_n^{(eq)}(\mathbf{r}_1 \ldots \mathbf{r}_n|\mathbf{R}; \nu_0) G_M(\mathbf{P}) \prod_{j=1}^{n} G_m(\mathbf{p}_j) ,
\end{align*}
\]

where

\[
G_m(\mathbf{p}) = (2\pi Tm)^{-3/2} \exp(-\mathbf{p}^2/2Tm)
\]
is Maxwell momentum distribution of a particle with mass \(m\), and \(F_n^{(eq)}(\mathbf{r}_1 \ldots \mathbf{r}_n|\mathbf{R}; \nu_0)\) is usual thermodynamically equilibrium joint DF of coordinates of \(n\) atoms and BP corresponding to the canonical ensemble. Of course, eventually we are most interested in evolution of \(F_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; \nu_0)\) and especially in probability distribution of BP’ path,

\[
V_0(t, \Delta \mathbf{R}; \nu_0) = \int F_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; \nu_0) d\mathbf{P} \quad (\Delta \mathbf{R} \equiv \mathbf{R} - \mathbf{R}_0)
\]

It is important that \(F_n\) by their definition naturally satisfy weakening of correlations between distant particles. Under initial conditions \[1\] and \[5\] this property concretizes to

\[
\begin{align*}
F_1(t, \mathbf{r}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1|\mathbf{R}_0; \nu_0) &\rightarrow F_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; \nu_0) G_m(\mathbf{p}_1) , \\
F_1^{(eq)}(\mathbf{r}_1|\mathbf{R}_0; \nu_0) &\rightarrow 1 , \\
F_n(\ldots \mathbf{r}_k \ldots |\mathbf{p}_k \ldots ) &\rightarrow F_n(\ldots \mathbf{r}_k \ldots ) G_m(\mathbf{p}_k) , \\
F_n^{(eq)}(\ldots \mathbf{r}_k \ldots ) &\rightarrow F_n^{(eq)}(\ldots \mathbf{r}_k \ldots ) ,
\end{align*}
\]

when \(\mathbf{r}_1 \rightarrow \infty\) and \(\mathbf{r}_k \rightarrow \infty\), respectively.

It will be convenient, again following \[1\], to collect all the DF into one generating functional

\[
\mathcal{F}\{t, \mathbf{R}, \mathbf{P}, \psi|\mathbf{R}_0; \nu_0\} = F_0(t, \mathbf{R}, \mathbf{P}|\mathbf{R}_0; \nu_0) + \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int_1 \ldots \int_n F_n(t, \mathbf{R}, \mathbf{r}^{(n)}, \mathbf{P}, \mathbf{p}^{(n)}|\mathbf{R}_0; \nu_0) \prod_{j=1}^{n} \psi(\mathbf{r}_j, \mathbf{p}_j)
\]

and correspondingly all the equations \[2\]–\[1\] into single equation for this functional:

\[
\begin{align*}
\frac{\partial \mathcal{F}}{\partial t} + \frac{\mathbf{P}}{M} \cdot \frac{\partial \mathcal{F}}{\partial \mathbf{R}} &= \hat{L} \left( \psi, \frac{\delta}{\delta \psi} \right) \\
&= - \int_1 \psi(\mathbf{x}_1) \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} \frac{\delta \mathcal{F}}{\delta \psi(\mathbf{x}_1)} + \\
&+ \int_1 \left[ 1 + \psi(\mathbf{x}_1) \right] \frac{\delta \mathcal{F}}{\delta \psi(\mathbf{x}_1)} + \frac{1}{2} \int_1 \int_2 \left[ 1 + \psi(\mathbf{x}_1) \right] \left[ 1 + \psi(\mathbf{x}_2) \right] \frac{\delta^2 \mathcal{F}}{\delta \psi(\mathbf{x}_1) \delta \psi(\mathbf{x}_2)}
\end{align*}
\]

For brevity here and below single argument \(x_j\) deputizes for the pair \(\{\mathbf{r}_j, \mathbf{p}_j\}\).

Equation \[7\] becomes direct analogue of equation \(7.9\) from \[1\] if replace functional argument \(u(x)\) by \(\nu_0 \psi(x)\) and use obvious identity \(\int_1 \int_2 \hat{L}_1^2 \cdots = 0\) \[1\]. Initial conditions \[5\] take the form

\[
\mathcal{F}\{0, \mathbf{R}, \mathbf{P}, \psi|\mathbf{R}_0; \nu_0\} = \delta(\mathbf{R} - \mathbf{R}_0) G_M(\mathbf{P}) \mathcal{F}^{(eq)}\{\phi|\mathbf{R}; \nu_0\}
\]

where generating functional for the equilibrium DF and new argument for this functional are introduced:

\[
\mathcal{F}^{(eq)}\{\phi|\mathbf{R}; \nu_0\} = 1 + \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int_1 \ldots \int F_n^{(eq)}(\mathbf{r}_1 \ldots \mathbf{r}_n|\mathbf{R}; \nu_0) \prod_{j=1}^{n} \phi(\mathbf{r}_j) d\mathbf{r}_j , \\
\phi(\mathbf{r}) \equiv \int \psi(\mathbf{r}, \mathbf{p}) G_m(\mathbf{p}) d\mathbf{p}
\]
From physical point of view, expression [S] represents thermodynamical equilibrium, since fixation of start BP's position in no way disturbs it. Nevertheless, [S] is not a fixed point of equation (7). The latter will be achieved at \( t \to \infty \) only, when BP's position \( R(t) \) becomes completely uncertain. Hence, formal statistical equilibrium is presented by functional \( G_M(P) \mathcal{F}^{(eq)} \{ \phi(R; \nu_0) \} \), and we can write

\[
\left[ -\frac{P}{M} \cdot \frac{\partial \mathcal{F}}{\partial R} + \hat{\mathcal{L}} \left( \psi, \frac{\delta}{\delta \psi} \right) \right] G_M(P) \mathcal{F}^{(eq)} \{ \phi(R; \nu_0) \} = 0
\]  

(9)

This equation easy transforms into another one in terms of \( \phi(r) \) itself:

\[
\left[ \frac{\partial}{\partial r} + \frac{\nabla \Phi(\mathbf{r} - \mathbf{R})}{T} \right] \frac{\delta \mathcal{F}^{(eq)}}{\delta \phi(r)} = \frac{1}{T} \int \left[ 1 + \phi(\mathbf{r'}) \right] \nabla \Phi_a(\mathbf{r'} - \mathbf{r}) \frac{\delta^2 \mathcal{F}^{(eq)}}{\delta \phi(r) \delta \phi(r')} d\mathbf{r'}
\]  

(10)

This is analogue of equation (2.14) in [I]. As combined with boundary conditions at infinity [O] it quite unambiguously determines \( DF \mathcal{F}^{(eq)}_n \) and thus initial condition to equation (2).

3. Correlation functions and historical correlations

Though \( DF \mathcal{F}^{(eq)}_n \) and thus \( F_n(t = 0, \ldots) \) include all equilibrium inter-particle correlations and at \( t > 0 \) our system remains in equilibrium, nevertheless at \( t > 0 \) some excess correlations do arise, so that

\[
F_n(t, R_1 \ldots R_n, P_1 \ldots P_n | R_0; \nu_0) \neq F_0(t, R, P | R_0; \nu_0) F_n^{(eq)}(R_1 \ldots R_n | R; \nu_0) \prod_j G_m(p_j)
\]

as opposed to what one could think. To describe a difference between left and right-hand side here, let us introduce “correlation functions” (CF) \( V_n(t, R_1 \ldots R_n, P_1 \ldots P_n | R_0; \nu_0) \) and their generating functional

\[
\mathcal{V} \{ t, R, P, \psi | R_0; \nu_0 \} = V_0(t, R, P | R_0; \nu_0) + \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int \ldots \int V_n(t, R, \mathbf{r}^{(n)}, P, \mathbf{p}^{(n)} | R_0; \nu_0) \prod_{j=1}^{n} \psi(r_j, p_j)
\]

and define all them in the language of functionals be relation

\[
\mathcal{F} \{ t, R, P, \psi | R_0; \nu_0 \} = \mathcal{F}^{(eq)} \{ \phi | R_0; \nu_0 \} \mathcal{V} \{ t, R, P, \psi | R_0; \nu_0 \},
\]

(11)

where \( \phi(r) = \int \psi(r, p) G_m(p) dp \) as in [S]. The term “correlation functions” is traditionally used in statistical mechanics for various corrections to equilibrium or quasi-equilibrium distributions (see e.g. [2][3][4]). By this definition, in particular,

\[
F_0(t, R, P | R_0; \nu_0) = V_0(t, R, P | R_0; \nu_0),
\]

\[
F_1(t, R, R_1, P, P_1 | R_0; \nu_0) = F_0(t, R, P | R_0; \nu_0) F_1^{(eq)}(R_1 | R; \nu_0) G_m(p_1) + V_1(t, R, R_1, P, P_1 | R_0; \nu_0)
\]

(12)

Initial conditions [S] transform to

\[
V_n(t = 0, \ldots) = \delta_{n, 0} \delta(R - R_0), \quad \mathcal{V} \{ t = 0, R, P, \psi | R_0; \nu_0 \} = \delta(R - R_0),
\]

(13)

while the boundary conditions [O] prescribe

\[
V_{n>0}(t, \ldots r_k \ldots) \to 0 \quad \text{at} \quad r_k \to \infty
\]

(14)

It should be underlined that presence in \( V_1 \) of start position of BP, \( R_0 \), is principally important. As we already mentioned, if \( R_0 \) was unknown then all the DF would be invariable, that is all \( V_{n>0} \) would turn to zero. This remark highlights two peculiarities of excess correlations described by \( V_{n>0} \). First, they are essentially \textit{spatial} correlations. Second, they connect current positions of atoms with not merely current
position of BP but its total previous displacement, or path, \( R - R_0 \), during time interval \((0, t)\). By this reason we can name them “historical correlations”. Further we will see that their actual extent is very closely related to statistics of the BP’s path \( R - R_0 \).

Substitution of (11) to equation (7) yields, with accounting for identity (9), equation for the generating functional of correlation functions:

\[
\frac{\partial \mathcal{V}}{\partial t} + \frac{\mathbf{P}}{M} \frac{\partial \mathcal{V}}{\partial \mathbf{R}} = \mathcal{L} \left( \psi, \frac{\delta}{\delta \psi^*} \right) \mathcal{V} + \mathcal{L}^\prime \left( \nu_0, \psi, \frac{\delta}{\delta \psi^*} \right) \mathcal{V},
\]

where action of operator \( \mathcal{L} \) is described by expression (7) while action of new operator \( \mathcal{L}^\prime \) by

\[
\mathcal{L}^\prime \left( \nu_0, \psi, \frac{\delta}{\delta \psi^*} \right) \mathcal{V} = \left\{ \int [1 + \phi(\mathbf{r})] \nabla \Phi_b(\mathbf{R} - \mathbf{r}) \frac{\delta \ln \mathcal{F}^{(eq)}(\phi; \nu_0)}{\delta \phi(\mathbf{r})} d\mathbf{r} \right\} \left( \frac{\mathbf{P}}{MT} + \frac{\partial}{\partial \mathbf{P}} \right) \mathcal{V} + \int \int_1^2 \left[ 1 + \psi(x_1) \right] \left[ 1 + \psi(x_2) \right] \frac{\delta \ln \mathcal{F}^{(eq)}(\phi; \nu_0)}{\delta \phi(r_2)} G_m(\mathbf{p}_2) \frac{\delta \mathcal{V}}{\delta \psi(x_1)}
\]

So complicated expression is payment for simple initial condition (13). After that, variational derivatives of (15) at \( \psi = 0 \) give BBGKY equation in terms of the CF. The first of them looks quite similar to (2):

\[
\frac{\partial \mathcal{V}_0}{\partial t} = -\frac{\mathbf{P}}{M} \frac{\partial \mathcal{V}_0}{\partial \mathbf{R}} + \nu_0 \int \hat{L}_1 V_1
\]

Since \( \mathcal{V}_0 \equiv F_0 \), comparison of (17) with (2) shows that quasi-equilibrium part of the pair DF \( F_1 \), i.e. first right-hand term in (12), does not contribute to the collision term in (2), and collisions of BP with atoms are wholly represented by pair CF \( \mathcal{V}_1 \). The second BBGKY equation becomes

\[
\frac{\partial \mathcal{V}_1}{\partial t} = \hat{L}_1 V_1 + \nu_0 \int \hat{L}_2 V_2 + \nu_0 \int \hat{L}_12 [V_2 + F_1^{(eq)}(1) G_m(1) V_1(2) + F_1^{(eq)}(2) G_m(2) V_1(1)] + \]

\[
+ G_m(1) \left\{ \nabla \Phi_b(\mathbf{R} - \mathbf{r}_1) F_1^{(eq)}(1) + \nu_0 \int \nabla \Phi_b(\mathbf{R} - \mathbf{r}) C_2^{(eq)}(\mathbf{r}, \mathbf{r}_1; \mathbf{R}; \nu_0) d\mathbf{r} \right\} \left( \frac{\mathbf{P}}{MT} + \frac{\partial}{\partial \mathbf{P}} \right) \mathcal{V}_0
\]

with \( F_1^{(eq)}(\mathbf{k}) \equiv F_1^{(eq)}(\mathbf{k}| \mathbf{R}; \nu_0) \), \( V_1(\mathbf{k}) \equiv V_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_k| \mathbf{R}_0; \nu_0) \) and \( G_m(\mathbf{k}) \equiv G_m(\mathbf{p}_k) \). The function

\[
C_2^{(eq)}(\mathbf{r}_1, \mathbf{r}_2; \nu_0) \equiv F_2^{(eq)}(\mathbf{r}_1, \mathbf{r}_2| \mathbf{R}; \nu_0) - F_1^{(eq)}(\mathbf{r}_1| \mathbf{R}; \nu_0) F_1^{(eq)}(\mathbf{r}_2| \mathbf{R}; \nu_0)
\]
is pair CF of the fluid under given BP’s position.

4. Equilibrium generating functional and its invariant transformations

Next, consider more carefully the equilibrium generating functional \( \mathcal{F}^{(eq)} \). It is of interest for us here since operator (10) includes its logarithmic variational derivative. Let us write the latter as

\[
\frac{\delta \ln \mathcal{F}^{(eq)}(\phi; \nu_0)}{\delta \phi(\mathbf{r})} = \nu_0 C_{R}(\mathbf{r}, \phi| \mathbf{R}; \nu_0) =
\]

\[
= \nu_0 \left[ 1 + C_{1}^{(eq)}(\mathbf{r}| \mathbf{R}; \nu_0) + \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int \int \int C_{n+1}^{(eq)}(\mathbf{r}_1, \mathbf{r}_2| \mathbf{R}; \nu_0) \prod_{j=1}^{n} \phi(r_j) d\mathbf{r}_j \right],
\]

where \( C_{1}^{(eq)}(\mathbf{r}| \mathbf{R}; \nu_0) = F_1^{(eq)}(\mathbf{r}| \mathbf{R}; \nu_0) - 1 \), pair correlation function \( C_2^{(eq)}(\mathbf{r}, \mathbf{r}_1; \mathbf{R}; \nu_0) \) was presented just above, third-order correlation function or, to be precise, cumulant function is

\[
C_3^{(eq)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) = F_3^{(eq)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) + 2 F_1^{(eq)}(\mathbf{r}) F_2^{(eq)}(\mathbf{r}_1) F_1^{(eq)}(\mathbf{r}_2) -
\]

\[
- F_1^{(eq)}(\mathbf{r}) F_2^{(eq)}(\mathbf{r}_1, \mathbf{r}_2) - F_1^{(eq)}(\mathbf{r}_1) F_2^{(eq)}(\mathbf{r}, \mathbf{r}_2) - F_1^{(eq)}(\mathbf{r}_2) F_2^{(eq)}(\mathbf{r}, \mathbf{r}_1),
\]
for brevity omitting arguments \( R \) and \( \nu_0 \), and so on. Then equation (10) transforms to

\[
\left[ \frac{\partial}{\partial r} + \frac{\nabla \Phi_b(r - R)}{T} \right] C_{\text{eq}} \{ r, \phi | R; \nu_0 \} = \frac{1}{T} \int \left[ 1 + \frac{\phi(r')}{1 + \sigma} \right] \frac{\nabla \Phi_a(r' - r)}{\delta \phi(r')} \frac{\delta C_{\text{eq}} \{ r, \phi | R; \nu_0 \}}{\delta \phi(r')} \, dr' + \\
+ C_{\text{eq}} \{ r, \phi | R; \nu_0 \} \nu_0 \int \left[ 1 + \frac{\phi(r')}{1 + \sigma} \right] \frac{\nabla \Phi_a(r' - r)}{\delta \phi(r')} C_{\text{eq}} \{ r', \phi | R; \nu_0 \} \, dr'
\]

(20)

This nonlinear equation can not be solved in a closed form but it will help us to perceive important features of functional \( C_{\text{eq}} \).

With this purpose, first, notice that due to the DF’s asymptotic at infinity (6) at any reasonable potentials of atom-atom and atom-BP interactions, similar to (14),

\[
C_{n+1}^{(eq)}(r, r_1 \ldots r_n | R; \nu_0) \rightarrow 0 \quad \text{if} \quad r_j - r \rightarrow \infty ,
\]

\[
C_1^{(eq)}(r_1 | R; \nu_0) \rightarrow 0 \quad \text{if} \quad R - r_1 \rightarrow \infty ,
\]

\[
C_{n>1}^{(eq)}(r_1 \ldots r_n | R; \nu_0) \rightarrow C_{n>1}^{(eq)}(r_1 \ldots r_n | \nu_0) \quad \text{if} \quad R - r_j \rightarrow \infty ,
\]

where cumulant functions \( C_n^{(eq)}(r_1 \ldots r_n | \nu_0) \) describe fluid without BP and satisfy

\[
C_{n+1}^{(eq)}(r, r_1 \ldots r_n | \nu_0) \rightarrow 0 \quad \text{if} \quad r_j - r \rightarrow \infty
\]

Moreover, any of the cumulant functions \( C_{n>1}^{(eq)}(r_1 \ldots r_n | R; \nu_0) \) tend to zero at \( r_j \rightarrow \infty \) in so fast way that all they are integrable in respect to \( r_1 \ldots r_n \).

Consequently, functional \( C^{(eq)} \) keeps a sense when \( \phi(r) \) turns into nonzero constant, \( \phi(r) \rightarrow \sigma = \text{const} \), as well as when one replaces \( \phi(r) \) by \( \sigma + \phi(r) \) with \( \sigma = \text{const} \). Thus we can introduce function

\[
C(\sigma, \nu_0) = \lim_{R - r \rightarrow \infty} C^{(eq)} \{ r, \sigma | R; \nu_0 \} = 1 + \sum_{n=1}^{\infty} \frac{\nu_0^n \sigma^n}{n!} \int \ldots \int C_{n+1}^{(eq)}(r, r_1 \ldots r_n | \nu_0) \, dr_1 \ldots dr_n ,
\]

(22)

where, clearly, integrals actually do not depend on \( r \). Besides, introduce new functional

\[
C_{\sigma}^{(eq)} \{ r, \phi | R \} = \frac{C_{\text{eq}} \{ r, \sigma + \phi | R; \nu_0 \}}{lim_{R - r \rightarrow \infty} C_{\text{eq}} \{ r, \sigma | R; \nu_0 \}} = \frac{C_{\text{eq}} \{ r, \sigma + \phi | R; \nu_0 \}}{C(\sigma, \nu_0)}
\]

(23)

Under change \( \phi(r) \rightarrow \sigma + \phi(r) \) equation (20) evidently turns to equation for \( C_{\sigma}^{(eq)} \{ r, \phi | R \} \) as follows,

\[
\left[ \frac{\partial}{\partial r} + \frac{\nabla \Phi_b(r - R)}{T} \right] C_{\sigma}^{(eq)} \{ r, \phi | R \} = \frac{1}{T} \int \left[ 1 + \frac{\phi(r')}{1 + \sigma} \right] \frac{\nabla \Phi_a(r' - r)}{\delta \phi(r')} \frac{\delta C_{\sigma}^{(eq)} \{ r, \phi | R \}}{\delta \phi(r')} \, dr' + \\
+ C_{\sigma}^{(eq)} \{ r, \phi | R \} \nu_0 C(\sigma, \nu_0) \frac{1 + \sigma}{1 + \sigma} \int \left[ 1 + \frac{\phi(r')}{1 + \sigma} \right] \frac{\nabla \Phi_a(r' - r)}{\delta \phi(r')} \frac{\delta C_{\sigma}^{(eq)} \{ r, \phi | R \}}{\delta \phi(r')} \, dr'
\]

(24)

Second, a simple analysis of structure of equation (20) shows that it uniquely determines its solution in the form of expansion (19) if coefficients of the expansion satisfy conditions (21).

Third, coefficients of similar series expansion of the functional (23) satisfy absolutely similar conditions, because, in consequence of (21),

\[
\int \ldots \int C_{n+k+1}^{(eq)}(r, r_1 \ldots r_n, \rho_1 \ldots \rho_k | R; \nu_0) \, d\rho_1 \ldots d\rho_k \rightarrow 0 \quad \text{if} \quad r_j - r \rightarrow \infty ,
\]

\[
C_{\sigma}^{(eq)} \{ r, \phi = 0 | R \} \rightarrow 1 \quad \text{if} \quad R - r \rightarrow \infty
\]

(25)

Fourth, the only formal difference of equation (24) from (20) is mere change of its two independent variables, concretely, \( \phi(r) \rightarrow \phi(r)/(1 + \sigma) \) and \( \nu_0 \rightarrow \nu(\sigma, \nu_0) \), where

\[
\nu(\sigma, \nu_0) = \nu_0 C(\sigma, \nu_0) (1 + \sigma)
\]

(26)
These observations taken together mean that a proper solution to equation (24), $C^{(eq)}(\nu, \phi | R; \nu_0)$, is nothing but $C^{(eq)}(\nu, \phi / (1 + \sigma) | R; \nu_0)$, that is, in view of (23) and (26), for any $\sigma = \text{const}$ identity

$$
\nu_0 C^{(eq)}(\nu, \phi + \phi | R; \nu_0) = \frac{\nu(\sigma, \nu_0)}{1 + \sigma} C^{(eq)} \left\{ \nu, \frac{\phi}{1 + \sigma} | R; \nu(\sigma, \nu_0) \right\}
$$

(27)

takes place. In essence two latter formulas define a group of such transformations of equilibrium generating functional $C^{(eq)}(\nu, \phi | R; \nu_0)$ which do not change its value:

$$
\hat{T}(\sigma) C^{(eq)}(\nu, \phi | R; \nu_0) = \frac{\nu(\sigma, \nu_0)}{(1 + \sigma) \nu_0} C^{(eq)} \left\{ \nu, \frac{1 + \phi}{1 + \sigma} - 1 | R; \nu(\sigma, \nu_0) \right\} = C^{(eq)}(\nu, \phi | R; \nu_0),
$$

(28)

$$
\hat{T}(\sigma_2) \hat{T}(\sigma_1) = \hat{T}(\sigma_1 + \sigma_2 + \sigma_1 \sigma_2),
$$

$$
\nu(\sigma_2, \nu(\sigma_1, \nu_0)) = \nu(\sigma_1 + \sigma_2 + \sigma_1 \sigma_2, \nu_0)
$$

At that, obviously, the group parameter should satisfy $\sigma > -1$, and similar restriction should be imposed upon $\phi(\mathbf{r})$. But this restriction disappears if write $\sigma = \exp(a) - 1$, so that in terms of new parameter

$$
\hat{T}(\sigma_2) \hat{T}(\sigma_0) = \hat{T}(\sigma_0 + \alpha_2)
$$

Infinitesimal form of functional identities (27) or (28) looks better in terms of particular cumulants:

$$
\left\{ n \varphi(\nu) + \left[ 1 + \varphi(\nu) \right] \nu \frac{\partial}{\partial \nu} \right\} C^{(eq)}(\nu_1 \ldots \nu_n | \mathbf{R}; \nu) + \delta_{n, 1} = \nu \int C^{(eq)}(\nu_1 \ldots \nu_n, \nu' | \mathbf{R}; \nu) \, d\nu',
$$

$$
\varphi(\nu) \equiv - \left[ \frac{\partial C(\sigma, \nu)}{\partial \sigma} \right]_{\sigma = 0} = \nu \int C^{(eq)}(\nu_0 | \mathbf{R}) \, d\nu
$$

(29)

Recall that

$$
1 + \varphi(\nu) = T \left( \frac{\partial \nu}{\partial P} \right)_T,
$$

with $P$ being pressure, is isothermal compressibility of a fluid [34][15].

5. Invariance group of the historical correlations functional and virial relations

Now, turn our attention to evolution equation (13) for the generating functional of correlation functions, $\mathcal{V}(t, \mathbf{R}, \mathbf{P}, \mathbf{R}_0; \nu_0)$, and consider its principal properties implied by structure of operator $\mathcal{L} + \mathcal{L}'$, above mentioned properties of factor $\delta \ln \mathcal{F}(\nu_0) / \delta \phi(\mathbf{r}) = \nu_0 C^{(eq)}(\nu, \phi | R; \nu_0)$ which enters $\mathcal{L}'$, initial condition (13) and, of course, asymptotic boundary conditions (14).

What is important, the initial condition for $\mathcal{V}$ does not include independent variables $\psi = \psi(\mathbf{r}, \mathbf{p})$ and $\nu_0$ at all. Therefore all effects of their transformations are purely determined by properties of $\mathcal{L} + \mathcal{L}'$ itself under boundary conditions (14). One role of the latter is as just above: they allow to extend functional $\mathcal{V}(t, \mathbf{R}, \mathbf{P}, \mathbf{R}_0; \nu_0)$ to argument $\sigma + \psi(\mathbf{r}, \mathbf{p})$ with $\sigma = \text{const}$ in place of $\psi(\mathbf{r}, \mathbf{p})$. Another role of conditions (14) is that due to them, and according to definition (7) of operator $\hat{\mathcal{L}}$, variable $\psi(x_1)$ in the first term of $\hat{\mathcal{L}} \mathcal{V}$ can be shifted by arbitrary constant:

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

where $\sigma = \text{const}$, e.g. $\sigma = 1$. This is principal difference of expression $\hat{\mathcal{L}} \mathcal{V}$ from $\hat{\mathcal{L}} \mathcal{F}$. As the consequence, taking in mind action of $\hat{\mathcal{L}}$ onto $\mathcal{V}$, one can write

$$
\hat{\mathcal{L}} \left( \sigma + \psi, \frac{\delta}{\delta \psi} \right) = \hat{\mathcal{L}} \left( \psi, \frac{\delta}{1 + \sigma} \frac{\delta}{\delta \psi} \right)
$$

(30)
Visual study of operator \( \hat{L}' \) defined by (16), with taking into account identity (27) for \( \nu_0 \mathcal{C}(eq) \{ r, \phi | R; \nu_0 \} \), shows that \( \hat{L}' \) possesses the same invariance property, if transformation of \( \psi(r, p) \) is accompanied by transformation of the density argument \( \nu_0 \) in conformity with (20) and (22):

\[
\hat{L}' \left( \nu_0, \sigma + \psi, \frac{\delta}{\delta \psi} \right) = \hat{L}' \left( \nu(\sigma, \nu_0), \frac{\psi}{1 + \sigma}, \frac{\delta}{\delta \psi/(1 + \sigma)} \right) \quad (31)
\]

Because of (30) and (31) equation (15) under initial condition (13) implies similar invariance property for its solution:

\[
\mathcal{V}\{ t, R, P, \sigma + \psi | R_0; \nu_0 \} = \mathcal{V}\{ t, R, P, \frac{\psi}{1 + \sigma} | R_0; \nu(\sigma, \nu_0) \} \quad (32)
\]

with arbitrary \( \sigma(r) = \text{const} \). In other words, the generating functional \( \mathcal{V} \) of time-dependent "historical correlations" also is invariant under above mentioned group of transformations:

\[
\hat{T}(\sigma) \mathcal{V}\{ t, R, P, \psi | R_0; \nu_0 \} = \mathcal{V}\{ t, R, P, 1 + \psi \frac{\partial}{\partial \psi} - 1 | R_0; \nu(\sigma, \nu_0) \} = \mathcal{V}\{ t, R, P, \psi | R_0; \nu_0 \} \quad (33)
\]

where left identity, as combined with (20) and (22), defines action of the group onto \( \mathcal{V} \).

This is main formal result of the present paper. It would be difficult to obtain this result from a chain of equations for particular DF, (24)-(26) or all the more (17), (18), etc. Thus, perhaps, for the first time a real profit of Bogolyubov’s generating functional for non-equilibrium DF has been demonstrated.

Infinitesimal form of (33) reads

\[
\left\{ n \kappa(\nu) + [1 + \kappa(\nu)] \nu \frac{\partial}{\partial \nu} \right\} V_n(t, R, r^{(n)}, P, p^{(n)} | R_0; \nu) = \\
= \nu \int_{n+1} V_{n+1}(t, R, r^{(n+1)}, P, p^{(n+1)} | R_0; \nu) , \quad (34)
\]

thus at \( n > 0 \) connecting derivative of any BP-atoms correlation in respect to density of atoms and next-order correlation integrated over variables of additional outer atom. At \( n = 0 \) we connect derivative of the very BP’s probability distribution and integrated pair historical correlation:

\[
[1 + \kappa(\nu)] \frac{\partial V_0(t, R, P | R_0; \nu)}{\partial \nu} = \left( \int V_1(t, R, r_1, P, p_1 | R_0; \nu) \right) \quad (35)
\]

with \( \kappa(\nu) \) defined in (29).

From the other hand, if considering \( \psi(r, p) \) as infinitesimal parameter instead of \( \sigma \) and performing in (32) \( k \)-order variational differentiation over \( \psi \) at point \( \psi = 0 \), one comes to rather different type of relations. At \( k > 0 \),

\[
\left[ \frac{\nu(\sigma, \nu_0)}{(1 + \sigma)\nu_0} \right]^k V_k(t, R, r^{(k)}, P, p^{(k)} | R_0; \nu(\sigma, \nu_0)) = \\
= V_k(t, R, r^{(k)}, P, p^{(k)} | R_0; \nu_0) + \sum_{n=1}^{\infty} \frac{\nu_0^k \sigma^n}{n!} \int_{k+1} \int V_{k+n}(t, R, r^{(k+n)}, P, p^{(k+n)} | R_0; \nu_0) \quad (36)
\]

For \( k = 0 \), i.e. merely under putting on \( \psi = 0 \), identity (32) yields

\[
V_0(t, R, P | R_0; \nu(\sigma, \nu_0)) = V_0(t, R, P | R_0; \nu_0) + \sum_{n=1}^{\infty} \frac{\nu_0^0 \sigma^n}{n!} \int V_n(t, R, r^{(n)}, P, p^{(n)} | R_0; \nu_0) \quad (37)
\]

Of course, all terms in this formula actually depend on the BP’s path \( \Delta R = R - R_0 \) only.

Formulas (37) and (30), by their sense, can be interpreted as a sort of virial expansion of the BP’s probability distribution and BP’s correlations with fluid, with those peculiarity that in opposite to usual
virial expansions of thermodynamic quantities \cite{15} or kinetic coefficients \cite{16} our ones are expansions over relative change of density, \( \nu/\nu_0 - 1 \), rather than its absolute value. Then corresponding differential forms \cite{35} and \cite{41} can be named “virial relations”.

6. Some principal consequences of the virial relations

Although invariance property \cite{32} of the functional \( \mathcal{V} \) does not substitute solving the equation \cite{15} of its evolution, corresponding virial relations bring important information about structure of correlations functions and, eventually, character of evolution of the BP’s probability distribution

\[
V_0(t, \Delta R, P|\nu) \equiv V_0(t, R, P|R_0; \nu)
\]

For example, let us consider relation \cite{35} supposing for simplicity that fluid density \( \nu \) and correlations. For instance, if the hypothetical Gaussian asymptotic \cite{3,4,5} of BP’s distribution at \( \pi r \) to a dilute gas: \( 4 \nu^2 r^4 \nu/3 \ll 1 \) (characteristic radii of interactions \( r_a \) and \( r_b \) were introduced above). Then \( \nu(\nu) \ll 1 \) and, as it is known (see e.g. \cite{16}), mean free path of our molecular-size BP and mean free path of atoms both are inversely proportional to gas density: \( \Lambda_b \sim (\pi r_b^2 \nu)^{-1} \), \( \Lambda_a \sim (\pi r_a^2 \nu)^{-1} \), together with diffusivity of BP, \( D_b = D_b(\nu) \sim \nu_0 \Lambda_b \propto \nu^{-1} \), and diffusivity of atoms, \( D_a(\nu) \sim \nu_0 \Lambda_a \propto \nu^{-1} \), where \( v_b = \sqrt{T/M} \) and \( v_a = \sqrt{T/m} \) are thermal velocities. Besides, we take in mind large enough temporal and spatial scales: \( |\Delta R| > \Lambda_b \) and \( t > \tau_b \) with \( \tau_b \sim \Lambda_b/v_b \) being mean free-flight time of BP.

First, it is useful to compare relation \cite{35}, along with \cite{33}, and relations \cite{29}. In the latter, in general, \( \max |C^{(eq)}_n| \sim 1 \) while characteristic scale of equilibrium inter-atom correlations equals to \( r_a \). Therefore right-hand sides of \cite{29} can be roughly but surely estimated as

\[
\int C^{(eq)}_{n+1}(r_1 \ldots r_n, r' | \nu) \, dr' \sim r^3_a C^{(eq)}_n(r_1 \ldots r_n | \nu)
\]

On the left, consequently,

\[
\frac{\partial C^{(eq)}_n(r_1 \ldots r_n | \nu)}{\partial \nu} \sim \nu r^3_a C^{(eq)}_n(r_1 \ldots r_n | \nu) \ll C^{(eq)}_n(r_1 \ldots r_a | \nu),
\]

in particular, \( \nu(\nu) \ll 1 \). In opposite, in \cite{33}-\cite{35} we can at first roughly but surely estimate left sides:

\[
\nu \frac{\partial V_n(t, R, r^{(n)}, P, p^{(n)} | R_0; \nu)}{\partial \nu} \sim V_n(t, R, r^{(n)}, P, p^{(n)} | R_0; \nu)
\]

Indeed, a relatively small variation of gas density results in similar relative variation of BP’s diffusivity and therefore in comparable relative change of probability of its displacement, as well as connected probabilities and correlations. For instance, if the hypothetical Gaussian asymptotic \cite{31,13} of BP’s distribution at \( t > \tau_b \) and \( |\Delta R| \sim \sqrt{D_b t} \gg \Lambda_b \) realized,

\[
V_0(t, \Delta R, P | \nu) \rightarrow V_G(t, \Delta R, P | \nu) \equiv [4\pi D_b(\nu)t]^{-3/2} \exp \left[ -\frac{\Delta R^2}{4D_b(\nu)t} \right] G_M(P),
\]

then one would have, evidently,

\[
\nu \frac{\partial V_0(t, \Delta R, P | \nu)}{\partial \nu} \sim V_0(t, \Delta R, P | \nu) \left[ \frac{3}{2} - \frac{\Delta R^2}{4D_b(\nu)t} \right].
\]

Hence, for right-hand sides of \cite{33} and \cite{35} we obtain estimates \( \int_{n+1}^{\infty} V_{n+1} \sim \partial V_n/\partial \nu \sim \nu^{-1} V_n \) and

\[
\frac{1}{V_1(t, R, r_1, P, p_1 | R_0; \nu)} \sim \frac{\partial V_0(t, \Delta R, P | \nu)}{\partial \nu} \sim \nu^{-1} V_0(t, \Delta R, P | \nu)
\]

with coefficient \( \nu^{-1} \) which is \( (r^3_a \nu)^{-1} \gg 1 \) times greater than in case of equilibrium correlations.

This observation prompts that characteristic volume, \( \Omega_\nu \), occupied by a historical correlation between BP and an atom by order of magnitude is equal to \( \nu^{-1} \), that is volume displayed per one atom of fluid.
Physically, such statement follows also from almost trivial syllogism:

(a) historical correlation between BP and atom springs from their current (or soon forthcoming or just happening) collision;
(b) collision is (or will be or was) possible among those particles only whose relative position vector \( \mathbf{r}_1 - \mathbf{R} \) belongs to the “collision cylinder”; the latter has radius \( \approx r_b \), is oriented along relative velocity of BP and atom, \( \mathbf{v}_1 - \mathbf{V}_0 = \mathbf{p}_1/m - \mathbf{P}_0/M \), and its length in this direction has an order of \( \Lambda_b \) (assuming for simplicity that \( r_a \sim r_b \) and \( \Lambda_a \sim \Lambda_b \) ) since collision of stronger separated particles is prevented by other particles;
(c) consequently, volume of the pair correlation \( \Omega_c \sim \pi r_b^2 \Lambda_b \sim \nu^{-1} \).

Formally, such statement, i.e., \( \Omega_c \sim \nu^{-1} \), follows from (40) if one presumes that

\[
\max_{\mathbf{R}_0} |V_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1|\mathbf{R}_0; \nu)| \sim \left| \nu \frac{\partial V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu)}{\partial \nu} \right| G_m(\mathbf{p}_1) \sim V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu) G_m(\mathbf{p}_1),
\]

where maximum is achieved somewhere at \( |\mathbf{r}_1 - \mathbf{R}| \sim r_b \). This presumption seems likely from the point of view of equation (18) and well agrees with considerations of pair correlations in conventional theory 3415.

However, the resulting conclusion that \( \Omega_c \sim \nu^{-1} \) contradicts conventional models of molecular diffusion (“hybrid” models, in terms of [4], as they combine dynamics and stochastics). In order to see this, let us consider relation (12) (in fact, definition of \( V_1 \)) taking \( |\mathbf{r}_1 - \mathbf{R}| > r_b \). Since left side of (12) represents a probability density, it is certainly non-negative. Therefore everywhere in the mentioned region, including most part of the collision cylinder,

\[
V_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1|\mathbf{R}_0; \nu) \geq - V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu) G_m(\mathbf{p}_1) \quad (41)
\]

Hence, according to the estimate \( \Omega_c \sim \nu^{-1} \),

\[
\int V_1(t, \mathbf{R}, \mathbf{r}_1, \mathbf{P}, \mathbf{p}_1|\mathbf{R}_0; \nu) \geq - \Omega_c V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu) \sim - \nu^{-1} V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu) \quad (42)
\]

regardless of \( t \) and \( \Delta \mathbf{R} \). This inequality as combined with [35] or [40] and confronted with [39] clearly shows that formula [38] can not represent a true asymptotic of the BP’s probability distribution!

A more rigorous substantiation of this striking statement was suggested in [1112]. There (see also [10]) it was shown that true asymptotic of \( V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu) \) as a function of \( \Delta \mathbf{R} \) possesses power-law long tails cut off at \( |\Delta \mathbf{R}| \sim \nu_0 t \). This qualitative prediction agrees with quantitative result of approximate analysis of the BBGKY hierarchy undertaken in [9]:

\[
V_0(t, \Delta \mathbf{R}, \mathbf{P}|\nu) \to \frac{\Gamma(7/2)}{4\pi D_b(\nu \nu_b t)^{5/2}} \left[ 1 + \frac{\Delta \mathbf{R}^2}{4D_b(\nu \nu_b t)} \right]^{-7/2} \Theta \left( \frac{\Delta \mathbf{R}}{\nu_0 t} \right) G_M(\mathbf{P}), \quad (43)
\]

where function \( \Theta(x) \approx 1 \) at \( x \ll 1 \) and in a fast way tends to zero at \( x > 1 \). An origin of such statistics of equilibrium molecular Brownian motion was discussed more than once as long ago as in [1718] and later in [78910] (see also references therein). In short, such statistics says merely that dynamics of a very many-particle system always is unique and can not be imitated by primitive stochastic processes.

7. Conclusion

To resume, first, in this paper we rigorously formulated the problem of random walk of small molecular-size Brownian particle (BP) in classical thermodynamically equilibrium fluid. We considered corresponding BBGKY hierarchy in terms of Bogolyubov type generating functionals and derived a linear evolution equation for generating functional of time-dependent “historical correlations” which together accumulate statistics of collisions of BP with fluid atoms and eventually determine statistics of BP’s path.

Second, we showed that both the evolution equation and its solution, along with generating functional of static equilibrium correlations, are invariant with respect to definite continuous group of transformations...
of their independent variables including fluid density. As the consequence, we found an infinite set of original exact “virial relations” which connect the BP’s path probability distributions and various correlation functions at different values of the density.

Notice that particular relation $\{37\}$ first was found in $\{10\}$ in the form integrated over BP’s momentum and in $\{11,12\}$ in the full form. There it was derived from most general properties of the Liouville operator, as an example of the “generalized fluctuation-dissipation relations” $\{13,14\}$. Here, formula $\{37\}$ appeared, in company with infinitely many new relations $\{34\}$ and $\{36\}$, as consequence of hidden symmetry of the BBGKY hierarchy. In principle, of course, these are allied approaches. Nevertheless, they use very different formal techniques, therefore confirmation of previous results certainly is useful. The more so as it produces much wider results which give a new sight of the BBGKY theory.

Third, we demonstrated that virial relations bring significant information about solutions to the BBGKY hierarchy even without literal solving it. In particular, they impose principal restrictions on possible asymptotic profile of the BP’s path probability distribution, definitely forbidding the Gaussian profile implied by invented stochastic or hybrid models of random walks $\{34-35\}$, in agreement with results previously obtained by approximate methods in $\{7\}$ (or see $\{8\}$) and in $\{9\}$.

Undoubtedly, this is not all of the benefits from the invariance group of BBGKY hierarchy represented by virial relations. It can extended, from one hand, to non-equilibrium random walks at presence of an external force acting onto BP. From the other hand, to more usual problems when probability distributions under interest describe not information on position of some distinct particle but hydrodynamic fields of initially non-equilibrium or externally disturbed fluid. Curious feature of the virial relations $\{36-37\}$ is that they establish contacts between states of a fluid under arbitrary different values of pressure, e.g. between dense liquid and dilute gas. May be this will help in constructing approximate solutions to the BBGKY equations. Anyway there is a lot of interesting tasks for the future.

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