Subdynamics of fluctuations in an equilibrium classical many-particle system and generalized linear Boltzmann and Landau equations

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Exact completely closed homogeneous generalized master equations (GMEs) governing the evolution in time of equilibrium two-time correlation functions for dynamic variables of a subsystem of s particles ($s < N$) selected from $N \gg 1$ particles of a classical many-body system are obtained. These time-convolution and time-convolutionless GMEs differ from the known GMEs (e.g., Nakajima-Zwanzig GME) by the absence of inhomogeneous terms containing correlations between all N particles at the initial moment of time and preventing the closed description of s-particle subsystem evolution. Closed homogeneous GMEs describing the subdynamics of fluctuations are obtained by applying a special projection operator to the Liouville-type equation governing the dynamics of the correlation function with the related to the Gibbs distribution initial state, which is more natural than the conventional factorized initial state. No common approximation, like the "molecular chaos," is needed. In the linear approximation in the particles' density, the linear generalized Boltzmann equation accounting for initial correlations and valid at all timescales is obtained. This equation for a weak interparticle interaction converts into the generalized linear Landau equation in which the initial correlations are also accounted for. The connection of these equations to the nonlinear Boltzmann and Landau equations is discussed. The same approach is applicable to studying the kinetics of the conventional reduced s-particle distribution functions for a classical N-particle system driven from an equilibrium state by an external force.

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I. INTRODUCTION

One of the long-standing problems of statistical physics of N-particle ($N \gg 1$) systems remains the derivation of the closed kinetic equations for s-particle ($s < N$) distribution functions (statistical operators) sufficient for calculation of the measurable values characterizing a nonequilibrium state of the many-particle system. The natural starting point is the Liouville (classical system) or von Neumann (quantum system) linear equation for an N-particle distribution function or statistical operator. In the reduced description method leading to the Born-Bogoliubov-Green-Kirkwood-Yvon (BBGKY) chain, the closed Boltzmann kinetic equation can be obtained by employing the Boltzmann "molecular chaos" approximation at any time moment (beginning from the initial state) or more sophisticated Bogoliubov principle of weakening of initial correlations [1]. In the latter case, in the first approximation in particles' density, the nonlinear Boltzmann equation follows from the BBGKY chain on a large (kinetic) timescale. Note that nonlinearity of the Boltzmann equation, obtained from the linear Liouville (or von Neumann) equation, is a consequence of the above-mentioned approximations. Lanford's derivation of the Boltzmann equation (however, only on a small timescale and for a hard-sphere system) [2] seems to be the most relevant result in the mathematical foundation of the kinetic theory. Some aspects of the rigorous mathematical approach to this problem can be found in [3].

For the case of a small interparticle interaction, the nonlinear Landau equation follows from the nonlinear Boltzmann equation (see, e.g., [4]). But, strictly speaking, the Landau equation should be derived from the particles' system dynamics (the Liouville equation) in the weak-coupling limit. The partial result in this direction (for the short timescale) was obtained in [5]. The linear versions of these equations (linear Boltzmann and Landau equations) also rely on the molecular chaos approximation (see, e,g, [6]).

In the projection operators' approach leading to the generalized master equations (GMEs) (see, e.g., [7]), in order to obtain the completely closed (homogeneous) linear equation for the reduced s-particle ($s < N$) distribution function (statistical operator), the undesired inhomogeneous term (a source) containing all N-particle initial correlations should be disregarded (which is incorrect in principle [8]). The mentioned procedures allowing for obtaining the desired closed kinetic equations are not completely satisfactory: They imply, e.g., the "propagation of chaos" in time hypothesis for the factorized initial state, the general proof of which is still lacking (see, e.g., [9]), and do not allow for considering the evolution process on any timescale for an arbitrary initial state. The natural desire then arises to abandon the molecular chaos (or other mentioned assumption) and include initial correlations into consideration. This can be effectively done, e.g., by deriving from the Liouville (von Neumann) equation the completely closed (homogeneous with no source)

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evolution equations valid on any timescale and accounting for initial correlations in the kernel governing the evolution of the reduced s-particle distribution function (statistical operator). For arbitrary initial conditions, it has been attempted in [10–13].

It is widely recognized that the selected initial state plays an essential role in deriving the effective equations describing the evolution of the multiparticle system. For example, the very special (and not very realistic [8]) factorized initial state allows for deriving the nonlinear Boltzmann equation from the linear Liouville equation. On the other hand, there is a natural initial condition: the equilibrium state of the whole system at some initial time moment t_0. The evolution of the system in that case can be studied either under the influence of an external force (switched on at $t > t_0$) or by means of equilibrium correlation functions. But, with the help of the traditional projection operator [see Eq. (12) below] we again obtain the inhomogeneous Nakajima-Zwanzig equation.

However, the equilibrium initial state provides an opportunity for including initial correlations into consideration. For a quantum system, the closed homogeneous linear evolution equations accounting for initial correlations were obtained in [14,15] with application to the polaron mobility problem. It turns out that the initial equilibrium state in the classical physics case is even more favorable than the case of quantum physics, for realization of the program with no molecular chaos (factorized initial state) assumption. In this paper we show that there is a special projection operator selecting the relevant part of the N-particle function satisfying the Liouville-type equation and governing the evolution of an equilibrium two-time s-particle ($s < N$) correlation function that obeys the exact time-convolution (TC) or time-convolutionless (TCL) homogeneous GMEs. Thus, it is shown that there is a subdynamics in the subspace of s particles and, therefore, the evolution equation for the correlation function (thermal fluctuations) is completely closed (no undesirable terms defined on the full phase space of N particles). It has become possible due to the fact that the initial condition for the Liouville-type equation, defining the evolution of the correlation function, is related to the Gibbs equilibrium distribution. The initial correlations are now "hidden" in the projection operator, and the kernels of obtained homogeneous equations can effectively be expanded in the particle density n or in a small interparticle interaction. In the first case, the linear generalized Boltzmann equation accounting for initial correlations and valid at all timescales follows from the obtained homogeneous TC GME in the first order in n expansion of the kernel governing the evolution of a one-particle correlation function. We show how this equation leads to the linear Boltzmann equation but with an additional term related to initial correlations. In the case of small interparticle interaction, we obtain from this equation the linear equation for one-particle correlation function in the second order in the interaction and discuss its connection to the Landau equation.

The suggested approach, although valid only for an initial equilibrium state for the full system (which, however, looks more natural than the factorized state), is not restricted to the derivation of the closed equations for correlation functions. The same type of exact closed homogeneous equations for the conventional reduced s-particle distribution functions (marginals), considered in classical statistical physics, can be obtained in the case, when the system is driven from the equilibrium state by an external force [16]. These equations, however, differ by the terms caused by an external force. The results, obtained in this paper and those of [16], complement each other.

II. PROJECTION OPERATOR FORMALISM FOR s-PARTICLE EQUILIBRIUM CORRELATION FUNCTION

We consider an N-particle ($N \gg 1$) system of interacting classical particles. Let us select the subsystem s, i.e., the complex of s ($s < N$) particles (s complex), which interacts with the environment Σ of remaining $N - s$ particles. Note that the particles, making up a subsystem, can be different from the environment particles' sort. Then, we assume that the Hamilton function of the full system can be presented as

$$H = H_s + H_\Sigma + \widetilde{H}_{s\Sigma}, \tag{1}$$

where H_s, H_Σ, and $\widetilde{H}_{s\Sigma}$ are the Hamilton functions of the subsystem s, the environment Σ, and the subsystem-environment interaction $\widetilde{H}_{s\Sigma}$, respectively. More specific forms of these functions will be considered later.

We consider a two-time equilibrium correlation function for the subsystem's dynamic functions A_s and B_s, which depend on the set of variables characterizing the subsystem, i.e., on $x_i = (\mathbf{r}_i, \mathbf{p}_i)$, $i = 1, 2, \ldots, s$, where x_i is the coordinate of the ith particle in the phase space. The time dependence of dynamic functions is given by $A_s(t) = \exp(Lt)A_s(0)$, $B_s(t) = \exp(Lt)B_s(0)$, where L is the Liouville operator $L = L_s + L_\Sigma + \widetilde{L}_{s\Sigma}$ related to the Hamilton function (1) and defined by the Poisson bracket. Thus, we consider the correlation function

$$\varphi_{AB}(t) = \langle A_s(t)B_s(0)\rangle = \langle A_s(0)B_s(-t)\rangle = \int \ldots \int dx^s A_s(0)\left[\int \ldots \int dx^\Sigma G_N(t,\beta)\right],$$
$$G_N(t,\beta) = \rho(\beta)\exp(-Lt)B_s(0), \quad dx^s = dx_1 \ldots dx_s, \quad dx^\Sigma = dx_{s+1} \ldots dx_N. \tag{2}$$

Here,

$$\rho(\beta) = Z^{-1}\exp(-\beta H), \quad Z = \int \ldots \int dx^N \exp(-\beta H), \quad \beta = 1/k_B T, \quad dx^N = dx^s dx^\Sigma,$$
$$LC_N = \{H, C_N\}_p = \sum_{i=1}^{N}\left[\frac{\partial C_N}{\partial \mathbf{r}_i}\frac{\partial H}{\partial \mathbf{p}_i} - \frac{\partial C_N}{\partial \mathbf{p}_i}\frac{\partial H}{\partial \mathbf{r}_i}\right], \tag{3}$$

$\{H, C_N\}_p$ is the Poisson bracket, C_N is some dynamic function defined on the full phase space of the N-particle system under consideration. We see that the dynamics of correlation function (2) is defined by the function $G_N(t,\beta)$, which depends on the whole set of variables $x_1, \ldots, x_N$ and obeys the Liouville-type equation

$$\frac{\partial}{\partial t}G_N(t,\beta) = -\rho(\beta)L\exp(-Lt)B_s(0) = -LG_N(t,\beta), \quad (4)$$

where we used that $\rho(\beta)$ commutes with L [more generally $\rho(\beta)$ commutes with $\exp(-Lt)$]. The formal solution to Eq. (4) is

$$G_N(t,\beta) = U(t,0)G_N(0,\beta),$$
$$U(t,0) = \exp(-Lt),\ G_N(0,\beta) = \rho(\beta)B_s(0). \quad (5)$$

However, one can see from the definition (2) that dynamics of the subsystem fluctuations is governed by the function dependent on much smaller number of variables $x_1, \ldots, x_s$ than the whole set of N variables $x_1, \ldots, x_N$, i.e., by the function $G_N(t,\beta)$ integrated over the environment variables $x_{s+1}, \ldots, x_N$:

$$F_s(t,\beta) = \int \ldots \int dx^{\Sigma} G_N(t,\beta). \quad (6)$$

From (2) and (6) one can see that $F_s(t,\beta)$ can be viewed as the distribution function for $A_s(0)$.

In order to obtain the equation for the reduced distribution function $F_s(t,\beta)$ [Eq. (6)], it is convenient to employ the projection operator technique [17–19] and to break $G_N(t,\beta)$ by some projection operators P and $Q = 1 - P$ (with the properties $P^2 = P,\ Q^2 = Q,\ P + Q = 1,\ PQ = 0$) into the relevant $R_N(t,\beta)$ and irrelevant $I_N(t,\beta)$ parts

$$G_N(t,\beta) = R_N(t,\beta) + I_N(t,\beta),$$
$$R_N(t,\beta) = PG_N(t,\beta),$$
$$I_N(t,\beta) = QG_N(t,\beta) = G_N(t,\beta) - R_N(t,\beta). \quad (7)$$

We note that the relevant and irrelevant parts generally depend on coordinates and momenta of all N particles in contrast to the reduced function $F_s(t,\beta)$. The relevant part $R_N(t,\beta)$ is conveniently defined in such a way that it comprises the reduced function of interest $F_s(t,\beta)$ as a multiplier. Thus, we consider the projection operators of the form

$$P = \Phi_{s\Sigma}\int \ldots \int dx^{\Sigma}, \quad (8)$$

where the function $\Phi_{s\Sigma}$ generally depends on the coordinates of a subsystem and an environment and normalized as

$$\int \ldots \int \Phi_{s\Sigma}dx^{\Sigma} = 1. \quad (9)$$

Then, it is easily seen that for projectors given by (8) and (9), the correlation function (2) is completely defined by the relevant part of $G_N(t,\beta)$:

$$\varphi_{AB}(t) = \int \ldots \int dx^{s}\int \ldots \int dx^{\Sigma}A_s(0)R_N(t,\beta). \quad (10)$$

If, e.g.,

$$\Phi_{s\Sigma} = \rho_{\Sigma} = Z_{\Sigma}^{-1}\exp(-\beta H_{\Sigma}),$$
$$Z_{\Sigma} = \int \ldots \int dx^{\Sigma}\exp(-\beta H_{\Sigma}), \quad (11)$$

then we have the "standard" projectors (see, e.g., [7])

$$P = P_{\Sigma} = \rho_{\Sigma}\int \ldots \int dx^{\Sigma},\ Q_{\Sigma} = 1 - P_{\Sigma} \quad (12)$$

conventionally used for such types of problems (interaction of a subsystem with a reservoir). Note that the formal introduction of the distribution function ρ_{Σ} does not necessarily mean that the environment of $N - s$ particles is in the equilibrium state.

By application of operators (12) to Eq. (4), we obtain the equations for the relevant and irrelevant parts of $G_N(t,\beta)$:

$$\frac{\partial}{\partial t}R_N(t,\beta) = -P_{\Sigma}L[R_N(t,\beta) + I_N(t,\beta)],$$
$$\frac{\partial}{\partial t}I_N(t,\beta) = -Q_{\Sigma}L[R_N(t,\beta) + I_N(t,\beta)], \quad (13)$$

where now

$$R_N(t,\beta) = P_{\Sigma}G_N(t,\beta) = G_N^r(t,\beta) = \rho_{\Sigma}F_s(t,\beta),$$
$$I_N(t,\beta) = G_N(t,\beta) - \rho_{\Sigma}F_s(t,\beta) = G_N^i(t,\beta). \quad (14)$$

Finding $G_N^i(t,\beta)$ from the second equation (13) as a function of $G_N^r(\tau,\beta)$ and $G_N^i(0,\beta)$ and inserting it in the first equation (13), we arrive at the conventional exact time-convolution generalized master equation (TC-GME) known as the Nakajima-Zwanzig equation for the relevant part of $G_N^r(t,\beta)$ [17,18]:

$$\frac{\partial}{\partial t}G_N^r(t,\beta) = -P_{\Sigma}LG_N^r(t,\beta) + \int_0^t P_{\Sigma}LU_{Q_{\Sigma}}(t,\tau)Q_{\Sigma}LG_N^r \times(\tau,\beta)d\tau - P_{\Sigma}LU_{Q_{\Sigma}}(t,0)G_N^i(0,\beta),$$
$$U_{Q_{\Sigma}}(t,\tau) = \exp[-Q_{\Sigma}LQ_{\Sigma}(t-\tau)]. \quad (15)$$

Equation (15), which, in fact, gives the equation for the reduced function $F_s(t,\beta)$, is quite general and formally closed. Serving as a basis for many applications [7], this equation, nevertheless, contains the undesirable and non-negligible inhomogeneous initial condition term [the last term in the right-hand side of (15)]

$$G_N^i(0,\beta) = G_N(0,\beta) - P_{\Sigma}G_N(0,\beta) = [\rho(\beta) - \rho_s\rho_{\Sigma}]B_s(0),$$
$$\rho_s = \int \ldots \int dx^{\Sigma}\rho(\beta) \quad (16)$$

[see (2) and (12)]. This term is not equal to zero due to initial (at $t = 0$) correlations $[\rho(\beta) \neq \rho_s\rho_{\Sigma}]$. Therefore, Eq. (15) does not provide for a complete reduced description of a multiparticle system in terms of the relevant (reduced) function $F_s(t,\beta)$. Applying Bogoliubov's principle of weakening of initial correlations, allowing to eliminate the influence of initial correlations on the large enough timescale $t \gg t_{\rm cor}$ ($t_{\rm cor}$ is the time for damping of initial correlations) or using a factorized initial condition, when $\rho(\beta) = \rho_s\rho_{\Sigma}$, one can achieve the desirable goal and obtain the homogeneous GME for $F_s(t,\beta)$, i.e., Eq. (15) with no initial condition term. However,

obtained in such a way homogeneous GME is either approximate and valid only on a large enough timescale (when all initial correlations vanish) or applicable only for a rather artificial (actually unreal, as pointed in [8]) initial conditions (no correlations at an initial instant of time). In addition, Eq. (15) poses the problem to deal with due to its time nonlocality. However, it is possible to obtain the time-local equation for the relevant part $G_N^r(t,\beta)$ [7,20,21] which also contains the inhomogeneous source term.

III. COMPLETELY CLOSED (HOMOGENEOUS) GMEs FOR *s*-PARTICLE CORRELATION FUNCTION

Let us now introduce the following projection operators P_s and Q_s:

$$P = P_s = \rho_\Sigma^s \int \dots \int dx^\Sigma, \quad Q = Q_s = 1 - P_s,$$
$$\rho_\Sigma^s = \frac{1}{Z_\Sigma^s} \exp[-\beta(H_\Sigma + \widetilde{H}_{s\Sigma})],$$
$$Z_\Sigma^s = \int \dots \int dx^\Sigma \exp[-\beta(H_\Sigma + \widetilde{H}_{s\Sigma})]. \tag{17}$$

It is not difficult to see that $P_s^2 = P_s$, $Q_s^2 = Q_s$, $P_s Q_s = 0$. Then, we can divide $G_N(t,\beta)$ into the relevant $g_N^r(t,\beta)$ and irrelevant $g_N^i(t,\beta)$ components as

$$G_N(t,\beta) = g_N^r(t,\beta) + g_N^i(t,\beta),$$
$$g_N^r(t,\beta) = P_s G_N(t,\beta) = \rho_\Sigma^s F_S(t,\beta),$$
$$g_N^i(t,\beta) = Q_s G_N(t,\beta) = G_N(t,\beta) - \rho_\Sigma^s F_S(t,\beta). \tag{18}$$

It is not difficult to see that the dynamics of the correlation function (2) is completely defined by the relevant part $g_N^r(t,\beta)$ of $G_N(t,\beta)$, i.e.,

$$\varphi_{AB}(t) = \int \dots \int dx^s A_s(0) F_s(t,\beta)$$
$$= \int \dots \int dx^N A_s(0) g_N^r(t,\beta). \tag{19}$$

The projection operator P_s, Eq. (17), has an interesting property, namely,

$$P_s \rho(\beta) = \rho(\beta), \;\; Q_s G_N(0,\beta) = 0. \tag{20}$$

Thus, by applying the introduced projection operators P_s and Q_s, Eq. (17), to Eq. (4), we arrive at the following exact homogeneous time-convolution GME [compare with (15)]:

$$\frac{\partial}{\partial t} g_N^r(t,\beta) = -P_s L g_N^r(t,\beta) + \int_0^t P_s L U_{Q_s}(t,\tau) Q_s L g_N^r(\tau,\beta) d\tau,$$
$$U_{Q_s}(t,\tau) = \exp[-Q_s L(t-\tau)]. \tag{21}$$

Equation (21) is a completely closed equation which defines the evolution in time of the relevant part of the correlation function that we are looking for. It shows that in the considered case, the dynamics of correlation function (2) can be exactly projected on the dynamics within its relevant subspace. It follows that the dynamics of fluctuations of the selected complex of *s* particles can be described by the *linear* equation in the subspace of the corresponding coordinates $x_i = (\mathbf{r}_i, \mathbf{p}_i)$ $(i = 1, \dots, s)$. To make it more clear, we rewrite Eq. (21) as the equation for an *s*-particle function $F_s(t,\beta)$ [Eq. (6)] governing the subsystem's fluctuations in time [see also (2) and (18)]:

$$\frac{\partial}{\partial t} F_s(t,\beta) = -\left[\int \dots \int dx^\Sigma L \rho_\Sigma^s\right] F_s(t,\beta)$$
$$+ \left[\int \dots \int dx^\Sigma L \int_0^t d\tau U_{Q_s}(t,\tau) Q_s L \rho_\Sigma^s\right]$$
$$\times F_s(\tau,\beta). \tag{22}$$

Generally, the evolution equation (21) poses some problem to deal with due to its time nonlocality. It is possible, however, to obtain the exact homogeneous time-local equation for the relevant part of the correlation function. The idea is to take advantage of the evolution of $G_N(t,\beta)$, defined by (5), which leads to the relation

$$G_N(\tau,\beta) = U^{-1}(t,\tau) G_N(t,\beta),$$
$$U^{-1}(t,\tau) = \exp[L(t-\tau)]. \tag{23}$$

Using (23) and the conventional projection operator (12), the well known time-convolutionless equation for the relevant part $G_N^r(t,\beta)$ of $G_N(t,\beta)$, which contains the undesirable inhomogeneous term (16) comprising the initial correlations, can be obtained (see [7,20,21]).

We will show now that the use of the projector (17) instead of (12) leads to the completely closed homogeneous time-convolutionless GME for the relevant part of the correlation function. We will briefly conduct the derivation which is rather a standard one. First, we apply the projector (17) to (23) and obtain additional equation connecting the relevant and irrelevant parts of $G_N(t,\beta)$:

$$g_N^r(\tau,\beta) = P_s U^{-1}(t,\tau)\left[g_N^r(t,\beta) + g_N^i(t,\beta)\right]. \tag{24}$$

We also have the equation for the irrelevant part $g_N^i(t,\beta)$ which follows from the solution of the second equation (13) with the projection operator (17):

$$g_N^i(t,\beta) = -\int_0^t U_{Q_s}(t,\tau) Q_s L g_N^r(\tau,\beta) d\tau, \tag{25}$$

where $U_{Q_s}(t,\tau)$ is given by (21) and the property (20) was used. From two equations (24) and (25) one finds that

$$g_N^i(t,\beta) = [1-\alpha(t)]^{-1}\alpha(t) g_N^r(t,\beta),$$
$$\alpha(t) = -\int_0^t U_{Q_s}(t,\tau) Q_s L P_s U^{-1}(t,\tau) d\tau. \tag{26}$$

Substituting $g_N^i(t,\beta)$, Eq. (26), into the projected by P_s, Eq. (4),

$$\frac{\partial}{\partial t} g_s^r(t,\beta) = -P_s L\left[g_N^r(t,\beta) + g_N^i(t,\beta)\right], \tag{27}$$

we finally obtain

$$\frac{\partial}{\partial t} g_N^r(t,\beta) = -P_s L [1-\alpha(t)]^{-1} g_N^r(t,\beta). \tag{28}$$

If it is possible to expand the operator $[1-\alpha(t)]^{-1}$ into the series in $\alpha(t)$, then the first two terms of this expansion result

in the following time-local equation [compare with (21)]:

$$\frac{\partial}{\partial t}g_N^r(t,\beta) = -P_sLg_N^r(t,\beta) + P_sL\int_0^t d\tau U_{Q_s}(t,\tau)Q_sLP_sU^{-1}(t,\tau)g_N^r(t,\beta). \tag{29}$$

Equations (21) and (28) present the main results of this section. They show that the projector (17) allows for selecting the relevant part $g_N^r(t,\beta)$ of the multiparticle function $G_N(t,\beta)$ governing the dynamics of correlation function (2) which satisfies the completely closed linear time-convolution and time-convolutionless equations. They, in fact, describe the evolution of the s-particle marginals (6) on the arbitrary timescale. Thus, one remains in the scope of the linear evolution given by the Liouville equation (4) but should pay for this simplification by accounting for initial correlations, which are conventionally ignored, but now are included in the kernels of Eqs. (21) and (28) by means of the new projection operator (17). It is also worth noting that the developed formalism only works in the framework of classical physics [when the terms of the Hamilton function (1) commute with each other]. For quantum physics a different approach is needed (see [14,15]).

IV. EQUATIONS FOR A MORE SPECIFIC CASE

Let us specify the Hamilton function H [Eq. (1)] for the case of the identical particles with the two-body interparticle interaction V_{ij} as

$$\begin{aligned} H &= H_s + H_\Sigma + \widetilde{H}_{s\Sigma},\\ H_s &= \sum_{i=1}^{s}\frac{\mathbf{p}_i^2}{2m} + \sum_{1\leqslant i<j\leqslant s}V_{ij}(|\mathbf{r}_i-\mathbf{r}_j|) + \langle H_{s\Sigma}\rangle_\Sigma,\\ H_\Sigma &= \sum_{i=s+1}^{N}\frac{\mathbf{p}_i^2}{2m} + \sum_{s+1\leqslant i<j\leqslant N}V_{ij}(|\mathbf{r}_i-\mathbf{r}_j|),\\ \widetilde{H}_{s\Sigma} &= H_{s\Sigma} - \langle H_{s\Sigma}\rangle_\Sigma, \quad H_{s\Sigma} = \sum_{i=1}^{s}\sum_{j=s+1}^{N}V_{ij}(|\mathbf{r}_i-\mathbf{r}_j|). \end{aligned} \tag{30}$$

Here, for convenience, we introduce the energy of the mean field $\langle H_{s\Sigma}\rangle_\Sigma$ acting on the s complex by the "equilibrium" environment

$$\langle H_{s\Sigma}\rangle_\Sigma = \int\ldots\int dx^\Sigma \rho_\Sigma H_{s\Sigma}, \tag{31}$$

where ρ_Σ is given by (11). Note that $\langle H_{s\Sigma}\rangle_\Sigma$ depends only on the coordinates of s selected particles $\mathbf{r}_i$ $(i=1,\ldots,s)$.

The corresponding to (30) Liouville operator L is

$$\begin{aligned} L &= L_s + L_\Sigma + \widetilde{L}_{s\Sigma},\\ L_s &= \sum_{i=1}^{s}\left[\mathbf{v}_i\cdot\nabla_i - (\nabla_i\langle H_{s\Sigma}\rangle_\Sigma)\cdot\frac{\partial}{\partial\mathbf{p}_i}\right] - \sum_{1\leqslant i<j\leqslant s}(\nabla_iV_{ij})\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right),\\ L_\Sigma &= \sum_{i=s+1}^{N}\mathbf{v}_i\cdot\nabla_i - \sum_{s+1\leqslant i<j\leqslant N}(\nabla_iV_{ij})\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right),\\ \widetilde{L}_{s\Sigma} &= -\sum_{i=1}^{s}\sum_{j=s+1}^{N}(\nabla_iV_{ij})\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right) + \sum_{i=1}^{s}(\nabla_i\langle H_{s\Sigma}\rangle_\Sigma)\cdot\frac{\partial}{\partial\mathbf{p}_i},\\ \mathbf{v}_i &= \mathbf{p}_i/m, \quad \nabla_i = \frac{\partial}{\partial\mathbf{r}_i}, \quad V_{ij} = V_{ij}(|\mathbf{r}_i-\mathbf{r}_j|). \end{aligned} \tag{32}$$

Equations (21) and (28) can be rewritten in the simplified form if we take into account the following operator properties:

$$\begin{aligned} &P_sL_s = P_sL_sP_s = \rho_\Sigma^sL_s\int\ldots\int dx^\Sigma, P_sL_sQ_s = 0, \quad Q_sL_sP_s = L_sP_s - \rho_\Sigma^sL_s\int\ldots\int dx^\Sigma,\\ &P_sL_\Sigma = 0,\ P_sL_\Sigma Q_s = 0,\ Q_sL_\Sigma P_s = L_\Sigma P_s, \quad P_s\widetilde{L}_{s\Sigma}P_s = \sum_{i=1}^{s}\left[\langle\mathbf{F}_i\rangle_\Sigma^s - \langle\mathbf{F}_i\rangle_\Sigma\right]\cdot\frac{\partial}{\partial\mathbf{p}_i}P_s, \end{aligned} \tag{33}$$

where

$$\mathbf{F}_i = -\sum_{j=s+1}^{N}(\nabla_iV_{ij}), \langle\ldots\rangle_\Sigma^s = \int\ldots\int dx^\Sigma(\ldots\rho_\Sigma^s), \tag{34}$$

i.e., $\mathbf{F}_i$ is the force acting on the i particle $(i=1,\ldots,s)$ from the "environment" of $N-s$ particles. Here and further on, we use, as usual, that all functions $\Phi(x_1,\ldots,x_N;t)$, defined on the phase space, and their derivatives vanish at the boundaries of the configurational space and at $\mathbf{p}_i=\pm\infty$.

Now, Eq. (21) can be presented as

$$\frac{\partial}{\partial t}F_s(t,\beta) = -\left[L_s + \sum_{i=1}^{s}\left(\langle \mathbf{F}_i\rangle_\Sigma^s - \langle \mathbf{F}_i\rangle_\Sigma\right)\cdot\frac{\partial}{\partial \mathbf{p}_i}\right]F_s(t,\beta) + C(t,\beta), \tag{35}$$

where the collision term $C(t,\beta)$ is defined by

$$C(t,\beta) = \int_0^t d\tau \int\cdots\int dx^\Sigma \widetilde{L}_{s\Sigma}U_{Q_s}(\tau,0)\left[\widetilde{L}_{s\Sigma}\rho_\Sigma^s + \left(L_s\rho_\Sigma^s\right) + L_\Sigma\rho_\Sigma^s - \sum_{i=1}^{s}\left(\langle \mathbf{F}_i\rangle_\Sigma^s - \langle \mathbf{F}_i\rangle_\Sigma\right)\cdot\rho_\Sigma^s\frac{\partial}{\partial \mathbf{p}_i}\right]F_s(t-\tau,\beta), \tag{36}$$

and $(L_s\rho_\Sigma^s)$ means that L_s acts only on ρ_Σ^s. Note that if we use in (35) and (36) the standard projector (12), i.e., substitute ρ_Σ^s with ρ_Σ, then Eq. (35) will acquire the "standard" form

$$\frac{\partial}{\partial t}F_s(t,\beta) = -L_sF_s(t,\beta) + \int_0^t d\tau\int\ldots\int dx^\Sigma\widetilde{L}_{s\Sigma}U_{Q_s}(\tau,0)\widetilde{L}_{s\Sigma}\rho_\Sigma F_s(t-\tau,\beta) \tag{37}$$

if we neglect in (15) the inhomogeneous source term. Thus, we see that the extra terms in Eq. (35) are due to initial correlations which are "hidden" in the projector (17).

V. EVOLUTION EQUATION FOR ONE-PARTICLE CORRELATION FUNCTION IN THE FIRST APPROXIMATION IN THE PARTICLE DENSITY

For what follows, we consider the equation for $F_1(t,\beta) = F_1(\mathbf{r}_1,\mathbf{p}_1;t,\beta)$. One can see that for $s=1$ the Hamilton function (30) and the Liouville operator (32) have more simple form. In order to expand the kernel of Eq. (35) in the density of particles $n = N/V$ (V is the system's volume), we need the expansion for the distribution function ρ_Σ^1. In order to do that, it is convenient to express $\exp(-\beta H_\Sigma)$ and $\exp(-\beta H_{1\Sigma})$ in terms of the Mayer functions f_{ij} [22]. Then,

$$\rho_\Sigma^1 = \frac{\exp(-\beta H_\Sigma)\exp(-\beta H_{1\Sigma})}{\int\ldots\int dx^\Sigma\exp(-\beta H_\Sigma)\exp(-\beta H_{1\Sigma})} = \rho_\Sigma(\mathbf{p})\frac{\prod_{2\leqslant i<j\leqslant N}(1+f_{ij})\prod_{j=2}^N(1+f_{1j})}{\int\ldots\int d\mathbf{r}^\Sigma\prod_{2\leqslant i<j\leqslant N}(1+f_{ij})\prod_{j=2}^N(1+f_{1j})}, \quad d\mathbf{r}^\Sigma = d\mathbf{r}_2\ldots d\mathbf{r}_N, \tag{38}$$

where

$$f_{ij} = e^{-\beta V_{ij}} - 1,\ V_{ij} = V(|\mathbf{r}_i - \mathbf{r}_j|), \quad \rho_\Sigma(\mathbf{p}) = \exp[-\beta H_\Sigma(\mathbf{p})]\Big/\int\ldots\int d\mathbf{p}^\Sigma\exp[-\beta H_\Sigma(\mathbf{p})],$$
$$H_\Sigma(\mathbf{p}) = \sum_{j-2}^{N}p_j^2/2m, \quad d\mathbf{p}^\Sigma = d\mathbf{p}_2\ldots d\mathbf{p}_N, \tag{39}$$

and we used that $\exp(\beta\langle H_{1\Sigma}\rangle_\Sigma)$ does not depend on the "environment" Σ variables and is canceled out of ρ_Σ^1.

Let us consider the denominator of ρ_Σ^1:

$$\begin{aligned}
&\int\ldots\int d\mathbf{r}^\Sigma\prod_{2\leqslant i<j\leqslant N}(1+f_{ij})\prod_{j=2}^N(1+f_{1j})\\
&= \int d\mathbf{r}_2\ldots\int d\mathbf{r}_N(1+f_{23}+f_{24}+f_{34}+\cdots+f_{N-1,N}+f_{23}f_{24}+\cdots)(1+f_{12}+f_{13}+\cdots+f_{12}f_{13}+\cdots)\\
&= V^{N-1} + (N-1)V^{N-2}\int f_{12}d\mathbf{r}_2 + N(N-1)V^{N-3}\int d\mathbf{r}_2\int d\mathbf{r}_3(f_{23}+f_{12}f_{13}) + \cdots\\
&= V^{N-1}\left[1 + n\int d\mathbf{r}_2f_{12} + n^2\int d\mathbf{r}_2\int d\mathbf{r}_3(f_{23}+f_{12}f_{13}) + \cdots\right],\ N\gg 1.
\end{aligned} \tag{40}$$

One can see that the terms with one integration over the particle coordinate is proportional to n, while the terms with integration over coordinates of two, three, and more particles are proportional to n^2, n^3, and higher powers of n, respectively. In what follows, we will restrict ourselves to the linear in n approximation to the kernel of Eq. (35) and, therefore, only the terms with one integration over the particle coordinate should be taken into consideration. The products of terms with one integration over the particle coordinate will also be (naturally) disregarded. Thus, within the linear in n accuracy,

$$\rho_\Sigma^1 = \frac{1}{V^{N-1}}\rho_\Sigma(\mathbf{p})\left(1+\sum_{j=2}^{N}f_{1j}\right)\left(1 - n\int d\mathbf{r}_2f_{12}\right), \tag{41}$$

where we approximated $\prod_{j=2}^{N}(1+f_{1j})$ by $1+\sum_{j=2}^{N} f_{1j}$ for the above-mentioned reasons (in view of the further integration over the environment $N-s$ particle coordinates). In the same way we can consider the difference between ρ_{Σ}^{1} and ρ_{Σ}. In the linear in n approximation

$$\rho_{\Sigma}^{1}-\rho_{\Sigma}=\frac{1}{V^{N-1}}\rho_{\Sigma}(\mathbf{p})\left[\left(\sum_{j=2}^{N} f_{1j}\right)\left(1-n\int d\mathbf{r}_2 f_{12}\right)-n\int d\mathbf{r}_2 f_{12}\right], \tag{42}$$

where we used that in this approximation $\rho_{\Sigma}=\frac{1}{V^{N-1}}\rho_{\Sigma}(\mathbf{p})$. Then, applying $\int\cdots\int dx^{\Sigma}$ to (42), we see that in the adopted approximation

$$\langle\mathbf{F}_1\rangle_{\Sigma}^{1}-\langle\mathbf{F}_1\rangle_{\Sigma}=-n\int d\mathbf{r}_2 f_{12}(\nabla_1 V_{12}). \tag{43}$$

Thus, Eq. (35) for $s=1$ in the linear in n approximation acquires the form

$$\frac{\partial}{\partial t}F_1(t,\beta)=-\left[\mathbf{v}_1\cdot\nabla_1-(\nabla_1\langle H_{1\Sigma}\rangle_{\Sigma})\cdot\frac{\partial}{\partial\mathbf{p}_1}-n\int d\mathbf{r}_2 f_{12}(\nabla_1 V_{12})\cdot\frac{\partial}{\partial\mathbf{p}_1}\right]F_1(t,\beta),+C_{\rm col}(t,\beta)+C_{ic}(t,\beta), \tag{44}$$

where $C_{\rm col}(t,\beta)$ is the collision term

$$\begin{aligned}
C_{\rm col}(t,\beta)&=n\int_0^t d\tau\int d\mathbf{r}_2\int d\mathbf{p}_2 L_{12}'\exp[-(L_{12}\tau)]L_{12}'\rho^0(\mathbf{p}_2)e^{-\beta V_{12}}F_1(t-\tau,\beta)\\
&=n\int_0^t d\tau\int d\mathbf{r}_2\int d\mathbf{p}_2\partial_{12}\cdot\mathbf{F}_{12}\exp[-(L_{12}\tau)]\mathbf{F}_{12}\cdot\partial_{12}\rho^0(\mathbf{p}_2)e^{-\beta V_{12}}F_1(t-\tau,\beta)\\
L_{12}&=L_1^0+L_2^0+L_{12}',\quad L_1^0=\mathbf{v}_1\cdot\nabla_1, L_2^0=\mathbf{v}_2\cdot\nabla_2,\\
L_{12}'&=\mathbf{F}_{12}\cdot\partial_{12},\quad \mathbf{F}_{12}=-(\nabla_1 V_{12}),\partial_{12}=\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2},\\
\rho^0(\mathbf{p}_2)&=\exp\big(-\beta p_2^2/2m\big)\Big/\int d\mathbf{p}_2\exp\big(-\beta p_2^2/2m\big),
\end{aligned} \tag{45}$$

and $C_{ic}(t,\beta)$ is the additional term due to initial correlations

$$\begin{aligned}
C_{ic}(t,\beta)&=n\int_0^t d\tau\int d\mathbf{r}_2\int d\mathbf{p}_2 L_{12}'\exp[-(L_{12}\tau)]\mathbf{g}_{12}\cdot(\nabla_1 f_{12})\rho^0(\mathbf{p}_2)F_1(t-\tau,\beta)\\
&=n\beta\int_0^t d\tau\int d\mathbf{r}_2\int d\mathbf{p}_2\partial_{12}\cdot\mathbf{F}_{12}\exp[-(L_{12}\tau)]\mathbf{F}_{12}\cdot\mathbf{g}_{12}\rho^0(\mathbf{p}_2)e^{-\beta V_{12}}F_1(t-\tau,\beta),\\
\mathbf{g}_{12}&=\mathbf{v}_1-\mathbf{v}_2.
\end{aligned} \tag{46}$$

Here, we used Eqs. (30)–(32) and (41) and that in the linear in n approximation

$$\langle H_{1\Sigma}\rangle_{\Sigma}=n\int d\mathbf{r}_2 V_{12}, \tag{47}$$

and also that $\nabla_1 f_{12}=-\nabla_2 f_{12}$.

Obtained Eq. (44) is the main result of this section and can be considered as a generalized linear Boltzmann equation accounting for initial correlations. The term (45) is the generalized linear version of the Boltzmann collision term. We see that the tagged particle 1, the evolution of which we follow by means of obtained equation, collides with the tagged second particle in the equilibrium state described by $\rho^0(\mathbf{p}_2)e^{-\beta V_{12}}$.

In the space-homogeneous case when $F_1(t,\beta)=F_1(\mathbf{p}_1;t,\beta)$, $\nabla_1\langle H_{1\Sigma}\rangle_{\Sigma}=0$, and $\int d\mathbf{r}_2 f_{12}(\nabla_1 V_{12})=0$, Eq. (44) reduces to

$$\frac{\partial}{\partial t}F_1(\mathbf{p}_1;t,\beta)=C_{\rm col}(t,\beta)+C_{ic}(t,\beta), \tag{48}$$

where $C_{\rm col}(t,\beta)$ and $C_{ic}(t,\beta)$ are given by (45) and (46) but with $F_1(t-\tau,\beta)=F_1(\mathbf{p}_1;t-\tau,\beta)$.

We see that the evolution in time in Eqs. (45) and (46) is defined by the exact two-particle propagator which satisfies the integral equation

$$\exp[-(L_{12}\tau)]=U_{12}(\tau)=U_{12}^0(\tau)+\int_0^{\tau} d\tau_1 U_{12}^0(\tau-\tau_1)L_{12}'U_{12}(\tau_1), \tag{49}$$

where $U_{12}^0(\tau)=\exp[-(L_1^0+L_2^0)\tau]$ is a "free" two-particle propagator.

VI. CONNECTION TO THE BOLTZMANN EQUATION

Note that Eqs. (44) and (48) are the reversible in time ones. They become irreversible if it is possible to extend in them the upper limit of integration over τ to infinity (and this limit exists). It can be the case of the short time interparticle interaction $\tau_{\rm cor}$, when

$$\tau_{\rm cor} \ll t \sim \tau_{\rm rel}, \tag{50}$$

where $\tau_{\rm rel}$ is the timescale on which the $F_1(t,\beta)$ changes (see also below). Then, in the obtained equations we can approximate the one-particle function as $F_1(t-\tau,\beta) \approx F_1(t,\beta)$ and simultaneously extend the upper limit of integration to infinity. The latter can be done, e.g., if the time-dependent force-force correlation function in Eqs. (45) and (46)

$$\int d\mathbf{r}_2 \mathbf{F}_{12} \cdot \exp[-(L_{12}\tau)]\mathbf{F}_{12} \tag{51}$$

quickly vanishes on the timescale $\tau_{\rm cor} \sim r_{\rm cor}/v \ll \tau_{\rm rel}$ ($r_{\rm cor}$ is a radius of the interparticle interaction V_{ij} and v is the average particle velocity), i.e., when the interaction is rather a short-range one. Thus, in this case, Eqs. (44) and (48) on the timescale $t \sim \tau_{\rm rel}$ become Markovian (time local) and irreversible.

Let us consider (following the approach of [4]) in this approximation and in the space-homogeneous case the collision term (45), which in the new convenient variables $\mathbf{v}_i = \mathbf{p}_i/m$, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, and $\mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2$ can be written as

$$C_{\rm col}(\mathbf{v}_1;t,\beta) = n\int d\mathbf{v}_2 J(\mathbf{v}_1,\mathbf{v}_2), \quad J(\mathbf{v}_1,\mathbf{v}_2) = \int d\mathbf{r}\int_0^\infty d\tau\, L'U(\tau)L'\varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta),$$

$$L' = -[\nabla V(\mathbf{r})]\cdot\partial, \quad \nabla = \frac{\partial}{\partial\mathbf{r}}, \quad \partial = \frac{2}{m}\frac{\partial}{\partial\mathbf{g}},$$

$$\varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) = \rho^0(\mathbf{v}_2)e^{-\beta V(\mathbf{r})}F_1(\mathbf{v}_1;t,\beta), \quad \rho^0(\mathbf{v}_2) = \exp\big(-\beta m v_2^2/2\big)\Big/\int d\mathbf{v}_2 \exp\big(-\beta m v_2^2/2\big), \tag{52}$$

where we assumed that in the space-homogeneous case $B_1(0)$, hidden in $F_1(\mathbf{v}_1;t,\beta)$, depends only on $\mathbf{v}_1$ and dropped for brevity the indices 12 in (45), which cannot lead to misunderstanding because we deal in the adopted first order in n approximation only with a tagged pair of particles. It can be easily shown that the integral over τ in (52) can be presented as [see (49)]

$$Z = G + GL'Z, \quad G = \lim_{p\to+0}\int_0^\infty d\tau\, e^{-p\tau}U^0(\tau), \quad Z = \lim_{p\to+0}\int_0^\infty d\tau\, e^{-p\tau}U(\tau). \tag{53}$$

In the matrix form, $Z(\mathbf{r},\mathbf{g};\mathbf{r}',\mathbf{g}')$ satisfies the equation

$$\{\mathbf{g}\cdot\nabla - [\nabla V(\mathbf{r})]\cdot\partial\}Z(\mathbf{r},\mathbf{g};\mathbf{r}',\mathbf{g}') = \delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{g}-\mathbf{g}'), \tag{54}$$

i.e., it is the Green's function of the two-particle Liouville equation [see (32)], whereas the matrix $G(\mathbf{r},\mathbf{g};\mathbf{r}',\mathbf{g}')$ is diagonal with respect to velocity indices $G(\mathbf{r},\mathbf{g};\mathbf{r}',\mathbf{g}') = G^0(\mathbf{r}-\mathbf{r}')\delta(\mathbf{g}-\mathbf{g}')$ and $G^0(\mathbf{r},\mathbf{g};\mathbf{r}',\mathbf{g}')$ is Green's function of the unperturbed Liouville equation

$$\mathbf{g}\cdot\nabla G^0(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{55}$$

If we introduce the function

$$f(\mathbf{r},\mathbf{g};t,\beta) = \varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) + \int d\mathbf{r}'\int d\mathbf{g}' Z(\mathbf{r},\mathbf{g};\mathbf{r}',\mathbf{g}')[\nabla' V(\mathbf{r}')]\cdot\partial'\varphi(\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}';t,\beta), \tag{56}$$

then it is not difficult to show, using (54), that

$$\{\mathbf{g}\cdot\nabla - [\nabla V(\mathbf{r})]\cdot\partial\}f(\mathbf{r},\mathbf{g};t,\beta) = \mathbf{g}\cdot\nabla\varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta), \quad \lim_{V(r)\to0} f(\mathbf{r},\mathbf{g};t,\beta) = \rho^0(\mathbf{v}_2)F_1(\mathbf{v}_1;t,\beta). \tag{57}$$

Thus, it is easy to verify that the function $f(\mathbf{r},\mathbf{g};t,\beta)$, presented as

$$f(\mathbf{r},\mathbf{g};t,\beta) = \varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) + \int d\mathbf{r}' G^0(\mathbf{r}-\mathbf{r}')[\nabla' V(\mathbf{r}')]\cdot\partial f(\mathbf{r}',\mathbf{g};t,\beta), \tag{58}$$

satisfies the equation (57).

Now we can write the function $J(\mathbf{v}_1,\mathbf{v}_2)$, defining the collision term (52), as

$$J(\mathbf{v}_1,\mathbf{v}_2) = \int d\mathbf{r}[\nabla V(\mathbf{r})]\cdot\partial[f(\mathbf{r},\mathbf{g};t,\beta) - \varphi(\mathbf{v_1},\mathbf{v_2},\mathbf{r};t,\beta)] = \int d\mathbf{r}\,\mathbf{g}\cdot\nabla V(\mathbf{r}) f(\mathbf{r},\mathbf{g};t,\beta). \tag{59}$$

Here, we used (56) and (57) and that $\varphi(\mathbf{v_1},\mathbf{v_2},\mathbf{r};t,\beta)$ depends on the relative distance r as $\exp[-\beta V(r)]$ and, therefore, $\int d\mathbf{r}[\nabla V(\mathbf{r})]\exp[-\beta V(r)] = -\beta^{-1}\int d\mathbf{r}\,\nabla\{\exp[-\beta V(r)]\} = 0$ in the space-homogeneous case.

Let us select the coordinate system in which axis z is directed along vector $\mathbf{g}$. Then, the Green's function $G^0(\mathbf{r}-\mathbf{r}')$ has the form

$$G^0(\mathbf{r}-\mathbf{r}') = g^{-1}\delta(x-x')\delta(y-y')\theta(z-z'), \quad \theta(x)=1,\ x>0 \quad \theta(x)=0,\ x<0 \tag{60}$$

which is in agreement with Eq. (55). Inserting (60) in (58), we obtain

$$\begin{aligned} f(\mathbf{r},\mathbf{g};t,\beta) &= \varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) + \int_{-\infty}^{z} dz' g^{-1}[\nabla' V(x,y,z')]\cdot\partial f(x,y,z',g;t,\beta) \\ &= \varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) + \int_{-\infty}^{z} dz'\left(\frac{\partial}{\partial z'}\right)[f(x,y,z',g;t,\beta) - \varphi(\mathbf{v}_1,\mathbf{v}_2,z';t,\beta)] \\ &= \varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) + \int_{-\infty}^{z} dz'\left(\frac{\partial}{\partial z'}\right) f(x,y,z',g;t,\beta) \\ &= \varphi(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r};t,\beta) + \Phi(x,y,z,g;t,\beta), \quad \Phi(x,y,z,g,\beta) = \int_{-\infty}^{z} dz'\left(\frac{\partial}{\partial z'}\right) f(x,y,z',g;t,\beta). \end{aligned} \tag{61}$$

Finally, introducing (61) in (59), we obtain

$$\begin{aligned} J(\mathbf{v}_1,\mathbf{v}_2) &= \int d\mathbf{r}\,\mathbf{g}\cdot\nabla V(\mathbf{r}) f(\mathbf{r},\mathbf{g};t,\beta) = \int_{-\infty}^{\infty} dz\, g\left(\frac{\partial}{\partial z}\right)\Phi(x,y,z) = g[\Phi(x,y,\infty,g;t,\beta) - \Phi(x,y,-\infty,g;t,\beta)] \\ &= g\int_{-\infty}^{\infty} dz'\left(\frac{\partial}{\partial z'}\right) f(x,y,z',g;t,\beta) = g[f(x,y,+\infty,g;t,\beta) - f(x,y,-\infty,g;t,\beta)]. \end{aligned} \tag{62}$$

It is then evident from (62) that function $f(x,y,-\infty,g;t,\beta)$ can be identified with the distribution function (52) $\varphi(\mathbf{v}_1,\mathbf{v}_2,-\infty;t,\beta)$ prior to collision, i.e.,

$$\varphi(\mathbf{v}_1,\mathbf{v}_2,-\infty;t,\beta) = \rho^0(\mathbf{v}_2)F_1(\mathbf{v}_1;t,\beta), \tag{63}$$

where we used that $\exp[-\beta V(\pm\infty)] = 1$ $[V(\pm\infty)=0]$. Function $f(x,y,+\infty,g;t,\beta)$ can be considered as the distribution function of particles after collision with the relative velocity $\mathbf{g}$. But due to Liouville-type dynamics given by Eq. (4), this distribution function is equal to the distribution function before collision with velocities $\mathbf{v}_1'$, $\mathbf{v}_2'$ which correspond to the velocities $\mathbf{v}_1$, $\mathbf{v}_2$ (the Liouville-type theorem), i.e.,

$$f(x,y,+\infty,g;t,\beta) = \rho^0(\mathbf{v}_2')F_1(\mathbf{v}_1';t,\beta), \quad \mathbf{v}_1+\mathbf{v}_2 = \mathbf{v}_1'+\mathbf{v}_2', \quad v_1^2+v_2^2 = v_1'^2+v_2'^2. \tag{64}$$

Taking into account that in the adopted coordinate system with $\mathbf{g}$ directed along the z axis

$$dx\,dy = bdbd\varphi, \tag{65}$$

where b is the impact parameter and φ is the azimuth angle. As a result, we arrive at the linear Boltzmann collision term in Eq. (48):

$$C_{\rm col}(\mathbf{v}_1;t,\beta) = n\int d\mathbf{v}_2\int d\varphi\, db\, bg[\rho^0(\mathbf{v}_2')F_1(\mathbf{v}_1';t,\beta) - \rho^0(\mathbf{v}_2)F_1(\mathbf{v}_1;t,\beta)], \tag{66}$$

i.e., the Boltzmann collision term with the Maxwell distribution function for the second tagged particle. Making in (66) the substitutions

$$F_1(\mathbf{v}_1;t,\beta) = \rho^0(\mathbf{v}_1)W(\mathbf{v}_1,t), \quad F_1(\mathbf{v}_1';t,\beta) = \rho^0(\mathbf{v}_1')W(\mathbf{v}_1',t), \tag{67}$$

the collision term for the function W can be rewritten as (see, e.g. [23])

$$C_{\rm col}(\mathbf{v}_1;t,\beta) = \rho^0(\mathbf{v}_1)n\int d\mathbf{v}_2\int d\varphi\, db\, bg\rho^0(\mathbf{v}_2)[W(\mathbf{v}_1',t) - W(\mathbf{v}_1,t)], \tag{68}$$

where we used that according to definition (45) for $\rho^0(\mathbf{v})$ and the conservation of energy (64)

$$\rho^0(\mathbf{v}_1)\rho^0(\mathbf{v}_2) = \rho^0(\mathbf{v}_1')\rho^0(\mathbf{v}_2'). \tag{69}$$

Note that $\rho^0(\mathbf{v}_1)$ can be canceled out in Eq. (48) written for function $W(\mathbf{v}_1,t)$ with no initial correlation term $C_{ic}(t,\beta)$.

VII. CONNECTION TO THE LANDAU EQUATION

It is interesting to consider Eq. (44) for the case of a weak interparticle interaction when

$$\left\langle p_i^2/2m\right\rangle \backsim k_BT \gg V_{ij}, \tag{70}$$

i.e., the interparticle interaction is small as compared to the average particle's kinetic energy. Then, in the second order in the small parameter, defined by inequality (70), the collision term (45) can be rewritten as

$$C_{\rm col}(t,\beta) = n\int_0^t d\tau \int d\mathbf{r}_2 \int d\mathbf{p}_2 \mathbf{F}_{12}\cdot\partial_{12}\exp[-(\mathbf{v}_1\cdot\nabla_1+\mathbf{v}_2\cdot\nabla_2)\tau]\mathbf{F}_{12}\cdot\partial_{12}\rho^0(\mathbf{p}_2)e^{\mathbf{v}_1\cdot\nabla_1\tau}F_1(t,\beta). \tag{71}$$

Here, in order to remain within adopted accuracy, we took $F_1(t-\tau,\beta)$ in the zero in the interaction approximation [see (44)]

$$F_1(t-\tau,\beta) = \exp[-\mathbf{v}_1\nabla_1(t-\tau)]F_1(0,\beta) = e^{\mathbf{v}_1\nabla_1\tau}F_1(t,\beta). \tag{72}$$

In the same approximation

$$C_{ic}(t,\beta) = n\beta\int_0^t d\tau \int d\mathbf{r}_2 \int d\mathbf{p}_2 \mathbf{F}_{12}\cdot\partial_{12}\exp[-(\mathbf{v}_1\nabla_1+\mathbf{v}_2\nabla_2)\tau]\mathbf{F}_{12}\cdot\mathbf{g}_{12}\rho^0(\mathbf{p}_2)e^{\mathbf{v}_1\nabla_1\tau}F_1(t,\beta). \tag{73}$$

Then, we have for any function of the particles coordinates $\Phi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$

$$\exp[-(\mathbf{v}_1\nabla_1+\mathbf{v}_2\nabla_2)\tau]\Phi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \Phi(\mathbf{r}_1-\mathbf{v}_1\tau,\mathbf{r}_2-\mathbf{v}_2\tau,\mathbf{r}_3,\ldots,\mathbf{r}_N). \tag{74}$$

If we also take into account the commutation rule

$$[\exp[-(\mathbf{v}_1\nabla_1+\mathbf{v}_2\nabla_2)\tau],\partial_{12}] = \exp[-(\mathbf{v}_1\nabla_1+\mathbf{v}_2\nabla_2)\tau]\frac{\tau}{m}(\nabla_1-\nabla_2), \tag{75}$$

the collision term acquires the final form

$$C_{\rm col}(t,\beta) = n\int_0^t d\tau\int d\mathbf{p}_2\partial_{12}G_L(x_1,\mathbf{g}_{12};\tau)\Big(\partial_{12}+\frac{\tau}{m}\nabla_1\Big)\rho^0(\mathbf{p}_2)F_1(x_1;t,\beta),$$
$$G_L(\mathbf{r}_1,\mathbf{g}_{12};\tau) = \int d\mathbf{r}_2\mathbf{F}_{12}(0)\mathbf{F}_{12}(\tau), \quad \mathbf{F}_{12}(\tau) = -\nabla_1V(\mathbf{r}_1-\mathbf{r}_2-\mathbf{g}_{12}\tau). \tag{76}$$

Using (74), the initial correlation term (73) can be rewritten as

$$C_{ic}(t,\beta) = n\beta\int_0^t d\tau\int d\mathbf{p}_2\partial_{12}G_L(\mathbf{r}_1,\mathbf{g}_{12};\tau)\mathbf{g}_{12}\rho^0(\mathbf{p}_2)F_1(x_1;t,\beta). \tag{77}$$

The collision integral (76) coincides with the corresponding collision integral in the nonlinear equation for inhomogeneous system of weakly interacting classical particles (see [4]) if in the latter, the distribution function for the particle, with which the tagged particle collides, is replaced by the equilibrium distribution function for this particle $\rho^0(\mathbf{p}_2)$. In addition, for such a coincidence, the integral over $d\tau$ should be extended to infinity. It can be done, if the interaction is rather a short-range one and if for the timescale (50) the force acting on the particle vanishes [$\mathbf{F}_{12}(t)=0$].

In the space-homogeneous case, Eq. (48) for a small interparticle interaction reads as

$$\frac{\partial}{\partial t}F_1(\mathbf{p}_1;t,\beta) = n\int_0^t d\tau\int d\mathbf{p}_2\partial_{12}G_L(\mathbf{r}_1,\mathbf{g}_{12};\tau)(\partial_{12}+\beta\mathbf{g}_{12}) \times\rho^0(\mathbf{p}_2)F_1(\mathbf{p}_1;t,\beta). \tag{78}$$

The first (collision) term in the right-hand side of Eq. (78) coincides with the Landau collision integral if it is possible to extend the integral over τ to infinity (short-range interparticle interaction) and to replace the distribution function for the second tagged particle with $\rho^0(\mathbf{p}_2)$ [which seems natural for considered second order in interaction approximation for the kernel governing evolution of $F_1(\mathbf{p}_1;t,\beta)$]. The second term in the right-hand side of (78) is caused by initial correlations and is formally of the same order as the first term.

VIII. CONCLUSION

We have rigorously derived the exact completely closed (homogeneous) generalized master equations governing the evolution in time of an equilibrium two-time correlation function for dynamic variables of a selected group of s ($s<N$) particles of an N-particle ($N\gg1$) system of classical particles. These time-convolution and time-convolutionless GMEs differ from known equations (such as Nakajima-Zwanzig equation) by the absence of undesirable inhomogeneous terms containing the correlations of all N particles in the initial moment of time. Such closed reduced description has become possible through the use of a special projection operator (17).

This projection operator (comprising initial correlations) can be expanded into a series in the density of particles or in the weak interparticle interaction. In the linear in n approximation for the kernel governing the evolution of a one-particle correlation function, the generalized linear Boltzmann equation accounting for initial correlations and valid at any timescale has been rigorously obtained. At the timescale $t\sim\tau_{\rm rel}\gg\tau_{\rm cor}$ and for a short-range interaction, this equation becomes irreversible with the collision integral of the linear

Boltzmann equation (for the space-homogeneous case) but with an additional term due to initial correlations.

If in addition the interparticle interaction is weak, the generalized linear Boltzmann equation converts into the generalized linear Landau equation accounting for initial correlations and valid on all timescales. Again, at the timescale $t \sim \tau_{\rm rel} \gg \tau_{\rm cor}$ and for a short-range interaction this equation becomes irreversible. For the space-homogeneous case, the collision integral coincides with the Landau collision integral in which the distribution function of the second tagged particle is replaced with the equilibrium Maxwell distribution function. But, there is also an additional term in the kernel governing the evolution of a one-particle correlation function caused by initial correlations.

The approach suggested in this paper with no traditional approximations (molecular chaos, propagation of chaos, Bogoliubov principle of weakening of initial correlations) works only for the initial equilibrium state for the full system, which in the considered case of equilibrium correlation function (2) can be conveniently taken in the form $\rho(\beta)B_s(0)$ [see (5)]. This approach is not restricted only to the case of equilibrium correlation functions (2). It is easily seen that for the case when a system is driven from an initial (at $t = t_0$) Gibbs equilibrium state $\rho(\beta)$ by an external force (applied at $t > t_0$), the same method works and the similar completely closed (homogeneous) GMEs (but with the additional external force terms) can be obtained for the conventional reduced s-particle distribution functions (see recently published work [16], where, as an application, a small interparticle interaction case was considered, which resulted in the linear generalized Landau equation).

Thus, the natural initial equilibrium state for the full system allows for rigorous derivation of the generalized linear Boltzmann and Landau equations with the terms caused by initial correlations. Note that the known linear Boltzmann and Landau equations are conventionally derived using the above-mentioned unproven approximations (i.e., in fact by neglecting the initial correlations) [6] as well as the conventional nonlinear Boltzmann and Landau equations. The linearity of the obtained in this paper equations naturally follows from the linear Liouville equation.

In summary, the long-standing problem of the rigorous derivation of the completely closed evolution equations for s-particle marginals from the Liouville equation seems to be resolved in the case of equilibrium initial state for the full N-particle ($N > s$) classical system (at least on the level of rigor adopted in this paper). The obtained homogeneous GMEs are the linear ones. The rigorous derivation of the nonlinear (Boltzmann-type) closed equations for arbitrary timescale is still an open problem. The linear Boltzmann and Landau equations, which follow from the obtained in this paper homogeneous GMEs, differ from the known equations by additional terms due to accounting for initial correlation between the s-particle subsystem and environment of $N - s$ particles. These additional terms can contribute to the kinetic properties of the system under consideration, as it was demonstrated for the polaron mobility in the papers [14,15], in which the initial correlations for the quantum mechanical problem of interaction of a subsystem with a heat bath were taken into account by different method.

It should also be noted that the application of the obtained equations to a specific calculation of the measurable values for realistic potentials may lead to some mathematical problems, as it is, e.g., in the case of the Landau equation, applied to a plasma, when a cutoff has to be included [4].

[1] N. N. Bogoliubov, *Problems of Dynamical Theory in Statistical Physics* (Gostekhizdat, Moscow, 1946, in Russian); English translation: *Stud. Statist. Mech.* **1** (North-Holland, Amsterdam, 1962).

[2] O. E. Lanford, Time evolution of large classical systems, in *Dynamical Systems, Theory and Applications*, Lecture Notes in Physics, Vol. 38, edited by J. Moser (Springer, Berlin, 1975), pp. 1–111.

[3] C. Cercignani, R. Illner, and M. Pulvirenti, *The Mathematical Theory of Dilute Gases*, Applied Mathematical Sciences, Vol. 106 (Springer-Verlag, New York, 1994).

[4] R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975).

[5] A. Bobylev, M. Pulvirenti, and C. Saffirio, Commun. Math. Phys. **319**, 683 (2013).

[6] B. Vacchini and K. Hornberger, Phys. Rep. **478**, 71 (2009).

[7] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, New York, 2002).

[8] N. G. van Kampen, J. Stat. Phys. **115**, 1057 (2004).

[9] M. Kac, *Probability and Related Topics in Physical Sciences* (Interscience, London, 1959).

[10] V. F. Los, J. Phys. A: Math. Gen. **34**, 6389 (2001).

[11] V. F. Los, J. Stat. Phys. **119**, 241 (2005).

[12] V. F. Los, in *Evolution Equations*, edited by A. Claes (Nova Science, New York, 2012), p. 251.

[13] V. F. Los, Theor. Math. Phys. **160**, 1124 (2009).

[14] V. F. Los, J. Stat. Phys. **168**, 857 (2017).

[15] V. F. Los, Physica A (Amsterdam) **503**, 476 (2018).

[16] V. F. Los, Physica A (Amsterdam) **554**, 124704 (2020).

[17] S. Nakajima, Prog. Theor. Phys. **20**, 948 (1958).

[18] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).

[19] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience, New York, 1962).

[20] F. Shibata, Y. Takahashi, and N. Hashitsume, J. Stat. Phys. **17**, 171 (1977).

[21] F. Shibata and T. Arimitsu, J. Phys. Soc. Jpn. **49**, 891 (1980).

[22] J. E. Mayer and E. W. Montroll, J. Chem. Phys. **9**, 2 (1941).

[23] N. Catapano, Kinet. Relat. Models **11**, 647 (2018).