Dense inhomogeneous fluids: Functional perturbation theory, the generalized Langevin equation, and kinetic theory

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We present a functional perturbation theory (FPT) to describe the dynamical behavior of dense, inhomogeneous fluid mixtures, and from this show rigorously that the generalized Langevin equations are a first order form of this FPT. These equations lead to linearized kinetic equations for the singlet dynamical distribution function and for the higher distribution functions. These kinetic equations for inhomogeneous fluid mixtures reduce to those of Sung and Dahler [J. Chem. Phys. **80**, 3025 (1984)] in the case of homogeneous fluids. Finally, we prove that the kinetic equations derived can be used to derive a "smoothed density" postulate, in which the local transport coefficients for inhomogeneous fluids are equated to those for a homogeneous fluid of the same smoothed density.

I. INTRODUCTION

Although several theoretical approaches to the microscopic theory of transport processes are available for homogeneous fluids,[1–5] there have been few attempts to develop the kinetic theory for strongly inhomogeneous fluids, and in particular for inhomogeneous fluids of liquid-like density. Such a theory is needed for the study of fluids near interfaces and in microporous media,[6–8] where the pores are often in the size range 5–20 Å. The most successful approach to such fluids was suggested[9] and later developed[10,11] by Davis and co-workers; it was based on an intuitively reasonable extension of the revised Enskog theory.[12–14] At an *ad hoc* level, it has been postulated that local transport coefficients in inhomogeneous fluids can be set equal to those for a homogeneous fluid whose density is set equal to some "smoothed" density obtained by averaging over densities in the immediate region of the point of interest in the inhomogeneous system.[15] Such an approach follows the successful use of such smoothed density ideas for equilibrium inhomogeneous fluids; although the use of such smoothed densities rests on rigorous foundations for the equilibrium case,[16] no analogous foundation exists so far for their use for nonequilibrium fluids.

In this work we present a new attempt to establish a more rigorous microscopic theory for the description of nonequilibrium behavior of strongly inhomogeneous fluids, and in particular liquids. The approach is based on the generalized Langevin equation (GLE) method originally suggested by Zwanzig,[17] generalized and developed by Mori,[18] and heuristically extended by Akcasu and Duderstadt.[19] As a method of deriving time evolution equations for time correlation functions of fluids, the GLE approach has proved its usefulness over almost three decades.[20–24] The GLE approach has also been used as a starting point for deriving kinetic equations by Sung and Dahler,[25,26] who showed that mean field kinetic equations (MFKEs) for homogeneous fluids obtained in such an approach were identical in form to the linearized version of the revised Enskog equations[12] (REEs) for hard sphere mixtures. These REEs have been proved[13,14] to be consistent with the Onsager reciprocal relations, for which an entropy functional exists. The important difference between MFKEs and REEs is that the structure factors (radial and direct correlation functions) take into account the soft attractive intermolecular forces in the former case, whereas they do not in the latter. Thus MFKEs lead to hydrodynamical equations and transport coefficients which are in good agreement with experimental data for densities and viscosities of homogeneous liquids. The MFKEs can be regarded as an extension of REEs to fluids with intermolecular interaction potentials that include soft attractive parts. Also, the MFKEs were proved[27] to coincide with analogous equations of linearized kinetic variational theory.[5,27]

The theory for inhomogeneous fluids presented here was inspired by the work of Sung and Dahler[26] for homogeneous fluids. In Secs. II and III we develop a functional perturbation theory (FPT) scheme and prove rigorously that the GLEs of Refs. 18 and 19 can be considered to be exact equations of the first order FPT with respect to thermal disturbances of the collective dynamical variables. Attempts to develop such a scheme were taken originally by Sauermann *et al.*[28] for dynamical systems under the time-dependent external fields, and by Pozhar[29] for scalar dynamical variables describing time evolution of dynamical systems with thermal disturbances. In the present investigation we develop ideas of Ref. 29 for vector dynamical variables. The FPT scheme developed below is based on (a) the Liouville equation for collective dynamical variables, together with (b) functional Taylor expansions of the time derivatives of these variables, and (c) some specific mathematical features of the Laplace transforms. In the framework of the FPT, the GLE is a linearization of the more complicated equation describing time evolution of the collective dynamical variables. Thus the GLE leads to linearized kinetic equations, both for singlet distribution functions and more complicated correlation functions of fluids. The FPT scheme also permits us to

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derive nonlinear master equations for collective dynamical variables of the n-th order with respect to thermal disturbances of the collective dynamical variables. These could be of significant interest for the description of the time evolution of dynamical systems with strong memory effects.

In Sec. IV we extend Sung and Dahler's approach,[26] and use the GLEs to derive mean field kinetic equations for singlet distribution functions of strongly inhomogeneous fluid mixtures; these reduce to the MFKEs of Sung and Dahler[26] if the equilibrium numerical densities of the components are independent of coordinates. At the end of Sec. IV we analyze the equations derived, and establish their compatibility with the "smoothed" local density postulate,[15] in which local transport coefficients for inhomogeneous fluids are equated to those for a homogeneous fluid of the same smoothed density.

II. MAIN ASSUMPTIONS AND EXPANSIONS OF COLLECTIVE DYNAMICAL VARIABLES

We choose a set of N collective dynamical variables $\{B_i(\mathbf{q},\mathbf{p},t)\}$ where $i = 1,2,...N$, that are sufficient for a complete description of the system's collective behavior; for example, for a fluid mixture system these dynamical variables would include the phase space densities of species, momenta, angular moments, and energy. For further convenience, and without loss of generality, we can consider their invariant parts to be zero, and that the ergodicity conditions hold,

$$\lim_{T\to\infty}(1/T)\int_0^T B_i(\mathbf{q},\mathbf{p},t)\,dt = 0. \qquad (2.1)$$

We expect[18] the first time derivative of $B_i(\mathbf{q},\mathbf{p},t)$ to take the form [Though $\mathbf{q},\mathbf{p}$ above are independent of t, we use the notation (d/dt) for the derivative to stress the fact that $B_i(\mathbf{q},\mathbf{p},t)$ depends on t through the coordinates and momenta $\mathbf{q}^\alpha(t),\mathbf{p}^\alpha(t)$ of particles from the dynamical system, which we have not included explicitly as arguments of the B_i.]

$$\frac{d}{dt}B_i(\mathbf{q},\mathbf{p},t) = F(\mathbf{q},\mathbf{p},t) = F_1\left[\{B_j(\mathbf{x},\mathbf{u},\tau)\}_{j=1}^N,\ \infty \geqslant \mathbf{x},\mathbf{u} \geqslant -\infty,\ t \geqslant \tau \geqslant t_0\right] + F_2^{(i)}(\mathbf{q},\mathbf{p},t), \qquad (2.2)$$

where $F_1[\ ]$ is an operator acting in a Hilbert space of the dynamical variables and depending on the previous history of $\{B_i(\mathbf{q},\mathbf{p},t)\}_{i=1}^N$, and $F_2(\mathbf{q},\mathbf{p},t)$ represents contributions of other degrees of freedom of the system. Due to our choice of $\{B_i(\mathbf{q},\mathbf{p},t)\}_{i=1}^N$ with invariant parts equal to zero, and considering $F_1[\ ]$ as an analytical operator and setting $t_0 = 0$, we can rewrite (2.2) in the form[30,31]

$$\frac{d}{dt}B_i(\mathbf{p},t) = \sum_{n=1}^{\infty}\frac{1}{n!}\underbrace{\sum\cdots\sum_{j<k<\cdots<m=1}^{N}}_{n}\int_0^t d\tau_1\cdots d\tau_n\int_{-\infty}^{\infty}d\mathbf{u}_1\cdots d\mathbf{u}_n \times\Theta^{(i)}_{jk\cdots m}(\mathbf{p},t;\tau_1,...,\tau_n,\mathbf{u}_1,...,\mathbf{u}_n)B_m(\mathbf{u}_n,\tau_n)\times\cdots\times B_k(\mathbf{u}_2,\tau_2)B_j(\mathbf{u}_1,\tau_1) + F_2^{(i)}(\mathbf{p},t), \qquad (2.3)$$

where we have used a Taylor series for the operator $F_1[\ ]$, and $\mathbf{p}$ to denote $(\mathbf{q},\mathbf{p})$, and $\mathbf{u}$ to denote dummy variables $(\mathbf{u},\mathbf{x})$ of integration. We require the functions $\Theta^{(i)}_{jk...m}$ and contributions $F_2^{(i)}(\mathbf{p},t)$ to belong to the space C^∞ of infinitely differentiable functions. Also, for most dynamical systems we can expect that the $\Theta^{(i)}_{jk\cdots m}$ are symmetrical functions with respect to any permutation of their arguments in sets $\{\mathbf{u}_1,...,\mathbf{u}_n\}$ and $\{\tau_1,...,\tau_n\}$, and also

$$\Theta^{(i)}_{jk\cdots m}(\mathbf{p},t;\tau_1,...,\tau_n,\mathbf{u}_1,...\mathbf{u}_n) = \Theta^{(i)}_{jk\cdots m}(\mathbf{p};t-\tau_1,...,t-\tau_n,\mathbf{u}_1,...,\mathbf{u}_n). \qquad (2.4)$$

In order to make practical use of (2.3) we should restrict our consideration to some limited number M terms in the sum in the right-hand side of (2.3), so that the other terms with $n > M$ are included into $F_2^{(i)}(\mathbf{p},t)$. We should emphasize here that the idea of a collective mode description of the many-body system time evolution assumes that the restricted sum in the right-hand side of (2.3) defines the evolution, so that $F_2^{(i)}(\mathbf{p},t)$ should be thought of as terms of the next order with respect to the M-th term in the sum. We now make the M-multiple Laplace–Carson (LC) transforms[32,33] of Eq. (2.3),

$$\mathrm{LC}(f(t)) = f(z) = z\int_0^\infty e^{-zt}f(t)\,dt. \qquad (2.5)$$

For the first order terms in $B_i(\mathbf{u},t)$ in the right-hand side of (2.3), after changing the order of integration and integrating by parts, we obtain

$$\mathrm{LC}\left(\int_0^t \Theta_k^{(i)}(\mathbf{p},t;\tau,\bar{\mathbf{u}})B_k(\bar{\mathbf{u}},\tau)\,d\tau\right) = z_1\int_0^\infty d\tau\int_\tau^\infty dt\, e^{-z_1 t}\Theta_k^{(i)}(\mathbf{p},t;\tau,\bar{\mathbf{u}})B_k(\bar{\mathbf{u}},\tau) = \sum_{l=1}^{\infty}\sum_{m=0}^{\infty}\frac{1}{z_1^{(l+m)}}C^{(l-1)}_{(l+m)}(\bar{\mathbf{u}})\frac{d^{(l-1)}}{dt^{(l-1)}}B_k(\bar{\mathbf{u}},0), \qquad (2.6)$$

where the coefficients $C_j^l(\mathbf{u})$ are complicated combinations of $\Theta_k^{(i)}(\mathbf{p},t;\tau,\mathbf{u})$ and its' derivatives with respect to τ and/or t calculated at $t = \tau = 0$. Here and elsewhere in this paper we use the standard convention of integrating over the domain of an overscored variable, e.g.,

$$f(\bar{\mathbf{u}},\mathbf{y})g(\bar{\mathbf{u}},\mathbf{v}) = \int d\mathbf{u}\, f(\mathbf{u},\mathbf{y})g(\mathbf{u},\mathbf{v}).$$

Since the LC transform in the left-hand side of Eq. (2.6) is a function of z_1 and is uniquely determined by its LC preimage $\int_0^t \Theta_k^{(i)}(\mathbf{p},t;\tau,\bar{\mathbf{u}})B_k(\bar{\mathbf{u}},\tau)d\tau$, the whole sum on the right-hand side of (2.6) has to converge to the result of the LC transform of the left-hand side. On the other hand, the coefficients $C_j^l(\mathbf{u})$ are numbers at every given $\mathbf{u}$, so the whole dependence of the series Σ_m in the right-hand side of Eq. (2.6) on z_i is represented by factors $1/z_1^{(l+m)}$ that multiply $C_j^l(\mathbf{u})$. Also, each series Σ_m is multiplied by $B_k(\mathbf{u},t)$ or it's derivatives calculated at $t=0$, which are also independent of z_1 at every given $\mathbf{u}$.

Thus, it follows from the above that at every given $\mathbf{u}$ each series Σ_m should converge to one unique function of z_1, say, $\xi_l^{i(k)}(\mathbf{p};z_1,\mathbf{u})$ which is the sum of the corresponding series. Since the space of LC images of infinite differentiable functions is complete, the sums $\xi_l^{i(k)}(\mathbf{p};z_1,\mathbf{u})$ should belong to this space. Thus expression (2.6) could be written in the form

$$\mathrm{LC}\left\{\int_0^t \Theta_k^{(i)}(\mathbf{p},t;\tau,\bar{\mathbf{u}})B_k(\bar{\mathbf{u}},\tau)d\tau\right\} = \sum_{l=0}^{\infty}\xi_l^{i(k)}(\mathbf{p};z_1,\bar{\mathbf{u}})\frac{d^lB_k(\bar{\mathbf{u}},0)}{dt^l}. \quad (2.7)$$

Reasons analogous to those given above permit us to obtain the LC image of the n-th term in the sum from the right-hand side of Eq. (2.3),

$$\mathrm{LC}\left\{\int_0^t d\tau_1\cdots d\tau_n\Theta_{jk\cdots m}^{(i)}(\mathbf{p},t;\tau_1,\ldots,\tau_n,\bar{\mathbf{u}}_1,\ldots,\bar{\mathbf{u}}_n)B_m(\bar{\mathbf{u}}_n,\tau_n)\times\cdots\times B_k(\bar{\mathbf{u}}_2,\tau_2)B_j(\bar{\mathbf{u}}_1,\tau_1)\right\}$$
$$=\sum_{l_1,\ldots,l_n=0}^{\infty}\cdots\sum^{\infty}\xi_{l_1\cdots l_n}^{i(jk\cdots m)}(\mathbf{p},z_1,\ldots,z_n,\bar{\mathbf{u}}_1,\ldots,\bar{\mathbf{u}}_n)\frac{d^{l_n}B_m(\bar{\mathbf{u}}_n,0)}{dt^{l_n}}\times\cdots\times\frac{d^{l_2}B_k(\bar{\mathbf{u}}_2,0)}{dt^{l_2}}\frac{d^{l_1}B_j(\bar{\mathbf{u}}_1,0)}{dt^{l_1}}. \quad (2.8)$$

where the functions $\xi_{l_1\cdots l_n}^{i(jk\cdots m)}$ have a meaning analogous to the functions $\xi_l^{i(k)}$ above.

Thus, the result of the M-multiple LC transforms of Eq. (2.3) has the form

$$B_i(\mathbf{p},z_1)=B_i(\mathbf{p},0)+\frac{1}{z_1}\sum_{n=1}^{M}\frac{1}{n!}\underbrace{\sum^{N}\cdots\sum^{N}}_{\substack{j<k<\cdots<m\\ n}}\sum_{l_1,\ldots,l_n=0}^{\infty}\cdots\sum^{\infty}\xi_{l_1\cdots l_n}^{i(jk\cdots m)}(\mathbf{p};z_1,\ldots,z_n,\bar{\mathbf{u}}_1,\ldots,\bar{\mathbf{u}}_n)$$
$$\times\frac{d^{l_n}B_m(\bar{\mathbf{u}}_n,0)}{dt^{l_n}}\times\cdots\times\frac{d^{l_1}B_j(\bar{\mathbf{u}}_1,0)}{dt^{l_1}}+\frac{1}{z_1}F_2^{(i)}(\mathbf{p},z_1). \quad (2.9)$$

We can now make the inverse M-multiple LC transforms of (2.9) with respect to $t_1=t_2=\cdots=t_m=t$ to obtain an expansion

$$B_i(\mathbf{p},t)=\sum_{n=1}^{M}\frac{1}{n!}\underbrace{\sum_{j<k<}^{N}\cdots\sum_{<m=1}^{N}}_{n}\sum_{l_1,}^{\infty}\cdots\sum_{l_n=0}^{\infty}\int_{-\infty}^{\infty}d\mathbf{u}_1\cdots d\mathbf{u}_n\xi_{l_1\cdots l_n}^{i(jk\cdots m)}(\mathbf{p},t;\mathbf{u}_1,\ldots,\mathbf{u}_n)$$
$$\times\frac{d^{l_n}B_m(\mathbf{u}_n,0)}{dt^{l_n}}\times\cdots\times\frac{d^{l_1}B_j(\mathbf{u}_1,0)}{dt^{l_1}}+\tilde{F}_2^{(i)}(\mathbf{p},t). \quad (2.10)$$

where functions $\xi_{l_1\cdots l_n}^{i(jk\cdots m)}(\mathbf{p},t;\mathbf{u}_1,\ldots,\mathbf{u}_n)$ are defined uniquely by their LC preimages, $\xi_{l_1\cdots l_n}^{i(jk\cdots m)}(\mathbf{p};z_1,\ldots,z_n,\mathbf{u}_1,\ldots,\mathbf{u}_n)$, and $\tilde{F}_2^{(i)}(\mathbf{p},t)=\mathrm{LC}^{-1}\{(1/z_1)F_2(\mathbf{p},z_1)\}$.

The expansion (2.10) can be written in more compact form if we introduce column vectors

$$\mathbf{A}_{l_1\cdots l_n}^{n}(\mathbf{u}_n\cdots\mathbf{u}_1,\tau_n\cdots\tau_1)=\left|\begin{matrix}\frac{d^{l_n}B_1(\mathbf{u}_n,\tau_n)}{dt^{l_n}}\times\cdots\times\frac{d^{l_2}B_1(\mathbf{u}_2,\tau_2)}{dt^{l_2}}\times\frac{d^{l_1}B_1(\mathbf{u}_1,\tau_1)}{dt^{l_1}}\\ \vdots\\ \frac{d^{l_n}B_i(\mathbf{u}_n,\tau_n)}{dt^{l_n}}\times\cdots\times\frac{d^{l_2}B_k(\mathbf{u}_2,\tau_2)}{dt^{l_2}}\times\frac{d^{l_1}B_j(\mathbf{u}_1,\tau_1)}{dt^{l_1}}\\ \vdots\\ \frac{d^{l_n}B_N(\mathbf{u}_n,\tau_n)}{dt^{l_n}}\times\cdots\times\frac{d^{l_2}B_N(\mathbf{u}_2,\tau_2)}{dt^{l_2}}\times\frac{d^{l_1}B_N(\mathbf{u}_1,\tau_1)}{dt^{l_1}}\end{matrix}\right| \quad (2.11)$$

and, in particular,

$$A_0^1(\mathbf{p},t)=\left|\begin{matrix}B_1(\mathbf{p},t)\\ \vdots\\ B_N(\mathbf{p},t)\end{matrix}\right|\equiv\mathbf{B}(\mathbf{p},t).$$

Then from Eqs. (2.10) and (2.11) we can obtain a matrix form of the expansion (2.10),

$$\mathbf{B}(\mathbf{p},t)=\sum_{n=1}^{M}\frac{1}{n!}\Phi_n(\mathbf{p},t;\bar{\mathbf{u}}_1,\ldots,\bar{\mathbf{u}}_n)\cdot\mathbf{A}^n(\bar{\mathbf{u}}_n\cdots\bar{\mathbf{u}}_1)+\tilde{F}_2(\mathbf{p},t), \quad (2.12)$$

where the matrices $\mathbf{A}^n(\mathbf{u}_n\cdots\mathbf{u}_1)$ are composed of column vectors $\mathbf{A}_{l_1\cdots l_n}^n$ above, calculated at $\tau_1=\tau_2=\cdots\tau_n=0$, the dot $\cdot$ denotes matrix product, and matrices $\Phi_n(\mathbf{p},t;\mathbf{u}_1\cdots\mathbf{u}_n)$ are composed of row vectors

$$\Phi_n^{l_1\cdots l_n}(\mathbf{p},t;\mathbf{u}_1,\ldots\mathbf{u}_n)\equiv\left\{\xi_{l_1\cdots l_n}^{\overbrace{11\cdots1}^{n}}(\mathbf{p},t;\mathbf{u}_1,\ldots,\mathbf{u}_n),\ldots,\right.$$

$$\xi^{\overbrace{ik\cdots j}^{n}}_{l_1\cdots l_n}(\mathbf{p},t;\mathbf{u}_1,...,\mathbf{u}_n),...,\xi^{\overbrace{NN\cdots N}^{n}}_{l_1\cdots l_n}(\mathbf{p},t;\mathbf{u}_1,...,\mathbf{u}_n)\Big\},$$

$\mathring{F}_2(\mathbf{p},t)$ is the column vector

$$\begin{vmatrix} \mathring{F}_2^{(1)}(\mathbf{p},t) \\ \vdots \\ \mathring{F}_2(N)(\mathbf{p},t) \end{vmatrix},$$

and

$$\xi^{ik\cdots j}_{l_1\cdots l_n}(\mathbf{p},t;\mathbf{u}_1,...,\mathbf{u}_n) = \sum_{m=1}^{N} \xi^{m(ik\cdots j)}_{l_1\cdots l_n}(\mathbf{p},t;\mathbf{u}_1,...,\mathbf{u}_n).$$

Further on we also use the vectors $\mathbf{B}^n \equiv \mathbf{A}^n_{0\cdots 0}$; vectors $\mathbf{A}^n_{0\cdots 0}$ are defined by Eq. (2.11). We should emphasize that the expansions (2.10) and (2.12) have been derived from Eq. (2.3) without any restrictions on the functions $\Theta^{(i)}_{jk\cdots m}(\mathbf{p},t;\tau_1\cdots\tau_n,\mathbf{u}_1,\cdots\mathbf{u}_n)$, except their infinite differentiability. If we now use the physically reasonable restriction (2.4), then the right-hand side of Eq. (2.3) will contain convolutions. As a result, in assumption (2.4) the expansion (2.12) of the vector $\mathbf{B}(\mathbf{p},t)$ will contain only vectors $\mathbf{A}^n_{0\cdots 0}(\mathbf{u}_n\cdots\mathbf{u}_1)$.

In the vector notations above the expansion (2.3) can be rewritten in the form

$$\mathbf{B}(\mathbf{p},t) = \sum_{n=1}^{M} \frac{1}{n!}\int_0^t d\tau_1\cdots d\tau_n \times\Theta_n(\mathbf{p};t-\tau_1,...,t-\tau_n,\bar{\mathbf{u}}_1,...,\bar{\mathbf{u}}_n) \cdot\mathbf{B}^n(\bar{\mathbf{u}}_n\cdots\bar{\mathbf{u}}_1,\tau_n\cdots\tau_1) + \mathring{F}_2(\mathbf{p},t), \quad (2.13)$$

where the matrices Θ_n are composed of row vectors $\Theta_{jk\cdots m} \equiv (\Theta^{(1)}_{jk\cdots m},...,\Theta^{(n)}_{jk\cdots m})$. Then the LC transforms of Eq. (2.13) give

$$\mathbf{B}(\mathbf{p},z_1) = \mathbf{B}(\mathbf{p}) + \frac{1}{z_1}\sum_{n=1}^{M}\Big(1/n!\prod_{l=1}^{n} z_l\Big) \times\Theta_n(\mathbf{p};z_1,...,z_n,\bar{\mathbf{u}}_1,...,\bar{\mathbf{u}}_n) \cdot\mathbf{B}^n(\bar{\mathbf{u}}_n\cdots\bar{\mathbf{u}}_1,z_n\cdots z_1) + \frac{1}{z_1}F_2(\mathbf{p},z_1), \quad (2.14)$$

where matrices Θ_n are defined uniquely by their LC preimages,

$$\Theta_n(\mathbf{p};t-\tau_1,...,t-\tau_n,\mathbf{u}_1\cdots\mathbf{u}_n).$$

Since Eq. (2.14) holds for any z_i we have derived, in fact, a system of nonlinear algebraic equations for $\mathbf{B}(\mathbf{p},z_1)$ (due to the structure of the vectors $\mathbf{B}^n(\mathbf{u}_n\cdots\mathbf{u}_1,z_n\cdots z_1)$) which could be solved, for example, by an iteration procedure.[34] In the first order FPT Eq. (2.14) has an exact solution which generalizes Mori's one,[18]

$$B(\mathbf{u},z_1) = \Lambda^{-1}(\mathbf{p},z_1,\mathbf{u})\delta(\mathbf{p}-\mathbf{u})\cdot\mathbf{B}(\mathbf{u}) + \frac{1}{z_1}\Lambda^{-1}(\mathbf{p},z_1,\mathbf{u})\delta(\mathbf{p}-\mathbf{u})\cdot F_2(\mathbf{u},z_1), \quad (2.15)$$

where $\Lambda^{-1}(\mathbf{p},z_1,\mathbf{u})$ is the matrix inverse of the matrix $\Lambda(\mathbf{p},z_1,\mathbf{u}) \equiv [\delta(\mathbf{p}-\mathbf{u})\mathbf{I} - (1/z_1^2)\Phi_1(\mathbf{p};z_1,\mathbf{u})]$ and $\mathbf{I}$ is the unit matrix. Then the inverse LC transform of Eq. (2.15) gives

$$\mathbf{B}(\mathbf{u},t) = \Lambda^{-1}(\mathbf{p},t,\mathbf{u})\delta(\mathbf{p}-\mathbf{u})\cdot\mathbf{B}(\mathbf{u}) + \int_0^t d\tau\,\Lambda^{-1}(\mathbf{p},t-\tau,\mathbf{u})\delta(\mathbf{p}-\mathbf{u})\cdot F_2(\mathbf{u},\tau). \quad (2.15')$$

From above we can now see that the expansions (2.10)–(2.15) have the character of the projection of a vector upon a system of mutual orthogonal vectors from the sets $\mathbb{A}\{\mathbf{A}^n(\mathbf{u}_1\cdots\mathbf{u}_n)\}_1^M$ or $\mathbb{A}\equiv\{\mathbf{B}^n(\mathbf{u}_1\cdots\mathbf{u}_n)\}_1^M$. It is possible to obtain such expansions because the LC (or L) transforms have the property of introducing $f(0)$ when transforming time derivatives of any functions $f(t)$.

The expansions (2.10)–(2.15′) are of limited use until we use some additional properties of the collective dynamical variables. Their main property is that their time evolution is governed by the Liouville equation. In Sec. III we use this fact together with results of this section to construct a projection operator technique.

III. PROJECTION OPERATOR TECHNIQUE

We consider a Hilbert space $\mathscr{H}$ of the dynamical variables, which are all functions of vectors $\langle B(\mathbf{p},t)|$, where $\langle B(\mathbf{p},t)|$ are column vectors composed of collective dynamical variables $\{B_i(\mathbf{p},t)\}_1^M$ whose invariant parts are set equal to zero. Let $\langle F|G\rangle$, $\langle F|,\langle G|\in\mathscr{H}$ be a scalar product in $\mathscr{H}$. In addition to the standard properties of a scalar product,

$$\langle F(\mathbf{p}_n\cdots\mathbf{p}_1,t)|G(\mathbf{p}_n\cdots\mathbf{p}_1,t)\rangle = [\langle G(\mathbf{p}_n\cdots\mathbf{p}_1,t)|F(\mathbf{p}_n\cdots\mathbf{p}_1,t)\rangle]^\dagger;$$
$$\langle G(\mathbf{p}_n\cdots\mathbf{p}_1,t)|G(\mathbf{p}_n\cdots\mathbf{p}_1,t)\rangle > 0, \quad \forall\langle G(\mathbf{p}_n\cdots\mathbf{p}_1,t)|\neq 0; \quad (3.1)$$
$$\Big\langle\sum_{i=1}^{n} c_i F_i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|G(\mathbf{p}_n\cdots\mathbf{p}_1,t)\Big\rangle = \sum_{i=1}^{n} c_i\langle F_i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|G(\mathbf{p}_n\cdots\mathbf{p}_1,t)\rangle,$$

$\forall\langle F|,\langle G|\in\mathscr{H}$, and c_i are numbers, we require that the Liouville operator L,

$$iL\equiv\begin{cases}\displaystyle\sum_{j=1}^{N}\frac{\partial H}{\partial\mathbf{p}_j}\frac{\partial}{\partial\mathbf{r}_j}-\frac{\partial H}{\partial\mathbf{r}_j}\frac{\partial}{\partial\mathbf{p}_j}, & \text{(the classical case)}\\ (i/\hbar)[H,\ ], & \text{(the quantum case)}\end{cases} \quad (3.2)$$

be Hermitian[18] with respect to the scalar product (3.1). In (3.2) H is the Hamiltonian of the dynamical system in question, $\mathbf{r}_j,\mathbf{p}_j$ denote the coordinate and momentum of the j-th particle, respectively, and † in Eq. (3.1) means Hermitian conjugation, and [,] denotes commutator.

A collective dynamical variable $\langle B(\mathbf{p},t)|\in\mathscr{H}$ is governed by the Liouville equation

$$\frac{d}{dt}\langle B(\mathbf{p},t)| = iL < B(\mathbf{p},t)|, \quad (3.3)$$

whose formal solution has the form

$$\langle B(\mathbf{p},t)| = \exp[tiL]\langle B(\mathbf{p})|, \quad (3.4)$$

where we have omitted the index $t=0$ in the right-hand side of (3.4) and will use analogous reduced notation below.

Since $\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1)|\in\mathbb{A}$ are also dynamical variables from $\mathscr{H}$ they should be governed by the Liouville equation as well. Below, in order to treat the most general case, we consider the Γ number of dynamical variables $\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1)|\in\mathbb{A}$ with $l\neq n$, because the method of organization of vectors $\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1)|$ in sets $\mathbb{A}$ and the enumeration of vectors in the $\mathbb{A}$ is not unique.

Due to the absence in (2.10)–(2.15′) of terms of the form $\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1)|F_2(\mathbf{p}_n\cdots\mathbf{p}_1,t)\rangle$, these expressions can be considered to be expansions of the vectors $\langle B(\mathbf{p},t)|\in\mathscr{H}$ on the systems of the mutual orthogonal vectors from $\mathbb{A}=\{\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1)|\}_1^\Gamma$ and $\langle F_2(\mathbf{p},t)|\in\mathscr{H}$,

$$\sum_{j=1}^{\Gamma}\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1)|A^j(\bar{\mathbf{p}}_k''\cdots\bar{\mathbf{p}}_1'')\rangle \times\langle A^j(\bar{\mathbf{p}}_k''\cdots\bar{\mathbf{p}}_1'')|A^l(\mathbf{p}_m'\cdots\mathbf{p}_1')\rangle^{-1} =\delta_{il}\delta_{nm}\delta(\mathbf{p}_1-\mathbf{p}_1')\times\cdots\times\delta(\mathbf{p}_n-\mathbf{p}_m'),$$

$$\forall\langle A^k(\mathbf{p}_n\cdots\mathbf{p}_1)|\in\mathbb{A},$$

$$\langle F_2(\mathbf{p},t)|A^k(\mathbf{p}_n\cdots\mathbf{p}_1)\rangle=0, \tag{3.5}$$

where $\mathbf{p}''$ are dummy variables that are integrated over.

The relations (3.5) represent those additional properties of the scalar products (3.1) which permit us to construct a generalized projection scheme for vectors $\langle B(\mathbf{p},t)|$. We have to stress here that the variables $\mathbf{p}_n,\ldots,\mathbf{p}_1$ above are points in the coordinate-momentum space and are not momenta of any particular particles from the dynamical system in question. The correlations (3.5) are generalizations of those considered by Mori,[18] Akcasu and Duderstadt,[19] and Pozhar.[29]

As was pointed out above, the vectors $\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1)|\in\mathbb{A}$ are also collective dynamical variables by their definition, belonging to $\mathscr{H}$. We denote their values at $t>0$ by $\langle A^l(\mathbf{p}_n\cdots\mathbf{p}_1,t)|$. Thus, using Eq. (3.5) permits us to find a projection of any vector $\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|\in\mathscr{H}$ onto the Γ-dimensional subspace $\mathscr{H}_\Gamma\subset\mathscr{H}$ which is spanned by the vectors $\{A^l(\mathbf{p}_k\cdots\mathbf{p}_1)|\}_1^\Gamma=\mathbb{A}$, $P\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|$

$$P\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)| =\sum_{j<l=1}^{\Gamma}\sum^{\Gamma}\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|A^l(\bar{\mathbf{u}}_k\cdots\bar{\mathbf{u}}_1)\rangle \times\langle A^l(\bar{\mathbf{u}}_k\cdots\bar{\mathbf{u}}_1)|A^j(\bar{\mathbf{v}}_m\cdots\bar{\mathbf{v}}_1)\rangle^{-1}\langle A^j(\bar{\mathbf{v}}_m\cdots\bar{\mathbf{v}}_1)|. \tag{3.6}$$

The operator P defined by (3.6) and satisfying the condition $P(1-P)=0$ is also a linear Hermitian operator, and thus P is a projection operator.

Now we write down the explicit expression for the projection $\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m)$ of a vector $\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|\in\mathscr{H}$ on a vector $\langle A^j(\mathbf{p}_m'\cdots\mathbf{p}_1')|\in\mathbb{A}$,

$$\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m) =\sum_{l=1}^{\Gamma}\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|A^l(\bar{\mathbf{u}}_k\cdots\bar{\mathbf{u}}_1)\rangle \times\langle A^l(\bar{\mathbf{u}}_k\cdots\bar{\mathbf{u}}_1)|A^j(\mathbf{p}_m'\cdots\mathbf{p}_1')\rangle^{-1}. \tag{3.7}$$

Below we also use symbols $\Psi_j^i(A^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m)$, $\dot\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m)$, and $\dot\Psi_j^i(A^i,\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m)$ to denote the values of the functions Ψ_j^i defined by Eq. (3.7) at $t=0$, and their first time derivative calculated at $t=t$ and $t=0$, respectively. Due to Eqs. (3.6) and (3.7) the expansions of the vectors $\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|$ onto the set $\mathbb{A}$ take the form

$$\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|=\sum_{j=1}^{\Gamma}\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\bar{\mathbf{p}}'\}_1^l) \times\langle A^j(\bar{\mathbf{p}}_l'\cdots\mathbf{p}_1')|+\langle A'^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|, \tag{3.8}$$

where

$$\langle A'^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|=(1-P)\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|, \tag{3.9}$$

and the operator $(1-P)$ projects a vector $\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|\in\mathscr{H}$ onto the subspace $\mathscr{H}_\perp\subset\mathscr{H}$, where $\mathscr{H}_\Gamma\oplus\mathscr{H}_\perp=\mathscr{H}$.

After differentiating Eq. (3.8) with respect to t and using the Liouville equation (3.3) for $\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|$ one obtains

$$\langle\dot A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)=iL\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)| =\sum_{j=1}^{\Gamma}\dot\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^l)\langle A^j(\bar{\mathbf{p}}_l'\cdots\bar{\mathbf{p}}_1')| +\langle\dot A'^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|, \tag{3.10}$$

and then from Eq. (3.10) at $t=0$,

$$\langle\dot A^i(\mathbf{p}_n\cdots\mathbf{p}_1)|=iL\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1)| =\sum_{j=1}^{\Gamma}\dot\Psi_j^i(A^i;\{\mathbf{p}\}_1^n\{\bar{\mathbf{p}}'\}_1^l) \times\langle(A^j(\bar{\mathbf{p}}_l'\cdots\bar{\mathbf{p}}_1')|+\langle\dot A'^i(\mathbf{p}_n\cdots\mathbf{p}_1), \tag{3.11}$$

where $\langle\dot A^i(\ )|$ denotes the total first time derivative of the vector $\langle A^i(\ )|$.

Below we use the expressions

$$\langle\dot A'^i(\mathbf{p}_n\cdots\mathbf{p}_1)|=\langle K(A^i,\mathbf{p}_n\cdots\mathbf{p}_1)|, \tag{3.12}$$

where $\langle K(A^i,\mathbf{p}_n\cdots\mathbf{p}_1)|$ is the time-independent vector introduced and discussed by Sachs,[35] and Mori and Kawasaki,[36,18] which is defined uniquely by the time reversal operator of Ref. 35.

We now proceed directly with the generalization of the projection operator method of Mori,[18] Akcasu and Duderstadt,[19] and Pozhar.[29] By differentiating Eq. (3.7) with respect to t and taking into account Eqs. (3.9)–(3.12) one can prove

$$\frac{d}{dt}\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m)=\sum^{\Gamma}\sum_{l,k,\gamma=1}^{\Gamma}\sum^{\Gamma}\dot{\Psi}_k^l(A^i;\{\mathbf{p}\}_1^n\{\bar{\mathbf{u}}\}_1^\rho)\Psi_\gamma^k(tA^k;\{\bar{\mathbf{u}}\}_1^\rho\{\bar{\mathbf{v}}\}_1^\alpha)$$
$$\times\langle A^\gamma(\bar{\mathbf{v}}_\alpha\cdots\bar{\mathbf{v}}_1)|A^l(\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1)\rangle\langle A^l\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1)|A^j(\mathbf{p}'_m\cdots\mathbf{p}'_1)\rangle^{-1}+\sum_{l=1}^{\Gamma}\langle K(A^i;\mathbf{p}_n\cdots\mathbf{p}_1)|A^l(\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1,-t)\rangle$$
$$\times\langle(A^l(\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1)|A^j(\mathbf{p}'_m\cdots\mathbf{p}'_1)\rangle^{-1}, \tag{3.13}$$

where Hermitianness of the Liouville operator has been used.

Operating using $(1-P)$ on the Liouville equation for $\langle A'^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|$ and using Eqs. (3.8), (3.11), and (3.12) one obtains

$$\frac{d}{dt}\langle A'^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|$$
$$=(1-P)iL\,\langle A'^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|$$
$$+\sum_{k=1}^{\Gamma}\Psi_k^l(tA^l;\{\mathbf{p}''\}_1^\omega\{\bar{\mathbf{w}}\}_1^\sigma)\langle K(A^k;\bar{\mathbf{w}}_\sigma\cdots\bar{\mathbf{w}}_1)|. \tag{3.14}$$

Equation (3.14) is integrated to yield

$$\langle A'^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|=\int_0^t ds\, e^{(t-s)(1-P)iL}$$
$$\times\sum_{k=1}^{\Gamma}\Psi_k^l(sA^k;\{\mathbf{p}''\}_l^\omega(\bar{\mathbf{w}}_1^\sigma)$$
$$\times\langle K(A^k;\bar{\mathbf{w}}_\sigma\cdots\bar{\mathbf{w}}_1)|. \tag{3.15}$$

We now introduce the notations,

$$U(t)\equiv\exp[t(1-P)iL], \tag{3.16}$$

$$\langle\mathfrak{F}_l(t,\{\mathbf{p}\}_1^n|\equiv U(t)\langle K(A^l;\mathbf{p}_n\cdots\mathbf{p}_1)|. \tag{3.17}$$

Then the solution (3.15) takes the form

$$A'^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|=\int_0^t ds\sum_{k=1}^{\Gamma}\Psi_k^l(sA^k;\{\mathbf{p}''\}_1^\omega\{\bar{\mathbf{w}}\}_1^\sigma)$$
$$\times\langle\mathfrak{F}_k((t-s),\{\bar{\mathbf{w}}\}_1^\sigma)|. \tag{3.18}$$

The propagator $U(t)$ defined by Eq. (3.16) and the "random forces" (3.17) have the same form as those of Refs. 18, 19, and 29.

From Eq. (3.8) written for $\langle A^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|$ and Eq. (3.18) it immediately follows that for the conjugation $|A^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,-t)\rangle$ of the vector $\langle A^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,t)|$ one obtains

$$|A^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1,-t\rangle=\sum_{k=1}^{\Gamma}|A^k(\bar{\mathbf{w}}_\sigma\cdots\bar{\mathbf{w}}_1)\rangle$$
$$\times\Psi_k^{l\dagger}(tA^l;\{\mathbf{p}''\}_1^\omega\{\bar{\mathbf{w}}\}_1^\sigma)$$
$$+\int_0^{-t}ds\sum_{k=1}^{\Gamma}|\mathfrak{F}_k((-t-s),\{\bar{\mathbf{w}}\}_1^\sigma\rangle$$
$$\times\Psi_k^{l\dagger}(sA^k;\{\mathbf{p}''\}_1^\omega\{\bar{\mathbf{w}}\}_1^\sigma,), \tag{3.19}$$

where † means Hermitian conjugation, and the Hermitianness of the Liouville operator has been used.

Substituting Eq. (3.19) into Eq. (3.13) one obtains

$$\frac{d}{dt}\Psi_j^i(tA^i;\{\mathbf{p}\}_1^n\{\mathbf{p}'\}_1^m=\sum\sum\sum_{l,k,\gamma=1}^{\Gamma\,\Gamma\,\Gamma}\dot{\Psi}_k^l(A^i;\{\mathbf{p}\}_1^n\{\bar{\mathbf{u}}\}_1^\rho)\Psi_\gamma^k(tA^k;\{\bar{\mathbf{u}}\}_1^\rho\{\bar{\mathbf{v}}\}_1^\alpha)\langle A^\gamma(\{\bar{\mathbf{v}}_\alpha\cdots\bar{\mathbf{v}}_1)|A^l(\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1)\rangle$$
$$\times\langle A^l(\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1)|A^j(\mathbf{p}'_m\cdots\mathbf{p}'_1)\rangle^{-1}+\sum\sum_{l,k=1}^{\Gamma\,\Gamma}\int_0^{-t}ds\langle K(A^i;\mathbf{p}_n\cdots\mathbf{p}_1)|\mathfrak{F}_k((-t-s),\{\mathbf{w}\}_1^\sigma\rangle$$
$$\times\Psi_k^{l\dagger}(sA^k;\{\bar{\mathbf{p}}''\}_1^\omega\{\bar{\mathbf{w}}\}_1^\sigma)\langle A^l(\bar{\mathbf{p}}''_\omega\cdots\bar{\mathbf{p}}''_1)|A^j(\mathbf{p}'_m\cdots\mathbf{p}'_1)\rangle^{-1}. \tag{3.20}$$

From Eq. (3.7) and Hermitianness of the Liouville operator it follows that

$$\Psi_k^{l\dagger}(sA^k;\{\mathbf{p}''\}_1^\omega\{\mathbf{w}\}_1^\sigma)$$
$$=\sum\sum_{m,\gamma=1}^{\Gamma\,\Gamma}\langle A^k(\mathbf{w}_\sigma\cdots\mathbf{w}_1)|A^m(\bar{\mathbf{v}}_\alpha\cdots\bar{\mathbf{v}}_1)\rangle^{-1}\Psi_\gamma^m(-sA^k;\{\bar{\mathbf{v}}\}_1^\alpha\{\bar{\mathbf{v}}'\}_1^\beta)\langle A^\gamma(\bar{\mathbf{v}}'_\beta\cdots\bar{\mathbf{v}}'_1)|A^l(\mathbf{p}''_\omega\cdots\mathbf{p}''_1)\rangle. \tag{3.21}$$

We now introduce definitions of damping functions

$$\varphi^{km}_{(i)}(sA^k;\{\mathbf{p}\}^n_1\{\mathbf{v}\}^\alpha_1) = -\langle\mathfrak{F}_i(\{\mathbf{p}\}^n_1)|\mathfrak{F}_k(-t,\{\overline{\mathbf{w}}\}^\sigma_1)\rangle \times\langle A^k(\overline{\mathbf{w}}_\sigma\cdots\overline{\mathbf{w}}_1)|A^m(\mathbf{v}_\alpha\cdots\mathbf{v}_1)\rangle^{-1}, \quad (3.22)$$

where Eq. (3.17) has given $\langle\mathfrak{F}_k(\{\mathbf{p}\}^n_1)| = \langle K(A^k;\mathbf{p}_n\cdots\mathbf{p}_1)|$. Then, substituting Eq. (3.21) into Eq. (3.20), taking into account Eq. (3.5), using definitions (3.22), and changing the time variable s to $(s-t)$ one can prove that

$$\frac{d}{dt}\Psi^i_j(tA^i;\{\mathbf{p}\}^n_1\{\mathbf{p}'\}^m_1) = \sum_{k=1}^{\Gamma}\dot\Psi^i_k(A^i;\{\mathbf{p}\}^n_1\{\overline{\mathbf{u}}\}^\rho_1)\,\Psi^k_j(tA^k;\{\overline{\mathbf{u}}\}^\rho_1\{\mathbf{p}'\}^m_1) + \sum_{k,m=1}^{\Gamma}\sum^{\Gamma}\int_0^t ds \times\varphi^{km}_{(i)}(s,\{\mathbf{p}\}^n_1\{\overline{\mathbf{v}}\}^\alpha_1)\Psi^m_j((t-s)A^m;\{\overline{\mathbf{v}}\}^\alpha_1\{\mathbf{p}'\}^m_1). \quad (3.23)$$

The LC transform of Eq. (3.23) with respect to t is

$$\Psi^i_j(zA^i;\{\mathbf{p}\}^n_1\{\mathbf{p}'\}^m_1) = \Psi^i_j(A^i;\{\mathbf{p}\}^n_1\{\mathbf{p}'\}^m_1) + \frac{1}{z}\sum_{k=1}^{\Gamma}\dot\Psi^i_k(A^i;\{\mathbf{p}\}^n_1\{\overline{\mathbf{u}}\}^\rho_1)\Psi^k_j(zA^k;\{\overline{\mathbf{u}}\}^\rho_1\{\mathbf{p}'\}^m_1) + \frac{1}{z^2}\sum_{k,m=1}^{\Gamma}\sum^{\Gamma}\varphi^{km}_{(i)}(z,\{\mathbf{p}\}^n_1\{\overline{\mathbf{v}}\}^\alpha_1)\Psi^m_j(zA^m;\{\overline{\mathbf{v}}\}^\alpha_1\{\mathbf{p}'\}^m_1). \quad (3.24)$$

We have derived a system of Γ^2 matrix equations for the LC images $\Psi^i_j(zA^i,\{\mathbf{p}\}^n_1\{\mathbf{p}'\}^m_1)$ of projections of vectors $\langle A^i(\mathbf{p}_n\cdots\mathbf{p}_1,t)|$ on the vectors $\langle A^j(\mathbf{p}'_m\cdots\mathbf{p}'_1)|\in\mathbb{A}$, where $\varphi^{km}_{(i)}(z,\{\mathbf{p}\}^n_1\{\mathbf{v}\}^\alpha_1)$ represent the LC images of damping functions defined by Eq. (3.22). Equations (3.24) are a generalization of Eq. (37) derived by Mori[18] and Eqs. (2.21) of Ref. 29, and the fluctuation–dissipation relations (3.22) generalize those of Refs. 18, 19, and 29. The system of integral matrix equations (3.24) can be solved after explicit introduction of the set $\mathbb{A}$.

We demonstrate the projection scheme above in its first order form, and derive the GLE. In the first order FPT scheme, instead of the set $\mathbb{A}$ we have the unique vector $\langle B(\mathbf{p},0)|$, as can be easily seen from Eq. (2.15), and from Eqs. (3.6) and (3.7) one can obtain

$$P\langle B(\mathbf{p}_1,t)| = \langle B(\mathbf{p}_1,t)|B(\overline{\mathbf{p}}')\rangle\langle B(\overline{\mathbf{p}}')|B(\overline{\mathbf{p}}_2)\rangle^{-1}\langle B(\overline{\mathbf{p}}_2)|, \quad (3.25)$$

and

$$\Psi^1_1(tB;\mathbf{p}_1,\mathbf{p}_2) = \langle B(\mathbf{p}_1,t)|B(\overline{\mathbf{p}}')\rangle\langle B(\overline{\mathbf{p}}')|B(\mathbf{p}_2)\rangle^{-1}. \quad (3.26)$$

Taking into account Eq. (3.5) at $t=0$, from Eq. (3.26) it follows that

$$\Psi^1_1(B;\mathbf{p}_1,\mathbf{p}_2) = \delta(\mathbf{p}_1-\mathbf{p}_2)\mathbf{I}, \quad (3.27)$$

where $\mathbf{I}$ is the unit matrix. Substituting Eq. (3.27) into Eq. (3.24) one obtains an integral matrix equation

$$\Psi^1_1(zB;\mathbf{p}_1,\mathbf{p}_2) = \delta(\mathbf{p}_1-\mathbf{p}_2)\mathbf{I} + \frac{1}{z}\dot\Psi^1_1(B;\mathbf{p}_1,\overline{\mathbf{p}}')\Psi^1_1(zB;\overline{\mathbf{p}}',\mathbf{p}_2) + \frac{1}{z_2}\varphi^{11}_{(1)}(z,\mathbf{p}_1,\overline{\mathbf{p}}')\Psi^1_1(zB;\overline{\mathbf{p}}',\mathbf{p}_2), \quad (3.28)$$

with $\varphi^{11}_{(1)}(z,\mathbf{p}_1,\mathbf{p}')$ defined by its LC-preimage (3.22),

$$\varphi^{11}_{(1)}(t,\mathbf{p}_1,\mathbf{p}') = -\langle\mathfrak{F}_1(\mathbf{p}_1)|\mathfrak{F}_1(-t,\overline{\mathbf{p}}'')\rangle \times\langle B(\overline{\mathbf{p}}'')|B(\mathbf{p}')\rangle^{-1}.$$

The solution of Eq. (3.28) is

$$\Psi^1_1(zB;\mathbf{u},\mathbf{p}_2) = \Lambda^{-1}_\psi(\mathbf{p}_1,z,\mathbf{u})\delta(\mathbf{p}_2-\mathbf{u})\delta(\mathbf{p}_1-\mathbf{u}), \quad (3.29)$$

where $\Lambda^{-1}_\psi(\mathbf{p}_1,z,\mathbf{u})$ is the matrix inverse to the matrix

$$\Lambda_\psi(\mathbf{p}_1,z,\mathbf{u}) = \delta(\mathbf{p}_1-\mathbf{u})\mathbf{I} - \frac{1}{z}\dot\Psi^1_1(B;\mathbf{p}_1,\mathbf{u}) - \frac{1}{z^2}\varphi^{11}_{(1)}(z,\mathbf{p}_1,\mathbf{u}). \quad (3.30)$$

Then Eq. (3.8) takes the form

$$\langle B(\mathbf{p}',z)| = \Lambda^{-1}_\Psi(\mathbf{p},z,\mathbf{p}')\delta(\mathbf{p}-\mathbf{p}') \times\langle B(\mathbf{p}')| + \langle\mathbf{B}'(\mathbf{p}',z)|, \quad (3.31)$$

wherein $\langle\mathbf{B}'(\mathbf{p}',t)|$ is defined by Eq. (3.18) with $\langle\mathfrak{F}_1(t,\mathbf{p})| = \langle\mathbf{F}_2(\mathbf{p},t)|$. Comparing Eq. (3.31) with Eq. (2.15′) one can derive

$$\Theta_1(\mathbf{p},z,\mathbf{p}') = z\dot\Psi^1_1(B;\mathbf{p},\mathbf{p}') + \varphi^{11}_{(1)}(z,\mathbf{p},\mathbf{p}'). \quad (3.32)$$

The inverse LC transform of Eq. (3.32) with respect to z gives

$$\Theta_1(\mathbf{p},t,\mathbf{p}') = 2\delta(t)\dot\Psi^1_1(B;\mathbf{p},\mathbf{p}') + \varphi^{11}_{(1)}(t,\mathbf{p},\mathbf{p}'). \quad (3.33)$$

On the other hand, from Eq. (2.3) one can obtain for the case under consideration

$$\frac{d}{dt}\mathbf{B}(\mathbf{p},t) = \int_0^t d\tau\,\Theta_1(\mathbf{p},t-\tau,\overline{\mathbf{p}}')\mathbf{B}(\overline{\mathbf{p}}',\tau) + F_2(\mathbf{p},t). \quad (3.34)$$

Substituting Eq. (3.33) into Eq. (3.34) gives

$$\frac{d}{dt}\mathbf{B}(\mathbf{p},t) - \dot{\Psi}_1^1(B;\mathbf{p},\bar{\mathbf{p}}')\mathbf{B}(\bar{\mathbf{p}}',t) - \int_0^t d\tau\, \varphi_{(1)}^{11}((t-\tau),\mathbf{p},\mathbf{p}')\mathbf{B}(\bar{\mathbf{p}}',\tau). \tag{3.35}$$

Thus, we have proved that the master equation (3.35) is an exact equation of the first order FPT with respect to thermal disturbances. Since the above development is general, master equations of different FPT orders can be derived in the above way for any quantities whose time evolution is governed by the Liouville equation. Taking into account the differences in notations and in the definition of $\varphi_{(1)}^{11}(t,\mathbf{p},\mathbf{p}')$, which in the investigation presented above differs in its sign from those of Refs. 18 and 19, the master equation (3.35) is the GLE of Refs. 18 and 19. For a scalar dynamical variable the scheme developed above leads to a generalization of the corresponding equation of Ref. 29. The second order FPT master equation for a vector dynamical variable can also be obtained; in view of its complicated structure we do not describe it here.

There are mathematical questions of separability and completeness of the Hilbert space $\mathscr{H}$ introduced at the beginning of this section which have not been solved here, nor in Refs. 18, 19, or 29. We leave these questions to mathematicians, and go on to derive mean field kinetic equations for the singlet distribution functions of strongly inhomogeneous fluids in Sec. IV.

IV. KINETIC EQUATIONS FOR STRONGLY INHOMOGENEOUS FLUID MIXTURES

We consider an inhomogeneous fluid mixture of nonreactive structureless molecules numbered with Greek indices $\alpha, \beta,\ldots,$ of species i,j, etc., labeled with Latin indices. The fluid–fluid particle interactions are assumed to be pairadditive, central and decomposable into the sum

$$\varphi_I(q_{ij}^{\alpha\beta}) = \varphi_H(q_{ij}^{\alpha\beta}) + \varphi_S(q_{ij}^{\alpha\beta}), \tag{4.1}$$

where φ_H is a hard core repulsive contribution,

$$\varphi_H(q_{ij}^{\alpha\beta}) = \begin{cases} +\infty, & q_{ij}^{\alpha\beta} < \sigma_{ij}, \\ 0, & q_{ij}^{\alpha\beta} > \sigma_{ij}, \end{cases} \tag{4.2}$$

and $\varphi_S(q_{ij}^{\alpha\beta})$ represents an attractive soft interaction that is assumed to be continuous and $q_{ij}^{\alpha\beta} = q_{ij}^{\alpha\beta}\hat{\mathbf{q}}_{ij}^{\alpha\beta} = \mathbf{q}_j^\beta - \mathbf{q}_i^\alpha, \mathbf{q}_i^\alpha$ and $\mathbf{q}_j^\beta$ are vector coordinates of the particles α, β belonging to species i, j, respectively. The inhomogeneity of the fluid mixture is caused by an external field potential. We consider two cases of external field potentials.

(1) $\nu_i^E(q_i^\alpha)$ is a continuous potential of a general kind with $\mathbf{q}_i^\alpha = q_i^\alpha \hat{\mathbf{q}}_i^\alpha$; and (2) a fluid-wall potential of the type

$$\nu_{iw}^E(q_{iw}^{\alpha w}) = \nu_H^E(q_{iw}^{\alpha w}) + \nu_{Siw}^E(q_{iw}^{\alpha w}), \tag{4.3}$$

where the hard-core contribution is

$$\nu_H^E(q_{iw}^{\alpha w}) = \begin{cases} +\infty, & q_{iw}^{\alpha w} < \sigma_{iw}, \\ 0, & q_{iw}^{\alpha w} > \sigma_{iw}, \end{cases} \tag{4.4}$$

and $\nu_{Siw}^E(q_{iw}^{\alpha w})$ is the attractive part of the interaction between the α-th fluid particle of species i and the w-th particle belonging to a structured solid wall consisting of particles of species w. The wall restricts the fluid volume, and is impenetrable to fluid particles. We also assume that fluid mixture particles cannot react with wall particles, and that the latter are structureless, all of the same species, and cannot move from their average positions in the walls, $\mathbf{q}_w = q_w \hat{\mathbf{q}}_w$.

The evolution of a fluid collective dynamical variable $A[\Gamma(t)]$, where $\Gamma(t) = \{\mathbf{q}_i^\alpha(t), \mathbf{p}_i^\alpha(t)\}(\mathbf{p}_i^\alpha = m_i \mathbf{v}_i^\alpha$ is the momentum of the α-th particle of species i, $\mathbf{v}_i^\alpha$ and m_i are its velocity and mass) is a dynamical state of the fluid system, is described by the Liouville equation (3.3) with the solution

$$A(t) = \begin{cases} \exp(itL_+)A(0), & t>0, \\ \exp(itL_-)A(0), & t<0, \end{cases} \tag{4.5}$$

which follows from the singularity of the potentials $\varphi_I(q_{ij}^{\alpha\beta})$ and $\nu_{iw}^E(q_{iw}^{\alpha w})$, which contain hardcore repulsive contributions. The Liouville operator $iL_\pm$ is the sum of free particle, iL^0, fluid–fluid interaction, $iL_\pm^I$, and fluid–external field (case 1), iL^E, or fluid–wall interaction (case 2), $iL_\pm^E$, operators,

$$iL^0 = \sum_i \sum_{\alpha=1}^{N_i} \frac{\mathbf{p}_i^\alpha}{m_i} \cdot \frac{\partial}{\partial \mathbf{q}_i^\alpha}, \tag{4.6}$$

$$iL_\pm^I = \frac{1}{2}\sum_i \sum_j \sum_{\alpha,\beta=1;}^{N_i} \sum_{\alpha\neq\beta}^{N_j} I_{ij\pm}^{\alpha\beta}, \tag{4.7}$$

wherein

$$I_{ij\pm}^{\alpha\beta} = -\frac{\partial}{\partial \mathbf{q}_i^\alpha}\varphi_S(q_{ij}^{\alpha\beta})\cdot\left(\frac{\partial}{\partial \mathbf{p}_i^\alpha} - \frac{\partial}{\partial \mathbf{p}_j^\beta}\right) + |\mathbf{v}_{ij}^{\alpha\beta}\cdot\hat{\mathbf{q}}_{ij}^{\alpha\beta}|\Theta(\mp \mathbf{v}_{ij}^{\alpha\beta}\cdot\hat{\mathbf{q}}_{ij}^{\alpha\beta})\delta(q_{ij}^{\alpha\beta} - \sigma_{ij}) \times(\mathbf{b}_{ij}^{\alpha\beta} - 1), \quad \mathbf{v}_{ij}^{\alpha\beta} \equiv \mathbf{v}_j^\beta - \mathbf{v}_i^\alpha; \tag{4.8}$$

$$iL^E = -\sum_i \sum_{\alpha=1}^{N_i} \frac{\partial}{\partial \mathbf{q}_i^\alpha}\nu_i^E(q_i^\alpha)\cdot\frac{\partial}{\partial \mathbf{p}_i^\alpha} \quad \text{(case 1)} \tag{4.9}$$

or

$$iL_\pm^E = \sum_i \sum_{\alpha=1}^{N_i} \sum_{w=1}^{N_w} I_{i\pm}^{E\alpha w}, \quad \text{(case 2)} \tag{4.10}$$

wherein

$$I_{i\pm}^{E\alpha w} = -\frac{\partial}{\partial \mathbf{q}_i^\alpha}\nu_{iw}^E(q_{iw}^{\alpha w})\cdot\frac{\partial}{\partial \mathbf{p}_i^\alpha} + T_i^{\alpha w}(\mathbf{v}_i^\alpha,\mathbf{q}_i^\alpha,\mathbf{q}_w), \tag{4.11}$$

$$T_i^{\alpha w}(\mathbf{v}_i^\alpha,\mathbf{q}_i^\alpha,\mathbf{q}_w) = |\mathbf{v}_i^\alpha\cdot\hat{\mathbf{q}}_{iw}^{\alpha w}|\Theta(\mp \mathbf{v}_i^\alpha\cdot\hat{\mathbf{q}}_{iw}^{\alpha w}) \times\delta(q_{iw}^{\alpha w} - \sigma_{iw})(\mathbf{b}_i^\alpha - 1),$$

$$\mathbf{q}_{iw}^{\alpha w} = \mathbf{q}_w - \mathbf{q}_i^\alpha = q_{iw}^{\alpha w}\hat{\mathbf{q}}_{iw}^{\alpha w}.$$

In Eqs. (4.9)–(4.11) $\Theta(x)$ denotes the unit step function, and $\mathbf{b}_{ij}^{\alpha\beta}$ are the hard core collision operators[26] for fluid–fluid interactions, and

$$\mathbf{b}_i^\alpha \mathbf{v}_i^\alpha \equiv \mathbf{v}_i^{\alpha *} = \mathbf{v}_i^\alpha + 2(\mathbf{v}_i^\alpha\cdot\mathbf{q}_{iw}^{\alpha w})\hat{\mathbf{q}}_{iw}^{\alpha w},$$

where $\mathbf{v}_i^\alpha, \mathbf{v}_i^{\alpha *}$ mean the pre- and postcollisional velocities of a fluid particle, respectively.

A. Generalized Langevin equations for the species phase space and singlet distribution functions of inhomogeneous fluid mixtures

We consider the collective dynamical variable

$$A_i(\mathbf{q},\mathbf{p},t) = \sum_{\alpha=1}^{N_i} \delta(\mathbf{q}-\mathbf{q}_i^\alpha(t))\delta(\mathbf{v}-\mathbf{v}_i^\alpha(t)) - \left\langle \sum_{\alpha=1}^{N_i} \delta(\mathbf{q}-\mathbf{q}_i^\alpha(t))\delta(\mathbf{v}-\mathbf{v}_i^\alpha(t)) \right\rangle = \sum_{\alpha=1}^{N_i} \delta(\mathbf{q}-\mathbf{q}_i^\alpha(t))\delta(\mathbf{v}-\mathbf{v}_i^\alpha(t)) - n_i(\mathbf{q})\Phi_i(v), \tag{4.12}$$

which is the deviation from equilibrium of the phase space density of species i. The bracket $\langle\ \rangle$ denotes averaging over the grand canonical equilibrium ensemble; here temperature is $T=1/\kappa_B\beta$, N_i is the number of molecules of species i, $n_i(\mathbf{q})$ is the equilibrium number density of species i, and $\Phi_i(v)$ is the Maxwell–Boltzmann velocity distribution function. The GLE (3.35) in component representation is

$$\frac{\partial}{\partial t} A_i(\mathbf{q},\mathbf{v};t) - i\Omega_{ij}(\mathbf{q},\mathbf{v};\bar{\mathbf{q}}',\bar{\mathbf{v}}',)A_j(\bar{\mathbf{q}}',\bar{\mathbf{v}}';t) + \int_0^t ds\, \Sigma_{ij}(\mathbf{q};\mathbf{v};\bar{\mathbf{q}}',\bar{\mathbf{v}}';t-s)A_j(\bar{\mathbf{q}}',\bar{\mathbf{v}}';s) = \mathfrak{F}_i^+(\mathbf{q},\mathbf{v};t), \tag{4.13}$$

where for convenience of comparing our results with those of Ref. 26 we have introduced for the matrices $\dot{\Psi}_1^1, \varphi_{(1)}^{11}$ and the vector $\mathbf{F}_2(\mathbf{p},t)$ the following notations

$$\dot{\Psi}_1^1(A;\mathbf{p},\mathbf{p}') \equiv i\Omega(\mathbf{q},\mathbf{v};\mathbf{q}',\mathbf{v}'), \tag{4.14}$$

$$\varphi_{(1)}^{11}((t-s),\mathbf{p},\mathbf{p}') \equiv -\Sigma(\mathbf{q},\mathbf{v};\mathbf{q}',\mathbf{v}';t-s), \tag{4.15}$$

$$\mathbf{F}_2(\mathbf{p},t) \equiv \mathfrak{F}^+(\mathbf{q},\mathbf{v};t), \tag{4.16}$$

so that, corresponding to Eqs. (3.26), (3.22), and (3.25),

$$i\Omega_{ij}(\mathbf{q},\mathbf{v};\mathbf{q}',\mathbf{v}') = \langle\{iL_+ A_i(\mathbf{q},\mathbf{v})\}A_k^*(\bar{\mathbf{q}}'',\bar{\mathbf{v}}'')\rangle \times \langle A_k(\bar{\mathbf{q}}'',\bar{\mathbf{v}}'')A_j^*(\mathbf{q}',\mathbf{v}')\rangle^{-1} \tag{4.17}$$

is an element of the frequency matrix describing an instantaneous response of the system, * means complex conjugation and

$$\Sigma_{ij}(\mathbf{q},\mathbf{v};\mathbf{q}',\mathbf{v}') = \langle \mathfrak{F}_1^+(\mathbf{q},\mathbf{v};t)\mathfrak{F}_k^{-*}(\bar{\mathbf{q}}'',\bar{\mathbf{v}}'')\rangle \times \langle A_k(\bar{\mathbf{q}}'',\bar{\mathbf{v}}'')A_j^*(\mathbf{q}',\mathbf{v}')\rangle^{-1} \tag{4.18}$$

is an element of the dynamic memory matrix describing the delayed response. The projection operator (3.25) and the random forces $\mathfrak{F}_1^+$ defined by (3.17), (4.16) take the same form as those of Ref. 26.

Introducing averaging over the nonequilibrium grand canonical ensemble in the same way as that of Ref. 26 one can find that the GLEs (4.13) averaged over the nonequilibrium ensemble give the kinetic equations (2.17) of Ref. 26.

As was discussed in Secs. II and III, the terms $\mathfrak{F}_1^+(\mathbf{q},\mathbf{v};t)$ in the GLEs (4.13) should be considered to be terms of the next order of smallness with respect to other terms in Eq. (4.13), in order to give meaning to the collective dynamical variables description of the time evolution of the system. Also, the ensemble average of the fluctuating term $\mathfrak{F}_i^+$ tends to zero after many collisions have occurred if the initial state of the system is near equilibrium.[37] As we have seen in Secs. II and III, the GLEs are rigorous equations of the first order FPT, and thus we can only use them correctly if the state of the dynamical system in question is near to a stationary or an equilibrium one. The conclusion of Ref. 37 that $\langle \mathfrak{F}_i^+(\mathbf{q},\mathbf{v},t)\rangle_{ne} \to 0$ is also consistent (without restriction on the fluid density) with Bogoliubov's hypothesis describing the kinetic stage of the many-body system time evolution in terms of singlet distribution functions, as was pointed out by Sung and Dahler.[26] Thus, $\langle \mathfrak{F}_i^+(\mathbf{q},\mathbf{v};t)\rangle_{ne}$ can be set equal to zero. The next step in the investigation of Eqs. (2.17) of Ref. 26 is to find an appropriate approximation for the dynamic response Σ_{ij}. As in Ref. 26, it seems to be logically justified to consider a zeroth order approximation $\Sigma_{ij}=0$ at first. The results derived in Ref. 26 using such an approximation when deriving mean-field kinetic equations of homogeneous fluids proved this approximation remains informative and permits one to prove reasonable and tractable kinetic equations. Thus, as the first step in investigating the kinetic state of the inhomogeneous system time evolution, we also adopt a zero approximation for Σ_{ij}. Following Ref. 26, we consider the coupled set of mean-field kinetic equations

$$\frac{\partial}{\partial t}\delta F_i(\mathbf{q},\mathbf{v};t) - i\Omega_{ij}(\mathbf{q},\mathbf{v};\bar{\mathbf{q}}',\bar{\mathbf{v}}')\delta F_j(\bar{\mathbf{q}}',\bar{\mathbf{v}}';t) = 0 \tag{4.19}$$

as the starting point for studying the time evolution of the inhomogeneous fluid mixture described by the departure from equilibrium, δF_i, of the nonequilibrium singlet distribution functions $F_i(\mathbf{q},\mathbf{v};t)$. [In Eqs. (4.19), as in most cases in this section, we use the standard convention of summing on a repeated index.]

As we shall see, Eqs. (4.19) can be rewritten in explicit form in the case of an inhomogeneous fluid mixture as well, and generalize those of Ref. 26.

B. The explicit form of the mean-field kinetic equation for inhomogeneous fluid mixtures

To write down an explicit form of the kinetic equations (4.19) one should calculate the frequency matrix $i\Omega_{ij}$ of Eq. (4.17) which can be represented in the form

$$i\Omega_{ij}(x,x') = i\Omega_{ij}^0(x,x') + i\Omega_{ij}^I(x,x') + i\Omega_{ij}^E(x,x'), \tag{4.20}$$

where x denotes $(\mathbf{q},\mathbf{v})$ and

$$i\Omega_{ij}^r(x,x') = \langle\{iL'A_i(x)\}A_l^*(\bar{x}'')\rangle \times \chi_{lj}^{-1}(\bar{x}'',x') \quad r=0,I,E, \tag{4.21}$$

and χ^{-1} defined by

$$\chi_{il}^{-1}(x,\bar{x}'')\chi_{lj}(\bar{x}'',x') = \delta_{ij}\delta(x-x') \tag{4.22}$$

is the inverse of the static correlation matrix with elements

$$\chi_{ij}(x,x') = \langle A_i(x)A_j^*(x')\rangle, \tag{4.23}$$

where $\delta(x-x')=\delta(\mathbf{q}-\mathbf{q}')\delta(\mathbf{v}-\mathbf{v}')$ is the product of the Dirac δ functions.

After simple calculations (see Appendix A) one can obtain

$$\chi_{ij}(x,x') = \delta_{ij}\delta(x-x')n_i(\mathbf{q})\Phi_i(v) + n_i(\mathbf{q})n_j(\mathbf{q}')\Phi_i(v)\Phi_j(v')h_{ij}(\mathbf{q},\mathbf{q}'), \quad (4.24)$$

wherein

$$h_{ij}(\mathbf{q},\mathbf{q}') = g_{ij}(\mathbf{q},\mathbf{q}') - 1, \quad (4.25)$$

and the pair correlation function $g_{ij}(\mathbf{q},\mathbf{q}')$ of the inhomogeneous fluid mixture specific to the two species i and j is defined according to van Hove,[38]

$$n_i(\mathbf{q})n_j(\mathbf{q}')g_{ij}(\mathbf{q},\mathbf{q}') = \left\langle \sum_{\alpha\neq\beta}\sum \delta(\mathbf{q}-\mathbf{q}_i^{\alpha})\delta(\mathbf{q}'-\mathbf{q}_j^{\beta})\right\rangle. \quad (4.26)$$

Then from Eqs. (4.22) and (4.24) it follows that

$$\chi_{ij}^{-1}(x,x') = \delta_{ij}\delta(x-x') \times [n_j(\mathbf{q}')\Phi_j(v')]^{-1} - C_{ij}(\mathbf{q},\mathbf{q}'), \quad (4.27)$$

where the functions

$$C_{ij}(\mathbf{q},\mathbf{q}') = \int d\mathbf{q}''\, d\mathbf{v}''\, \chi_{ik}^{-1}(\mathbf{q},\mathbf{v};\mathbf{q}'',\mathbf{v}'') \times n_k(\mathbf{q}'')\Phi_k(v'')h_{kj}(\mathbf{q}'',\mathbf{q}') \quad (4.28)$$

satisfy the Ornstein–Zernike relations,

$$C_{ij}(\mathbf{q},\mathbf{q}') + \int d\mathbf{q}''\, C_{ik}(\mathbf{q},\mathbf{q}'')n_k(\mathbf{q}'')h_{kj}(\mathbf{q}'',\mathbf{q}') = h_{ij}(\mathbf{q},\mathbf{q}'), \quad (4.29)$$

and have all the other properties of the direct correlation functions (see Appendix B). Thus, they are the direct correlation functions for the inhomogeneous fluid mixture.

Using Eqs. (4.27), (4.29), from (4.21) at $r=0$, after some calculations (see Appendix C), one can derive

$$i\Omega_{ij}^{0}(x,x') = \delta_{ij}\int d\mathbf{q}^1 \frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial \mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\} \times\delta(\mathbf{q}^1-\mathbf{q}')\delta(\mathbf{v}-\mathbf{v}'). \quad (4.30)$$

Thus, it follows from Eq. (4.30) that

$$\sum_j\int dx'\, i\Omega_{ij}^{0}(x,x')\delta F_j(x';t) = \int d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}\delta F_i(\mathbf{q}^1,\mathbf{v};t) = -\mathbf{v}\frac{\partial}{\partial\mathbf{q}}\delta F_i(\mathbf{q},\mathbf{v},t), \quad (4.31)$$

where we have used the δ-function derivative property (C5) of Appendix C.

The most complicated calculations are connected with deriving an explicit expression for the fluid–fluid interaction contribution $i\Omega_{ij}^{I}(x,x')$ to the frequency matrix. They are discussed in Appendix D where a method analogous to that of Ref. 26 has been used. In Appendix E we calculate the external field contribution $i\Omega_{ij}^{E}(x,x')$ to the frequency matrix. Thus, summing up the expressions (D14) and (E2) of Appendices D and E, respectively, in case 1 (an external field potential of a general kind v_i^E) one can derive

$$\begin{aligned}
i\Omega_{ij}^{I}(x,x') + i\Omega_{ij}^{E}(x,x') = {} & \delta_{ij}\sum_l\int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2\{I_{il}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}^1-\mathbf{v}')\delta(\mathbf{q}^1-\mathbf{q}')\delta(\mathbf{q}-\mathbf{q}^1)\\
& \times n_l(\mathbf{q}^2)\Phi_l(v^2)g_{il}(\mathbf{q}^1,\mathbf{q}^2) + \int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2\\
& \times\{I_{ij}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}^2-\mathbf{v}')\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}'-\mathbf{q}^2)\\
& \times n_i(\mathbf{q}^1)\Phi_i(v^1)g_{ij}(\mathbf{q}^1,\mathbf{q}^2) + \delta_{ij}\int d\mathbf{q}^1\, d\mathbf{v}^1\{I_i^{E1}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^1-\mathbf{q}')\delta(\mathbf{v}^1-\mathbf{v}')\\
& + n_i(\mathbf{q})\Phi_i(v)\mathbf{v}\left\{\frac{\partial C_{ij}(\mathbf{q},\mathbf{q}')}{\partial\mathbf{q}} + \beta g_{ij}(\mathbf{q},\mathbf{q}')\frac{\partial\Psi_{ij}(\mathbf{q},\mathbf{q}')}{\partial\mathbf{q}}\right\} + \frac{\partial n_i(\mathbf{q})}{\partial\mathbf{q}}\Phi_i(v)\mathbf{v}\Big[1 + C_{ij}(\mathbf{q},\mathbf{q}')\\
& - \sum_l\int d\mathbf{q}^3\, n_l(\mathbf{q}^3)C_{lj}(\mathbf{q}^3,\mathbf{q}')\Big],
\end{aligned} \quad (4.32)$$

where we have taken into account that

$$\sum_l\int d\mathbf{q}^2\frac{\partial\Psi_{il}(\mathbf{q},\mathbf{q}^2)}{\partial\mathbf{q}}n_l(\mathbf{q}^2)g_{il}(\mathbf{q},\mathbf{q}^2) + \frac{\partial v_i^E(\mathbf{q})}{\partial\mathbf{q}} = 0, \quad (4.33)$$

as the resulting force acting on a particle of species i at point $\mathbf{q}$ in equilibrium is zero. The quantity $\psi_{il}(\mathbf{q},\mathbf{q}')$ is defined in Appendix D.

An analogous expression in case 2 [external field potential v_{iw}^E defined by (4.3)] can be proved by summing up the expressions (D15) and (E4) of Appendices D and E, respectively.

$$i\Omega_{ij}^{I}(x,x') + i\Omega_{ij}^{E}(x,x') = \delta_{ij}\sum_{l}\int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2\{I_{il}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}^1-\mathbf{v}')\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^1-\mathbf{q}')$$
$$\times n_l(\mathbf{q}^2)\Phi_l(v^2)g_{il}(\mathbf{q}^1,\mathbf{q}^2) + \int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2\{I_{ij}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}^2-\mathbf{v}')\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^2-\mathbf{q}')$$
$$\times n_i(\mathbf{q}^1)\Phi_i(v^1)g_{ij}(\mathbf{q}^1,\mathbf{q}^2) + \delta_{ij}\int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\{I_i^{E1w}\delta(\mathbf{v}-\mathbf{v}')\}$$
$$\times\delta(\mathbf{v}^1-\mathbf{v}')\}\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^1-\mathbf{q}')n_w(\mathbf{q}^2)g_{iw}(\mathbf{q}^1,\mathbf{q}^2) + n_i(\mathbf{q})\Phi_i(v)\mathbf{v}$$
$$\times\left\{\frac{\partial C_{ij}(\mathbf{q},\mathbf{q}')}{\partial\mathbf{q}} + \beta g_{ij}(\mathbf{q},\mathbf{q}')\frac{\partial\Psi_{ij}(\mathbf{q},\mathbf{q}')}{\partial\mathbf{q}}\right\}$$
$$+\frac{\partial n_i(\mathbf{q})}{\partial\mathbf{q}}\Phi_i(v)\mathbf{v}\left[1 + C_{ij}(\mathbf{q},\mathbf{q}') - \sum_l\int d\mathbf{q}^3\, n_l(\mathbf{q}^3)C_{lj}(\mathbf{q}^3,\mathbf{q}')\right], \tag{4.34}$$

where we have also made use of multipliers

$$\sum_k\int d\mathbf{q}^2\, n_k(\mathbf{q}^2)g_{ik}(\mathbf{q},\mathbf{q}^2)\frac{\partial\Psi_{ik}(\mathbf{q},\mathbf{q}^2)}{\partial\mathbf{q}} + \int d\mathbf{q}^2\frac{\partial V_{iw}^{E}(\mathbf{q},\mathbf{q}^2)}{\partial\mathbf{q}}n_w(\mathbf{q}^2)g_{iw}(\mathbf{q},\mathbf{q}^2) = 0, \tag{4.35}$$

which represent the resulting force acting on a fluid particle of species i at point $\mathbf{q}$ in equilibrium in case 2. The quantities $V_{iw}^{E}(\mathbf{q},\mathbf{q}')$ and $n_w(\mathbf{q})$ are defined in Appendices D and E.

Substituting Eqs. (4.31) and (4.32) in Eq. (4.19) one can derive in case 1 of a general external potential ν_i^E,

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\frac{\partial}{\partial\mathbf{q}}\right)\delta F_i(\mathbf{q},\mathbf{v};t) = \sum_j\left\{\left[\int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2\{I_{ij}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{q}-\mathbf{q}^1)n_j(\mathbf{q}^2)\Phi_j(v^2)\right.\right.$$
$$\times g_{ij}(\mathbf{q}^1,\mathbf{q}^2)\delta F_i(\mathbf{q}^1,\mathbf{v}^1;t) + \int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2\{I_{ij}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{q}-\mathbf{q}^1)$$
$$\times n_i(\mathbf{q}^1)\Phi_i(v^1)g_{ij}(\mathbf{q}^1,\mathbf{q}^2)\delta F_j(\mathbf{q}^2,\mathbf{v}^2;t) + n_i(\mathbf{q})\Phi_i(v)\mathbf{v}\int d\mathbf{q}'$$
$$\times\left\{\frac{\partial C_{ij}(\mathbf{q},\mathbf{q}')}{\partial\mathbf{q}} + \beta g_{ij}(\mathbf{q},\mathbf{q}')\frac{\partial\Psi_{ij}(\mathbf{q},\mathbf{q}')}{\partial\mathbf{q}}\right\}\delta F_j(\mathbf{q}',\bar{\mathbf{v}}';t) + \frac{\partial n_i(\mathbf{q})}{\partial\mathbf{q}}\Phi_i(v)\mathbf{v}\int d\mathbf{q}'\left[1 + C_{ij}(\mathbf{q},\mathbf{q}')\right.$$
$$\left.\left.-\sum_l\int d\mathbf{q}''\, n_l(\mathbf{q}'')C_{lj}(\mathbf{q}'',\mathbf{q}')\right]\delta F_j(\mathbf{q}',\bar{\mathbf{v}}';t)\right\} + \int d\mathbf{q}^1\, d\mathbf{v}^1\{I_i^{E1}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{q}-\mathbf{q}^1)\delta F_i(\mathbf{q}^1,\mathbf{v}^1;t). \tag{4.36}$$

So far we have not used any properties of the fluid–fluid interaction potential except its pairwise nature together with Eq. (4.1), where we have considered φ_S to be of a general form $\varphi_S(\mathbf{q}_i^\alpha,\mathbf{q}_j^\beta)$. We now make use of the fact that $\varphi_S(\mathbf{q}_i^\alpha,\mathbf{q}_j^\beta) = \varphi_S(|\mathbf{q}_i^\alpha - \mathbf{q}_j^\beta|)$. Then from Eq. (4.36), definitions (4.38), and (4.39), (4.31), (4.32), (4.19), (4.33), and (C6) of Appendix C, one can derive in case 1 of the external potential ν_i^E

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_i\frac{\partial}{\partial\mathbf{q}_i}\right)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t) = \sum_j\left\{\left[\int d\mathbf{q}_j\, d\mathbf{v}_j\, T_{ij}\{n_j(\mathbf{q}_j)\Phi_j(v_j)g_{ij}(\mathbf{q}_1,\mathbf{q}_j)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)\right.\right.$$
$$+ n_i(\mathbf{q}_i)\Phi_i(v_i)g_{ij}(\mathbf{q}_i,\mathbf{q}_j)\delta F_j(\mathbf{q}_j,\mathbf{v}_j;t)\}$$
$$+ n_i(\mathbf{q}_i)\Phi_i(v_i)\mathbf{v}_i\int d\mathbf{q}_j\left(\frac{\partial C_{ij}(\mathbf{q}_i,\mathbf{q}_j)}{\partial\mathbf{q}_i} - g_{ij}(\mathbf{q}_1,\mathbf{q}_j)\frac{\partial f_{ij}^H(q_{ij})}{\partial\mathbf{q}_{ij}}\right)\delta F_j(\mathbf{q}_j,\bar{\mathbf{v}}_j;t)$$
$$\left.+\frac{\partial n_i(\mathbf{q}_i)}{\partial\mathbf{q}_i}\Phi_i(v_i)\mathbf{v}_i\int d\mathbf{q}_j\left[1 + C_{ij}(\mathbf{q}_i\mathbf{q}_j) - \sum_l\int d\mathbf{q}_l\, n_l(\mathbf{q}_l)C_{lj}(\mathbf{q}_l,\mathbf{q}_j)\right]\delta F_j(\mathbf{q}_j,\bar{\mathbf{v}}_j;t)\right\}, \tag{4.37}$$

where the quantity

$$f_{ij}^H(q_{ij}) = \exp[-\beta\varphi_H(q_{ij})] - 1 = \Theta(q_{ij} - \sigma_{ij}) - 1, \quad q_{ij} = |\mathbf{q}_1 - \mathbf{q}_j|, \tag{4.38}$$

is the Mayer function specific to the hard-core fluid–fluid interaction, and we have used the operators

$$I_{ij} = \frac{\partial\varphi_S(\mathbf{q}_1,\mathbf{q}_j)}{\partial\mathbf{q}_1}\cdot\left(\frac{1}{m_i}\frac{\partial}{\partial\mathbf{v}_i} - \frac{1}{m_j}\frac{\partial}{\partial\mathbf{v}_j}\right) + T_{ij}, \tag{4.39}$$
$$T_{ij} = \delta(|\mathbf{q}_i - \mathbf{q}_j| - \sigma_{ij})|\mathbf{v}_{ij}\cdot\hat{\mathbf{q}}_{ij}|\{\Theta(\mathbf{v}_{ij}\cdot\hat{\mathbf{q}}_{ij})\mathbf{b}_{ij} - \Theta(-\mathbf{v}_{ij}\cdot\hat{\mathbf{q}}_{ij})\}$$

$$= \sigma_{ij}^2 \int d\hat{\sigma} |\mathbf{v}_{ij}\cdot\hat{\sigma}| \Theta(-\mathbf{v}_{ij}\cdot\hat{\sigma}) \{\delta(\mathbf{q}_i - \mathbf{q}_j + \sigma_{ij}\hat{\sigma}) - \delta(\mathbf{q}_i - \mathbf{q}_j - \sigma_{ij}\hat{\sigma})\}, \tag{4.40}$$

$$\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j, \quad \mathbf{b}_{ij} = \mathbf{b}_{ij}^{\alpha\beta} \text{ with } \alpha = i, \beta = j,$$

and where we have also changed notations $(\mathbf{q},\mathbf{v})$ and $(\mathbf{q}',\mathbf{v}')$ on $(\mathbf{q}_i,\mathbf{v}_i)$ and $(\mathbf{q}_j,\mathbf{v}_j)$, respectively.

Using the same procedure which has lead to Eq. (4.37), from Eqs. (4.31), (4.34), and (4.19) we can prove in case 2 (external potential ν_{iw}^E),

$$\left\{\frac{\partial}{\partial t} + \mathbf{v}_i \frac{\partial}{\partial \mathbf{q}_i} - \frac{1}{\beta m_i}\int d\mathbf{q}_w \frac{\partial f_{iw}^H(q_{iw})}{\partial \mathbf{q}_i} n_w(\mathbf{q}_w) g_{iw}(\mathbf{q}_i,\mathbf{q}_w)\frac{\partial}{\partial \mathbf{v}_i}\right\}\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)$$
$$= \sum_j \Bigg\{ \int d\mathbf{q}_j\, d\mathbf{v}_j\, T_{ij}\{n_j(\mathbf{q}_j)\Phi_j(v_j)g_{ij}(\mathbf{q}_i,\mathbf{q}_j)\delta F_i(\mathbf{q}_1,\mathbf{v}_1;t) + n_i(\mathbf{q}_i)\Phi_i(v_i)g_{ij}(\mathbf{q}_i,\mathbf{q}_j)\delta F_j(\mathbf{q}_j,\mathbf{v}_j;t)\}$$
$$+ n_i(\mathbf{q}_i)\Phi_i(v_i)\mathbf{v}_i \int d\mathbf{q}_j\left(\frac{\partial C_{ij}(\mathbf{q}_i,\mathbf{q}_j)}{\partial \mathbf{q}_i} - g_{ij}(\mathbf{q}_i,\mathbf{q}_j)\frac{\partial f_{ij}^H(q_{ij})}{\partial \mathbf{q}_{ij}}\right)\delta F_j(\mathbf{q}_j,\bar{\mathbf{v}}_j;t)$$
$$+ \frac{\partial n_i(\mathbf{q}_i)}{\partial \mathbf{q}_i}\Phi_i(v_i)\mathbf{v}_1\int d\mathbf{q}_j\left[1 + C_{ij}(\mathbf{q}_i,\mathbf{q}_j) - \sum_l \int d\mathbf{q}_l\, n_l(\mathbf{q}_l)C_{lj}(\mathbf{q}_l,\mathbf{q}_j)\right]\delta F_j(\mathbf{q}_j,\bar{\mathbf{v}}_j;t)\Bigg\}$$
$$+ \int d\mathbf{q}_w\, T_i^{iw}(\mathbf{v}_i,\mathbf{q}_i,\mathbf{q}_w) n_w(\mathbf{q}_w) g_{iw}(\mathbf{q}_i,\mathbf{q}_w)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t), \tag{4.41}$$

where we have also denoted $(\mathbf{q},\mathbf{v})$, $(\mathbf{q}',\mathbf{v}')$, $(\mathbf{q}^3,\mathbf{v}^3)$, $(\mathbf{q}^2,\mathbf{v}^2)$ by $(\mathbf{q}_i,\mathbf{v}_i)$, $(\mathbf{q}_j,\mathbf{v}_j)$, $(\mathbf{q}_l,\mathbf{v}_l)$, and $(\mathbf{q}_w,\mathbf{v}_w)$, respectively, and T_i^{iw} is $T_i^{\alpha w}$ from Eq. (4.11) at $\alpha = i$. We note here that, in principle, Eq. (4.41) can be obtained from Eq. (4.37) directly by using the time smoothing procedure introduced by Karkheck and Stell.[39]

Equations (4.37) can be reduced to Eq. (2.31) of Ref. 26 for a homogeneous fluid mixture, assuming $n_i(\mathbf{q}_i)$, $n_j(\mathbf{q}_j)$ are equal to constants. Similarly to Eq. (2.31), Eq. (4.37) and (4.41) do not contain explicitly the soft fluid–fluid and fluid–wall interaction potentials, so the effect of the soft interactions are confined to their contributions to the equilibrium correlation functions. Thus, Eqs. (4.37) and (4.41) can be regarded as extensions of Eqs. (2.31) of Ref. 26 for homogeneous fluid mixtures to inhomogeneous ones, where the external potentials can be of a general kind ν_i^E or a pairwise kind ν_{kw}^E. Moreover, Eq. (2.31) of Ref. 26 were proved to be a near-equilibrium linearized homogeneous generalization (without restrictions on fluid number densities) of the BBGKY equations for fluid mixtures with hard-core fluid–fluid interactions to interaction potentials containing soft parts. Thus, Eqs. (4.37) and (4.41) should be treated as near-equilibrium linearized inhomogeneous generalizations (without restrictions on fluid number densities) of the BBGKY equations. The linearity of the generalizations above follows from the liner nature of the GLEs, as was shown in Sec. III.

The absence in Eq. (4.37) and (4.41) of terms explicitly containing soft fluid–fluid or fluid–wall interactions has important consequences. To see this we note that instead of the definitions (4.12) for the collective dynamical variables one could introduce collective dynamical variables $\tilde{A}_i(\mathbf{q}_i,\mathbf{v}_i,t)$,

$$\tilde{A}_i(\mathbf{q},\mathbf{v};t) = \sum_{\alpha=1}^{N_i}\delta(\mathbf{q}-\mathbf{q}_i^\alpha(t))\delta(\mathbf{v}-\mathbf{v}_i^\alpha(t)) - \left\langle\sum_{\alpha=1}^{N_i}\delta(\mathbf{q}-\mathbf{q}_i^\alpha(t))\delta(\mathbf{v}-\mathbf{v}_i^\alpha(t))\right\rangle_\sim$$
$$= \sum_{\alpha=1}^{N_i}\delta(\mathbf{q}-\mathbf{q}_i^\alpha(t))\delta(\mathbf{v}-\mathbf{v}_i^\alpha(t)) - \tilde{n}_i(\mathbf{q})\Phi_i(v), \tag{4.42}$$

where $\langle\ \rangle_\sim$ means "near-to-point-**q**-space-smoothed" averaging over the equilibrium grand canonical ensemble, and

$$\tilde{n}_i(\mathbf{q}_i)\cdots\tilde{n}_k(\mathbf{q}_k)\tilde{g}_{i\cdots k}(\mathbf{q}_i,\dots,\mathbf{q}_k) = \sum_{\alpha\neq\cdots\neq\gamma}\cdots\sum\delta(\mathbf{q}_i-\mathbf{q}_i^\alpha(t))\cdots\delta(\mathbf{q}_k-\mathbf{q}_k^\gamma(t)) \tag{4.43}$$

defines the "smoothed" equilibrium specific van Hove correlation functions $\tilde{g}_{i\cdots k}(\mathbf{q}_i,\dots,\mathbf{q}_k)$. The quantities (4.17), (4.18), and the projection operator should also be redefined so that they be expressed through the average $\langle\ \rangle_\sim$ instead of $\langle\ \rangle$. The sense of space "smoothing" above is to introduce $\tilde{n}_i(\mathbf{q}_i)$ so that $\partial\tilde{n}_i(\mathbf{q}_i)/\partial\mathbf{q}_i \propto \delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)$. If we require Eqs. (4.33) and (4.35) to hold for "smoothed" $\tilde{n}_k(\mathbf{q}_k)$, $\tilde{g}_{ik}(\mathbf{q}_i,\mathbf{q}_k)$, then Eqs. (4.37) for an inhomogeneous fluid mixture in a general external potential ν_i^E take the same *form* as Eq. (2.31) of Ref. 26 for a homogeneous fluid,

$$\left(\frac{\partial}{\partial t}+\mathbf{v}_i\frac{\partial}{\partial \mathbf{q}_i}\right)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)=\sum_j\left\{\iint d\mathbf{q}_j\,d\mathbf{v}_j\,T_{ij}\{\tilde{n}_j(\mathbf{q}_j)\Phi_j(v_j)\tilde{g}_{ij}(\mathbf{q}_i,\mathbf{q}_j)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)\right.$$
$$+\tilde{n}_i(\mathbf{q}_i)\Phi_i(v_i)\tilde{g}_{ij}(\mathbf{q}_i,\mathbf{q}_j)\delta F_j(\mathbf{q}_j,\mathbf{v}_j;t)+\tilde{n}_i(\mathbf{q}_i)\Phi_i(v_i)\mathbf{v}_i$$
$$\left.\times\int d\mathbf{q}_j\left[\frac{\partial\tilde{C}_{ij}(\mathbf{q}_i,\mathbf{q}_j)}{\partial\mathbf{q}_i}-\tilde{g}_{ij}(\mathbf{q}_i,\mathbf{q}_j)\,\frac{\partial f^H_{ij}(q_{ij})}{\partial\mathbf{q}_i}\right]\delta F_j(\mathbf{q}_j,\bar{\mathbf{v}}_j;t)\right\},\tag{4.44}$$

and analogous equations (4.41) for an inhomogeneous fluid mixture in an external field v^E_{iw} can be written as

$$\left\{\frac{\partial}{\partial t}+\mathbf{v}_1\,\frac{\partial}{\partial\mathbf{q}_i}-\frac{1}{\beta m_i}\int d\mathbf{q}_w\,\frac{\partial f^H_{iw}(q_{iw})}{\partial\mathbf{q}_{iw}}\,\tilde{n}_w(\mathbf{q}_w)\tilde{g}_{iw}(\mathbf{q}_i,\mathbf{q}_w)\frac{\partial}{\partial\mathbf{v}_i}\right\}\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)$$
$$=\sum_j\left\{\iint d\mathbf{q}_j\,d\mathbf{v}_j\,T_{ij}\{\tilde{n}_j(\mathbf{q}_j)\Phi_j(v_j)\tilde{g}_{ij}(\mathbf{q}_i,\mathbf{q}_j)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t)+\tilde{n}_i(\mathbf{q}_i)\Phi_i(v_i)\tilde{g}_{ij}(\mathbf{q}_i\mathbf{q}_j)\delta F_j(\mathbf{q}_j,\mathbf{v}_j;t)\}\right.$$
$$\left.\times\tilde{n}_i(\mathbf{q}_i)\Phi_i(v_i)\mathbf{v}_i\int d\mathbf{q}_j\left[\frac{\partial\tilde{C}_{ij}(\mathbf{q}_i,\mathbf{q}_j)}{\partial\mathbf{q}_i}-\tilde{g}_{ij}(\mathbf{q}_i,\mathbf{q}_j)\,\frac{\partial f^H_{ij}(q_{ij})}{\partial\mathbf{q}_i}\right]\delta F_j(\mathbf{q}_j,\bar{\mathbf{v}}_j;t)\right\}$$
$$+\int d\mathbf{q}_w\,T^{iw}_i(\mathbf{v}_i,\mathbf{q}_i,\mathbf{q}_w)\tilde{n}_w(\mathbf{q}_w)\tilde{g}_{iw}(\mathbf{q}_i,\mathbf{q}_j)\delta F_i(\mathbf{q}_i,\mathbf{v}_i;t),\tag{4.45}$$

where $\tilde{n}_w(\mathbf{q}_w)$ is a smoothed surface number density for the wall molecules.

Equations (4.44) and (4.45) can also be derived directly from (4.37) and (4.41), respectively, by assuming $\tilde{n}_j(\mathbf{q}_j)$, instead of $n_j(\mathbf{q}_j)$, and taking into account that all other equilibrium quantities there that are functionals[40,41] of $n_j(\mathbf{q}_j)$ should be changed to ones corresponding to $\tilde{n}_j(\mathbf{q}_j)$.

V. CONCLUSIONS

In the investigation presented above we have developed a rigorous functional perturbation theory (FTP) scheme by means of the generalized Mori projection operator technique. This permits us, in principle, to derive the master equation for any order of FPT describing the evolution of collective dynamical variables of a many-body system. In particular, we have proved that the generalized Langevin equation is an exact equation of the first order FPT above. The master equations for the higher orders FPT can also be derived and should be useful for the description of the time behavior of dynamical systems with strong memory effects. We have also used the GLE to derive kinetic equations for strongly inhomogeneous fluid mixtures under the assumption that the dynamic memory matrix in the GLE is equal to zero. The kinetic equations for inhomogeneous fluids with first order dynamic memory effects can be derived from the GLE with appropriate approximations for the dynamic memory matrix. We have considered two cases each of which includes an external time-independent potential field of a general kind and pairwise fluid particle–wall particle interactions. Such equations have been proved to be a natural generalization of those derived by Sung and Dahler[26] for homogeneous fluid mixtures. We have been able to establish that these equations can be rewritten in the same *form* as those for homogeneous fluid mixtures,[26] by introducing a space-smoothing procedure for *equilibrium* structure factors (number densities, pair and direct correlation functions).

Unfortunately, from a general point of view, one cannot introduce a unique procedure for "smoothing." Such a procedure should be developed additionally for any particular system under consideration. The "smoothing" procedure for simple equilibrium fluids confined in narrow capillary pores has been widely discussed (see, e.g., Ref. 42), however, and seems to be established.

As follows from Eqs. (4.44) and (4.45), nonequilibrium singlet distribution functions $F_j(\mathbf{q}_j,\mathbf{v}_j,t)$ for inhomogeneous fluid mixtures should be expected to be functions of "smoothed" equilibrium local number densities $\tilde{n}_j(\mathbf{q}_j)$. As a result, local transport coefficients of strongly inhomogeneous fluids near to equilibrium can be expressed as functions of $\tilde{n}_j(\mathbf{q}_j)$. Thus, we have provided a rigorous foundation for the heuristic idea proposed by Davis *et al.*[15] for simple fluids confined in narrow capillary pores, namely, that local transport coefficients of inhomogeneous fluids in narrow capillary pores can be set equal to the transport coefficients of homogeneous fluids at the "smoothed" local densities. We have also extended this idea to the whole class of strongly inhomogeneous fluid mixtures.

In a future paper we shall consider a velocity moment method to derive from Eqs. (4.37), (4.41) and (4.44), (4.45) hydrodynamic equations and explicit expressions for the transport coefficients of strongly inhomogeneous fluids near to equilibrium.

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APPENDIX A: CALCULATION OF THE STATIC CORRELATION MATRIX

Noticing that

$$\langle \sum_{\alpha\neq\beta}^{N_iN_j}\sum \delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{q}'-\mathbf{q}_j^\beta)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\delta(\mathbf{v}'-\mathbf{v}_j^\beta)\rangle$$
$$=\delta_{ij}\delta(x-x')n_i(\mathbf{q})\Phi_i(v) + n_i(\mathbf{q})n_j(\mathbf{q}')\Phi_i(v)\Phi_j(v')g_{ij}(\mathbf{q},\mathbf{q}'),$$

one can obtain the expression (4.24) of the text from Eqs. (4.12) and (4.23).

APPENDIX B: SOME PROPERTIES OF THE MATRIX χ AND FUNCTIONS $C_{ij}(\mathbf{q},\mathbf{q}')$

By definition Eq. (4.23) in classical statistic mechanics one can derive

$$\chi_{ij}(x,x')=\chi_{ji}(x',x) \tag{B1}$$

so $\chi_{ij}(x,x')$ are symmetric functions of the simultaneous permutation of index sets $(i;x)$ and $(j;x')$. The same property applies to the pair correlation functions (4.26), then from Eqs. (4.22) and (B1) it follows that

$$\chi_{jk}^{-1}(x_j,x_k)=\chi_{kj}^{-1}(x_k,x_j), \tag{B2}$$

so that from Eqs. (4.27) and (B2) one can derive

$$C_{ij}(\mathbf{q},\mathbf{q}')=\delta_{ij}\delta(x-x')\{[n_j(\mathbf{q}')\Phi_j(v')]^{-1} - [n_i(\mathbf{q})\Phi_i(v)]^{-1}\}+C_{ji}(\mathbf{q}',\mathbf{q}). \tag{B3}$$

Thus, from Eq. (B3) it follows that $C_{ij}(\mathbf{q},\mathbf{q}')=C_{ji}(\mathbf{q}',\mathbf{q})$.

APPENDIX C: CALCULATION OF $i\Omega_{ij}^0(x,x')$

We first calculate the average

$$\langle\{iL^0A_i(x)\}A_k(x'')\rangle = \left\langle\left\{\sum_\alpha \frac{p_i^\alpha}{m_i}\frac{\partial}{\partial\mathbf{q}_i^\alpha}\delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\right\} \times\left[\sum_{\beta=1}^{N_k}\delta(\mathbf{q}''-\mathbf{q}_k^\beta)\delta(\mathbf{v}''-\mathbf{v}_k^\beta)-n_k(\mathbf{q}'')\Phi_k(v'')\right]\right\rangle = I_1+I_2, \tag{C1}$$

where

$$I_1=\left\langle\left\{\sum_\alpha \frac{\mathbf{p}_i^\alpha}{m_i}\frac{\partial}{\partial\mathbf{q}_i^\alpha}\delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\right\}\times\sum_{\beta=1}^{N_k}\delta(\mathbf{q}''-\mathbf{q}_k^\beta)\delta(\mathbf{v}''-\mathbf{v}_k^\beta)\right\rangle$$
$$=\delta_{ik}\int d\mathbf{q}^1\,d\mathbf{v}^1\left\{\frac{\mathbf{p}^1}{m_i}\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}\delta(\mathbf{v}-\mathbf{v}^1)\times\delta(\mathbf{q}^1-\mathbf{q}'')\delta(\mathbf{v}^1-\mathbf{v}'')n_i(\mathbf{q}^1)\Phi_i(v^1)$$
$$+\int d\mathbf{q}^1\,d\mathbf{v}^1\left\{\frac{\mathbf{p}^1}{m_i}\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}\delta(\mathbf{v}-\mathbf{v}^1)n_i(\mathbf{q})\times n_k(\mathbf{q}'')\Phi_k(v'')g_{ik}(\mathbf{q}^1,\mathbf{q}'') \tag{C2}$$

and

$$I_2=-\left\langle\sum_\alpha \frac{\mathbf{p}_i^\alpha}{m_i}\frac{\partial}{\partial\mathbf{q}_i^\alpha}\delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\right\rangle n_k(\mathbf{q}'')\Phi_k(v'')$$
$$=-\int d\mathbf{q}^1\,d\mathbf{v}^1\left\{\frac{\mathbf{p}^1}{m_i}\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}\delta(\mathbf{v}-\mathbf{v}^1)\times n_i(\mathbf{q}^1)\Phi_i(v^1)n_k(\mathbf{q}'')\Phi_k(v''). \tag{C3}$$

Then from Eqs. (4.21) and (4.27) at $r=0$ one can obtain

$$i\Omega_{ij}^0(x,x')=\delta_{ij}\int d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}\delta(\mathbf{q}^1-\mathbf{q}')\delta(\mathbf{v}-\mathbf{v}^1)-\int d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}$$
$$\times n_i(\mathbf{q}^1)\Phi_i(v)C_{ij}(\mathbf{q}^1;\mathbf{q}')+\int d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}n_i(\mathbf{q}^1)\Phi_i(v)g_{ij}(\mathbf{q}^1,\mathbf{q}')$$
$$-\sum_k\int d\mathbf{q}''\,d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}n_i(\mathbf{q}^1)\Phi_i(v)n_k(\mathbf{q}'')g_{ik}(\mathbf{q}^1,\mathbf{q}'')C_{kj}(\mathbf{q}'',\mathbf{q}')$$
$$-\int d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}n_i(\mathbf{q}^1)\Phi_i(v)+\sum_k\int d\mathbf{q}''\,d\mathbf{q}^1\frac{\mathbf{p}}{m_i}\left\{\frac{\partial}{\partial\mathbf{q}^1}\delta(\mathbf{q}-\mathbf{q}^1)\right\}n_i(\mathbf{q}^1)$$
$$\times\Phi_i(v)n_k(\mathbf{q}'')\Phi_k(v''). \tag{C4}$$

The expression (4.30) follows from Eq. (C4) after using the δ-function derivative property

$$\int_{-\infty}^{\infty} f_1(\tau)\{f_2(\tau)\delta'(\tau-a)\}=\int_{-\infty}^{\infty}d\tau\{f_1(\tau)f_2(\tau)\}\delta'(\tau-a)$$
$$=-[f_1(\tau)f_2(\tau)]'_{\tau=a}=-f_1'(a)f_2(a)-f_1(a)f_2'(a), \tag{C5}$$

together with the symmetry properties (Appendix B) of the functions $g_{ij}(\mathbf{q},\mathbf{q}'),C_{ij},(\mathbf{q},\mathbf{q}')$ and the OZ equation (4.29).

APPENDIX D: CALCULATION OF $i\Omega_{ij}^I(x,x')$

Corresponding to Eqs. (4.7), (4.17), and (4.21) one can write

$$i\Omega_{ij}^I(x,x')=\langle\{iL_+^IA_i(x)\}A_l^*(\bar{x}'')\rangle\chi_{lj}^{-1}(\bar{x}'',x'), \tag{D1}$$

where

$$iL^{I}_{+}A_i(x)=\frac{1}{2}\sum_{\alpha\neq\beta}\sum\left\{I^{\alpha\beta}_{ii}+\sum_{j\neq i}[I^{\alpha\beta}_{ij}+I^{\alpha\beta}_{ji}]\right\}A_i(x)$$

$$=\sum_{\alpha\neq\beta}\sum\Bigg(I^{\alpha\beta}_{ii}[\delta(\mathbf{q}-\mathbf{q}^{\alpha}_i)\delta(\mathbf{v}-\mathbf{v}^{\alpha}_i)-n_i(\mathbf{q})\Phi_i(v)]+\frac{1}{2}\sum_{i\neq j}\sum I^{\alpha\beta}_{ij}[\delta(\mathbf{q}-\mathbf{q}^{\alpha}_i)$$

$$\times\delta(\mathbf{v}-\mathbf{v}^{\alpha}_i)-n_i(\mathbf{q})\Phi_i(v)]+\frac{1}{2}\sum_{i\neq j}\sum I^{\alpha\beta}_{ji}[\delta(\mathbf{q}-\mathbf{q}^{\beta}_i)\delta(\mathbf{v}-\mathbf{v}^{\beta}_i)-n_i(\mathbf{q})\phi_i(v)]\Bigg), \tag{D2}$$

where the Latin subscripts and Greek superscripts correspond to species and particle labels, respectively. Since the second and third terms in Eq. (D2) give the same contributions, Eq. (D2) can be written in the form

$$i\Omega^{I}_{ij}(x,x')=\sum_{p=1}^{4}\mathscr{L}^{(p)}_{il}(x,\bar{x}'')\chi^{-1}_{lj}(\bar{x}'',x') \tag{D3}$$

with

$$\mathscr{L}^{(1)}_{il}(x,x')=\delta_{il}\sum_j\int d\mathbf{q}^1\,d\mathbf{v}^1\,d\mathbf{q}^2\,d\mathbf{v}^2\{I^{12}_{ij}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}'-\mathbf{v}^1)\delta(\mathbf{q}-\mathbf{q}^1)$$
$$\times\delta(\mathbf{q}'-\mathbf{q}^1)n_i(\mathbf{q}^1)n_j(\mathbf{q}^2)\Phi_i(v^1)\Phi_j(v^2)g_{ij}(\mathbf{q}^1,\mathbf{q}^2), \tag{D4}$$

$$\mathscr{L}^{(2)}_{il}(x,x')=\sum_j\delta_{jl}\int d\mathbf{q}^1\,d\mathbf{v}^1\,d\mathbf{q}^2\,d\mathbf{v}^2\{I^{12}_{ij}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}'-\mathbf{v}^2)\delta(\mathbf{q}-\mathbf{q}^1)$$
$$\times\delta(\mathbf{q}'-\mathbf{q}^2)n_i(\mathbf{q}^1)n_j(\mathbf{q}^2)\Phi_i(v^1)\Phi_j(v^2)g_{ij}(\mathbf{q}^1,\mathbf{q}^2), \tag{D5}$$

$$\mathscr{L}^{(3)}_{il}(x,x')=\sum_j\int d\mathbf{q}^1\,d\mathbf{v}^1\,d\mathbf{q}^2\,d\mathbf{v}^2\,d\mathbf{q}^3\,d\mathbf{v}^3\{I^{12}_{ij}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}'-\mathbf{v}^3)$$
$$\times\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}'-\mathbf{q}^3)n_i(\mathbf{q}^1)n_j(\mathbf{q}^2)n_l(\mathbf{q}^3)\Phi_i(v^1)\Phi_j(v^2)\Phi_l(v^3)g_{ijl}(\mathbf{q}^1,\mathbf{q}^2,\mathbf{q}^3), \tag{D6}$$

$$\mathscr{L}^{(4)}_{il}(x,x')=-\sum_j n_l(\mathbf{q}')\Phi_l(v')\int d\mathbf{q}^1\,d\mathbf{v}^1\,d\mathbf{q}^2\,d\mathbf{v}^2\{I^{12}_{ij}\delta(\mathbf{v}-\mathbf{v}^1)\}$$
$$\times\delta(\mathbf{q}-\mathbf{q}^1)n_i(\mathbf{q}^1)n_j(\mathbf{q}^2)\Phi_i(v^1)\Phi_j(v^2)g_{ij}(\mathbf{q}^1,\mathbf{q}^2). \tag{D7}$$

We can now compute the products $\mathscr{L}^{(p)}_{il}\chi^{-1}_{lj}$ using the formula (4.27) for χ^{-1}_{lj} and the formula (C14) of Ref. 25 which in our case takes the form

$$\int d\mathbf{v}^1 d\mathbf{v}^2\{I^{12}_{il}\delta(\mathbf{v}-\mathbf{v}^1)\}\Phi_i(\mathbf{v}^1)\Phi_l(v^2)=\frac{1}{m_i}\frac{\partial}{\partial\mathbf{v}}\Phi_i(v)\frac{\partial}{\partial\mathbf{q}^1}\Psi_{il}(\mathbf{q}^1,\mathbf{q}^2), \tag{D8}$$

with

$$\Psi_{il}(\mathbf{q}^1,\mathbf{q}^2)=\varphi_S(\mathbf{q}^1,\mathbf{q}^2)-\beta^{-1}\Theta(|\mathbf{q}^1-\mathbf{q}^2|-\sigma_{il}), \tag{D9}$$

where the notations $\Psi_{il}(\mathbf{q}^1,\mathbf{q}^2)$ and $\varphi_S(\mathbf{q}^1,\mathbf{q}^2)$ stress the fact that we have not used so far any properties of the soft interaction potentials except their pairwise nature.

Further on, using the formula (D8) one can compute the product $\mathscr{L}^{(2)}_{il}(x,\bar{x}'')\chi^{-1}_{lk}(\bar{x}'',x')$. The third of these products can be written in the form

$$\mathscr{L}^{(3)}_{il}(x,\bar{x}'')\chi^{-1}_{lk}(\bar{x}'',x')=\frac{1}{m_i}\frac{\partial\Phi_i(v)}{\partial\mathbf{v}}n_i(\mathbf{q})$$
$$\times\sum_{j,l}\int d\mathbf{q}''d\mathbf{q}^2\frac{\partial\Psi_{ij}(\mathbf{q},\mathbf{q}^2)}{\partial\mathbf{q}}n_j(\mathbf{q}^2)g_{ijl}(\mathbf{q},\mathbf{q}^2,\mathbf{q}'')[\delta_{lk}\delta(\mathbf{q}''-\mathbf{q}')-n_l(\mathbf{q}'')C_{lk}(\mathbf{q}'',\mathbf{q}')], \tag{D10}$$

where the expression (D8) has also been used. The last of the products, Eq. (D7), can be transformed to the form

$$\mathscr{L}^{(4)}_{il}(x,\bar{x}'')\chi^{-1}_{lk}(\bar{x}'',x')=\sum_j\frac{1}{m_i}\frac{\partial\Phi_i(v)}{\partial\mathbf{v}}n_i(\mathbf{q})\int d\mathbf{q}^2\frac{\partial\Psi_{ij}(\mathbf{q},\mathbf{q}^2)}{\partial\mathbf{q}}n_j(\mathbf{q}^2)g_{ij}(\mathbf{q},\mathbf{q}^2)$$
$$+\sum_{j,l}\sum\frac{1}{m_i}\frac{\partial\Phi_i(v)}{\partial\mathbf{v}}n_i(\mathbf{q})\int d\mathbf{q}''\,d\mathbf{q}^2\,n_l(\mathbf{q}'')n_j(\mathbf{q}^2)\frac{\partial\Psi_{ij}(\mathbf{q},\mathbf{q}^2)}{\partial\mathbf{q}}g_{ij}(\mathbf{q},\mathbf{q}^2)C_{lk}(\mathbf{q}'',\mathbf{q}'). \tag{D11}$$

The expression (D10) can be transformed using the second equilibrium BBGKY relationship for inhomogeneous fluids.[40] We consider two cases of external field potentials discussed at the beginning of Sec. IV. Thus, in case 1 for the external potential $\nu_i^E(q_i^\alpha)$ of a general kind the corresponding BBGKY relationship takes the form

$$\sum_j \int d\mathbf{q}^2 \frac{\partial \Psi_{ij}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_i(\mathbf{q}) n_j(\mathbf{q}^2) g_{ilj}(\mathbf{q},\mathbf{q}'',\mathbf{q}^2)$$

$$= -\beta^{-1} n_i(\mathbf{q}) \frac{\partial g_{il}(\mathbf{q},\mathbf{q}'')}{\partial \mathbf{q}} - \beta^{-1} g_{il}(\mathbf{q},\mathbf{q}'') \frac{\partial n_i(\mathbf{q})}{\partial \mathbf{q}} - n_i(\mathbf{q}) g_{il}(\mathbf{q},\mathbf{q}'') \frac{\partial \Psi_{il}(\mathbf{q},\mathbf{q}'')}{\partial \mathbf{q}} - n_i(\mathbf{q}) g_{il}(\mathbf{q},\mathbf{q}'') \frac{\partial \nu_i^E(\mathbf{q})}{\partial \mathbf{q}}. \quad \text{(D12)}$$

The notation $\nu_i^E(\mathbf{q})$ emphasizes the fact that we have not used any special properties of ν_i^E. In case 2 of the external potential $\nu_{iw}^E(q_{iw}^{\alpha w})$ the result from the second BBGKY relationship can be written as

$$\sum_j \int d\mathbf{q}^2 \frac{\partial \Psi_{ij}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_i(\mathbf{q}) n_j(\mathbf{q}^2) g_{ilj}(\mathbf{q},\mathbf{q}'',\mathbf{q}^2)$$

$$= -\beta^{-1} n_i(\mathbf{q}) \frac{\partial g_{il}(\mathbf{q},\mathbf{q}'')}{\partial \mathbf{q}} - \beta^{-1} g_{il}(\mathbf{q},\mathbf{q}'') \frac{\partial n_i(\mathbf{q})}{\partial \mathbf{q}}$$

$$- n_i(\mathbf{q}) g_{il}(\mathbf{q},\mathbf{q}'') \frac{\partial \Psi_{il}(\mathbf{q},\mathbf{q}'')}{\partial \mathbf{q}} - \int d\mathbf{q}^3 \frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^3)}{\partial \mathbf{q}} n_i(\mathbf{q}) n_w(\mathbf{q}^3) g_{ilw}(\mathbf{q},\mathbf{q}'',\mathbf{q}^3), \quad \text{(D13)}$$

where

$$V_{iw}^E(\mathbf{q},\mathbf{q}^3) \equiv \nu_{Siw}^E(\mathbf{q},\mathbf{q}^3) - \beta^{-1}\Theta(|\mathbf{q}-\mathbf{q}^3| - \sigma_{iw}),$$

[with notations $V_{iw}^E(\mathbf{q},\mathbf{q}_3)$ we indicate that we do not need any other properties of the soft external potentials except their pairwise nature], $n_w(\mathbf{q}^3)$ is the surface number density of the wall particles and $g_{ijw}(\mathbf{q},\mathbf{q}'',\mathbf{q}^3)$ represents the three-particle correlation function specific to i,j—fluid particle and w-wall particle correlations.

Thus, the expression (D1) calculated for a general potential $\nu_i^E(\mathbf{q})$ takes the form

$$i\Omega_{ij}^I(x,x') = \delta_{ij} \sum_l \int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2 \{I_{il}^{12} \delta(\mathbf{v}-\mathbf{v}^1)\} \delta(\mathbf{v}^1-\mathbf{v}')\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^1-\mathbf{q}')$$

$$\times n_l(\mathbf{q}^2)\Phi_l(v^2) g_{il}(\mathbf{q}^1,\mathbf{q}^2) + \beta\Phi_i(v) n_i(\mathbf{q}) \mathbf{v} \sum_l \int d\mathbf{q}^2 \frac{\partial \Psi_{il}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_l(\mathbf{q}^2) g_{il}(\mathbf{q},\mathbf{q}^2)$$

$$\times C_{ij}(\mathbf{q},\mathbf{q}') + \int d\mathbf{q}^1\, d\mathbf{q}^2\, d\mathbf{v}^1\, d\mathbf{v}^2 \{I_{ij}^{12}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{v}^2-\mathbf{v}')\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^2-\mathbf{q}') n_i(\mathbf{q}^1)\Phi_i(v^1)$$

$$\times g_{ij}(\mathbf{q}^1,\mathbf{q}^2) + \Phi_i(v)\mathbf{v}\Bigg[\frac{\partial C_{ij}(\mathbf{q},\mathbf{q}')}{\partial \mathbf{q}} n_i(\mathbf{q}) + \beta n_i(\mathbf{q}) g_{ij}(\mathbf{q},\mathbf{q}') \frac{\partial \Psi_{ij}(\mathbf{q},\mathbf{q}')}{\partial \mathbf{q}} + \beta n_i(\mathbf{q}) g_{ij}(\mathbf{q},\mathbf{q}') \frac{\partial \nu_i^E(\mathbf{q})}{\partial \mathbf{q}}$$

$$+ \frac{\partial n_i(\mathbf{q})}{\partial \mathbf{q}} \left[1 + C_{ij}(\mathbf{q},\mathbf{q}') - \sum_l \int d\mathbf{q}'' n_l(\mathbf{q}'') C_{lj}(\mathbf{q}'',\mathbf{q}')\right] - \beta n_i(\mathbf{q}) \frac{\partial \nu_i^E(\mathbf{q})}{\partial \mathbf{q}} \sum_l \int d\mathbf{q}''\, g_{il}(\mathbf{q},\mathbf{q}'')$$

$$\times n_l(\mathbf{q}'') C_{lj}(\mathbf{q}'',\mathbf{q}') + \beta n_i(\mathbf{q}) \sum_l \int d\mathbf{q}^2 \frac{\partial \Psi_{il}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_l(\mathbf{q}^2) g_{il}(\mathbf{q},\mathbf{q}^2)$$

$$- \beta n_i(\mathbf{q}) \sum_{l,k} \int d\mathbf{q}''\, d\mathbf{q}^2\, n_l(\mathbf{q}'') n_k(\mathbf{q}^2) g_{ik}(\mathbf{q},\mathbf{q}^2) C_{lj}(\mathbf{q}'',\mathbf{q}') \frac{\partial \Psi_{ik}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}}\Bigg]. \quad \text{(D14)}$$

For the pair-additive external potential $\nu_{iw}^E(\mathbf{q}^1,\mathbf{q}^2)$ an analogous expression can be found,

$$i\Omega_{ij}^I(x,x') = i\Omega_{ij}^I(x,x')|_{(\text{D14;3})} + \Phi_i(v)\mathbf{v}\Bigg\{\frac{\partial C_{ij}(\mathbf{q},\mathbf{q}')}{\partial \mathbf{q}} n_i(\mathbf{q})$$

$$+ \beta n_i(\mathbf{q}) g_{ij}(\mathbf{q},\mathbf{q}') \frac{\partial \Psi_{ij}(\mathbf{q},\mathbf{q}')}{\partial \mathbf{q}} + \beta n_i(\mathbf{q}) \int d\mathbf{q}^3 \frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^3)}{\partial \mathbf{q}} n_w(\mathbf{q}^3) g_{iwj}(\mathbf{q},\mathbf{q}^3,\mathbf{q}')$$

$$+ \frac{\partial n_i(\mathbf{q})}{\partial \mathbf{q}} \left[1 + C_{ij}(\mathbf{q},\mathbf{q}') - \sum_l \int d\mathbf{q}''\, n_l(\mathbf{q}'') C_{lj}(\mathbf{q}'',\mathbf{q}')\right] - \beta n_i(\mathbf{q}) \sum_l \int d\mathbf{q}''\, n_l(\mathbf{q}'')$$

$$\times C_{lj}(\mathbf{q}'',\mathbf{q}') \int d\mathbf{q}^3 \frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^3)}{\partial \mathbf{q}} n_w(\mathbf{q}^3) g_{iwl}(\mathbf{q},\mathbf{q}^3,\mathbf{q}') + \beta n_i(\mathbf{q}) \sum_l \int d\mathbf{q}^2 \frac{\partial \Psi_{il}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}}$$

$$\times n_l(\mathbf{q}^2) g_{il}(\mathbf{q},\mathbf{q}^2) - \beta n_i(\mathbf{q}) \sum_{l,k} \int d\mathbf{q}^2\, n_k(\mathbf{q}^2) g_{ik}(\mathbf{q},\mathbf{q}^2) \frac{\partial \Psi_{ik}(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} \int d\mathbf{q}''\, n_l(\mathbf{q}'') C_{lj}(\mathbf{q}'',\mathbf{q}')\Bigg\}, \quad \text{(D15)}$$

where $i\Omega_{ij}^I(x,x')|_{(\text{D14;3})}$ denotes the sum of the first three terms in (D14).

As is obvious from the above, the expressions derived for $i\Omega_{ij}^{I}(x,x')$ are also valid for general fluid–fluid and fluid–wall pairwise interaction potentials, after replacing V_{iw}^{E} and Ψ_{il} by the corresponding continuous potentials.

APPENDIX E: CALCULATION OF $i\Omega_{ij}^{E}$

1. $i\Omega_{ij}^{E}$ for the potential of a general kind

Denoting by

$$I_i^{E\alpha} \equiv -\frac{\partial}{\partial \mathbf{q}_i^\alpha} v_i^E(\mathbf{q}_i^\alpha)\cdot\frac{\partial}{\partial \mathbf{p}_i^\alpha}$$

we obtain

$$iL^E = \sum_i \sum_{\alpha=1}^{N_i} I_i^{E\alpha},$$

so that

$$iL^E A_i(x) = \sum_i \sum_\alpha^{N_i} I_i^{E\alpha}\{\delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\}.$$

Then for

$$P_{il}(x,x'') = \langle\{iL^E A_i(x)\}A_l^*(x'')\rangle$$

one can obtain

$$P_{il}(x,x'') = \left\langle \sum_{\alpha,\gamma}\sum \{I_i^{E\alpha}\delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\}\delta(\mathbf{q}''-\mathbf{q}_l^\gamma)\delta(\mathbf{v}''-\mathbf{v}_l^\gamma)\right\rangle - \left\langle \sum_\alpha \{I_i^{E\alpha}\delta(\mathbf{q}-\mathbf{q}_i^\alpha)\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\}\right\rangle n_l(\mathbf{q}'')\Phi_l(v''). \tag{E1}$$

Then from Eqs. (4.21), (4.27), and (E1) after simple calculations one can derive

$$\begin{aligned} i\Omega_{ij}^E(x,x') &= \delta_{ij}\int d\mathbf{q}^1\, d\mathbf{v}^1\{I_i^{E1}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{q}^1-\mathbf{q}')\delta(\mathbf{v}^1-\mathbf{v}') + \beta n_i(\mathbf{q})\Phi_i(v)\mathbf{v} \\ &\times\left\{\frac{\partial v_i^E(\mathbf{q})}{\partial \mathbf{q}} C_{ij}(\mathbf{q},\mathbf{q}') - \frac{\partial v_i^E(\mathbf{q})}{\partial \mathbf{q}} g_{ij}(\mathbf{q},\mathbf{q}') + \frac{\partial v_i^E(\mathbf{q})}{\partial \mathbf{q}}\sum_l \int d\mathbf{q}^2\, n_l(\mathbf{q}^2) g_{il}(\mathbf{q},\mathbf{q}^2) C_{lj}(\mathbf{q}^2,\mathbf{q}')\right. \\ &\left.+ \frac{\partial v_i^E(\mathbf{q})}{\partial \mathbf{q}} - \frac{\partial v_i^E(\mathbf{q})}{\partial \mathbf{q}}\sum_l \int d\mathbf{q}^2\, n_l(\mathbf{q}^2) C_{lj}(\mathbf{q}^2,\mathbf{q}')\right\}, \end{aligned} \tag{E2}$$

where we have also made use of the expression (D9).

2. $i\Omega_{ij}^{E}$ for pairwise fluid particle–wall particle interactions

In this case [see Eqs. (4.10) and (4.11)] we have

$$iL_+^E A_i(x) = \sum_\alpha \sum_w I_i^{E\alpha w}\{\delta(\mathbf{v}-\mathbf{v}_i^\alpha)\delta(\mathbf{q}-\mathbf{q}_i^\alpha) - n_i(\mathbf{q})\Phi_i(v)\},$$

so that

$$P_{il}(x,x'') \equiv \langle\{iL_+^E A_i(x)\}A_l(x'')\rangle$$

and

$$i\Omega_{ij}^E(x,x') = P_{il}(x,\bar{x}'')\chi_{lj}^{-1}(\bar{x}'',x').$$

Then using Eq. (4.27) and the expression

$$\int d\mathbf{v}^1\{I_i^{E1w}\delta(\mathbf{v}-\mathbf{v}^1)\}\Phi_i(v^1) = \frac{1}{m_i}\frac{\partial \Phi_i(v)}{\partial \mathbf{v}}\frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}_w)}{\partial \mathbf{q}} \tag{E3}$$

we can derive

$$\begin{aligned} i\Omega_{ij}^E(x,x') &= \delta_{ij}\int d\mathbf{v}^1\, d\mathbf{q}^1\, d\mathbf{q}^2\{I_i^{E1w}\delta(\mathbf{v}-\mathbf{v}^1)\}\delta(\mathbf{q}-\mathbf{q}^1)\delta(\mathbf{v}'-\mathbf{v}^1)\delta(\mathbf{q}^1-\mathbf{q}')n_w(\mathbf{q}^2)g_{iw}(\mathbf{q}^1,\mathbf{q}^2) \\ &+ \beta\Phi_i(v)n_i(\mathbf{q})\mathbf{v}\left[\int d\mathbf{q}^2\frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_w(\mathbf{q}^2)g_{iw}(\mathbf{q},\mathbf{q}^2)C_{ij}(\mathbf{q},\mathbf{q}') - \int d\mathbf{q}^2\frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}}\right. \\ &\times n_w(\mathbf{q}^2)g_{iwj}(\mathbf{q},\mathbf{q}^2,\mathbf{q}') + \sum_l\int d\mathbf{q}^3\, d\mathbf{q}^2\frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_w(\mathbf{q}^2)n_l(\mathbf{q}^3)g_{iwl}(\mathbf{q},\mathbf{q}^2,\mathbf{q}^3)C_{lj}(\mathbf{q}^3,\mathbf{q}') \\ &\left.+\int d\mathbf{q}^2\frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_w(\mathbf{q}^2)g_{iw}(\mathbf{q},\mathbf{q}^2) - \int d\mathbf{q}^2\frac{\partial V_{iw}^E(\mathbf{q},\mathbf{q}^2)}{\partial \mathbf{q}} n_w(\mathbf{q}^2)g_{iw}(\mathbf{q},\mathbf{q}^2)\sum_l\int d\mathbf{q}''\, n_l(\mathbf{q}'')C_{lj}(\mathbf{q}'',\mathbf{q}')\right]. \end{aligned} \tag{E4}$$

We have introduced above the two- and three-particle correlation functions $g_{iw}(\mathbf{q}^1,\mathbf{q}^2)$ and $g_{iwj}(\mathbf{q}^1,\mathbf{q}^2,\mathbf{q}^3)$ [or $g_{ijw}(\mathbf{q}^1,\mathbf{q}^3,\mathbf{q}^2)$], respectively, specific to correlations between fluid particles i,j and a wall particle w, and defined by[38]

$$n_i(\mathbf{q}^1)n_w(\mathbf{q}^2)g_{iw}(\mathbf{q}^1,\mathbf{q}^2) = \left\langle \sum_{\alpha}^{N_i}\sum_{w}^{N_w}\delta(\mathbf{q}^1-\mathbf{q}_i^\alpha)\delta(\mathbf{q}^2-\mathbf{q}_w)\right\rangle,$$

$$n_i(\mathbf{q}^1)n_w(\mathbf{q}^2)n_j(\mathbf{q}^3)g_{iwj}(\mathbf{q}^1,\mathbf{q}^2,\mathbf{q}^3) = \sum\sum\sum_{\alpha\neq\beta\ w}^{N_iN_jN_w}\delta(\mathbf{q}^1-\mathbf{q}_i^\alpha)\delta(\mathbf{q}^2-\mathbf{q}_w)\delta(\mathbf{q}^3-\mathbf{q}_j^\beta) \quad .$$

When calculating $i\Omega_{ij}^I$ and $i\Omega_{ij}^E$ for case 2 (external field potential v_{iw}^E), we have taken into consideration the wall particles. Thus, the average $\langle\ \rangle$ in this case includes averaging over the wall particles.

[1] J. Karkheck and G. Stell, J. Chem. Phys. **75**, 1475 (1981).
[2] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Fluids* (Interscience, New York, 1965).
[3] A. R. Altenberger, J. S. Dahler, and M. Tirrell, J. Chem. Phys. **86**, 2909 (1987).
[4] H. T. Davis, Adv. Chem. Phys. **XXIV**, 257 (1973), edited by I. Prigogine and S. Rice.
[5] G. Stell, Y. Karkheck, and H. van Beijeren, J. Chem. Phys. **79**, 3166 (1983).
[6] M. Baus and C. F. Tejero, J. Chem. Phys. **78**, 483 (1983).
[7] D. Ronis and I. Oppenheim, Physica **A117**, 317 (1983).
[8] D. Ronis, Physica **A121**, 1 (1983).
[9] H. T. Davis, J. Chem. Phys. **86**, 1474 (1987); Chem. Engn. Commun. **58**, 413 (1987).
[10] T. K. Vanderlick and H. T. Davis, J. Chem. Phys. **87**, 1791 (1987).
[11] I. Bitsanis, T. K. Vanderlick, M. Tirrell, and H. T. Davis, J. Chem. Phys. **89**, 3152 (1988).
[12] H. V. Beijeren and M. H. Ernst, Physica **68**, 437 (1973).
[13] P. Resibois, Phys. Rev. Lett. **40**, 1409 (1978).
[14] P. Resibois, J. Stat. Phys. **19**, 593 (1978).
[15] I. Bitsanis, J. Magda, M. Tirrell, and H. T. Davis, J. Chem. Phys. **87**, 1733 (1987).
[16] R. Evans, Adv. Phys. **28**, 143 (1979).
[17] R. Zwanzig, *Lectures in Theoretical Physics* (Interscience, New York, 1961), Vol. 3.
[18] H. Mori, Prog. Theoret. Phys. **33**, 423 (1965).
[19] A. Z. Akcasu and J. J. Duderstadt, Phys. Rev. **188**, 188 (1969).
[20] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw Hill, New York, 1980).
[21] D. Loss and H. Schoeller, Physica **A150**, 199 (1988).
[22] M. W. Evans and D. M. Heyes, Mol. Phys. **65**, 1441 (1988).
[23] M. W. Evans, Mol. Phys. **67**, 1195 (1989).
[24] G. C. Joslin and C. G. Gray, Mol. Phys. **66**, 757 (1989).
[25] W. Sung and J. S. Dahler, J. Chem. Phys. **78**, 6264 (1983).
[26] W. Sung and J. S. Dahler, J. Chem. Phys. **80**, 3025 (1984).
[27] R. C. Castillo, E. Martina, M. Lopez de Haro, Y. Karkheck, and G. Stell, Phys. Rev. A **39**, 3106 (1989).
[28] G. Sauermann, W. Just, K.-P. Karmann, and V. Zhang, Physica **140A**, 597 (1987).
[29] L. A. Pozhar, Ukr. Phys. J. **34**, 779 (1989) (in Russian).
[30] V. Volterra, *Theory of functionals and integral and integrodifferential equations* (Dover, New York, 1959).
[31] J. Killingbeck and G. H. A. Cole, *Mathematical Technique and Physical Applications* (Academic, New York, 1959).
[32] V. A. Ditkin and A. P. Prudnikov, *Handbook of Operation Calculus* (Vysch. Shk. Publ., Moscow, 1965) (in Russian).
[33] F. B. Hildebrand, *Advanced Calculus for Applications*, 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1976).
[34] A. H. Nayfeh, *Introduction to Perturbation Techniques* (Wiley, New York, 1981).
[35] R. G. Sachs, *Nuclear Theory* (Addison-Wesley, Cambridge, MA, 1953).
[36] H. Mori and K. Kawasaki, Progr. Theoret. Phys. **27**(3), 529 (1962).
[37] B. J. Berne, *Modern Theoretical Chemistry*, edited by B. J. Berne (Plenum, New York, 1977), p. 1.
[38] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976), p. 211.
[39] J. Karkheck and G. Stell, Phys. Rev. A **25**, 3302 (1982).
[40] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids, V. I. Fundamentals* (Clarendon, Oxford, 1984), Chap. 3.
[41] G. Stell, *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), p. II-171.
[42] B. K. Peterson, K. E. Gubbins, G. S. Heffelfinger, U. Marini Bettolo Marconi, and F. van Swol, J. Chem. Phys. **88**, 6487 (1988).