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Zwanzig-Mori equation for the time-dependent pair distribution function

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We develop a microscopic theoretical framework for the time-dependent pair distribution function starting from the Liouville equation. An exact Zwanzig-Mori equation of motion for the time-dependent pair distribution function is derived based on the projection-operator formalism. It is demonstrated that, under the Markovian approximation, our equation reduces to the so-called telegraph equation that includes the potential of mean force acting between the pair particles. With the additional approximation neglecting the inertia term, our equation takes the form of Smoluchowski's equation, which has been previously introduced with intuitive arguments and shown to satisfactorily reproduce the simulation results of the particle-pair dynamics.

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I. INTRODUCTION

The time-dependent pair distribution function $g(\boldsymbol{r},\boldsymbol{r}',t)$, describing the probability density of finding a pair of particles separated by $\boldsymbol{r}$ at time t given that they were separated by $\boldsymbol{r}'$ at time zero, is one of the fundamental quantities characterizing liquid-state dynamics [1]. It is a central quantity determining collision-induced absorption and depolarized Rayleigh and Raman scattering spectra [2,3]. Its knowledge also enables the calculation of the first encounter time distribution and survival probability of reactive molecules [4,5], and it has played an important role in the rigorous formulation of the diffusion-influenced bimolecular reaction kinetics [6,7]. However, the theoretical development for $g(\boldsymbol{r},\boldsymbol{r}',t)$ is still in the primitive stage compared to that for the van Hove correlation functions [1].

The function $g(\boldsymbol{r},\boldsymbol{r}',t)$ was first introduced by Oppenheim and Bloom [8] in their study of nuclear magnetic relaxation in fluids. However, their theory is valid only in the limit of free particles and leads to unsatisfactory results even for the short-time regime in the presence of interparticle interactions [9]. The exact short-time dynamics of $g(\boldsymbol{r},\boldsymbol{r}',t)$ were subsequently derived by Balucani and Vallauri [10], but calculating the dynamics in the longer time regime was outside the scope of their work. On the other hand, Haan [11] studied the dynamic behavior of $g(\boldsymbol{r},\boldsymbol{r}',t)$ from a different approach and demonstrated that Smoluchowski's equation with a potential of mean force satisfactorily reproduces the simulation results of the particle-pair dynamics. However, his approach resorts to intuitive arguments and is not based on a first-principle theory. The pair distribution function has also been investigated based on the kinetic theory [12], but its applicability is limited to the low-density regime.

In this paper, we develop a basic theoretical framework for the time-dependent pair distribution function, starting from the Liouville equation and using the projection-operator technique. Such a rigorous framework has served as a basis for developing successful liquid-state theories for the van Hove correlation functions [1]. It is demonstrated that the exact short-time behavior derived before and Smoluchowski's equation, which satisfactorily reproduced the simulation results in the longer time regime, naturally follow from the exact equation of motion for $g(\boldsymbol{r},\boldsymbol{r}',t)$ that we will derive in the present work. Our result will therefore provide a rigorous basis for developing improved theories dealing with the time-dependent pair distribution function.

The paper is organized as follows. In the next section, we derive an exact Zwanzig-Mori equation of motion for the time-dependent pair distribution function, starting from the Liouville equation for the whole system comprising a central particle pair and surrounding solvent particles. Section III discusses the implications of the derived equation, and the Appendix is devoted to a derivation of the initial value of the memory function.

II. EXACT EQUATION OF MOTION

A. Liouville equation

We consider a classical fluid of N spherical particles of mass m at a temperature T confined in a volume V, in which two tagged particles, A and B, are dissolved. For simplicity, the tagged particles are assumed to be mechanically identical to solvent particles. The Hamiltonian of the total system is given by

$$H = K + U, \tag{1}$$

with the kinetic energy part

$$K = \frac{\boldsymbol{p}_A^2}{2m} + \frac{\boldsymbol{p}_B^2}{2m} + \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m}, \tag{2}$$

and the potential energy part

$$U = \phi(r_{AB}) + \sum_{i=1}^{N}[\phi(r_{Ai}) + \phi(r_{Bi})] + \frac{1}{2}\sum_{i,j\,(i\neq j)}^{N} \phi(r_{ij}). \tag{3}$$

Here, $\boldsymbol{p}_i$ and $\boldsymbol{r}_i$ denote the momentum and position vectors of the particle i, respectively, and we have assumed that the total potential is represented by a sum of radially symmetric potential functions $\phi(r_{ij})$ that depend only on the particle separation $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$.

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According to classical mechanics, Newton's equation of motion of a dynamical variable—say, $A(t)$—can be written in the form

$$\frac{d}{dt}A(t) = \{H,A(t)\} \equiv i\mathcal{L}A(t), \quad (4)$$

which is called the Liouville equation [1]. Here the symbol { , } denotes a classical Poisson bracket, and the Liouville operator $i\mathcal{L}$ of the total system is given by

$$i\mathcal{L} = \sum_{i=A,\,B,\,1,\,\ldots,\,N} \left[\frac{\boldsymbol{p}_i}{m}\cdot\frac{\partial}{\partial \boldsymbol{r}_i} - \frac{\partial U}{\partial \boldsymbol{r}_i}\cdot\frac{\partial}{\partial \boldsymbol{p}_i} \right]. \quad (5)$$

B. Time-dependent pair distribution function

Of primary interest in the present work is the joint probability distribution function

$$G(\boldsymbol{r},\boldsymbol{r}',t) \equiv V\langle \delta(\boldsymbol{r}-\boldsymbol{r}_{AB}(t))\delta(\boldsymbol{r}'-\boldsymbol{r}_{AB}(0))\rangle. \quad (6)$$

Here, $\boldsymbol{r}_{AB}(t) = \boldsymbol{r}_A(t) - \boldsymbol{r}_B(t)$ denotes the separation of the particles A and B at time t, and $\langle\cdots\rangle$ represents the canonical ensemble average

$$\langle\cdots\rangle = \frac{1}{Z}\int \prod_{i=A,\,B,\,1,\,\ldots,\,N} [d\boldsymbol{p}_i d\boldsymbol{r}_i]\, e^{-\beta H}\cdots. \quad (7)$$

In this expression, $\beta = 1/(k_B T)$, with k_B being Boltzmann's constant and Z denoting the partition function

$$Z = \int \prod_{i=A,\,B,\,1,\,\ldots,\,N} [d\boldsymbol{p}_i d\boldsymbol{r}_i]\, e^{-\beta H}. \quad (8)$$

The initial value of $G(\boldsymbol{r},\boldsymbol{r}',t)$ is given by

$$G(\boldsymbol{r},\boldsymbol{r}',0) = V\delta(\boldsymbol{r}-\boldsymbol{r}')\langle\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')g(r) \quad (9)$$

in terms of the radial distribution function $g(r)$ [1]. This result accounts for the name time-dependent pair distribution function given to $G(\boldsymbol{r},\boldsymbol{r}',t)$. In the long-time limit, the average in Eq. (6) can be factored, yielding

$$\lim_{t\to\infty} G(\boldsymbol{r},\boldsymbol{r}',t) = \frac{1}{V}\, g(r)g(r'). \quad (10)$$

Let us also introduce the conditional distribution function

$$g(\boldsymbol{r},\boldsymbol{r}',t) \equiv G(\boldsymbol{r},\boldsymbol{r}',t)/g(r'), \quad (11)$$

which is proportional to the probability of finding a pair of particles separated by $\boldsymbol{r}$ at time t, given that they were separated by $\boldsymbol{r}'$ at time zero. The initial value and the long-time limit are given by

$$g(\boldsymbol{r},\boldsymbol{r}',0) = \delta(\boldsymbol{r}-\boldsymbol{r}') \text{ and } \lim_{t\to\infty} g(\boldsymbol{r},\boldsymbol{r}',t) = \frac{1}{V}\, g(r). \quad (12)$$

The time-dependent pair distribution function obeys the Liouville equation

$$\frac{d}{dt}G(\boldsymbol{r},\boldsymbol{r}',t) = i\mathcal{L}G(\boldsymbol{r},\boldsymbol{r}',t), \quad (13)$$

and so does the conditional distribution function $g(\boldsymbol{r},\boldsymbol{r}',t)$. In the following, we shall rewrite this equation of motion using the projection-operator formalism.

C. Projection-operator formalism

Here, we summarize the projection-operator formalism that is to be used in deriving the exact equation of motion for $G(\boldsymbol{r},\boldsymbol{r}',t)$. Let us consider time-correlation functions formed with a set of dynamical variables $\{A_i(\boldsymbol{r})\}$:

$$C_{ij}(\boldsymbol{r},\boldsymbol{r}',t) \equiv (A_i(\boldsymbol{r},t),A_j(\boldsymbol{r}',0)) \equiv V\langle A_i(\boldsymbol{r},t)A_j(\boldsymbol{r}',0)\rangle. \quad (14)$$

Hereafter, the absence of the argument t implies that associated quantities are evaluated at time $t=0$. For example, we shall denote the initial value of $C_{ij}(\boldsymbol{r},\boldsymbol{r}',t)$ as

$$C_{ij}(\boldsymbol{r},\boldsymbol{r}') = (A_i(\boldsymbol{r}),A_j(\boldsymbol{r}')) = V\langle A_i(\boldsymbol{r})A_j(\boldsymbol{r}')\rangle. \quad (15)$$

Let us introduce the projection operator onto a set of dynamical variables $\{A_i(\boldsymbol{r})\}$ via

$$\mathcal{P}X(\boldsymbol{r}) \equiv \sum_{j,\ell}\int d\boldsymbol{r}'\int d\boldsymbol{r}''\,(X(\boldsymbol{r}),A_j(\boldsymbol{r}'))\,C^{-1}_{j\ell}(\boldsymbol{r}',\boldsymbol{r}'')\,A_\ell(\boldsymbol{r}''). \quad (16)$$

Here, C^{-1}_{ij} denotes an element of the inverse matrix of C_{ij} defined through

$$\sum_\ell \int d\boldsymbol{r}''\, C_{i\ell}(\boldsymbol{r},\boldsymbol{r}'')\,C^{-1}_{\ell j}(\boldsymbol{r}'',\boldsymbol{r}') = \delta_{ij}\,\delta(\boldsymbol{r}-\boldsymbol{r}'). \quad (17)$$

The complementary operator is defined by $\mathcal{Q} \equiv I - \mathcal{P}$, with I being the identity operator. One can easily show that the operators $\mathcal{P}$ and $\mathcal{Q}$ are idempotent and Hermitian.

Once the projection operator satisfying the idempotency and Hermitianity is introduced, it is straightforward to obtain from the Liouville equation

$$\frac{d}{dt}C_{ij}(\boldsymbol{r},\boldsymbol{r}',t) = i\mathcal{L}C_{ij}(\boldsymbol{r},\boldsymbol{r}',t) \quad (18)$$

the following exact Zwanzig-Mori equation of motion [1]:

$$\frac{d}{dt}C_{ij}(\boldsymbol{r},\boldsymbol{r}',t) = \sum_\ell \int d\boldsymbol{r}''\, i\Omega_{i\ell}(\boldsymbol{r},\boldsymbol{r}'')\,C_{\ell j}(\boldsymbol{r}'',\boldsymbol{r}',t) - \sum_\ell \int d\boldsymbol{r}''\int_0^t d\tau\, K_{i\ell}(\boldsymbol{r},\boldsymbol{r}'',t-\tau) \times C_{\ell j}(\boldsymbol{r}'',\boldsymbol{r}',\tau). \quad (19)$$

Here, the frequency matrix is defined by

$$i\Omega_{ij}(\boldsymbol{r},\boldsymbol{r}') = \sum_\ell \int d\boldsymbol{r}''\,(i\mathcal{L}A_i(\boldsymbol{r}),A_\ell(\boldsymbol{r}''))\,C^{-1}_{\ell j}(\boldsymbol{r}'',\boldsymbol{r}'), \quad (20)$$

while the memory-function matrix reads

$$K_{ij}(\boldsymbol{r},\boldsymbol{r}',t) = \sum_\ell \int d\boldsymbol{r}''\,(R_i(\boldsymbol{r},t),R_\ell(\boldsymbol{r}''))\,C^{-1}_{\ell j}(\boldsymbol{r}'',\boldsymbol{r}'), \quad (21)$$

in terms of the fluctuating force given by

$$R_i(\boldsymbol{r},t) = e^{i\mathcal{Q}\mathcal{L}\mathcal{Q}t}R_i(\boldsymbol{r}), \quad (22)$$

with

$$R_i(\boldsymbol{r}) = i\mathcal{L}A_i(\boldsymbol{r}) - \sum_{\ell} \int d\boldsymbol{r}'\, i\Omega_{i\ell}(\boldsymbol{r},\boldsymbol{r}')\, A_\ell(\boldsymbol{r}'). \tag{23}$$

D. Exact equation of motion for the time-dependent pair distribution function

Here we derive the exact equation of motion for $G(\boldsymbol{r},\boldsymbol{r}',t)$ using the result from the previous subsection. To this end, we introduce dynamical variables

$$\rho(\boldsymbol{r},t) = \delta(\boldsymbol{r} - \boldsymbol{r}_{AB}(t)), \tag{24}$$

$$\boldsymbol{j}(\boldsymbol{r},t) = \boldsymbol{v}_{AB}(t)\,\delta(\boldsymbol{r} - \boldsymbol{r}_{AB}(t)), \tag{25}$$

so that $A_0(\boldsymbol{r}) = \rho(\boldsymbol{r})$, $A_1(\boldsymbol{r}) = j_x(\boldsymbol{r})$, $A_2(\boldsymbol{r}) = j_y(\boldsymbol{r})$, and $A_3(\boldsymbol{r}) = j_z(\boldsymbol{r})$. Here, $\boldsymbol{v}_{AB} = \boldsymbol{p}_A/m - \boldsymbol{p}_B/m$ denotes the relative velocity. Notice that the function $G(\boldsymbol{r},\boldsymbol{r}',t)$ in which we are interested is given by the (0,0) component of $C_{ij}(\boldsymbol{r},\boldsymbol{r}',t)$,

$$C_{00}(\boldsymbol{r},\boldsymbol{r}',t) = G(\boldsymbol{r},\boldsymbol{r}',t). \tag{26}$$

For later convenience, let us also introduce the following notation:

$$H_x(\boldsymbol{r},\boldsymbol{r}',t) \equiv C_{10}(\boldsymbol{r},\boldsymbol{r}',t), \quad H_y(\boldsymbol{r},\boldsymbol{r}',t) \equiv C_{20}(\boldsymbol{r},\boldsymbol{r}',t),$$
$$H_z(\boldsymbol{r},\boldsymbol{r}',t) \equiv C_{30}(\boldsymbol{r},\boldsymbol{r}',t). \tag{27}$$

We first evaluate the elements $C_{ij}(\boldsymbol{r},\boldsymbol{r}')$ and $C^{-1}_{ij}(\boldsymbol{r},\boldsymbol{r}')$. For static ensemble averages formed with the variables in Eqs. (24) and (25), we obtain

$$\langle \rho(\boldsymbol{r})\rho(\boldsymbol{r}')\rangle = \frac{1}{V}\delta(\boldsymbol{r} - \boldsymbol{r}')\, g(r'), \tag{28}$$

$$\langle \rho(\boldsymbol{r}) j_\beta(\boldsymbol{r}')\rangle = \langle j_\alpha(\boldsymbol{r})\rho(\boldsymbol{r}')\rangle = 0, \tag{29}$$

$$\langle j_\alpha(\boldsymbol{r}) j_\beta(\boldsymbol{r}')\rangle = \frac{1}{V}\,\delta_{\alpha\beta}\, v^2\, \delta(\boldsymbol{r} - \boldsymbol{r}')\, g(r'). \tag{30}$$

Here, α and β refer to x, y, or z, and $v^2 \equiv k_{\rm B}T/\mu$ is the thermal velocity with the reduced mass $\mu = m/2$. We therefore obtain from the definition (15)

$$\boldsymbol{C}(\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')\, g(r) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & v^2 & 0 & 0 \\ 0 & 0 & v^2 & 0 \\ 0 & 0 & 0 & v^2 \end{pmatrix}, \tag{31}$$

and from Eq. (17), the inverse is given by

$$\boldsymbol{C}^{-1}(\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')\, \frac{1}{g(r)} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/v^2 & 0 & 0 \\ 0 & 0 & 1/v^2 & 0 \\ 0 & 0 & 0 & 1/v^2 \end{pmatrix}. \tag{32}$$

We next calculate static ensemble averages involving time derivatives to obtain the expression for $i\boldsymbol{\Omega}(\boldsymbol{r},\boldsymbol{r}')$. Due to the time-reversal symmetry, the following equations hold:

$$\langle [i\mathcal{L}\rho(\boldsymbol{r})]\rho(\boldsymbol{r}')\rangle = 0, \quad \langle [i\mathcal{L} j_\alpha(\boldsymbol{r})] j_\beta(\boldsymbol{r}')\rangle = 0. \tag{33}$$

For the rest, we use the continuity equation

$$i\mathcal{L}\rho(\boldsymbol{r}) = -\boldsymbol{v}_{AB}\cdot \nabla\delta(\boldsymbol{r} - \boldsymbol{r}_{AB}) = -\nabla\cdot \boldsymbol{j}(\boldsymbol{r}), \tag{34}$$

to obtain

$$\langle [i\mathcal{L}\rho(\boldsymbol{r})] j_\alpha(\boldsymbol{r}')\rangle = -\frac{1}{V}\, v^2\, \nabla_\alpha[\delta(\boldsymbol{r} - \boldsymbol{r}')g(r)], \tag{35}$$

$$\langle [i\mathcal{L} j_\alpha(\boldsymbol{r})]\rho(\boldsymbol{r}')\rangle = -\langle j_\alpha(\boldsymbol{r})[i\mathcal{L}\rho(\boldsymbol{r}')]\rangle = \frac{1}{V}\, v^2\, \nabla'_\alpha[\delta(\boldsymbol{r} - \boldsymbol{r}')g(r)], \tag{36}$$

where we have used the Hermitian property of $\mathcal{L}$, which can easily be derived from the definition (5). Here and in the following, ∇_α and ∇'_α refer to the x, y, or z component of $\boldsymbol{\nabla} \equiv \partial/\partial\boldsymbol{r}$ and $\boldsymbol{\nabla}' \equiv \partial/\partial\boldsymbol{r}'$. Let us notice

$$\frac{1}{g(r')}\nabla_\alpha[\delta(\boldsymbol{r} - \boldsymbol{r}')g(r)] = \nabla_\alpha\delta(\boldsymbol{r} - \boldsymbol{r}'), \tag{37}$$

whereas

$$\begin{aligned} &\frac{1}{g(r')}\nabla'_\alpha[\delta(\boldsymbol{r} - \boldsymbol{r}')g(r)] \\ &= \nabla'_\alpha\delta(\boldsymbol{r} - \boldsymbol{r}') + \delta(\boldsymbol{r} - \boldsymbol{r}')\nabla'_\alpha \log[g(r')] \\ &= -\nabla_\alpha\delta(\boldsymbol{r} - \boldsymbol{r}') - \beta\delta(\boldsymbol{r} - \boldsymbol{r}')\nabla_\alpha w(r), \end{aligned} \tag{38}$$

where we have introduced the potential of mean force [1]

$$w(r) \equiv -k_{\rm B}T \log g(r). \tag{39}$$

Using the results so far, we obtain from Eq. (20)

$$i\boldsymbol{\Omega}(\boldsymbol{r},\boldsymbol{r}') = \begin{pmatrix} 0 & -\nabla_x\delta(\boldsymbol{r} - \boldsymbol{r}') & -\nabla_y\delta(\boldsymbol{r} - \boldsymbol{r}') & -\nabla_z\delta(\boldsymbol{r} - \boldsymbol{r}') \\ -v^2\nabla_x\delta(\boldsymbol{r} - \boldsymbol{r}') - \beta v^2\delta(\boldsymbol{r} - \boldsymbol{r}')\nabla_x w(r) & 0 & 0 & 0 \\ -v^2\nabla_y\delta(\boldsymbol{r} - \boldsymbol{r}') - \beta v^2\delta(\boldsymbol{r} - \boldsymbol{r}')\nabla_y w(r) & 0 & 0 & 0 \\ -v^2\nabla_z\delta(\boldsymbol{r} - \boldsymbol{r}') - \beta v^2\delta(\boldsymbol{r} - \boldsymbol{r}')\nabla_z w(r) & 0 & 0 & 0 \end{pmatrix}. \tag{40}$$

Now we can calculate $\boldsymbol{R}(\boldsymbol{r})$ from Eq. (23). Using the continuity equation (34), we have

$$^{t}\boldsymbol{R}(\boldsymbol{r}) = (0 \quad R_x(\boldsymbol{r}) \quad R_y(\boldsymbol{r}) \quad R_z(r)), \tag{41}$$

where the superscript "t" denotes the transpose, and

$$R_\alpha(\boldsymbol{r}) = i\mathcal{L} j_\alpha(\boldsymbol{r}) + v^2 \nabla_\alpha \rho(\boldsymbol{r}) + \beta v^2 \rho(\boldsymbol{r}) \nabla_\alpha w(r). \tag{42}$$

One therefore obtains from Eqs. (21) and (32)

$$\boldsymbol{K}(\boldsymbol{r},\boldsymbol{r}',t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & K_{xx}(\boldsymbol{r},\boldsymbol{r}',t) & K_{xy}(\boldsymbol{r},\boldsymbol{r}',t) & K_{xz}(\boldsymbol{r},\boldsymbol{r}',t) \\ 0 & K_{yx}(\boldsymbol{r},\boldsymbol{r}',t) & K_{yy}(\boldsymbol{r},\boldsymbol{r}',t) & K_{yz}(\boldsymbol{r},\boldsymbol{r}',t) \\ 0 & K_{zx}(\boldsymbol{r},\boldsymbol{r}',t) & K_{zy}(\boldsymbol{r},\boldsymbol{r}',t) & K_{zz}(\boldsymbol{r},\boldsymbol{r}',t) \end{pmatrix}, \tag{43}$$

with

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t) \equiv \frac{V}{v^2} \langle R_\alpha(\boldsymbol{r},t) R_\beta(\boldsymbol{r}') \rangle / g(r'). \tag{44}$$

The initial value of $K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t)$ is evaluated in the Appendix, and the result under Kirkwood's superposition approximation for a triple-density correlation function [see Eqs. (A36) and (A37)] is given in Eq. (A38).

Summarizing the results so far, we obtain the following set of exact equations of motion involving $G(\boldsymbol{r},\boldsymbol{r}',t)$ and $H_\alpha(\boldsymbol{r},\boldsymbol{r}',t)$:

$$\frac{d}{dt} G(\boldsymbol{r},\boldsymbol{r}',t) = -\nabla \cdot \boldsymbol{H}(\boldsymbol{r},\boldsymbol{r}',t), \tag{45}$$

$$\begin{aligned} \frac{d}{dt} H_\alpha(\boldsymbol{r},\boldsymbol{r}',t) &= -v^2 \nabla_\alpha G(\boldsymbol{r},\boldsymbol{r}',t) - \beta v^2 G(\boldsymbol{r},\boldsymbol{r}',t) \nabla_\alpha w(r) \\ &\quad - \sum_\beta \int d\boldsymbol{r}'' \int_0^t d\tau\, K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}'',t-\tau) H_\beta(\boldsymbol{r}'',\boldsymbol{r}',\tau). \end{aligned} \tag{46}$$

Combining these two equations, one obtains

$$\begin{aligned} \frac{d^2}{dt^2} G(\boldsymbol{r},\boldsymbol{r}',t) &= v^2 \nabla^2 G(\boldsymbol{r},\boldsymbol{r}',t) + \beta v^2 \nabla \cdot \{G(\boldsymbol{r},\boldsymbol{r}',t) \nabla w(r)\} \\ &\quad + \sum_{\alpha,\beta} \int d\boldsymbol{r}'' \int_0^t d\tau\, \nabla_\alpha K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}'',t-\tau) \\ &\quad \times H_\beta(\boldsymbol{r}'',\boldsymbol{r}',\tau). \end{aligned} \tag{47}$$

The equation just derived is still not in a useful form, and further manipulation shall therefore be performed in the following subsection.

E. Further manipulation

The manipulation we will do here is to eliminate H_β in favor of G from the last term in Eq. (47). This is possible by exploiting the isotropy of the system, according to which the current density can be decomposed into the longitudinal and transverse components

$$\boldsymbol{j}(\boldsymbol{r},t) = \boldsymbol{j}_L(\boldsymbol{r},t) + \boldsymbol{j}_T(\boldsymbol{r},t), \tag{48}$$

satisfying

$$\nabla \times \boldsymbol{j}_L(\boldsymbol{r},t) = 0, \tag{49}$$

$$\nabla \cdot \boldsymbol{j}_T(\boldsymbol{r},t) = 0. \tag{50}$$

The longitudinal component $j_{L,\alpha}(\boldsymbol{r},t)$ can be written in terms of a scalar function $\psi(\boldsymbol{r},t)$ as

$$j_{L,\alpha}(\boldsymbol{r},t) = \nabla_\alpha \psi(\boldsymbol{r},t). \tag{51}$$

Since the density fluctuation couples only with the longitudinal current fluctuation in the isotropic system, there holds

$$\begin{aligned} H_\alpha(\boldsymbol{r},\boldsymbol{r}',t) &= (j_\alpha(\boldsymbol{r},t),\rho(\boldsymbol{r}',0)) = (j_{L,\alpha}(\boldsymbol{r},t),\rho(\boldsymbol{r}',0)) \\ &= \nabla_\alpha \Psi(\boldsymbol{r},\boldsymbol{r}',t), \end{aligned} \tag{52}$$

where in the final equality we have introduced the time-correlation function

$$\Psi(\boldsymbol{r},\boldsymbol{r}',t) \equiv (\psi(\boldsymbol{r},t),\rho(\boldsymbol{r}',0)). \tag{53}$$

It then follows from Eq. (45) that

$$\frac{d}{dt} G(\boldsymbol{r},\boldsymbol{r}',t) = -\nabla^2 \Psi(\boldsymbol{r},\boldsymbol{r}',t). \tag{54}$$

Thus, H_α and G are connected via the function Ψ through Eqs. (52) and (54).

To see a more direct connection, it is more convenient to work in the Fourier space. Let us introduce the Fourier transform (FT) of $G(\boldsymbol{r},\boldsymbol{r}',t)$ via

$$F(\boldsymbol{k},\boldsymbol{k}',t) = \int d\boldsymbol{r}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \int d\boldsymbol{r}'\, e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}'} G(\boldsymbol{r},\boldsymbol{r}',t), \tag{55}$$

and its inverse relation by

$$G(\boldsymbol{r},\boldsymbol{r}',t) = \frac{1}{(2\pi)^6} \int d\boldsymbol{k}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \int d\boldsymbol{k}'\, e^{i\boldsymbol{k}'\cdot\boldsymbol{r}'} F(\boldsymbol{k},\boldsymbol{k}',t). \tag{56}$$

The FTs of other functions shall be defined similarly. One then obtains from Eqs. (52) and (54)

$$H_\alpha(\boldsymbol{k},\boldsymbol{k}',t) = -ik_\alpha \Psi(\boldsymbol{k},\boldsymbol{k}',t), \quad \frac{d}{dt} F(\boldsymbol{k},\boldsymbol{k}',t) = k^2\, \Psi(\boldsymbol{k},\boldsymbol{k}',t), \tag{57}$$

and hence

$$H_\alpha(\boldsymbol{k},\boldsymbol{k}',t) = -i \frac{k_\alpha}{k^2} \frac{d}{dt} F(\boldsymbol{k},\boldsymbol{k}',t). \tag{58}$$

Let us use this result to rewrite the last term in Eq. (47). Using the product rule

$$\begin{aligned} &\int d\boldsymbol{r} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \int d\boldsymbol{r}' e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}'} \left[\int d\boldsymbol{r}''\, A(\boldsymbol{r},\boldsymbol{r}'')\, B(\boldsymbol{r}'',\boldsymbol{r}') \right] \\ &= \frac{1}{(2\pi)^3} \int d\boldsymbol{k}''\, A(\boldsymbol{k},\boldsymbol{k}'')\, B(\boldsymbol{k}'',\boldsymbol{k}'), \end{aligned} \tag{59}$$

the FT of the last term in Eq. (47) is found to be given by

$$\begin{aligned} &\text{FT of} \left\{ \sum_{\alpha,\beta} \int d\boldsymbol{r}'' \int_0^t d\tau\, \nabla_\alpha K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}'',t-\tau) H_\beta(\boldsymbol{r}'',\boldsymbol{r}',\tau) \right\} \\ &= -\int d\boldsymbol{k}'' \int_0^t d\tau\, K_L(\boldsymbol{k},\boldsymbol{k}'',t-\tau) \frac{d}{d\tau} F(\boldsymbol{k}'',\boldsymbol{k}',\tau), \end{aligned} \tag{60}$$

where we have introduced

$$K_L(\boldsymbol{k},\boldsymbol{k}',t) \equiv \sum_{\alpha,\beta} \frac{k_\alpha k'_\beta}{(k')^2} K_{\alpha\beta}(\boldsymbol{k},\boldsymbol{k}',t). \tag{61}$$

Equation (47) can then be written as

$$\begin{aligned}\frac{d^2}{dt^2}G(\boldsymbol{r},\boldsymbol{r}',t)\\ &= v^2\nabla^2 G(\boldsymbol{r},\boldsymbol{r}',t) + \beta v^2 \nabla\cdot\{G(\boldsymbol{r},\boldsymbol{r}',t)\nabla w(r)\}\\ &\quad -\int d\boldsymbol{r}''\int_0^t d\tau\, K_L(\boldsymbol{r},\boldsymbol{r}'',t-\tau)\frac{d}{d\tau}G(\boldsymbol{r}'',\boldsymbol{r}',\tau),\end{aligned} \tag{62}$$

with the memory kernel $K_L(\boldsymbol{r},\boldsymbol{r}',t)$, which is an inverse FT of $K_L(\boldsymbol{k},\boldsymbol{k}',t)$.

Finally, we notice that all of the differential operators in Eq. (62) do not involve $\boldsymbol{r}'$, so this equation holds also for the conditional distribution function $g(\boldsymbol{r},\boldsymbol{r}',t)$ introduced in Eq. (11).

III. DISCUSSION

In this section, we discuss implications of the exact Zwanzig-Mori equation (62) in connection with the previous related work and with the corresponding equation for the van Hove self-correlation function. We start from the short-time expansion of $G(\boldsymbol{r},\boldsymbol{r}',t)$,

$$G(\boldsymbol{r},\boldsymbol{r}',t) = G(\boldsymbol{r},\boldsymbol{r}',0) + \frac{t^2}{2}\ddot{G}(\boldsymbol{r},\boldsymbol{r}',0) + O(t^4), \tag{63}$$

in which only even powers of time appear, due to the time-reversal symmetry. The initial value is given in Eq. (9). For the initial second time derivative, one obtains by setting $t=0$ in Eq. (62) and using the definition (39) for the potential of mean force

$$\begin{aligned}\ddot{G}(\boldsymbol{r},\boldsymbol{r}',0) &= v^2\nabla^2 G(\boldsymbol{r},\boldsymbol{r}',0) - v^2\nabla\cdot\{G(\boldsymbol{r},\boldsymbol{r}',0)\nabla\log[g(r)]\}\\ &= v^2\nabla^2\{\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)\} - v^2\nabla\cdot\{\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla g(r)\}.\end{aligned} \tag{64}$$

This expression can be rewritten in a more symmetrical form with respect to $\boldsymbol{r}$ and $\boldsymbol{r}'$ as

$$\ddot{G}(\boldsymbol{r},\boldsymbol{r}',0) = -v^2\nabla\cdot\nabla'[\delta(\boldsymbol{r}-\boldsymbol{r}')\,g(r')], \tag{65}$$

showing that $\ddot{G}(\boldsymbol{r},\boldsymbol{r}',0)$ is negative definite when viewed as a matrix with indices $\boldsymbol{r}$ and $\boldsymbol{r}'$. This result agrees with the one derived in the previous work [1,10]. The short-time expansion for $g(\boldsymbol{r},\boldsymbol{r}',t)$ can be obtained in a similar manner, with the result

$$g(\boldsymbol{r},\boldsymbol{r}',t) = g(\boldsymbol{r},\boldsymbol{r}',0) + \frac{t^2}{2}\ddot{g}(\boldsymbol{r},\boldsymbol{r}',0) + O(t^4), \tag{66}$$

in which $g(\boldsymbol{r},\boldsymbol{r}',0) = \delta(\boldsymbol{r}-\boldsymbol{r}')$ and

$$\ddot{g}(\boldsymbol{r},\boldsymbol{r}',0) = v^2\nabla^2\delta(\boldsymbol{r}-\boldsymbol{r}') + \beta v^2\nabla\cdot[\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla w(r)]. \tag{67}$$

We next consider the long-time diffusive regime. Let us introduce the following Markovian approximation for the memory kernel

$$K_L(\boldsymbol{r},\boldsymbol{r}',t) \approx \frac{v^2}{D_r}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t), \tag{68}$$

in terms of the relative diffusion constant D_r. One then obtains from Eq. (62) for $g(\boldsymbol{r},\boldsymbol{r}',t)$ [see the comment below Eq. (62)]

$$\begin{aligned}\frac{d^2}{dt^2}g(\boldsymbol{r},\boldsymbol{r}',t) &= v^2\nabla^2 g(\boldsymbol{r},\boldsymbol{r}',t) + \beta v^2\nabla\cdot[g(\boldsymbol{r},\boldsymbol{r}',t)\nabla w(r)]\\ &\quad -\frac{v^2}{D_r}\frac{d}{dt}g(\boldsymbol{r},\boldsymbol{r}',t).\end{aligned} \tag{69}$$

By introducing

$$D_r = \frac{k_{\mathrm{B}}T}{\zeta_r} \quad \text{and} \quad \bar{\beta} = \frac{\zeta_r}{\mu}, \tag{70}$$

Eq. (69) can be rewritten as

$$\begin{aligned}\bar{\beta}^{-1}\frac{d^2}{dt^2}g(\boldsymbol{r},\boldsymbol{r}',t) + \frac{d}{dt}g(\boldsymbol{r},\boldsymbol{r}',t)\\ = \frac{k_{\mathrm{B}}T}{\zeta_r}\nabla\cdot[\nabla g(\boldsymbol{r},\boldsymbol{r}',t) + \beta g(\boldsymbol{r},\boldsymbol{r}',t)\nabla w(r)].\end{aligned} \tag{71}$$

This equation is formally identical to the so-called telegraph equation [13]. The telegraph equation is conventionally derived starting from the Fokker-Planck equation [13], but it also follows from the Liouville equation, as we have demonstrated here.

If one further neglects the inertia term in Eq. (69), one obtains the following equation, which takes the form of Smoluchowski's equation

$$\frac{d}{dt}g(\boldsymbol{r},\boldsymbol{r}',t) = D_r\{\nabla^2 g(\boldsymbol{r},\boldsymbol{r}',t) + \beta\nabla\cdot[g(\boldsymbol{r},\boldsymbol{r}',t)\nabla w(r)]\}. \tag{72}$$

This equation is the one proposed by Haan with intuitive arguments, and has been shown to satisfactorily reproduce the simulation result for $g(\boldsymbol{r},\boldsymbol{r}',t)$ [11].

Finally, let us compare the equations for the time-dependent pair distribution function $g(\boldsymbol{r},\boldsymbol{r}',t)$ with the corresponding equations for the more familiar van Hove self-correlation function $G_s(\boldsymbol{r},t)$ [1] to highlight the new feature in the former equations. The van Hove self-correlation function, defined by $G_s(\boldsymbol{r},t) \equiv \langle\delta(\boldsymbol{r}-[\boldsymbol{r}_A(t)-\boldsymbol{r}_A(0)])\rangle$, is associated with the probability that a single tagged particle moves to a position that is separated by $\boldsymbol{r}$ from its initial position during the time t. The initial value and the long-time limit are given by $G_s(\boldsymbol{r},0) = \delta(\boldsymbol{r})$ and $\lim_{t\to\infty} G_s(\boldsymbol{r},t) = 1/V$, which are to be compared with those for $g(\boldsymbol{r},\boldsymbol{r}',t)$ given in Eq. (12). Using the similar projection-operator technique presented in Sec. II, one obtains the following Zwanzig-Mori equation for $G_s(\boldsymbol{r},t)$ [1]:

$$\begin{aligned}\frac{d^2}{dt^2}G_s(\boldsymbol{r},t) &= v_s^2\nabla^2 G_s(\boldsymbol{r},t)\\ &\quad -\int d\boldsymbol{r}''\int_0^t d\tau\, K_{s,L}(\boldsymbol{r}-\boldsymbol{r}'',t-\tau)\frac{d}{d\tau}G_s(\boldsymbol{r}'',\tau),\end{aligned} \tag{73}$$

where $v_s^2 = k_{\mathrm{B}}T/m$ and $K_{s,L}(\boldsymbol{r},t)$ is the corresponding memory kernel, which is to be compared with Eq. (62). From this equation, the short-time expansion is given by

$$G_s(\boldsymbol{r},t) = G_s(\boldsymbol{r},0) + \frac{t^2}{2}\ddot{G}_s(\boldsymbol{r},0) + O(t^4), \tag{74}$$

with $G_s(\boldsymbol{r},0) = \delta(\boldsymbol{r})$ and

$$\ddot{G}_s(\boldsymbol{r},0) = v_s^2 \nabla^2 \delta(\boldsymbol{r}), \tag{75}$$

to be compared with Eq. (67). Under the Markovian approximation $K_{s,L}(\boldsymbol{r},t) = (v_s^2/D_s)\delta(\boldsymbol{r})\delta(t)$, with D_s denoting the diffusion constant, and neglecting the inertia term, one obtains from Eq. (73) the ordinary diffusion equation

$$\frac{d}{dt} G_s(\boldsymbol{r},t) = D_s \nabla^2 G_s(\boldsymbol{r},t), \tag{76}$$

to be compared with Eq. (72). Thus, the essential difference between the equations for $g(\boldsymbol{r},\boldsymbol{r}',t)$ and the corresponding equations for $G_s(\boldsymbol{r},t)$ is in the appearance of the term involving the potential of mean force $w(r) = -k_B T \log g(r)$ in the former, and this holds in both the short-time and long-time regimes. In fact, while $G_s(\boldsymbol{r},t \to \infty) = 1/V$ is a steady-state solution to Eq. (76), the structural effects enter even into the long-time limit $g(\boldsymbol{r},\boldsymbol{r}',t \to \infty) = (1/V)g(r)$ that solves Eq. (72) in the steady-state limit. It is thus expected that, unlike the dynamics of $G_s(\mathbf{r},t)$, whose relaxation from the initial delta function toward the long-time limit $1/V$ is rather structureless, the dynamics of $g(\boldsymbol{r},\boldsymbol{r}',t)$ are strongly affected by the structural effects in the whole time regime. Indeed, molecular-dynamics simulation results for $g(\boldsymbol{r},\boldsymbol{r}',t)$ in Refs. [11,14] have demonstrated that its time evolution is characterized by a relaxation toward certain favored separations associated with the peaks of $g(r)$: Particles initially separated by a distance corresponding to a peak of $g(r)$ tend to retain that separation for a long time, whereas those initially not in a favored position quickly lose their initial separation and attain separations associated with the peaks of $g(r)$. Our exact equation of motion provides a microscopic basis for understanding such structural effects that show up in the dynamics of $g(\boldsymbol{r},\boldsymbol{r}',t)$.

In this paper, we derived an exact Zwanzig-Mori equation of motion for the time-dependent pair distribution function, starting from the Liouville equation and based on the projection-operator formalism. The derived Eq. (62) reproduces the exact short-time behavior that has been derived before and reduces to Smoluchowski's equation, which has been demonstrated to yield satisfactory results in the diffusion regime. For the intermediate time regime, on the other hand, one needs to take into account non-Markovian effects in the memory kernel. The simplest approximation would be the so-called viscoelastic model, in which the time dependence of the memory kernel is assumed to be exponential [1]. This approximation becomes even more tractable when it is combined with the method in [15,16], which estimates the relaxation time in the viscoelastic model solely based on the initial value of the memory kernel. Such an approximation is feasible for $g(\boldsymbol{r},\boldsymbol{r}',t)$, since we have derived the initial value of the memory kernel [see Eq. (A38)]. Another possibility is to develop a mode-coupling theory that does not assume the decay form of the memory kernel [1], which, however, requires further theoretical work. The basic theoretical framework for the time-dependent pair distribution function we presented here will serve as a basis for such developments.

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APPENDIX: INITIAL VALUE OF THE MEMORY KERNEL

In this Appendix, we derive the expression for the initial value of the memory kernel, $K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0)$, which according to Eqs. (42) and (44) is given by

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = \frac{V}{v^2 g(r')} \langle R_\alpha(\boldsymbol{r}) R_\beta(\boldsymbol{r}') \rangle, \tag{A1}$$

with

$$R_\alpha(\boldsymbol{r}) = \dot{j}_\alpha(\boldsymbol{r}) + v^2 \nabla_\alpha \rho(\boldsymbol{r}) + \beta v^2 \rho(\boldsymbol{r}) \nabla_\alpha w(r). \tag{A2}$$

Here and in the following discussion, the dot denotes the time derivative, $\dot{A} = (d/dt)A = i\mathcal{L}A$. From the definition in (25), the time derivative of $j_\alpha(\boldsymbol{r})$ is given by

$$\dot{j}_\alpha(\boldsymbol{r}) = \dot{v}_{AB}^\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_{AB}) - \sum_\gamma v_{AB}^\alpha v_{AB}^\gamma \nabla_\gamma \delta(\boldsymbol{r} - \boldsymbol{r}_{AB}). \tag{A3}$$

Substituting Eq. (A2) into Eq. (A1) yields

$$\begin{aligned} K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = \frac{V}{v^2 g(r')} \{ &\langle \dot{j}_\alpha(\boldsymbol{r}) \dot{j}_\beta(\boldsymbol{r}') \rangle + v^2 \nabla'_\beta \langle \dot{j}_\alpha(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle + \beta v^2 [\nabla'_\beta w(r')] \langle \dot{j}_\alpha(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle + v^2 \nabla_\alpha \langle \rho(\boldsymbol{r}) \dot{j}_\beta(\boldsymbol{r}') \rangle \\ &+ v^4 \nabla_\alpha \nabla'_\beta \langle \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle + \beta v^4 [\nabla'_\beta w(r')] \nabla_\alpha \langle \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle + \beta v^2 [\nabla_\alpha w(r)] \langle \rho(\boldsymbol{r}) \dot{j}_\beta(\boldsymbol{r}') \rangle \\ &+ \beta v^4 [\nabla_\alpha w(r)] \nabla'_\beta \langle \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle + \beta^2 v^4 [\nabla_\alpha w(r)][\nabla'_\beta w(r')] \langle \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle \}. \end{aligned} \tag{A4}$$

Using Eq. (28) for the terms involving $\langle \rho(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle$, one obtains

$$\begin{aligned} K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = &\frac{V}{v^2 g(r')} \{ \langle \dot{j}_\alpha(\boldsymbol{r}) \dot{j}_\beta(\boldsymbol{r}') \rangle + v^2 \nabla'_\beta \langle \dot{j}_\alpha(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle + \beta v^2 [\nabla'_\beta w(r')] \langle \dot{j}_\alpha(\boldsymbol{r}) \rho(\boldsymbol{r}') \rangle \\ &+ v^2 \nabla_\alpha \langle \rho(\boldsymbol{r}) \dot{j}_\beta(\boldsymbol{r}') \rangle + \beta v^2 [\nabla_\alpha w(r)] \langle \rho(\boldsymbol{r}) \dot{j}_\beta(\boldsymbol{r}') \rangle \} \\ &+ \frac{v^2}{g(r')} \{ \nabla_\alpha \nabla'_\beta [\delta(\boldsymbol{r} - \boldsymbol{r}') g(r)] + \beta [\nabla'_\beta w(r')] \nabla_\alpha [\delta(\boldsymbol{r} - \boldsymbol{r}') g(r)] \\ &+ \beta [\nabla_\alpha w(r)] \nabla'_\beta [\delta(\boldsymbol{r} - \boldsymbol{r}') g(r)] + \beta^2 [\nabla_\alpha w(r)][\nabla'_\beta w(r')] \delta(\boldsymbol{r} - \boldsymbol{r}') g(r) \}. \end{aligned} \tag{A5}$$

In the following, we shall calculate the terms involving the averages $\langle \dot{j}_\alpha(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle$, $\langle \dot{j}_\alpha(\boldsymbol{r})\rho(\boldsymbol{r}')\rangle$, and $\langle \rho(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle$.

1. Calculation of the terms involving $\langle \dot{j}_\alpha(\boldsymbol{r})\rho(\boldsymbol{r}')\rangle$ and $\langle \rho(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle$

Using Eq. (A3), one can derive

$$\langle \dot{j}_\alpha(\boldsymbol{r})\rho(\boldsymbol{r}')\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\alpha_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle - \frac{v^2}{V}\nabla_\alpha[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)]. \tag{A6}$$

Similarly, there holds

$$\langle \rho(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\beta_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle - \frac{v^2}{V}\nabla'_\beta[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)]. \tag{A7}$$

Now, we need to calculate $\langle \dot{v}^\alpha_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle$.

From Newton's equation of motion, we have

$$\dot{v}^\alpha_{AB} = -\frac{1}{m}\frac{\partial U}{\partial r^\alpha_A} + \frac{1}{m}\frac{\partial U}{\partial r^\alpha_B}, \tag{A8}$$

where U denotes the potential of the total system given in Eq. (3). We therefore obtain

$$\langle \dot{v}^\alpha_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle = -\frac{1}{m}\left\langle \frac{\partial U}{\partial r^\alpha_A}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle + \frac{1}{m}\left\langle \frac{\partial U}{\partial r^\alpha_B}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle. \tag{A9}$$

Here, we use the following well-known relation [1],

$$\left\langle \frac{\partial U}{\partial r^\alpha_A} f\right\rangle = k_{\mathrm{B}}T\left\langle \frac{\partial f}{\partial r^\alpha_A}\right\rangle, \tag{A10}$$

to obtain

$$\langle \dot{v}^\alpha_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle = \frac{v^2}{V}\nabla_\alpha\, g(r). \tag{A11}$$

Using this result, one gets from Eqs. (A6) and (A7)

$$\langle \dot{j}_\alpha(\boldsymbol{r})\rho(\boldsymbol{r}')\rangle = \frac{v^2}{V}\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\alpha\, g(r) - \frac{v^2}{V}\nabla_\alpha[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)], \tag{A12}$$

$$\langle \rho(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle = \frac{v^2}{V}\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\beta\, g(r) - \frac{v^2}{V}\nabla'_\beta[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)]. \tag{A13}$$

Substituting these results into Eq. (A5) yields

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = \frac{V}{v^2 g(r')}\langle \dot{j}_\alpha(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle + \frac{v^2}{g(r')}\{\nabla'_\beta[\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\alpha\, g(r)] - \beta^2[\nabla_\alpha w(r)][\nabla'_\beta w(r')]\delta(\boldsymbol{r}-\boldsymbol{r}')g(r) + \nabla_\alpha[\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\beta\, g(r)] - \nabla_\alpha\nabla'_\beta[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)]\}. \tag{A14}$$

2. Calculation of the term involving $\langle \dot{j}_\alpha(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle$

We next consider the term involving $\langle \dot{j}_\alpha(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle$. From Eq. (A3), one obtains

$$\langle \dot{j}_\alpha(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\alpha_{AB}\dot{v}^\beta_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle - v^2\nabla'_\beta\big[\delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\alpha_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle\big] - v^2\nabla_\alpha\big[\delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\beta_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle\big] + \sum_{\gamma,\gamma'}\langle v^\alpha_{AB}v^\gamma_{AB}v^\beta_{AB}v^{\gamma'}_{AB}\nabla_\gamma\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\nabla'_{\gamma'}\delta(\boldsymbol{r}'-\boldsymbol{r}_{AB})\rangle. \tag{A15}$$

The last term survives only when (i) $\alpha=\beta=\gamma=\gamma'$, (ii) $\alpha=\beta$ and $\gamma=\gamma'$ or $\alpha\neq\gamma$, (iii) $\gamma=\alpha$ and $\gamma'=\beta$, and (iv) $\gamma=\beta$ and $\gamma'=\alpha$—that is, the following condition holds:

$$\text{last term in Eq. (A15)} = \frac{v^4}{V}\left(\nabla_\alpha\nabla'_\beta + \nabla'_\alpha\nabla_\beta + \delta_{\alpha\beta}\sum_\gamma\nabla_\gamma\nabla'_\gamma\right)[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)], \tag{A16}$$

in deriving which we have used $\langle (v^\alpha_{AB})^4\rangle = 3v^4$ and $\langle (v^\alpha_{AB})^2\rangle = v^2$. Using Eq. (A11) for the second and third terms on the right-hand side of Eq. (A15), we obtain

$$\langle \dot{j}_\alpha(\boldsymbol{r})\dot{j}_\beta(\boldsymbol{r}')\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\alpha_{AB}\dot{v}^\beta_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle - \frac{v^4}{V}\nabla'_\beta[\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\alpha\, g(r)] - \frac{v^4}{V}\nabla_\alpha[\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\beta\, g(r)] + \frac{v^4}{V}\left(\nabla_\alpha\nabla'_\beta + \nabla'_\alpha\nabla_\beta + \delta_{\alpha\beta}\sum_\gamma\nabla_\gamma\nabla'_\gamma\right)[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)]. \tag{A17}$$

Substituting this result into Eq. (A14) gives

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = \frac{V}{v^2 g(r')}\delta(\boldsymbol{r}-\boldsymbol{r}')\langle \dot{v}^\alpha_{AB}\dot{v}^\beta_{AB}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle + \frac{v^2}{g(r')}\left\{\left(\nabla'_\alpha\nabla_\beta + \delta_{\alpha\beta}\sum_\gamma\nabla_\gamma\nabla'_\gamma\right)[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)] - \beta^2[\nabla_\alpha w(r)][\nabla'_\beta w(r')]\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)\right\}. \tag{A18}$$

Now we are left with the average $\langle \dot{v}_{AB}^{\alpha}\dot{v}_{AB}^{\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle$. From Eq. (A8), we have

$$\langle \dot{v}_{AB}^{\alpha}\dot{v}_{AB}^{\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle = \frac{1}{m^2}\left\langle \frac{\partial U}{\partial r_A^\alpha}\frac{\partial U}{\partial r_A^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle - \frac{1}{m^2}\left\langle \frac{\partial U}{\partial r_A^\alpha}\frac{\partial U}{\partial r_B^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle - \frac{1}{m^2}\left\langle \frac{\partial U}{\partial r_B^\alpha}\frac{\partial U}{\partial r_A^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle + \frac{1}{m^2}\left\langle \frac{\partial U}{\partial r_B^\alpha}\frac{\partial U}{\partial r_B^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle. \tag{A19}$$

Let us start from the first term. Using the relation (A10), we obtain the following result:

$$\text{first term in Eq. (A19)} = \frac{k_\mathrm{B}T}{m^2}\left\langle\left(\frac{\partial^2 U}{\partial r_A^\alpha \partial r_A^\beta}\right)\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle + \left(\frac{k_\mathrm{B}T}{m}\right)^2\left\langle\frac{\partial^2}{\partial r_A^\alpha \partial r_A^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle. \tag{A20}$$

The second term in this expression can be written as

$$\left\langle\frac{\partial^2}{\partial r_A^\alpha \partial r_A^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle = \left\langle\frac{\partial^2}{\partial r_{AB}^\alpha \partial r_{AB}^\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle = \frac{1}{V}\nabla_\alpha\nabla_\beta\, g(r). \tag{A21}$$

Using Eq. (3), the second derivative of the total potential reads

$$\frac{\partial^2 U}{\partial r_A^\alpha \partial r_A^\beta} = \frac{\partial^2\phi(r_{AB})}{\partial r_A^\alpha \partial r_A^\beta} + \sum_{i=1}^{N}\frac{\partial^2\phi(r_{Ai})}{\partial r_A^\alpha \partial r_A^\beta} = \frac{\partial^2\phi(r_{AB})}{\partial r_{AB}^\alpha \partial r_{AB}^\beta} + \sum_{i=1}^{N}\frac{\partial^2\phi(r_{Ai})}{\partial r_{Ai}^\alpha \partial r_{Ai}^\beta}, \tag{A22}$$

and hence, the first term in Eq. (A20) is given by

$$\begin{aligned}\left\langle\left(\frac{\partial^2 U}{\partial r_A^\alpha \partial r_A^\beta}\right)\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle &= \left\langle\left(\frac{\partial^2\phi(r_{AB})}{\partial r_{AB}^\alpha \partial r_{AB}^\beta}\right)\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle + \sum_{i=1}^{N}\left\langle\left(\frac{\partial^2\phi(r_{Ai})}{\partial r_{Ai}^\alpha \partial r_{Ai}^\beta}\right)\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\right\rangle \\ &= [\nabla_\alpha\nabla_\beta\,\phi(r)]\langle\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle + \sum_{i=1}^{N}\int d\boldsymbol{r}''\,[\nabla_\alpha''\nabla_\beta''\,\phi(r'')]\langle\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\delta(\boldsymbol{r}''-\boldsymbol{r}_{Ai})\rangle \\ &= \frac{1}{V}[\nabla_\alpha\nabla_\beta\,\phi(r)]g(r) + \frac{\rho}{V}\int d\boldsymbol{r}''\,[\nabla_\alpha''\nabla_\beta''\,\phi(r'')]g_{AB;A}^{(3)}(\boldsymbol{r},\boldsymbol{r}''),\end{aligned} \tag{A23}$$

where we have introduced the triple-density correlation function involving the particles A and B and a solvent particle:

$$\frac{\rho}{V}g_{AB;A}^{(3)}(\boldsymbol{r},\boldsymbol{r}'') \equiv \sum_{i=1}^{N}\langle\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\delta(\boldsymbol{r}''-\boldsymbol{r}_{Ai})\rangle, \tag{A24}$$

with $\rho = N/V$ being the average number density of the solvent. We therefore obtain

$$\text{first term in Eq. (A19)} = \frac{k_\mathrm{B}T}{Vm^2}\left\{[\nabla_\alpha\nabla_\beta\phi(r)]g(r) + \rho\int d\boldsymbol{r}''[\nabla_\alpha''\nabla_\beta''\phi(r'')]g_{AB;A}^{(3)}(\boldsymbol{r},\boldsymbol{r}'')\right\} + \frac{1}{V}\left(\frac{k_\mathrm{B}T}{m}\right)^2\nabla_\alpha\nabla_\beta\, g(r). \tag{A25}$$

The other terms in Eq. (A19) can be handled in a similar manner, with the results

$$\text{second term in Eq. (A19)} = \frac{1}{V}\frac{k_\mathrm{B}T}{m^2}[\nabla_\alpha\nabla_\beta\,\phi(r)]g(r) + \frac{1}{V}\left(\frac{k_\mathrm{B}T}{m}\right)^2\nabla_\alpha\nabla_\beta\, g(r), \tag{A26}$$

$$\text{third term in Eq. (A19)} = \frac{1}{V}\frac{k_\mathrm{B}T}{m^2}[\nabla_\alpha\nabla_\beta\,\phi(r)]g(r) + \frac{1}{V}\left(\frac{k_\mathrm{B}T}{m}\right)^2\nabla_\alpha\nabla_\beta\, g(r), \tag{A27}$$

$$\text{fourth term in Eq. (A19)} = \frac{1}{V}\frac{k_\mathrm{B}T}{m^2}\left\{[\nabla_\alpha\nabla_\beta\,\phi(r)]g(r) + \rho\int d\boldsymbol{r}''\,[\nabla_\alpha''\nabla_\beta''\,\phi(r'')]g_{AB;B}^{(3)}(\boldsymbol{r},\boldsymbol{r}'')\right\} + \frac{1}{V}\left(\frac{k_\mathrm{B}T}{m}\right)^2\nabla_\alpha\nabla_\beta\, g(r). \tag{A28}$$

Summarizing Eqs. (A19), (A25), and (A26)–(A28), we obtain

$$\langle \dot{v}_{AB}^{\alpha}\dot{v}_{AB}^{\beta}\delta(\boldsymbol{r}-\boldsymbol{r}_{AB})\rangle = \frac{\beta v^4}{V}[\nabla_\alpha\nabla_\beta\,\phi(r)]g(r) + \frac{v^4}{V}\nabla_\alpha\nabla_\beta\, g(r) + \frac{\rho k_\mathrm{B}T}{Vm^2}\int d\boldsymbol{r}''\,[\nabla_\alpha''\nabla_\beta''\,\phi(r'')]g_{AB;A}^{(3)}(\boldsymbol{r},\boldsymbol{r}'') + \frac{\rho k_\mathrm{B}T}{Vm^2}\int d\boldsymbol{r}''\,[\nabla_\alpha''\nabla_\beta''\,\phi(r'')]g_{AB;B}^{(3)}(\boldsymbol{r},\boldsymbol{r}''). \tag{A29}$$

Substituting the result (A29) into Eq. (A18) yields

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = \frac{v^2}{g(r')}\left(\nabla'_\alpha\nabla_\beta + \delta_{\alpha\beta}\sum_\gamma \nabla_\gamma\nabla'_\gamma\right)[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)] + \frac{v^2}{g(r')}\delta(\boldsymbol{r}-\boldsymbol{r}')\{\nabla_\alpha\nabla_\beta\, g(r) - \beta^2[\nabla_\alpha w(r)][\nabla'_\beta w(r')]g(r)\}$$
$$+ \frac{1}{g(r')}\delta(\boldsymbol{r}-\boldsymbol{r}')\left\{\beta v^2[\nabla_\alpha\nabla_\beta\,\phi(r)]g(r) + \frac{\rho k_{\mathrm{B}}T}{v^2m^2}\int d\boldsymbol{r}''\,[\nabla''_\alpha\nabla''_\beta\,\phi(r'')]g^{(3)}_{AB;A}(\boldsymbol{r},\boldsymbol{r}'')\right.$$
$$\left. + \frac{\rho k_{\mathrm{B}}T}{v^2m^2}\int d\boldsymbol{r}''\,[\nabla''_\alpha\nabla''_\beta\,\phi(r'')]g^{(3)}_{AB;B}(\boldsymbol{r},\boldsymbol{r}'')\right\}. \tag{A30}$$

Here, we notice that

$$\nabla_\alpha\nabla_\beta\,\log[g(r)] = \nabla_\alpha\left[\frac{\nabla_\beta\, g(r)}{g(r)}\right] = \frac{[\nabla_\alpha\nabla_\beta\, g(r)]\,g(r) - [\nabla_\beta\, g(r)]\,[\nabla_\alpha\, g(r)]}{g(r)^2}$$
$$= \frac{1}{g(r)}\nabla_\alpha\nabla_\beta\, g(r) - \{\nabla_\alpha\,\log[g(r)]\}\,\{\nabla_\alpha\,\log[g(r)]\} = \frac{1}{g(r)}\nabla_\alpha\nabla_\beta\, g(r) - \beta^2[\nabla_\alpha w(r)]\,[\nabla_\beta w(r)], \tag{A31}$$

which leads to

$$\frac{1}{g(r')}\delta(\boldsymbol{r}-\boldsymbol{r}')\nabla_\alpha\nabla_\beta\, g(r) = \delta(\boldsymbol{r}-\boldsymbol{r}')\{-\beta\nabla_\alpha\nabla_\beta w(r) + \beta^2[\nabla_\alpha w(r)]\,[\nabla_\beta w(r)]\}. \tag{A32}$$

Using this result, Eq. (A30) can be rewritten as

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = \frac{v^2}{g(r')}\left(\nabla'_\alpha\nabla_\beta + \delta_{\alpha\beta}\sum_\gamma \nabla_\gamma\nabla'_\gamma\right)[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r)] + \delta(\boldsymbol{r}-\boldsymbol{r}')\,\beta v^2\nabla_\alpha\nabla_\beta\,[\phi(r) - w(r)]$$
$$+ \delta(\boldsymbol{r}-\boldsymbol{r}')\,\frac{\rho k_{\mathrm{B}}T}{v^2m^2}\int d\boldsymbol{r}''\,[\nabla''_\alpha\nabla''_\beta\,\phi(r'')]\big[g^{(3)}_{AB;A}(\boldsymbol{r},\boldsymbol{r}'')/g(r)\big]$$
$$+ \delta(\boldsymbol{r}-\boldsymbol{r}')\,\frac{\rho k_{\mathrm{B}}T}{v^2m^2}\int d\boldsymbol{r}''[\nabla''_\alpha\nabla''_\beta\,\phi(r'')]\,\big[g^{(3)}_{AB;B}(\boldsymbol{r},\boldsymbol{r}'')/g(r)\big]. \tag{A33}$$

3. Further manipulations

Equation (A33) shall further be manipulated to eliminate the radial distribution function appearing in the denominator. For the first two terms in Eq. (A33), we proceed as follows:

$$\frac{1}{g(r')}\nabla'_\alpha\nabla_\beta[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r')] = \frac{1}{g(r')}\nabla'_\alpha[g(r')\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}')] = \frac{1}{g(r')}\{[\nabla'_\alpha\, g(r')][\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}')] + g(r')\nabla'_\alpha\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}')\}$$
$$= -\beta[\nabla'_\alpha w(r')]\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}') + \nabla'_\alpha\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{A34}$$

$$\frac{1}{g(r')}\nabla_\gamma\nabla'_\gamma[\delta(\boldsymbol{r}-\boldsymbol{r}')g(r')] = -\beta[\nabla'_\gamma w(r')]\nabla_\gamma\,\delta(\boldsymbol{r}-\boldsymbol{r}') + \nabla_\gamma\nabla'_\gamma\,\delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{A35}$$

For the triple-density correlations in Eq. (A33), we use Kirkwood's superposition approximation [1]:

$$g^{(3)}_{AB;A}(\boldsymbol{r},\boldsymbol{r}'') \approx g(r)g(r'')g(|\boldsymbol{r}-\boldsymbol{r}''|), \tag{A36}$$

$$g^{(3)}_{AB;B}(\boldsymbol{r},\boldsymbol{r}'') \approx g(r)g(|\boldsymbol{r}+\boldsymbol{r}''|)g(r''). \tag{A37}$$

Thereby, we arrive at the following expression for $K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0)$:

$$K_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',0) = -\beta v^2\big[\nabla'_\alpha w(r')\big][\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}')] + v^2\nabla'_\alpha\nabla_\beta\,\delta(\boldsymbol{r}-\boldsymbol{r}') + \delta_{\alpha\beta}v^2\sum_\gamma\{-\beta[\nabla'_\gamma w(r')][\nabla_\gamma\,\delta(\boldsymbol{r}-\boldsymbol{r}')] + \nabla_\gamma\nabla'_\gamma\,\delta(\boldsymbol{r}-\boldsymbol{r}')\}$$
$$+ \delta(\boldsymbol{r}-\boldsymbol{r}')\,\beta v^2\nabla_\alpha\nabla_\beta\,[\phi(r) - w(r)] + \delta(\boldsymbol{r}-\boldsymbol{r}')\,\frac{\rho v^2}{2k_{\mathrm{B}}T}\int d\boldsymbol{r}''\,[\nabla''_\alpha\nabla''_\beta\,\phi(r'')]g(r'')g(|\boldsymbol{r}-\boldsymbol{r}''|). \tag{A38}$$

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