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バージョン：

Time-Dependent Density Functional Theory Formulated using the Interaction-Site Model

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A theory for studying nonlinear dynamics of molecular liquids is developed. The theory is based on the extension of the time-dependent density functional theory to a rigid interaction-site model. From the theory, one can calculate time changes in interaction-site densities using molecular parameters such as the inertial moment of a molecule. The theory has a differential and integral basic equation with a kernel function, which is not included in the time-dependent density functional theory of simple liquids. The application of the theory to diatomic and three-site molecules allows one to obtain explicit expressions of kernel functions.

KEYWORDS: theoretical method of classical liquid dynamics, molecular liquid, time-dependent density functional theory, rotational invariant expansion, interaction-site density

1. Introduction

In studies of dynamical properties of a solution system, one of the unsolved and important problems is given by the dynamics of a molecular liquid in an inhomogeneous field. A solution system consists of liquid solvents and solutes, which include large molecules, such as proteins. Although various inhomogeneous fields can be considered in the system, particularly important effects of inhomogeneous fields are due to the interaction of solute molecules to solvent molecules. Such a field causes an inhomogeneous distribution of solvent molecules. Although the inhomogeneous distribution affects the dynamics of solvent molecules significantly, the understanding of the effects has not advanced significantly.

Many phenomena show profound effects of inhomogeneous fields due to solutes on the dynamics of molecular liquids. When a solute particle is small[1–5] and solvents are mixtures,[5–15] the solute affects solvation dynamics nonlinearly. The effects of the solute also cause a deviation in solvation dynamics from the Gaussian process. The deviation has been observed by time-resolved fluorescence spectra.[16–19] Some authors have

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recently discussed the dynamics of water around a charged solute molecule.[20–22] In these phenomena, an inhomogeneous distribution of solvent molecules around a solute molecule plays an important role.

Besides the above phenomena, the motions of a solute often affect the dynamics of solvent molecules around the solute. The modification of solvent dynamics due to solutes has been found to be important for the diffusion of large particles such as proteins.[23–25] The modification is caused by the inhomogeneous distribution of solvent molecules.

To study such effects, the time-dependent density functional theory (TDDFT) has been developed,[4–6, 26–36] although studies using the theory have been restricted to simple liquids. The TDDFT can adequately deal with the inhomogeneous distribution of solvent molecules caused by solute molecules. The inhomogeneity can be studied using nonlinear terms in the basic equations of the TDDFT. In fact, the TDDFT has been successful in studying nonlinear effects on the solvation dynamics of simple liquids.[4–6, 26–32] Since the TDDFT, however, is applied only to simple liquids, it is necessary to extend the theory to molecular liquids.

In studying molecular liquids, the formulation of the TDDFT in molecular liquids is efficient, if one can formulate it in the same way as that in simple liquids. Since the TDDFT allows one to solve many problems in simple liquids, one can also expect to solve problems in molecular liquids. In addition, if the basic equations have the same nonlinear terms as that in simple liquids, the TDDFT of molecular liquids has the same merits as that of simple liquids. Using the nonlinear term, for instance, one can study solute effects on molecular liquid dynamics. Thus, the TDDFT formulated for molecular liquids is useful, if the formulation includes only approximations similar to that in simple liquids.

In the present study, molecular liquids are described by the rigid interaction-site model.[37] Many authors have thoroughly studied the equilibrium properties of the rigid interaction-site model.[38] Nonequilibrium properties of the model have been studied using the mode coupling theory.[39–41] The TDDFT of the rigid interaction-site model, however, has not been developed although a deformable model has already been studied.[42, 43]

Other formulation for the study of molecular liquids is given by rotational invariants.[32, 44–47] The rotational invariants are employed to deal with rotational freedoms explicitly. By the rotational invariant, the only linearized TDDFT has been formulated,[32] although no nonlinear version has been studied. This is because the formulation is too complex to be used in calculating molecular liquids.

The purpose of the present study is to formulate the TDDFT using the rigid interaction-site model. For the formulation, the projection operator method[48,49] is employed in the same way as the derivation of the TDDFT about simple liquids.[34] The formulation is applied to diatomic molecules, so that explicit expressions are obtained.

2. General Formulation

2.1 Projection operator methods

To formulate the TDDFT using the rigid interaction-site model, the Kawasaki-Gunton projection operator[34,48,49] is introduced using the interaction-site density. The interaction-site density is defined by

$$\hat{\rho}_a(\mathbf{r}) \equiv \sum_i \delta(\mathbf{r} - \mathbf{r}_i^a), \tag{1}$$

where $\mathbf{r}_i^a$ is the position of site a in molecule i. The site density allows one to define the Kawasaki-Gunton projection operator by[34]

$$P_t \hat{X} \equiv \langle \hat{X} \rangle_{lt} + \sum_a \int d\mathbf{r} \frac{\delta \langle \hat{X} \rangle_{lt}}{\delta \langle \hat{\rho}_a(\mathbf{r}) \rangle_{lt}} \delta_t \rho_a(\mathbf{r}), \tag{2a}$$

where $\hat{X}$ is an arbitrary function of a phase space and $\delta_t \rho_a(\mathbf{r}) = \hat{\rho}_a(\mathbf{r}) - \langle \hat{\rho}_a(\mathbf{r}') \rangle_{lt}$. By the projection operator, phase space functions are projected on a space consisting of constants and $\delta_t \rho_a(\mathbf{r})$, using the scaler product defined by $\langle \cdots \rangle_{lt}$.

The average $\langle \cdots \rangle_{lt}$ included in the projection operator is defined by[50]

$$\langle \hat{X} \rangle_{lt} \equiv \frac{\langle \hat{X} \exp[-\beta \int d\mathbf{r} \sum_a \hat{\rho}_a(\mathbf{r}) \psi_a(\mathbf{r})] \rangle}{\langle \exp[-\beta \int d\mathbf{r} \sum_a \hat{\rho}_a(\mathbf{r}) \psi_a(\mathbf{r})] \rangle}, \tag{2b}$$

where $\langle \cdots \rangle$ denotes the usual average by the equilibrium distribution. In addition, $\beta = 1/k_{\mathrm{B}}T$ where k_{B} is Boltzmann's constant and T is the absolute temperature. One can determine the fictional external field $\psi_a(\mathbf{r})$ using

$$\langle \hat{\rho}(\mathbf{r}) \rangle_{lt} = \rho_a(\mathbf{r}, t), \tag{2c}$$

where $\rho_a(\mathbf{r}, t)$ is the average for $\hat{\rho}_a(\mathbf{r})$ by a nonequilibrium distribution. The nonequilibrium distribution allows $\rho_a(\mathbf{r}, t)$ to depend on time.

By the projection operator, one can derive exact equations of the site density.[34] The equations are given by

$$\frac{\partial \rho_a(\mathbf{r}, t)}{\partial t} = \sum_b \int_0^t dt' \int d\mathbf{r}' M_{ab}(t, t'; \mathbf{r}, \mathbf{r}') \beta \psi_b(\mathbf{r}), \tag{3a}$$

where

$$M_{ab}(t,t';\mathbf{r},\mathbf{r}') \quad = \quad \langle R_a(t',t';\mathbf{r})R_b(t',t;\mathbf{r}')\rangle_{lt'} \tag{3b}$$

$$R_a(t',t;\mathbf{r}) \quad = \quad Q_{t'}U(t',t)iL\,\hat{\rho}_a(\mathbf{r}). \tag{3c}$$

Here, $Q_t = 1 - P_t$, $U(t',t)$ is defined by

$$\frac{\partial}{\partial t}U(t',t) = U(t',t)iLQ_t, \tag{3d}$$

with $U(t,t) = 1$, and iL is the Liouville operator. One can associate $\psi_b(\mathbf{r})$ with the free energy functional of the site density[51,52] by

$$\psi_b(\mathbf{r}) = -\frac{\delta F[\rho_a(\mathbf{r},t)]}{\delta\rho_b(\mathbf{r}',t)}, \tag{4a}$$

where the free energy functional $F[\rho_a(\mathbf{r},t)]$ is defined by

$$F[\rho_a(\mathbf{r})] = F_\psi[\psi_a(\mathbf{r})] - \sum_a \int \rho_a(\mathbf{r})\psi_a(\mathbf{r})d\mathbf{r}, \tag{4b}$$

with

$$F_\psi[\psi_a(\mathbf{r})] = -k_{\mathrm{B}}T\ln\left\langle \exp[-\beta\sum_a\int\rho_a(\mathbf{r})\psi_a(\mathbf{r})d\mathbf{r}]\right\rangle. \tag{4c}$$

The substitution of eq. (4a) into eq. (3a) yields

$$\frac{\partial\rho_a(\mathbf{r},t)}{\partial t} = \sum_b\int_0^t dt'\int d\mathbf{r}' M_{ab}(t,t';\mathbf{r},\mathbf{r}')\left\{-\frac{\delta\beta F[\rho_a(\mathbf{r},t)]}{\delta\rho_b(\mathbf{r}',t)}\right\}. \tag{5}$$

A closed equation of the site density is derived using the Markovian approximation. Here, the nonequilibrium average $\langle\rho_a(\mathbf{r},t)\rangle_{lt}$ and the deviation from the average $\delta_t\rho_a(\mathbf{r})$ are assumed to change with time more slowly than the other variables. Then, the Markovian approximation is given by[53]

$$M_{ab}(t,t';\mathbf{r},\mathbf{r}') \approx \langle R_a(t,t;\mathbf{r})R_b(t,t;\mathbf{r}')\rangle_{lt}\tau\delta(t-t'). \tag{6}$$

The substitution of eq. (6) into eq. (5) yields

$$\frac{\partial\rho_a(\mathbf{r},t)}{\partial t} = \sum_b\frac{\tau}{2}\int d\mathbf{r}' M_{ab}(t,t;\mathbf{r},\mathbf{r}')\left\{-\frac{\delta\beta F[\rho_a(\mathbf{r},t)]}{\delta\rho_b(\mathbf{r}',t)}\right\}, \tag{7a}$$

where

$$M_{ab}(t,t;\mathbf{r},\mathbf{r}') = \left\langle[iL\,\hat{\rho}_a(\mathbf{r})][iL\,\hat{\rho}_b(\mathbf{r}')]\right\rangle. \tag{7b}$$

Rewriting the closed equation of the site density, one can obtain the basic equation of the TDDFT formulated using the rigid interaction-site model. Since $iL\,\hat{\rho}_a(\mathbf{r}) = -\nabla\cdot$

$\hat{\mathbf{J}}_a(\mathbf{r})$ with

$$\hat{\mathbf{J}}_a(\mathbf{r}) = \sum_i \mathbf{v}_i^a \delta(\mathbf{r} - \mathbf{r}_i^a), \tag{8}$$

where $\mathbf{v}_i^a$ is the velocity of site a in molecule i, one obtains

$$\frac{\partial \rho_a(\mathbf{r},t)}{\partial t} = \sum_b \frac{\tau}{2} \int d\mathbf{r}' [\nabla \cdot \mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')] \cdot \nabla' \frac{\delta \beta F[\rho_a(\mathbf{r},t)]}{\delta \rho_b(\mathbf{r}',t)}, \tag{9a}$$

where

$$\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}') = \left\langle \hat{\mathbf{J}}_a(\mathbf{r})\, \hat{\mathbf{J}}_b(\mathbf{r}') \right\rangle_{lt}, \tag{9b}$$

and ∇' denotes the differentiation with respect to $\mathbf{r}'$. In addition, eq. (9b) shows that the $\alpha\beta$-component of the tensor $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ is given by $\left\langle \hat{J}_a^{\alpha}(\mathbf{r})\, \hat{J}_b^{\beta}(\mathbf{r}') \right\rangle_{lt}$, where $\hat{J}_a^{\alpha}(\mathbf{r})$ is the α-component of the vector $\hat{\mathbf{J}}_a(\mathbf{r})$. If eq. (9a) is written in the form

$$\frac{\partial \rho_a(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}_a(\mathbf{r},t), \tag{10a}$$

then

$$\mathbf{J}_a(\mathbf{r},t) = -\sum_b \frac{\tau}{2} \int d\mathbf{r}' [\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')] \nabla' \frac{\delta F[\rho_a(\mathbf{r},t)]}{\delta \rho_b(\mathbf{r}',t)}. \tag{10b}$$

The obtained basic equation of the TDDFT shows differentiation and integration with the kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$. To calculate the equation, one needs an explicit expression of $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$, in particular. The kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ will be expressed by microscopic parameters of molecules for the rest of the section.

2.2 *Dividing of kernel functions* $\boldsymbol{M}_{ab}^{tot}(\mathbf{r},\mathbf{r}')$

The kernel functions $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ included in the obtained equation show no correlation between different molecules. The substitution of eq. (8) into eq. (9b) yields

$$\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}') = \left\langle \sum_{ij} \mathbf{v}_i^a \mathbf{v}_j^b \delta(\mathbf{r} - \mathbf{r}_i^a) \delta(\mathbf{r}' - \mathbf{r}_j^b) \right\rangle_{lt}. \tag{11}$$

Since one can find that velocity distributions for molecules i and j $(\neq i)$ are independent using the classical statistical mechanics, one obtains

$$\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}') = \left\langle \sum_{i} \mathbf{v}_i^a \mathbf{v}_i^b \delta(\mathbf{r} - \mathbf{r}_i^a) \delta(\mathbf{r}' - \mathbf{r}_i^b) \right\rangle_{lt}. \tag{12}$$

In the case of simple liquids, straightforward calculations give $(k_{\mathrm{B}}T/m)\rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ exactly,[34] where $\rho(\mathbf{r})$ is the density field of the simple liquid.

One can divide $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ into translational and rotational parts. The site velocity $\mathbf{v}_i^a$ is divided into two parts by $\mathbf{v}_i^a = \mathbf{v}_i^G + \Delta\mathbf{v}_a$, where $\mathbf{v}_i^G$ is the velocity of the center of mass. The other part $\Delta\mathbf{v}_a$ is given by $\boldsymbol{\omega}_i \times \delta\mathbf{r}_i^a$, where $\boldsymbol{\omega}_i$ is the angular velocity of molecule i and $\delta\mathbf{r}_i^a = \mathbf{r}_i^a - \mathbf{r}_i^G$ with the position of the center of mass $\mathbf{r}_i^G$. The substitution of $\mathbf{v}_i^a = \mathbf{v}_i^G + \Delta\mathbf{v}_a$ into eq. (12) yields

$$\mathbf{M}_{ab}^{\text{tot}}(\mathbf{r},\mathbf{r}') = \mathbf{M}_{ab}^{\text{G}}(\mathbf{r},\mathbf{r}') + \mathbf{M}_{ab}^{\text{R}}(\mathbf{r},\mathbf{r}'), \tag{13a}$$

where

$$\mathbf{M}_{ab}^{\text{G}}(\mathbf{r},\mathbf{r}') = \left\langle \sum_i \mathbf{v}_i^G \mathbf{v}_i^G \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle_{lt} \tag{13b}$$

$$\mathbf{M}_{ab}^{\text{R}}(\mathbf{r},\mathbf{r}') = \left\langle \sum_i \Delta\mathbf{v}_a \Delta\mathbf{v}_b \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle_{lt}, \tag{13c}$$

because $\left\langle \mathbf{v}_i^G \Delta\mathbf{v}_a \right\rangle = 0$. The translational and rotational parts are given by $\mathbf{M}_{ab}^{\text{G}}(\mathbf{r},\mathbf{r}')$ and $\mathbf{M}_{ab}^{\text{R}}(\mathbf{r},\mathbf{r}')$, respectively.

The translational part of the kernel functions is calculated using the statistical independences of the position and velocity. From the average defined by eq. (2b), one can average the position and velocity in eq. (13b) independently as follows:

$$\mathbf{M}_{ab}^{\text{G}}(\mathbf{r},\mathbf{r}') = \sum_i \left\langle \mathbf{v}_i^G \mathbf{v}_i^G \right\rangle \left\langle \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle_{lt}. \tag{14}$$

Since

$$\left\langle \mathbf{v}_i^G \mathbf{v}_i^G \right\rangle = \frac{k_{\text{B}}T}{m}\mathbf{U}, \tag{15}$$

where $\mathbf{U}$ is the unit tensor and m is the mass of the molecule, one can obtain

$$\mathbf{M}_{ab}^{\text{G}}(\mathbf{r},\mathbf{r}') = \frac{k_{\text{B}}T}{m}\mathbf{U} w_{ab}^{lt}(\mathbf{r},\mathbf{r}'), \tag{16a}$$

where

$$w_{ab}^{lt}(\mathbf{r},\mathbf{r}') \equiv \sum_i \left\langle \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle_{lt}. \tag{16b}$$

The rotational part $\mathbf{M}_{ab}^{\text{R}}(\mathbf{r},\mathbf{r}')$ given by eq. (13c) will be calculated in the next subsection.

2.3 Calculation of the rotational part in kernel functions $\boldsymbol{M}_{ab}^{R}(\mathbf{r},\mathbf{r}')$

To calculate the rotational part $\mathbf{M}_{ab}^{\text{R}}(\mathbf{r},\mathbf{r}')$ of kernel functions, an approximation is introduced. The approximation is given by

$$\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}') \approx \frac{\left\langle \sum_i \Delta\mathbf{v}_a \Delta\mathbf{v}_b \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle}{\rho w_{ab}(\mathbf{r}-\mathbf{r}')}, \tag{17a}$$

where

$$\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}') \equiv \frac{\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r},\mathbf{r}')}{w^{lt}_{ab}(\mathbf{r},\mathbf{r}')}. \tag{17b}$$

Here, ρ is the equilibrium density of the molecules and $w_{ab}(\mathbf{r}) \equiv \left\langle \delta(\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\right\rangle$.

By the approximation, one can expand the rotational part of the kernel function in rotational invariants.[37,44] Because of the approximation, $\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')$ depends only on $\Delta\mathbf{r} = \mathbf{r}-\mathbf{r}'$, so that

$$\left\langle \sum_i \Delta\mathbf{v}_a\Delta\mathbf{v}_b\delta(\mathbf{r}-\mathbf{r}^a_i)\delta(\mathbf{r}'-\mathbf{r}^b_i)\right\rangle = \rho\left\langle \Delta\mathbf{v}_a\Delta\mathbf{v}_b\delta(\Delta\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\right\rangle. \tag{18}$$

Then, the expansion is given by

$$\mathbf{A}\cdot\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')\cdot\mathbf{B} = \sum_{J=0}^{2} C_J\Phi^{11J}(\Omega_A,\Omega_B,\Omega_{\Delta r}), \tag{19a}$$

where $\mathbf{A}$ and $\mathbf{B}$ are arbitrary unit vectors.

The rotational invariant $\Phi^{11J}(\Omega_A,\Omega_B,\Omega_{\Delta r})$ is defined by[44]

$$\Phi^{11J}(\Omega_A,\Omega_B,\Omega_{\Delta r}) = f^J\sum_{\mu\nu\lambda}\begin{pmatrix}1 & 1 & J\\ \mu & \nu & \lambda\end{pmatrix} R^1_{\mu 0}(\Omega_A)R^1_{\nu 0}(\Omega_B)R^J_{\lambda 0}(\Omega_{\Delta r}). \tag{19b}$$

Here, f^J is an arbitrary nonzero constant, $\begin{pmatrix}m & n & J\\ \mu & \nu & \lambda\end{pmatrix}$ is the $3j$ symbol,[54] and Ω_A, Ω_B, and $\Omega_{\Delta r}$ denote the polar angles describing the orientation of the vectors $\mathbf{A}$, $\mathbf{B}$, and $\Delta\mathbf{r}$, respectively. In addition, $R^m_{\mu\mu'}(\Omega)$ is a generalized spherical harmonic defined by Messiah.[54] In the present case, $R^m_{\mu 0}(\Omega)$ is proportional to a simple spherical harmonic.

The coefficients of the expansion are given by three integrals with respect to polar angles. When $a = b$, C_0 alone is nonzero because $\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')$ does not depend on $\Omega_{\Delta r}$. The coefficients C_J for $a \neq b$ are given by

$$C_J = \frac{1}{I^J}\int\!\!\int\!\!\int d\Omega_A d\Omega_B d\Omega_{\Delta r}\frac{\left\langle(\mathbf{A}\cdot\Delta\mathbf{v}_a)(\mathbf{B}\cdot\Delta\mathbf{v}_b)\delta(\Delta\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\right\rangle}{w_{ab}(\mathbf{r}-\mathbf{r}')}\Phi^{11J*}(\Omega_A,\Omega_B,\Omega_{\Delta r}), \tag{20a}$$

where $\Phi^{11J*}(\Omega_A,\Omega_B,\Omega_{\Delta r})$ is the complex conjugate of $\Phi^{11J}(\Omega_A,\Omega_B,\Omega_{\Delta r})$, and

$$I^J = \frac{(4\pi)^3(f^J)^2}{9(2J+1)}. \tag{20b}$$

Within the present approximation, $\mathbf{X}_{ab}(-\mathbf{r},-\mathbf{r}') = \mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')$, so that $C_1 = 0$.

The two of three integrals can be calculated by the generalized spherical harmonics.

Since

$$(\mathbf{A}\cdot\Delta\mathbf{v}_a)=\Delta v_a\sum_{\mu'}(-1)^{\mu'}R^1_{\mu'0}(\Omega_A)R^1_{-\mu'0}(\Omega_{\Delta v_a}), \tag{21}$$

with $\Delta v_a=|\Delta\mathbf{v}_a|$, if $R^{1*}_{\mu0}(\Omega_A)$ is the complex conjugate of $R^1_{\mu0}(\Omega_A)$, one has[54]

$$\int d\Omega_A(\mathbf{A}\cdot\Delta\mathbf{v}_a)R^{1*}_{\mu0}(\Omega_A)=\frac{4\pi}{3}\Delta v_a(-1)^{\mu}R^1_{-\mu0}(\Omega_{\Delta v_a}). \tag{22}$$

The integration with respect to Ω_B in the same way yields

$$\begin{aligned}C_J=\frac{(4\pi)^2}{9I^J}\int d\Omega_{\Delta r}\frac{1}{w_{ab}(\mathbf{r}-\mathbf{r}')}\Big\langle\Delta v_a\Delta v_b\delta(\Delta\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\\ \times f^J\sum_{\mu\nu\lambda}(-1)^{\mu+\nu}\begin{pmatrix}1&1&J\\ \mu&\nu&\lambda\end{pmatrix}R^1_{-\mu0}(\Omega_{\Delta v_a})R^1_{-\nu0}(\Omega_{\Delta v_b})R^{J*}_{\lambda0}(\Omega_{\Delta r})\Big\rangle.\end{aligned} \tag{23}$$

From $R^{J*}_{\lambda0}(\Omega_{\Delta r})=(-1)^{\lambda}R^J_{-\lambda0}(\Omega_{\Delta r})$,

$$\begin{pmatrix}1&1&J\\ -\mu&-\nu&-\lambda\end{pmatrix}=(-1)^{1+1+J}\begin{pmatrix}1&1&J\\ \mu&\nu&\lambda\end{pmatrix}, \tag{24}$$

and $\mu+\nu+\lambda=0$,[54] one has

$$C_J=\frac{(4\pi)^2}{9I^J}(-1)^J\int d\Omega_{\Delta r}\frac{\big\langle\Delta v_a\Delta v_b\delta(\Delta\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\Phi^{11J}(\Omega_{\Delta v_a},\Omega_{\Delta v_b},\Omega_u)\big\rangle}{w_{ab}(\mathbf{r}-\mathbf{r}')}, \tag{25}$$

where Ω_u denotes the polar angle of the unit vector $\mathbf{u}$ of $\mathbf{r}^a_i-\mathbf{r}^b_i$.

The other integral in eqs (20) is calculated by the division of the average. The rotational invariant $\Phi^{11J}(\Omega_{\Delta v_a},\Omega_{\Delta v_b},\Omega_u)$ is independent of the coordinate system. Thus, if choosing the body-fixed molecular frame, one has

$$\begin{aligned}&\big\langle\Delta v_a\Delta v_b\delta(\Delta\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\Phi^{11J}(\Omega_{\Delta v_a},\Omega_{\Delta v_b},\Omega_u)\big\rangle\\ &\qquad=\big\langle\Delta v_a\Delta v_b\Phi^{11J}(\Omega_{\Delta v_a},\Omega_{\Delta v_b},\Omega_u)\big\rangle\big\langle\delta(\Delta\mathbf{r}-\mathbf{r}^a_i+\mathbf{r}^b_i)\big\rangle.\end{aligned} \tag{26}$$

The substitution of eq. (26) into eq. (25) yields

$$C_J=\frac{(4\pi)^3}{9I^J}(-1)^J\big\langle\Delta v_a\Delta v_b\Phi^{11J}(\Omega_{\Delta v_a},\Omega_{\Delta v_b},\Omega_u)\big\rangle. \tag{27}$$

From eq. (20b), one can obtain

$$C_J=\frac{2J+1}{(f^J)^2}(-1)^J\big\langle\Delta v_a\Delta v_b\Phi^{11J}(\Omega_{\Delta v_a},\Omega_{\Delta v_b},\Omega_u)\big\rangle. \tag{28}$$

2.4 Approximation to $w^{lt}_{ab}(\mathbf{r},\mathbf{r}')$

Equations (16a) and (17b) include $w^{lt}_{ab}(\mathbf{r},\mathbf{r}')$, which one cannot exactly calculate, so that, in the present study, a form of $w^{lt}_{ab}(\mathbf{r},\mathbf{r}')$ is assumed. The assumption is given by

$$w^{lt}_{ab}(\mathbf{r},\mathbf{r}') = f(\rho_a(\mathbf{r}))f(\rho_b(\mathbf{r}'))w_{ab}(\mathbf{r}-\mathbf{r}'), \tag{29}$$

where an unknown function $f(x)$ is later determined. Using eq. (29), one can prove the H-theorem given by $\nabla'\delta F[\rho_a(\mathbf{r},t)]/\delta\rho_a(\mathbf{r}',t) \to 0$ at $t \to \infty$.[36] The theorem is needed for the system to reach the equilibrium state as time advances. The proof of the H-theorem is given by the Appendix.

One can determine the unknown function $f(x)$ included in the assumed form of $w^{lt}_{ab}(\mathbf{r},\mathbf{r}')$ by considering some limiting cases. Equation (16b) reduces to $w^{lt}_{ab}(\mathbf{r},\mathbf{r}') = \rho_a(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ in the first limiting case given by $\mathbf{r}^a_i = \mathbf{r}^b_i$. Considering the limiting case, one finds that the TDDFT of molecular liquids agrees with that of simple liquids when all bond lengths between sites are zero. In contrast to the first case, if all bonds are broken, the TDDFT should agree with that of multicomponent mixtures in simple liquids (the second limiting case). In the third limiting case, omitting the nonlinear terms of density fields, one obtains the linear Langevin equations developed by Chong and Hirata.[55]

In the limiting cases, the present form of $w^{lt}_{ab}(\mathbf{r},\mathbf{r}')$ gives exact values if $f(x) = \sqrt{x}$. One can easily show that $f(x) = \sqrt{x}$ gives exact limiting values in the first limiting case for $\mathbf{r}^a_i = \mathbf{r}^b_i$ because $w_{ab}(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$. In Appendix, the proofs in the other cases are given.

From $f(x) = \sqrt{x}$, one can obtain the final expression of $\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r},\mathbf{r}')$. The substitution of $f(x) = \sqrt{x}$ into eq. (29) yields

$$w^{lt}_{ab}(\mathbf{r},\mathbf{r}') = \sqrt{\rho_a(\mathbf{r})}\sqrt{\rho_b(\mathbf{r}')}w_{ab}(\mathbf{r}-\mathbf{r}'). \tag{30}$$

If f^J is appropriately chosen, from eqs. (17b) and (19a), one obtains

$$\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r},\mathbf{r}') = C_0\sqrt{\rho_a(\mathbf{r})}\sqrt{\rho_b(\mathbf{r}')}w_{ab}(\mathbf{r}-\mathbf{r}')\mathbf{U} + C_2(1-\delta_{ab})\sqrt{\rho_a(\mathbf{r})}\sqrt{\rho_b(\mathbf{r}')}w_{ab}(\mathbf{r}-\mathbf{r}')\mathbf{D}(\mathbf{r}-\mathbf{r}'), \tag{31}$$

where $\mathbf{D}(\mathbf{r}) = 3\mathbf{r}\mathbf{r} - \mathbf{U}$. Substituting eq. (28) into eq. (31), one can obtain

$$\begin{aligned}\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r},\mathbf{r}') = {} & \frac{1}{3}\left\langle(\Delta\mathbf{v}_a\cdot\Delta\mathbf{v}_b)\right\rangle\sqrt{\rho_a(\mathbf{r})}\sqrt{\rho_b(\mathbf{r}')}w_{ab}(\mathbf{r}-\mathbf{r}')\mathbf{U} \\ & + \frac{1}{6}(1-\delta_{ab})\left\langle(\Delta\mathbf{v}_a\cdot\mathbf{D}(\mathbf{u})\cdot\Delta\mathbf{v}_b)\right\rangle\sqrt{\rho_a(\mathbf{r})}\sqrt{\rho_b(\mathbf{r}')}w_{ab}(\mathbf{r}-\mathbf{r}')\mathbf{D}(\mathbf{r}-\mathbf{r}'). \end{aligned} \tag{32}$$

3. Application to Some Molecules

3.1 Diatomic molecules

By calculating two coefficients for $J = 0$ and 2, one can apply the general formulation derived in the previous section to diatomic molecules.[56] From eq. (28), the rotational part of the kernel function $\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r}, \mathbf{r}')$ is expressed by molecular parameters, such as I and z_a. Here, I and z_a are the inertial moment of the diatomic molecule and the z coordinate of site a. In the present section, the coordinate system is given by the body-fixed molecular frame, where the origin is taken to be the center of mass. In addition, the z-axis is along the principal axis of the molecule.

The calculation of the coefficient for $J = 0$ by eq. (28) requires the average for $\Phi^{110}(\Omega_{\Delta v_a}, \Omega_{\Delta v_b}, \Omega_u) = (\Delta\mathbf{v}_a \cdot \Delta\mathbf{v}_b)$. One has

$$\left\langle \omega_i^\alpha \omega_i^\beta \right\rangle = \delta_{\alpha\beta} \frac{k_{\mathrm{B}}T}{I}, \tag{33}$$

where ω_i^α is the α-component of $\boldsymbol{\omega}_i$. In addition, in the case of the diatomic molecule, $\delta\mathbf{r}_i^a$ and $\delta\mathbf{r}_i^b$ have the same direction. Using these, one can easily calculate the average using

$$\left\langle \Delta v_a \Delta v_b \Phi^{110}(\Omega_{\Delta v_a}, \Omega_{\Delta v_b}, \Omega_u) \right\rangle = \langle (\Delta\mathbf{v}_a \cdot \Delta\mathbf{v}_b) \rangle = 2 z_a z_b \frac{k_{\mathrm{B}}T}{I}. \tag{34}$$

The coefficient for $J = 2$ is also given by $(\Delta\mathbf{v}_a \cdot \Delta\mathbf{v}_b)$. The right-hand side of eq. (28) for $J = 2$ is calculated using

$$\left\langle \Delta v_a \Delta v_b \Phi^{112}(\Omega_{\Delta v_a}, \Omega_{\Delta v_b}, \Omega_u) \right\rangle = \langle (\Delta\mathbf{v}_a \cdot \mathbf{D}(\mathbf{u}) \cdot \Delta\mathbf{v}_b) \rangle \tag{35a}$$

$$= \langle 3(\Delta\mathbf{v}_a \cdot \mathbf{u})(\Delta\mathbf{v}_b \cdot \mathbf{u}) - (\Delta\mathbf{v}_a \cdot \Delta\mathbf{v}_b) \rangle . \tag{35b}$$

Since $\mathbf{u}$ is parallel to $\delta\mathbf{r}_i^a$ and $\delta\mathbf{r}_i^b$ in the case of the diatomic molecule, $\mathbf{u}$ is normal to $\Delta\mathbf{v}_a$ and $\Delta\mathbf{v}_b$, so that $(\Delta\mathbf{v}_a \cdot \mathbf{u}) = (\Delta\mathbf{v}_b \cdot \mathbf{u}) = 0$. From eq. (34), one obtains

$$\langle 3(\Delta\mathbf{v}_a \cdot \mathbf{u})(\Delta\mathbf{v}_b \cdot \mathbf{u}) - (\Delta\mathbf{v}_a \cdot \Delta\mathbf{v}_b) \rangle = -2 z_a z_b \frac{k_{\mathrm{B}}T}{I}. \tag{36}$$

Finally, substituting eqs. (34) and (36) into eq. (32), one can obtain

$$\begin{aligned} \mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r}, \mathbf{r}') = {} & \frac{2}{3} z_a z_b \frac{k_{\mathrm{B}}T}{I} \sqrt{\rho_a(\mathbf{r})} \sqrt{\rho_b(\mathbf{r}')} w_{ab}(\mathbf{r} - \mathbf{r}') \mathbf{U} \\ & - \frac{1}{3}(1 - \delta_{ab}) z_a z_b \frac{k_{\mathrm{B}}T}{I} \sqrt{\rho_a(\mathbf{r})} \sqrt{\rho_b(\mathbf{r}')} w_{ab}(\mathbf{r} - \mathbf{r}') \mathbf{D}(\mathbf{r} - \mathbf{r}'). \end{aligned} \tag{37}$$

3.2 Three-site molecules

Since the rotational invariants are employed in the present formulation, one can easily apply it to complex molecules such as water. Using the rotational invariants, one can freely choose the coordinate system, so that the inertial tensor can be diagonalized. In the present subsection, it is applied to three-site molecules where sites 2 and 3 have the same mass as well as the same distance from site 1. To diagonalize the inertial tensor, the z- and x-axes are chosen along the direction from the center of mass to site 1 and the direction from site 2 to site 3. Because of the diagonal inertial tensors, I_x, I_y and I_z, one can obtain simple expressions of $\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r},\mathbf{r}')$ from eq. (28) or (32).

The average of $(\Delta\mathbf{v}_a\cdot\Delta\mathbf{v}_b)$ in eq. (32) is easy to calculate because the coordinate system is appropriately chosen by the rotational invariants. Since the present coordinate system gives the diagonalized inertial tensor, eq. (33) is also valid in the same way as the diatomic molecules. Thus, one obtains

$$\langle(\Delta\mathbf{v}_a\cdot\Delta\mathbf{v}_b)\rangle=\sum_{\alpha\neq\beta}\frac{k_{\mathrm{B}}T}{I_\alpha}\delta r^{\beta}_{a}\delta r^{\beta}_{b},\tag{38}$$

where δr^{β}_{a} is the β-component of $\delta\mathbf{r}^{a}_{i}$. By the present coordinate system, since $\delta r^{y}_{a}=0$, $\delta r^{x}_{1}=0$, $\delta r^{x}_{2}=-\delta r^{x}_{3}$, and $\delta r^{z}_{2}=\delta r^{z}_{3}$, one can obtain

$$\left\langle\Delta\mathbf{v}_1^2\right\rangle=\left(\frac{k_{\mathrm{B}}T}{I_x}+\frac{k_{\mathrm{B}}T}{I_y}\right)(\delta r^{z}_{1})^2,\tag{39a}$$

$$\left\langle\Delta\mathbf{v}_2^2\right\rangle=\left\langle\Delta\mathbf{v}_3^2\right\rangle=k_{\mathrm{B}}T\left\{\left(\frac{1}{I_y}+\frac{1}{I_z}\right)(\delta r^{x}_{2})^2+\left(\frac{1}{I_x}+\frac{1}{I_y}\right)(\delta r^{z}_{2})^2\right\},\tag{39b}$$

$$\langle(\Delta\mathbf{v}_1\cdot\Delta\mathbf{v}_2)\rangle=\langle(\Delta\mathbf{v}_1\cdot\Delta\mathbf{v}_3)\rangle=\left(\frac{k_{\mathrm{B}}T}{I_x}+\frac{k_{\mathrm{B}}T}{I_y}\right)\delta r^{z}_{1}\delta r^{z}_{2},\tag{39c}$$

$$\langle(\Delta\mathbf{v}_2\cdot\Delta\mathbf{v}_3)\rangle=k_{\mathrm{B}}T\left\{\left(\frac{1}{I_y}+\frac{1}{I_z}\right)\delta r^{x}_{2}\delta r^{x}_{3}+\left(\frac{1}{I_x}+\frac{1}{I_y}\right)(\delta r^{z}_{2})^2\right\}.\tag{39d}$$

For the same reason as that for the average of $(\Delta\mathbf{v}_a\cdot\Delta\mathbf{v}_b)$, the calculation of $\langle(\Delta\mathbf{v}_a\cdot\mathbf{u})(\Delta\mathbf{v}_b\cdot\mathbf{u})\rangle$ in eq. (32) is also straightforward. Using eq. (33), one can generally show that

$$\langle(\Delta\mathbf{v}_a\cdot\mathbf{u})(\Delta\mathbf{v}_b\cdot\mathbf{u})\rangle=\sum_{\alpha}(\delta\mathbf{r}^{a}_{i}\times\mathbf{u})_\alpha\frac{k_{\mathrm{B}}T}{I_\alpha}(\delta\mathbf{r}^{b}_{i}\times\mathbf{u})_\alpha,\tag{40}$$

where $(\delta\mathbf{r}^{a}_{i}\times\mathbf{u})_\alpha$ is the α-component of $\delta\mathbf{r}^{a}_{i}\times\mathbf{u}$. In the case of the present three-site molecules, one obtains

$$\langle(\Delta\mathbf{v}_1\cdot\mathbf{u})(\Delta\mathbf{v}_2\cdot\mathbf{u})\rangle=\langle(\Delta\mathbf{v}_1\cdot\mathbf{u})(\Delta\mathbf{v}_3\cdot\mathbf{u})\rangle=-\frac{k_{\mathrm{B}}T}{I_y}\delta r^{z}_{1}u_x^2,\tag{41a}$$

$$\langle(\Delta\mathbf{v}_2\cdot\mathbf{u})(\Delta\mathbf{v}_3\cdot\mathbf{u})\rangle=0.\tag{41b}$$

Substituting eqs. (39) and (41) into eq. (32) and calculating $\Delta\mathbf{v}_a\cdot\mathbf{D}(\mathbf{u})\cdot\Delta\mathbf{v}_b$ using eq. (35b), one can obtain explicit expressions of $\mathbf{M}^{\mathrm{R}}_{ab}(\mathbf{r},\mathbf{r}')$.

4. Discussion

The present results have shown that the kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ is needed for the TDDFT formulated by the interaction site model.[56] Such kernel functions are not included in the TDDFT of simple liquids. Since the kernel function cannot exactly be calculated, one needs approximations.

Because of the kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$, the molecular TDDFT has different characteristic properties from simple liquids. Equation (10b) shows that different positions, components, and sites are coupled between the two vectors $\mathbf{J}_a(\mathbf{r})$ and $\nabla'\delta F[\rho_a(\mathbf{r},t)]/\delta\rho_a(\mathbf{r}',t)$. Different positions and sites are coupled because $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ has a value even for $a \neq b$ and $\mathbf{r} \neq \mathbf{r}'$. Different components are coupled by off-diagonal elements of the tensor. In contrast, the TDDFT of simple liquids does not have such coupling, though the current density $\mathbf{J}_a(\mathbf{r})$ can be expressed by the functional derivative of the free energy.

Although $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ does not include the correlation between different molecules, the correlation is included in the free energy functional. The exclusion of the correlation from $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ can exactly be derived from the classical statistical mechanics. Since the correlation, however, is considered using the free energy functional, the present theory can deal with dense molecular liquids where the effects of the correlation are significant. The point is the same as the formulation of the TDDFT for simple liquids. In contrast to the formulation for simple liquids, $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ includes the correlation between sites in the same molecule.

Since $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ cannot exactly be calculated, the two approximations have been introduced. The approximations are given by eqs. (17a) and (29). Equation (17a) is an approximation to the rotational part $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$ of $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$. Equation (29) makes an assumption about $w_{ab}^{lt}(\mathbf{r},\mathbf{r}')$ included in $\mathbf{M}_{ab}^{\mathrm{G}}(\mathbf{r},\mathbf{r}')$ as well as in $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$.

The first approximation is about $\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')$ defined by eq. (17b), where $\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')$ is a conditional average. Equation (17b) shows that $\mathbf{X}_{ab}(\mathbf{r},\mathbf{r}')$ is the average for $\Delta\mathbf{v}_a\Delta\mathbf{v}_b$ under the condition that the positions of the two sites $\mathbf{r}_i^a$ and $\mathbf{r}_i^b$ are fixed to $\mathbf{r}$ and $\mathbf{r}'$, respectively. Thus, one has to only average it over a rotation around $\mathbf{r}_i^a - \mathbf{r}_i^b$ and velocity. The first approximation is given by omitting $\psi_a(\mathbf{r})$ from the average.

Even if $\psi_a(\mathbf{r})$ is omitted by the first approximation, exact values are obtained in the case of linear molecules such as a diatomic molecule. The omission of $\psi_a(\mathbf{r})$ affects the rotational average alone because $\psi_a(\mathbf{r})$ does not affect velocity. Thus, the omission of

$\psi_a(\mathbf{r})$ does not have any effects on linear molecules because of the symmetry about the rotation. The omission in the other cases does not lead to large errors, if the shape of a liquid molecule deviates slightly from a linear molecule.

In addition, even if a molecule is not linear, one has the case in which the first approximation given by eq. (17a) does not lead to large errors. The case is given when the center of mass is almost located in site a, as can be seen in water. If $\mathbf{r}_i^a \approx \mathbf{r}_i^G$, then $\delta\mathbf{r}_i^a = \mathbf{r}_i^a - \mathbf{r}_i^G$ and $\Delta\mathbf{v}_a = \boldsymbol{\omega}_i \times \delta\mathbf{r}_i^a$ have small values. Thus, from eq. (13c), one can find that $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$ is small, so that $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}') << \mathbf{M}_{ab}^{\mathrm{G}}(\mathbf{r},\mathbf{r}')$. In such a case, the approximation to $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$ does not contribute to the calculation of $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$.

Since the second approximation using eq. (29) gives the exact values in limiting cases (Appendix), one can expect a small deviation from exact values in similar cases to the limits. When the distance between sites is small, or when $\rho_a(\mathbf{r})$ deviates slightly from ρ, the values calculated using eq. (29) approximate exact values. One, however, can consider other forms giving the exact values in limiting cases. Equation (29) is one of the simplest forms giving the exact values.

When an explicit expression of $w_{ab}^{lt}(\mathbf{r},\mathbf{r}')$ is considered, satisfying the H-theorem is more important than including some effects omitted in eq. (29). In eq. (29), the effects of the correlation between different molecule and the effects of $\rho_a(\mathbf{r}'')$ at other positions $\mathbf{r}'' \neq \mathbf{r}$ and $\mathbf{r}'' \neq \mathbf{r}'$, are omitted. In the expression of $w_{ab}^{lt}(\mathbf{r},\mathbf{r}')$, if the effect of $\rho_a(\mathbf{r}'')$ is considered, one should include functionals of $\rho_a(\mathbf{r}'')$. Since such effects lead to a complex expression of $w_{ab}^{lt}(\mathbf{r},\mathbf{r}')$, one can consider that eq. (29) is appropriate as the first step in approximations of $w_{ab}^{lt}(\mathbf{r},\mathbf{r}')$. Satisfying the H-theorem in eq. (29), in particular, is important because one cannot calculate the relaxation of molecular liquids to equilibrium states if it is not satisfied.

Here, besides the kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$, one should discuss how the present results are limited by the Markovian approximation given by eq. (6). The Markovian approximation requires that the nonequilibrium average of the site density should change more slowly than other variables. One can consider a velocity field as the candidate for variables slower than the average site density. The relaxation times of the velocity field in common molecular liquids are 1 to 2 ps. Thus, the present results are valid in time regions longer than the time; one cannot study the inertial effects on solvation dynamics, for instance.

In addition, approximations to the free energy functional $F[\rho_a(\mathbf{r})]$ should be discussed: one has some cases in which the present results are not limited by the approximations. The present results require an explicit form of $F[\rho_a(\mathbf{r})]$ in eq. (9a), which cannot exactly be calculated. To calculate the explicit form of $F[\rho_a(\mathbf{r})]$, one can employ approximations by the reference interaction site model (RISM) theory, which has some limitations. One, however, has many cases to which one can apply the present formulation without limitations: one of the cases is given by small solvent molecules around a large simple solute. In addition, in the present framework, the solute-solvent interaction is regarded as an external field; one can easily employ the three-dimensional RISM theory.

Finally, it is noted that the derived expression given by eq. (9a) includes the nonlinearity of the site density through $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r}, \mathbf{r}')$ in the same way as that in simple liquids. Equation (9a) shows such a nonlinearity because of $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r}, \mathbf{r}')$, even if the nonlinearity is not included in the functional derivative of the free energy. This is because $w_{ab}^{lt}(\mathbf{r}, \mathbf{r}')$ has the term $\sqrt{\rho_a(\mathbf{r})}$ in eq. (30), though $\mathbf{X}_{ab}(\mathbf{r}, \mathbf{r}')$ does not include $\rho_a(\mathbf{r})$ in eq. (17a). The basic equations in the TDDFT of simple liquids have the same nonlinearity, which is the characteristic property of the TDDFT.

Considering the validity of these approximations with the nonlinearity, one can conclude that the TDDFT has been extended to the interaction-site model. Basic equations of the extended TDDFT given by eq. (9a) can be calculated using molecular parameters and the free energy functional. Thus, one can apply the extended TDDFT to various nonlinear phenomena in molecular liquids, such as solvation dynamics and the transport of large particles. The application is the subject of future work.

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Appendix A: Proof of the *H*-Theorem

In Appendix, the H-theorem[36] is proved within the approximations eqs (17a) and (29). In the present case, the H-theorem is given by $\nabla' \delta F[\rho_a(\mathbf{r}, t)]/\delta \rho_a(\mathbf{r}', t) \to 0$ at $t \to \infty$. The theorem shows that the system reaches the equilibrium state for an infinite time.

The H-theorem can be proved when $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r}, \mathbf{r}')$ in eq. (9a) is positive definite. If the free energy functional defined by eqs (4) is differentiated with respect to t, then

$$\frac{dF[\rho_a(\mathbf{r},t)]}{dt} = \sum_a \int d\mathbf{r} \frac{\delta F[\rho_a(\mathbf{r},t)]}{\delta \rho_a(\mathbf{r},t)} \frac{\partial \rho_a(\mathbf{r},t)}{\partial t}. \tag{A$\cdot$1}$$

Substituting eq. (9a) into eq. (A·1) and integrating eq. (A·1) by parts, one has

$$\frac{dF[\rho_a(\mathbf{r},t)]}{dt} = -\sum_{ab} \frac{\tau}{2} \int d\mathbf{r}d\mathbf{r}' \left(\nabla \frac{\delta F[\rho_a(\mathbf{r},t)]}{\delta \rho_a(\mathbf{r},t)} \right) \cdot \mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}') \cdot \left(\nabla' \frac{\delta \beta F[\rho_a(\mathbf{r},t)]}{\delta \rho_b(\mathbf{r}',t)} \right). \tag{A$\cdot$2}$$

If $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ is positive definite, the H-theorem can be proved because $dF[\rho_a(\mathbf{r},t)]/dt \leq 0$.

Even when the present approximations are introduced, one can prove that $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ is positive definite. The kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ is positive definite if both of $\mathbf{M}_{ab}^{\mathrm{G}}(\mathbf{r},\mathbf{r}')$ and $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$ are positive definite. Substituting eq. (29) into eq. (16a), one can easily prove that $\mathbf{M}_{ab}^{\mathrm{G}}(\mathbf{r},\mathbf{r}')$ is positive definite. In addition, using eqs (17), $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$ is written in the form

$$\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}') = w_{ab}^{lt}(\mathbf{r},\mathbf{r}') \frac{\left\langle \sum_i \Delta\mathbf{v}_a \Delta\mathbf{v}_b \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle}{\rho w_{ab}(\mathbf{r}-\mathbf{r}')}. \tag{A$\cdot$3}$$

One finds that $\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}')$ is also positive definite because the substitution of eq. (29) into eq. (A·3) yields

$$\mathbf{M}_{ab}^{\mathrm{R}}(\mathbf{r},\mathbf{r}') = \frac{1}{\rho} f(\rho_a(\mathbf{r})) f(\rho_b(\mathbf{r}')) \left\langle \sum_i \Delta\mathbf{v}_a \Delta\mathbf{v}_b \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle. \tag{A$\cdot$4}$$

Appendix B: The Bond-Breaking Limit

If all bonds of molecules are broken, the TDDFT of molecular liquids should agree with that of multicomponent simple liquids. When all bonds are broken, $\mathbf{v}_i^a$ and $\mathbf{v}_i^b$ are statistically independent if $a \neq b$. In addition, $\mathbf{v}_i^a$ is also independent of $\mathbf{r}_i^a$. Then, in the limit, one should have the exact relation

$$\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}') = \frac{k_{\mathrm{B}}T}{m_a} \mathbf{U} \delta_{ab} \rho_a(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}'), \tag{B$\cdot$1}$$

where m_a is the mass of a particle for component a. If eq. (B·1) is substituted into eq. (9a), eq. (9a) is in agreement with the basic equation of multicomponent simple liquids.

The kernel function $\mathbf{M}_{ab}^{\mathrm{tot}}(\mathbf{r},\mathbf{r}')$ is rewritten to show the agreement within the present approximations. Since $\mathbf{v}_i^G$ is independent of $\mathbf{r}_i^a$ even without the limit, one can write

$$\left\langle \mathbf{v}_i^G \mathbf{v}_i^G \right\rangle = \frac{\left\langle \sum_i \mathbf{v}_i^G \mathbf{v}_i^G \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle}{\rho w_{ab}(\mathbf{r}-\mathbf{r}')}. \tag{B$\cdot$2}$$

Substituting eq. (B·2) into eq. (14) and using eq. (13a) with eqs (17), one obtains

$$\mathbf{M}^{\mathrm{tot}}_{ab}(\mathbf{r},\mathbf{r}') = \frac{\left\langle \sum_i \mathbf{v}_i^a \mathbf{v}_i^b \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b)\right\rangle}{\rho w_{ab}(\mathbf{r}-\mathbf{r}')} w^{lt}_{ab}(\mathbf{r},\mathbf{r}'). \tag{B·3}$$

Equation (B·3) is satisfied without the limit.

Using the rewritten expression of $\mathbf{M}^{\mathrm{tot}}_{ab}(\mathbf{r},\mathbf{r}')$ given by eq. (B·3), one can show that the present TDDFT is in agreement with that of multicomponent simple liquids in the limit. In the limit, since $\mathbf{v}_i^a$ is independent of $\mathbf{r}_i^a$, one obtains

$$\mathbf{M}^{\mathrm{tot}}_{ab}(\mathbf{r},\mathbf{r}') = \left\langle \mathbf{v}_i^a \mathbf{v}_i^b \right\rangle w^{lt}_{ab}(\mathbf{r},\mathbf{r}'). \tag{B·4}$$

In the limit,

$$\left\langle \mathbf{v}_i^a \mathbf{v}_i^b \right\rangle = \frac{k_{\mathrm{B}}T}{m_a}\mathbf{U}\delta_{ab}, \tag{B·5}$$

so that one obtains

$$\mathbf{M}^{\mathrm{tot}}_{ab}(\mathbf{r},\mathbf{r}') = \frac{k_{\mathrm{B}}T}{m_a}\mathbf{U}\delta_{ab} w^{lt}_{aa}(\mathbf{r},\mathbf{r}'). \tag{B·6}$$

One can obtain eq. (B·1) because eq. (30) for $a = b$ reduces to

$$w^{lt}_{aa}(\mathbf{r},\mathbf{r}') = \rho_a(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'). \tag{B·7}$$

Appendix C: Linearization

If the present equation is linearized, one should obtain the results given by Chong and Hirata.[55] Expanding eq. (9a) in $\Delta\rho_a(\mathbf{r},t) = \rho_a(\mathbf{r},t) - \rho$, one neglects the terms higher than second order. Then, one has

$$\frac{\partial \rho_a(\mathbf{r},t)}{\partial t} = \sum_{bc} \frac{\tau}{2} \int d\mathbf{r}' \int d\mathbf{r}'' [\nabla \cdot \mathbf{M}^{L}_{ab}(\mathbf{r},\mathbf{r}')] \cdot \nabla' \frac{\delta^2 \beta F[\rho_a(\mathbf{r},t)]}{\delta\rho_b(\mathbf{r}',t)\delta\rho_c(\mathbf{r}'',t)} \Delta\rho_c(\mathbf{r}'',t), \tag{C·1}$$

where

$$\mathbf{M}^{L}_{ab}(\mathbf{r}-\mathbf{r}') = \left\langle \sum_i \mathbf{v}_i^a \mathbf{v}_i^b \delta(\mathbf{r}-\mathbf{r}_i^a)\delta(\mathbf{r}'-\mathbf{r}_i^b) \right\rangle. \tag{C·2}$$

Chong and Hirata[55] have exactly obtained the Fourier transform of eq. (C·2).

One can show that the linearization agrees with the results of Chong and Hirata[55] within the present approximation. The kernel function $\mathbf{M}^{\mathrm{tot}}_{ab}(\mathbf{r},\mathbf{r}')$ should agree with $\mathbf{M}^{L}_{ab}(\mathbf{r}-\mathbf{r}')$ given by eq. (C·2) when $\rho_a(\mathbf{r}) = \rho$, because $\rho_a(\mathbf{r}) = \rho$ is equivalent to $\psi_a(\mathbf{r}) = 0$. Even when the approximations are employed, one can obtain eq. (C·2) by substituting eq. (30) for $\rho_a(\mathbf{r}) = \rho_b(\mathbf{r}) = \rho$ into eq. (B·3).

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