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Microscopic derivation of time-dependent density functional methods

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Time-dependent density functional methods (TDDFM) are studied from the microscopic viewpoint using projection operator methods in classical liquids. A density field is defined without averaging, so that a time evolution equation of the density field is derived with a random force. The derived equation includes a free energy functional, which is different from that defined in the TDDFM. The projection operator method provides the exact expression of the free energy functional. Another definition of the density field by an average leads to the equation of the TDDFM. In addition, an equation describing fluctuations is also derived.

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I. INTRODUCTION

The time-dependent density functional method (TDDFM) is successful in studies on dynamical properties of classical liquids [1–13]. The method was early applied to solvation dynamics [1–3]. The solvation dynamics in mixtures, in particular, has shown agreement between the TDDFM and molecular dynamics simulations [4,10]. In addition, the TDDFM has reproduced values of viscosity obtained by molecular dynamics simulations [6]. It can also provide the dynamic structure factor [5] and self-diffusion constant [6]. Some authors have extended the method to supercooled liquids [8,9] and molecular liquids [11–13].

In addition, recently, the TDDFM has been applied to Brownian fluids such as colloidal systems [14–20]. The TDDFM for the system was compared with numerical simulations of Brownian dynamics. Marconi and Tarazona have shown excellent agreement in a two-dimensional rod system [14]. In three-dimensional systems, Dzubiella and Likos have also found agreement using a Gaussian interaction fluid [17].

No-one, however, to our knowledge has derived the TDDFM from the Liouville equation using a microscopic Hamiltonian [10,21]. Some authors have discussed the derivation in Brownian fluids [14,18–20]. These discussions started from Langevin equations of interacting particles. Since the TDDFM is succesful for atomic liquids, one should study the microscopic base in Hamiltonian mechanics. The difference between the Hamiltonian system and Brownian dynamics is given by momentum relaxation.

When the TDDFM is derived, the derived equation should have the same free energy functional as that in the density functional theory (DFT) [10,22]. In the basic equation of the TDDFM, the functional derivative of the free energy provides the time evolution of a density field. Then, the free energy functional is defined by the DFT. This is because the TDDFM is the dynamical extension of the DFT.

Some authors have derived the DFT free energy functional in the TDDFM for Brownian fluids, using an assumption [14,18–20]. The assumption is that the two-particle correlation in a nonequilibrium fluid is the same as that in an equilibrium fluid with the corresponding desnity field. This is the local equilibrium assumption. The physical interpretation of the assumption is, however, not clear.

On the other hand, one obtains the free energy functional with different definitions from that of the DFT, if the nonlinear Langevin equation theory is applied to atomic fluids [21,23,24]. The nonlinear Langevin equation theory provides similar equations to the TDDFM, which describe the time evolution of a density field. In addition, the equations include the "free energy functional," though its definition is different from that in the DFT. From the difference of the definition, one finds that the equations are different from that of the TDDFM.

One can expect that the Kawasaki-Gunton operator method [25–27] provides the same free energy functional as that of the DFT. The Kawasaki-Gunton operator was originally introduced by Kawasaki and Gunton to study the nonlinear shear viscosity [25]. Some authors have employed it to derive transport equations exactly [26,27]. The Kawasaki-Gunton operator method is formulated using the relevant distribution obtained by the generalization of the Gibbs ensemble [27]. On the other hand, in the nonlinear Langevin equation theory, one employs a distribution including δ functions, which is similar to that of the microcanonical ensemble. Thus, Kawasaki has called the two operator methods canonical and microcanonical descriptions [26]. One can expect that the canonical description leads to the free energy functional of the DFT.

Discussions also arise as to random force in the TDDFM with the microscopic derivation. Some authors have employed the TDDFM with a random force to study supercooled liquids and glass [8,9]. One can obtain a random force by nonlinear Langevin equation theory [23,24]. Marconi and Tarazona [14,19], however, have derived the TDDFM without a random force. They insisted that the TDDFM should not have a random force. In the Brownian fluid system, Archer and Rauscher have shown that the problem depends on the definition of the density field [20].

An additional problem is caused by the explicit expressions of the free energy functional defined in the nonlinear Langevin equation theory. The definition is different from that in the density functional theory and the TDDFM. Frusawa and Hayakawa [28] have obtained the explicit expres-

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sion on a discrete lattice. Woo and Song [29], however, have shown that the method causes difficulties for hard-sphere liquids. Thus, explicit expressions valid for all interactions between liquid particles have not yet been obtained.

The purpose of the present study is to derive the TDDFM from the Liouville equation for atomic liquids using projection operators. In addition, the relation of the free energy functional to the derivation is established. Projection operator methods provide a systematic derivation and clear interpretation of the approximation. First, the time evolution of a density field is studied without coarse graining using the nonlinear Langevin equation theory. Next, the TDDFM is derived using the Kawasaki-Gunton operators.

In the present study, the nonlinear Langevin equation theory is also studied to compare it with the Kawasaki-Gunton operator method. The nonlinear Langevin equation theory leads to a random force. Thus, by using the nonlinear Langevin equation theory, one can establish the role of a random force in the derivation of the TDDFM. In addition, the theory provides the free energy functional discussed by Frusawa and Hayakawa [28] and Woo and Song [29]. For these reasons, the nonlinear Langevin equation theory will be discussed in the next section.

II. THE NONLINEAR LANGEVIN EQUATION THEORY

In the present section, a density field is defined without coarse graining. The time evolution equation of a density field $\rho(\mathbf{r},t)$ depends on its definition [20]. If one has

$$\hat{\rho}(\mathbf{r},t) \equiv \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i(t)), \tag{1}$$

the first definition is given by $\rho(\mathbf{r},t)=\hat{\rho}(\mathbf{r},t)$. Here, $\mathbf{r}_i(t)$ is the position of particle i.

The nonlinear Langevin equation theory [21,30,31] is applied to the first definition $\rho(\mathbf{r},t)=\hat{\rho}(\mathbf{r},t)$. In the nonlinear Langevin equation theory, slow variables play an essential role. The time changes of the slow variables are projected on the nonlinear functional space of the variables. The projection provides closed equations for the variables when the memory functions are obtained. If time changes of the chosen variables are slow enough, one can employ the Markovian approximation. The present slow variable is $\hat{\rho}(\mathbf{r},t)$.

To apply the nonlinear Langevin equation theory, the projection operator is defined by

$$P\hat{X} \equiv \langle \hat{X};\hat{\rho}(\mathbf{r})\rangle \equiv \frac{\langle \hat{X}\delta(\hat{\rho}(\mathbf{r})-\rho(\mathbf{r},t))\rangle}{\langle \delta(\hat{\rho}(\mathbf{r})-\rho(\mathbf{r},t))\rangle}. \tag{2}$$

Here, $\hat{X}$ is a function of the phase space with $t=0$, $\hat{\rho}(\mathbf{r})=\hat{\rho}(\mathbf{r},0)$, and $\langle\cdots\delta(\hat{\rho}(\mathbf{r})-\rho(\mathbf{r},t))\rangle$ denotes the average restricted to $\hat{\rho}(\mathbf{r})=\rho(\mathbf{r},t)$ over the phase space with $t=0$.

The usual procedure of the projection operator method [32] provides a generalized nonlinear Langevin equation. The equation is given by

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = \int_0^t dt'\langle iLR(\mathbf{r},t-t');\rho(\mathbf{r},t')\rangle + R(\mathbf{r},t), \tag{3}$$

where

$$R(\mathbf{r},t) = e^{tQiL}QiL\rho(\mathbf{r},0). \tag{4}$$

Here, iL is the Liouville operator and $Q\equiv 1-P$.

The Markovian approximation leads one to the nonlinear Langevin equation. The present Markovian approximation is given by [24]

$$\langle iLR(\mathbf{r},t-t');\rho(\mathbf{r},t')\rangle \approx \langle iLR(\mathbf{r},0);\rho(\mathbf{r},t')\rangle\tau\delta(t-t'). \tag{5}$$

The substitution of Eq. (5) into Eq. (3) yields

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = \frac{\tau}{2}\langle iLR(\mathbf{r},0);\rho(\mathbf{r},t')\rangle + R(\mathbf{r},t). \tag{6}$$

The nonlinear Langevin equation is rewritten in a form including the free energy functional. The first term in the right hand side of Eq. (6) reduces to

$$\langle iLR(\mathbf{r},0);\rho(\mathbf{r},t)\rangle = \int d\mathbf{r}' M(\mathbf{r},\mathbf{r}',t)\frac{\delta(-\beta F'[\rho(\mathbf{r},t)])}{\delta\rho(\mathbf{r}',t)} + \int d\mathbf{r}'\frac{\delta M(\mathbf{r},\mathbf{r}',t)}{\delta\rho(\mathbf{r}',t)}, \tag{7}$$

where $M(\mathbf{r},\mathbf{r}',t)=\langle[iL\rho(\mathbf{r})][iL\rho(\mathbf{r}')];\rho(\mathbf{r},t)\rangle$. The free energy functional

$$-\beta F'[\rho(\mathbf{r})] \equiv \ln\langle\delta(\hat{\rho}(\mathbf{r})-\rho(\mathbf{r}))\rangle \tag{8}$$

is different from that of the DFT in its definition. This is the one discussed by Frusawa and Hayakawa [28] and Woo and Song [29]. Since

$$M(\mathbf{r},\mathbf{r}',t) = \nabla\cdot\left[\frac{k_{\mathrm{B}}T\rho(\mathbf{r},t)}{m}\nabla'\delta(\mathbf{r}-\mathbf{r}')\right], \tag{9}$$

where m is the mass of the particle, one can find that the second term in Eq. (7) vanishes and then

$$\langle iLR(\mathbf{r},0);\rho(\mathbf{r},t)\rangle = \nabla\cdot\left[\frac{k_{\mathrm{B}}T\rho(\mathbf{r},t)}{m}\nabla\frac{\delta\beta F'[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}\right]. \tag{10}$$

The substitution of Eq. (10) into Eq. (6) yields

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = D\nabla\cdot\left[\rho(\mathbf{r},t)\nabla\frac{\delta\beta F'[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}\right] + R(\mathbf{r},t), \tag{11}$$

where $D=k_{\mathrm{B}}T\tau/(2m)$.

On the other hand, one can obtain a different expression for the nonlinear Langevin equation. Calculating the first term in the right hand side of Eq. (6) directly, one has

$$iLR(\mathbf{r},0) = -\,\boldsymbol{\nabla}\cdot\left[\sum_{i=1}^{N}\mathbf{v}_i\,\boldsymbol{\nabla}\cdot\mathbf{v}_i\delta(\mathbf{r}-\mathbf{r}_i)+\sum_{i=1}^{N}\dot{\mathbf{v}}_i\delta(\mathbf{r}-\mathbf{r}_i)\right], \tag{12}$$

where $\mathbf{v}_i$ is the velocity of particle i. In addition, $\dot{\mathbf{v}}_i = iL\mathbf{v}_i$ is given by the equation of motion $m\dot{\mathbf{v}}_i = -\Sigma_{j\neq 1}\boldsymbol{\nabla}_i v(\mathbf{r}_i,\mathbf{r}_j)$ when one considers only a two-particle interaction $v(\mathbf{r}_i,\mathbf{r}_j)$. Averaging Eq. (12), one can obtain

$$\begin{aligned}\langle iLR(\mathbf{r},0);\rho(\mathbf{r},t)\rangle &= -\frac{1}{m}\boldsymbol{\nabla}\cdot\Bigg[-k_{\mathrm{B}}T\,\boldsymbol{\nabla}\,\rho(\mathbf{r},t)-\rho(\mathbf{r},t)\,\boldsymbol{\nabla}\\ &\quad\times\int d\mathbf{r}'v(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}',t)+\rho(\mathbf{r},t)\,\boldsymbol{\nabla}\,v(\mathbf{r},\mathbf{r})\Bigg].\end{aligned} \tag{13}$$

Then one has

$$\begin{aligned}\frac{\partial\rho(\mathbf{r},t)}{\partial t} &= \frac{\tau k_{\mathrm{B}}T}{2m}\nabla^2\rho(\mathbf{r},t)\\ &\quad+\frac{\tau}{2m}\boldsymbol{\nabla}\cdot\left[\rho(\mathbf{r},t)\,\boldsymbol{\nabla}\int d\mathbf{r}'v(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}',t)\right]\\ &\quad-\frac{\tau}{2m}\boldsymbol{\nabla}\cdot[\rho(\mathbf{r},t)\,\boldsymbol{\nabla}\,v(\mathbf{r},\mathbf{r})]+R(\mathbf{r},t),\end{aligned} \tag{14}$$

which is equivalent to the equation derived by Dean [33] and Frusawa and Hayakawa [34] for the Langevin process.

The two expressions provide an exact form of the first free energy functional $F'[\rho(\mathbf{r})]$. Comparing Eqs. (10) and (13), one has

$$\begin{aligned}\beta F'[\rho(\mathbf{r})] &= \int\rho(\mathbf{r})\ln\rho(\mathbf{r})d\mathbf{r}\\ &\quad+\frac{\beta}{2}\int d\mathbf{r}\int d\mathbf{r}'v(\mathbf{r},\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')\\ &\quad-\beta\int d\mathbf{r}\,v(\mathbf{r},\mathbf{r})\rho(\mathbf{r})+A\int\rho(\mathbf{r})d\mathbf{r}+B,\end{aligned} \tag{15}$$

because $F'[\rho]$ is independent of $\mathbf{r}$ if ρ is independent of $\mathbf{r}$. This agrees with the result derived by Frusawa and Hayakawa [28]. In contrast to their derivation, it is valid for all interactions because no discrete lattices are employed in the present derivation. Equation (15), however, has arbitrary constants A and B.

III. THE KAWASAKI AND GUNTON PROJECTION OPERATOR

The second projection operator is introduced because the first projection operator does not provide the TDDFM. The second projection operator has been developed by Kawasaki and Gunton [25,26]. The projection operator is applied to the second definition $\rho(\mathbf{r},t) = \langle\hat{\rho}(\mathbf{r})\rangle_t$ where the average is given by a nonequilibrium distribution.

The second projection operator is defined by [25,26]

$$P_t\hat{X} \equiv \langle\hat{X}\rangle_{lt}+\int d\mathbf{r}\frac{\delta\langle\hat{X}\rangle_{lt}}{\delta\langle\hat{\rho}(\mathbf{r})\rangle_{lt}}\delta_t\rho(\mathbf{r},0). \tag{16}$$

The expression in brackets $\langle\cdots\rangle_{lt}$ is given by

$$\langle\hat{X}\rangle_{lt} \equiv \frac{\langle\hat{X}\exp[-\beta\int d\mathbf{r}\,\hat{\rho}(\mathbf{r})\psi(\mathbf{r})]\rangle}{\langle\exp[-\beta\int d\mathbf{r}\,\hat{\rho}(\mathbf{r})\psi(\mathbf{r})]\rangle}, \tag{17}$$

where the virtual external field $\psi(\mathbf{r})$ is determined by

$$\langle\hat{\rho}(\mathbf{r})\rangle_{lt} = \langle\hat{\rho}(\mathbf{r})\rangle_t. \tag{18}$$

Here, $\langle\cdots\rangle_t$ is the average using a nonequilibrium distribution, and

$$\langle\hat{\rho}(\mathbf{r})\rangle_t = \langle\hat{\rho}(\mathbf{r},t)\rangle_0. \tag{19}$$

In addition,

$$\frac{\delta\langle\hat{X}\rangle_{lt}}{\delta\langle\hat{\rho}(\mathbf{r})\rangle_{lt}} = \int d\mathbf{r}'\langle\hat{X}\,\delta_t\hat{\rho}(\mathbf{r}',0)\rangle_{lt}\left\{\frac{\delta\psi(\mathbf{r}')}{\delta\langle\hat{\rho}(\mathbf{r})\rangle_{lt}}\right\}$$

and $\delta_t\rho(\mathbf{r},t') = \hat{\rho}(\mathbf{r},t')-\langle\hat{\rho}(\mathbf{r}')\rangle_{lt}$. The second projection operator depends on time in contrast to the first projection operator given by Eq. (2).

The second projection operator provides a exact equation for $\hat{\rho}(\mathbf{r},t)$. The time development of $\hat{\rho}(\mathbf{r},t)$ is given by

$$\begin{aligned}\frac{\partial\hat{\rho}(\mathbf{r},t)}{\partial t} &= \int_0^t dt'e^{t'iL}P_{t'}iLQ_{t'}U(t',t)iL\hat{\rho}(\mathbf{r})\\ &\quad+\int_0^t dt'e^{t'iL}\dot{Q}_{t'}U(t',t)iL\hat{\rho}(\mathbf{r})+Q_0U(0,t)iL\hat{\rho}(\mathbf{r}),\end{aligned} \tag{20}$$

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

$$\frac{\partial}{\partial t}U(t',t) = U(t',t)iLQ_t, \tag{21}$$

with $U(t,t) = 1$, and $R(t',t;\mathbf{r}) \equiv Q_{t'}U(t',t)iL\hat{\rho}(\mathbf{r})$. Equation (20) is rewritten in the form

$$\begin{aligned}\frac{\partial\hat{\rho}(\mathbf{r},t)}{\partial t} &= \int_0^t dt'\Bigg\{\langle iLR(t',t;\mathbf{r})\rangle_{lt'}\\ &\quad+\int d\mathbf{r}'\frac{\delta\langle iLR(t',t;\mathbf{r})\rangle_{lt'}}{\delta\langle\hat{\rho}(\mathbf{r}',0)\rangle_{lt'}}\delta_{t'}\rho(\mathbf{r},t')\Bigg\}\\ &\quad+\int_0^t dt'e^{t'iL}\dot{Q}_{t'}U(t',t)iL\hat{\rho}(\mathbf{r})+R(0,t;\mathbf{r}).\end{aligned} \tag{22}$$

The first term on the right hand side of Eq. (22) reduces to

$$\langle iLR(t',t;\mathbf{r})\rangle_{lt'} = \int d\mathbf{r}'M(t,t';\mathbf{r},\mathbf{r}')\beta\psi(\mathbf{r}), \tag{23}$$

where $M(t,t';\mathbf{r},\mathbf{r}') = \langle R(t',t';\mathbf{r})R(t',t;\mathbf{r}')\rangle_{lt'}$ and [10]

$$\psi(\mathbf{r}) = \frac{\delta F[\rho(\mathbf{r},t)]}{\delta \rho(\mathbf{r}',t)}. \tag{24}$$

The second free energy functional $F[\rho(\mathbf{r})]$ is exactly the same as that in the DFT. Calculating $\dot{Q}_{t'}$, one has

$$\begin{aligned}\frac{\partial \hat{\rho}(\mathbf{r},t)}{\partial t} = {} & \int_0^t dt' \Bigg[\int d\mathbf{r}' M(t,t';\mathbf{r},\mathbf{r}')\beta\psi(\mathbf{r}) \\ & + \int d\mathbf{r}' \frac{\delta \langle \hat{i}LR(t',t;\mathbf{r})\rangle_{lt'}}{\delta \langle \hat{\rho}(\mathbf{r}',0)\rangle_{lt'}} \delta_{t'}\rho(\mathbf{r}',t') \Bigg] \\ & - \int_0^t dt' \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta^2 \langle U(t',t) iL\hat{\rho}(\mathbf{r})\rangle_{lt'}}{\delta \langle \hat{\rho}(\mathbf{r}',0)\rangle_{lt'} \delta \langle \hat{\rho}(\mathbf{r}'',0)\rangle_{lt'}} \\ & \times \delta_{t'}\rho(\mathbf{r}',t')\dot{\rho}(\mathbf{r}'',t') + R(0,t;\mathbf{r}). \end{aligned} \tag{25}$$

Averaging the equation, one can obtain an equation for $\rho(\mathbf{r},t) = \langle \hat{\rho}(\mathbf{r})\rangle_t$. If $\langle \cdots \rangle_0$ is applied to Eq. (25), the second and third terms in the right hand side vanish, because $\langle \delta_{t'}\rho(\mathbf{r},t')\rangle_0 = 0$. In addition, assuming that for the initial distribution

$$\langle \hat{X}\rangle_0 = \langle \hat{X}\rangle_{l0}, \tag{26}$$

where $\hat{X}$ is an arbitrary function of the phase space, one can show $\langle R(0,t;\mathbf{r})\rangle_0 = 0$. Thus, considering $\langle \partial\hat{\rho}(\mathbf{r},t)/\partial t\rangle_0 = (\partial/\partial t)\langle \hat{\rho}(\mathbf{r},t)\rangle_0$, one can obtain

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = \int_0^t dt' \int d\mathbf{r}' M(t,t';\mathbf{r},\mathbf{r}')\beta\psi(\mathbf{r}). \tag{27}$$

If the Markovian approximation is applied to the averaged equation, one can obtain the TDDFM equation. In a similar way to Eq. (5), the approximation is given by [24]

$$M(t,t';\mathbf{r},\mathbf{r}') \approx \langle R(t,t;\mathbf{r})R(t,t;\mathbf{r}')\rangle_{lt}\tau\delta(t-t'). \tag{28}$$

Using $P_{t'} iL\hat{\rho}(\mathbf{r}) = 0$, one has

$$\langle R(t,t;\mathbf{r})R(t,t;\mathbf{r}')\rangle_{lt} = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla}' \frac{k_B T}{m}\rho(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}'). \tag{29}$$

The substitution of Eqs. (28) and (29) into Eq. (27) yields

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = D\boldsymbol{\nabla} \cdot \left[\rho(\mathbf{r},t)\boldsymbol{\nabla}\frac{\delta \beta F[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}\right] \tag{30}$$

where $D = k_B T\tau/(2m)$. This is the equation of the TDDFM.

In addition, one also obtains an equation for fluctuations $\delta_t\rho(\mathbf{r},t)$. From Eqs. (25) and (27), one gets

$$\begin{aligned}\frac{\partial \delta_t\rho(\mathbf{r},t)}{\partial t} = {} & \int_0^t dt' \int d\mathbf{r}' \frac{\delta \langle iLR(t',t;\mathbf{r})\rangle_{lt'}}{\delta \langle \hat{\rho}(\mathbf{r}',0)\rangle_{lt'}} \delta_{t'}\rho(\mathbf{r}',t') \\ & - \int_0^t dt' \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta^2 \langle U(t',t) iL\hat{\rho}(\mathbf{r})\rangle_{lt'}}{\delta \langle \hat{\rho}(\mathbf{r}',0)\rangle_{lt'} \delta \langle \hat{\rho}(\mathbf{r}'',0)\rangle_{lt'}} \\ & \times \delta_{t'}\rho(\mathbf{r}',t')\dot{\rho}(\mathbf{r}'',t') + R(0,t;\mathbf{r}). \end{aligned} \tag{31}$$

Two Markovian approximations are assumed [24],

$$\langle \delta_{t'}\rho(\mathbf{r},0) iLR(t',t;\mathbf{r})\rangle_{lt'} \approx \langle \delta_t\rho(\mathbf{r},0) iLR(t,t;\mathbf{r})\rangle_{lt'}\tau\delta(t-t'), \tag{32a}$$

$$\begin{aligned}& \langle \delta_{t'}\rho(\mathbf{r},0)\delta_{t'}\rho(\mathbf{r}',0)U(t',t) iL\hat{\rho}(\mathbf{r})\rangle_{lt'} \\ & \quad \approx \langle \delta_t\rho(\mathbf{r},0)\delta_t\rho(\mathbf{r},0)U(t,t) iL\hat{\rho}(\mathbf{r})\rangle_{lt}\tau\delta(t-t'). \end{aligned} \tag{32b}$$

Using the approximations, the first term on the right hand side of Eq. (31) reduces to

$$\begin{aligned}& \int_0^t dt' \int d\mathbf{r}' \frac{\delta \langle iLR(t',t;\mathbf{r})\rangle_{lt'}}{\delta \langle \hat{\rho}(\mathbf{r}',0)\rangle_{lt'}} \delta_{t'}\rho(\mathbf{r}',t') \\ & \quad = \frac{\tau}{2}\int d\mathbf{r}' \frac{\delta \langle iLR(t,t;\mathbf{r})\rangle_{lt}}{\delta\rho(\mathbf{r}',t)} \delta_{t'}\rho(\mathbf{r}',t'). \end{aligned} \tag{33}$$

Since $\langle \delta_t\rho(\mathbf{r},0)\delta_t\rho(\mathbf{r},0) iL\hat{\rho}(\mathbf{r})\rangle_{lt} = 0$, the second term vanishes. Thus, one can obtain

$$\frac{\partial \delta_t\rho(\mathbf{r},t)}{\partial t} = \int d\mathbf{r}' \left[\frac{\delta}{\delta\rho(\mathbf{r}',t)}\frac{\delta\rho(\mathbf{r},t)}{\partial t}\right]\delta_{t'}\rho(\mathbf{r}',t') + R(0,t;\mathbf{r}). \tag{34}$$

Here $\partial\rho(\mathbf{r},t)/\partial t$ is given by Eq. (30).

IV. DISCUSSION

In the present study, the TDDFM has been derived using the Kawasaki-Gunton operator. The derivation shows that the TDDFM is applicable when the distribution in the phase space approaches fast that in the local equilibrium. The local equilibrium average is expressed by Eq. (17). It was an assumption when the TDDFM was derived for Brownian fluids [14,18–20]. The present derivation does not have any approximations when Eq. (17) is defined. The present main approximation is the Markovian approximation Eq. (28). The approximation is valid if the relaxation of $\langle R(t',t';\mathbf{r})R(t',t;\mathbf{r}')\rangle_{lt}$ is faster than the average density field $\rho(\mathbf{r},t) = \langle \hat{\rho}(\mathbf{r})\rangle_t$. This correlation function vanishes if the distribution is not in perfect equilibrium but in local equilibrium. This shows that the approximation of the TDDFM is valid if the distribution approaches fast that in the local equilibrium. The projection operator method provides the physical interpretation of the approximation.

In addition to the fast approach to the local equilibrium distribution, the TDDFM requires that the initial distribution also should be in local equilibrium. One can find the condition from Eq. (26). This condition was not discussed for Brownian fluids.

The Kawasaki-Gunton operator method has also provided an equation of fluctuations as well as the TDDFM. It includes nonlocal effects, where the calculation of a value at the position $\mathbf{r}$ needs a value of $\mathbf{r}'$. Equation (34) allows one to calculate the time evolution of the dispersion $\langle \delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t)\rangle$, which plays an important role in solvation dynamics. Some experiments on solvation dynamics have shown that the spectral bandwidths have relaxed more slowly than the peak shifts [35,36]. If the spectral bandwidth is given by the dispersion, the time evolution equation of the dispersion is useful in studying the experimental results.

In the present derivation, the TDDFM does not have random force when the free energy functional agrees with that in the DFT. This is because the density field is defined by $\rho(\mathbf{r},t)=\langle\hat{\rho}(\mathbf{r})\rangle_t$. Archer and Rauscher have shown that the random force depends on the definition of the density field [20]. The present results show that the free energy functional is also relevant to the random force. If $\rho(\mathbf{r},t)=\hat{\rho}(\mathbf{r},t)$, one can obtain an alternative equation (11) including a random force. The equation, however, has a different free energy functional from that in the DFT. This is consistent with the discussion of Marconi and Tarazona [14,19].

One cannot apply the TDDFM to the glass transition without a random force. Studies of the glass transition require a random force because the system is trapped at a local minimum. However, one cannot employ Eq. (30) even if one has a random force. This is because the functional derivative of the free energy defined by the DFT can have discontinuities at the glass transition point. If it has discontinuities, one cannot calculate Eq. (30). Thus, one needs different equations describing the time development of the density field to study the glass transition.

Some authors have studied other definitions of a density field to obtain the random force. Diving a system into cells, Munakata has defined a density field by the average over the cell [24]. Archer and Rauscher have defined a density field by the average over a time period [20]. Such definitions provide equations of a density field including a free energy functional with random force. One, however, cannot generally prove that the free energy functional is the same as that in the DFT.

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