

# Generalized Langevin theory on the dynamics of simple fluids under external fields

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A theory on the time development of the density and current fields of simple fluids under an external field is formulated through the generalized Langevin formalism. The theory is applied to the linear solvation dynamics of a fixed solute regarding the solute as the external field on the solvent. The solute-solvent-solvent three-body correlation function is taken into account through the hypernetted-chain integral equation theory, and the time correlation function of the random force is approximated by that in the absence of the solute. The theoretical results are compared with those of molecular-dynamics (MD) simulation and the surrogate theory. As for the transient response of the density field, our theory is shown to be free from the artifact of the surrogate theory that the solvent can penetrate into the repulsive core of the solute during the relaxation. We have also found a large quantitative improvement of the solvation correlation function compared with the surrogate theory. In particular, the short-time part of the solvation correlation function is in almost perfect agreement with that from the MD simulation, reflecting that the short-time expansion of the theoretical solvation correlation function is exact up to  $t^2$  with the exact three-body correlation function. A quantitative improvement is found in the long-time region, too. Our theory is also applied to the force-force time correlation function of a fixed solute, and similar improvement is obtained, which suggests that our present theory can be a basis to improve the mode-coupling theory on the solute diffusion. © 2005 American Institute of Physics. [DOI: 10.1063/1.1955455]

## I. INTRODUCTION

Liquids under external fields, such as those at interface, those in porous media and gels, and water around biomolecules, have been of certain interest for both academic and engineering reasons. The theory on the dynamics of liquids under external fields is required because in addition to their structural and thermodynamic properties, we sometimes need to understand their dynamics.

The solute-solvent interaction is often regarded as the external field on solvent molecules in the liquid-state theory.<sup>1</sup> From this point of view, we can also think of the dynamics of solvent molecules around a solute as the dynamics of liquids under external fields, provided that the effect of the motion of the solute is neglected.

The response of the solvent around the solute to the sudden change in the solute-solvent interaction, usually called “solvation dynamic,” has been intensively studied by ultrafast laser spectroscopy during the last decades. In the time-resolved fluorescence measurement, for instance, the solute molecule is excited to its excited state by a pulsed laser, and the time development of the transition energy between the excited and ground states is monitored as the dynamic Stokes shift of the fluorescence spectrum. Although the observed phenomenon is specific to the ultrafast laser spectroscopy, the dynamics of solvents it probes is related to

various other dynamic properties of the solute. For example, the response of the dipolar solvent molecules to the sudden change of the dipolar moment of the solute, called “polar solvation dynamics,” is related to the dielectric friction on ions in polar solvents, and it also has something to do with electron transfer reactions.<sup>2</sup>

The similarity between the solute diffusion and the solvation dynamics is also found in their theoretical treatments. In the surrogate theory for the solvation dynamics,<sup>3–14</sup> the solvation correlation function is approximated as the linear combination of the dynamic structure factor of the neat solvent. The coefficient of the linear combination, describing the coupling strength between the electronic transition of the solute and the density field of the solvent, is equal to the difference in the direct correlation functions of the ground and excited states. On the other hand, under the mode-coupling approximation,<sup>1,15–18</sup> the memory function on the translational diffusion of a solute is approximated as the linear combination of the biproduct of the dynamic structure factor of the solvent and the self-part of the dynamic structure factor of the solute. The coupling coefficient between the translational motion of the solute and the density field of the solvent is described as the derivative of the direct correlation function, which is the difference in the direct correlation functions before and after the infinitely small amount of the translational displacement of the solute. The self-part of the dynamic structure factor of the solute is negligible when the motion of the solute is slow compared with that of the

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solvent. The mode-coupling theory for the diffusion of massive solutes is therefore equivalent to the surrogate theory for the solvation dynamics.

In both the surrogate and mode-coupling theories, the dynamics of the solvent density around the solute is approximated as that of the neat solvent, so long as the dynamics of the solvent is described by the dynamic structure factor of the neat fluid. Although it is convenient and useful as a first approximation, sometimes we have to consider how the presence of the solute modifies the dynamic response of the solvent molecules around the solute. In the polar solvation dynamics, a small amount of the solute dependence is reported both experimentally and theoretically.<sup>19–21</sup> We recently investigated the transient response of the solvation shell of cations in water by molecular-dynamics (MD) simulation, and found that the motion of water molecules around small ions as  $\text{Li}^+$  and  $\text{Na}^+$  is significantly different from that around large ions or neutral molecules due to the strong attractive interaction between ion and water, and that the change in the dynamics of hydrating water appears as the oscillatory behavior in the memory function of ions.<sup>22</sup> The dissolution of a hydrophobic molecule into water is known to retard the mobility of water in the hydration shell of the solute, and it is yet to be resolved how the retardation of the mobility of water affect the mobility of the solute molecule.<sup>23,24</sup> In order to achieve a better understanding of the dynamic properties of a solute, it is therefore required to develop a theory to treat the dynamics of solvent molecules under the effect of the solute-solvent interaction.

The generalized Langevin formalism is the theory that has been successfully applied to the dynamics of neat simple liquids.<sup>1,15,16</sup> Our purpose for the present work is to extend the theory to fluids under external fields and apply it to the solvation dynamics of an immobile solute. The numerical results of the present theory are compared with MD simulations and the surrogate theory. The surrogate theory is chosen for comparison, because it is a representative microscopic theory for solvation dynamics, and also because our theory can be regarded as its extension, as will be described in Sec. II. We treat three model systems for the test of the theory. The first and the second ones are the change in the attractive and repulsive parts, respectively, of the isotropic solute-solvent interaction. Since the characteristics of the nonpolar solvation dynamics strongly depend on the nature of the solute-solvent interaction involved,<sup>25</sup> we believe that the demonstration of the applicability of the theory to both systems is necessary. The third one is the response of the solvent to the translational displacement of the solute. As will be elucidated below, it is closely related to the translational diffusion of the solute, so that the test of the present theory for this particular system is crucial to the extension of the theory to that of the translational diffusion. Although our numerical application is limited to the solute-solvent system, the formulation of the theory is quite general, so that it is applicable to various kinds of external fields.

## II. THEORY

### A. Generalized Langevin equation for inhomogeneous fluid

The system we consider is the fluid which is composed of monoatomic molecules whose mass is  $m$ . The external field,  $U(\mathbf{r})$ , is imposed on the fluid, and the equilibrium mean number density under the external field is denoted as  $\langle \rho(\mathbf{r}) \rangle$ . The pair of angular brackets stands for the equilibrium average throughout this work. The external field converges to zero as  $r \equiv |\mathbf{r}|$  goes to infinity, and the equilibrium number density at infinite distance is simply denoted as  $\rho_0$ .

In order to apply the generalized Langevin formalism, we have to choose slow variables of explicit concern. As is the case of the theory of homogeneous liquids,<sup>1,15,16</sup> we consider explicitly the fluctuation of the number density,  $\delta\rho(\mathbf{r})$ , and current density,  $\mathbf{j}(\mathbf{r})$ , as

$$\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \langle \rho(\mathbf{r}) \rangle, \quad (1)$$

$$\rho(\mathbf{r}) \equiv \sum_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (2)$$

$$\mathbf{j}(\mathbf{r}) \equiv \sum_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (3)$$

where  $i$  is the index for each molecule, and  $\mathbf{r}_i$  and  $\mathbf{v}_i$  mean the position and velocity of the molecule  $i$ , respectively.

According to the standard procedure of the generalized Langevin theory based on the projection operator, the time development of the density and current-density fields is derived as follows:<sup>15</sup>

$$\delta\dot{\rho}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t), \quad (4)$$

$$\begin{aligned} \dot{\mathbf{j}}(\mathbf{r}, t) = & - \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{j}(\mathbf{r}) \otimes \mathbf{j}(\mathbf{r}_1) \rangle \\ & \cdot \nabla_1 [\langle \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \rangle^{-1} \delta\rho(\mathbf{r}_2, t)] \\ & - \int_0^t d\tau \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{R}(\mathbf{r}, 0) \otimes \mathbf{R}(\mathbf{r}_1, \tau) \rangle \\ & \cdot \langle \mathbf{j}(\mathbf{r}_1) \otimes \mathbf{j}(\mathbf{r}_2) \rangle^{-1} \cdot \mathbf{j}(\mathbf{r}_2, t - \tau) + \mathbf{R}(\mathbf{r}, t), \end{aligned} \quad (5)$$

$$\mathbf{R}(\mathbf{r}, t) \equiv e^{iQLQ} \mathbf{Q} \mathbf{j}(\mathbf{r}). \quad (6)$$

Here,  $\mathbf{Q} \equiv 1 - \mathcal{P}$ , and  $\mathcal{P}$  stands for the projection operator onto the subspace generated by  $\{\delta\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ . The tensor product of two vectors is denoted as  $\otimes$ . Equation (4) is the continuity equation that describes the conservation of the number of molecules. Equation (5) is the equation of motion, and its right-hand side (rhs) describes the forces acting on the molecule at the position  $\mathbf{r}$ . The first term comes from the distortion of the liquid structure, the second one is the dissipation, and the last one is the excitation due to the thermal fluctuation.

Equations (4) and (5) reduce to the generalized Langevin equation for homogeneous simple fluids when the external fields on the fluid are absent. Owing to the translational symmetry, the variables of different wave numbers are uncorrelated in the homogeneous fluids, so that the decoupled sets of

the equations are obtained in the reciprocal space. On the other hand, we cannot decouple the equations either in the real or reciprocal spaces in the presence of the external fields, since the translational symmetry is lost due to the external fields.

## B. Approximations for correlation functions

Although Eq. (5) is formally exact, it is of no practical use unless we can evaluate explicitly the correlation functions there. We shall summarize the approximation for these correlation functions in this subsection.

First, the static correlation function of the current fields is given by

$$\begin{aligned} \langle \mathbf{j}(\mathbf{r}) \otimes \mathbf{j}(\mathbf{r}') \rangle &= \frac{k_B T}{m} \langle \rho(\mathbf{r}) \rangle \delta(\mathbf{r} - \mathbf{r}') \mathbf{1} \\ &\equiv \frac{\rho_0 k_B T}{m} g(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \mathbf{1}, \end{aligned} \quad (7)$$

where  $k_B$ ,  $T$ , and  $\mathbf{1}$  stand for the Boltzmann constant, absolute temperature, and unit tensor, respectively. The function  $g(\mathbf{r})$  is defined as

$$g(\mathbf{r}) \equiv \frac{\langle \rho(\mathbf{r}) \rangle}{\rho_0}. \quad (8)$$

Equation (7) is an exact relationship, contrary to the approximate ones described below.

Another static correlation function we need is the two-point density-density one,  $\langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle$ , which appears in the first term of the rhs of Eq. (5). In the absence of the external field, it is expressed by the ordinary radial distribution function, which is obtained by either MD simulation or liquid-state theories. The two-body correlation function in the presence of the external field, which corresponds to the solute-solvent-solvent three-body correlation function in the solute-solvent systems, is the function of six variables. Although its direct evaluation by MD simulation is not impossible, the computational cost is much higher than the calculation of the average structure,  $g(\mathbf{r})$ . It is therefore desirable to devise an approximate expression for  $\langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle$  that we can calculate easily.

The starting point of our approximation is the exact relationship for the two-point correlation function as

$$\langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle = -k_B T \frac{\delta \langle \rho(\mathbf{r}) \rangle}{\delta U(\mathbf{r}')} = -\rho_0 k_B T \frac{\delta g(\mathbf{r})}{\delta U(\mathbf{r}')}. \quad (9)$$

An approximate expression for the functional derivative at the rhs can be derived from the hypernetted-chain (HNC) integral equation theory as<sup>1</sup>

$$h(\mathbf{r}) = c(\mathbf{r}) + \rho_0 \int d\mathbf{r}' c_0(|\mathbf{r} - \mathbf{r}'|) h(\mathbf{r}'), \quad (10)$$

$$\ln g(\mathbf{r}) = -\frac{U(\mathbf{r})}{k_B T} + h(\mathbf{r}) - c(\mathbf{r}). \quad (11)$$

Here,  $h(\mathbf{r}) \equiv g(\mathbf{r}) - 1$  and  $c(\mathbf{r})$  denote the total and direct correlation functions, respectively, and  $c_0(r)$  stands for the

solvent-solvent direct correlation function. The differentiation of Eqs. (10) and (11) yields

$$\delta g(\mathbf{r}) = \delta c(\mathbf{r}) + \rho_0 \int d\mathbf{r}' c_0(|\mathbf{r} - \mathbf{r}'|) \delta g(\mathbf{r}'), \quad (12)$$

$$\frac{\delta g(\mathbf{r})}{g(\mathbf{r})} = -\frac{\delta U(\mathbf{r})}{k_B T} + \delta g(\mathbf{r}) - \delta c(\mathbf{r}). \quad (13)$$

From Eqs. (11) and (12), we can eliminate  $\delta c(\mathbf{r})$  as

$$\frac{\delta U(\mathbf{r})}{k_B T} = -\frac{\delta g(\mathbf{r})}{g(\mathbf{r})} + \rho_0 \int d\mathbf{r}' c_0(|\mathbf{r} - \mathbf{r}'|) \delta g(\mathbf{r}'). \quad (14)$$

Comparing Eqs. (9) and (14), the two-point density correlation function in Eq. (9) is derived as

$$\langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle^{-1} = \frac{1}{\rho_0 g(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}') - c_0(|\mathbf{r} - \mathbf{r}'|). \quad (15)$$

The substitution of Eqs. (7) and (15) into the first term of the rhs of Eq. (5) yields a physically transparent expression as

$$\begin{aligned} & - \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{j}(\mathbf{r}) \otimes \mathbf{j}(\mathbf{r}_1) \rangle \\ & \quad \cdot \nabla_1 [ \langle \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \rangle^{-1} \delta\rho(\mathbf{r}_2, t) ] \\ & = -\frac{1}{m} \left[ \{ \nabla W(\mathbf{r}) \} \delta\rho(\mathbf{r}, t) + k_B T \nabla \delta\rho(\mathbf{r}, t) \right. \\ & \quad \left. + \int d\mathbf{r}' \rho_0 g(\mathbf{r}') \nabla' \{ -k_B T c_0(|\mathbf{r} - \mathbf{r}'|) \} \delta\rho(\mathbf{r}, t) \right], \end{aligned} \quad (16)$$

where  $W(\mathbf{r})$  stands for the potential of mean force due to the external field, which is defined as

$$W(\mathbf{r}) \equiv -k_B T \ln g(\mathbf{r}). \quad (17)$$

The first term of Eq. (16) denotes the force due to  $W(\mathbf{r})$ . The second one comes from the thermal motion of the solvent. The third one is read as the mean force from other solvent molecules, since  $-k_B T c_0(r)$  has the meanings of the effective interaction between solvent molecules. This expression of the force is close to that used in the generalized nonlinear Smolchovski-Vlasov theory for solvation dynamics developed by Egorov.<sup>26</sup>

In addition to the physical transparency, Eq. (16) has an advantage in numerical calculations. The exact two-body correlation function is a nonlocal function in both the real and reciprocal spaces. On the other hand, the first and second terms of Eq. (16) are local in the real space, while the third term is local in the reciprocal space. We can therefore evaluate them by treating the former and the latter in the real and reciprocal spaces, respectively.

Now we turn to the random force,  $\mathbf{R}(\mathbf{r}, t)$ . The approximation employed here is simply to assume that the statistical properties of the random force are not affected by the presence of the external field. Explicitly, the time correlation function of the random force is given by

$$\begin{aligned} & \langle \mathbf{R}^*(\mathbf{k}, 0) \otimes \mathbf{R}(\mathbf{k}', t) \rangle \\ & \simeq \frac{\rho_0 k_B T}{m} \left[ \frac{\mathbf{k} \otimes \mathbf{k}}{k^2} K_L(k, t) + \left( 1 - \frac{\mathbf{k} \otimes \mathbf{k}}{k^2} \right) K_T(k, t) \right] \\ & \quad \times \delta(\mathbf{k} - \mathbf{k}'), \end{aligned} \quad (18)$$

$$\mathbf{R}(\mathbf{k}, t) \equiv \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{R}(\mathbf{r}, t), \quad (19)$$

where the asterisk stands for the complex conjugate. The functions in Eq. (18),  $K_L(k, t)$  and  $K_T(k, t)$ , are the longitudinal and transverse parts, respectively, of the memory function of the bulk fluid, which are related to the dynamic structure factor,  $F(k, t)$ , and the transverse current correlation function,  $C_T(k, t)$ , of the bulk fluid as

$$\ddot{F}(k, t) + \frac{k^2 k_B T}{m S(k)} F(k, t) + \int_0^t d\tau K_L(k, t - \tau) \dot{F}(k, \tau) = 0, \quad (20)$$

$$\dot{C}_T(k, t) + \int_0^t d\tau K_T(k, t - \tau) C_T(k, \tau) = 0. \quad (21)$$

A lot of approximations are available for the memory functions of bulk fluids, and we can also evaluate it from the MD simulation.

### C. Momentum conservation

The conservation laws play a crucial role in physics. The conserved quantities are the particle number, momentum, and energy in the case of the liquid-state theory. In our theory, Eq. (4) assures the number-density conservation. The energy is not conserved because we are not treating the energy density in an explicit way. In this subsection, we show that the momentum conservation is satisfied in an approximate way in our theory. Although the momentum conservation is usually not considered in the theory of solvation dynamics, it plays an important role in the translational diffusion. The Stokes–Einstein relationship is derived by solving the Navier–Stokes equation around the solute, which describes the conservation law of the momentum of the solvent. The momentum conservation is therefore essential to treat the relationship between the microscopic and hydrodynamic theories on diffusion.

Equation (5) is integrated over the whole space to yield the equation as

$$\begin{aligned} \frac{d}{dt} \int d\mathbf{r} \mathbf{j}(\mathbf{r}, t) &= - \int d\mathbf{r} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{j}(\mathbf{r}) \\ & \quad \otimes \mathbf{j}(\mathbf{r}_1) \rangle \cdot \nabla_1 [ \langle \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \rangle^{-1} \delta\rho(\mathbf{r}_2, t) ] \\ & \quad - \int_0^t d\tau \int d\mathbf{r} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{R}(\mathbf{r}, 0) \\ & \quad \otimes \mathbf{R}(\mathbf{r}, \tau) \rangle \cdot \langle \mathbf{j}(\mathbf{r}_1) \otimes \mathbf{j}(\mathbf{r}_2) \rangle^{-1} \cdot \mathbf{j}(\mathbf{r}_2, t - \tau) \\ & \quad + \int d\mathbf{r} \mathbf{R}(\mathbf{r}, t). \end{aligned} \quad (22)$$

In the absence of the external field, the space integration of the random force vanishes as

$$\int d\mathbf{r} \mathbf{R}(\mathbf{r}, t) \equiv \int d\mathbf{r} e^{i\mathbf{Q} \cdot \mathbf{r}} \mathbf{Q} \cdot \mathbf{j}(\mathbf{r}) = e^{i\mathbf{Q} \cdot \mathbf{r}} \mathbf{Q} \int d\mathbf{r} \mathbf{j}(\mathbf{r}) = 0, \quad (23)$$

where the last equation comes from the conservation of the total momentum in the absence of the external field. Since we have assumed in Sec. II B that the statistical properties of the random force is not affected by the presence of the external field, we can utilize Eq. (23) in the inhomogeneous case. As a result, we can neglect the second and third terms of Eq. (22).

Substituting Eqs. (7) and (9) into Eq. (22) gives

$$\begin{aligned} m \frac{d}{dt} \int d\mathbf{r} \mathbf{j}(\mathbf{r}, t) &= - \int d\mathbf{r} \int d\mathbf{r}_2 k_B T \langle \rho(\mathbf{r}) \rangle \nabla \\ & \quad \times \left[ \left\{ - \frac{1}{k_B T} \frac{\delta U(\mathbf{r}_2)}{\delta \rho(\mathbf{r})} \right\} \delta\rho(\mathbf{r}_2, t) \right] \\ &= - \int d\mathbf{r} \nabla U(\mathbf{r}) \delta\rho(\mathbf{r}, t). \end{aligned} \quad (24)$$

The left-hand side is the time derivative of the total momentum possessed by the liquid molecules. The rhs is the total force on the liquid molecules exerted by the external force. Since there is no source of the momentum in the system other than the external field, Eq. (24) means that the momentum balance of the system is satisfied. It should be noted here, however, that Eq. (24) is not an exact relationship under our approximations, because the two-body correlation function obtained from Eq. (15) does not satisfy Eq. (9) unless we calculate  $g(\mathbf{r})$  with the HNC integral equation theory.

### D. Application to the linear solvation dynamics

The problem we shall consider in this work is the following one. First, the system is in thermal equilibrium under the external field  $U(\mathbf{r})$  at the time  $t < 0$ . If the field changes suddenly at  $t = 0$  by  $\delta U(\mathbf{r})$ , the system relaxes to the new equilibrium under  $U(\mathbf{r}) + \delta U(\mathbf{r})$ . What we want to obtain are the time development of the density and current fields, denoted as  $\langle \rho(\mathbf{r}, t) \rangle_{\text{ne}}$  and  $\langle \mathbf{j}(\mathbf{r}, t) \rangle_{\text{ne}}$ , respectively. The average of the “transition energy,”  $\langle u(t) \rangle_{\text{ne}}$ , is also discussed, where  $u(t)$  is defined as

$$u(t) \equiv \int d\mathbf{r} \delta U(\mathbf{r}) \rho(\mathbf{r}, t). \quad (25)$$

Here,  $\langle \cdots \rangle_{\text{ne}}$  stands for the nonequilibrium average.

This problem is equivalent to the solvation dynamics in which the solute molecule is fixed. The initial external field,  $U(\mathbf{r})$ , is regarded as the solute-solvent interaction when the solute is in its ground state. After the solute is excited to the excited state at  $t = 0$ , the solute-solvent interaction becomes  $U(\mathbf{r}) + \delta U(\mathbf{r})$ . Since  $\delta U(\mathbf{r})$  is the solute-solvent interaction part of the transition energy, what we obtain in the experimental measurement of the solvation dynamics is  $\langle u(t) \rangle_{\text{ne}}$ , and  $\langle \rho(\mathbf{r}, t) \rangle_{\text{ne}}$  represents the microscopic mechanism of  $\langle u(t) \rangle_{\text{ne}}$ .



According to the linear-response theory, these nonequilibrium averages are approximated by the equilibrium time correlation function when  $\delta U(\mathbf{r})$  is small as follows:

$$\bar{\mathbf{j}}(\mathbf{r}, t) \equiv \langle \mathbf{j}(\mathbf{r}, t) \rangle_{\text{ne}} - \langle \mathbf{j}(\mathbf{r}, t = \infty) \rangle_{\text{ne}} = \frac{1}{k_B T} \langle u(t=0) \mathbf{j}(\mathbf{r}, t) \rangle, \quad (26)$$

$$\begin{aligned} \bar{\rho}(\mathbf{r}, t) &\equiv \langle \rho(\mathbf{r}, t) \rangle_{\text{ne}} - \langle \rho(\mathbf{r}, t = \infty) \rangle_{\text{ne}} \\ &= \frac{1}{k_B T} \langle u(t=0) \delta \rho(\mathbf{r}, t) \rangle. \end{aligned} \quad (27)$$

In particular, the initial conditions of  $\bar{\mathbf{j}}(\mathbf{r}, t)$  and  $\bar{\rho}(\mathbf{r}, t)$  are given by

$$\bar{\mathbf{j}}(\mathbf{r}, 0) = \mathbf{0}, \quad (28)$$

$$\bar{\rho}(\mathbf{r}, 0) = \frac{1}{k_B T} \langle u(t=0) \delta \rho(\mathbf{r}, t=0) \rangle, \quad (29)$$

and they relax to zero as  $t \rightarrow \infty$ . From the definition of  $u(t)$  [Eq. (25)] the time development of the transition energy is given by

$$\begin{aligned} \bar{u}(t) &\equiv \langle u(t) \rangle_{\text{ne}} - \langle u(t = \infty) \rangle_{\text{ne}} \\ &= \int d\mathbf{r} \delta U(\mathbf{r}) \bar{\rho}(\mathbf{r}, t) = \frac{1}{k_B T} \langle u(t=0) u(t) \rangle. \end{aligned} \quad (30)$$

Since the equilibrium fluctuation of  $\mathbf{j}(\mathbf{r}, t)$  and  $\delta \rho(\mathbf{r}, t)$  follows Eqs. (4) and (5), respectively, the time development of  $\bar{\mathbf{j}}(\mathbf{r}, t)$  and  $\bar{\rho}(\mathbf{r}, t)$  are given by

$$\bar{\rho}(\mathbf{r}, t) = -\nabla \cdot \bar{\mathbf{j}}(\mathbf{r}, t), \quad (31)$$

$$\begin{aligned} \bar{\mathbf{j}}(\mathbf{r}, t) &= - \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{j}(\mathbf{r}) \\ &\otimes \mathbf{j}(\mathbf{r}_1) \rangle \cdot \nabla_1 [ \langle \delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \rangle^{-1} \bar{\rho}(\mathbf{r}_2, t) ] \\ &- \int_0^t d\tau \int d\mathbf{r}_1 \int d\mathbf{r}_2 \langle \mathbf{R}(\mathbf{r}, 0) \otimes \mathbf{R}(\mathbf{r}_1, \tau) \rangle \cdot \langle \mathbf{j}(\mathbf{r}_1) \\ &\otimes \mathbf{j}(\mathbf{r}_2) \rangle^{-1} \cdot \bar{\mathbf{j}}(\mathbf{r}_2, t - \tau). \end{aligned} \quad (32)$$

The combination of Eqs. (25), (27), and (29) gives the exact value of  $\bar{u}(0)$ . In addition, the short-time expansion of  $\bar{\rho}(\mathbf{r}, t)$  from Eqs. (31) and (32) is exact up to  $t^2$ , provided that the two-body correlation function  $\langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle$  is exact. Our theory therefore gives the response function of the transition energy whose short-time expansion is exact up to  $t^2$ . On the other hand, our theory can provide a good description of the long-time part of the response function, since the collective slow density modes are taken into account. Therefore, our present theory can be a candidate to describe both the short- and long-time parts of the solvation dynamics in a unified manner.

In the surrogate theory for the solvation dynamics, the bare coupling between the state transition of the solute and the density field of the solvent,  $\delta U(\mathbf{r})$ , is replaced by the difference in the solute-solvent direct correlation functions of

two states,  $c(\mathbf{r})$ , multiplied by  $-k_B T$ , and the dynamics of the solvent around the solute is approximated by that in the absence of the solute. The former approximation corresponds to the replacement of  $\delta U(\mathbf{r})$  with  $-k_B T \delta c(\mathbf{r})$  in Eq. (25). The latter one does to the use of static correlation functions of the bulk fluids for Eq. (32). Explicitly, the substitution of unity into  $g(\mathbf{r})$  in Eqs. (7) and (15) is required to alter our theory to the surrogate one. In the linear solvation dynamics, the response of the direct correlation function to the finite change of the solute-solvent interaction can be replaced by its linear response as

$$\delta c(\mathbf{r}) = \int d\mathbf{r}' \frac{\delta c(\mathbf{r})}{\delta U(\mathbf{r}')} \delta U(\mathbf{r}'). \quad (33)$$

Since our theory has a simple relationship with the surrogate theory, the former can be regarded as the natural extension of the latter.

### E. Force-force time correlation function

Consider that a spherical solute is fixed in a simple fluid at  $t < 0$ . The position of the solute is taken to be the origin. The solute-solvent interaction is isotropic, denoted as  $U(\mathbf{r})$ . Suppose that the position of the solute is suddenly displaced at  $t=0$  to the  $z$  direction by a small amount,  $\Delta z$ . The change of the solute-solvent interaction due to the translational displacement of the solute is given by

$$\delta U(\mathbf{r}) = U(\mathbf{r}) - U(\mathbf{r} + \Delta z \hat{z}) \simeq -\frac{\partial U(\mathbf{r})}{\partial z} \Delta z, \quad (34)$$

where  $\hat{z}$  is the unit vector parallel to the  $z$  axis. Regarding the states before and after the displacement as the ground and excited states, respectively, we can utilize the theoretical formulation for the solvation dynamics described in Sec. II D. In this case,  $u(t)$  is given by

$$u(t) = - \int d\mathbf{r} \frac{\partial U(\mathbf{r})}{\partial z} \Delta z \bar{\rho}(\mathbf{r}, t) = F_z(t) \Delta z, \quad (35)$$

where  $F_z(t)$  stands for the  $z$  component of the force felt by the solute.

According to Eq. (30), the response of  $u(t)$  is described as

$$\frac{\bar{u}(t)}{\Delta z^2} = \frac{1}{k_B T} \langle F_z(0) F_z(t) \rangle, \quad (36)$$

which is the massive-solute limit of the memory function of the translational diffusion of the solute. In addition, the response of the density field is given by

$$\frac{\bar{\rho}(\mathbf{r}, t)}{\Delta z} = \frac{1}{k_B T} \langle F_z(0) \rho(\mathbf{r}, t) \rangle, \quad (37)$$

which is also equivalent to the massive-solute limit of the response of the solvent density field to the translational diffusion of the solute recently formulated by us.<sup>22</sup>

As for the translational displacement of the solute, the linear response of the direct correlation function is equal to the simple derivative as

$$\delta c(\mathbf{r}) = \frac{dc(r)}{dr} \frac{z}{r} \Delta z. \quad (38)$$

The surrogate approximation for  $\bar{u}(t)$  is therefore given by

$$\frac{\bar{u}(t)}{\Delta z^2} = \frac{\rho_0 k_B T}{6\pi^2} \int_0^\infty dk k^4 c^2(k) F(k, t), \quad (39)$$

which is equivalent to the mode-coupling expression of the memory function of the translational diffusion in the immobile limit of the solute.<sup>15,17</sup>

### III. MODEL SYSTEMS

The solvent fluid calculated in this work is the Lennard-Jones (LJ) liquid near the triple point. The temperature and the density of the liquid is 0.75 and 0.85, respectively, where the LJ reduced unit is employed throughout this work. The LJ reduced unit is the unit that scales  $\epsilon$  and  $\sigma$  in the LJ potential;  $m$  and  $k_B$  are unity. In particular, the unit of time is  $\sqrt{m\sigma^2/\epsilon}$ , which corresponds to a few picoseconds for typical liquids. As the external field, the LJ solute is fixed at the origin, whose LJ parameters are the same as those of the solvent.

Three systems with different functional forms of  $\delta U(\mathbf{r})$  are considered here. The first two are the nonpolar solvation dynamics studied by Yamaguchi *et al.*<sup>25</sup> The last one is the translational displacement of the solute. Explicitly,  $\delta U(\mathbf{r})$  of the first system is given by

$$\delta U(\mathbf{r}) = \begin{cases} -1 & (r < 2^{1/6}) \\ 4[r^{-12} - r^{-6}] & (r > 2^{1/6}), \end{cases} \quad (40)$$

which is the attractive part of the LJ potential in the sense of Weeks *et al.*<sup>27</sup> Hereafter we call this system the “attractive solvation dynamics.”

The potential change in the second system is described as

$$\delta U(\mathbf{r}) = \begin{cases} 4[r^{-12} - r^{-6}] + 1 & (r < 2^{1/6}) \\ 0 & (r > 2^{1/6}), \end{cases} \quad (41)$$

which is the repulsive part of the LJ potential. This system is therefore called the “repulsive solvation dynamics.”

The third one is the “translational displacement,” which is expressed as

$$\delta U(\mathbf{r}) = -\frac{\partial U(\mathbf{r})}{\partial z}. \quad (42)$$

Owing to the spherical symmetry of  $U(\mathbf{r})$  and  $\delta U(\mathbf{r})$ , the three-dimensional functions  $\bar{\rho}(\mathbf{r}, t)$  and  $\bar{\mathbf{j}}(\mathbf{r}, t)$  can be reduced to the one-dimensional ones by the spherical harmonics expansion. In the cases of attractive and repulsive solvation dynamics, they are described as

$$\bar{\rho}(\mathbf{r}, t) = \rho_0(r, t), \quad (43)$$

$$\bar{\mathbf{j}}(\mathbf{r}, t) = \frac{\mathbf{r}}{r} j_1(r, t). \quad (44)$$

As for the translational displacement of the solute, they are given by

$$\bar{\rho}(\mathbf{r}, t) = \frac{z}{r} \rho_1(r, t), \quad (45)$$

$$\bar{\mathbf{j}}(\mathbf{r}, t) = \hat{z} j_0(r, t) + \frac{3z\mathbf{r} - r^2 \hat{z}}{r^2} j_2(r, t). \quad (46)$$

The current densities of the former two systems are purely longitudinal. On the other hand, both the longitudinal and transverse components are included in that of the last system in a natural manner. The response function of the last system can be regarded as the immobile-solute limit of the memory function of the translational diffusion of a solute, and the coupling between the translational diffusion of the solute and the transverse current of the solvent is important to bridge the gap between the microscopic theory and the hydrodynamic one as the Stokes–Einstein relationship.

### IV. NUMERICAL METHOD

#### A. Molecular-dynamics simulation

We performed the equilibrium MD simulations of the three systems, in order to obtain the equilibrium correlation functions used in the theoretical calculations. The MD simulation is also utilized for the comparison with the theoretical calculations.

The system under the MD simulation is composed of 500 LJ particles. One of them is fixed at the origin, which is regarded as the solute. The simulation cell is cubic, and the periodic boundary condition is applied. The equation of motion is integrated by the leap-frog algorithm. The length of a time step is 0.001. The temperature of the system is controlled by the Nose–Hoover thermostat. The total length of the simulation run is  $1 \times 10^6$  steps. The initial 130 000 steps are used for equilibration, and the remaining trajectories are analyzed.

In addition to the systems with a fixed solute, the simulation of the bulk liquids, containing 500 mobile molecules, is performed to obtain the bulk properties of the fluid.

#### B. Equilibrium correlation functions

The solvent-solvent radial distribution function, which is equal to the solute-solvent one in our model, is obtained from the MD simulation, and extrapolated by the method similar to that proposed by Verlet.<sup>28,29</sup> In the extrapolation, the distribution function inside a certain cutoff distance is equated to the simulation one, and the HNC equation [Eq. (11)] is assumed outside the cutoff. The cutoff distance is taken to be 2.5. The solvent-solvent direct correlation function is calculated from the Fourier transform of the extrapolated correlation function.

The initial value of the density relaxation,  $\bar{\rho}(\mathbf{r}, t=0)$ , is also evaluated by the MD simulation from Eq. (29). The linear response of the direct correlation function is calculated from  $g(\mathbf{r})$  in the same way to that used for the extrapolation of the radial distribution function in the cases of the attractive and repulsive solvation dynamics. Explicitly,  $g(\mathbf{r})$  from the simulation is used inside the cutoff radius, and Eq. (13) is assumed outside the cutoff. The combination of them with

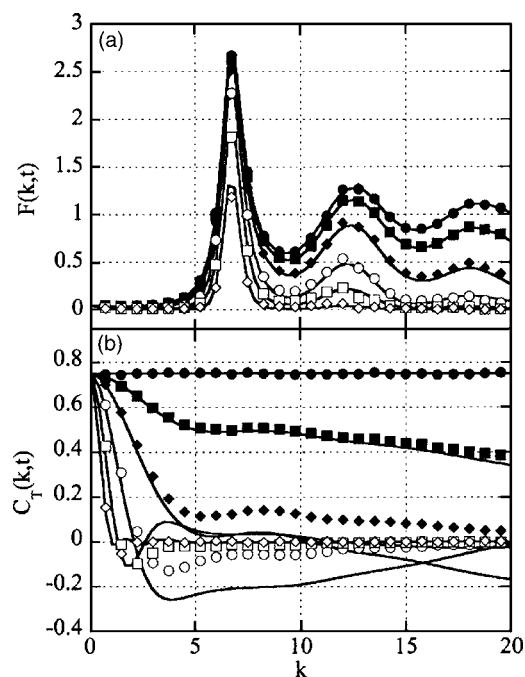


FIG. 1. The exponential model for the dynamic structure factor,  $F(k, t)$ , and the transverse current correlation function,  $C_T(k, t)$ , are compared with the MD simulation in (a) and (b), respectively. The functions from the theory and the simulation are described by the lines and symbols, respectively. Filled circles:  $t=0$ , filled squares:  $t=0.049$ , filled diamonds:  $t=0.098$ , open circles:  $t=0.197$ , open squares:  $t=0.393$ , and open diamonds:  $t=0.798$ .

Eq. (12) yields  $\delta c(\mathbf{r})$ . The linear response of the direct correlation function for the translational displacement of the solute is evaluated by Eq. (38).

### C. Approximation for the memory function

We employ the exponential models for the memory functions of the longitudinal and transverse currents of the bulk fluid,  $K_L(k, t)$  and  $K_T(k, t)$ . The exponential model for  $K_L(k, t)$  is proposed by Lovesey.<sup>1,30</sup> It requires the zeroth-, second-, and fourth-order derivatives of  $F(k, t)$  with respect to  $t$  at  $t=0$ , all of which can be evaluated from the radial distribution function and intermolecular interaction. The dynamic structure factor from the exponential model is compared with that from the MD simulation in Fig. 1(a). Both functions agree well with each other. In particular, the decay rate of the density fluctuation at the peak of the structure factor,  $k=7$ , is reproduced by the theory. We therefore believe that the error in the approximation for  $K_L(k, t)$  hardly affects the theoretical results on the dynamics of solvent molecules around the solute.

The exponential model for  $K_T(k, t)$  is less popular than that for  $K_L(k, t)$ . It was recently used by Egorov in his study on the mode-coupling theory for the solute diffusion in supercritical fluids.<sup>31</sup> In this model, the time dependence of the second-order memory function [memory function for  $K_T(k, t)$ ] is assumed to be exponential. The initial values of the first- and second-order memory functions are determined from the short-time expansion of  $C_T(k, t)$ , and the relaxation time of the exponential function is adjusted to reproduce the shear viscosity in the hydrodynamic limit. The zeroth- and second-order time derivatives of  $C_T(k, t)$  can be calculated

from the radial distribution function and intermolecular interaction.<sup>16</sup> The evaluation of the fourth-order derivative requires the three-body correlation function, for which we employ the superposition approximation. We utilize the efficient algorithm for the numerical calculation of the fourth-order derivative proposed by Bansal and Pathak.<sup>16,32</sup> The shear viscosity of the bulk fluid is 3.2, which is taken from the MD simulation performed by Yamaguchi and Kimura.<sup>33</sup> The theoretical transverse current correlation function is compared with that from the MD simulation in Fig. 1(b). The agreement is fairly good, although it is worse than that for the dynamic structure factor.

### D. Numerical procedures

Given the static correlation functions, initial values of  $\bar{\rho}(\mathbf{r}, t)$ , and memory functions of the bulk solvents, we can evaluate  $\bar{\rho}(\mathbf{r}, t)$  at all times by integrating Eqs. (31) and (32). In the numerical calculations, the functions in the three-dimensional space are first reduced to the one-dimensional one using the spherical symmetry as is described in Sec. III. These functions are then discretized linearly at the interval of  $\Delta r=0.02$  from  $r=0$  to  $r_{\text{cut}}=10.24$ . The functions are simply cut off at  $r=r_{\text{cut}}$ , and no long-range correction is performed. The equation of motion [Eq. (32)] is integrated by the implicit algorithm, which is essential to obtain the stability of the solution. The factor  $1/g(\mathbf{r})$  appears sometimes in Eq. (32) through Eqs. (7) and (15). The value of  $g(\mathbf{r})$  is essentially zero inside the repulsive core of the solute, so that its direct evaluation is numerically impossible. In this work,  $1/g(\mathbf{r})$  is replaced by  $1/g_{\text{min}}$  when  $g(\mathbf{r})$  is smaller than  $g_{\text{min}}$ . The value of  $g_{\text{min}}$  is taken to be  $10^{-40}$ . It is confirmed that the value of  $g_{\text{min}}$  does not affect the numerical results provided that it is sufficiently small.

## V. RESULTS AND DISCUSSIONS

### A. Nonpolar solvation dynamics

Figures 2(a) and 2(b) shows the response functions of the transition energy,  $\bar{u}(t)$ , of the systems of attractive and repulsive solvation dynamics, respectively. The results of the present theory are compared with those of the surrogate theory and MD simulation. The results of the MD simulation do not agree with those previously reported by Yamaguchi *et al.*,<sup>25</sup> since the solute is fixed in the present model, while it is mobile in the previous one.

In the case of the attractive solvation dynamics, the results of the present theory approximately follows that of the MD simulation. In contrast, it is clearly seen that the initial value and the decay rate of  $\bar{u}(t)$  are overestimated in the surrogate theory. It can therefore be said that the present theory provides a significant improvement of the surrogate theory for the attractive solvation dynamics.

The agreement between the MD simulation and the theory is not so good in the repulsive case. The response function from the simulation is composed of two parts, the short- and long-time ones. The former decays within  $t < 0.1$ , and the tail of small amplitude remains in the long-time region, on which a small oscillation is imposed. While the short-time part of the response function is almost perfectly

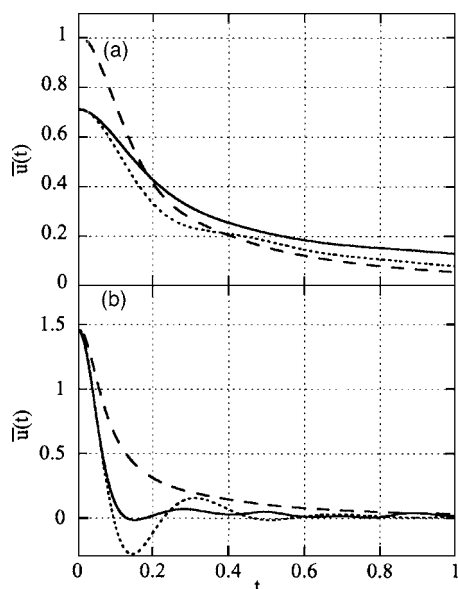


FIG. 2. The response functions of the transition energy,  $\bar{u}(t)$ , of the attractive and repulsive solvation dynamics are shown in (a) and (b), respectively. The solid, dashed, and dotted lines stand for the MD simulation, surrogate theory, and our present theory, respectively.

reproduced by the theory, the oscillation in the long-time region is overemphasized. However, we consider that our present theory has improved the response function compared with the surrogate theory.

The short-time part of  $\bar{u}(t)$  of both systems are described well by our theory, in harmony with the statement in Sec. II D that the short-time expansion of  $\bar{u}(t)$  is exact up to the order of  $t^2$ , if the approximation for the two-body density correlation function [Eq. (15)] is exact. In the MD simulation study on the nonpolar solvation dynamics, Yamaguchi *et al.* suggested an idea that the equilibrium amount of the fluctuation of the solvent around the solute is the principal factor that determines the relaxation rate of the solvation correlation function in the short-time regime.<sup>25</sup> The present results are consistent with their idea in that the better description of the fluctuation of the solvent density around the solute has improved the short-time behavior of the response function compared with the surrogate theory.

The time development of the density response,  $\rho_0(r, t)$ , is demonstrated in Figs. 3 and 4 for the detailed comparison among the theories and the simulation. Figures 3 and 4 are those of the attractive and the repulsive solvation dynamics, respectively.

The most important point in Fig. 3 we have to stress is that the finite amount of the solvent density response is found inside the repulsive core of the solute in the surrogate theory, whereas no response is observed there in both the present theory and MD simulation. The existence of the response inside the repulsive core of the solute is reported in previous studies on polar solvation dynamics using the surrogate theory.<sup>4,6-8</sup> Since the solvent is excluded from the repulsive core throughout the relaxation, the response of the solvent density field must not be found there. The finite response inside the core has thus been regarded as one of the

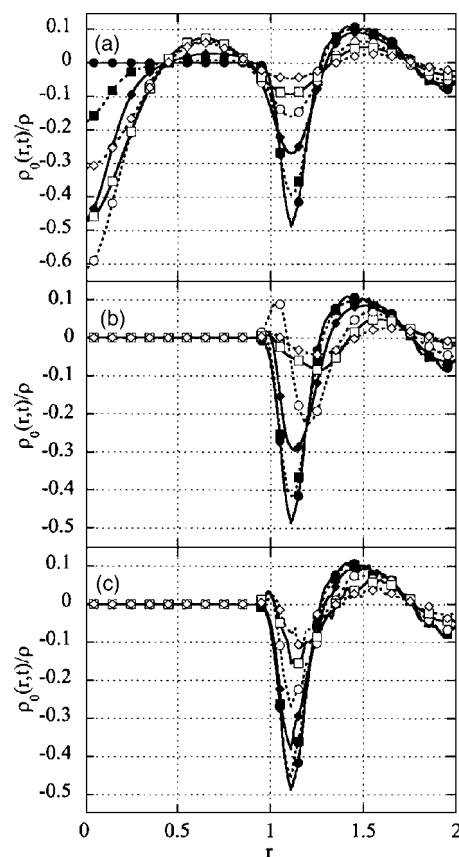


FIG. 3. The normalized density response of the attractive solvation dynamics,  $\rho_0(r, t)$ , are plotted. The results of the surrogate theory, our present one, and the MD simulation are shown in (a)–(c), respectively. The times indicated by the symbols are the same as those in Fig. 1.

artifacts of the surrogate theory on the solvation dynamics, and our present theory provides the remedy for it.

The improvement in the present theory that leads to the physically correct behavior inside the repulsive core is the inclusion of the two-body density fluctuation as Eq. (15). The structure of the solvent around the solute is taken into account as the first term,  $\delta(\mathbf{r}-\mathbf{r}')/\rho_0 g(\mathbf{r})$ . Since  $g(\mathbf{r})$  is equal to zero inside the core,  $\langle \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') \rangle^{-1}$  diverges to infinity when  $\mathbf{r}$  or  $\mathbf{r}'$  is included in the core, which forbids the solvent density fluctuation there. On the other hand, the factor of  $g(\mathbf{r})$  is neglected in the surrogate theory, so that the fluctuation of the solvent density is allowed anywhere.

In Fig. 4, the dynamics of solvent near the repulsive wall of the solute is compared in the case of repulsive solvation dynamics. The peak of  $\rho_0(r, t=0)$  found at  $r \sim 1$  represents the solvent molecules under the repulsive potential of the solute. We can see in Fig. 4 that the motion of the peak is different among the two theories and the MD simulation. In the present theory and MD simulation [Figs. 4(b) and 4(c), respectively], the solvent molecule is repelled from the solute after the solute-solvent repulsive interaction is strengthened, in harmony with our physical intuition. In contrast, the solvent is drawn by the repulsive potential of the solute, and it finally penetrates into the repulsive core of the solute, which can by no means be realized in real systems.

Although the direction of the solvent motion is reproduced by the present theory, there are some quantitative dif-



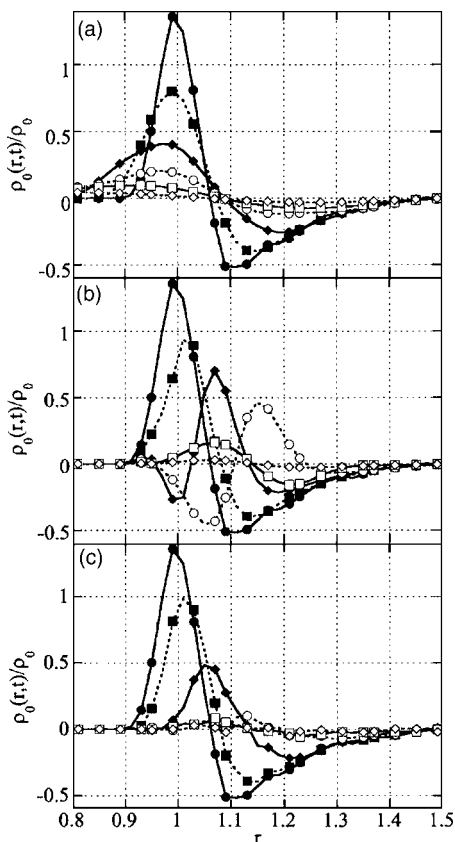


FIG. 4. The normalized density response of the repulsive solvation dynamics,  $\rho_0(r,t)$ , are plotted. The results of the surrogate theory, our present one, and the MD simulation are shown in (a)–(c), respectively. The times indicated by the symbols are the same as those in Fig. 1.

ferences between the theory and the MD simulation. In the theory [Fig. 4(b)] the peak goes to  $r \sim 1.05$  at  $t = 0.197$ . It makes the negative contribution to  $\rho_0(r,t)$  around  $r \sim 1.05$  by its excluded volume, which leads to the negative part of  $\bar{u}(t)$  found around  $t \sim 0.15$ . The peak then moves back to the solute, and oscillates within the first well of the potential of the mean force. The oscillation persists up to  $t \sim 1$ , as is found in  $\bar{u}(t)$  shown in Fig. 2(b). On the other hand, the decay of the peak is faster in the simulation. Although the small oscillation is also found in  $\bar{u}(t)$  of the simulation in Fig. 2(b), its amplitude is smaller than that of the theory.

We consider that there can be two reasons for the rather quantitative difference between the theory and the simulation. The first one is the error in the HNC approximation. It has been well known that the HNC approximation is not so good as the Percus–Yevick (PY) one for hard-sphere fluids,<sup>1</sup> which suggests that the HNC theory does not work for the correlation of the solvent near the repulsive core of the solute. The second one is the approximation introduced in Eq. (18) that the statistic properties of the random force are not affected by the presence of the external field. We can elucidate the difference between the theory and the simulation if the friction on the solvent within the first solvation shell of the solute is larger in reality than that assumed in Eq. (18). Although both reasons may be working, we consider the latter one more probable, since the breakdown of the HNC approximation has to appear also in the short-time dynamics.

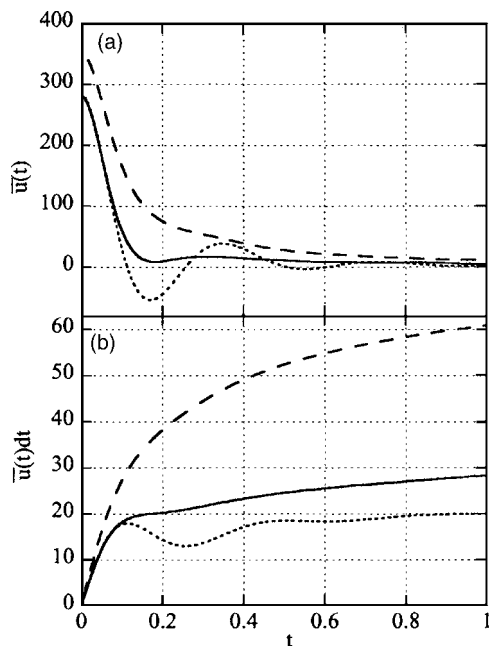


FIG. 5. The response functions of the transition energy,  $\bar{u}(t)$ , to the translational displacement of the solute are exhibited in (a), and the running integrals,  $\int_0^t d\tau \bar{u}(\tau)$ , are shown in (b). The meanings of the lines are the same as those in Fig. 2.

We shall note here that the error in the exponential model for the memory function of the transverse current correlation function, as is shown in Fig. 1(b), does not affect the theoretical results on the isotropic solvation dynamics, because the solvent current density is purely transverse, as is elucidated in Sec. III.

## B. Translational displacement of the solute

Figure 5(a) shows the response function,  $\bar{u}(t)$ , to the translational displacement of the solute, which is the immobile-solute approximation of the memory function of the translational diffusion of the solute. The characteristic features of Fig. 5(a) are quite similar to that of the repulsive solvation dynamics [Fig. 2(b)]. The response function from the MD simulation is composed of short- and long-time components. The short-time part is reproduced by the present theory almost perfectly. In the long-time region, the theoretical response function oscillates around the long-time tail of  $\bar{u}(t)$  from the simulation. The surrogate theory overestimates both the short- and long-time parts of the response function.

The similarity between the repulsive solvation dynamics and the response to the translational displacement suggests the following two things. One is that the repulsive part of the solute-solvent interaction is dominant in the force felt by the solute, which is consistent with that the repulsive interaction is the principal factor in the determination of the structure of dense simple liquids. The other is that the solvent response to the solute-solvent repulsive interaction is controlled by the local interaction and structure, and it is rather insensitive to the global symmetry of the interaction.

In the mode-coupling theory of the translational diffusion of a solute, the short-time part of the memory function is assigned to the solute-solvent binary collision, and the

long-time tail is attributed to the correlated collisions as the backscatter effect. Although it may belong to the issue of the terminology, it sounds interesting to see that the description of the binary part is improved by our present theory that takes the solute-solvent-solvent three-body correlation function into account.

The most important property of the response function,  $\bar{u}(t)$ , to the translational displacement of the solute is its integrated value over the time, because it is inversely proportional to the diffusion coefficient of the solute in its massive limit. Figure 5(b) shows the running integral of the response function,  $\int_0^t d\tau \bar{u}(\tau)$ , in order to show how the discrepancy  $\bar{u}(t)$  between the theory and simulation affects the difference in their integrated values. Comparing the present theory and the MD simulation, the contributions of the binary parts agree well with each other. Interestingly, the oscillation of the theoretical response function in the long-time region ( $t > 0.3$ ) is averaged out by the integration, and its contribution to the integrated value of  $\bar{u}(t)$  is comparable with that of the MD simulation. The integrated value of the theoretical response function up to  $t=1$  is 20.1, which is about 0.7 times as large as that of the simulation, 28.2. The origin of their difference comes from the time region of the transition from the binary to the collective parts,  $t \sim 0.2$ . A large negative dip is found in the theoretical response function, whose strength is quite small in the MD simulation. The integrated value of the response function of the surrogate theory up to  $t=1$  is 60.9, which is more than twice larger than the corresponding value of the MD simulation.

Figure 6 shows the response of the solvent density to the translational displacement of the solute. As is the case of  $\bar{u}(t)$ , the response to the translational displacement of the solute resembles that to the change of the solute-solvent repulsive interaction [Fig. 4]. The solvent penetrates into the repulsive core of the solute in the surrogate theory. The oscillation of the solvent within the first minimum of the potential of the mean force is observed in the present theory, which results in the oscillatory response in  $\bar{u}(t)$ . The decay of the peak describing the collision pair is relatively fast, and small backscatter effect is found in the MD simulation.

We shall comment here that the oscillation of the solvent within the first well of the potential of the mean force, although not observed in the MD simulation, is not unphysical. We have very recently investigated the response of the solvent structure to the translational diffusion of the solute by MD simulations.<sup>22</sup> In the presence of the strong solute-solvent attractive interaction, as is the case of lithium ion in water, the solvent molecules are bound to the first solvation shell, and the oscillation of the solvent within the first solvation shell is actually observed. We therefore believe that the difference between the present theory and the MD simulation is quantitative, rather than qualitative, resulting from the underestimation of the friction on the solvent within the first solvation shell of the solute.

Figure 7 plots the response of the solvent density in the reciprocal space. The response function of the density in the reciprocal space,  $\bar{\rho}_k(\mathbf{k}, t)$ , is defined as

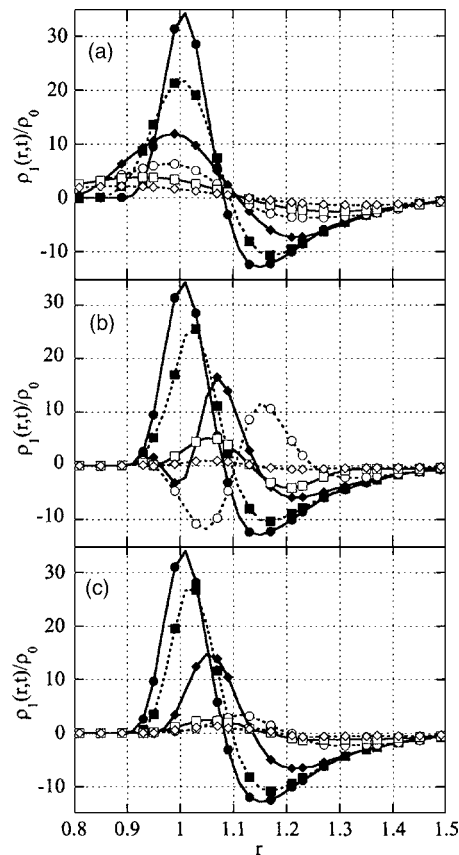


FIG. 6. The normalized response of the solvent to the translational displacement of the solute,  $\rho_1(r, t)/\rho_0$ , are plotted. (a)–(c) show the results of the surrogate theory, our present one, and the MD simulation, respectively. The times indicated by the symbols are the same as those in Fig. 1.

$$\begin{aligned} \bar{\rho}_k(\mathbf{k}, t) &\equiv \frac{1}{k_B T} \langle u(t=0) \delta \rho_k(\mathbf{k}, t) \rangle \\ &= \frac{1}{k_B T} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \langle u(t=0) \delta \rho(\mathbf{r}, t) \rangle, \end{aligned} \quad (47)$$

$$\delta \rho_k(\mathbf{k}, t) \equiv \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \delta \rho(\mathbf{r}, t). \quad (48)$$

Owing to the spherical symmetry of the system, the three-dimensional function  $\bar{\rho}(\mathbf{k}, t)$  is reduced to the one-dimensional one like Eq. (45) as

$$\bar{\rho}_k(\mathbf{k}, t) = \frac{k_z}{k} \rho_{1k}(k, t). \quad (49)$$

The functions shown in Fig. 7 correspond to the response of the solvent density to the translational diffusion of the solute in the reciprocal space we have shown in Fig. 3 of Ref. 22. It is to be noted here that  $\rho_{1k}(k, t)$  is purely imaginary, so that only the imaginary part is plotted in Fig. 7.

The negative peaks are found in Fig. 7 around  $k \sim 7$ , where the peak of the static structure factor of the solvent exists. Since the solvent fluctuation around this wave vector is large and its relaxation is slow, it is natural to find the large and slow response of the solvent density at this wave vector.<sup>15</sup> Quantitatively, the relaxation of the peak in the surrogate theory is slower than that in the MD simulation, in

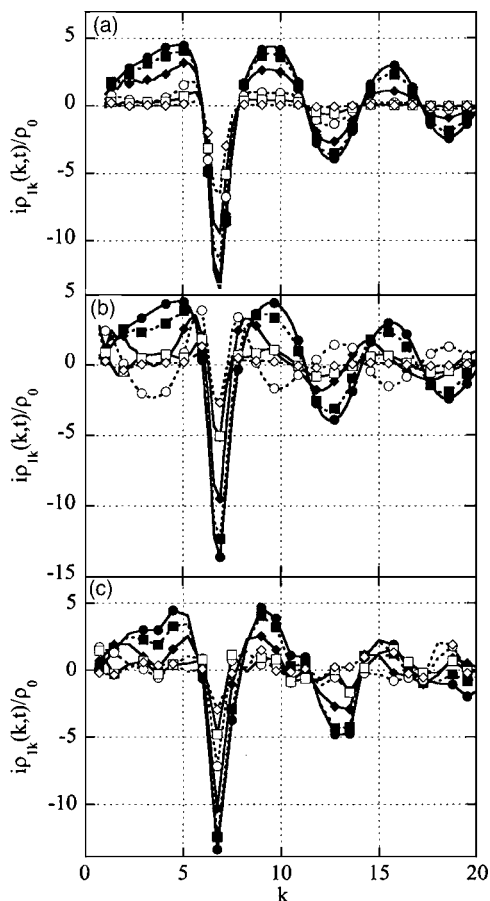


FIG. 7. The normalized response of the solvent to the translational displacement of the solute are plotted in the reciprocal space as  $i\rho_{1k}(k,t)/\rho_0$ . (a)–(c) show the results of the surrogate theory, our present one, and the MD simulation, respectively. The times indicated by the symbols are the same as those in Fig. 1.

harmony with the large amplitude of the long-time tail of  $\bar{u}(t)$  shown in Fig. 5. It is also consistent with the result of our previous work that the factorization approximation underestimates the relaxation rate of the peak of the density response to the translational diffusion of the solute.<sup>22</sup> On the other hand, the relaxation of the peak is reproduced well by our present study. Therefore it is safely said that, in addition to the short-time dynamics, the description of the relaxation of slow modes is also improved by our present theory compared with that of the surrogate one.

Figure 8 demonstrates  $\rho_1(r,t)$  at  $t=0.786$ . The results of the present theory and MD simulation agrees well. In contrast, the oscillation of the density response is overestimated and the solvent penetrates into the repulsive core of the solute in the surrogate theory. Therefore it can be seen also in the real-space response function that the present theory is good for the long-time dynamics of the solvent. The present theory includes explicitly the fluctuation of the solvent density around the solute, which forbids the fluctuation within the repulsive core of the solute. As a result, the amplitude of the soft mode of the solvent density around the solute will be also suppressed, which we consider is the reason for the fast relaxation of the solvent density around the solute compared with the surrogate theory.

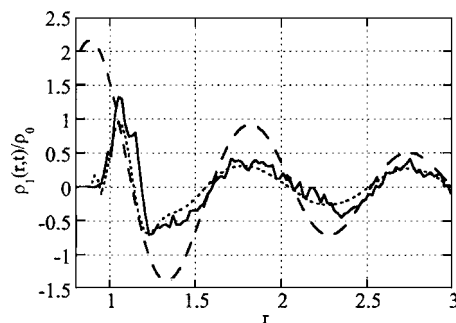


FIG. 8. The density responses of the solvent to the translational displacement of the solute at  $t=0.798$  obtained from the surrogate and present theories and the MD simulation are compared. The meanings of the lines are the same as those in Fig. 2.

## VI. SUMMARY

A theory on the time development of the solvent density under the external field is formulated based on the generalized Langevin formalism. An approximate expression for the two-body solvent density correlation function that appears in the generalized Langevin equation is given by the HNC integral equation theory. The expression of the force on molecules is physically transparent in that the force due to the potential of the mean force produced by the presence of the external field and the mean force from other molecules are divided. The memory function, which is the autocorrelation function of the random force, is approximated as that in the absence of the external field.

The theory developed here is applied to the solvation dynamics in the Lennard-Jones liquid near the triple point, regarding the solute-solvent interaction as the external field on the solvent. Three models are investigated, in which the change in the solute-solvent is different. In the first and second models, the attractive and repulsive parts, respectively, of the solute-solvent interaction change, while the solute is translationally displaced in the third one. In all the models, the present theory gives agreements with MD simulations better than the surrogate theory does. The agreement in the former two systems demonstrates the applicability of our theory to various systems, and that in the last model suggests that the present theory can be a basis to improve the mode-coupling theory for solute diffusion.

The agreement of the short-time part of the response function of the transition energy is almost perfect, in particular, in harmony with the consideration based on the short-time expansion. The long-time parts are also improved in our theory compared with the surrogate theory. However, the underdamped oscillation is imposed on the theoretical response function, which is found in the MD simulation only slightly. The oscillation of the response function reflects the oscillatory motion of the solvent within the first solvation shell of the solute, which in turn is attributed to the underestimation of the friction on solvent molecules there.

We are now trying to analyze the solute diffusion based on the present theory. In the conventional treatment of the memory function of the translational diffusion of a solute, the short- and long-time parts are handled in separate ways. The former, called “binary part,” is usually approximated as

a simple function as the Gaussian one, whose parameters are determined by the short-time expansion of the memory function. The mode-coupling approximation, which is similar to the surrogate theory for the solvation dynamics, is applied to the latter. In contrast, our theory has a potential ability to handle both the short- and long-time parts in a unified way. The short-time expansion will be satisfied by incorporating the solute-solvent-solvent three-body correlation function in an approximate way. The description of the long-time part will be improved upon the mode-coupling theory, since the present theory on the solvation dynamics is better than the surrogate theory in the long-time region, although an underdamped oscillation may appear in the memory function, whose effect on the diffusion coefficient will be rather small. In addition, our present theory satisfies the momentum conservation, and the coupling with the transverse current density is naturally incorporated, and the dynamics of the transverse current density reduces to the hydrodynamic Navier-Stokes equation at the position far from the solute. Since the momentum conservation and the coupling with the transverse current density are the origin of the hydrodynamic effect on the translational diffusion, we believe that our approach is suitable to treat the long-range hydrodynamic effects that are difficult to handle by molecular simulations.<sup>1,34,35</sup>

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