Nonlinear Langevin equations and the time dependent density functional method

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To study the time dependent density functional method (TDDFM), two streaming velocity (reversible) terms are reformulated in the nonlinear Langevin equation. Mori's [Prog. Theor. Phys. **33**, 423 (1965)] projection operator method shows a variety of nonlinear Langevin equations. This is because the equations depend on the choice of phase space functions employed in the projection. If phase space functions include particular functions, however, the streaming velocity term has an invariable form. The form is independent of the choice of other phase space functions. Since the invariable streaming velocity term does not introduce the TDDFM, the second viewpoint is presented. In this, the linearization of the streaming velocity term agrees with the frequency term in the linear Langevin equation. Since only the second streaming velocity term introduces the TDDFM, one needs to be cautious in the derivation of the TDDFM. [S1063-651X(99)10506-3]

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I. INTRODUCTION

Many authors have employed the time dependent density functional method (TDDFM) [1,2] to examine dynamical properties of classical liquids [2–10]. Linear [3–5] and nonlinear [5,6] TDDFM's have brought out a deep understanding of solvation dynamics. With the TDDFM, Araki and Munakata calculated shear viscosity and a self-diffusion constant [9]. In addition to normal liquids, the TDDFM has recently been applied to supercooled liquids or glass states [2,10].

Though the TDDFM has been extensively employed, few authors have studied its microscopic derivation [11]. The TDDFM was not developed from the Liouville equation that provides a microscopic basis. One cannot explain, in particular, the origin of the term including a free energy functional derivative in the basic equation of the TDDFM.

If the TDDFM is related to nonlinear generalized Langevin equations, one can microscopically derive it. This is because nonlinear generalized Langevin equations are derived from the Liouville equation. The nonlinear generalized Langevin equation is divided into three parts: the streaming velocity term, the memory term, and the random force. The streaming velocity term does not contribute to entropy production, so that it is also called the reversible term [12]. One can expect that the streaming velocity term causes the free energy functional term in the TDDFM, if the velocity and number densities are selected as the dynamical variables. Their relation, however, has not yet been established.

A nonlinear generalized Langevin equation has been formulated from the Liouville equation [13]. After Green [14] and Zwanzig [15] derived the Fokker-Planck equation, Mori and Fujisaka [13] have formulated the generalized nonlinear Langevin equation. Mori and Fujisaka projected the Liouville equation onto the δ functions of the dynamical variables. Their streaming velocity term was the same as that in the Fokker-Planck equation derived by Green [14] and Zwanzig [15].

One cannot establish the TDDFM from the nonlinear Langevin equation formulated by Mori and Fujisaka because of the difference in the definitions of free energy. Mori and Fujisaka formulated the free energy by the δ functions. On the other hand, the free-energy functional in the TDDFM is thermodynamically defined by the cumulant function or the fictional external fields [16–18]. The two kinds of free energy agree at the long-wavelength limit of fluctuations in density. Small-wavelength fluctuations in density, however, have a large difference.

The TDDFM is possibly established from other nonlinear Langevin equations than that derived by Mori and Fujisaka. This is because various kinds of projections lead to various nonlinear Langevin equations [19]. While Mori and Fujisaka employed projection onto the δ functions, one can also derive another Langevin equation from another kind of projection. For example, the projection onto the dynamical variables themselves leads to Mori's linear Langevin equation [20]. Thus the TDDFM is possibly related to other projections than that by Mori and Fujisaka.

In the relation between the TDDFM and nonlinear Langevin equations, the streaming velocity term plays an important role. The free energy definition in the TDDFM is different from that in the equation by Mori and Fujisaka. For the TDDFM, the free energy functional is included in the streaming velocity term, if the velocity and number densities are selected as the dynamical variables.

In addition, studying the streaming velocity term is important because one can exactly calculate the term from the microscopic viewpoint. The calculation of the streaming velocity term requires information only on equilibrium states, while the memory term and random force require a dynamical knowledge. This allows one to learn the form of the streaming velocity term definitely, though one can only approximately estimate the other two terms. Thus one needs to establish the microscopic derivation of the streaming velocity term for the application.

The purpose of the present study is to study the streaming velocity term in nonlinear Langevin equations to establish the microscopic derivation of the TDDFM. It focuses on the streaming velocity term corresponding to the TDDFM. In addition, a physical meaning is established for the difference between the streaming velocity term corresponding to the TDDFM and that derived by Mori and Fujisaka.

For the purpose, two streaming velocity terms are reformulated in nonlinear Langevin equations. The first streaming velocity term is formulated so that the form is independent of projection in Mori's identity if particular functions belong to the subspace (Sec. II). The streaming velocity term is the same as the term derived by Green [14], Zwanzig [15], and Mori and Fujisaka [13]. The second streaming velocity term is formulated so that its linearization agrees with the frequency term in the linear Langevin equation (Sec. III). The TDDFM is developed from the second streaming velocity term. The two streaming velocity terms agree at the thermodynamic limit.

II. INVARIABLE FORMS OF STREAMING VELOCITY TERMS

Mori's projection operator method shows that nonlinear generalized Langevin equations depend on the phase space functions employed in the projection. In the present study, the equations describe the time evolution of a set of dynamical variables, $\{X_i\}=\{X_1,\ldots,X_N\}$. Then the phase space functions are denoted by $\mathbf{A}=(X_1,\ldots,X_N,A_{N+1}(\{X_i\}),A_{N+2}(\{X_i\}),\ldots)$. Here $A_{N+j}(\{X_i\})$ is a function of $\{X_i\}$. By projecting the Liouville equation onto $\mathbf{A}$, one can derive generalized Langevin equations

$$\dot{X}_i=\sum_\alpha i\Omega_{i\alpha}A_\alpha-\sum_\alpha\int_0^t M_{i\alpha}(t-s)A_\alpha(s)ds+R_i(t), \tag{1a}$$

where $A_i=X_i$, $i=1,\ldots,N$. In Eq. (1a), one has

$$i\Omega_{i\alpha}=\sum_\beta\langle\dot{X}_iA_\beta\rangle(\mathbf{AA})^{-1}_{\beta\alpha}, \tag{1b}$$

$$M_{i\alpha}(t)=\sum_\beta\langle R_i(t)R_\beta(0)\rangle(\mathbf{AA})^{-1}_{\beta\alpha}, \tag{1c}$$

$$R_\alpha(t)=e^{QiLQt}QiLA_\alpha. \tag{1d}$$

Here $Q=1-P$, where P is the projection operator onto $\mathbf{A}$, and iL is the Liouville operator. In addition, $\langle\cdots\rangle$ is the average by the canonical ensemble, and $(\mathbf{AA})^{-1}$ is the inverse of the matrix with the element $\langle A_\alpha A_\beta\rangle$. Since $i\Omega_{i\alpha}$, $M_{i\alpha}(t)$, and $R_\alpha(t)$ are functionals of $\mathbf{A}$, they have different forms if one of $\{A_{N+j}(\{X_i\})\}$ is replaced by other functions. This shows that a variety of equations is possible because of the choice of $\{A_{N+j}(\{X_i\})\}$.

Furthermore, in the Markovian approximation, nonlinear Langevin equations also depend on the projection. If motions except $\mathbf{A}$ are slow enough, the Markovian approximation leads to

$$\dot{X}_i=\sum_\alpha i\Omega_{i\alpha}A_\alpha-\sum_\alpha L_{i\alpha}A_\alpha+R_i(t), \tag{2a}$$

where

$$L_{i\alpha}=\int_0^\infty M_{i\alpha}(t)dt \tag{2b}$$

is the transport coefficient. Since it is a functional of $\mathbf{A}$ again, the replacement of $\{A_{N+j}(\{X_i\})\}$ changes values of $L_{i\alpha}$.

In the nonlinear Langevin equations, one can establish an invariable form of the streaming velocity term if the phase space functions $\{A_{N+j}(\{X_i\})\}$ include particular ones. The invariable streaming velocity term does not change the form even if others of $\{A_{N+j}(\{X_i\})\}$ are replaced.

If the particular function and another arbitrary function are denoted by $f_i(\{X_i\})$ and $h(\{X_i\})$, then $\mathbf{A}=(X_i,f_i(\{X_i\}),h(\{X_i\}))$ and

$$i\Omega_{i\alpha}=\delta_{f_i,\alpha}. \tag{3}$$

Here $\delta_{f_i,\alpha}$ has the value of unity if α corresponds to $f_i(\{X_i\})$; otherwise its value is zero. Equation (3) shows that the streaming velocity term in Eqs. (1a) and (2a) is independent of changes in $h(\{X_i\})$.

Equation (3) provides the invariable form of the streaming velocity term. From Eq. (1b), Eq. (3) is rewritten as

$$\langle\dot{X}_iA_\alpha\rangle=\langle f_i(\{X_i\})A_\alpha\rangle. \tag{4}$$

When $A_\alpha=h(\{X_i\})$, the functional differentiation with respect to an arbitrary function, $h(\{x_i\})$, yields

$$\langle\dot{X}_i\delta(X-x)\rangle=f_i(\{x_i\})\langle\delta(X-x)\rangle, \tag{5}$$

where $\delta(X-x)=\Pi_i\delta(X_i-x_i)$. Thus, to satisfy Eq. (3), the function $f_i(\{x_i\})$ should have the following form:

$$f_i(\{x_i\})=\frac{\langle\dot{X}_i\delta(X-x)\rangle}{\langle\delta(X-x)\rangle}. \tag{6}$$

Equation (6) agrees exactly with the streaming velocity term obtained by Green [14], Zwanzig [15], and Mori and Fujisaka [13].

The invariable streaming velocity terms do not introduce the TDDFM. If the free energy functional is defined by $-k_BT\ln\langle\delta(X-x)\rangle$, Eq. (6) reduces to the reversible term in the TDDFM. For the TDDFM, however, the free energy functional is usually defined in a different manner.

One can also derive the invariable form of the other terms in the Langevin equation. Appendix A provides the details. The expressions closely agree with those in the generalized Langevin equation derived by Mori and Fujisaka [13].

III. STREAMING VELOCITY TERMS INTRODUCING THE TDDFM

One needs another viewpoint because the streaming velocity terms derived in Sec. II do not introduce the TDDFM. The viewpoint is that the linearized form of the streaming velocity term agrees with the frequency term in the linear Langevin equation. The linear Langevin equation is derived from the Liouville equation in only one manner, unlike the nonlinear generalized Langevin equation. Thus the viewpoint gives a definite form of the second streaming velocity term.

The viewpoint is formulated using the linear generalized Langevin equation [20] for $\delta X_i=X_i-\langle X_i\rangle$:

$$\delta\dot{X}_i=\sum_j i\omega_{i,j}\delta X_j-\sum_j \int_0^t \gamma_{i,j}(t-s)\delta X_j(s)ds+r_i. \quad (7)$$

Here $i\omega_{i,j}$, $\gamma_{i,j}(t)$, and r_i are the frequency term, the memory function and the random force in the linear generalized Langevin equation.

From the viewpoint, the second streaming velocity term is given by

$$i\omega_{i,j}=\frac{\partial}{\partial x_j}f_i(\{x_i\})|_{x_i=\langle X_i\rangle}. \quad (8)$$

Equation (8) shows that the integration of $i\omega_{i,j}$ yields $f(\{X_i\})$. Such a linearization principle never holds for the memory function or random force. The linearization of the terms does not agree with those in the linear Langevin equation. This is because both the linear and nonlinear generalized Langevin equations are exactly derived from the Liouville equation. The memory function or random force includes the nonlinear terms in the linear generalized Langevin equation [13].

To derive the second streaming velocity term, the extended Gibbs ensemble is introduced [21]. The integration of $i\omega_{i,j}$ in Eq. (8) needs changes in a value of the average, $\langle X_i\rangle$. To change the value, fictional external fields are employed as follows:

$$\langle X_i\rangle_\lambda\equiv\frac{\int X_i\exp\left[-\beta H+\sum_j \lambda_j X_j\right]d\Gamma}{\int \exp\left[-\beta H+\sum_j \lambda_j X_j\right]d\Gamma}. \quad (9)$$

Here $\beta=(k_BT)^{-1}$, where T is the temperature and k_B is Boltzmann's constant, H is the Hamiltonian, and $d\Gamma$ is the volume element in the phase space. In addition, the parameter, λ_i is the function of $\{x_i\}$ given by

$$x_i=\langle X_i\rangle_\lambda. \quad (10)$$

Equation (9) describes the extended Gibbs ensemble developed in Ref. [21]. The distribution corresponds to the maximal information entropy for average values given by Eq. (10). In the ensemble, the parameter λ_i has often been called the ''thermodynamic force,'' because it is associated with the gradient of free energy in

$$\lambda_i=\frac{\partial\beta F(\{x_i\})}{\partial x_i}, \quad (11)$$

where

$$F(\{x_i\})=-k_BT\left(\ln\int \exp\left[-\beta H+\sum_i \lambda_i X_i\right]d\Gamma\right)+k_BT\sum_i \lambda_i x_i. \quad (12)$$

is the free energy.

The extended Gibbs ensemble leads to the streaming velocity term. Attaching λ to the definition of $i\omega_{i,j}$, one has

$$i\omega_{i,j}=\sum_k \langle\delta\dot{X}_i\delta X_k\rangle_\lambda(\langle\delta X\delta X\rangle_\lambda)^{-1}_{k,j}, \quad (13)$$

where $(\langle\delta X\delta X\rangle_\lambda)^{-1}_{k,j}$ is element k, j of the inverse matrix of $\langle\delta X_i\delta X_j\rangle_\lambda$. In Eq. (13), the matrix, $\langle\delta\dot{X}_i\delta X_j\rangle_\lambda$, is rewritten as

$$\langle\delta\dot{X}_i\delta X_j\rangle_\lambda=\frac{\partial}{\partial\lambda_j}\langle\dot{X}_i\rangle_\lambda. \quad (14)$$

In addition, since the matrix, $\langle\delta X_i\delta X_j\rangle_\lambda$, is given by

$$\langle\delta X_i\delta X_j\rangle_\lambda=\frac{\partial\langle X_i\rangle_\lambda}{\partial\lambda_j}=\frac{\partial x_i}{\partial\lambda_j}, \quad (15)$$

the inverse is

$$(\langle\delta X\delta X\rangle_\lambda)^{-1}_{k,j}=\frac{\partial\lambda_k}{\partial x_j}. \quad (16)$$

The substitution of Eqs. (14) and (16) into Eq. (13) yields

$$i\omega_{i,j}=\frac{\partial}{\partial x_j}\langle\dot{X}_i\rangle_\lambda. \quad (17)$$

The integration provides

$$f_i(\{x_i\})=\langle\dot{X}_i\rangle_\lambda. \quad (18)$$

Equation (18) shows the streaming velocity term from the second principle.

The TDDFM is established by the second streaming velocity term. To establish the TDDFM, the velocity density $\mathbf{J}(\mathbf{r})=\Sigma_i\mathbf{v}_i\delta(\mathbf{r}_i-\mathbf{r})$ and the number density $\rho(\mathbf{r})=\Sigma_i\delta(\mathbf{r}_i-\mathbf{r})$ are considered, where $\mathbf{v}_i$ and $\mathbf{r}_i$ are the velocity and position of particle i. If $\{X_i\}=\{\mathbf{J}(\mathbf{r}),\rho(\mathbf{r})\}$, as shown in Appendix B, one has

$$\langle\dot{\mathbf{J}}(\mathbf{r})\rangle_\lambda=k_BT\int d\mathbf{r}'\langle\{\mathbf{J}(\mathbf{r}),\mathbf{J}(\mathbf{r}')\}_{\mathrm{PB}}\rangle_\lambda\frac{\delta\beta F}{\delta\mathbf{J}(\mathbf{r}')}+k_BT\int d\mathbf{r}'\langle\{\mathbf{J}(\mathbf{r}),\rho(\mathbf{r}')\}_{\mathrm{PB}}\rangle_\lambda\frac{\delta\beta F}{\delta\rho(\mathbf{r}')}. \quad (19)$$

Here $\{\ \}_{\mathrm{PB}}$ is the Poisson bracket and the free energy functional F is defined in the same manner as Eq. (12). Since $\langle\{\mathbf{J}(\mathbf{r}),\rho(\mathbf{r}')\}_{\mathrm{PB}}\rangle_\lambda=m^{-1}\nabla_{\mathbf{r}'}\rho(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, where m is the mass of the particle, one derives the hydrodynamic Langevin equations [1]

$$\dot{\mathbf{J}}(\mathbf{r})=-\frac{\rho(\mathbf{r})}{m}\nabla\frac{\delta F}{\delta\rho(\mathbf{r})}-\int d\mathbf{r}'\int_0^t G(\mathbf{r},\mathbf{r}',t-s)\mathbf{J}(\mathbf{r},s)ds+\mathbf{f}(\mathbf{r},t), \quad (20a)$$

$$\dot{\rho}(\mathbf{r})=-\nabla\cdot\mathbf{J}(\mathbf{r}). \quad (20b)$$

Here, the first term representing the advection in Eq. (19) was neglected. By the Markovian approximation and diffusive limit, Eqs. (20) reduce to the TDDFM including the random current [1]

$$\dot{\rho}(\mathbf{r})=D\boldsymbol{\nabla}\left\{\rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta F}{\delta\rho(\mathbf{r})}-m\mathbf{f}(\mathbf{r},t)\right\}. \tag{21}$$

The second streaming velocity term derived in the present section agrees asymptotically with that in Sec. II at the thermodynamic limit. The Fourier transformation for the δ function in Eq. (6) yields

$$\langle\dot{X}_i\delta(X-x)\rangle=\int_{-\infty}^{\infty}\Pi_i dk_i\left\langle\dot{X}_i\exp\left[i\sum_j k_j(X_j-x_j)\right]\right\rangle \tag{22a}$$

$$=\int_{-\infty}^{\infty}\Pi_i dk_i\langle\dot{X}_i\rangle_{ik}\exp\left[-i\sum_j k_jx_j-\beta\mathcal{F}(ik)\right], \tag{22b}$$

where

$$\exp[-\beta\mathcal{F}(ik)]=\frac{\int d\Gamma\,\exp\left[-\beta H+i\sum_j k_jX_j\right]}{\int d\Gamma\,\exp[-\beta H]}. \tag{22c}$$

The integral in Eq. (22b) is estimated by the saddle point method as follows [22]:

$$\langle\dot{X}_i\delta(X-x)\rangle\cong A\langle\dot{X}_i\rangle_\lambda\exp\left[-\sum_j \lambda_jx_j-\beta\mathcal{F}(\lambda)\right]. \tag{23}$$

Here the integral in Eq. (22b) was translated to an integral over the line $k_j=\lambda_j/i+\kappa_j$, where κ_j is real, through the standard contour integral methodology. The constant A is calculated from $\beta\partial^2\mathcal{F}/\partial\kappa_i\partial\kappa_j$. The pure imaginary saddle point λ/i is given by

$$\beta\frac{\partial\mathcal{F}(\lambda)}{\partial\lambda_i}=-x_i. \tag{24}$$

Equation (22c) shows that Eq. (24) is the same as Eq. (10). In the same manner as Eq. (23), one has

$$\langle\,\delta(X-x)\rangle\cong A\,\exp\left[-\sum_j \lambda_jx_j-\beta\mathcal{F}(\lambda)\right]. \tag{25}$$

From Eqs. (23) and (25), one can obtain

$$\langle\dot{X}_i\rangle_\lambda\cong\frac{\langle X_i\delta(X-x)\rangle}{\langle\,\delta(X-x)\rangle}. \tag{26}$$

One can employ the saddle point method only when $\mathcal{F}(\lambda)$ and x_i have sufficiently large values. If X_i is proportional to the particle number N, then $\mathcal{F}(\lambda)$ and x_i have large values at the large-number limit of particles ($N\to\infty$), because $\mathcal{F}(\lambda)\propto N$ in Eq. (22c). This limit is given by the thermodynamic limit.

IV. DISCUSSION

The analysis by the invariable form has revealed the physical meaning of the streaming velocity term obtained in previous study [13–15]. The physical meaning is that the streaming velocity term is obtained by the projection onto the subspace consisting of arbitrary functions of $\{X_i\}$. One can find it by the result that the streaming velocity term does not change though the phase space functions $\{A_\alpha\}$ in Eq. (1a) include arbitrary functions, $h(\{X_i\})$. This physical meaning is not surprising. Mori and Fujisaka obtained the term by the projection onto δ functions [13]. The projection onto the δ function is equivalent to that onto the arbitrary functions [19].

The physical meaning of the streaming velocity term shows that the invariable form is important for the Markovian approximation. In particular, the invariable streaming velocity term is superior to the frequency term in the linear Langevin equation. This is because $\{A_\alpha\}$ in Eq. (1a) include the arbitrary function $h(\{X_i\})$, while only $\{X_i\}$ themselves are selected in the linear Langevin equation. The Markovian approximation works well only when slow variables are selected as $\{A_\alpha\}$. Usually, if values of $\{X_i\}$ vary slowly, a value of an arbitrary function $h(\{X_i\})$ also varies slowly. Then the Markovian approximation is applicable only to the invariable streaming velocity term.

The second streaming velocity terms in Sec. III are linked with some phenomenological theories without the advantage in the Markovian approximation. In some phenomenological theories, the linearization of a nonlinear reversible term yields the frequency term in the linear Langevin equation. A good example is given by the hydrodynamic equations, such as the Navier-Stokes equation. The linearization of the hydrodynamic equations yields the linear Langevin equations [12]. This shows that the reversible terms in the hydrodynamic equations are obtained in the same manner as that in Sec. III.

The TDDFM does not have the advantage of the arbitrary-function projection in the same manner as other phenomenological theories. The free energy functional term in the TDDFM does not agree exactly with the invariable form of the streaming velocity term. However, Eq. (26) shows that the term approximates to the invariable form when density fluctuates on a large scale. This is because one can apply the saddle point method to the large-scale fluctuation including many particles. The term in the TDDFM for short-scale fluctuations, however, is different from the invariable form because they include only a few particles. Nevertheless, the TDDFM has been available for many dynamical properties of liquids even in small-scale fluctuations [2–9]. The reason for this has never been clear.

The second streaming velocity term can be formulated by a transport equation, though the present study treated it in the Langevin equation. Using the Kawasaki-Gunton projection operator, Zubarev, Morozov, and Röpke developed the same streaming velocity term as that from the second principle in the present study [21]. In addition, they also derived the irreversible term in the transport equation. In the Langevin equation with the second streaming velocity term, the memory function and random force will be discussed elsewhere [23].

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APPENDIX A: INVARIABLE FORMS OF THE IRREVERSIBLE TERM AND RANDOM FORCE

In this appendix, the invariable forms are established for the second and third terms on the right-hand side in Eq. (2a). First, equations similar to Eq. (3) are written for the transport coefficient and random force. These equations lead to the invariable form of the irreversible term. In addition, it is shown that the random force has an invariable form.

If $\{A_\alpha\}$ includes the new particular functions $g_i(\{X_i\})$ in addition to $f_i(\{X_i\})$, then for the irreversible term and random force one has

$$L_{i\alpha}=\delta_{g_i,\alpha}, \tag{A1a}$$

$$\frac{\delta R_i(t)}{\delta h(\{X_i\})}=0. \tag{A1b}$$

Here $\delta_{g_i,\alpha}$ has a similar definition as per $\delta_{f_i,\alpha}$. Equations (A1) show that the irreversible term and random force are independent of an arbitrary function, $h(\{X_i\})$.

Equations (A1) lead to the irreversible terms. Using Eqs. (1c) and (2b), Eq. (A1a) is rewritten as

$$\int_0^\infty dt\langle R_i(t)R_\alpha(0)\rangle=\langle g_i(\{X_i\})A_\alpha\rangle. \tag{A2}$$

When $A_\alpha=h(\{X_i\})$, the functional differentiation with respect to $h(\{x_i\})$ yields

$$g_i(\{x_i\})\langle\delta(X-x)\rangle=\int_0^\infty dt\left\{\left\langle\frac{\delta R_i(t)}{\delta h(\{x_i\})}R_h(0)\right\rangle+\left\langle R_i(t)\frac{\delta}{\delta h(\{x_i\})}iLh(\{X_i\})\right\rangle\right\}. \tag{A3}$$

Here $\langle R_i(t)QA\rangle=\langle R_i(t)A\rangle$ was employed, where A is an arbitrary operator. Then, using Eq. (A1b), one can obtain the irreversible term from Eq. (A3) by

$$g_i(\{x_i\})=\frac{1}{\langle\delta(X-x)\rangle}\int_0^\infty dt\langle R_i(t)iL\,\delta(X-x)\rangle \tag{A4a}$$

$$=\frac{1}{\langle\delta(X-x)\rangle}\int_0^\infty dt\sum_j\left\langle R_i(t)(iLX_j)\frac{\partial}{\partial X_j}\delta(X-x)\right\rangle \tag{A4b}$$

$$=-\frac{1}{\langle\delta(X-x)\rangle}\int_0^\infty dt\sum_j\frac{\partial}{\partial x_j}\langle R_i(t)(iLX_j)\,\delta(X-x)\rangle. \tag{A4c}$$

For the random force, Eq. (A1b) is satisfied, if $f_i(\{x_i\})$ is given by Eq. (6) and $M_{i\alpha}(t)=\delta(t)\,\delta_{\alpha,g}$. Since Eq. (6) satisfies Eq. (3), one has

$$R_i(0)=\dot{X}_i-f_i(\{X_i\}). \tag{A5}$$

Thus

$$\frac{\delta R_i(0)}{\delta h(\{x_i\})}=0. \tag{A6}$$

Next the time evolution of $\delta R_i(t)/\delta h(\{x_i\})$ is considered. From

$$\frac{\delta R_i(t)}{\delta h(\{x_i\})}=\frac{\delta}{\delta h(\{x_i\})}(e^{QiLQt}R_i(0)), \tag{A7a}$$

one has

$$\frac{d}{dt}\frac{\delta R_i(t)}{\delta h(\{x_i\})}=\frac{\delta}{\delta h(\{x_i\})}(QiLQ\,R_i(t)). \tag{A7b}$$

If $M_{i\alpha}(t)=\delta(t)\,\delta_{\alpha,g}$, then

$$QiLQ\,R_i(t)=iL\,R_i(t)+\delta(t)g_i(\{x_i\}). \tag{A8}$$

Thus

$$\frac{\delta}{\delta h(\{x_i\})}QiLQ\,R_i(t)=iL\frac{\delta R_i(t)}{\delta h(\{x_i\})}. \tag{A9}$$

The substitution of Eq. (A9) into Eq. (A7b) yields

$$\frac{d}{dt}\frac{\delta R_i(t)}{\delta h(\{x_i\})}-iL\frac{\delta R_i(t)}{\delta h(\{x_i\})}=0. \tag{A10}$$

From Eqs. (A10) and (A6), one can obtain Eq. (A1b).

The summation of these terms yields a nonlinear Langevin equation

$$\dot{X}_i = f_i(\{X_i\}) - g_i(\{X_i\}) + R_i(t). \tag{A11}$$

Here $f_i(\{X_i\})$ and $g_i(\{X_i\})$ are given by Eqs. (6) and (A4c).

APPENDIX B: DERIVATION OF TDDFM

This appendix gives the calculation of Eq. (19). Using the Poisson bracket,

$$\langle \dot{\mathbf{J}}(\mathbf{r}) \rangle_\lambda = \langle \{\mathbf{J}(\mathbf{r}), H\}_{\mathrm{PB}} \rangle_\lambda \tag{B1a}$$

$$= -\beta^{-1} \int d\Gamma \{\mathbf{J}(\mathbf{r}), \rho_e\}_{\mathrm{PB}} \exp\left[\sum_i \lambda_i X_i\right] \times \left\langle \exp\left[\sum_i \lambda_i X_i\right]\right\rangle^{-1}. \tag{B1b}$$

Here ρ_e is the distribution function in the canonical ensemble. The integration by parts yields

$$-\beta^{-1} \int d\Gamma \{\mathbf{J}(\mathbf{r}), \rho_e\}_{\mathrm{PB}} \exp\left[\sum_i \lambda_i X_i\right] \left\langle \exp\left[\sum_i \lambda_i X_i\right]\right\rangle^{-1} = k_B T \left\langle \left\{ \mathbf{J}(\mathbf{r}), \exp\left[\sum_i \lambda_i X_i\right]\right\}_{\mathrm{PB}} \right\rangle \left\langle \exp\left[\sum_i \lambda_i X_i\right]\right\rangle^{-1} \tag{B2a}$$

$$= k_B T \left\langle \left\{ \mathbf{J}(\mathbf{r}), \sum_i \lambda_i X_i \right\}_{\mathrm{PB}} \exp\left[\sum_i \lambda_i X_i\right] \right\rangle \left\langle \exp\left[\sum_i \lambda_i X_i\right]\right\rangle^{-1} \tag{B2b}$$

$$= k_B T \sum_i \lambda_i \langle \{\mathbf{J}(\mathbf{r}), X_i\}_{\mathrm{PB}} \rangle_\lambda \tag{B2c}$$

Substituting $\{X_i\} = \{\mathbf{J}(\mathbf{r}), \rho(\mathbf{r})\}$, one can obtain Eq. (19).

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