Time-dependent density-functional theory with H theorems

Toyonori Munakata
Department of Applied Mathematics and Physics, Kyoto University, Kyoto 606, Japan
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The density-functional theory, which is widely used to study static aspects of various phase transitions, such as a liquid-crystal and a glass transition, is generalized so that one can discuss the dynamical behavior of a density profile. The main emphasis is put on the H theorems and the nature of the random current in the Langevin diffusion equation.

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The density-functional theory (DFT) [1] has now become a useful tool to study quantitatively various phase transitions in condensed matter, such as freezing [2], the glass transition [3], and interface properties [4]. We note, however, that the DFT gives only static information on the (quasi)equilibrium density profile $n_{\rm eq}(\mathbf{r})$ and the related free energy $F_{\rm eq} \equiv F[n_{\rm eq}(\mathbf{r})]$, with $F[n(\mathbf{r})]$ denoting free-energy functional, a quantity of paramount importance in the DFT [1].

If we could introduce dynamics to the DFT, with $F[n(\mathbf{r})]$ as the only input to the dynamics, this would make it possible to study how the density $n(\mathbf{r};t)$ evolves in time starting from a given initial condition $n(\mathbf{r};t=0)$. It is to be expected that $n(\mathbf{r};t)$ will develop a density wave if the equilibrium phase is not a uniform liquid but a crystalline solid. However, it could also happen that $n(\mathbf{r};t)$ be trapped in a local minimum of $F[n]$ for a long time, thus enabling us to explore the dynamics and the details of the energy surface $F[n]$.

The purpose of this paper is first to make the DFT time dependent (TD) [5] and to open a way to study dynamical aspects of various transitions and interface properties, and secondly to discuss general properties of the TD-DFT. We first derive a Langevin diffusion equation and the corresponding Fokker-Planck (FP) equation for the distribution functional $f[n(\mathbf{r});t]$. A TD-DFT is required to satisfy the condition that the stationary distribution functional $P_{\rm st}[n(\mathbf{r})]$ to the FP equation should be proportional to $\exp\{-\beta F[n(\mathbf{r})]\}$ with $\beta=(k_B T)^{-1}$.

With this guiding principle in mind, let us start from the following (phenomenological) hydrodynamic equation for the density $n(\mathbf{r};t)$ and the momentum density $\mathbf{g}(\mathbf{r};t)$:

$$\partial n(\mathbf{r};t)/\partial t = -\nabla\cdot\mathbf{g}(\mathbf{r};t)/m \ , \tag{1}$$

$$\partial \mathbf{g}(\mathbf{r};t)/\partial t = -n(\mathbf{r},t)\nabla\delta F/\delta n(\mathbf{r};t) - \int d\mathbf{r}' \int_0^t dt' G(\mathbf{r},\mathbf{r}';t-t') \times \mathbf{g}(\mathbf{r}',t') + \mathbf{f}(\mathbf{r};t) \ , \tag{2}$$

where $-\nabla\delta F/\delta n(\mathbf{r};t)$ represents a generalized force on a particle at $\mathbf{r}$ [6] and the fluctuation-dissipation (FD) theorem expresses the damping matrix $G_{ij}(\mathbf{r},\mathbf{r}';t)=\Gamma(\mathbf{r},\mathbf{r}';t)\delta_{ij}$ in terms of the correlation function of the random forces

$$\langle f_i(\mathbf{r};t) f_j(\mathbf{r}';t')\rangle = F(\mathbf{r},\mathbf{r}';t-t')\delta_{ij}$$

as

$$\Gamma(\mathbf{r};\mathbf{r}';t)\delta_{ij} = \sum_k \int d\mathbf{r}'' F(\mathbf{r},\mathbf{r}'';t)\delta_{ik}\{\langle \mathbf{g}(\mathbf{r}'')\mathbf{g}(\mathbf{r}')\rangle^{-1}\}_{kj} \ . \tag{3}$$

The static momentum density correlation function is given by [7]

$$\langle g_i(\mathbf{r}) g_j(\mathbf{r}')\rangle = m k_B T \delta(\mathbf{r}-\mathbf{r}') n_{\rm eq}(\mathbf{r})\delta_{ij} \ . \tag{4}$$

Since the density field $n(\mathbf{r};t)$ is assumed to be the only relevant dynamical variable (order parameter) that changes slowly in time, the crucial step to derive the desired TD-DFT is that we replace the equilibrium density $n_{\rm eq}(\mathbf{r})$ in Eq. (4) by a time-dependent (nonequilibrium) $n(\mathbf{r};t)$. Thus inserting Eq. (4) with $n_{\rm eq}(\mathbf{r})$ replaced by $n(\mathbf{r};t)$ into Eq. (3) and assuming for simplicity

$$\Gamma(\mathbf{r},\mathbf{r}';t) = 2\Gamma_0\delta(\mathbf{r}-\mathbf{r}')\delta(t)$$

with Γ_0 a constant, we arrive at a modified FD theorem

$$\langle f_i(\mathbf{r};t) f_j(\mathbf{r}';t')\rangle = 2mk_B T\Gamma_0 n(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\delta_{ij} \ , \tag{5}$$

and Eq. (2) reduces to

$$\partial\mathbf{g}(\mathbf{r};t)/\partial t = -n(\mathbf{r},t)\nabla\delta F/\delta n(\mathbf{r};t) - \Gamma_0\mathbf{g}(\mathbf{r},t) + \mathbf{f}(\mathbf{r};t) \ . \tag{6}$$

Since we are interested in long time behavior, we employ an adiabatic approximation for Eq. (6), yielding

$$\mathbf{g}(\mathbf{r};t) = \{-n(\mathbf{r};t)\nabla\delta F/\delta n(\mathbf{r};t) + \mathbf{f}(\mathbf{r};t)\}/\Gamma_0 \ . \tag{7}$$

From Eqs. (7) and (1) we finally obtain the Langevin diffusion equation

$$\partial n(\mathbf{r};t)/\partial t = -\nabla\cdot\{-n(\mathbf{r};t)\nabla\delta F/\delta n(\mathbf{r};t) + \mathbf{f}(\mathbf{r};t)\}/(m\Gamma_0) \equiv -\nabla\cdot\{\mathbf{j}+\mathbf{j}_R\} \ , \tag{8}$$

with the FD theorem (5). $\mathbf{j}$ and $\mathbf{j}_R$ in Eq. (8) denote the systematic and the random current, respectively.

From the FD theorem (5) it is seen that the random current $\mathbf{j}_R(\mathbf{r};t) \equiv \mathbf{f}(\mathbf{r};t)/m\Gamma_0$ is a multiplicative noise [8] and one must specify how one interprets the noise. Here for our purpose it is to be treated as an Ito type noise. If we express the increment of $n(\mathbf{r})$ between t and $t+\Delta t$ by $\Delta n(\mathbf{r})$ we readily see from Eqs. (8) and (5) that

$$\langle \Delta n(\mathbf{r}) \rangle / \Delta t = -\nabla \cdot \mathbf{j}(\mathbf{r};t) \ ,$$
$$\langle \Delta n(\mathbf{r}) \Delta n(\mathbf{r}') \rangle / \Delta t = 2D(\nabla \cdot \nabla') n(\mathbf{r};t) \delta(\mathbf{r}-\mathbf{r}') \ , \quad (9)$$

with $D \equiv k_B T / m\Gamma_0$. Denoting by $f[n(\mathbf{r});t]$ the probability functional for the density field $n(\mathbf{r})$ at time t, the FP equation is given from Eq. (9) straightforwardly as

$$\partial f/\partial t = \int d\mathbf{r} [\delta/\delta n(\mathbf{r})] \{ f \nabla \cdot \mathbf{j}(\mathbf{r}) \} + D \int d\mathbf{r} \int d\mathbf{r}' [\delta^2 / \delta n(\mathbf{r}) \delta n(\mathbf{r}')] \times \{ f \nabla \cdot \nabla' n(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}') \} \ . \quad (10)$$

The second term on the right-hand side of Eq. (10) is

$$-D \int d\mathbf{r} [\delta/\delta n(\mathbf{r})] \nabla \cdot \int d\mathbf{r}' [\delta/\delta n(\mathbf{r}')] \times \{ f n(\mathbf{r}) \nabla \delta(\mathbf{r}-\mathbf{r}') \} \ .$$

Since

$$[\delta/\delta n(\mathbf{r}')] \{ f n(\mathbf{r}) \nabla \delta(\mathbf{r}-\mathbf{r}') \} = -n(\mathbf{r}) [\delta f / \delta n(\mathbf{r}')] \nabla' \delta(\mathbf{r}-\mathbf{r}')$$

and $\delta(\mathbf{r}) \nabla \delta(\mathbf{r}) = 0$, it holds that

$$[\delta/\delta n(\mathbf{r}')] \{ f n(\mathbf{r}) \nabla \delta(\mathbf{r}-\mathbf{r}') \} = -n(\mathbf{r}) [\delta f / \delta n(\mathbf{r}')] \nabla' \delta(\mathbf{r}-\mathbf{r}')$$

and

$$\int d\mathbf{r}' [\delta/\delta n(\mathbf{r}')] \{ f n(\mathbf{r}) \nabla \delta(\mathbf{r}-\mathbf{r}') \} = n(\mathbf{r}) \nabla \delta f / \delta n(\mathbf{r}) \ .$$

Thus we obtain from Eq. (10) the following FP equation:

$$\partial f / \partial t = -\int d\mathbf{r} [\delta / \delta n(\mathbf{r})] J(f) \ , \quad (11)$$

$$J(f) \equiv D \{ \beta f \nabla \cdot n(\mathbf{r}) \nabla \delta F / \delta n(\mathbf{r}) + \nabla \cdot n(\mathbf{r}) \nabla \delta f / \delta n(\mathbf{r}) \} \ . \quad (12)$$

When f is proportional to $\exp(-\beta F[n])$,

$$\nabla \cdot n(\mathbf{r}) \nabla \delta f / \delta n(\mathbf{r}) = \nabla \cdot n(\mathbf{r}) \{ -\beta f \nabla \delta F / \delta n(\mathbf{r}) \} = -\beta f \nabla \cdot n(\mathbf{r}) \nabla \delta F / \delta n(\mathbf{r}) \ ,$$

and we confirm that the stationary solution is given by $\exp(-\beta F)$. In other words, the Langevin diffusion equation (8) actually samples, in a steady state, the density field $n(\mathbf{r})$ according to the weight $\exp(-\beta F)$. Tracing our derivation of the FP equation (11) we notice that the replacement of $n_{\text{eq}}(\mathbf{r})$ by $n(\mathbf{r};t)$ in the FD theorem (5) and the Ito interpretation of the noise current $\mathbf{j}_R(\mathbf{r};t)$ are the important ingredients of a TD-DFT. This point will be discussed from a different viewpoint.

Next we turn to the H theorems satisfied by the FP equation (11). First we neglect the random current $\mathbf{j}_R$ and consider the diffusion equation

$$\partial n(\mathbf{r};t)/\partial t = \beta D \nabla \cdot n(\mathbf{r};t) \nabla \delta F / \delta n(\mathbf{r};t) = -\nabla \cdot \mathbf{j}(\mathbf{r};t) \ . \quad (13)$$

First H theorem. When the density field $n(\mathbf{r};t)$ evolves in time according to Eq. (13), $F[n]$ decreases in time until $\mathbf{j}(\mathbf{r};t)$ vanishes.

This is readily shown from

$$dF/dt = \int d\mathbf{r} [\delta F / \delta n(\mathbf{r};t)] \partial n(\mathbf{r};t) / \partial t = -\beta D \int d\mathbf{r} \{ \nabla \delta F / \delta n(\mathbf{r};t) \}^2 n(\mathbf{r};t) = -(\beta D)^{-1} \int d\mathbf{r} \{ \mathbf{j}(\mathbf{r};t) \}^2 / n(\mathbf{r};t) \le 0 \ . \quad (14)$$

When $\mathbf{j}(\mathbf{r};t)$ vanishes, we see that

$$\delta F / \delta n(\mathbf{r}) = \mu \ , \quad (15)$$

where μ is a constant. Equation (15) denotes the variational condition in the DFT to determine the equilibrium density field [1,2].

The free-energy functional can be expanded in terms of the (generalized) direct correlation function $C_k(\mathbf{r}_1, \ldots, \mathbf{r}_k)$ of a uniform reference liquid as [2]

$$\beta F[n] = \int dr\, n(\mathbf{r}) \{ \ln[n(\mathbf{r}) \Lambda^3] - 1 \} - \sum_{k=1}^{\infty} \int d\mathbf{r}_1 \cdots d\mathbf{r}_k \{ C_k(\mathbf{r}_1, \ldots, \mathbf{r}_k)/k! \} \times \{ n(\mathbf{r}_1) - n_l \} \cdots \{ n(\mathbf{r}_k) - n_l \} \ , \quad (16)$$

where Λ and n_l denote the thermal wavelength and the density of the reference liquid, respectively. From Eqs. (13) and (16) we obtain the so-called Vlasov-Smoluchowski equation [9]

$$\partial n(\mathbf{r};t)/\partial t = D \nabla^2 n(\mathbf{r};t) + \beta D \nabla \cdot n(\mathbf{r};t) \nabla \int d\mathbf{r}' v_{\text{eff}}(|\mathbf{r}-\mathbf{r}'|) \times n(\mathbf{r}';t) \ , \quad (17)$$

with the effective potential $v_{\text{eff}}(|\mathbf{r}-\mathbf{r}'|)$ given by

$$v_{\text{eff}}(|\mathbf{r}-\mathbf{r}'|) = -k_B T \sum_{k=2}^{\infty} \int d\mathbf{r}_3 \cdots d\mathbf{r}_k \{ C_k(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \ldots, \mathbf{r}_k)/(k-1)! \} \{ n(\mathbf{r}_3) - n_l) \} \cdots \{ n(\mathbf{r}_k) - n_l \} \ . \quad (18)$$

If we retain in Eq. (18) only the term with $k=2$, we obtain the widely used relation

$$v_{\text{eff}}(|\mathbf{r}-\mathbf{r}'|) = -k_B T C_2(\mathbf{r}, \mathbf{r}') \equiv -k_B T C(|\mathbf{r}-\mathbf{r}'|) \ ,$$

with $C(r)$ the two-body direct correlation function of a uniform liquid [2,7]. Equation (17) has been used to study dynamical properties of a supercooled liquid [9].

Now we turn to the full Langevin diffusion equation (8).

Second H theorem. When the distribution functional

$f[n;t]$ evolves in time according to the FP equation (11), the generalized free-energy functional $F_G[f]$ defined by

$$F_G[f]=\int DnF[n]f[n;t]+k_BT\int Dnf[n]\ln(f[n]) \quad (19)$$

decreases in time monotonically until $f[n;t]$ takes the form

$$f_{\rm st}[n]=\text{const}\times\exp[-F[n]/k_BT] . \quad (20)$$

We note that $\int Dn$ denotes the integration over the function space of $n(\mathbf{r})$. The theorem is proved as follows. From Eq. (19) we have

$$dF_G/dt=\int DnF[n]\partial f/\partial t+k_BT\int Dn(\partial f/\partial t)\ln(f) +k_BT(d/dt)\int Dnf[n;t] . \quad (21)$$

The last term on the right-hand side of Eq. (21) vanishes due to the conservation of probability. Now from the FP equation (11) we have

$$\begin{aligned} dF_G/dt&=\int Dn\int d\mathbf{r}\{F[n]+k_BT\ln(f)\}[\delta/\delta n(\mathbf{r})]\{f\nabla\cdot\mathbf{j}(\mathbf{r})-D\nabla\cdot n(\mathbf{r})\nabla\delta f/\delta n(\mathbf{r})\}\\ &=-\int Dn\int d\mathbf{r}\{\delta F/\delta n(\mathbf{r})+k_BTf^{-1}\delta f/\delta n(\mathbf{r})\}\{f\nabla\cdot\mathbf{j}(\mathbf{r})-D\nabla\cdot n(\mathbf{r})\nabla\delta f/\delta n(\mathbf{r})\} . \end{aligned} \quad (22)$$

The right-hand side of Eq. (22) consists of four parts, each of which is separately calculated and summed to give

$$dF_G/dt=-\int Dn\int d\mathbf{r}\{[k_BTf/Dn(\mathbf{r})]^{1/2}\mathbf{j}(\mathbf{r}) -[Dk_BTn(\mathbf{r})/f]^{1/2}\nabla\delta f/\delta n(\mathbf{r})\}^2\le 0 . \quad (23)$$

When the integrand of Eq. (23) is zero, we have Eq. (20). Comparing the two theorems it is seen that the noise $\mathbf{j}_R$ prevents the density field $n(\mathbf{r};t)$ from being trapped in a local minimum of the functional $F[n]$. That is to say, there can be many solutions to Eq. (15), which determines the (local) extremum of $F[n]$ [1–3].

Now we comment on the FD theorem (5) from the point of view of the internal noise, first proposed by Mikhailov [10]. In order to make the comparison easier, we take as the free-energy functional $F[n]$ that of the free gas with all the direct correlation functions C_k put equal to zero. Then from Eq. (16)

$$\beta F[n]=\int d\mathbf{r}\, n(\mathbf{r})\{\ln[n(\mathbf{r})\Lambda^3]-1\}$$

and the Langevin diffusion equation (8) and the corresponding FP equation (10) become

$$\partial n(\mathbf{r};t)/\partial t=D\nabla^2 n(\mathbf{r};t)-\nabla\cdot\mathbf{f}(\mathbf{r};t) , \quad (24)$$

$$\partial f[n;t]/\partial t=\int d\mathbf{r}[\delta/\delta n(\mathbf{r})]\{f\nabla^2 n(\mathbf{r})\} +D\int d\mathbf{r}\int d\mathbf{r}'[\delta^2/\delta n(\mathbf{r})\delta n(\mathbf{r}')] \times\{f\nabla\cdot\nabla' n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\} . \quad (25)$$

Now let us consider a hopping process of particles among a set of interconnected cells $j=0,\pm1,\ldots$ put on a linear chain. The microscopic state of the system is specified by a set of numbers n_j of the particles in the cell j. The master equation for the distribution function $f(\{n_j\};t)$ is given by

$$\partial f(\{n_j\};t)/\partial t=w\sum_j[(n_j+1)f(n_{j-1}-1,n_j+1) +(n_j+1)f(n_j+1,n_{j+1}-1) -2n_jf(\{n_j\})] , \quad (26)$$

where w denotes the hopping rate for one particle and the hopping is assumed only between the neighboring cells. If the occupation numbers $\{n_j\}$ are sufficiently large one can treat $\{n_j\}$ as a continuum and Eq. (26) is transformed to

$$\begin{aligned} \partial f/\partial t=&-w\sum_j(\partial/\partial n_j)[(n_{j+1}+n_{j-1}-2n_j)f]\\ &+(w/2)\sum_j(\partial^2/\partial n_j^2)[(n_{j+1}+n_{j-1}+2n_j)f]\\ &-(w/2)\sum_j(\partial^2/\partial n_j\partial n_{j-1})(2n_jf)\\ &-(w/2)\sum_j(\partial^2/\partial n_j\partial n_{j+1})(2n_jf) , \end{aligned} \quad (27)$$

where approximations like

$$f(n_{j-1}-1,n_j+1)=f-\partial f/\partial n_{j-1}+\partial f/\partial n_j +2^{-1}\partial^2 f/\partial n_j^2+2^{-1}\partial^2 f/\partial n_{j-1}^2 -\partial^2 f/\partial n_j\partial n_{j-1} \quad (28)$$

have been used. Mikhailov [10] shows that Eq. (27) is equivalent to the functional FP equation

$$\partial f/\partial t=-D\int dx[\delta/\delta n(x)](f\partial^2 n/\partial x^2) +D\int dx\, dx'[\delta^2/\delta n(x)\delta n(x')] \times\{f(\partial^2/\partial x\,\partial x')[n(x)\delta(x-x')]\} , \quad (29)$$

where D is the diffusion constant. Equation (29) is just the one-dimensional version of the FP equation (25) and the corresponding Langevin diffusion equation (A11) of Ref. [10] coincides with Eqs. (24) and (5). Thus the multiplicativeness of the noise, Eq. (5), which was obtained by modifying the equilibrium FD theorem, Eq. (4), can be interpreted based on the internal noise, which results from the atomistic nature of the constituent (diffusing) particles.

In concluding this paper we note that our discussion can be easily generalized to multicomponent systems. In fact, we recently [11] applied TD-DFT to the reference interaction site model, which has been formulated based on the DFT by Chandler, McCoy, and Singer [12].

[1] For reviews, see R. Evans, Adv. Phys. **28**, 143 (1979); A. D. J. Haymet, Annu. Rev. Phys. Chem. **38**, 89 (1987); Y. Singh, Phys. Rep. **207**, 351 (1991).

[2] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979); A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981); D. W. Oxtoby and A. D. J. Haymet, J. Chem. Phys. **76**, 6262 (1982).

[3] Y. Singh, J. P. Stoessel, and P. G. Wolynes, Phys. Rev. Lett. **54**, 1059 (1985); P. G. Wolynes, J. Non. Cryst. Solids **75**, 443 (1979).

[4] P. Harrowell and D. W. Oxtoby, J. Chem. Phys. **80**, 1639 (1984).

[5] Part of this paper is published in T. Munakata, J. Phys. Soc. Jpn. **58**, 2434 (1989).

[6] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).

[7] J. P. Hansen and I. R. MacDonald, *Theory of Simple Liquids* (Academic, New York, 1986).

[8] C. W. Gardner, *Handbook of Stochastic Methods* (Springer, Berlin, 1982).

[9] T. Munakata, J. Phys. Soc. Jpn. **43**, 1723 (1979); D. F. Calef and P. G. Wolynes, J. Chem. Phys. **78**, 4145 (1983).

[10] A. S. Mikhailov, Phys. Rep. **184**, 307 (1989).

[11] F. Hirata and T. Munakata (unpublished).

[12] D. Chandler, John D. McCoy, and Sherwin J. Singer, J. Chem. Phys. **85**, 5971 (1986); *ibid.* **85**, 5977 (1986).