

Time-dependent Density Functional Theory and Its Application to Liquid Dynamics*

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Abstract

The density functional theory for classical (equilibrium) statistical mechanics is generalised so that one can discuss various dynamical processes associated with density fluctuations in liquids. This is effected by deriving a Langevin-diffusion equation for the density field, which satisfies a novel H-theorem. As applications of our theory we consider density fluctuations in both supercooled liquids and molecular liquids, interface dynamics and transport coefficients.

1. Introduction

The density functional theory (DFT) (for reviews see Evans 1979; Haymet 1987; Oxtoby 1990; Singh 1991) has become a useful method to study a freezing transition from a quantitative standpoint. The crystal–liquid interface (Haymet and Oxtoby 1981; Oxtoby and Haymet 1982; Harrowell and Oxtoby 1987), nucleation (Harrowell and Oxtoby 1984; Grant and Gunton 1985) and a glass transition (Kirkpatrick and Wolynes 1989; Singh *et al.* 1985) are also investigated within the framework of the DFT. The DFT is now generalised to deal with complex systems such as molecular liquids (Chandler *et al.* 1986) and liquid crystals (Singh 1991).

It is to be noted that the DFT is basically concerned with the (quasi)equilibrium density profile $n_{\text{eq}}(\mathbf{r})$ and the corresponding free-energy $F_{\text{eq}} = F[n_{\text{eq}}(\mathbf{r})]$, where $F[n(\mathbf{r})]$ denotes the free-energy functional of the system and plays the central role in the DFT. If we could introduce dynamics to the DFT and follow time evolution of the density field $n(\mathbf{r}, t)$, this might enable us to study some dynamic aspects of the various processes mentioned above. In this paper we present time-dependent (TD) DFT together with some (preliminary) applications of the TD-DFT.

In Section 2 the DFT is briefly reviewed to make this paper self-contained and also to introduce some physical variables which play important roles in latter sections. In Section 3 we present a TD-DFT by deriving a Langevin-diffusion (L-D) equation for the density field $n(\mathbf{r}, t)$. Stochastic properties of the L-D equation are discussed with emphases put on an H-theorem. The close relation between the random current in the L-D equation and the ‘internal noise’, proposed

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by Mikhailov (1989) in connection with hopping diffusion, is presented. In Section 4 we consider, as applications of a TD-DFT, some dynamical processes such as density fluctuations in liquids, crystal-liquid interface dynamics and mass flow around a fixed particle to calculate transport coefficients of liquids. Section 5 contains a summary of this paper.

2. Density Functional Theory (DFT) and Phase Transitions

Let us start from the grand-canonical ensemble

$$f_G(\Gamma_N) = \exp\{-\beta(H_N - \mu N)\} / \Xi(\mu, T, V), \quad (1)$$

where $\beta \equiv 1/k_B T$, $\Gamma_N = \{\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N\}$ and V, μ and T denote volume, chemical potential and temperature respectively. The Hamiltonian H_N for an N -particle system is given by

$$H_N = \sum \mathbf{p}_i^2 / 2m + \sum_{i < j} \phi(r_{ij}) + \sum \phi_{\text{ext}}(\mathbf{r}_i) \equiv H_{N,0} + \sum \phi_{\text{ext}}(\mathbf{r}_i), \quad (2)$$

where $\phi_{\text{ext}}(\mathbf{r})$ denotes an external field and a two-body interaction is assumed for simplicity. The grand potential $\Omega_G(\mu, T, V)$ is obtained from the grand partition function Ξ ,

$$\Xi \equiv \Sigma(1/h^{3N} N!) \int d\Gamma_N \exp[-\beta(H_N - \mu N)] \equiv \text{Tr} \exp[-\beta(H_N - \mu N)], \quad (3)$$

by the relation

$$\Omega_G \equiv -k_B T \ln(\Xi) = -pV \quad (p = \text{pressure}). \quad (4)$$

The foundation of the DFT consists in the following two theorems (proofs are given in Hansen and McDonald 1986):

Theorem 1: Consider a functional

$$\Omega[f_0] \equiv \text{Tr} f_0 [H_N - \mu N + k_B T \ln(f_0)] \quad (5)$$

of a distribution f_0 . Then for an arbitrary f_0 , which satisfies the normalisation $\text{Tr} f_0 = 1$, $\Omega[f_0] \geq \Omega[f_G] = \Omega_G$.

Theorem 2: Consider an arbitrary density field $n(\mathbf{r})$. Then there exists a unique external field $\phi_{\text{ext}}(\mathbf{r})$, which produces the $n(\mathbf{r})$ by the relation

$$n(\mathbf{r}) = \text{Tr} f_G \sum_{i=0}^{i=N} \delta(\mathbf{r} - \mathbf{r}_i) \equiv \text{Tr} f_G n_M(\mathbf{r}). \quad (6)$$

Theorem 2 allows us to use a notation $\phi_{\text{ext}}(\mathbf{r}|n)$, expressing the fact that this external field is determined functionally by $n(\mathbf{r})$, and accordingly to define two density functionals,

$$F[n] \equiv \text{Tr} f_G (H_{N,0} + k_B T \ln(f_G)), \quad (7)$$

$$\Omega[n, \phi_{\text{ext}}] \equiv F[n] - \int d\mathbf{r} [\mu - \phi_{\text{ext}}(\mathbf{r})] n(\mathbf{r}). \quad (8)$$

We note first that the external field $\phi_{\text{ext}}(\mathbf{r})$ in f_G on the rhs of (7), see (1) and (2), is determined by (6) and $F[n]$ has nothing to do with $\phi_{\text{ext}}(\mathbf{r})$, even if the system of interest is under the influence of an external field. Secondly $\Omega[n, \phi_{\text{ext}}]$ is regarded as a functional of two independent functions $n(\mathbf{r})$ and $\phi_{\text{ext}}(\mathbf{r})$.

With these preparations we arrive at the following fundamental theorem:

Variational Principle: As a functional of $n'(\mathbf{r})$ with $\phi_{\text{ext}}(\mathbf{r})$ fixed, $\Omega[n', \phi_{\text{ext}}]$ is minimised for $n'(\mathbf{r}) = n(\mathbf{r})$ where $n(\mathbf{r})$ is related to $\phi_{\text{ext}}(\mathbf{r})$ by (6).

Proof: Suppose that an external field $\phi'_{\text{ext}}(\mathbf{r})$ and a density field $n'(\mathbf{r})$ satisfy the relation $\phi'_{\text{ext}}(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}|n')$ and that the grand ensemble f_G' is given by (1) with $\phi_{\text{ext}}(\mathbf{r})$ replaced by $\phi_{\text{ext}}(\mathbf{r}|n')$. Then using (5) and (7) $\Omega[f_G'] = \text{Tr} f_G' [H_{N,0} + \sum \phi_{\text{ext}}(\mathbf{r}_i) - \mu N + k_B T \ln(f_G')] = F[n'] + \int d\mathbf{r} n'(\mathbf{r}) [\phi_{\text{ext}}(\mathbf{r}) - \mu] = \Omega[n', \phi_{\text{ext}}]$. From theorem 1 we see that $\Omega[n', \phi_{\text{ext}}] \geq \Omega[f_G]$. However, it is readily seen that $\Omega[f_G] = \Omega[n, \phi_{\text{ext}}]$ and thus $\Omega[n', \phi_{\text{ext}}] \geq \Omega[n, \phi_{\text{ext}}]$.

From the variational principle, we obtain an equation to determine the equilibrium density profile $n_{\text{eq}}(\mathbf{r})$:

$$\frac{\delta \Omega[n, \phi_{\text{ext}}]}{\delta n(\mathbf{r})} = \frac{\delta F[n]}{\delta n(\mathbf{r})} - \mu + \phi_{\text{ext}}(\mathbf{r}) = 0. \quad (9)$$

We note that all the difficulties of a many-body problem are embedded in the free-energy functional $F[n]$ and there have been many methods already proposed (Oxtoby 1990). All the approaches divide $F[n]$ into an ideal gas part $F_{\text{id}}[n]$ and an interaction (excess) part $-\Phi[n]$, with F_{id} exactly given by

$$F_{\text{id}}[n] = k_B T \int d\mathbf{r} n(\mathbf{r}) [\ln(n(\mathbf{r})\Lambda^3) - 1], \quad (10)$$

with Λ the thermal wavelength $(h^2/2\pi m k_B T)^{1/2}$. Standard perturbational approaches employ a functional Taylor expansion around the uniform liquid state $n(\mathbf{r}) = n_L$, a constant,

$$\begin{aligned} \Phi[n] &= \sum (1/m!) \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_m \delta^m \Phi / \delta n(\mathbf{r}_1) \cdots \delta n(\mathbf{r}_m) |_{n_L} \\ &\quad \times (n(\mathbf{r}_1) - n_L) \cdots (n(\mathbf{r}_m) - n_L) \\ &\equiv k_B T \sum (1/m!) \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_m c_m(\mathbf{r}_1, \dots, \mathbf{r}_m) \\ &\quad \times (n(\mathbf{r}_1) - n_L) \cdots (n(\mathbf{r}_m) - n_L), \end{aligned} \quad (11)$$

which is usually truncated after $m = 2$ (Ramakrishnan and Yussouff 1979). In this case $F[n]$ takes the form

$$F[n] \approx F_{\text{id}}[n] - \{\Phi[n_L] + k_B T \int d\mathbf{r}_1 c_1[n(\mathbf{r}_1) - n_L] \quad (12)$$

$$+ (k_B T/2) \int d\mathbf{r}_1 \int d\mathbf{r}_2 c_2(|\mathbf{r}_2 - \mathbf{r}_1|)[n(\mathbf{r}_1) - n_L][n(\mathbf{r}_2) - n_L]\},$$

where use is made of the fact that for a uniform system c_1 is a constant and c_2 is a function of $|\mathbf{r}_2 - \mathbf{r}_1|$. It is not difficult to derive the relation between c_2 and the radial distribution function $g(r) = h(r) + 1$,

$$h(r) = c_2(r) + n_L \int d\mathbf{r}' h(r') c_2(|\mathbf{r} - \mathbf{r}'|). \quad (13)$$

Equation (13) is the familiar Ornstein–Zernike relation and hereafter we denote the direct correlation function $c_2(r)$ as $c(r)$. Inserting (12) into (9) we obtain, when there is no external field,

$$n_{\text{eq}}(\mathbf{r}) = \Lambda^{-3} \exp\{\beta\mu + c_1 + \int d\mathbf{r}_1 c(|\mathbf{r} - \mathbf{r}_1|)[n_{\text{eq}}(\mathbf{r}_1) - n_L]\}. \quad (14)$$

Since $n_{\text{eq}}(\mathbf{r}) = \Lambda^{-3} \exp\{\beta\mu + c_1\}$ is the trivial solution to (14), it is rewritten as

$$n_{\text{eq}}(\mathbf{r}) = n_L \exp\{\int d\mathbf{r}_1 c(|\mathbf{r} - \mathbf{r}_1|)[n_{\text{eq}}(\mathbf{r}_1) - n_L]\}. \quad (14')$$

If we could find some solutions to (14') [usually two, one representing a liquid phase $n_{\text{eq}}(\mathbf{r}) = n_L$ and the other a crystalline phase], we could calculate the grand potential based on (8) with $\phi_{\text{ext}}(\mathbf{r}) = 0$ and choose the solution $n_{\text{eq}}(\mathbf{r})$, which gives the smallest value for Ω , as representing the equilibrium phase. At the point where two solutions give the same Ω , namely the same pressure, the phase transition takes place. Of course, there are a lot of subtle points in the actual calculations and we refer to Haymet and Oxtoby (1986).

Finally we remark that non-perturbative approaches in the DFT attract considerable attention due to slow convergence of the expansion (11) (Tarazona 1985; Curtin and Ashcroft 1985; Denton and Ashcroft 1989).

3. Time-dependent Density Functional Theory (TD-DFT)

We now derive a Langevin-diffusion (L-D) equation for the density field $n(\mathbf{r}, t)$ and the corresponding Fokker–Planck (FP) equation for the distribution functional $f[n(\mathbf{r}), t]$, and discuss general properties of the TD-DFT (Munakata 1989, 1994). For the purpose let us start from the following phenomenological hydrodynamic equation for the density $n(\mathbf{r}, t)$ and the momentum density $\mathbf{g}(\mathbf{r}, t)$:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = \nabla \cdot \mathbf{g}(\mathbf{r}, t)/m, \quad (15)$$

$$\begin{aligned} \frac{\partial \mathbf{g}(\mathbf{r}, t)}{\partial t} = & -n(\mathbf{r}, t) \nabla \frac{\delta F}{\delta n(\mathbf{r}, t)} \\ & - \int d\mathbf{r}' \int_0^t dt' G(\mathbf{r}, \mathbf{r}', t - t') \mathbf{g}(\mathbf{r}', t') + \mathbf{f}(\mathbf{r}, t), \end{aligned} \quad (16)$$

where $-\nabla \delta F / \delta n(\mathbf{r}, t)$ represents a generalised force on a particle at $\mathbf{r}$ (Kirkpatrick and Wolynes 1987) 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 force $\langle f_i(\mathbf{r}, t) f_j(\mathbf{r}', t') \rangle = F(\mathbf{r}, \mathbf{r}', t - t') \delta_{ij}$ as

$$\Gamma(\mathbf{r}, \mathbf{r}', t) \delta_{ij} = \sum_k \int d\mathbf{r}'' F(\mathbf{r}, \mathbf{r}'', t) \delta_{ik} \{ \langle \mathbf{g}(\mathbf{r}'') \mathbf{g}(\mathbf{r}') \rangle^{-1} \}_{kj}. \quad (17)$$

The static momentum density correlation function is given by (Hansen and McDonald 1986)

$$\langle g_i(\mathbf{r}) g_j(\mathbf{r}') \rangle = m k_B T \delta(\mathbf{r} - \mathbf{r}') n_{\text{eq}}(\mathbf{r}) \delta_{ij}. \quad (18)$$

Since the density field $n(\mathbf{r}, t)$ is assumed to be the only 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 $n_{\text{eq}}(\mathbf{r})$ in (18) by a time-dependent (non-equilibrium) $n(\mathbf{r}, t)$. Thus inserting (18) with $n_{\text{eq}}(\mathbf{r})$ replaced by $n(\mathbf{r}, t)$ into (17) 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

$$\langle f_i(\mathbf{r}, t) f_j(\mathbf{r}', t') \rangle = 2m k_B T \Gamma_0 n(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \delta_{ij}, \quad (19)$$

and (16) reduces to

$$\frac{\partial g(\mathbf{r}, t)}{\partial t} = -n(\mathbf{r}, t) \nabla \frac{\delta F}{\delta n(\mathbf{r}, t)} - \Gamma_0 g(\mathbf{r}, t) + \mathbf{f}(\mathbf{r}, t). \quad (20)$$

Since we are interested in long time behaviour, we employ an adiabatic approximation for (20), yielding

$$g(\mathbf{r}, t) = \left(-n(\mathbf{r}, t) \nabla \frac{\delta F}{\delta n(\mathbf{r}, t)} + \mathbf{f}(\mathbf{r}, t) \right) / \Gamma_0. \quad (21)$$

From (21) and (15) we finally obtain the L-D equation,

$$\begin{aligned} \frac{\partial n(\mathbf{r}, t)}{\partial t} &= -\nabla \cdot \left(-n(\mathbf{r}, t) \nabla \frac{\delta F}{\delta n(\mathbf{r}, t)} + \mathbf{f}(\mathbf{r}, t) \right) / m\Gamma_0 \\ &\equiv -\nabla \cdot \{ \mathbf{j}_S + \mathbf{j}_R \}, \end{aligned} \quad (22)$$

with the FD theorem (19). Here $\mathbf{j}_S$ and $\mathbf{j}_R$ denote the systematic and the random current respectively. From the FD theorem (19) 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 (Gardiner 1982) and one must specify how one interprets the noise. Here for our purpose it is to be treated as an Ito type. Following a routine procedure (Gardiner 1982) to derive an FP equation from a Langevin equation, we see that the distribution functional $f[n(\mathbf{r}, t)]$ evolves in time, with $D \equiv k_B T / m\Gamma_0$, according to

$$\frac{\partial f}{\partial t} = -\int d\mathbf{r} \frac{\delta}{\delta n(\mathbf{r})} J(f), \quad (23)$$

$$J(f) \equiv D \left(\beta f \nabla \cdot n(\mathbf{r}) \nabla \frac{\delta F}{\delta n(\mathbf{r})} + \nabla \cdot n(\mathbf{r}) \nabla \frac{\delta f}{\delta n(\mathbf{r})} \right). \quad (24)$$

When f is proportional to $\exp(-\beta F[n])$, $\nabla \cdot n(\mathbf{r}) \nabla \delta f / \delta n(\mathbf{r}) = \nabla \cdot n(\mathbf{r}) \times \{-\beta f \nabla \delta F / \delta n(\mathbf{r})\} = -\beta f \nabla \cdot n(\mathbf{r}) \nabla \delta F / \delta n(\mathbf{r})$ and we confirm that the stationary solution is given by $\exp(-\beta F)$. In other words, the L-D equation (22) 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 (23) we notice that the replacement of $n_{\text{eq}}(\mathbf{r})$ by $n(\mathbf{r}, t)$ in the FD theorem (19) 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 later in this section.

General properties of the TD-DFT are most concisely represented by the following two H-theorems, the proofs of which are given in Munakata (1994). First we neglect the random current $\mathbf{j}_R$ and consider the diffusion equation

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = \beta D \nabla \cdot n(\mathbf{r}, t) \nabla \frac{\delta F}{\delta n(\mathbf{r}, t)} = -\nabla \cdot \mathbf{j}_S(\mathbf{r}, t). \quad (25)$$

First H-theorem: When the density field $n(\mathbf{r}, t)$ evolves in time according to (25), $F[n]$ decreases in time according to $dF/dt = -(\beta D)^{-1} \int d\mathbf{r} \{ \mathbf{j}_S(\mathbf{r}, t) \}^2 / n(\mathbf{r}, t) \leq 0$, until $\mathbf{j}_S(\mathbf{r}, t)$ vanishes, and it holds that $\delta F / \delta n(\mathbf{r}) = \mu$, representing the variational condition (9) in the DFT to determine the equilibrium density field for the case $\phi_{\text{ext}}(\mathbf{r}) = 0$.

Now we turn to the full L-D equation (22):

Second H-theorem: When the distribution functional $f[n, t]$ evolves in time according to the FP equation (23) the generalised free-energy functional $F_g[f]$ defined by

$$F_g[f] = \int Dn F[n] f[n; t] + k_B T \int Dn f[n] \ln(f[n]), \quad (26)$$

decreases in time monotonically according to

$$\begin{aligned} \frac{dF_g}{dt} = & - \int Dn \int d\mathbf{r} \{ (k_B T f / Dn(\mathbf{r}))^{\frac{1}{2}} \mathbf{j}_S(\mathbf{r}) \\ & - (Dk_B T n(\mathbf{r}) / f)^{\frac{1}{2}} \nabla (\delta f / \delta n \mathbf{r}) \}^2 \leq 0, \end{aligned} \quad (27)$$

until $f[n, t]$ takes the form

$$f_{\text{st}}[n] = \text{const.} \exp(-F[n] / k_B T). \quad (28)$$

We note that $\int Dn$ denotes the integration over the function space of $n(\mathbf{r})$. When the integrand of (27) is zero, we have (28). 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 (9) (Dasgupta and Ramaswamy 1992), which determines the (local) extremum of $F[n]$.

Finally we comment on the FD theorem (19) from the point of view of the internal noise, proposed by Mikhailov (1989). In order to make our discussion clearer, we take as the free-energy functional $F[n]$ the one for a free gas with all the direct correlation functions put equal to zero. Then the L-D equation (22) becomes

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \nabla^2 n(\mathbf{r}, t) - \nabla \cdot \mathbf{f}(\mathbf{r}, t). \quad (29)$$

Now let us consider, following Mikhailov, a hopping process of particles among a set of interconnected cells $j = 0, \pm 1, \dots$ 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

$$\begin{aligned}
\frac{\partial f(\{n_j\}; t)}{\partial t} = & w \sum_j [(n_j + 1)f(n_{j-1} - 1, n_j + 1) \\
& + (n_j + 1)f(n_j + 1, n_{j+1} - 1) \\
& - 2n_j f(\{n_j\})], \tag{30}
\end{aligned}$$

where w denotes the hopping rate for one particle, and the hopping is assumed only between neighbouring cells. If the occupation numbers $\{n_j\}$ are sufficiently large one can treat $\{n_j\}$ as a continuum and (30) is transformed to

$$\begin{aligned}
\frac{\partial f}{\partial t} = & -w \sum \partial / \partial n_j [(n_{j+1} + n_{j-1} - 2n_j)f] \\
& + \frac{1}{2}w \sum \partial^2 / \partial n_j^2 [(n_{j+1} + n_{j-1} + 2n_j)f] \\
& - \frac{1}{2}w \sum \partial^2 / \partial n_j \partial n_{j-1} (2n_j f) - \frac{1}{2}w \sum \partial^2 / \partial n_j \partial n_{j+1} (2n_j f), \tag{31}
\end{aligned}$$

where a continuum approximation like

$$\begin{aligned}
f(n_{j-1} - 1, n_j + 1) = & f - \frac{\partial f}{\partial n_{j-1}} + \frac{\partial f}{\partial n_j} + \frac{1}{2} \frac{\partial^2 f}{\partial n_j^2} \\
& + \frac{1}{2} \frac{\partial^2 f}{\partial n_{j-1}^2} - \frac{\partial^2 f}{\partial n_j \partial n_{j-1}} \tag{32}
\end{aligned}$$

has been used. Changing from a box j to a smooth x description, Mikhailov (1989) showed that (31) is equivalent to the (one-dimensional version of the) L-D equation (29) with the FD theorem (19). Thus the multiplicativeness of the noise (19), which was obtained by modifying the equilibrium FD theorem (18), can be interpreted based on the internal noise, which results from the atomistic nature of the constituent (diffusing) particles.

4. Applications of TD-DFT

In this section we apply TD-DFT developed in the previous section to study dynamic density fluctuations (4a), liquid-solid interface dynamics (4b) and transport coefficients (4c). In these studies the approximation (12) for the free-energy functional is employed since we have no reliable information on higher-order direct correlation functions $c_n(n \geq 3)$.

(4a) Dynamic Structure Factor

Inserting (12) with (10) into (22) we obtain the following L-D equation:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \nabla^2 n - D \nabla \cdot n(\mathbf{r}, t) \nabla \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) [n(\mathbf{r}', t) - n_L] - \nabla \cdot \mathbf{j}_R. \tag{33}$$

We note that the second term on the rhs describes a diffusion process, which is induced by the Vlasov field $V_F \equiv -k_B T \int d\mathbf{r}' c(|\mathbf{r}-\mathbf{r}'|)[n(\mathbf{r}', t)-n_L]$. Equation (33) with or without the random current (Munakata 1977, 1989), together with its generalisation to a two-component system (Bagchi 1987) and to polar liquids (Calef and Wolynes 1983; Hirata 1992), has played an important role and is now generally called a Smoluchowski–Vlasov equation. Here we calculate the dynamic structure factor (see e.g. Hansen and MacDonald 1986),

$$G(\mathbf{q}, t) = \langle n(\mathbf{q}, t) n(-\mathbf{q}, 0) \rangle / \langle n(\mathbf{q}) n(-\mathbf{q}) \rangle, \quad (34)$$

with $n(\mathbf{q}, t) \equiv \int d\mathbf{r} \{n(\mathbf{r}, t) - n_L\} \exp(-i\mathbf{q} \cdot \mathbf{r}) / N^{\frac{1}{2}}$, based on the nonlinear L-D equation (33). Fourier-transformation of (33) and the FD theorem (19) yields

$$\frac{\partial n(\mathbf{q}, t)}{\partial t} = -\gamma(\mathbf{q}) n(\mathbf{q}, t) + \sum_{\mathbf{k}} V(\mathbf{q}, \mathbf{k}) n(\mathbf{k}, t) n(\mathbf{q} - \mathbf{k}, t) + \xi(\mathbf{q}, t), \quad (35)$$

$$\langle \xi(\mathbf{q}, t) \xi(\mathbf{q}', t') \rangle = -2D\mathbf{q} \cdot \mathbf{q}' \delta(t - t') \{ \delta_{\mathbf{q}+\mathbf{q}', 0} + n(\mathbf{q} + \mathbf{q}', t) / N^{\frac{1}{2}} \}, \quad (36)$$

where $\gamma(\mathbf{q}) = Dq^2/s(\mathbf{q})$, with $s(\mathbf{q})$ denoting the static structure factor, $c(\mathbf{q}) = 1 - 1/s(\mathbf{q})$, and $V(\mathbf{q}, \mathbf{k}) = Dc(\mathbf{k})\mathbf{q} \cdot \mathbf{k} / N^{\frac{1}{2}}$. If we neglect the effects of both nonlinearity in (35) and the multiplicativeness of the noise, $n(\mathbf{q}, t)$ becomes a simple Ornstein–Uhlenbeck process (Gardiner 1986) and $G(\mathbf{q}, t)$ and the dynamic structure factor $G''(\mathbf{q}, w) = \frac{1}{2} \int dt G(\mathbf{q}, t) \exp(iwt)$ are given by

$$G_0(\mathbf{q}, t) = \exp[-\gamma(\mathbf{q})t] \quad \text{and} \quad G_0''(\mathbf{q}, w) = \gamma(\mathbf{q}) / [\gamma(\mathbf{q})^2 + w^2] \quad (37)$$

respectively, where the subscript 0 on G means that we regard it as the zeroth approximation to G .

In calculating $G(\mathbf{q}, t)$ based on (35) and (36), we follow a nonlinear theory of fluctuations by Mori and Fujisaka (1973). Referring the details of the calculation to Munakata (1990), we only give the final mode-coupling equation for $G(\mathbf{q}, t)$:

$$\frac{dG(\mathbf{q}, t)}{dt} = i\Omega(\mathbf{q}) G(\mathbf{q}, t) - \int_0^t ds \Psi(\mathbf{q}, t-s) G(\mathbf{q}, s), \quad (38)$$

where, under a decoupling approximation, $i\Omega(\mathbf{q}) = -\gamma(\mathbf{q})$ and

$$\Psi(\mathbf{q}, t) = \sum_{\mathbf{k}} W(\mathbf{q}, \mathbf{k}) G(\mathbf{k}, t) G(|\mathbf{q} - \mathbf{k}|, t), \quad (39)$$

with the vertex function of the form

$$W(\mathbf{q}, \mathbf{k}) = \frac{D^2}{Ns(\mathbf{q})} c(\mathbf{k}) \mathbf{q} \cdot \mathbf{k} \{ s(\mathbf{k})(q^2 - \mathbf{q} \cdot \mathbf{k}) - s(|\mathbf{q} - \mathbf{k}|)(q^2 s(\mathbf{k}) - \mathbf{q} \cdot \mathbf{k}) \}. \quad (40)$$

To calculate $G(\mathbf{q}, t)$ we use (38) where $\Psi(\mathbf{q}, t)$ is obtained from (39) with $G(\mathbf{k}, t)$ appearing on the rhs of (39) replaced by $G_0(\mathbf{k}, t)$ from (37). Thus, we avoid

the full-scale iteration calculation to obtain $G(q, t)$, as is often done in the mode-coupling calculation (Bosse and Munakata 1982).

Numerical calculation is performed for a hard sphere system characterised by a packing fraction $p = \pi\sigma^3 n_L/6$. The Percus-Yevick approximation is used to supply the structural information. If we choose $\tau \equiv \sigma^2/D$ and σ as the unit of time and length, respectively, the numerical results do not depend on D , a parameter in our theory. In Fig. 1, we compare $G_0''(q, w)$ and $G''(q, w)$ at $q\sigma = 1.25$ for various values of p . As p becomes large we observe a narrowing of the central peak, reflecting a slowing down of the density fluctuations due to nonlinear coupling in (35). At $p = 0.53$ a dynamic 'instability' occurs where the effective diffusion constant crosses zero. As is well known, the hard sphere system freezes at $p \approx 0.5$ and the DFT in its various versions, has been applied to study the transition (Haymet and Oxtoby 1986). It is interesting to note that the interaction part (11) of the free energy gives rise to the equilibrium transition on the one hand and it also gives rise to the instability through the nonlinear coupling in the L-D equation (35).

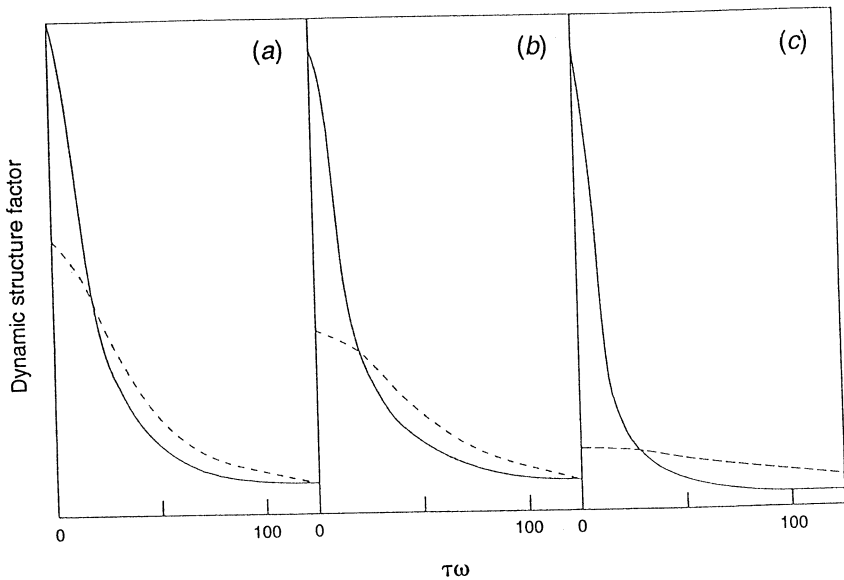


Fig. 1. Dynamic structure factor $G''(q, w)$ at $q\sigma = 1.25$ for the hard sphere system for (a) $p = 0.4$, (b) $p = 0.45$ and (c) $p = 0.5$. The dashed curves correspond to the linear approximation (37).

Before leaving this section we note that if we take the free-energy functional as given by Chandler *et al.* (1986) for molecular (polyatomic) liquids, we obtain from (22) a L-D equation for each of the atomic species constituting the molecules, which is very similar to (35). After linearisation as in (37), we obtain a linear diffusion equation, which was used by Hirata (1992) to investigate the dynamic structure factors of water.

(4b) Liquid-Solid Interface Dynamics

Recently (quasi)microscopic approaches to interface dynamics were initiated based on the DFT (Harrowell and Oxtoby 1987). Interest has been centred

around the interface velocity or growth rate v , which may depend on various factors such as the degree of supercooling, anisotropy, interface disorder, and so on. Time evolution of the order parameter(s) in the theory is usually assumed to be governed by a time-dependent Ginzburg–Landau (TD–GL) equation of the form

$$\frac{\partial \mu_i}{\partial t} = -\Gamma_i \frac{\delta H}{\delta \mu_i(\mathbf{r})}, \quad (41)$$

for a non-conserved order parameter and

$$\frac{\partial \mu_0}{\partial t} = \Gamma_0 \nabla^2 \frac{\delta H}{\delta \mu_0(\mathbf{r})} \quad (42)$$

for a conserved one. Usually one deals with either (41) or (42) depending on the problem at hand. However, as we show below, in the problem of liquid–solid interface dynamics, conserved and non-conserved order parameters are coupled to each other and thus give rather complicated problems.

Let us start from (14'), which is based on the approximate free-energy functional (12). Before proceeding to dynamics we first consider how the interface in an equilibrium state is dealt with, following Haymet and Oxtoby (1981) and Oxtoby and Haymet (1982). For a uniform solid, the density profile is assumed to be

$$n_s(\mathbf{r}) = n_L [1 + \mu_0 + \sum_{i>0} \mu_i \exp(i \mathbf{G}_i \cdot \mathbf{r})], \quad (43)$$

where $\mathbf{G}_i$ denotes the reciprocal lattice vector of the crystal and $\{\mu_i\}$ constitute the order parameters of the problem. At the transition point $\{\mu_i = \mu_{i,s}\}$, the difference in the grand potential $\Omega_S - \Omega_L \equiv k_B T n_L W(\{\mu_i\})$ becomes zero where

$$W(\{\mu_i\}) = (c_0 - 1)\mu_0 + c_0 \mu_0^2/2 + \sum_{i>0} c_i \mu_i^2 \quad (44)$$

and c_i denotes the Fourier transform of $c(r)$ at the wavevector $\mathbf{q} = \mathbf{G}_i$. Since $c_0 < 0$ and the density usually increases on freezing ($\mu_0 > 0$), the first two terms on the rhs are negative and the third one is positive since $c_i > 0$. If we consider a flat interface we assume that the parameters μ_i in (43) are slowly varying functions of z , which is perpendicular to the surface. If $z = \infty$ ($-\infty$) corresponds to a solid (liquid) phase we have $\mu_i(\infty) = \mu_{i,s}$ and $\mu_i(-\infty) = 0$. Under the circumstances, one applies a square gradient approximation, i.e.

$$\mu_i(z_1) \approx \mu_i(z) + \frac{\partial \mu_i}{\partial z} (z_1 - z) + \frac{1}{2} \frac{\partial^2 \mu_i}{\partial z^2} (z_1 - z)^2 \quad (45)$$

to the convolution integral in (14') to derive a coupled set of differential equations for $\{\mu_i(z)\}$. These equations are shown to be equivalent to the Lagrange variational equation for the interface free-energy functional

$$\Delta \Omega = n_L k_B T \int d\mathbf{r} \left\{ f(z) - \frac{1}{4} c_0'' \left(\frac{d\mu_0}{dz} \right)^2 - \sum_{i>0} c_i'' \alpha_i^2 \left(\frac{d\mu_i}{dz} \right)^2 \right\}, \quad (46)$$

where $f(z) = W(\{\mu_i\}) - \beta U_0(z)(1 + \mu_0) - \beta \sum_{i>0} U_i(z)\mu_i$, α_i is a direction cosine of $\mathbf{G}_i$ and the z -axis, and $c_0'' = dc_0/dq^2$. Here U_i , each function of $\{\mu_i\}$, represents the effective force necessary to stabilise the uniform crystal with order parameters $\{\mu_i\}$; thus for $\{\mu_{i,s}\}$ and $\{\mu_i = 0\}$, $\{U_i = 0\}$.

In order to deal with dynamical situations, we now generalise the order parameters to be a function of z and t . First, we linearise the L-D equation (22) and neglect the random current $\mathbf{j}_R$ to obtain $\partial n(\mathbf{r}, t)/\partial t = (n_L/m\Gamma_0)\nabla^2 \delta F/\delta n(\mathbf{r})$, and then use the functional (46) for F together with the identity

$$\frac{\delta F}{\delta n(\mathbf{r})} = n_L^{-1} \left(\frac{\delta F}{\delta \mu_0(\mathbf{r})} + \sum_{i>0} \frac{\delta F}{\delta \mu_i(\mathbf{r})} \exp(-i \mathbf{G}_i \cdot \mathbf{r}) \right) \quad (47)$$

to derive

$$\frac{\partial}{\partial t} \{ \mu_0 + \sum_{i>0} \mu_i \exp(i \mathbf{G}_i \cdot \mathbf{r}) \} = D \nabla^2 \{ A_0 + \sum_{i>0} A_i \exp(-\mathbf{G}_i \cdot \mathbf{r}) \}, \quad (48)$$

where $A_i \equiv \partial f/\partial \mu_i - |c_i''| \mu_i''/2$. Since A_i is a slowly varying function of z , we neglect ∇A_i compared with $\nabla \exp[i \mathbf{G}_i \cdot \mathbf{r}]$ and finally we arrive at the following coupled TD-GL equations for the conserved (μ_0) and non-conserved ($\mu_i, i > 0$) parameters:

$$\frac{\partial \mu_0}{\partial t} = D \frac{\partial^2 A_0}{\partial z^2}, \quad \frac{\partial \mu_i}{\partial t} = -D G_i^2 A_i. \quad (49)$$

Similar equations have been used to analyse the dynamics of the liquid-(bcc) solid interface by Harrowell and Oxtoby (1987).

(4c) Some Transport Coefficients

In this subsection we put a particle at the origin in a velocity field $\mathbf{u}(\mathbf{r})$ and study the effects of flow on a stationary density profile $n_{st}(\mathbf{r})$. When there is no flow $\mathbf{u}(\mathbf{r}) = \mathbf{0}$, $n_{st}(\mathbf{r})$ is obviously given by $n_L g(r)$, with $g(r)$ a radial distribution function. Due to the flow $\mathbf{u}(\mathbf{r})$, this equilibrium distribution is distorted and from the distortion we can calculate transport coefficients such as the viscosity and friction constant, as we show below.

We consider a one-component system and neglect random current $\mathbf{j}_R$ in (33) to obtain

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}_S(\mathbf{r}, t), \quad (50)$$

$$\mathbf{j}_S(\mathbf{r}, t) = -D \nabla n - \beta D n \nabla [\int d\mathbf{r}' v_{eff}(|\mathbf{r} - \mathbf{r}'|) n(\mathbf{r}', t) + \phi(r)] + n \mathbf{u}, \quad (51)$$

where $v_{eff}(r) = -k_B T c(r)$ and $\phi(r)$, the two-body interaction of equation (2), represents effects of the particle fixed at $\mathbf{r} = \mathbf{0}$. The last term on the rhs of (51) represents particle flow due to the velocity field $\mathbf{u}(\mathbf{r})$. We are interested in a stationary density profile $n_{st}(\mathbf{r})$ around the fixed particle.

First we consider the equilibrium solution $n_{eq}(\mathbf{r})$ when $\mathbf{u} = \mathbf{0}$. In this case the particle flow is $\mathbf{j}_S = \mathbf{0}$ and from (51) we readily obtain

$$\begin{aligned} \ln[g(r)] &\equiv \ln[n_{\text{eq}}(r)/n_L] \\ &= -\beta \int d\mathbf{r}' v_{\text{eff}}(|\mathbf{r} - \mathbf{r}'|) n_L [g(r') - 1] - \beta\phi(r), \end{aligned} \quad (52)$$

where the boundary condition $n_{\text{eq}}(\mathbf{r}) \rightarrow n_L$ as $r \rightarrow \infty$ is taken into account. From the relation (13) between h and c , we observe immediately that (52) is equivalent to the HNC equation to determine $g(r)$. Thus our theory, when applied to an equilibrium situation, gives the HNC result for $g(r)$ (Hansen and McDonald 1986).

Now let us turn to specific effects of the flow field $\mathbf{u}(\mathbf{r})$ on $n_{\text{st}}(\mathbf{r})$. We consider shear flow

$$\mathbf{u}(\mathbf{r}) = \gamma y \mathbf{e}_x, \quad (53)$$

where $\mathbf{e}_x$ denotes a unit vector in the x -direction. In this case we assume a solution of the form

$$n_{\text{st}}(\mathbf{r}) = n_L g(r) [1 + w(\mathbf{r})\gamma/D + O(\gamma)], \quad (54)$$

where $O(\gamma)/\gamma \rightarrow 0$. Inserting (54) into (50) with $\partial n/\partial t = 0$, we obtain

$$\begin{aligned} g \nabla^2 w - n_L g \nabla^2 \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) g(r') w(\mathbf{r}') + \nabla g \cdot \nabla w \\ - n_L \nabla g \cdot \nabla \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) g(r') w(\mathbf{r}') = xy g'(r)/r. \end{aligned} \quad (55)$$

With use of a Fourier transformation it is seen that (55) has a solution of the form

$$w(\mathbf{r}) = xy a(r), \quad (56)$$

and $a(r)$ satisfies a complicated integro-differential equation, which we do not write down here.

The final step to obtain the shear viscosity η is to calculate the xy component of the stress tensor σ_{xy} , which is expressed, on the one hand, in terms of η and γ as

$$\sigma_{xy} = \eta\gamma, \quad (57)$$

and also microscopically as (Evans and Morriss 1991)

$$\sigma_{xy} = (n_L/2) \int d\mathbf{r} n_{\text{st}}(\mathbf{r}) xy \phi'(r)/r, \quad (58)$$

where $\phi'(r) \equiv d\phi/dr$ and we have neglected the kinetic contribution, which is very small at a liquid density. Use of the solution (56) together with (57) and (58) gives

$$\eta = (n_L^2/2D) \int d\mathbf{r} (xy)^2 g(r) \phi'(r) a(r)/r. \quad (59)$$

If we fix a particle in a uniform flow $\mathbf{u}(\mathbf{r}) = u_0 \mathbf{e}_x$, we can calculate the friction constant ξ from a stationary force on a fixed particle by following similar lines of reasoning as above.

Our preliminary results for shear viscosity η of a soft-core system with $\phi(r) = \epsilon(\sigma/r)^{12}$ show that the main contribution in the integrand in (56) comes from the region $r \approx (V/N)^{1/3}$ (of course in the high-density state) and that η increases sharply as a function of $\rho^* \equiv (\epsilon/k_B T)^{1/4}(N\sigma^3/V)$. Although detailed analysis of η and ξ based on our TD-DFT needs some time to be completed, it seems that our approach is promising in view of the fact that we have at the moment no (microscopic) theory for η and ξ , especially for dense complex systems like water.

5. Summary

In this paper we have given a dynamic extension of the DFT, by deriving a L-D equation (22) with the fluctuation-dissipation theorem (19). We showed that the stochastic equation correctly samples the density field according to the probability $\exp\{-\beta F[n]\}$ in (28), based on the second H-theorem (27). At this point we note, however, that our TD-DFT is phenomenological and it is desirable to have a first-principles dynamics generalisation of DFT.

As applications of the TD-DFT, we considered density fluctuations in liquids, interface dynamics and transport coefficients. We are currently trying to solve the L-D equation in real space-time to study slow dynamics in supercooled liquids. This study may be considered a dynamic counterpart of the work by Dasgupta and Ramaswamy (1992), and as a similar attempt we mention the work by Lust and Valls (1993). We expect that our L-D equation has many fields of application. One example is dynamics in molecular liquids, as noted at the end of Section 4a, which is a very important field in connection with chemical reactions in solutions but, at the same time, is very complex to deal with from first principles.

References

- Bagchi, B. (1987). *Physica* **145A**, 273.
- Bosse, J., and Munakata, T. (1982). *Phys. Rev. A* **25**, 2676.
- Calef, D. F., and Wolynes, P. G. (1983). *J. Chem. Phys.* **78**, 4145.
- Chandler, D., McCoy, J. D., and Singer, S. J. (1986). *J. Chem. Phys.* **85**, 5971; 5977.
- Curtin, W. A., and Ashcroft, N. W. (1985). *Phys. Rev. A* **32**, 2909.
- Dasgupta, C., and Ramaswamy, S. C. (1992). *Physica A* **186**, 314.
- Denton, A. R., and Ashcroft, N. W. (1989). *Phys. Rev. A* **39**, 426.
- Evans, R. (1979). *Adv. Phys.* **28**, 143.
- Gardiner, C. W. (1982). 'Handbook of Stochastic Methods' (Springer: Berlin).
- Grant, M., and Gunton, J. D. (1985). *Phys. Rev. B* **32**, 7299.
- Hansen, J. P., and McDonald, I. R. (1986). 'Theory of Simple Liquids' (Academic: New York).
- Harrowell, P. R., and Oxtoby, D. W. (1984). *J. Chem. Phys.* **80**, 1639.
- Harrowell, P. R., and Oxtoby, D. W. (1987). *J. Chem. Phys.* **86**, 2932.
- Haymet, A. D. J. (1987). *Ann. Rev. Phys. Chem.* **38**, 89.
- Haymet, A. D. J., and Oxtoby, D. W. (1981). *J. Chem. Phys.* **74**, 2559.
- Haymet, A. D. J., and Oxtoby, D. W. (1986). *J. Chem. Phys.* **84**, 1769.
- Hirata, F. (1992). *J. Chem. Phys.* **96**, 4619.
- Kirkpatrick, T. R., and Wolynes, P. G. (1987). *Phys. Rev. A* **35**, 3072.
- Lust, L. M., and Valls, V. (1993). *Phys. Rev. E* **48**, 1787.
- Mikhailov, A. S. (1989). *Phys. Rep.* **184**, 307.
- Mori, H., and Fujisaka, H. (1973). *Prog. Theor. Phys.* **49**, 764.
- Munakata, T. (1977). *J. Phys. Soc. Jpn* **43**, 1723.
- Munakata, T. (1989). *J. Phys. Soc. Jpn* **58**, 2434.
- Munakata, T. (1990). *J. Phys. Soc. Jpn* **59**, 1299.

- Munakata, T. (1994). *Phys. Rev. E* **50**, 2347.
- Oxtoby, D. W. (1990). In 'Liquid, Freezing, and the Glass Transition' (Eds J. P. Hansen, D. Levesque and J. Zinn-Justin) (Elsevier: New York).
- Oxtoby, D. W., and Haymet, A. D. J. (1982). *J. Chem. Phys.* **76**, 6262.
- Ramakrishnan, T. V., and Yussouff, M. (1979). *Phys. Rev. B* **19**, 2775.
- Singh, Y. (1991). *Phys. Rep.* **207**, 351.
- Singh, Y., Stoessel, J. P., and Wolynes, P. G. (1985). *Phys. Rev. Lett.* **54**, 1059.
- Tarazona, P. (1985). *Phys. Rev. A* **31**, 2672.

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