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Markovian approximation and dynamic density functional theory for classical dense liquids

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A kinetic description of dense liquids is one of the long-standing problems in statistical mechanics. We apply here a well-known Markovian approximation to the Mori-Fujisaka nonlinear generalized Langevin equation. This enables us to derive systematically and without further approximations the Smoluchowski equation for an interacting many-body system and the dynamic density functional theory (DDFT), which are playing important roles for the glass transition and dynamics in supercooled liquids. The free energy functional in our DDFT may be termed microcanonical as compared with the grand-canonical one widely used in the equilibrium theory of liquids.

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\[ \Psi(t) = (\hat{R}(t), \hat{R}) \cdot (\hat{A}, \hat{A})^{-1}. \] (5)

The MA to the GLE (1) consists in

\[ \Psi(t) = \Psi(0) \tau \delta(t), \] (6)

where it is assumed that the kernel \( \Psi(t) \) decays to zero rapidly in time \( \tau \), which may be small in the time scale of \( \hat{A} \). [See the lines below Eq. (11) for more details.] It is important to notice that \( \Psi(0) \) is an equilibrium quantity which can be calculated in principle exactly. As examples, we first take the velocity autocorrelation function (VAF) \( \Phi(t) = \langle v_x(t), v_x(0) \rangle \) of a Brownian particle put in a liquid. Here \( v_x \) is the \( x \) component of the velocity of the particle. Taking \( A = v_x \), we have from Eq. (1)

\[ d\Phi(t)/dt = -\int_0^t ds \Psi(t-s)\Phi(s), \] (7)

which, under the MA, gives an exponential VAF

\[ \Phi(t) = \exp[-\tau \Psi(0)] \Phi(0) \exp[-\tau \Psi(0)] \langle \frac{1}{2} k_B T/m \rangle \] with \( k_B \) and \( m \) the Boltzmann constant and the mass of the Brownian particle, respectively. In this case \( \Psi(0) = \omega^2 \) where \( \omega \) represents the so-called Einstein frequency with which the Brownian particle oscillates in the sea of the surrounding particles [4].

As a second example, we take the incoherent scattering function, for which we choose \( A = n_0(q) \exp[iq \cdot r_0] \) with \( r_0 \) denoting the position of a tagged particle and \( \Phi_q(t) = n_0(q) \). The MA (6) gives \( \Psi(t) = (q^2 k_B T/\pi m) \delta(t) = q^2 D \delta(t) \) and

\[ \Phi_q(t) = \exp[-q^2 D t], \] (8)

which is the well-known result from the diffusion approximation, which is valid for small \( q \) [4,5].

Although these types of the MA are used widely in studies of the dynamics in liquids, we notice that the information from the MA is rather limited in the sense that MA cannot present relaxation mechanism behind the exponential correlation functions. In order to overcome this situation, we consider the nonlinear version of the GLE (1), NGLE [2], which is equivalent to the mode-coupling equation expanded to in-
finite order [2.6]. As in the GLE we are interested in the dynamics of the variable $\hat{A}$, but in the NGLE we consider the distribution of $\hat{A}$, microscopically defined by

$$\hat{g}(a) = \delta(\hat{A} - a) = \prod_{i=1}^{K} \delta(\hat{A}_i - a_i).$$

(9)

We notice that $\hat{g}(a)$, now characterized by a continuous parameter $a$, is equivalent to the collection of all the powers of $\hat{A}$. Using the similar projection technique as used in deriving Eq. (1), one can easily arrive at the following NGLE:

$$d\hat{g}(a,t)/dt = \int da' \left[ \sum_{a'} \hat{\Psi}[a,a',t - s] \cdot \hat{g}(a',s) \right] + \hat{\mathbb{R}}(a,t).$$

(10)

The evolution equation for the distribution function $g(a,t)$ of $\hat{A}$ is obtained by taking the average of Eq. (10) over an (non-equilibrium) initial distribution in the phase space, which results in Eq. (10) without the random force $\hat{\mathbb{R}}(a,t)$ for rather general class of the initial ensemble and we call this equation hereafter the Fokker-Planck (FP) equation for $g(a,t)$. As Eq. (6), the MA to the NGLE consists in assuming that

$$\Psi[a,a',t] = \Psi[a,a',0] \tau(\hat{t}).$$

(11)

Within the idea of the mode-coupling theory, this $\tau$ can be assumed to be less sensitive to the thermodynamic state and to be smaller in the time scale of the (slow) variables $\hat{A}$ as compared with the $\tau$ in Eq. (6). As exemplified below [see Eqs. (17) and (36)], $\tau$ could be absorbed in the time scale of the resulting equation because usually the first term on the right-hand side of Eq. (10) vanishes. In order to avoid further approximation, one has to calculate $\Psi[a,a',0]$ exactly, which gives some important information on the dynamics through its dependence on $a$ and $a'$. Before going into our main problem of the dynamic density functional theory (DDFT), we first consider the case of Brownian motion in a (solvent) liquid, which is described by the Hamiltonian of the general form

$$H = H_B + H_{\text{solv}} + H_{\text{int}},$$

(12)

where $H_{\text{solv}}$ and $H_{\text{int}}$ denote the Hamiltonian of the solvent particles and the interaction between the Brownian particle(s) and the solvent, respectively, whose explicit form we do not need below. For the Hamiltonian of the $N$ Brownian particles $H_B$ we take the following:

$$H_B = \sum_{i=1}^{N} \left[ \hat{p}_i^2/(2m) + V(\hat{r}_i) \right] + \sum_{i<j} \phi(\hat{r}_{ij}),$$

(13)

where $V(\hat{r}_i)$ is the external field in which Brownian particle is put and $\phi(\hat{r}_{ij})$ is the interaction of the two Brownian particles at $\hat{r}_i$ and $\hat{r}_j$ with $\hat{r}_{ij} = \hat{r}_i - \hat{r}_j$. Let us choose as $A$ the $N$ position vectors $A = \{\hat{r}_1, \hat{r}_2, \ldots, \hat{r}_N\}$ and from Eq. (9),

$$\hat{g}(r) = \hat{g}(r_1, r_2, \ldots, r_N) = \delta(\hat{r}_1 - r_1) \cdots \delta(\hat{r}_N - r_N).$$

(14)

We easily have

$$(\hat{g}(r), \hat{g}(r')) = g\exp(-r / (k_B T)) \delta(r - r').$$

(15)

Here, $g(r) = \exp[-F(r)/(k_B T)]/Z$ denotes the equilibrium distribution function of the Brownian particles with the microcanonical free energy defined by $F(r) = -k_B T \ln \left[ \exp(-H(k_B T)) / \mathcal{D} \right]$, which is the volume element of the whole phase space. From $d\hat{g}(r)/dt = -\Sigma_j (p_j / m) \cdot \nabla \hat{g}(r)$, it is seen that $i\Omega = 0$ in Eq. (10) and

$$(d\hat{g}(r)/dt, d\hat{g}(r')/dt) = (m / k_B T)(\nabla \cdot \nabla \hat{g})(r, r').$$

(16)

From the MA, Eq. (11), we finally have

$$\partial g(r,t)/\partial t = D \sum_i \nabla \cdot \nabla \hat{g} + \beta g \nabla V(r).$$

(17)

This equation is usually called the Smoluchowski equation and

$$D = (k_B T / m) \tau.$$  

(18)

We make here two remarks. First, in the case of $N=1$ (single Brownian particle), we have

$$d\hat{g}(r,t)/dt = D \nabla \cdot \nabla \hat{g} + \beta g \nabla V(r),$$

(19)

which plays an important role in the theory of Brownian motion and chemical reaction [7,8]. Second, starting from Eq. (17) without an external field, Szamel and Loh and [9] derived a mode-coupling equation, which represents the long-time limit of the mode-coupling theory for glass transition [10]. Let us now turn to the DDFT, which was first derived [11] based on the equilibrium or grand-canonical DFT [12] combined with a nonequilibrium idea presented in Ref. [13]. It is interesting to note that the same dynamic equation, but with different definition for the free energy functional $F[n(r)]$ from the grand-canonical DFT, is obtained from the MA.

We first divide our $d$ dimensional system with the volume $L^d$, described by the Hamiltonian (12), into the $N^d$ cells $\alpha, \alpha = 1, \ldots, N_c$, centered at $r_\alpha$, each with the volume $\Omega = a^d$ where $N_c = L^d/a$. The quantity of our interest $A$ is now the coarse grained or average density of the cell,

$$\hat{\rho}(r) = \int_a d\hat{\rho}(r)/\Omega,$$

(20)

where the microscopic density is defined by

$$\hat{n}(r) = \sum_{i=1}^{N} \delta(\hat{r}_i - r).$$

(21)

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Thus our problem is to apply the MA to the NGLE (10) for the microscopic probability of the density field \{\rho(\mathbf{r}_a)\}:

\[ \hat{g}[\rho] = \prod_a \delta(\rho(\mathbf{r}_a) - \rho(\mathbf{r}_a)). \]  

(22)

The calculation procedure, although a little more cumbersome, is basically the same as the one for the Smoluchowski equation.

First we note that

\[ \langle \hat{g}[\rho], \hat{g}[\rho'] \rangle = g_{eq}(\rho) \prod_a \delta(\rho(\mathbf{r}_a) - \rho'(\mathbf{r}_a)), \]  

(23)

where the equilibrium distribution function \( g_{eq}(\rho) \) is defined with use of the canonical distribution for the total system \( P_{eq}(\Gamma) \propto \exp[-\beta F] \) as

\[ g_{eq}(\rho) = \int d\Gamma \hat{g}[\rho] P_{eq}(\Gamma) = \langle \hat{g}[\rho] \rangle = \exp(\beta F - \beta F[\rho]), \]  

(24)

where

\[ F[\rho] = - (1/\beta) \ln \int d\Gamma \hat{g}[\rho] \exp[-\beta H] = - (1/\beta) \ln \mathcal{Z}[\rho], \]  

(25)

and \( F \) in Eq. (24) denotes the free energy of the system which normalizes \( g[\rho] \).

From the Hamilton’s equation of motion, it is seen that

\[ \frac{d\hat{g}[\rho]}{dt} = \sum_a (\hat{\partial}\hat{g}[\rho] / \partial \rho(\mathbf{r}_a)) \times \frac{1}{\Omega} \int d \mathbf{r} \sum_{\alpha} (p_\alpha / m) \mathbf{\nabla}_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_\alpha). \]  

(26)

The frequency matrix \( i\Omega \) in Eq. (10) vanishes due to the Gaussian property of the canonical distribution in momenta. To implement the MA it is necessary to calculate

\[ K[\rho, \rho'] = (\hat{d} \hat{g}[\rho] / \partial t, \hat{d} \hat{g}[\rho'] / \partial t), \]  

(27)

which is expressed from Eq. (26) as

\[ K[\rho, \rho'] = \left( \sum_a \hat{\partial} \hat{g}[\rho] / \partial \rho(\mathbf{r}_a) \right) \left( \sum_{\beta} \hat{\partial} \hat{g}[\rho] / \partial \rho(\mathbf{r}_\beta) \right) M, \]  

(28)

where

\[ M = (k_B T/m)(1/\Omega^2) \int d\mathbf{r} \int d\mathbf{r}' \mathbf{\nabla}_{\mathbf{r}} \hat{n}(\mathbf{r}) \cdot \mathbf{\nabla}_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}'). \]  

(29)

In order to express \( M \) in terms of the average density \( \{\rho(\mathbf{r}_a)\} \), we first introduce Fourier transformation by

\[ f(\mathbf{q}) = (1/L^d) \int d\mathbf{r} \hat{f}(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}). \]  

(30)

and obtain

\[ M = (k_B T/m)(1/L^d \Omega^2) \sum_{\mathbf{q}, \mathbf{q}'} \hat{n}(\mathbf{q}) \langle \mathbf{q} + \mathbf{q}' \rangle \cdot \hat{n}(\mathbf{q}) \int d\mathbf{r} \int d\mathbf{r}' \exp[-i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{r} + i\mathbf{q}' \cdot \mathbf{r}']. \]  

(31)

In the integration of Eq. (31), the new integration variables \( \mathbf{x} \) and \( \mathbf{y} \) are defined by \( \mathbf{r} = \mathbf{r}_a + \mathbf{x} \), \( \mathbf{r}' = \mathbf{r}_\beta + \mathbf{y} \), and we obtain

\[ M = (k_B T/m)(1/L^d \Omega^2)(\nabla_{\mathbf{r} a} \cdot \nabla_{\mathbf{r} \beta}) \sum_{\mathbf{q}, \mathbf{q}'} \hat{n}(\mathbf{q}) \times e(\mathbf{q} + \mathbf{q}') e(q') \exp[-i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{r}_a + i\mathbf{q}' \cdot \mathbf{r}_\beta], \]  

(32)

where \( e(q) \) is the Fourier transformation of the form factor \( e(r) \), which takes the value one in the cell centered at the origin \( (\mathbf{r}_a = 0) \) and zero outside of it. Inverse Fourier transformation yields the following concise form

\[ M = (k_B T/m)(1/\Omega)(\nabla_{\mathbf{r} a} \cdot \nabla_{\mathbf{r} \beta}) \hat{\rho}(\mathbf{r}_a) \delta(\mathbf{r}_a - \mathbf{r}_\beta), \]  

(33)

which in combination with Eqs. (28),(10) and under the MA, Eq. (11), finally leads to

\[ \partial g[\rho, t] / \partial t = -(D/\Omega) \sum_a [\partial / \partial \rho(\mathbf{r}_a)]g_{eq}(\rho) \mathbf{\nabla}_{\mathbf{r}} \cdot \rho(\mathbf{r}_a) \mathbf{\nabla}_{\mathbf{r}} \times [\partial / \partial \rho(\mathbf{r}_a)]g[\rho, t] / g_{eq}(\rho), \]  

(34)

where \( D \) is defined by Eq. (18). In the limit \( \Omega \to 0 \) we have from

\[ \sum_a (\partial / \partial \rho(\mathbf{r}_a)) \to d\mathbf{r} \partial / \partial \rho(\mathbf{r}), \]  

(35)

the following Fokker-Planck equation for the probability functional \( g[\rho, t] \):

\[ \partial g[\rho, t] / \partial t = - \int d\mathbf{r} \partial / \partial \rho(\mathbf{r}) J[\rho], \]  

(36)

\[ J = D \nabla_{\mathbf{r}} \rho(\mathbf{r}) \mathbf{\nabla}_{\mathbf{r}} g[\rho, t] / \partial \rho(\mathbf{r}) + g[\rho] \beta \mathbf{\nabla}_{\mathbf{r}} \delta F[\rho] / \partial \rho(\mathbf{r}). \]  

(37)

This is precisely the same as the one obtained before [11]. Some remarks are given in order. First, in our previous derivation of the DDFT [11], we started from a nonlinear Langevin equation for the density field \( n(\mathbf{r}, t) \) where some notions from the nonequilibrium thermodynamics such as the generalized force \(- \mathbf{\nabla} \delta F[\rho] / \partial \rho(\mathbf{r})\) [13] and from the stochastic theory such as a multiplicative noise [14] played important roles, and Eq. (34) or (36) was obtained as the corresponding Fokker-Planck equation. There the free energy \( F[\rho] \) was taken from the DFT of the equilibrium statistical
mechanics [12]. Here, however, as is seen from the definition, Eq. (24), $F[\rho]$ is better called a microcanonical, instead of grand-canonical one, because it is defined from the volume in the phase space, which satisfies some condition expressed by $\delta$-functions.

Second, if we start from the microscopic density field (21) instead of the average one, Eq. (20), Eqs. (36) and (37) are directly obtained. Also it is noted that effects of the solvent are to make the MA more implicit, in the sense that $H_{\text{sol}}+H_{\text{int}}$ does not play an explicit role in our derivation of the DDFT. Here we consider that the effects of the solvent are to make the MA more appropriate compared to the situation where there is no solvent.

Third, the DDFT, Eq. (36), has been applied already to study viscosity, and the conformation processes of a polymer in solvent [15]. Also the mode-coupling approach to Eq. (36) turned out to yield the equation for the density-density correlation function, which is in a sense the overdamped limit of the usual mode-coupling theory [16]. Since the Fokker-Planck equation or the corresponding Langevin equation for the density field describes fluctuations, or in the terminology of the mode-coupling theory, effects of thermal activation, we consider that Eq. (36) might be able to be applied to describe density fluctuations, which takes dynamical inhomogeneity into account and some progress is made in this direction, which will be reported elsewhere.

[16] K. Kawasaki, in Ref. [15].