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Principle of Maximum Entropy and Reduced Dynamics

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A new method to obtain a series of reduced dynamics at various stages of coarse-graining is proposed. This ranges from the most coarse-grained one which agrees with the deterministic time evolution equation for averages of the relevant variables to the least coarse-grained one which is the generalized Fokker-Planck equation for the probability distribution function of the relevant variables. The method is based on the extention of the Kawasaki-Gunton operator with the help of the principle of maximum entropy.

KEY WORDS: maximum entropy principle, deterministic dynamics, stochastic dynamics, projection operators

1. INTRODUCTION

Importance of understanding liquids has been greatly enhanced in recent years owing to their close association with life sciences. Here we are more concerned with the fact that living systems generally consist of materials in fluid state[3] However, theoretical progresss in the liquid state of matter has been hampered due to difficulties of incorporating short range correlations essential for liquids. Still we have seen significant advances, and one of the most successful ideas is the density functional theory[(3,4)] to deal with static aspects of liquids. This theory is firmly based on the existence of a variational principle.[(3)] It is then natural to attempt

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[3] This is discussed in Ref. 1 by contrasting liquid state of matter with solid state of matter which is associated with the mineral world and modern technology. Living matter is more often made of structured fluids.[(2)] Hence the basic understanding of the behavior of matter in fluid states should be quite relevant in life sciences.

to extend this theory to include dynamical aspects, which, however, is far from straightforward mainly due to the absence of any such variational principle. Such attempts resulted in what is commonly known as dynamical density functional theories (DDFT). There are the two limiting forms for the DDFT: deterministic and fully stochastic ones as explained below.

1. Closed deterministic equation for the averaged density profile $\rho(\mathbf{r}, t)$[5–10]

   Here DDFT takes the form of a deterministic time evolution equation for the averaged density profile to be denoted as $\rho(\mathbf{r}, t)$. One starts from BBGKY-like hierarchy equations for one body-, two body-... distribution functions for an interacting Brownian particle system. We assume establishment of a local equilibrium at each instant of time when one body distribution $\rho(\mathbf{r}, t)$ is given. In this manner multibody distribution functions ρ_n, $n = 2, 3, \ldots$ at a time t are expressed as fuctionals of $\rho(\mathbf{r}, t)$ at the same time t such that $\rho_2(\mathbf{r},\mathbf{r}', t) = \rho_2(\mathbf{r},\mathbf{r}'; \{\rho(\cdot, t)\})$, etc.

   We thus find

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left[\rho(\mathbf{r}, t) \frac{\delta \mathcal{F}\{\rho(t)\}}{\delta \rho(\mathbf{r}, t)} \right]$$

$$\mathcal{F}\{\rho(t)\} = \int d\mathbf{r}[\ln(\lambda^3 \rho(\mathbf{r}, t)) - 1] + \mathcal{F}_{ex}\{\rho(t)\} \tag{1.1}$$

   where $\mathcal{F}\{\rho\}$ is the equilibrium density functional with $\mathcal{F}_{ex}\{\rho(t)\}$ the excess contribution arising from interactions and λ the de Broglie length. Here and in (1.2) below the kinetic coefficient was chosen to be unity.

2. Fully stochastic DDFT[11–16]

   Time evolution can take either the form of a nonlinear Langevin equation or the form of a Fokker-Planck type equation. The latter equation for the distribution functional $D_M(\{\overline{\rho}\}, t)$ where $\overline{\rho}$ is a coarse-grained density profile as a stochastic variable reads

$$\frac{\partial D_M(\{\bar{\rho}, t\})}{\partial t} = -\int d\mathbf{r} \frac{\delta}{\delta \bar{\rho}(\mathbf{r})} \nabla \cdot \bar{\rho}(\mathbf{r}) \left[\frac{\delta}{\bar{\rho}(\mathbf{r})} + \frac{\delta \mathcal{H}\{\bar{\rho}\}}{\delta \bar{\rho}(\mathbf{r})} \right] D_M(\{\bar{\rho}, t)\} \tag{1.2}$$

   Here and after the Boltzmann constant times the absolute temperature will be taken to be unity, and the coarse-grained free energy functional is of the form,

$$\mathcal{H}\{\bar{\rho}\} \equiv \int d\mathbf{r} \bar{\rho}(\mathbf{r})[\ln(\lambda^3 \bar{\rho}(\mathbf{r})) - 1] + \mathcal{H}_{ex}\{\bar{\rho}\} \tag{1.3}$$

   Note in general $\mathcal{H}\{\overline{\rho}\} \neq \mathcal{F}\{\rho\}$ and $\mathcal{H}_{ex}\{\overline{\rho}\}$ is the excess contribution arising from interactions. Mapping between $\mathcal{H}\{\overline{\rho}\}$ and $\mathcal{F}\{\rho\}$ starts with defining a thermodynamic potential $\mathcal{G}\{\phi\}$ in an external field $\phi(\mathbf{r})$ through

$$e^{-\mathcal{G}\{\phi\}} = \int d\{\bar{\rho}\} e^{-\mathcal{H}\{\rho\}+\int d\mathbf{r}\phi(\mathbf{r})\bar{\rho}(\mathbf{r})} \tag{1.4}$$

We note that the coarse-grained density profile $\overline{\rho}(\mathbf{r})$ is generally different from the average density profile $\rho(\mathbf{r})$ because $\bar{\rho}(\mathbf{r})$ can still fluctuate to the degree that the coarse-graining does not incorporate all the fluctuation effects which are taken care of on the rhs of (1.4). Then a usual Legendre transformation $\phi(\mathbf{r}) \to \rho(\mathbf{r})$ enables one to obtain $\mathcal{F}\{\rho\}$ from $\mathcal{G}\{\phi\}$.

It is the purpose of this paper to propose a general treatment of reduced dynamics such as DDFT that includes the deterministic and fully stochastic dynamics as the two special cases. Indeed such a proposal was made by us recently[17] by starting from a projection operator formalism for general non-equilibrium situation.[19,20] Here we propose another such formalism that combines a projection operator technique with the principle of maximum entropy.[21] This maximum entropy formalism has a structure which permits a straightfoward extension of the Kawasaki-Gunton operator[19,20] for our purpose. Since the formalsim is not restricted to the density variable we use a more general framework of reduced dynamics as before.[17]

In this paper we first take up a classical system whose microscopic state is given by a point in the phase space simply denoted as $\hat{x}$. We must consider statistical properties of states which are contained in the phase space distribution functifunction $\hat{D}(\hat{x}, t)$ For brevity we introduce a notation Tr for trace operation as defined now. The trace Tr denotes phase space integration restricted by a fixed total energy for isolated systems, and for systems in contact with heat or particle reservoirs, this is to be properly generalized. For instance, for fluid systems in contact with heat and particle reservoirs, we have

$$\mathrm{Tr} \cdots = \sum_{\hat{N}=1}^{\infty} \frac{1}{\hat{N}!} \int d\mathbf{r}^{\hat{N}} d\mathbf{p}^{\hat{N}} e^{\mu\hat{N}-\hat{H}_{\hat{N}}} \cdots \tag{1.5}$$

where we have equated the Boltzmann constant times the absolute temperature as well as Planck's constant to unity and μ, $\hat{N}$ and $\hat{H}_{\hat{N}}$ are the chemical potential, the total partcle number and the system Hamiltonian with $\hat{N}$ particles, respectively. The symbol $d\mathbf{r}^{\hat{N}} d\mathbf{p}^{\hat{N}}$ is the volume element of the $6\hat{N}$-dimnesional phase space. Then our phase space distribution function $\hat{D}(\hat{x}, t)$ has components in different sectors with different values of $\hat{N}$, and reduces to a common constant in thermodynamic equilibrium. In the following we actually work in one sector with a fixed $\hat{N} = N$ when dealing with interacting particle systems.

The next section introduces a new set of projection operators with the help of maximum entropy principle. This enables us to define a set of reduced phase space distribution functions which interpolates deterministic and fully stochastic reduced dynamics. Section 3 describes time evolution of the probability distribution function of relevant variables associated with a reduced phase space distribution function. In Sec. 4 we take up the leading fluctuation correction to the deterministic reduced dynamics. Section 5 illustrates our general approach for two examples: a Brownian particle in a fluid and a one-component fluid. In Appendix B we derive fully stochastic reduced dynamics as a special case of our general approach.

Before concluding this section we add a few words on the fact that we will be basically dealing with those non-equilibrium states where certain slow time evolution can be discerned. This encompasses most situations encountered in condensed matter physics where collisions between particles dominate. Then there exist a time scale in which slow time evolution has not yet taken place, but fast time evolution not associated with slow degrees of freedom has already occurred. Under these circumstances a local equilibrium state provides a good reference state to describe slower processes although a projector technique *per se* is still formally exact without being thus restricted.

2. MAXIMUM ENTROPY PRINCIPLE AND PROJECTION OPERATORS

Dynamics of a system with a great number of degrees of freedom can be extremely complex for any sensible description. However, we have examples where much simpler reduced dynamical behavior of such systems are known. Macroscopic hydrodynamics provides an archetypical example. Then there must exist a set of variables hereafter called the relevant variables entering reduced description, which are smaller in number and are functions of microscopic variables such as phase space coordinates. The set of variables entering hydrodynamics provide again an archetypical example.[18,19]

In the traditional non-equilibrium statistical physics, a set of the relevant variables $\{a\}$ or a set of the corresponding phase space functions $\{\hat{A}(\hat{x})\}$ appear in construction of a local equilibrium phase space distribution function $\hat{D}_L(\hat{x}, t)$ of the form[19][4]

$$\hat{D}_L(\hat{x}, t) = e^{h_0(t) + \mathbf{h}_A^T(t)\cdot\delta_t\hat{\mathbf{A}}(\hat{x})} \tag{2.1}$$

where $\hat{\mathbf{A}}(\hat{x})$ is the set $\{\hat{A}(\hat{x})\}$ arranged as a column vector and $\mathbf{h}_A^T(t)$ is a row vector composed of the set of fields $\{h_A(t)\}$ conjugate to $\{\hat{A}(\hat{x})\}$. Also $\delta_t\mathbf{A}(\hat{x}) \equiv \mathbf{A}(\hat{x}) - \langle\mathbf{A}(\hat{x})\rangle(t)$, $\langle\cdots\rangle(t)$ being a non-equilibrium average at the time t. See below as well.

[4] In view of the definition of trace, (1.5), the usual phase space distribution function is obtained by multiplying $\hat{D}_L(\hat{x}, t)$ by the equilibrium phase space distribution function.

In general a local equilibrium state at a certain time is constructed in such a way that averages of the relevant variables computed in this state are identical to those computed in a true non-equilibrium state at the same time by adjusting conjugate fields $\{h_A(t)\}$. This prescription reflects the assumed existence of a time scale in which non-equilibrium averages of relevant variables (and hence their conjugate fields) hardly change, and a local eqilibrium state is attained with respect to other rapidly varying irrelevant degrees of freedom.

A utility of the maximum entropy principle[(21)] is that the phase space distribution function appearing here has formally the same structure as the local equilibrium distribution function just described if we extend the relevant variable set $\{\hat{A}\}$ to include their polynomial function series, which are here arranged in a column vector $\psi_W\{\hat{A}(\hat{x})\}$. We introduce the symbol W to specify a truncated polynomial function set $\psi_W\{\hat{A}(\hat{x})\}$ chosen from the complete set of functions. In constrast to the previous case,[(17)] we do not require them to be orthonormal, and hence these function themselves need not depend on time. The entropy functional $\mathcal{S}\{\hat{D}_W\}$ of the phase space distribution function $\hat{D}_W(\hat{x}, t)$ to be maximized is[5]

$$\mathcal{S}\{\hat{D}_W(\cdot, t)\} \equiv -\mathrm{Tr}\hat{D}_W(\cdot, t) \ln \hat{D}_W(\cdot, t) + \lambda_W{}^T(t) \cdot \mathrm{Tr}\psi_W \hat{D}_W(\cdot, t) \qquad (2.2)$$

where $\lambda_W^T(t)$, T being transpose, is a row vector conjugate to the column vector ψ_W whose first member $\lambda_0(t)$ corresponding to $\psi_0 = 1$ takes care of the normalization $\mathrm{Tr}\hat{D}_W(t) = 1$. Hereafter we sometimes skip the argument t as well as $\hat{x}$ and center dot $\cdot$. A center dot here denotes a point in phase space to be integrated over. We often suppress relevant variables $\{\hat{A}\}$ in the arguments of $\psi_W(\{\hat{A}\})$ as well. In passing we note that the definition (1.5) implies that the equilibrium phase space distribution function $\hat{D}_E(\hat{x})$ is in fact a constant independent of $\hat{x}$.

Then the extremum condition of (2.2),

$$\frac{\delta \mathcal{S}}{\delta \hat{D}_W} = -\ln \hat{D}_W + \lambda_W^T \cdot \psi_W \qquad (2.3)$$

yields

$$\hat{D}_W = e^{\lambda_W^T \cdot \psi_W} \qquad (2.4)$$

Here the unknown row vector λ_W^T is determined by matching averages of ψ_W over $\hat{D}_W(t)$ and $\hat{D}(t)$, the genuine non-equilibrium phase space distribution function at the time t. That is

$$\mathrm{Tr}\psi_W e^{\lambda_W^T \cdot \psi_W} = \mathrm{Tr}\psi_W \hat{D}(t) \qquad (2.5)$$

[5] The entropy maximized under various constraints is in fact more closely related to a free energy. However, we use the word entropy here following the convention.[(21)]

The normalization $\mathrm{Tr}\hat{D}_W(t) = 1$ then gives

$$\lambda_0 = -\ln e^{\lambda_W'^T \cdot \psi W}, \qquad \psi_0 = 1 \tag{2.6}$$

where λ' indicates exclusion of the first component λ_0.

Now we introduce a time dependent projector $P^W(t)$ by its operation on any phase space function $\hat{X}(\hat{x})$ as

$$P^W(t)\hat{X} = \hat{D}_W(t)\left[\mathrm{Tr}\hat{X} + \delta_t \psi_W^T \cdot \chi_W(t)^{-1} \cdot \mathrm{Tr}\delta_t \psi_W \hat{X}\right] \tag{2.7}$$

where $\delta_t \psi_W \equiv \psi_W - \langle \psi_W \rangle_W(t)$, and $\chi_W(t) \equiv \langle \delta_t \psi \delta_t \psi^T \rangle_W(t)$ the susceptibility matrix where $\langle \cdots \rangle_W(t)$ denotes an average over $\hat{D}_W(t)$. We immediately find

$$P^W(t)\hat{D}(t) = \hat{D}_W(t) \tag{2.8}$$

We can now see that $P^W(t)$ has the same properties as the K-G operator:[19,20]

$$P^W(t_2)P^W(t_1)\hat{X} = P^W(t_2)\hat{X}, \quad \dot{P}^W(t)\hat{D}(t) = 0 \tag{2.9}$$

where $\dot{P}^W(t)\hat{D}(t) \equiv \frac{d}{dt}[p^W(t)\hat{D}(t)] - P^W(t)\frac{d}{dt}\hat{D}(t)$. This implies that for any time-independent phase space function $\hat{X}(\hat{x})$, $\dot{P}^W(t)\hat{X}(\hat{x}) = \frac{d}{dt}P^W(t)\hat{X}(\hat{x})$. One consequence of the first property of (2.9) is, with $Q^W(t) \equiv 1 - P^W(t)$,

$$Q^W(t_2)Q^W(t_1)\hat{X} = Q^W(t_1)\hat{X} \tag{2.10}$$

These properties will be proven below and in Appendix A. We note that in constrast to the previous case[17] infinite powers of polynomial expansion are contained here.

We continue to discuss some further properties of the projection operators. First we consider the following:

$$P^{W_2}(t_2)P^{W_1}(t_1)\hat{X} = P^{W_2}(t_2)\hat{D}_{W_1}(t_1)\left[\mathrm{Tr}\hat{X} + \delta_{t_1}\psi_{W_1}^T \cdot \chi_{W_1}(t_1)^{-1} \cdot \mathrm{Tr}\delta_{t_1}\psi_{W_1}\hat{X}\right] \tag{2.11}$$

Using

$$\begin{aligned} P^{W_2}(t_2)\hat{D}_{W_1}(t_1) &= \hat{D}_{W_2}(t_2)\left[1 + \delta_{t_2}\psi_{W_2}^T \cdot \chi_{W_2}(t_2)^{-1} \cdot \langle \delta_{t_2}\psi_{W_2} \rangle W_1(t_1)\right] \\ P^{W_2}(t_2)\hat{D}_{W_1}(t_1)\delta_{t_1}\psi_{W_1} &= \hat{D}_{W_2}(t_2)\delta_{t_2}\psi_{W_2}^T \cdot \chi_{W_2}(t_2)^{-1}. \\ &\quad \times \left\langle \delta_{t_2}\psi_{W_2}\delta_{t_1}\psi_{W_1}^T \right\rangle_{W_1}(t_1) \end{aligned} \tag{2.12}$$

we find

$$\begin{aligned} &P^{W_2}(t_2)P^{W_1}(t_1)\hat{X} \\ &\quad = \hat{D}_{W_2}(t_2)\big\{\big[1 + \delta_{t_2}\psi_{W_2}^T \cdot \chi_{W_2}(t_2)^{-1} \cdot \langle\delta_{t_2}\psi_{W_2}\rangle_{W_1}(t_1)\big]\mathrm{Tr}\hat{X} \\ &\qquad + \delta_{t_2}\psi_{W_2}^T \cdot \chi_{W_2}(t_2)^{-1} \cdot \big\langle\delta_{t_2}\psi_{W_2}\delta_{t_1}\psi_{W_1}^T\big\rangle_{W_1}(t_1) \cdot \chi_{W_1}(t_1)^{-1}. \\ &\qquad \times \mathrm{Tr}\delta_{t_1}\psi_{W_1}\hat{X}\big]\big\} \end{aligned} \tag{2.13}$$

Consider now the two special cases:

1. $W_1 = W_2 = W, t_1 \neq t_2$
   We find

$$P^W(t_2)P^W(t_1)\hat{X} = \hat{D}_W(t_2)\big\{\mathrm{Tr}\hat{X} + \delta_{t_2}\psi_W^T \cdot \chi_W(t_2)^{-1} \cdot \hat{Y}\big\} \tag{2.14}$$

where

$$\begin{aligned} \hat{Y} &\equiv \langle\delta_{t_2}\psi_W\rangle_W(t_1)\mathrm{Tr}\hat{X} \\ &\quad + \big\langle\delta_{t_2}\psi_W\delta_{t_1}\psi_W^T\big\rangle_W(t_1) \cdot \chi_W(t_1)^{-1}\mathrm{Tr}\delta_{t_1}\psi_W\hat{X} \\ &= \mathrm{Tr}\delta_{t_2}\psi_W\hat{X} \end{aligned} \tag{2.15}$$

Therefore we recover the following:

$$\begin{aligned} P^W(t_2)P^W t_1\hat{X} &= \hat{D}_W(t_2)\big[\mathrm{Tr}\hat{X} + \delta_{t_2}\psi_W^T \cdot \chi_W(t_2)^{-1} \cdot \mathrm{Tr}\delta_{t_2}\psi_W\hat{X}\big] \\ &= P^W(t_2)\hat{X} \end{aligned} \tag{2.16}$$

2. $t_1 = t_2 = t$, $W_1 \neq W_2$ Here we find

$$P^{W_2}(t)P^{W_1}(t)\hat{X} = \hat{D}_{W_2}(t)\big[\mathrm{Tr}\hat{X} + \delta_{t_2}\psi_{W_2}^T \cdot \chi_{W_2}(t)^{-1} \cdot \mathrm{Tr}\hat{Z}\hat{X}\big] \tag{2.17}$$

with

$$\hat{Z} \equiv \langle\delta_t\psi_{W_2}\rangle_{W_1}(t) + \big\langle\delta_t\psi_{W_2}\delta_t\psi_{W_1}^T\big\rangle_{W_1}(t) \cdot \chi_{W_1}(t)^{-1} \cdot \delta_t\psi_{W_1} \tag{2.18}$$

We have not found intuitive or geometrical meaning of this result which is a double projection.

If the set $\{\psi_W(t)\}$ is restricted to linear functions of the $\hat{A}$'s, this reduces to the canonical case[20] $W = C$. On the other hand, if the set $\{\psi_W(t)\}$ constitutes a complete set, this is equivalent to having an arbitrary functions of the $\hat{A}$'s, or we can have $\delta\{a - \hat{A}(\hat{x})\}$ where the relevant variable set $\{a\}$ is regarded as an infinite set of parameters, which is the microcanonical case $W = M$.

3. EQUATION FOR TIME EVOLUTION

We consider time evolution governed by a Louville operator $\hat{L}$ appearing in the usual Liouville equation for a phase space distribution function $\hat{D}(\hat{x}, t)$,

$$\frac{\partial \hat{D}(\hat{x}, t)}{\partial t} = \hat{L}\hat{D}(\hat{x}, t) \tag{3.1}$$

We are interested in finding time evolution of the probability distribution function $D_W(\{a\}, t)$ for the set of relevant variables $\{a\}$ corresponding to the set of phase space functions $\{\hat{A}(\hat{x})\}$, which is defined as

$$D_W(\{a\}, t) \equiv \mathrm{Tr}\delta\{a - \hat{A}(\cdot)\}\hat{D}_W(\hat{x}, t) \tag{3.2}$$

The first step is to consider time evolution of the projected phase space distribution function $\hat{D}_W(\hat{x}, t)$, (2.8). The standard projector technique[19] yields a formally exact closed time evolution equation with memory for $\hat{D}(\hat{x}, t)$ with the assumption that initially at $t = 0$ we can start out at the projected state $\hat{D}(\hat{x}, 0) = \hat{D}_W(\hat{x}, 0)$. This follows from the basic premise of non-equilibrium statistical mechanics which excludes extremely improbable pathological initial states which can lead to violation of the second law of thermodynamics. The resulting time evolution equation is

$$\begin{aligned}\frac{\partial \hat{D}_W(\hat{x}, t)}{\partial t} &= P^W(t)\hat{L}\hat{D}_W(\hat{x}, t)\\ &\quad + \int_0^t ds P^W(t)\hat{L}e_+^{\int_s^t ds' Q^W(s')\hat{L}} Q^W(s)\hat{L}\hat{D}_W(\hat{x}, s)\end{aligned} \tag{3.3}$$

where $Q^W(t) \equiv 1 - P^W(t)$ and e_+ is the time ordered exponential. Derivation of this equation is given in Appendix A.

The next step is to realize that by (2.4) $\hat{D}_W(\hat{x}, t)$ depends on $\hat{x}$ only through $\{\hat{A}(\hat{x})\}$, which gives using (3.2) the following:

$$\hat{D}_W(\hat{x}, t) = e^{-S\{\hat{A}(\hat{x})\}} D_W(\{\hat{A}(\cdot)\}, t) \tag{3.4}$$

where a new "entropy" $S\{a\}$ is introduced through[6]

$$e^{S\{a\}} \equiv \mathrm{Tr}\delta\{a - \hat{A}(\hat{x})\} \tag{3.5}$$

Substituting (3.3) into the rhs of the following equatiton

$$\frac{\partial}{\partial t} D_W(\{a\}, t) = \mathrm{Tr}\delta\{a - \hat{A}(\hat{x})\}\frac{\partial}{\partial t}\hat{D}_W(\hat{x}, t) \tag{3.6}$$

[6] This is not to be confused with $\mathcal{S}$,(2.2), used to obtain $\hat{D}_W$ by maximizing.

and using (3.4) and (3.5) we obtain the set of equations valid irrespectively of actual structure of the projector,[17] which are written down as.

$$\frac{\partial}{\partial t} D_W(\{a\}, t) = \int d\{a'\}\mathcal{L}_W(\{a, a'\}; t) D_W(\{a'\}, t) + \int_0^t ds \int d\{a'\}\mathcal{M}_W(\{aa'\}; t, s) D_W(\{a'\}, s) \tag{3.7}$$

where

$$\mathcal{L}_W(\{a, a'\}; t) \equiv [\mathrm{Tr}\delta\{a - \hat{A}(\cdot)\}P^W(t)\hat{L}\delta\{a' - \hat{A}(\cdot)\}]e^{-S\{\hat{a}'\}} \tag{3.8}$$

and

$$\mathcal{M}_W(\{aa'\}; t, s) \equiv \left[\mathrm{Tr}\delta\{a - \hat{A}(\cdot)\}P^W(t)\hat{L}\hat{U}(ts)Q^W(s)\hat{L}\delta\{a' - \hat{A}(\cdot)\}\right] e^{-S\{\hat{a}'\}} \tag{3.9}$$

with $\hat{U}(ts) = e_+^{\int_s^t ds' Q^W(s')\hat{L}}$.

This formally exact time evolution equation for the probability distribution function $D(\{a\}, t)$ with memory will be our starting equation for the analyses that follow. Physically the first term on the rhs of (3.7) is the instantaneous part of change which will be the case if the system instantaneously follows change of the distribution function $D(\{a\}, t)$. This is generally not exact since other degrees of freedom not included in our reduced description affects delayed reaction, which is taken care of by the second term of (3.7).

We now undertake a task of transforming (3.7) into a more useful form which requires some algebrae. The results of these analyses will be summarized by Equations (3.35)–(3.39) at the end of this section. Let us thus consider

$$P^W(t)\hat{L}\hat{X} = \hat{D}_W(t)[\mathrm{Tr}\hat{L}\hat{X} + \delta_t\psi_W(\hat{A}) \cdot \chi_W(t)^{-1} \cdot \mathrm{Tr}\delta_t\psi_W\hat{L}\hat{X}] \tag{3.10}$$

as well as

$$\hat{L}\delta\{a - \hat{A}\} = \frac{\partial}{\partial a_j}\dot{\hat{A}}_j\delta\{a - \hat{A}\} \tag{3.11}$$

Here and after an overdot on a phase space function $\hat{X}$ means its time derivative, i.e. $\dot{\hat{X}} = -(\hat{L}\hat{X})$. Then we find after some algebra

$$\mathcal{L}_W(\{a, a'\}; t) = e^{-S\{a'\}} D_W(\{a\}, t) \times \frac{\partial}{\partial a'_j}[1 + \delta_t\psi_W\{a\} \cdot \chi_W(t)^{-1} \cdot \delta_t\psi_W\{a'\}]] \times \mathrm{Tr}\dot{\hat{A}}_j\delta\{a' - \hat{A}(\cdot)\} \tag{3.12}$$

The normalization is readily found using detailed balance for reversible part[25] as

$$\int d\{a\}\mathcal{L}_W(\{a,a'\};t) = \frac{\partial}{\partial a'_j}\mathrm{Tr}\dot{\hat{A}}_j\delta\{a'-\hat{A}(\cdot)\}$$
$$= \frac{\partial}{\partial a'_j}\langle\dot{\hat{A}}_j;\{a'\}\rangle_M e^{S\{a'\}} = 0 \tag{3.13}$$

with

$$\langle\hat{X};\{a\}\rangle_M \equiv \mathrm{Tr}\hat{X}\delta\{\hat{A}-a\}/\mathrm{Tr}\delta\{\hat{A}-a\}$$

We now have from (3.11)

$$\int d\{a'\}\mathcal{L}_W(\{a,a'\};t)D_W(\{a'\},t)$$
$$= -D_W(\{a\},t)\int d\{a'\}[1+\delta_t\psi_W\{a\}\cdot\chi_W(t)^{-1}\cdot\delta_t\psi_W\{a'\}]$$
$$\times\,\mathrm{Tr}\dot{\hat{A}}_j\delta\{a'-\hat{A}(\cdot)\}\frac{\partial}{\partial a'_j}e^{-S\{a'\},}D_W(\{a'\},t) \tag{3.14}$$

where summation convention is used for repeated indices here and after. From this we verify that $\int d\{a'\}\mathcal{L}_W(\{a,a'\};t)D_E(\{a'\},t) = 0$ with $D_E(\{a\},t)$ the equilibrium distribution independent of W. We define a microscopic driving force by

$$f_W^j(\{a\},t) \equiv -\frac{\partial}{\partial a_j}\ln\frac{D_W(\{a\},t)}{D_E(\{a\})} \tag{3.15}$$

This is basically identical with Mazur's phase space flow in his irreversible thermodynamic treatment of fluctuation phenomena.[7]

We now put together the results obtained so far.

$$\int d\{a'\}\mathcal{L}_W(\{a,a'\};t)D_W(\{a'\},t)$$
$$= D_W(\{a\},t)\int d\{a'\}\big[1+\delta_t\psi_W^T\{a\}\cdot\chi_W(t)^{-1}\cdot\delta_t\psi_W\{a'\}\big]$$
$$\times\,\langle\dot{\hat{A}}_j;\{a'\}\rangle_M f_W^j(\{a'\},t)D_W(\{a'\},t) \tag{3.16}$$

[7] Mazur[22] extended the conventional macroscopic irreversible thermodynamics in such a way that not only averages but also fluctuations of the macroscopic variables can be incorporated. He obtained an expression for an extra term for the average irreversible entropy production rate as a product of an average of probability flow rate in the space of ralevant variables a and a thermodynamic driving force conjugate to the flow. The expression for the latter quantity is identical to (3.15) in the text provided that the non-equilibrium probability distribution function is given by $D_W(\{a\},t)$.

with

$$\begin{aligned}\delta_i\psi_W\{a\} &\equiv \psi_W\{a\} - \mathrm{Tr}\psi_W\{\hat{A}\}\hat{D}_W(t)\\ \mathrm{Tr}\psi_W\{\hat{A}\}\hat{D}_W(t) &= \mathrm{Tr}\psi_W\{\hat{A}\}\hat{D}(t)\\ \chi_W(t) &= \langle\delta_t\psi_W\delta_t\psi_W^T\rangle W, \quad \text{(susceptibility matrix)}\\ \psi_W(\psi_W^T): &\quad \text{(column(row) vector)}\end{aligned} \tag{3.17}$$

We now turn to $\mathcal{M}$, (3.9), which is transformed into

$$\mathcal{M}_W(\{aa'\},ts) = e^{-S\{a'\}}\frac{\partial}{\partial a'_j}\mathrm{Tr}\delta\{a-\hat{A}\}P^W(t)\hat{L}\hat{U}^W(ts)Q^W(s)\hat{A}_j\delta\{a'-\hat{A}\} \tag{3.18}$$

Now, for an arbitrary phase space function $\hat{X}$ We can find

$$\begin{aligned}&\mathrm{Tr}\delta\{a-\hat{A}\}P^W(t)\hat{L}\hat{X}\\ &\quad= \mathrm{Tr}\delta\{a-\hat{A}\}\hat{D}_W(t)[\mathrm{Tr}\hat{L}\hat{X} + \delta_t\psi_W\{\hat{A}\}\cdot\chi_W(t)^{-1}\cdot\mathrm{Tr}\delta_t\psi_W\{\cdot\}\hat{L}\hat{X}]\\ &\quad= D_W(\{a\},t)\delta_t\psi_W\{a\}\cdot\chi_W(t)^{-1}\cdot\int d\{\underline{a}\}\frac{\partial\psi_W\{a\}}{\partial\underline{a}_j}\mathrm{Tr}\delta\{\underline{a}-\hat{A}\}\hat{A}_j\hat{X}\end{aligned} \tag{3.19}$$

where we have used $\mathrm{Tr}\hat{L}\hat{X} = 0$. Therefore, we have

$$\begin{aligned}&\int d\{a'\}\mathcal{M}_W(\{a,a'\},ts)D_W(\{a'\},s)\\ &\quad= -\int d\{a'\}\int d\{\underline{a}\}\left[\frac{\partial}{\partial a'_j}e^{-S\{a'\}}D_W(\{a'\},s)\right]D_W(\{a\},t)\psi_W\{a\}.\\ &\qquad\times\chi_W(t)^{-1}\cdot\frac{\partial\psi_W\{\underline{a}\}}{\partial\underline{a}_k}\mathrm{Tr}\delta\{\underline{a}-\hat{A}\}\hat{A}_k\hat{U}^W(ts)Q^W(s)\hat{A}_j\delta\{a'-\hat{A}\}\end{aligned} \tag{3.20}$$

$\mathcal{M}_W(\{aa'\},ts)$ can take a more convenient equivalent form:

$$\begin{aligned}\mathcal{M}_W(\{aa'\},ts) &\Rightarrow D_W(\{a\},t)\delta_t\psi_W\{a\}\cdot\chi_W(t)^{-1}\cdot\left[\int d\{\underline{a}\}\frac{\partial\psi_W\{\underline{a}\}}{\partial\underline{a}_k}e^{S\{\underline{a}\}-S\{a'\}}\right.\\ &\quad\left.\times\,\mathcal{T}^W_{kj}(\{\underline{a}a'\};ts)\right]f^j_W(\{a'\},s)\end{aligned} \tag{3.21}$$

where[8]

$$\mathcal{T}^W_{kj}(\{aa'\};ts) \equiv \langle\dot{\hat{A}}_k\hat{U}^W(ts)Q^W(s)\dot{\hat{A}}_j\delta\{a'-\hat{A}\};\{a\}\rangle_M \tag{3.22}$$

[8] Sometimes we have $\dot{\hat{A}}_j = V_j(\{\hat{A}\})$. In that case $Q^W\dot{\hat{A}}_j\delta\{a'-\hat{A}\} \neq 0$ in general unless $W = M$ due to the fact that $\dot{\hat{A}}_j\delta\{a'-\hat{A}\}$ need not be confined to the function space spanned by $\psi_W\{\hat{A}\}$.

Then the following normalization and stationarity properties can be seen immediately:

$$\int d\{a\}\mathcal{M}_W(\{aa'\}, ts) = 0, \quad \text{and} \quad \mathcal{M}_W(\{aa'\}, ts) = 0 \quad \text{for} \quad D_W = D_E \tag{3.23}$$

For subsequent analyses it is convenient to rewrite the preceding results in the following way:

$$\begin{aligned}\frac{\partial}{\partial t}&D_W(\{a\}, t)\\ &= D_W(\{a\}, t)\big[\mathcal{L}_0^W(\{a\}, t) + \delta_t\psi_W^T(\{a\}) \cdot \chi_W(t)^{-1} \cdot \mathcal{L}_1^W(\{a\}, t)\big]\\ &\quad + D_W(\{a\}, t)\delta_t\psi_W^T(\{a\}) \cdot \chi_W(t)^{-1} \cdot \mathcal{M}_1^W(\{a\}, t)\end{aligned} \tag{3.24}$$

where

$$\mathcal{L}_0^W(t) \equiv \int d\{a'\}\langle\dot{\hat{A}}_j; \{a'\}\rangle_M f_W^j(\{a'\}, t)D_W(\{a'\}, t) \tag{3.25}$$

$$\begin{aligned}\mathcal{L}_1^W(t) \equiv \int & D\{a'\}\delta_t\psi_W\{a'\}\langle\dot{\hat{A}}_j; \{a'\}\rangle_M\\ &\times f_W^j(\{a'\}, t)D_W(\{a'\}, t)\end{aligned} \tag{3.26}$$

$$\begin{aligned}\mathcal{M}_1^W(t) \equiv \int_0^t & ds \int d\{a'\} \int d\{\underline{a}\}\frac{\partial\psi_W\{a\}}{\partial\underline{a}_k}e^{S\{\underline{a}\}-S\{a'\}}\mathcal{T}_{kj}^W(\{\underline{a}a'\}; ts)\\ &\times f_W^j(\{a'\}, s)D_W(\{a'\}, s)\end{aligned} \tag{3.27}$$

On the other hand, we also find from (2.4)

$$\frac{\partial}{\partial t}D_W(\{a\}, t) = \dot{\lambda}_W(t)^T \cdot \psi_W\{a\}D_W(\{a\}, t) = \dot{\lambda}_W(t)^T \cdot \delta_t\psi_W\{a\}D_W(\{a\}, t) \tag{3.28}$$

where the last step is due to the following consequence of the normalization condition as applied to (3.28) and (3.24):

$$0 = \int d\{a\}\frac{\partial}{\partial t}D_W(\{a\}, t) = \dot{\lambda}_W(t)^T \cdot \langle\psi_W\{a\}\rangle W(t) = \mathcal{L}_0^W(t) \tag{3.29}$$

Therefore we finally find

$$\dot{\lambda}_W(t) = \chi_W(t)^{-1} \cdot \big[\mathcal{L}_1^W(t) + \mathcal{M}_1^W(t)\big] \tag{3.30}$$

Note in passing that, integrating (3.28) we have

$$D_W(\{a\}, t) = e^{\int_0^t ds\dot{\lambda}_W(s)^T\cdot\delta_s\psi_W\{a\}}D_W(\{a\}, 0) = e^{\lambda_W(t)\cdot\psi_W\{a\}} \tag{3.31}$$

Consistency of $\mathcal{L}_0^W(t) = 0$ readily follows:

$$\mathcal{L}_0^W(t) = \int d\{a'\}\langle\dot{\hat{A}}_j;\{a'\}\rangle_M \left[-\frac{\partial}{\partial a'_j}\ln\frac{D_W(\{a'\},t)}{D_E(\{a'\})}\right]D_W(\{a'\},t)$$
$$= \int d\{a'\}\langle\dot{\hat{A}}_j;\{a'\}\rangle_M \left[-\frac{\partial}{\partial a'_j}D_W(\{a'\},t) + \frac{D_W(\{a'\},t)}{D_E(\{a'\})}\frac{\partial}{\partial a'_j}D_E(\{a'\},t)\right]$$
$$= \int d\{a'\}\left[\frac{\partial}{\partial a'_j}\langle\dot{\hat{A}}_j;\{a'\}\rangle_M + \langle\dot{\hat{A}}_j;\{a'\}\rangle_M\frac{\partial S\{a'\}}{\partial a'_j}\right] \times D_W(\{a'\},t) = 0 \tag{3.32}$$

The last step used the detailed balance (3.13):

$$\frac{\partial}{\partial a'_j}\langle\dot{\hat{A}}_j;\{a'\}\rangle_M + \langle\dot{\hat{A}}_j;\{a'\}\rangle_M\frac{\partial S\{a'\}}{\partial a'_j} = 0 \tag{3.33}$$

We also find the following by computing average of $\dot{\psi}_W$ using (3.28):

$$\langle\dot{\psi}_W\rangle(t) \equiv \int d\{a\}\psi_W(\{a\})\frac{\partial}{\partial t}D_W(\{a\},t) = \chi_W(t)\cdot\dot{\lambda}_W(t) \tag{3.34}$$

Now, the evolution Eq. (3.24) is finally written as

$$\frac{\partial}{\partial t}D_W(\{a\},t) = D_W(\{a\},t)\delta_t\psi_W^T(\{a\})\cdot\chi_W(t)^{-1}\cdot[\mathcal{L}_W(t) + \mathcal{M}_W(t)] \tag{3.35}$$

where $\mathcal{L}_W$ and $\mathcal{M}_W$, which were previously written as $\mathcal{L}_1$ and $\mathcal{M}_1$, are now given by

$$\mathcal{L}_W(t) = \int d\{a'\}\delta_t\psi_W\{a'\}\langle\dot{\hat{A}}_j;\{a'\}\rangle_M f_W^j(\{a'\},t)D_W(\{a'\},t) \tag{3.36}$$

$$\mathcal{M}_W(t) = \int_0^t ds\int d\{a'\}\int d\{\underline{a}\}e^{s\{\underline{a}\}-S\{a'\}}\frac{\partial\psi_W\{\underline{a}\}}{\partial\underline{a}_k}\mathcal{T}^W(\{\underline{a}a'\};ts) \times f_W^j(\{a'\},s)D_W(\{a'\},s) \tag{3.37}$$

Then, as a final outcome of the long analyses of this section we obtain time evolution equation expressed in the following vector form:

$$\dot{\lambda}_W(t) = \chi_W(t)^{-1}\cdot[\mathcal{L}_W(t) + \mathcal{M}_W(t)] \tag{3.38}$$

or, equivqlently

$$\langle\dot{\psi}_W\rangle(t) = \chi_W(t)\cdot\dot{\lambda}_W(t) = \mathcal{L}_W(t) + \mathcal{M}_W(t) \tag{3.39}$$

Once we choose a set of relevant variables $\{\hat{A}(\hat{x})\}$ and a set of its polynomial functions or functionals arranged in a column vector $\psi_W\{\hat{A}(\cdot)\}$, the equation (3.38) or (3.39) gives time evolution at the level specified by W, although the equations have memory effects due to irrelevant processes projected out from P^W. The effects are embodied in $\mathcal{T}^W_{kj}(\{aa'\}; ts)$, (3.22), whose determination requires microscopic considerations outside the scope of this work. It would be more practical to adopt simplifying assumptions (see Sec. 5) or to devise well-focused computer analyses for this purpose.

In Appendix B we give a detailed analysis of the special case $W = M$ and recover the usual Fokker-Planck equation for the distribution function $D_M(\{a\}, t)$.

4. QUADRATIC CORRECTIONS TO THE CANONICAL CASE

We take up linear and quadratic functions for ψ_W to illustrate the general program of the preceding sections. This case is denoted as $W = 2$:

$$\lambda_2^T\cdot\psi_2 = \mathbf{h}_A^T(t)\cdot\delta_t\hat{\mathbf{A}}(\hat{x}) + \mathbf{h}_B^T : \hat{\mathbf{B}}_t(\hat{x}) \tag{4.1}$$

where the first term on the rhs contains the usual vectors with single indices with components such as $\delta_t\hat{A}_j$ whereas the second term contains vectors with two indices, for instance we can take

$$\hat{\mathbf{B}}_t \equiv \delta_t\hat{\mathbf{A}}\delta_t\hat{\mathbf{A}} - \langle\delta_t\hat{\mathbf{A}}\delta_t\hat{\mathbf{A}}\delta_t\hat{A}_j\rangle_2(t)\big[\chi_2^A(t)^{-1}\big]^{jk}\delta_t\hat{A}_k - \chi_2^A(t) \tag{4.2}$$

Here $\langle\cdot\rangle_2$ is an average over the reduced phase space distribution function $\hat{D}_2(t)$, and $\delta_t\hat{\mathbf{A}} \equiv \hat{\mathbf{A}} - \langle\hat{\mathbf{A}}\rangle_2(t)$. Hence we have

$$\langle\hat{\mathbf{B}}_t\rangle_2(t) = \langle\delta_t\hat{\mathbf{A}}\hat{\mathbf{B}}_t\rangle_2(t) = 0 \tag{4.3}$$

We now write down the reduced phase space distribution as

$$\hat{D}_2(\hat{x}, t) = \exp\big[\lambda_0(t) + \mathbf{h}_A^T(t)\cdot\delta_t\hat{\mathbf{A}}(\hat{x}) + \mathbf{h}_B^T(t) : \hat{\mathbf{B}}_t(\hat{x})\big] \tag{4.4}$$

with $\lambda_0(t)$ given by the normalization condition as

$$\lambda_0(t) = -\ln\mathrm{Tr}\exp\big[\mathbf{h}_A^T(t)\cdot\delta_t\hat{\mathbf{A}}(\hat{x}) + \mathbf{h}_B^T(t) : \hat{\mathbf{B}}_t(\hat{x})\big] \tag{4.5}$$

In view of orthogonality of $\delta_t\mathbf{A}$ and $\mathbf{B}$, the susceptibility matrix χ_2 splits into the two sections:

$$\chi_2(t) = \begin{pmatrix} \chi_2^A(t) & \mathbf{0} \\ \mathbf{0} & \chi_2^B(t) \end{pmatrix} \tag{4.6}$$

The time evolution equation is then

$$\langle\dot{\psi}_2(t)\rangle = \chi_2(t)\cdot\dot{\lambda}_2(t) = \mathcal{L}_2(t) + \mathcal{M}_2(t) \tag{4.7}$$

Here we have

$$\lambda_2(t) = \begin{pmatrix} \mathbf{h}_A(t) \\ \mathbf{h}_B(t) \end{pmatrix}, \quad \psi_2(t) = \begin{pmatrix} \delta_t\hat{\mathbf{A}}(t) \\ \hat{\mathbf{B}}_t \end{pmatrix} \tag{4.8}$$

The conditions for $\lambda_2(t)$ are such that

$$\langle\psi_2(t)\rangle(t) = \langle\psi_2(t)\rangle_2(t)(= 0) \tag{4.9}$$

Now, the terms on the rhs of (4.7) are written explicitly as

$$\mathcal{L}_2(t) = \begin{pmatrix} \left(\mathcal{L}^A_{2j}(t)\right) \\ \left(\mathcal{L}^B_{2jk}(t)\right) \end{pmatrix}, \quad \mathcal{M}_2(t) = \begin{pmatrix} \left(\mathcal{M}^A_{2j}(t)\right) \\ \left(\mathcal{M}^B_{2jk}(t)\right) \end{pmatrix} \tag{4.10}$$

where the $\mathcal{L}'$s are

$$\mathcal{L}^A_{2j}(t) = \int d\{a\} a_j \langle\dot{\hat{A}}_k;\{a\}\rangle_M f^k_2(\{a\},t) D_2(\{a\},t)$$

$$\mathcal{L}^B_{2jk}(t) = \int d\{a\} b_{jk}(\{a\},t)\langle\dot{\hat{A}}_l;\{a\}\rangle_M f^l_2(\{a\},t) D_2(\{a\},t) \tag{4.11}$$

with $b_{jl}(\{a\},t)$ the jl- component of the tensor $\hat{\mathbf{B}}_t$, (4.2), in which the $\hat{A}$'s are replaced by the a's.

Next, the $\mathcal{M}$'s are

$$\begin{aligned}\mathcal{M}^A_{2j}(t) &= \int_0^t ds \int d\{a\} \int d\{\underline{a}\} e^{S\{\underline{a}\}-S\{a\}} \frac{\partial \underline{a}_j}{\partial \underline{a}_k} \mathcal{T}^{(2)}_{km}(\{\underline{a}a\},ts) f^m_2(\{a\},s) \\ &\quad \times D_2(\{a\},s) \\ &= \int_0^t ds \int d\{a\} \int d\{\underline{a}\} e^{S\{\underline{a}\}-S\{a\}} \mathcal{T}^{(2)}_{ji}(\{\underline{a}a\},ts) f^l_2(\{a\},s) \\ &\quad \times D_2(\{a\},s)\end{aligned} \tag{4.12}$$

and

$$\begin{aligned}\mathcal{M}^B_{2jk}(t) &= \int_0^t ds \int d\{a\} \int d\{\underline{a}\} e^{S\{\underline{a}\}-S\{\ a\}} \frac{\partial b_{jk}(\{\underline{a}\};t)}{\partial \underline{a}_i} \mathcal{T}^{(2)}_{im}(\{\underline{a}a\},ts) \\ &\quad \times f^m_2(\{a\},s) D_2\{a\},s)\end{aligned} \tag{4.13}$$

Now we use

$$\frac{\partial b_{jk}(\{a\},t)}{\partial a_l} = \delta_{jl}\delta_t a_k + \delta_{kl}\delta_t a_j - \langle\delta_t a_j \delta_t a_k \delta_t a_p\rangle_2(t)\big[\chi^A_2(t)^{-1}/big]^{pl} \tag{4.14}$$

to obtain

$$
\begin{aligned}
\mathcal{M}^{B}_{2jk}(t) = \quad & \int_0^t ds \int d\{a\} \int d\{\underline{a}\} e^{S\{\underline{a}\}-S\{a\}} \Big[\delta_t \underline{a}_k \mathcal{T}^{(2)}_{jl}(\{\underline{a}a\}, ts) \\
& + \delta_t \underline{a}_j \mathcal{T}^{(2)}_{kl}(\{\underline{a}a\}, ts) \\
& - \langle \delta_t a_j \delta_t a_k \delta_t a_p \rangle_2(t) \big[\chi^{A}_2(t)^{-1}\big]^{pm} \\
& \times \mathcal{T}^{(2)}_{ml}(\{\underline{a}a\}, ts) \Big] f^{l}_2(\{a\}, s) D_2\{a\}, s)
\end{aligned} \tag{4.15}
$$

There is a subtlety associated with the lhs of (4.8) due to the explicit time dependence of $\mathbf{B}_t$ which has to be subracted off where $\delta_t \hat{\mathbf{A}}$ can be replaced by $\hat{\mathbf{A}}$ due to the normalization condition. Thus we have

$$
\begin{aligned}
\langle \dot{\psi}_2(t) \rangle_2(t) \equiv & \int d\{a\} \begin{pmatrix} \delta_t \mathbf{a} \\ \mathbf{b}_t \end{pmatrix} \frac{\partial}{\partial t} D_2(\{a\}, t) = \int d\{a\} \\
& \times \begin{pmatrix} (a_j) \\ (a_j a_l - \langle a_j \rangle_2(t) a_l - a_j \langle a_l \rangle_2(t) - c_{jlm}(t) a_m) \end{pmatrix} \\
& \times \frac{\partial}{\partial t} D_2(\{a\}, t) \\
= & \begin{pmatrix} \left(\frac{\partial}{\partial t} \langle a_j \rangle_2(t)\right) \\ \left(\frac{\partial}{\partial t}\big[\chi^{A}_2(t)\big]_{jl} - d_{jlm}(t) \frac{\partial}{\partial t} \langle a_m \rangle_2(t)\right) \end{pmatrix}
\end{aligned} \tag{4.16}
$$

with $c_{jlm}(t) \equiv \langle \delta_t a_j \delta_t a_l \delta_t a_k \rangle_2(t) [\chi^{A}_2(t)^{-1}]^{\mathrm{km}}$ and $d_{jlm}(t) \equiv \langle \delta_t a_j \delta_t a_l \delta_t a_k \rangle_2(t)$ $[\chi^{A}_2(t)^{-1}]^{\mathrm{km}}$. In the following we put down the explicit form of the evolution equation (4.7).

$$
\begin{aligned}
\frac{\partial}{\partial t} \langle a_j \rangle_(t) = & \mathcal{L}^{A}_{2j}(t) + \mathcal{M}^{2}_{2j}(t) \frac{\partial}{\partial t} \big[\chi^{A}_2(t)\big]_{jl} \\
& - \langle \delta_t a_j \delta_j a_l \delta_t a_k \rangle_2(t) \big[\chi^{A}_2(t)^{-1}\big]^{km} \frac{\partial}{\partial t} \langle a_m \rangle_2(t) \\
= & \mathcal{L}^{B}_{2ji}(t) + \mathcal{M}^{B}_{2jl}(t)
\end{aligned} \tag{4.17}
$$

4.1. Canonical Case

If we strike out everything related to **B** or **b**, we should recover the canonical case. From the first row of (4.7) we find

$$
\frac{\partial}{\partial t} \langle a_j \rangle(t) = \mathcal{L}^{C}_{j}(t) + \mathcal{M}^{C}_{j}(t) \tag{4.18}
$$

and $f^k_C(\{a\}, t) = -h^k(t)$ where superfixes and suffices C stand for "canonical." We have then

$$\mathcal{L}^C_j(t) = -\int d\{a\} a_j \langle \dot{\hat{A}}_k; \{a\}\rangle_M h^k(t) D_L(\{a\}, t) = -\Lambda_{jk}(t) h^k(t) \tag{4.19}$$

where

$$\Lambda_{jk}(t) \equiv \int d\{a\} a_j \langle \dot{\hat{A}}_k; \{a\}\rangle_M D_L(\{a\}, t) \tag{4.20}$$

Here a_j can be replaced by $\delta_t a_j$ due to the normalization (3.32) with $f^k_C(\{a\}, t) = -h^k(t)$. Next,

$$\begin{aligned}\mathcal{M}^C_j(t) &= -\int_0^t ds \int d\{a\} \int d\{\underline{a}\} e^{S\{\underline{a}\} - S\{a\}} \mathcal{T}^C_{jl}(\{\underline{a}, a\}, ts) h^l(s) D_L(\{a\}, s) \\ &= -\int_0^t ds \Upsilon_{jl}(ts) h^l(s)\end{aligned} \tag{4.21}$$

with

$$\Upsilon_{jl}(ts) \equiv \int d\{a\} \int d\{\underline{a}\} e^{S\{\underline{a}\} - S\{a\}} \mathcal{T}^C_{jl}(\{\underline{a} a\}, ts) D_L(\{a\}, s) \tag{4.22}$$

If we make a Markovian approximation, we have

$$\mathcal{M}^C_j(t) = -\zeta^C_{jl}(t) h^l(t);, \quad \zeta^C_{jl}(t) \equiv \int_0^t ds \Upsilon_{jl}(ts) \tag{4.23}$$

and hence, with $\bar{a}_j(t) \equiv \langle a_j \rangle_L(t)$, etc.,

$$\frac{d}{dt}\bar{a}_j(t) = -\left[\Lambda_{jl}(t) + \zeta^C_{jl}(t)\right] h^l(t) \tag{4.24}$$

This is the same deterministic equation for averaged relevant variables discussed in Ref. 17 apart from memory effects, and is also exemplified by (1.1).

5. EXAMPLES

In this section we illustrate the abstract formalism of the preceding sections with two concrete examples where, however, we do not intend to produce substantial new results yet.

5.1. A Brownian Particle in a Fluid

Let us consider a single particle immersed in a fluid which gives rise to a force $\hat{\xi}(t)$ on the particle. The relevant variables are taken to be the one-dimensional coordinate and momentum: $\{\hat{A}\} = \hat{X}, \hat{P}$. The equation of motion is

$$\dot{\hat{X}}(t) = \hat{P}(t)$$
$$\dot{\hat{P}}(t) = F(\hat{X}(t)) + \hat{\xi}(t) \tag{5.1}$$

where $F(\hat{X}(t)) = -U'(\hat{X}(t))$ is the external force and $U(\hat{X}(t))$ the associated potential. A prime stands for differentiation. The lower case relevant variables are $\{a\} = x, p$. We do not explicitly describe the fluid surrounding the particle and just write its variables collectively as y and their phase space functions as $\hat{y}.\hat{\xi}(t)$ is the force on the particle due to its interaction with fluid. See (5.4) below.

The purpose of this section is to facilitate understanding of the general and abstract formalism of the preceding sections. Thus we freely make simplifying assumptions like (5.22) and (5.38) below to rederive familiar results. We do not intend at this stage to obtain new results, which will be tasks of future works.

We point out that although we explicitly deal only with an actual Brownian particle, this can be generalized. The variable $\hat{X}, x$ can be for instance a reaction coordinate when we consider chemical reaction of a solute particle immersed in a solvent fluid. $\hat{P}, p$ is thus the momentum conjugate to $\hat{X}, x$

Then the phase space distribution function is $\hat{D}(\hat{X}, \hat{P}, \hat{y}; t)$ or simply $\hat{D}(t)$. Now, we introduce Tr operation by

$$\mathrm{Tr}(\cdots) \equiv \int d\hat{X} d\hat{P} d\hat{y} \hat{\mathcal{D}}_e(\hat{X}, \hat{P}, \hat{y})(\cdots) \tag{5.2}$$

with $\hat{\mathcal{D}}_e(\hat{X}, \hat{P}, \hat{y})$ the equlibrium phase space distribution function given by

$$\hat{\mathcal{D}}_e(\hat{X}, \hat{P}, \hat{y}) \equiv \exp\left[-\frac{1}{2}\hat{P}^2 - U(\hat{x}) - \hat{H}_f(\hat{y}; \hat{X})\right] \tag{5.3}$$

where the particle mass M and $k_B T$ are both taken to be unity, and $\hat{H}_f(\hat{y}; \hat{X})$ is the fluid Hamiltonian including interactions with the Brownian particle, and then we have

$$\hat{\xi} \equiv -\frac{\partial \hat{H}_f(\hat{y}; \hat{X})}{\partial \hat{X}} \tag{5.4}$$

The reduced equilibrium distribution function for the Brownian particle is then

$$\mathcal{D}_e(x, p) = \int d\hat{y} \hat{\mathcal{D}}_e(\hat{X}, \hat{P}, \hat{y})|_{\hat{X}=x, \hat{P}=p} = e^{S(x,p)} \tag{5.5}$$

The "entropy" $S(xp)$ was defined as in Eq. (3.5) through

$$e^{S(xp)} \equiv \mathrm{Tr}\delta(x - \hat{X})\delta(p - \hat{P}) = \int d\hat{X}d\hat{P}d\hat{y}\hat{\mathcal{D}}_e(\hat{X}, \hat{P}, \hat{y})\delta(x - \hat{X})\delta(p - \hat{P})$$
$$= \int d\hat{y}e^{-\frac{1}{2}p^2 - U(x) - \hat{H}_f(\hat{y};x)} = e^{-\frac{1}{2}p^2 - U(x) - \Delta U(x)} \tag{5.6}$$

with

$$e^{-\Delta U(x)} \equiv \int d\hat{y}e^{-\hat{H}_f(\hat{y};x)} \tag{5.7}$$

That is,

$$S(x, p) = -H_b(x, p) \equiv -\frac{1}{2}p^2 - U(x) - \Delta U(x) \tag{5.8}$$

where $H_b(x, p)$ plays the role of an effective Hamiltonian for the Brownian particle.

Next we consider the two special cases.

5.1.1. *Microcanonical case:* $W = M$

We make a simplifying Markovian aproximation as

$$\mathcal{T}_{kj}^M(\{aa'\}; ts) \to 2\zeta_k\delta_{kj}\delta\{a - a'\}\delta(t - s) \tag{5.9}$$

The second term of (3.35) or more appropriately the second term of (B.21) below then gives

$$\frac{\partial}{\partial a_k}e^{S\{a\}}\int_0^t ds\int d\{a'\}\mathcal{T}_{kj}^M(\{a, a'\}; ts)\frac{\partial}{\partial a'_j}\frac{D_M(\{a'\}, s)}{D_E\{a'\}}$$
$$\to \sum_k \zeta_k\frac{\partial}{\partial a_k}\left[\frac{\partial}{\partial a_k} - \frac{\partial S\{a\}}{\partial a_k}\right]D_M(\{a\}, t)$$
$$= \zeta_p\frac{\partial}{\partial p}\left[\frac{\partial}{\partial p} + p\right]D_M(\{a\}, t) \tag{5.10}$$

where we have noted

$$S\{a\} = S(x, p) = -\frac{p^2}{2} - U_{tot}(x), \quad U_{tot}(x) \equiv U(x) + \Delta U(x)$$
$$\zeta_x = 0, \quad \zeta_p \equiv \zeta \neq 0 \tag{5.11}$$

Also we have

$$\langle\dot{\hat{X}}; xp\rangle_M = p, \quad \langle\dot{\hat{P}}; xp\rangle_M = -U'_{tot}(x) \tag{5.12}$$

Putting together all these we get

$$\frac{\partial}{\partial t}D(x,p;t) = \left[-\frac{\partial}{\partial x}p + \frac{\partial}{\partial p}U'_{tot}(x) + \zeta\frac{\partial}{\partial p}\left(\frac{\partial}{\partial p}+p\right)\right]D(x,p;t) \quad (5.13)$$

This is known as Kramer's equation.[23]

5.1.2. Canonical case: $W = C$

We now explore the canonical case: $W = C$. The local equilibrium distribution is

$$\hat{D}_L(\hat{X},\hat{P},\hat{y};t) = \exp\{-\Phi(h^x(t),h^p(t)) + h^x(t)\hat{X} + h^p(t)\hat{P}\} \quad (5.14)$$

Then the normalization $\mathrm{Tr}\hat{D}_L = 1$ gives

$$\Phi(h^x(t),h^p(t)) = \ln \mathrm{Tr}\exp\{h^x(t)\hat{X} + h^p(t)\hat{P}\} \quad (5.15)$$

The Legendre transformation gives

$$\Psi(\bar{x}(t),\bar{p}(t)) = h^x(t)\bar{x}(t) + h^p(t)\bar{p}(t) - \Phi(h^x(t),h^p(t)) \quad (5.16)$$

with

$$\bar{x}(t) = \frac{\partial\Phi(h^x(t),h^p(t))}{\partial h^x(t)} = \frac{\left\langle \hat{X}e^{h^x(t)\hat{X}+h^p(t)\hat{P}}\right\rangle}{\left\langle e^{h^x(t)\hat{X}+h^p(t)\hat{P}}\right\rangle}$$

$$\bar{p}(t) = \frac{\partial\Phi(h^x(t),h^p(t))}{\partial h^x(t)} = \frac{\left\langle \hat{P}e^{h^x(t)\hat{X}+h^p(t)\hat{P}}\right\rangle}{\left\langle e^{h^x(t)\hat{X}+h^p(t)\hat{P}}\right\rangle} \quad (5.17)$$

and also

$$h^x(t) = \frac{\partial\Psi(\bar{x}(t),\bar{p}(t))}{\partial\bar{x}(t)} \qquad h^p(t) = \frac{\partial\Psi(\bar{x}(t),\bar{p}(t))}{\partial\bar{p}(t)(t)} \quad (5.18)$$

The averaged time evolution equations are

$$\dot{\bar{x}}(t) = -\Lambda_{xx}(t)h^x(t) - \Lambda_{xp}(t)h^p(t) - \int_0^t ds\,\Upsilon_{xx}(ts)h^x(s) - \int_0^t ds\,\Upsilon_{xp}(ts)h^p(s)$$

$$\dot{\bar{p}}(t) = -\Lambda_{px}(t)h^x(t) - \Lambda_{pp}(t)h^p(t) - \int_0^t ds\,\Upsilon_{px}(ts)h^x(s) - \int_0^t ds\,\Upsilon_{pp}(ts)h^p(s) \quad (5.19)$$

We now make a slow dynamics approximation where $|h^p|$ is assumed to be small but $|h^x|$ need not be small. Here we note

$$\langle \dot{\hat{X}}; \{x, p\}\rangle_M = p, \quad \langle \dot{\hat{P}}; \{x, p\}\rangle_M = -U'(x) - \Delta U'(x) \tag{5.20}$$

Then, noting $\hat{L}\hat{X} = -\hat{P}$, we obtain since the momentum distribution can be assumed to relax to the equilibrium one rapidly,

$$\begin{aligned}\Lambda_{xx}(t) &= \langle \delta_t xp\rangle_L \approx 0, \quad \Lambda_{xp}(t) = \langle \delta_t x F(x)\rangle_L = \langle \hat{X}(-\hat{L}\hat{P})\rangle_L \\ &= \langle (\hat{L}\hat{X})\hat{P}\rangle_L = -\langle \hat{P}^2\rangle_L \approx -1 \\ \Lambda_{px}(t) &= \langle p^2\rangle_L \approx 1, \quad \Lambda_{pp} = \langle \delta_t pF(x)\rangle_L \approx 0\end{aligned} \tag{5.21}$$

Next, since the Υ's involve only the parts projected out by P^C, the only remaining component without reversible mode coupling terms is Υ_{pp}. Thus we assume that the force on the Brownian particle by the surrounding fluid changes very rapidly, which permits us to put

$$\Upsilon_{pp}(ts) \approx 2\zeta\delta(t-s) \tag{5.22}$$

Finally we find

$$\begin{aligned}\dot{\bar{x}}(t) &= h^p(t) \\ \dot{\bar{p}}(t) &= -h^x(t) - \zeta h^p(t)\end{aligned} \tag{5.23}$$

Let us now consider

$$\Phi(h^x, h^p) = \ln \mathrm{Tr} e^{h^x\hat{X}+h^p\hat{P}} = \left(\ln \int d\hat{X} e^{-U_{tot}+h^x\hat{X}}\right) + \frac{(h^p)^2}{2} + cst. \tag{5.24}$$

where *cst* stands for an unimportant additive constant here and after. Next we find by Legendre transformation,

$$\begin{aligned}\Psi(\bar{x}, \bar{p}) &= h^x\bar{x} + h^p\bar{p} - \Phi(h^x, h^p) \\ &= h^x\bar{x} + h^p\bar{p} - \frac{(h^p)^2}{2} - \left(\ln \int d\hat{X} e^{-U_{tot}+h^x\hat{X}}\right) + cst.\end{aligned} \tag{5.25}$$

with

$$\bar{x} = \frac{\partial\Phi(h^x, h^p)}{\partial h^x} = \frac{\int d\hat{X}\hat{X} e^{-U_{tot}(\hat{X})+h^x\hat{X}}}{\int d\hat{X} e^{-U_{tot}(\hat{X})+h^x\hat{X}}} \tag{5.26}$$

This result can be inverted to give $h^x = h^x(\bar{x})$. Here h^p does not enter in the rhs of (5.26). We also have

$$\hat{\bar{p}} = \frac{\partial\Phi(h^x, h^p)}{\partial h^p} = h^p = \langle U'_{tot}\rangle \tag{5.27}$$

Therefore the time evolution equations are

$$\dot{\bar{x}} = h^p = \bar{p}$$
$$\dot{\bar{p}} = -h^x - \zeta h^p = -h^x(\bar{x}) - \zeta \bar{p} \tag{5.28}$$

Now we take a strong friction limit for ζ which requires to put the rhs of the second memeber of (5.28) to zero. Hence we get

$$\dot{\bar{x}} = -\frac{1}{\zeta} h^x(\bar{x}) \tag{5.29}$$

Now we take the limit of very steep symmtric double-well structure around $x = 0$ for $U_{tot}(x)$. The minimum occurs at $x = \pm x_m$ with $U_{min} = U_{\text{tot}}(\pm x_m)$. Then the contributions to $\bar{x}$ come mainly from these minima:

$$\bar{x} \simeq x_m \frac{-e^{-h^x x_m} + e^{h^x x_m}}{e^{-h^x x_m} + e^{h^x x_m}} = x_m \tanh(h^x x_m) \tag{5.30}$$

or its inverse

$$h^x \simeq \frac{1}{x_m} \tanh^{-1}\left(\frac{\bar{x}}{x_m}\right) \tag{5.31}$$

Hence the time evolution equation in this overdamped case is

$$\dot{\bar{x}} = -\frac{1}{\zeta x_m} \tanh^{-1}\left(\frac{\bar{x}}{x_m}\right) \tag{5.32}$$

It can be integrated to give

$$cst - t = \int^{\bar{x}} dx \frac{\zeta x_m}{\tanh^{-1}\left(\frac{x}{x_m}\right)} \tag{5.33}$$

We observe the following:

- $x = 0$ is a stable fixed point. Indeed near that point we get $\dot{\bar{x}} = -\frac{1}{\zeta x_m^2}\bar{x}$
- No trace of slow barrier crossing is found. Indeed the barrier height $U(0) - U_{\text{min}}$ never appears.
- No evidence of spontaneously broken symmetry appears.

These findings indicate inadequacies of the averaged equation. The same may be said for deterministic dynamical density functional theories.[5–10] It would be interesting to consider other cases than those two limiting cases of $W = M$ and $W = C$ that will serve to test our general approach.

5.2. One-Component Fluid

Here the relevant variables $\{\hat{A}\} \equiv \{\hat{\rho}(\mathbf{r}), \mathbf{g}(\mathbf{r})\}$, the particle number density and the momentum density, respectively, are defined through the following microscopic expressions:

$$\hat{\rho}(\mathbf{r}) \equiv \sum_j \delta(\mathbf{r}-\mathbf{r}_j), \quad \hat{\mathbf{g}}(\mathbf{r}) \equiv \sum_j \frac{\mathbf{p}_j}{m}\delta(\mathbf{r}-\mathbf{r}_j) \tag{5.34}$$

where $\mathbf{r}_j$ and $\mathbf{p}_j$ are the position vector and the momentum, respectively, of the particle j, and m its mass.

The local equilibrium distribution is

$$\hat{D}_L(\hat{x},t) = \exp\left(-\Phi(\{h^\rho(t), \mathbf{h}^{\mathbf{g}}(t)\} + \int d\mathbf{r}h^\rho(\mathbf{r},t)\hat{\rho}(\mathbf{r}) + \int d\mathbf{r}\mathbf{h}^{\mathbf{g}}(\mathbf{r},t)\cdot\hat{\mathbf{g}}(\mathbf{r})\right) \tag{5.35}$$

where $h^\rho(r,t)$ and $\mathbf{h}^{\mathbf{g}}(\mathbf{r},t)$ are, respectively, the local chemical potential and the local velocity.

Hereafter we only consider the canonical case and derive the deterministic dynamical density functional equation. The time evoulution equations with the Markovian approximation take the form:

$$\begin{aligned}
\frac{\partial}{\partial t}\bar{\rho}(\mathbf{r},t) &= -\int d\mathbf{r}'[\Lambda_{\rho\rho}(\mathbf{r}\mathbf{r}',t) + \zeta_{\rho\rho}(\mathbf{r}\mathbf{r}',t)]h^\rho(\mathbf{r}',t) \\
&\quad -\int d\mathbf{r}'[\Lambda_{\rho g}(\mathbf{r}\mathbf{r}',t) + \zeta_{\rho g}(\mathbf{r}\mathbf{r}',t)]\cdot\mathbf{h}^{\mathbf{g}}(\mathbf{r}',t) \\
\frac{\partial}{\partial t}\bar{\mathbf{g}}(\mathbf{r},t) &= -\int d\mathbf{r}'[\Lambda_{g\rho}(\mathbf{r}\mathbf{r}',t) + \zeta_{g\rho}(\mathbf{r}\mathbf{r}',t)]h^\rho(\mathbf{r}',t) \\
&\quad -\int d\mathbf{r}'[\Lambda_{gg}(\mathbf{r}\mathbf{r}',t) + \zeta_{gg}(\mathbf{r}\mathbf{r}',t)]\cdot\mathbf{h}^{g}(\mathbf{r}',t)
\end{aligned} \tag{5.36}$$

First we examine the Λ's.

$$\begin{aligned}
\Lambda_{\rho\rho}(\mathbf{r}\mathbf{r}',t) &= \langle\rho(\mathbf{r})\langle\nabla'\cdot\hat{\mathbf{g}}(\mathbf{r}');\{\rho\mathbf{g}\}\rangle_M\rangle_L(t) \\
&= \langle\rho(\mathbf{r})\nabla'\cdot\mathbf{g}(\mathbf{r}')\rangle_L(t) \simeq 0 \\
\Lambda_{\rho g}(\mathbf{r}\mathbf{r}',t) &= \langle\rho(\mathbf{r})\langle[-\hat{L}\hat{\mathbf{g}}(\mathbf{r}')];\{\rho\mathbf{g}\}\rangle_M\rangle_L(t) \\
&\simeq \langle[\hat{L}\hat{\rho}(\mathbf{r})]\hat{\mathbf{g}}(\mathbf{r}')\rangle_L(t) \\
&= \langle\nabla\cdot\hat{\mathbf{g}}(\mathbf{r})]\hat{\mathbf{g}}(\mathbf{r}')\rangle_L(t) \\
&\simeq \frac{1}{m}\nabla[\bar{\rho}(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}')] \\
\Lambda_{g\rho}(\mathbf{r}\mathbf{r}',t) &= \langle\mathbf{g}(\mathbf{r})\langle\dot{\hat{\rho}}(\mathbf{r}');\{\rho\mathbf{g}\}\rangle_M\rangle_L(t) \\
&= \langle\mathbf{g}(\mathbf{r})(-\nabla')\cdot\hat{\mathbf{g}}(\mathbf{r}')\rangle_L(t) \\
&\simeq -\frac{1}{m}\nabla'\bar{\rho}(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}') = \frac{1}{m}\bar{\rho}(\mathbf{r},t)\nabla\delta(\mathbf{r}-\mathbf{r}') \\
\Lambda_{gg}(\mathbf{r}\mathbf{r}',t) &\simeq 0
\end{aligned} \tag{5.37}$$

In the above we have used $\langle\hat{\mathbf{g}}(\mathbf{r})\hat{\mathbf{g}}(\mathbf{r}')\rangle_L(t) \simeq \frac{1}{m}\mathbf{1}\bar{\rho}(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}')$. As for dissipative parts the ζ's and the ζ's, we assume first $\zeta_{\rho\rho} \simeq \zeta_{\rho g} \simeq \zeta_{g\rho} \simeq 0$. For $\zeta_{gg}(\mathbf{r}-\mathbf{r}',t)$ we take up the idea that the momentum relaxation here is basically microscopic processes where conservation laws play no role. Thus we may assume

$$\zeta_{gg}(\mathbf{r}-\mathbf{r}',t) \simeq \tau^{-1}\bar{\rho}(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}') \tag{5.38}$$

so that τ has a meaning of momentum relaxation time.

On the other hand we have

$$h^{\rho}(\mathbf{r}) = \frac{\delta\Psi\{\bar{\rho},\bar{\mathbf{g}}\}}{\delta\bar{\rho}(\mathbf{r})}, \quad \mathbf{h}^{g}(\mathbf{r}) = \frac{\delta\Psi\{\bar{\rho},\bar{\mathbf{g}}\}}{\delta\mathbf{g}(\mathbf{r})} = \frac{\bar{\mathbf{g}}(\mathbf{r})}{\bar{\rho}(\mathbf{r})} \tag{5.39}$$

We thus have

$$\begin{aligned} \frac{\partial}{\partial t}\bar{\rho}(\mathbf{r},t) &= -\nabla\cdot\bar{\mathbf{g}}(\mathbf{r},t) \\ \frac{\partial}{\partial t}\bar{\mathbf{g}}(\mathbf{r},t) &= -\bar{\rho}(\mathbf{r},t)\nabla h^{\rho}(\mathbf{r},t) - \tau^{-1}\mathbf{g}(\mathbf{r},t) \end{aligned} \tag{5.40}$$

If the relaxation is strong enough so that the inertia term $\frac{\partial}{\partial t}\bar{\mathbf{g}}(\mathbf{r},t)$ above can be neglected, we have

$$\mathbf{g}(\mathbf{r},t) \simeq -\tau\bar{\rho}(\mathbf{r},t)\nabla h^{\rho}(\mathbf{r},t) \tag{5.41}$$

Substituting this into the rhs of the first member of (5.40) and using the first member of (5.39) we finally find

$$\frac{\partial}{\partial t}\bar{\rho}(\mathbf{r},t) = \tau\nabla\cdot\bar{\rho}(\mathbf{r},t)\nabla\frac{\delta\Psi\{\bar{\rho},\bar{\mathbf{g}}=0\}}{\delta\bar{\rho}(\mathbf{r})} \tag{5.42}$$

where we have put $\bar{\mathbf{g}} = 0$ in Ψ since fluctuation effects are already fully incorporated and the averaged momentum density is small. Thus we recover the known deterministic DDFT equation.[5,6]

Before closing we examine the momentum conservation associated with the reversible part of of the second member of (??) as reproduced below:

$$\frac{\partial}{\partial t}(\mathbf{r},t) = -\bar{\rho}(\mathbf{r},t)\nabla h^{\rho}(\mathbf{r},t) \tag{5.43}$$

Das and Mazenko[24] have shown that if $\Psi\{\bar{\rho}\} = \int d\mathbf{r}\varphi(\bar{\rho}(\mathbf{r},\nabla\bar{\rho}(\mathbf{r}))$ with φ some function, one can write $\bar{\rho}(\mathbf{r},t)\nabla\frac{\delta\Psi\{\bar{\rho}\}}{\delta\bar{\rho}(\mathbf{r})} = \nabla\cdot\Sigma$ which takes care of the short range force part of the free energy functional. For long range force part such that the force density is given by $\mathbf{F}(\mathbf{r}) = -\rho(\mathbf{r})\nabla\int d\mathbf{r}'U(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')$ with $U(\mathbf{r})$ the long range interaction potential, we can explicitly show that $\int d\mathbf{r}\mathbf{F}(\mathbf{r}) = 0$, which expresses Newton's law of action and reaction.

6. CONCLUDING REMARKS

We have presented a new approach to interpolate deterministic and fully stochastic reduced dynamics. So far this question has been mainly asked by people working on dynamical extentions of the density functional theories of liquid state which are enormously successful.[3,4] We have proposed a general formalism of reduced dynamics which correctly reproduced the two limiting cases: fully deterministic and fully stochastic.

The real value of our approach must be judged by the degree of successes when applied to situations where neither of the two limiting approaches is adequate. Perhaps the Brownian particle in an external field treated in section **5.1** can provide a testing ground for this purpose.

APPENDIX A: USEFUL PROPERTIES OF PROJECTION OPERATORS

A.1 Proof of $\dot{P}^W(t)\hat{D}(t) = 0$

We prove here the following:

$$\dot{P}^W(t)\hat{D}(t) = 0 \tag{A.1}$$

where we sometimes denote time derivative by an overdot. First note that by definition we have

$$\dot{P}^W(t)\hat{D}(t) = \frac{d}{dt}[P^W(t)\hat{D}(t)] - P^W(t)\dot{\hat{D}}(t) = \dot{\hat{D}}_W(t) \\ -\hat{D}_W(t)\big[\mathrm{Tr}\dot{\hat{D}}(t) + \delta_t\psi_W^T \cdot \chi_W(t)^{-1} \cdot \mathrm{Tr}\delta_t\psi_W\dot{\hat{D}}(t)\big] \tag{A.2}$$

We now use $\mathrm{Tr}\dot{\hat{D}}(t) = 0$. Differentiating $\mathrm{Tr}\delta_t\psi_W\hat{D}(t) = 0$ with respect to time we find $\mathrm{Tr}\delta_t\psi_W\dot{\hat{D}}(t) = \frac{\partial}{\partial t}\langle\psi_W\rangle(t) = \frac{\partial}{\partial t}\langle\psi_W\rangle_W(t)$. We thus find the following if we further note that $\hat{D}_W(t)$ depends on time only through $\lambda_W(t)$:

$$\dot{P}^W(t)\hat{D}(t) = \hat{D}_W(t)\big[\dot{\lambda}_W^{\mathrm{T}}(t)\cdot\psi_W - \delta_t\psi_W^T \cdot \chi_W(t)^{-1} \cdot \frac{\partial}{\partial t}\langle\psi_W\rangle_W(t)\big] \tag{A.3}$$

Now, writing $\mathrm{Tr}\dot{\hat{D}}_W(t) = 0$ explicitly we obtain

$$\mathrm{Tr}\dot{\lambda}_W^T(t)\cdot\psi_W\hat{D}_W(t) = \dot{\lambda}_W^T(t)\cdot\langle\psi_W\rangle_W(t) \\ = \frac{\partial\langle\psi_W^T\rangle_W(t)}{\partial t}\cdot\chi_W(t)^{-1}\cdot\langle\psi_W\rangle_W(t) = 0 \tag{A.4}$$

Therefore, (A.3) becomes

$$\dot{P}^W(t)\hat{D}(t) = \hat{D}_W(t)\left[\dot{\lambda}_W^T(t)\cdot\psi_W - \psi_W^T\cdot\chi_W(t)^{-1}\cdot\frac{\partial}{\partial t}\langle\psi_W\rangle_W(t)\right] = 0 \tag{A.5}$$

in view of the fact that a small change (expressed by a symbol δ) in $\lambda_W(t)$ is connected to that of $\langle\psi_W\rangle_W(t)$ by $\delta\lambda_W(t) = \chi_W(t)^{-1} \cdot \delta\langle\psi_W\rangle_W(t)$. The last property is also consistent with (3.34) derived there.

A.2 A Projector Identity for Time Evolution

We start from the following identities for constant projection operators P and $Q \equiv 1 - P$:

$$Le^{Lt} = LPe^{Lt} + L\int_0^t dse^{QL(T-s)}QLPe^{Ls} + Le^{QLt}Q \qquad \text{(A.6)}$$

Proof: The integrand of the middle term above is

$$Le^{QL(t-s)}QLPe^{Ls} = LQe^{LQ(t-s)}LPe^{Ls} = \frac{\partial}{\partial s}LQe^{LQ(t-s)}e^{Ls}$$

Thus the middle term of (A.6) is

$$LQe^{LQ(t-s)}e^{Ls}\Big|_{s=0}^{s=t} = LQe^{Lt} - LQe^{LQt} = LQe^{Lt} - Le^{QLt}Q$$

□

Next turn to the case of time-dependent projectors $P(t)$ and $Q(t) \equiv 1 - P(t)$. We will have a generalized version of (A.6) as

$$Le^{Lt} = LP(t)e^{Lt} + L\int_0^t dse_+^{\int_s^t ds'Q(s')L}Q(s)LP(s)e^{Ls} + Le_+^{\int_0^t Q(s)Lds}Q(0) \qquad \text{(A.7)}$$

Proof: For the integrand of the middle term above we get since $Q(s')Q(s) = Q(s)$,

$$Le_+^{\int_s^t ds'Q(x')L}Q(s)LP(s)e^{Ls} = Le_+^{\int_s^t ds'Q(s')LQ(s)'}Q(s)LP(s)e^{Ls}$$

$$= Le_+^{\int_s^t ds'LQ(x')L}Q(s)L(s)(1-Q(s))e^{Ls} = \frac{\partial}{\partial s}\left(Le_+^{\int_s^t dsQ(s')LQ(s')}\right)Q(s)e^{Ls}$$

$$+ Le_+^{\int_s^t ds'Q(s')LQ(s')}Q(s)Le^{LS}$$

Then we can put $Q(s)Le^{Ls} = Q(s)\frac{\partial}{\partial s}e^{Ls} = \frac{\partial}{\partial s}Q(s)e^{Ls}$ if we can assume $\dot{P}(s)e^{Ls} = 0$ which is valid for $P(t) = P^W(t)$ from (A. 1) for this case. Then we get

$$e_+^{\int_s^t ds' Q(s')L} Q(s)LP(s)e^{Ls} = \frac{\partial}{\partial s}\left(e_+^{\int_s^t ds' Q(s')LQ(s')} Q(s)e^{Ls}\right)$$

Thus the middle term of (A.7) is

$$Le_+^{\int_s^t ds' Q(s')LQ(s')} Q(s)e^{Ls}\Big|_{s=0}^{s=t} = LQ(t)e^{Lt} - Le_+^{\int_s^t ds Q(s)LQ(s)} Q(0)$$

$$= LQ(t)e^{Lt} - Le_+^{\int_0^t ds Q(s)L} Q(0)$$

□

In order to derive (3.3), we have to operate $P^W(t)$ onto (A.7) from the left and the resulting operator identity is acted upon $\hat{D}(\hat{x}, 0)$. The the last term of (A.7) drops out due to the particular choice of $\hat{D}(\hat{x}, 0)$, that is, $Q(0)\hat{D}(\hat{x}, 0) = Q(0)\hat{D}_W(\hat{x}, 0) = 0$.

APPENDIX B: MICROCANONICAL CASE: W=M

In this section we present a derivation of the usual Fokker-Planck type equation for the microcanonical probability distribution function $D_M(\{a\}, t)$ in the frame work of our approach. The steps of actual derivation are far from obvious although this is expected. So we go into some details.

The projected phase space distribution function for this case is

$$\hat{D}_M(\hat{x}, t) \equiv P^M \hat{D}(\hat{x}, t) = e^{-S\{\hat{A}(\hat{x})\}} D_M(\{\hat{A}(\hat{x})\}, t) = e^{\lambda_M(t)^T \cdot \psi_M\{\hat{A}(\hat{x})\}} \tag{B.1}$$

where the distribution function for $\{a\}$ is now given by

$$D_M(\{a\}, t) \equiv \mathrm{Tr}\delta\{a - \hat{A}(\cdot)\}\hat{D}_m(\cdot, t) \tag{B.2}$$

Hence we have

$$\lambda_M(t)^T \cdot \psi_M\{a\} = \psi_M\{a\}^T \cdot \lambda_M(t) = -S\{a\} + \ln D_M(\{a\}, t) \tag{B.3}$$

Now, the completeness of the set $\{\psi_M\}$ implies that we can alternatively take, suppressing the time argument t for a while,

$$\hat{D}_M(\hat{x}, t) = e^{\lambda\{\hat{A}(\hat{x})\}} \tag{B.4}$$

where $\lambda\{a\}$ is an arbitrary functional. Then we write discretizing the space of $\{a\}$

$$\lambda\{\hat{A}\} = \lambda_M^T \cdot \psi_M = \int \lambda\{a\}\delta\{a - \hat{A}\}d\{a\} \Longrightarrow \sum_{\{a\}} \lambda\{a\}\delta\{a - \hat{A}\}\Delta\{a\} \tag{B.5}$$

where $\Longrightarrow$ indicates transition to the discretized space of $\{a\}$. The above equation is explained in more detail. $\Delta\{a\}$ is the volume element of the space of $\{a\}$ which will be written simply as Δ_M hereafter. The components of vectors in the second member of (B.5) are labelled by $\{a\}$ that will appear as suffices, and are given by

$$[\lambda_M]_{\{a\}} \equiv \lambda\{a\}, \quad [\psi_M\{\hat{A}\}]_{\{a\}} \equiv \delta\{a - \hat{A}\} \Longrightarrow \Delta\{a - \hat{a}\} \tag{B.6}$$

Here $\delta\{a - a'\}d\{a\} \Longrightarrow \Delta\{a - a'\}$ is Kronecker's delta in the discretized space of $\{a\}$ such that $\Delta\{a - a'\} = 1$ for $\{a\} = \{a'\}$ and $\Delta\{a - a'\} = 0$ for $\{a\} \neq \{a'\}$.

Now, with the trial distibution $\hat{D}'_M(\hat{x})$, the entropy $\mathcal{S}\{\hat{D}'_M(\cdot)\}$, (2.2) becomes

$$S\{\hat{D}'_M(\cdot)\} = -\mathrm{Tr}\hat{D}'_M(\cdot)\ln \hat{D}'_M(\cdot) + \sum_{\{a\}} \lambda\{a\}\mathrm{Tr}\Delta\{a - \hat{A}(\cdot)\}\hat{D}'_M(\cdot) \tag{B.7}$$

The maximum entropy condidition gives

$$\hat{D}_M(\hat{x}) = e^{\lambda\{\hat{A}(\hat{x})\}} \tag{B.8}$$

with λ determinded by the following:

$$\mathrm{Tr}\Delta\{a - \hat{A}(\cdot)\}e^{\lambda(\{\hat{A}(\cdot)\},t)} = \mathrm{Tr}\Delta\{a - \hat{A}(\cdot)\}\hat{d}(\cdot, t) \tag{B.9}$$

The lhs and rhs of the above equation are, respectively,

$$\begin{aligned}\mathrm{Tr}\Delta\{a - \hat{A}(\cdot)\}e^{\lambda(\{\hat{A}(\cdot)\},t)} &= e^{\lambda(\{a\},t)}\mathrm{Tr}\Delta\{a - \hat{A}(\cdot)\} = e^{\lambda(\{a\},t)+S\{a\}}\Delta_M \\ \mathrm{Tr}\Delta\{a - \hat{A}(\cdot)\}\hat{D}(\cdot, t) &= \mathrm{Tr}\delta\{a - \hat{A}(\cdot)\}\hat{D}(\cdot, t)\Delta_M = D_M(\{a\}, t)\Delta_M\end{aligned} \tag{B.10}$$

Hence we obtain

$$\lambda(\{a\}, t) = -S\{a\} + \ln D_M(\{a\}, t)\left(= \ln \hat{D}_M(\{\hat{A} \to a\}, t)\right) \tag{B.11}$$

Let us return to the time evolution equation (3.38) which now becomes

$$\frac{\partial}{\partial t}\lambda(\{a\}, t) = \sum_{\{a'\}} \chi_M^{-1}(\{a\}\{a'\}, t)[\mathcal{L}_m(\{a'\}, t) + \mathcal{M}_M(\{a'\}, t)] \tag{B.12}$$

where $\mathcal{L}_M(\{a'\}, t) \equiv [\mathcal{L}_M(t)]_{\{a'\}}$ and $\mathcal{M}_M(\{a'\}, t) \equiv [\mathcal{M}_M(t)]_{\{a'\}}$ are components of the vectors $\mathcal{L}_M(t)$, (3.36), and $\mathcal{M}_M(t)$,(3.37). Now we obtain from (B.11)

$$\frac{\partial}{\partial t}\lambda(\{a\}, t) = D_M^{-1}(\{a\}, t)\frac{\partial}{\partial t}D_M(\{a\}, t) \tag{B.13}$$

On the other hand, using $\langle\Delta\{a - \hat{A}\}\rangle M(t) = D_M(\{a - \hat{A}\}, t)\Delta_M$ we have, denoting $\delta_t\hat{X} \equiv \hat{X} - \langle\hat{X}\rangle_M(t)$ for any phase space function $\hat{X}$.

$$\begin{aligned}\chi_M(\{a\}\{a'\}; t) &= \langle\delta_t\Delta\{a - \hat{A}\}\delta_t\Delta\{a' - \hat{A}\}\rangle_M(t) \\ &= \Delta_M^2[\delta\{a - a'\}D_M(\{a\}, t) - D_M(\{a\}, t)D_M\{a'\}, t]\end{aligned} \tag{B.14}$$

Now, in view of $\int \chi_M(\{a\}\{a'\};t)d\{a'\} = 0$, the matrix $\chi_M(\{a\}\{a'\};t)$ is singular. Thus we have to replace (B.12) by

$$\sum_{\{a'\}} \chi_M(\{a\}\{a'\},t)\frac{\partial}{\partial t}\lambda(\{a'\},t) = \mathcal{L}_M(\{a\},t) + \mathcal{M}_M(\{a\},t) \tag{B.15}$$

The lhs can be worked out using (B.13) and (B.14) to obtain

$$\sum_{\{a'\}} \chi_M(\{a\}\{a'\},t)\frac{\partial}{\partial t}\lambda(\{a'\},t) = \Delta_M \frac{\partial}{\partial t} D_M(\{a\},t) \tag{B.16}$$

We now analyze the rhs of (B.15). The Eq. (B.6), that is, $[\psi_M(\{a'\},t)]_{\{a\}} = \Delta\{a-a'\} = \Delta_M \delta\{a-a'\}$ gives $[(\partial/\partial \underline{a}_k)\psi_M(\{\underline{a}\},t)]_{\{a\}} = \Delta_M(\partial/\partial \underline{a}_k)\delta\{a-\underline{a}\}$ and $[\delta_t \psi_M(\{a'\},t)]_{\{a\}} = \Delta_M[\delta\{a-a'\} - D_M(\{a\},t)]$. Then we use these results and a consequence of the normalization (3.29) saying that $\int d\{a'\}\langle \dot{\hat{A}}_j;\{a'\}\rangle_M f_M^j(\{a'\},t)D_M(\{a'\},t) = 0$ to obtain

$$[\mathcal{L}_M]_{\{a\}} = \Delta_M \langle \dot{\hat{A}}_j;\{a\}\rangle_M f_M^j(\{a\},t)D_M(\{a\},t) \tag{B.17}$$

Next we turn to $[\mathcal{M}_M]_{\{a\}}$ which becomes after integrating by parts with respect to $\underline{a}_k$,

$$[\mathcal{M}_M]_{\{a\}} = -\int_0^t ds \int d\{a'\} e^{-S\{a'\}} \Delta_M \left[\frac{\partial}{\partial a_k} e^{S\{a\}} \mathcal{T}_{kj}^M(\{a,a'\};ts)\right] \times f_M^j(\{a'\},s)D_M(\{a'\},s) \tag{B.18}$$

We remind that we can write

$$f_M^j(\{a\},t)D_M(\{a\},t) = -D_E(\{a\},t)\frac{\partial}{\partial a_j}\frac{D_M(\{a\},t)}{D_E(\{a\},t)}$$

and also the detailed balance condition is given by $\frac{\partial \langle \dot{\hat{A}}_j;\{a\}\rangle_M D_E\{a\}}{\partial a_j} = 0$. We finally obtain

$$[\mathcal{L}_M]_{\{a\}} = -\Delta_M \frac{\partial}{\partial a_j}\langle \dot{\hat{A}}_j;\{a\}\rangle_M D_M(\{a\},t) \tag{B.19}$$

and

$$[\mathcal{M}_M]_{\{a\}} = \Delta_M \frac{\partial}{\partial a_k} e^{S\{a\}} \int_0^t ds \int d\{a'\} \mathcal{T}_{kj}^M(\{a,a'\};ts)\frac{\partial}{\partial a'_j}\frac{D_M(\{a'\},s)}{D_E\{a'\}} \tag{B.20}$$

Putting (B.15) and (B.16) together with (B.19) and (B.20) we recover the following Fokker-Planck type equation

$$\frac{\partial}{\partial t} D_M(\{a\}, t) = -\frac{\partial}{\partial a_j} \langle \dot{\hat{A}}_j; \{a\} \rangle_M D_M(\{a\}, t) + \frac{\partial}{\partial a_k} e^{S\{a\}} \int_0^t ds \int d\{a'\} \mathcal{T}_{kj}^M(\{a, a'\}; ts) \frac{\partial}{\partial a'_j} \frac{D_M(\{a'\}, s)}{D_E\{a'\}} \tag{B.21}$$

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