A. DONEV

The GENERIC Formalism of Hans Christian Öttinger

For an isolated system, i.e., the microcanonical ensemble, and assuming the internal energy can be written as a function of coarse-grained variables exactly, $E(x)$, then the GENERIC formalism of Öttinger is appropriate. It also requires expressing the entropy as a function of the coarse-grained variables, $S(x)$

EINSTEIN DISTRIBUTION

$$\boxed{P_{eq}(x) = Z^{-1} \exp\left[S(x)/k_B \right]}$$

A. Doney $\underline{\text{GENERIC}}$ equation for $X(t)$:

$$\dot{x} = L \cdot \frac{\partial E}{\partial x} + M \cdot \frac{\partial S}{\partial x} + \sqrt{2k_B}\ \tilde{M} \boxdot W(t)$$

kinetic

or Ito

+ DRIFT:

reversible (conservative)

irreversible (dissipative)

$$L^* = -L$$

(skew-adjoint)

$$M^* = M$$

(self-adjoint)

$$\boxed{\tilde{M}\tilde{M}^* = M}$$

fluctuation-dissipation balance

$$\boxed{L \cdot \frac{\partial S}{\partial x} = 0}$$

$$\boxed{M \cdot \frac{\partial E}{\partial x} = 0}$$

$\underline{\text{degeneracy}}$ conditions

$\underline{\text{Fokker - Planck}}$

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} \cdot \left\{ \left[L \cdot \frac{\partial E}{\partial x} + M \cdot \frac{\partial S}{\partial x} \right] P - k_B\ M \cdot \frac{\partial}{\partial x} P \right\}$$

which preserves $\exp[S/k_B]$

the GENERIC dynamics strictly conserves Energy: (3)

$$dE = \frac{\delta E}{\delta x}\cdot dx + \frac{\delta^2 E}{\delta x^2} : (k_B M)\, dt \quad \text{(Ito's formula)}$$

$$= k_B \left[\frac{\delta E}{\delta x}\cdot\left(\frac{\delta}{\delta x}\cdot M\right) + \left(\frac{\delta^2 E}{\delta x^2}\right) : M \right] dt$$

since $\frac{\delta E}{\delta x}\cdot L\cdot\frac{\delta E}{\delta x} = 0$ by antisymmetry

and $\tilde{M}\cdot\frac{\partial E}{\partial x} = 0$ $\quad \frac{\delta E}{\delta x}\cdot M\cdot\frac{\delta S}{dx} = 0$

$$= k_B \frac{\delta}{\delta x}\cdot\left[M\cdot\frac{\delta E}{\delta x}\right] = 0 \quad \text{identically}$$

If we do the same for entropy

$$dS = \frac{\delta S}{\delta x} \cdot dx + \frac{\delta^2 S}{\delta x^2} : (k_B M)\, dt =$$

$$= \Big[\underbrace{\frac{\delta S}{\delta x} \cdot M \cdot \frac{\delta S}{\delta x}}_{\geq 0} + \frac{\delta^2 S}{\delta x^2} : (k_B M) \Big] dt$$

$$+ \frac{\delta S}{\delta x} \cdot \sqrt{2 k_B}\, \tilde{M}\, dB$$

$$+ k_B \frac{\delta S}{\delta x} \cdot \left(\frac{\partial}{\partial x} \cdot M \right) dt \quad \text{from (drift)}$$

since M is SPD,

so on average $dS/dt \geq 0$ in deterministic limit ($k_B \to 0$). When fluctuations are present the second law is not strictly obeyed and entropy can decrease over individual paths.

Following Pep Español:

4a

Note however that the Gibbs–Jaynes entropy

$$\tilde{S} = -k_B \int P(x) \ln\left[\frac{P(x)}{P_{eq}(x)}\right] dx$$

does strictly increase with time even in the presence of fluctuations (and thus obeys a second law).

$$\frac{d\tilde{S}[P(x,t)]}{dt} = \int dx \, \frac{\delta\tilde{S}}{\delta P} \frac{\partial P}{\partial t}$$

$$= - \int dx \left[1 + \ln\frac{P}{P_{eq}}\right] \frac{\partial P}{\partial t}$$

Let us rewrite the FPE in the equivalent but instructive form: (46)

$$\text{flux} = \left[\frac{\partial S}{\partial x} - k_B \frac{\partial}{\partial x}\right] P =$$

where $P_{eq} = e^{S/k_B}$

$$= -\left[k_B P_{eq} \frac{\partial P_{eq}^{-1}}{\partial x} + k_B \frac{\partial}{\partial x}\right] P = -k_B F P$$

where the flux operator

$$F = P_{eq}(x) \frac{\partial}{\partial x} P_{eq}^{-1}$$

clearly $F P_{eq} = 0$

In this calculation we will ignore the reversible part (turns out not to affect ζ at all as expected)

Yet another way to write this (4C)

$$FP = P\frac{\partial}{\partial x}\ln\frac{P}{P_{eq}}$$

So we will take the FPE in the form

$$\frac{\partial P}{\partial t} = -k_B\frac{\partial}{\partial x}\cdot\left[MP\frac{\partial}{\partial x}\ln\left(\frac{P}{P_{eq}}\right)\right]$$

<u>or</u>

$$= -k_B\frac{\partial}{\partial x}\cdot\left[MP_{eq}\frac{\partial}{\partial x}\left(\frac{P}{P_{eq}}\right)\right]$$

Let's go back to the entropy

$$\frac{d\tilde{S}}{dt} = -\int dx \left(1 + \ln\frac{P}{P_{eq}}\right) \frac{\partial P}{\partial t} =$$

$$= +k_B \int dx \left(1 + \ln\frac{P}{P_{eq}}\right) \frac{\partial}{\partial x} \cdot \left[M\, P \frac{\partial}{\partial x} \ln\left(\frac{P}{P_{eq}}\right)\right]$$

integration by parts

$$= k_B \int P \underbrace{\left[\frac{\partial}{\partial x} \ln\left(\frac{P}{P_{eq}}\right)\right]}_{g} \cdot M \cdot \left[\frac{\partial}{\partial x} \ln\left(\frac{P}{P_{eq}}\right)\right] dx$$

$$= k_B \int P \; g \cdot M \cdot g \; dx \geq 0$$

because $M(x) \geq 0 \Rightarrow$

$\boxed{d\tilde{S}/dt \geq 0}$ strictly!

Importantly, the GENERIC dynamics is <u>time-reversible</u> with respect to the Einstein distribution $P(x) \sim e^{S/k_B}$ when $L=0$ and more generally it preserves this distribution.

<u>Dissipative</u> part:

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} \cdot \left\{ M \underbrace{\left[\frac{\partial S}{\partial x} - k_B \frac{\partial}{\partial x} \right] P}_{\text{zero flux}} \right\} = 0$$

does not affect Fluctuation-dissipation balance

So that part of the dynamics is time-reversible w.r.t. Einstein distribution.

Non-dissipative (reversible) part

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\cdot\left\{\left[L\cdot\frac{\partial E}{\partial x}\right]P\right\}$$

Assume $P \sim f(S)$ depends on entropy only

$$\frac{\partial P}{\partial t} = -\underbrace{\left(L : \frac{\partial^2 E}{\partial x^2}\right)}_{\text{zero since}} P - f' \underbrace{\frac{\partial S}{\partial x}\cdot L}_{\text{zero}}\cdot\frac{\partial E}{\partial x}$$

$$\boxed{\sum_{i,j} L_{ij}\frac{\partial^2 E}{\partial x_i\,\partial x_j} = -\sum L_{ij}\frac{\partial^2 E}{\partial x_i\,\partial x_j} = 0}$$

$$-\left(\frac{\partial}{\partial x}\cdot L\right)\cdot\frac{\partial E}{\partial x}P$$

must also be zero

So we need an additional condition

$$\boxed{\frac{\partial}{\partial x} \cdot L = 0}$$

More precisely, we want the $L \cdot \frac{\partial E}{\partial x}$ to be <u>Hamiltonian</u> (generalized here to non-canonical variables), which implies that the reversible dynamics preserves measures (volumes). In the GENERIC formalism this is expressed as stronger Jacobi identity relations in terms of Poisson brackets...

:

19-2011 10:46

One can generalize the Langevin description to more general sets of coarse-grained variables x.

For systems in the canonical ensemble i.e. isothermal systems, one considers a coarse-grained Hamiltonian or a free energy that represents the effective Hamiltonian in terms of the chosen variables [see entropy lectures]

$$\mathcal{H}(x) \equiv F(x)$$

OCT-18-2011 10:46

A Markovian stochastic dynamics for x that preserves the equilibrium distribution

$$P_{eq}(x) = Z^{-1} \exp\left[-\beta H(x)\right]$$

is

"reversible" "irreversible" "fluctuations"

$$\dot{x} = L \cdot \frac{\partial H}{\partial x} - \left(G G^*\right) \cdot \frac{\partial H}{\partial x} + (2kT)^{1/2} G \cdot W(t)$$

$$+ kT \frac{\partial}{\partial x} \cdot \left[G G^* - L \right]$$

Ito

spurious drift

Here $\boxed{M(x) = G G^* \succeq 0}$ or $G \cdot \left(\frac{\partial}{\partial x} \cdot G \right)$ less generally

P.011

A. Donev

Augmented Langevin equation:

coarse-grained Hamiltonian

$$\begin{cases} \dot{x} = L \cdot \frac{\partial H}{\partial x} - (GG^*) \cdot \frac{\partial H}{\partial x} + \sqrt{2kT} \cdot G \boxed{\cdot} W(t) & \text{[kinetic interpretation]} \\ \quad \underline{\underline{\text{or}}} + kT \frac{\partial}{\partial x} \cdot (GG^*) & \text{[Ito]} \\ L^* = -L \\ \frac{\partial}{\partial x} \cdot L = 0 & \text{(incompressibility)} \end{cases}$$

Corresponding $\underline{\underline{\text{FPE}}}$ (forward Kolmogorov)

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \cdot \left[(GG^*) \cdot \left(\frac{\partial H}{\partial x} P + kT \frac{\partial P}{\partial x} \right) \right]$$

$$- \frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial P}{\partial x}$$

A. Donev

It is easy to show that

$$P_{eq}(x) = Z^{-1} e^{-H(x)/kT}$$

is the equilibrium distribution since

$$\frac{\partial P_{eq}}{\partial x} = -\frac{1}{(kT)} \frac{\partial H}{\partial x} P_{eq}$$

$$\Rightarrow \quad \frac{\partial H}{\partial x} P_{eq} + kT \frac{\partial P_{eq}}{\partial x} = 0$$

so there is identically no-flux in phase space for any G, if L = 0 (think detailed balance versus balance)

Also: $\frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial P_{eq}}{\partial x} \sim \frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial H}{\partial x} = 0$ skew-symmetry