NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch. 8. Stochastic Descriptions

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Stochastic Descriptions

- Mesoscopic Models: Stochastic Processes
  - Brownian Motion: Langevin Equations
  - Mean-squared displacement and fluctuations
  - Fluctuation Dissipation relation
  - Fokker-Planck equation
  - Green-Kubo relation
- Micro to Macro: Multiscale expansion
- Micro to Meso: Projection Operators
- Path probabilities and barrier crossing

Mouvement Brownien : Processus de Langevin

Particule brownienne en suspension dans un liquide: rayon a = 1 μm.

équation de Newton pour son mouvement:

$$m\frac{d^2\boldsymbol{r}}{dt^2}=\boldsymbol{F}_{\mathrm{ext}}+\boldsymbol{F}_{\mathrm{liq}}$$

1) force due à un potentiel extérieur:

$$\boldsymbol{F}_{\mathrm{ext}}=-\frac{\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}$$

2) force due aux collisions avec les molécules environnantes:

$$\boldsymbol{F}_{\mathrm{liq}}=-\sum_{i=1}^{N}\frac{\partial U\left(\boldsymbol{r}-\boldsymbol{r}_i\right)}{\partial \boldsymbol{r}}$$

3) Approximation: Le liquide a deux effets : la particule donne énergie au liquide (*friction visqueuse*) et le liquide donne énergie à la particule (*fluctuations*) :

$$\boldsymbol{F}_{\mathrm{liq}}=\boldsymbol{F}_{\mathrm{visc}}+\boldsymbol{F}_{\mathrm{fluc}}$$

D'apres Stokes: $\boldsymbol{F}_{\mathrm{visc}}=-m\nu\frac{d\boldsymbol{r}}{dt}$ $\quad\nu=6\pi a\eta$

La force des flucutations est aléatoire.

Mouvement Brownien : Processus de Langevin

$$\boxed{m\frac{d^2\boldsymbol{r}}{dt^2}=-\frac{\partial U_{\text{ext}}}{\partial \boldsymbol{r}}-m\nu\frac{d\boldsymbol{r}}{dt}+\boldsymbol{F}_{\text{fluc}}}$$

L'équation de Newton avec cette force aléatoire ou stochastique
est appelée **équation de Langevin.**

4) La nature de la force stochastique

Pour décrire la force stochasique, on peut invoquer le théorème central limite selon lequel une somme de nombreuses variables est une distribution gaussienne. En particulier, sa moyenne statistique s'annule:

$$\langle \boldsymbol{F}_{\text{fluc}} \rangle = 0$$

Par ailleurs, les molécules se déplacent si vite que la force à un instant donné est essentiellement indépendante de celle à un instant suivant. Ceci se traduit en disant que la fonction de corrélation statistique de la force est égale à zéro dès que $t \neq t'$

$$\langle \boldsymbol{F}_{\text{fluc}}(t)\,\boldsymbol{F}_{\text{fluc}}(t') \rangle = 0, \quad t \neq t'$$

Mouvement Brownien : Processus de Langevin

4) ***La nature de la force stochastique***: pour élucider la nature de la force stochasique, nous étudions un système sans force exterior pour laquelle nous nous attendons le comportement diffusif.

Question: Quel est le déplacement quadratique moyenne? $\langle |\boldsymbol{r}(t)-\boldsymbol{r}(0)|^2 \rangle$

$$m\frac{d^2\boldsymbol{r}}{dt^2}=-m\nu\frac{d\boldsymbol{r}}{dt}+\boldsymbol{F}_{\text{fluc}}(t)$$

$$m e^{\nu t}\frac{d\boldsymbol{r}}{dt}-m e^{\nu t_0}\left(\frac{d\boldsymbol{r}}{dt}\right)_{t_0}=\int_{t_0}^{t} e^{\nu s}\boldsymbol{F}_{\text{fluc}}(s)\,ds$$

$$\boldsymbol{r}(t)-\boldsymbol{r}(t_0)=\nu^{-1}\left(1-e^{-\nu(t-t_0)}\right)\boldsymbol{v}(t_0)+\frac{1}{m}\int_{t_0}^{t} e^{-\nu s}\int_{t_0}^{s} e^{\nu s'}\boldsymbol{F}_{\text{fluc}}(s')\,ds'$$

$$=\nu^{-1}\left(1-e^{-\nu(t-t_0)}\right)\boldsymbol{v}(t_0)+\frac{1}{m\nu}\int_{t_0}^{t}\left(1-e^{\nu(s-t)}\right)\boldsymbol{F}_{\text{fluc}}(s)\,ds$$

$$\langle |\boldsymbol{r}(t)-\boldsymbol{r}(t_0)|^2\rangle=\nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2\langle \boldsymbol{v}(t_0)\boldsymbol{v}(t_0)\rangle$$

0 (causality)

$$+\frac{2}{m\nu^2}\left(1-e^{-\nu(t-t_0)}\right)\int_{t_0}^{t}\left(1-e^{\nu(s-t)}\right)\langle \boldsymbol{F}_{\text{fluc}}(s)\cdot\boldsymbol{v}(t_0)\rangle\,ds$$

$$+\frac{1}{(m\nu)^2}\int_0^t ds\int_0^t ds'\left(1-e^{\nu(s-t)}\right)\left(1-e^{\nu(s'-t)}\right)\langle \boldsymbol{F}_{\text{fluc}}(s)\cdot\boldsymbol{F}_{\text{fluc}}(s')\rangle$$

$\Rightarrow$ besoin de $\langle \boldsymbol{v}(t_0)\boldsymbol{v}(t_0)\rangle$, $\langle \boldsymbol{F}_{\text{fluc}}(s)\boldsymbol{F}_{\text{fluc}}(s')\rangle$

Mouvement Brownien : Processus de Langevin

4) ***La nature de la force stochastique***:

$$\left\langle \left|\boldsymbol{r}(t)-\boldsymbol{r}(t_0)\right|^2\right\rangle = \nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2\left\langle \boldsymbol{v}(t_0)\cdot\boldsymbol{v}(t_0)\right\rangle + \frac{1}{(m\nu)^2}\int_{t_0}^{t} ds \int_{t_0}^{t} ds'\left(1-e^{\nu(s-t)}\right)\left(1-e^{\nu(s'-t)}\right)\left\langle \boldsymbol{F}_{\text{fluc}}(s)\cdot\boldsymbol{F}_{\text{fluc}}(s')\right\rangle$$

Assumer la ***stationnarité***:

$$\left\langle \boldsymbol{F}_{\text{fluc}}(s)\boldsymbol{F}_{\text{fluc}}(s')\right\rangle = \left\langle \boldsymbol{F}_{\text{fluc}}(s+\tau)\boldsymbol{F}_{\text{fluc}}(s'+\tau)\right\rangle \underbrace{\rightarrow \left\langle \boldsymbol{F}_{\text{fluc}}(s-s')\boldsymbol{F}_{\text{fluc}}(0)\right\rangle}_{\tau=-s'} \equiv \boldsymbol{\gamma}(s-s')$$

$$\left\langle \left|\boldsymbol{r}(t)-\boldsymbol{r}(t_0)\right|^2\right\rangle = \nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2\left\langle \boldsymbol{v}(t_0)\cdot\boldsymbol{v}(t_0)\right\rangle + \frac{1}{(m\nu)^2}\int_{t_0}^{t} ds \int_{t_0}^{t} ds'\left(1-e^{\nu(s-t)}\right)\left(1-e^{\nu(s'-t)}\right) Tr\,\boldsymbol{\gamma}(s'-s)$$

$$= \nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2\left\langle \boldsymbol{v}(t_0)\cdot\boldsymbol{v}(t_0)\right\rangle + \frac{1}{(m\nu)^2}\int_{0}^{t-t_0} ds \int_{0}^{t-t_0} ds'\left(1-e^{\nu(s-(t-t_0))}\right)\left(1-e^{\nu(s'-(t-t_0))}\right) Tr\,\boldsymbol{\gamma}(s'-s)$$

Mouvement Brownien : Processus de Langevin

4) ***La nature de la force stochastique:***

la ***stationnarité***, $\Rightarrow$

$$\langle (\boldsymbol{r}(t)-\boldsymbol{r}(t_0))^2\rangle = \nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2 \langle \boldsymbol{v}(t_0)\cdot\boldsymbol{v}(t_0)\rangle$$
$$+\frac{1}{(m\nu)^2}\int_0^{t-t_0} ds \int_0^{t-t_0} ds' \left(1-e^{\nu(s-(t-t_0))}\right)\left(1-e^{\nu(s'-(t-t_0))}\right) Tr\,\boldsymbol{\gamma}(s'-s)$$

Le modèle le plus simple: $\langle \boldsymbol{F}_{\text{fluc}}(t)\,\boldsymbol{F}_{\text{fluc}}(t')\rangle = \boldsymbol{\gamma}\,\delta(t-t')$

$$\langle (\boldsymbol{r}(t)-\boldsymbol{r}(t_0))^2\rangle = \nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2 \langle \boldsymbol{v}(t_0)\cdot\boldsymbol{v}(t_0)\rangle + \frac{1}{(m\nu)^2} Tr\,\boldsymbol{\gamma}\int_0^{t-t_0} \left(1-e^{\nu(s-(t-t_0))}\right)^2 \; ds$$

$$= \nu^{-2}\left(1-e^{-\nu(t-t_0)}\right)^2 \langle \boldsymbol{v}(t_0)\cdot\boldsymbol{v}(t_0)\rangle + \frac{Tr\,\boldsymbol{\gamma}}{\nu(m\nu)^2}\left(\nu(t-t_0)-\frac{1}{2}\left(1-e^{-\nu(t-t_0)}\right)\left(3-e^{-\nu(t-t_0)}\right)\right)$$

$$\lim_{t-t_0\to\infty}\langle (\boldsymbol{r}(t)-\boldsymbol{r}(t_0))^2\rangle = \left(\frac{Tr\,\boldsymbol{\gamma}}{\nu(m\nu)^2}\right)\nu(t-t_0)(1+\ldots)$$

Mouvement Brownien : Processus de Langevin

4) La nature de la force stochastique

Diffusion: $$\frac{\partial P}{\partial t} = D\nabla^2 P \rightarrow \frac{\partial \langle \boldsymbol{r}\cdot\boldsymbol{r}\rangle}{\partial t} = \int \boldsymbol{r}\cdot\boldsymbol{r}\, D\nabla^2 P\, d\boldsymbol{r} = 2\,dD$$

$$2\,dD = \lim_{t-t_0 \gg 1/\nu} \frac{\partial}{\partial t}\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0)\right)^2 \rangle = Tr\,\frac{\boldsymbol{\gamma}}{(m\nu)^2}$$

"Fluctuation-dissipation relation"

$$m\frac{d^2\boldsymbol{r}}{dt^2} = -m\nu\frac{d\boldsymbol{r}}{dt} + \boldsymbol{F}_{\text{fluc}}(t), \quad \langle \boldsymbol{F}_{\text{fluc}}(t)\boldsymbol{F}_{\text{fluc}}(t')\rangle = 2D(m\nu)^2\,\mathbf{1}\,\delta(t-t')$$

Aussi,

$$\langle \frac{m}{2}\boldsymbol{v}(t)\cdot\boldsymbol{v}(t)\rangle = \frac{d}{2}k_B T \rightarrow \frac{m}{2}Tr\,\boldsymbol{\gamma}\,\frac{1}{2\nu m^2} = \frac{d}{2}k_B T \rightarrow Tr\,\boldsymbol{\gamma} = 2\,d\,\nu m k_B T \rightarrow m\nu D = k_B T$$

"Einstein relation"

Rélation entre l'équations de Langevin et de Fokker-Planck

Question:

Y a-t-il une relation plus formelle entre la dynamique mésoscopique (équation de Langevin)
et le comportement macroscopique (équation de diffusion)?

Rélation entre l'équations de Langevin et de Fokker-Planck

Equation de Langevin: $m\frac{d x_i}{dt}=b_i(x)+F_i(t), \quad \langle F_i(t) F_j(t')\rangle = 2\mathrm{D}_{ij}\delta(t-t')$

Discrétisé:

$$t \to t_k = k\tau$$

$$x_i(t) \to x_i(t_k) \equiv x_i^k$$

$$\frac{x_i^{k+1}-x_i^k}{\tau}=b_i(x^K)+F_i^k, \quad \langle F_i^k(t) F_j^{k'}(t')\rangle = 2\mathrm{D}_{ij}\frac{\delta_{kk'}}{\tau}$$

Distribution: $p(\boldsymbol{y};t) \equiv \langle \delta(\boldsymbol{x}(t)-\boldsymbol{y})\rangle \to p(\boldsymbol{y};k) \equiv \langle \delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle$

Equation de Fokker-Planck:

$$\frac{p(\boldsymbol{y};k+1)-p(\boldsymbol{y};k)}{\tau} = \langle \frac{\delta(\boldsymbol{x}^{k+1}-\boldsymbol{y})-\delta(\boldsymbol{x}^k-\boldsymbol{y})}{\tau}\rangle$$

$$=\langle \frac{x_i^{k+1}-x_i^k}{\tau}\frac{\partial}{\partial x_i^k}\delta(\boldsymbol{x}^k-\boldsymbol{y})+\frac{(x_i^{k+1}-x_i^k)(x_j^{k+1}-x_j^k)}{2\tau}\frac{\partial^2}{\partial x_i^k \partial x_j^k}\delta(\boldsymbol{x}^k-\boldsymbol{y})+\ldots\rangle$$

$$=-\frac{\partial}{\partial y_i}\langle \frac{x_i^{k+1}-x_i^k}{\tau}\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle+\frac{\partial^2}{\partial y_i \partial y_j}\langle \frac{(x_i^{k+1}-x_i^k)(x_j^{k+1}-x_j^k)}{2\tau}\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle+\ldots$$

$$=-\frac{\partial}{\partial y_i}\langle \left(b_i(\boldsymbol{x}^k)+F_i^k\right)\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle+\frac{1}{2}\frac{\partial^2}{\partial y_i \partial y_j}\langle \left(b_i(\boldsymbol{x}^k)+F_i^k\right)\left(b_j(\boldsymbol{x}^k)+F_j^k\right)\tau\,\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle+\ldots$$

Equations de Langevin et de Fokker-Planck

Equation de Langevin: $\frac{x_i^{k+1}-x_i^k}{\tau}=b_i(\boldsymbol{x}^k)+F_i^k, \quad \langle F_i^k F_j^{k'}\rangle=2\mathrm{D}_{ij}\frac{\delta_{kk'}}{\tau}$

Equation de Fokker-Planck:

$$\frac{p(\boldsymbol{y};k+1)-p(\boldsymbol{y};k)}{\tau}=-\frac{\partial}{\partial y_i}\langle\left(b_i(\boldsymbol{x}^k)+F_i^k\right)\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle$$

$$+\frac{1}{2}\frac{\partial^2}{\partial y_i\partial y_j}\tau\langle\left(b_i(\boldsymbol{x}^k)+F_i^k\right)\left(b_j(\boldsymbol{x}^k)+F_j^k\right)\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle+\dots$$

$$=-\frac{\partial}{\partial y_i}b_i(\boldsymbol{y})\langle\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle-\frac{\partial}{\partial y_i}\langle F_i^k\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle$$

$$+\frac{1}{2}\frac{\partial^2}{\partial y_i\partial y_j}\tau\langle F_i^k F_j^k\delta(\boldsymbol{x}^k-\boldsymbol{y})\rangle+\dots$$

$\boldsymbol{F}^k$ et $\boldsymbol{x}^k$ sont non corrélés à cause de causalité, ainsi $\langle\boldsymbol{F}^k\boldsymbol{x}^k\rangle=\langle\boldsymbol{F}^k\rangle\langle\boldsymbol{x}^k\rangle$, etc.

$$\frac{p(\boldsymbol{y};k+1)-p(\boldsymbol{y};k)}{\tau}=-\frac{\partial}{\partial y_i}b_i(\boldsymbol{y})\,p(\boldsymbol{y};k)+\frac{\partial^2}{\partial y_i\partial y_j}D_{ij}\,p(\boldsymbol{y};k)+O(\tau)$$

$$\Longrightarrow \quad \frac{dp(\boldsymbol{y};t)}{dt}=-\frac{\partial}{\partial y_i}\left(b_i(\boldsymbol{y})\,p(\boldsymbol{y};t)-\frac{\partial}{\partial y_j}D_{ij}\,p(\boldsymbol{y};t)\right)$$

Equations de Langevin et de Fokker-Planck

Equation de Langevin: $m\frac{d x_i}{dt} = b_i(x) + F_i(t), \quad \langle F_i(t) F_j(t')\rangle = 2\mathrm{D}_{ij}\delta(t-t')$

Equation de Fokker-Planck:

$$\frac{dp(\boldsymbol{y};t)}{dt} = -\frac{\partial}{\partial y_i}\left(b_i(\boldsymbol{y})\, p(\boldsymbol{y};t) - \frac{\partial}{\partial y_j} D_{ij}\, p(\boldsymbol{y};t)\right)$$

Notez: Si la dynamique déterminée est conservatrice

$$b_i(\boldsymbol{x}) = -K_{ij}\frac{\partial V(\boldsymbol{x})}{\partial x_j}$$

et s'il y a un relation fluctation-dissipation $K_{ij} = \epsilon D_{ij}$

il y a un état stationnaire.:
$$\begin{aligned} 0 &= -\frac{\partial}{\partial y_i}\left(-\epsilon D_{ij}\frac{\partial V}{\partial y_j} p(\boldsymbol{y};t) - \frac{\partial}{\partial y_j} D_{ij}\, p(\boldsymbol{y};t)\right) \\ &= \frac{\partial}{\partial y_i}\left(\frac{\partial}{\partial y_j} D_{ij}\, e^{\epsilon V}\, p(\boldsymbol{y};t)\right) \\ &\rightarrow p(\boldsymbol{y}) = A e^{-\epsilon V(\boldsymbol{y})} \end{aligned}$$

Fluctuation-dissipation relation <==> canonical distribution

Equations de Langevin et de Fokker-Planck

Equation de Langevin:

$$\frac{d\boldsymbol{r}}{dt}=\boldsymbol{v}$$

$$m\frac{d\boldsymbol{v}}{dt}=-m\nu\boldsymbol{v}-\frac{\partial U_{\text{ext}}}{\partial\boldsymbol{r}}+\boldsymbol{F}_{\text{fluc}}(t),\quad \langle\boldsymbol{F}_{\text{fluc}}(t)\boldsymbol{F}_{\text{fluc}}(t')\rangle=2D(m\nu)^2\mathbf{1}\delta(t-t')$$

Equation de Fokker-Planck: $p(\boldsymbol{r},\boldsymbol{v};t)$

$$\frac{\partial p}{\partial t}+\nabla\cdot\boldsymbol{J}=0\quad\text{avec}\quad J=\begin{bmatrix}\boldsymbol{v}\\ -\frac{1}{m}\frac{\partial U_{\text{ext}}}{\partial\boldsymbol{r}}-\nu\boldsymbol{v}\end{bmatrix}p-\begin{bmatrix}0 & 0\\ 0 & D\nu^2\mathbf{1}\end{bmatrix}\cdot\begin{bmatrix}\frac{\partial p}{\partial\boldsymbol{r}}\\ \frac{\partial p}{\partial\boldsymbol{v}}\end{bmatrix}$$

$$\frac{\partial p}{\partial t}+\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{v}\,p+\frac{\partial}{\partial\boldsymbol{v}}\cdot\left[\left(-\frac{1}{m}\frac{\partial u_{\text{ext}}}{\partial\boldsymbol{r}}-\nu\boldsymbol{v}\right)p\right]=D\nu^2\frac{\partial^2 p}{\partial^2 v}$$

Equation de Fokker-Planck

Equation de Fokker-Planck: $$\frac{\partial p}{\partial t}+\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{v}\,p+\frac{\partial}{\partial \boldsymbol{v}}\cdot\left[\left(-\frac{1}{m}\frac{\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}-\nu\,\boldsymbol{v}\right)p\right]=D\,\nu^2\frac{\partial^2 p}{\partial^2 v}$$

solution stationnaire d'équilibre: $$p_{eq}(\boldsymbol{r},\boldsymbol{v};t)=N\exp\left[-\frac{mv^2}{2\mathrm{k}_B T}-\frac{U_{\mathrm{ext}}(\boldsymbol{r})}{k_B T}\right]$$

vérification:

$$D\,\nu^2\frac{\partial^2 p}{\partial^2 v}=D\,\nu^2\frac{\partial}{\partial \boldsymbol{v}}\cdot\left(-\frac{m\,\boldsymbol{v}}{k_B T}\,p\right)=\frac{\partial}{\partial \boldsymbol{v}}\cdot\left(-\frac{mD\,\nu}{k_B T}\,\nu\,\boldsymbol{v}\,p\right)\underbrace{=}_{\text{Einstein relation}}\frac{\partial}{\partial \boldsymbol{v}}\cdot(-\nu\,\boldsymbol{v}\,p)$$

$$\frac{\partial}{\partial \boldsymbol{v}}\cdot\left[\left(-\frac{1}{m}\frac{\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}-\nu\,\boldsymbol{v}\right)p\right]=\left(-\frac{1}{m}\frac{\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}\right)\cdot\frac{\partial p}{\partial \boldsymbol{v}}+\frac{\partial}{\partial \boldsymbol{v}}\cdot[-\nu\,\boldsymbol{v}\,p]=\left(\frac{\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}\cdot\frac{\boldsymbol{v}}{k_B T}\,p\right)-\frac{\partial}{\partial \boldsymbol{v}}\cdot(\nu\,\boldsymbol{v}\,p)$$

$$\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{v}\,p=\frac{-\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}\cdot\frac{\boldsymbol{v}\,p}{k_B T}$$

Equation de Fokker-Planck: $$\boxed{\frac{\partial p}{\partial t}+\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{v}\,p+\frac{\partial}{\partial \boldsymbol{v}}\cdot\left[\left(-\frac{1}{m}\frac{\partial U_{\mathrm{ext}}}{\partial \boldsymbol{r}}-\nu\,\boldsymbol{v}\right)p\right]=\frac{\nu\,k_B T}{m}\frac{\partial^2 p}{\partial^2 v}}$$

Micro to Meso : Multiscale expansion

Example : Friction et fluctuations

Nous voulons avoir une connexion plus rigorous entre la dynamique microscopique (et déterministe) et l'idée de l'équation de Langevin (description macroscopique et stochastique).

L'idée fondamentale, c'est le concept de la séparation d'échelles de temps: il y a une partie du système mésoscopique et lent et une autre partie microscopique et vite.

Nous voulons avoir une dynamique pour la partie lente dans laquelle l'effet de la partie vite donne quelque chose comme l'équation de Langevin.

Plusieurs possibilités: l'analyse multi-eschelle, l'analyse projection opérateur, ...

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

Soit un système où il y a des coordinées vite, **z**, et un coordiné lent, “R”:

Hamiltonian: $H(\boldsymbol{z}; R(t)), \quad \dot{\boldsymbol{z}} \gg \dot{R}$

Distribution: $\rho(\boldsymbol{z}; t, R(t))$ ensemble sur les conditions initiales

L'equation de Liouville: $$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

Multiscale expansion: $$\rho(\boldsymbol{z}; t, R(t)) = \rho_0(\boldsymbol{z}; R(t_1)) + \epsilon \rho_1(\boldsymbol{z}; t, R(t_1)) + \ldots$$

$$t_1 = \epsilon t, \quad \epsilon \ll 1$$

Pour exemple, ε pourrait être le ratio de la masse du component vite et le component lent

$$\{\rho_0, H\} = 0, \quad O(\epsilon^0)$$

$$\frac{\partial \rho_0}{\partial R} \dot{R} + \frac{\partial \rho_1}{\partial t} + \{\rho_1, H\} = 0, \quad O(\epsilon^1)$$

etc.

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

0th ordre: $\{\rho_0, H\} = 0 \rightarrow \rho_0(\mathbf{z}; R(t_1)) = f_0(H(\mathbf{z}; R(t_1)); R(t_1))$

1 ordre: $\dfrac{\partial \rho_0}{\partial R}\dot{R} + \dfrac{\partial \rho_1}{\partial t} + \{\rho_1, H\} = 0 = \left(\dfrac{\partial f_0}{\partial R} + \dfrac{\partial f_0}{\partial H}\dfrac{\partial H}{\partial R}\right)\dot{R} + \dfrac{\partial \rho_1}{\partial t} + \{\rho_1, H\}$

Multipliez par une fonction de l'energie arbitraire et intégrez:

$$
\begin{aligned}
0 = &\int d\mathbf{z}\, g(H(\mathbf{z}; R(t_1)); R(t_1)) \left(\frac{\partial f_0}{\partial R} + \frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}\right)\dot{R} \\
&+ \int d\mathbf{z}\, g(H(\mathbf{z}; R(t_1)); R(t_1)) \frac{\partial \rho_1}{\partial t} \\
&+ \underbrace{\int d\mathbf{z}\, g(H(\mathbf{z}; R(t_1)); R(t_1)) \{\rho_1, H\}}_{=0}
\end{aligned}
$$

Ceci est typique de méthodes de multiéchelle : nous trouvons des fonctions arbitraires qui sont fixées en exigeant l'élimination de termes séculaires.

$$
\begin{aligned}
&\frac{\partial}{\partial t}\int d\mathbf{z}\, g(H(\mathbf{z}; R(t_1)); R(t_1)) \rho_1(H(\mathbf{z}; R(t_1)); t, R(t_1)) \\
&= \underbrace{-\int d\mathbf{z}\, g(H(\mathbf{z}; R(t_1)); R(t_1)) \left(\frac{\partial f_0}{\partial R} + \frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}\right)\dot{R}}_{\text{n'est pas de dependence sur } t \rightarrow 0}
\end{aligned}
$$

"*secular term*"

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

$$0=\int d\mathbf{z}\, g(H(\mathbf{z};R(t));R(t))\left(\frac{\partial f_0}{\partial R}+\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}\right)\dot{R}$$

$$=\int d\mathbf{z}\boxed{\int dE\quad \delta(E-H(\mathbf{z};R(t)))}g(H(\mathbf{z};R(t));R(t))\left(\frac{\partial f_0}{\partial R}+\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}\right)\dot{R}$$

$$=\int dE\, g(E;R(t))\left(\frac{\partial f_0(E,R)}{\partial R}\Sigma(R(t))+\frac{\partial f_0(E,R)}{\partial E}\Sigma(R(t))u(R)\right)\dot{R}$$

$$\Sigma(E,R)=\int d\mathbf{z}\,\delta(E-H(\mathbf{z};R))$$

$$u(E,R(t_1))\equiv\left\langle\frac{\partial H}{\partial R}\right\rangle_{(R(t_1),E)}\equiv\Sigma^{-1}(E,R(t_1))\int d\mathbf{z}\frac{\partial H}{\partial R}\delta(E-H(\mathbf{z},R(t_1)))$$

$$0=\int dE\, g(E;R(t))\left(\frac{\partial f_0(E,R)}{\partial R}+\frac{\partial f_0(E,R)}{\partial E}u(R)\right)\dot{R}\,\Sigma(R(t))$$

$$\boxed{g(E)\text{ arbitraire }\rightarrow 0=\frac{\partial f_0(E,R)}{\partial R}+\frac{\partial f_0(E,R)}{\partial E}u(R)}$$

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

$$0=\frac{\partial f_0(E,R)}{\partial R}+\frac{\partial f_0(E,R)}{\partial E}u(R)$$

Solution de 1 ordre:

$$\frac{\partial \rho_1}{\partial t}+\{\rho_1,H\}=-\frac{\partial \rho_0}{\partial R}\dot{R}$$

$$=-\left(\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}+\frac{\partial f_0}{\partial R}\right)\dot{R}$$

$$=-\left(\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}-\frac{\partial f_0}{\partial H}u(R)\right)\dot{R}$$

$$=-\frac{\partial f_0}{\partial H}\left(\frac{\partial H}{\partial R}-u(E,R)\right)\dot{R}$$

$$\rho_1=\rho_1^{homo}-\int_0^t dt'\, e^{L(t-t')}\frac{\partial f_0}{\partial H}\left(\frac{\partial H}{\partial R}-u(E,R)\right)\dot{R}$$

Évolution en arrière à temps utilisant l'Hamiltonien à R fixée.

$$\rho_1(\mathbf{z};t,R(t_1))=f_1(H(\mathbf{z};R(t_1));R(t_1))-\int_0^t dt'\left(\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial R}+\frac{\partial f_0}{\partial R}\right)_{(\mathbf{z}(t-t'))}\dot{R}(t_1)$$

$$=f_1(H(\mathbf{z};R(t_1));R(t_1))-\int_0^t dt'\,\frac{\partial f_0}{\partial H}\left(\frac{\partial H}{\partial R}-u(E,R(t_1))\right)_{(\mathbf{z}(t-t'))}\dot{R}(t_1)$$

Friction et fluctuations

$$\rho_1(\mathbf{z};t,R(t_1)) = f_1(H(\mathbf{z};R(t_1));R(t_1)) - \int_0^t dt'\,\frac{\partial f_0}{\partial H}\left(\frac{\partial H}{\partial R} - u(E,R(t_1))\right)_{(\mathbf{z}(t-t'))}\dot{R}(t_1)$$

$$\begin{aligned}
F &= -\int d\mathbf{z}\,\rho(\mathbf{z};t;R(t))\frac{\partial H}{\partial R} \\
&= -\int d\mathbf{z}\,(\rho_0(\mathbf{z};R(t)) + \rho_1(\mathbf{z};t,R(t)) + \ldots)\frac{\partial H}{\partial R} \\
&= -\int dE\,(f_0(E;R(t)) + f_1(E;R(t)))\,\Sigma(E)\left\langle\frac{\partial H}{\partial R}\right\rangle_{E,R} \\
&\quad + \int d\mathbf{z}\int_0^t dt'\,\frac{\partial f_0}{\partial H}\left(\frac{\partial H}{\partial R} - u(R(t))\right)_{(\mathbf{z}(t-t'))}\dot{R}(t)\frac{\partial H}{\partial R}
\end{aligned}$$

ajoute $\int dE\,\delta(E-H)$

$$\begin{aligned}
F &= -\int dE\,(f_0(E;R(t)) + f_1(E;R(t)))\,\Sigma(E)\left\langle\frac{\partial H}{\partial R}\right\rangle_{E,R} \\
&\quad + \dot{R}(t)\int dE\,\frac{\partial f_0(E,R)}{\partial E}\,\Sigma(E)\int_0^t dt'\left\langle\left(\frac{\partial H}{\partial R} - u(R(t_1))\right)_{(\mathbf{z}(t-t'))}\frac{\partial H}{\partial R}\right\rangle_{E,R}
\end{aligned}$$

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

$$F = -\boxed{\int dE\, f_0(E;R(t))\Sigma(E)\langle\frac{\partial H}{\partial R}\rangle_{E,R}} - \int dE\, f_1(E;R(t))\Sigma(E)\langle\frac{\partial H}{\partial R}\rangle_{E,R}$$

$$-\dot{R}(t)\int dE\, f_0(E,R)\frac{\partial}{\partial E}\Sigma(E)\int_0^t dt'\langle\left(\frac{\partial H}{\partial R}-u(R(t_1))\right)_{(\mathbf{z}(t-t'))}\frac{\partial H}{\partial R}\rangle_{E,R}$$

Pour $f_0(E,R(0))=\delta(E-E_0)/\Sigma(E,R(0))$ la solution est $f_0(E,R(t))=\delta(E-E')/\Sigma(E,R(t))$ ou $\int d\mathbf{z}\,\Theta(E'-H(\mathbf{z},R(t)))=\int d\mathbf{z}\,\Theta(E_0-H(\mathbf{z},R(0)))$

Donc,

$$0=\frac{\partial}{\partial R(t)}\int d\mathbf{z}\,\Theta(E'-H(\mathbf{z},R(t)))$$

$$=\frac{\partial E'}{\partial R(t)}\int d\mathbf{z}\,\delta(E'-H(\mathbf{z},R(t)))-\int d\mathbf{z}\,\delta(E'-H(\mathbf{z},R(t)))\frac{\partial H}{\partial R(t)}$$

$$=\frac{\partial E'}{\partial R(t)}\Sigma(E',R(t))-\Sigma(E',R(t))\langle\frac{\partial H}{\partial R(t)}\rangle_{E',R(t)}$$

$$\Rightarrow\quad \frac{\partial E'}{\partial R(t)}=\langle\frac{\partial H}{\partial R(t)}\rangle_{E',R(t)}=\int dE\,\delta(E-E')\langle\frac{\partial H}{\partial R(t)}\rangle_{E,R(t)}$$

$$=\boxed{\int dE\,\Sigma(E,R(t))f_0(E,R(t))\langle\frac{\partial H}{\partial R(t)}\rangle_{E,R(t)}}$$

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

$$F=-\frac{\partial E'}{\partial R(t)}-\overbrace{\int dE\, f_1(E;R(t))\Sigma(E)\left\langle\frac{\partial H}{\partial R}\right\rangle_{E,R}}^{\text{negligez}}$$

$$-\dot{R}(t)\int dE\, f_0(E,R)\frac{\partial}{\partial E}\Sigma(E)\int_0^t dt'\left\langle\left(\frac{\partial H}{\partial R}-u(R(t_1))\right)_{(\mathbf{z}(t-t'))}\frac{\partial H}{\partial R}\right\rangle_{E,R}$$

$$\delta(E-E')\ldots$$

$$F=-\frac{\partial E'}{\partial R(t)}-\dot{R}(t)\Sigma^{-1}(E',R(t))\frac{\partial}{\partial E'}\Sigma(E')\int_0^t dt'\left\langle\left(\frac{\partial H}{\partial R}-\frac{\partial E'}{\partial R}\right)_{(\mathbf{z}(t-t'))}\frac{\partial H}{\partial R}\right\rangle_{E',R}$$

$$\approx-\frac{\partial E'}{\partial R}-\dot{R}(t)\Sigma^{-1}(E',R(t))\frac{\partial}{\partial E'}\Sigma(E')\int_0^\infty dt'\left\langle\left(\frac{\partial H}{\partial R}-\frac{\partial E'}{\partial R}\right)_{(\mathbf{z}(t'))}\frac{\partial H}{\partial R}\right\rangle_{E',R}$$

$$\Sigma^{-1}(E',R(t))\frac{\partial}{\partial E'}\Sigma(E',R(t))=\frac{\partial}{\partial E'}\ln\Sigma(E',R(t))=\frac{1}{k_B T}$$

$$F\approx-\left(\frac{\partial E'}{\partial R}\right)-\dot{R}(t)\left(\beta+\frac{\partial}{\partial E'}\right)\int_0^\infty dt'\left\langle\left(\frac{\partial H}{\partial R}-\frac{\partial E'}{\partial R}\right)_{(\mathbf{z}(t'))}\frac{\partial H}{\partial R}\right\rangle_{E',R}$$

Friction et fluctuations

(d'apres Jarzynski, PRL 71, 839 (1993); Servantie et Gaspard, PRL 91 185501 (2003))

negligible

$$F \approx -\frac{\partial E'}{\partial R} - \dot{R}(t)\left(\beta + \cancel{\frac{\partial}{\partial E'}}\right)\int_0^\infty dt' \left\langle \left(\frac{\partial H}{\partial R} - \frac{\partial E'}{\partial R}\right)_{(\boldsymbol{z}(t'))} \frac{\partial H}{\partial R} \right\rangle_{E',R}$$

Force moyenne

Force fluctuant

$$\nu \approx \beta \int_0^\infty \langle F_{\text{fluc}}(t) F_{\text{fluc}}(0) \rangle dt$$

Micro to meso: Projection Operators

Dynamique microscopique Hamiltonienne

Espace des phases: $\Gamma=(\boldsymbol{q},\boldsymbol{p})=(\boldsymbol{q}_1,\boldsymbol{p}_1,\dots,\boldsymbol{q}_N,\boldsymbol{p}_N)\in M\,,\quad dim\,M=2\mathrm{f}=2\mathrm{Nd}$

Fonction hamiltonienne: $H=\sum_{i=1}^{N}\frac{p_i^2}{2m_i}+U(\boldsymbol{q}_1,\dots,\boldsymbol{q}_N)$

Equations d'Hamilton:
$$\dot{\boldsymbol{q}}_i=+\frac{\partial H}{\partial \boldsymbol{p}}\qquad\qquad \Rightarrow\{\boldsymbol{q}_i(t),\boldsymbol{p}_i(t)\}\equiv\Gamma_t$$
$$\dot{\boldsymbol{p}}_i=-\frac{\partial H}{\partial \boldsymbol{q}}$$

$$\frac{d}{dt}\Gamma_t=\{\Gamma_t,H(\Gamma_t)\}\equiv L_t\Gamma_t$$

Liouville's theorem: $d\Gamma_{t_1}=d\Gamma_{t_2}$

Micro to meso: Projection Operators

Distribution

Evolution of phases

$$\Gamma(0)=\Gamma_0$$

$$\frac{d}{dt}\Gamma_t=\{\Gamma_t, H(\Gamma_t)\}\equiv L_t\Gamma_t$$

$$\Rightarrow \Gamma_t(\Gamma_0)=e^{L_0 t}\Gamma_0$$

Probability density for initial conditions : $\rho_0(\Gamma_0)$

Average of arbitrary function of phase:

$$\langle A(\Gamma;t)\rangle=\int A(\Gamma_t(\Gamma_0))\rho_0(\Gamma_0)\,d\Gamma_0$$

$$=\int e^{L_0 t}A(\Gamma_0)\rho_0(\Gamma_0)\,d\Gamma_0$$
$$=\int A(\Gamma_0)e^{-L_0 t}\rho_0(\Gamma_0)\,d\Gamma_0$$
$$=\int A(\Gamma)e^{-Lt}\rho_0(\Gamma)\,d\Gamma$$

$$=\int A(\Gamma_t)\rho_0(\Gamma_0(\Gamma_t))\,d\Gamma_t$$
$$=\int A(\Gamma)\rho_0(\Gamma_{-t}(\Gamma))\,d\Gamma$$

Distribution:

$$\rho_t(\Gamma)\equiv\rho_0(\Gamma_{-t}(\Gamma))=e^{-Lt}\rho_0(\Gamma)$$

$$\frac{\partial}{\partial t}\rho_t(\Gamma)=-L\rho_t(\Gamma)$$

Stationary (Equilibrium)

$$L\rho_t(\Gamma)=0$$

Micro to meso: Projection Operators

Soit les variables de interet $\psi_\alpha(\Gamma), \quad \alpha = 1, \ldots, n \ll N \quad \Gamma = \{\boldsymbol{x}_i\}_{i=1,\ldots,N}$

$$\dot{\psi}_\alpha = L\psi_\alpha \Rightarrow \psi_\alpha(t) = e^{Lt}\psi_\alpha(0)$$

Ex.: Free streaming $\quad \psi_\alpha(t) = \psi_\alpha(\boldsymbol{q}_i(0) + \boldsymbol{p}_i(0)t\,;\boldsymbol{p}_i(0))$

Produit scalar $\quad \langle A(\Gamma), B(\Gamma)\rangle \equiv \int A(\Gamma)B(\Gamma)\rho(\Gamma)\,d\Gamma, \qquad L^{+}\rho = -L\rho = 0$

Projection Operator $\quad PX(\Gamma) = \langle X, \psi_\alpha\rangle g^{-1}_{\alpha\beta}\psi_\beta(\Gamma), \qquad g_{\alpha\beta} \equiv \langle \psi_\alpha, \psi_\beta\rangle$

Micro a macro: Projection Operators

$$\dot{\psi}_\alpha = L\psi_\alpha \Rightarrow \psi_\alpha(t) = e^{Lt}\psi_\alpha(0)$$

$$PX(\Gamma) = \langle X, \psi_\alpha\rangle g^{-1}_{\alpha\beta}\psi_\beta(\Gamma), \qquad g_{\alpha\beta} \equiv \langle \psi_\alpha, \psi_\beta\rangle, \qquad Q \equiv 1 - P$$

Claim: if $e^{Lt} = U(t)$ then $U(t) \equiv e^{Lt}P + \int_0^t d\tau\, e^{L(t-\tau)} PLe^{L'\tau}Q + e^{L't}Q, \quad t \geq 0 \qquad L' \equiv QLQ$

Proof: $\lim_{t\to 0} U(t) = P + Q = 1$

$$\begin{aligned}
\frac{\partial}{\partial t}U(t) &= Le^{Lt}P + \int_0^t d\tau\, Le^{L(t-\tau)} PLe^{L'\tau}Q + PLe^{L't}Q + L'e^{L't}Q \\
&= Le^{Lt}P + L\int_0^t d\tau\, e^{L(t-\tau)} PLe^{L'\tau}Q + PLe^{L't}Q + QLQe^{L't}Q \\
&= Le^{Lt}P + L\int_0^t d\tau\, e^{L(t-\tau)} PLe^{L'\tau}Q + PLe^{L't}Q + QLe^{L't}Q \\
&= Le^{Lt}P + L\int_0^t d\tau\, e^{L(t-\tau)} PLe^{L'\tau}Q + Le^{L't}Q \\
&= LU(t)
\end{aligned}$$

Micro a macro: Projection Operators

$$\dot{\psi}_\alpha = L\psi_\alpha \Rightarrow \psi_\alpha(t) = e^{Lt}\psi_\alpha(0)$$

$$PX(\Gamma) = \langle X, \psi_\alpha\rangle g^{-1}_{\alpha\beta}\psi_\beta(\Gamma), \qquad g_{\alpha\beta} \equiv \langle \psi_\alpha, \psi_\beta\rangle, \qquad Q \equiv 1 - P$$

$$e^{Lt} = e^{Lt}P + \int_0^t d\tau\, e^{L(t-\tau)} PLe^{L'\tau}Q + e^{L't}Q, \quad t \geq 0 \qquad L' \equiv QLQ$$

$$\dot{\psi}_\alpha(t) = Le^{Lt}\psi_\alpha(0)$$

$$= e^{Lt}L\psi_\alpha(0)$$

$$= e^{Lt}PL\psi_\alpha(0) + \int_0^t d\tau\, e^{L(t-\tau)}PLe^{L'\tau}QL\psi_\alpha(0) + e^{L't}QL\psi_\alpha(0)$$

$$= e^{Lt}\psi_\gamma(0)g^{-1}_{\gamma\beta}\langle\psi_\beta(0), L\psi_\alpha(0)\rangle + \int_0^t d\tau\, e^{L(t-\tau)}\psi_\gamma(0)g^{-1}_{\gamma\beta}\langle\psi_\beta Le^{L'\tau}QL\psi_\alpha(0)\rangle + e^{L't}QL\psi_\alpha(0)$$

$$= -\Omega_{\alpha\gamma}\psi_\gamma(t) - \int_0^t d\tau\, M_{\alpha\gamma}(\tau)\psi_\gamma(t-\tau) + f_\alpha(t)$$

$$= -\Omega_{\alpha\gamma}\psi_\gamma(t) - \int_0^t d\tau\, M_{\alpha\gamma}(t-\tau)\psi_\gamma(\tau) + f_\alpha(t)$$

$$\Omega_{\alpha\gamma} \equiv -g^{-1}_{\gamma\beta}\langle\psi_\beta, L\psi_\alpha\rangle$$

$$M_{\alpha\gamma}(\tau) \equiv -g^{-1}_{\gamma\beta}\langle\psi_\beta Le^{L'\tau}QL\psi_\alpha\rangle$$

$$f_\alpha(t) = e^{L't}QL\psi_\alpha$$

Micro a macro: Projection Operators

$$PX(\Gamma)=\langle X,\psi_\alpha\rangle g^{-1}_{\alpha\beta}\psi_\beta(\Gamma),\qquad g_{\alpha\beta}\equiv\langle\psi_\alpha,\psi_\beta\rangle,\qquad Q\equiv 1-P\qquad\qquad L'\equiv QLQ$$

$$\dot\psi_\alpha+\Omega_{\alpha\gamma}\psi_\gamma(t)+\underbrace{\int_0^t d\tau\, M_{\alpha\gamma}(t-\tau)\psi_\gamma(\tau)}_{\text{dissipitive term}}=\underbrace{f_\alpha(t)}_{\text{bruit}}$$

$$\Omega_{\alpha\gamma}\equiv -g^{-1}_{\gamma\beta}\langle\psi_\beta,L\psi_\alpha\rangle$$
$$M_{\alpha\gamma}(\tau)\equiv -g^{-1}_{\gamma\beta}\langle\psi_\beta L e^{L'\tau}QL\psi_\alpha\rangle$$
$$f_\alpha(t)=e^{L't}QL\psi_\alpha$$

$$\langle\psi_\alpha,f_\beta(t)\rangle=\langle\psi_\alpha,e^{L't}QL\psi_\beta\rangle=\langle\psi_\alpha,Qe^{L't}L\psi_\beta\rangle=0\Rightarrow f\ \text{ est bruit}$$

$$\begin{aligned}\langle f_\alpha(0)\,f_\beta(t)\rangle&=\langle(QL\psi_\alpha)e^{L't}QL\psi_\beta\rangle\\ &=\langle(L\psi_\alpha)e^{L't}QL\psi_\beta\rangle-\langle(PL\psi_\alpha)e^{L't}QL\psi_\beta\rangle\\ &=\langle\psi_\alpha L^{+}e^{L't}QL\psi_\beta\rangle-\langle\psi_\sigma L\psi_\alpha\rangle g^{-1}_{\sigma\mu}\langle\psi_\mu e^{L't}QL\psi_\beta\rangle\\ &=-\langle\psi_\alpha Le^{L't}QL\psi_\beta\rangle-\langle\psi_\sigma L\psi_\alpha\rangle g^{-1}_{\sigma\mu}\langle\psi_\mu \cancelto{0}{Qe^{L't}}L\psi_\beta\rangle\\ &=g_{\alpha\gamma}M_{\gamma\beta}(t)\end{aligned}$$

"fluctuation-dissipation relation"

Local in time:

$$M_{\alpha\beta}(t)=D_{\alpha\beta}\delta(t)\Rightarrow\dot\psi_\alpha+\Omega_{\alpha\gamma}\psi_\gamma(t)+D_{\alpha\gamma}\psi_\gamma(t)=f_\alpha(t),\qquad\langle f_\alpha(0)f_\beta(t)\rangle=g_{\alpha\gamma}D_{\gamma\beta}\delta(t)$$

Path probabilities and Transition paths

Langevin dynamics:

$$\frac{d}{dt}\boldsymbol{q}_i = \boldsymbol{v}_i$$

$$\frac{d}{dt}\boldsymbol{v}_i = -\frac{\partial U(\boldsymbol{q}^N)}{\partial \boldsymbol{q}_i} - \gamma \boldsymbol{v}_i + Q_{ij}\eta_j(t), \quad \langle \eta_i(t)\eta_j(t')\rangle = \delta_{ij}\delta(t-t')$$

Over-damped stochastic dynamics:

$$\gamma \gg 1 \Rightarrow \qquad 0 = -\frac{\partial U(\boldsymbol{q}^N)}{\partial \boldsymbol{q}_i} - \gamma \boldsymbol{v}_i + Q_{ij}\eta_j(t)$$

$$\boxed{\frac{d}{dt}\boldsymbol{q}_i = -\gamma^{-1}\frac{\partial U(\boldsymbol{q}^N)}{\partial \boldsymbol{q}_i} + \gamma^{-1} Q_{ij}\eta_j(t)}$$

Noise probabilities:

$$P(\eta_i(t) = \bar{\eta}_i) \equiv P(\bar{\eta}_t) = \pi^{-1/2} e^{-\frac{\bar{\eta}^2}{2}}$$

$$P(\eta_i(t_1) = \bar{\eta}_i(t_1), \eta_i(t_2) = \bar{\eta}_i(t_2)) = \pi^{-2/2} e^{-\frac{\bar{\eta}^2(t_1) + \bar{\eta}^2(t_2)}{2}}$$

Path probabilities and Transition paths

Over-damped stochastic dynamics:

$$\dot{\boldsymbol{q}}_i = b_i(\boldsymbol{q}) + Q_{ij}\eta_j(t), \quad \langle \eta_i(t)\eta_j(t')\rangle = \delta_{ij}\delta(t-t')$$

Noise probabilities have Gaussian statistics:

$$P(\eta_i(t)=\bar{\eta}_i) \equiv P(\bar{\eta}_t) = \pi^{-1/2} e^{-\frac{\bar{\eta}^2}{2}}$$

Discretize:

$$\boldsymbol{q}_i(t+dt) = \boldsymbol{q}_i(t) + dt\, b_i(\boldsymbol{q}(t)) + dt\, Q_{ij}\eta_j(t)$$

Probability that positions are $\boldsymbol{q}_i(t+dt)$

$$P(\boldsymbol{q}_i(t+dt)) = P(\boldsymbol{q}_i(t))\, P\left(\eta_j(t) = Q_{ji}^{-1}\left(\frac{\boldsymbol{q}_i(t+dt)-\boldsymbol{q}_i(t)}{dt} - b_i(\boldsymbol{q}(t))\right)\right)$$

Path Probabilities: $$P(\boldsymbol{q}(t);\dot{\boldsymbol{q}}(t)) \sim \pi^{-1/2}\exp\left[-\frac{1}{2}\left(\dot{\boldsymbol{q}}_i(t)-b_i(\boldsymbol{q})\right)Q_{ij}^{-2}\left(\dot{\boldsymbol{q}}_j(t)-b_j(\boldsymbol{q})\right)\right]$$

$$P(\boldsymbol{q}_0, t=0; \boldsymbol{q}_f, t=T) = \int D\boldsymbol{q}(\tau)\exp\left[-\frac{1}{2}\int_0^T dt\left(\frac{1}{2}\left(\dot{\boldsymbol{q}}_i(t)-b_i(\boldsymbol{q})\right)Q_{ij}^{-2}\left(\dot{\boldsymbol{q}}_j(t)-b_j(\boldsymbol{q})\right)+\frac{\partial b_i}{\partial q_i}\right)\right]$$

Path probabilities and Transition paths

$$\dot{\boldsymbol{q}}_i = b_i(\boldsymbol{q}) + Q_{ij}\eta_j(t)$$

$$P(\boldsymbol{q}_0, t=0; \boldsymbol{q}_f, t=T) = \int D\boldsymbol{q}(\tau)\exp[-S_{eff}]$$

$$S_{eff} = -\int_0^T dt \underbrace{\left(\frac{1}{2}(\dot{\boldsymbol{q}}_i(t) - b_i(\boldsymbol{q}))Q_{ij}^{-2}(\dot{\boldsymbol{q}}_j(t) - b_j(\boldsymbol{q})) + \frac{\partial b_i}{\partial q_i}\right)}_{\text{Lagrangian } L}$$

Most likely path:

$$\frac{\delta S_{eff}}{\delta q_i(t)} = 0 \quad \Rightarrow \frac{d}{dt}\frac{\delta L}{\delta \dot{q}_i(t)} - \frac{\delta L}{\delta q_i(t)} = 0$$

$$-\frac{d}{dt}\left(Q_{kj}^{-2}(\dot{\boldsymbol{q}}_j(t) - b_j(\boldsymbol{q}))\right) - \left(\frac{\partial}{\partial q_k} b_i(\boldsymbol{q})\right)Q_{ij}^{-2}(\dot{\boldsymbol{q}}_j(t) - b_j(\boldsymbol{q})) + \frac{\partial^2 b_i}{\partial q_i \partial q_k}$$
$$+\frac{1}{2}(\dot{\boldsymbol{q}}_i(t) - b_i(\boldsymbol{q}))\frac{\partial Q_{ij}^{-2}}{\partial q_k}(\dot{\boldsymbol{q}}_j(t) - b_j(\boldsymbol{q})) + \frac{\partial b_i}{\partial q_i} = 0$$

Weak noise approximation:

$$S_{eff} \approx -\frac{1}{2}\int_0^T dt\left(\frac{1}{2}(\dot{\boldsymbol{q}}_i(t) - b_i(\boldsymbol{q}))Q_{ij}^{-2}(\dot{\boldsymbol{q}}_j(t) - b_j(\boldsymbol{q}))\right)$$

Path probabilities and Transition paths

Most likely path:

$$-\frac{d}{dt}\left(Q_{kj}^{-2}\left(\dot{\boldsymbol{q}}_j(t)-b_j(\boldsymbol{q})\right)\right)-\left(\frac{\partial}{\partial q_k}b_i(\boldsymbol{q})\right)Q_{ij}^{-2}\left(\dot{\boldsymbol{q}}_j(t)-b_j(\boldsymbol{q})\right)+\frac{\partial^2 b_i}{\partial q_i \partial q_k}$$

$$+\frac{1}{2}\left(\dot{\boldsymbol{q}}_i(t)-b_i(\boldsymbol{q})\right)\frac{\partial Q_{ij}^{-2}}{\partial q_k}\left(\dot{\boldsymbol{q}}_j(t)-b_j(\boldsymbol{q})\right)+\frac{\partial b_i}{\partial q_i}=0$$

Weak noise approximation:

$$S_{eff}\approx-\frac{1}{2}\int_0^T dt\left(\frac{1}{2}\left(\dot{\boldsymbol{q}}_i(t)-b_i(\boldsymbol{q})\right)Q_{ij}^{-2}\left(\dot{\boldsymbol{q}}_j(t)-b_j(\boldsymbol{q})\right)\right)$$

Special case: crossing from a minum at A to another minimum at B

+ Conservative force: $b_i(\boldsymbol{x})=-K_{ij}(\boldsymbol{x})\frac{\partial V}{\partial x_j}$

+ weak noise approximation

+ fluctuation-dissipation relation $Q_{ij}^2(\boldsymbol{x})=\epsilon K_{ij}(\boldsymbol{x})$

==> MLP via gradient descent from critical point under the metric Q