NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch. 7. Stochastic Descriptions

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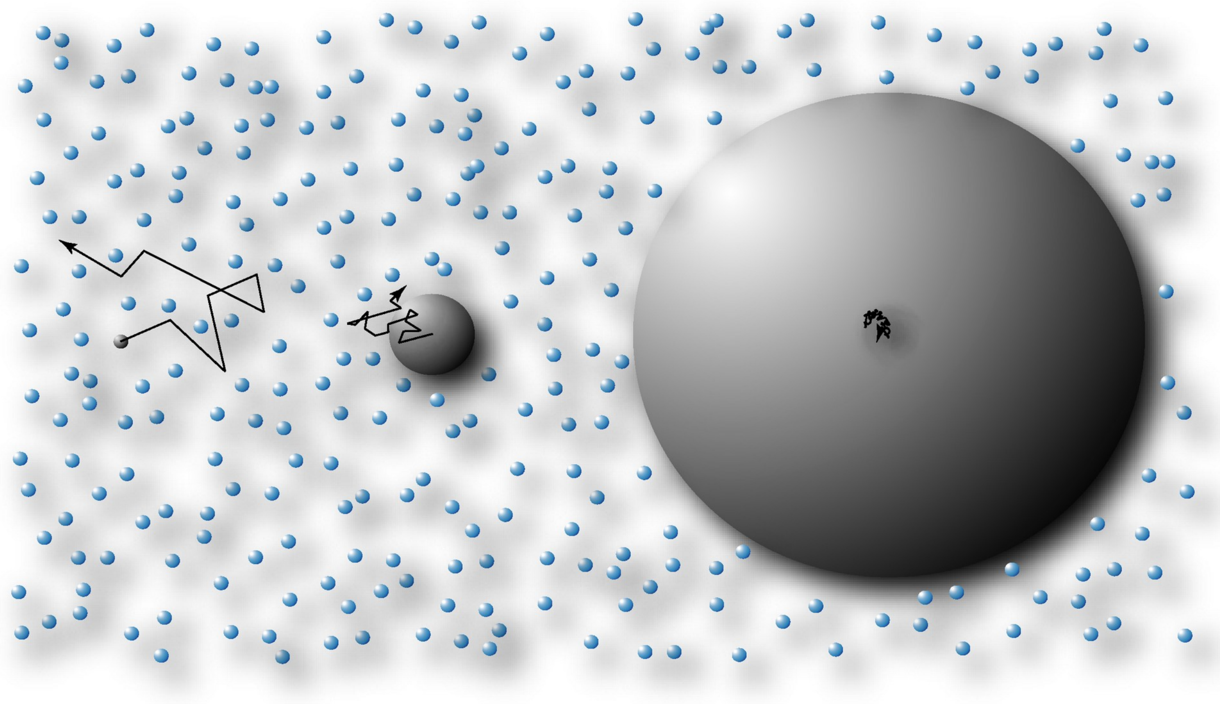
Stochastic Descriptions

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

Mouvement Brownien : Processus de Langevin



0,1-1 nm 1 µm 1 cm

Mouvement Brownien : Processus de Langevin

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

équation de Newton pour son mouvement: $$m\frac{d^2\boldsymbol{r}}{dt^2}=\boldsymbol{F}_{\text{ext}}+\boldsymbol{F}_{\text{liq}}$$

1) force due à un potentiel extérieur: $$\boldsymbol{F}_{\text{ext}}=-\frac{\partial U_{\text{ext}}}{\partial \boldsymbol{r}}$$

2) force due aux collisions avec les molécules environnantes:

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

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

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

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

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

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

$$m\frac{d^2\boldsymbol{r}}{dt^2}=-m\nu\frac{d\boldsymbol{r}}{dt}+\boldsymbol{F}_{\text{fluc}} \qquad \langle \boldsymbol{F}_{\text{fluc}}\rangle=0 \qquad \langle \boldsymbol{F}_{\text{fluc}}(t)\boldsymbol{F}_{\text{fluc}}(t')\rangle=0,\quad t\neq t'$$

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

Result:

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

Mouvement Brownien : Processus de Langevin

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

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

Assumer la ***stationnarité***: $\left\langle \boldsymbol{F}_{\text{fluc}}(s)\boldsymbol{F}_{\text{fluc}}(s') \right\rangle = \left\langle \boldsymbol{F}_{\text{fluc}}(s+\tau)\boldsymbol{F}_{\text{fluc}}(s'+\tau) \right\rangle$

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

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

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

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

Mouvement Brownien : Processus de Langevin

Pour la motion diffusif $\langle (\boldsymbol{r}(t)-\boldsymbol{r}(t_0))^2\rangle = \int (\boldsymbol{r}-\boldsymbol{r}_0)^2 P(\boldsymbol{r},t;\boldsymbol{r}_0,t_0)\,d\boldsymbol{r}$

$$\frac{\partial P(\boldsymbol{r},t;\boldsymbol{r}_0,t_0)}{\partial t} = D\nabla^2 P(\boldsymbol{r},t;\boldsymbol{r}_0,t_0), \qquad P(\boldsymbol{r},t_0;\boldsymbol{r}_0,t_0)=\delta(\boldsymbol{r}-\boldsymbol{r}_0)$$

$$\frac{\partial\langle \boldsymbol{r}\cdot\boldsymbol{r}\rangle}{\partial t} = \int \boldsymbol{r}\cdot\boldsymbol{r}\, D\nabla^2 P\, d\boldsymbol{r} = 2dD \qquad 2dD = \lim_{t-t_0 \gg 1/\nu} \frac{\partial}{\partial t}\langle (\boldsymbol{r}(t)-\boldsymbol{r}(t_0))^2\rangle = Tr\,\frac{\boldsymbol{\gamma}}{(m\nu)^2}$$

"Fluctuation-dissipation relation"

Aussi,

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

"Einstein relation"

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

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

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

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

Oui! Il s’appel la Fokker-Planck equation:

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

Connection: $p(\boldsymbol{y};t)\equiv\langle\delta(\boldsymbol{x}(t)-\boldsymbol{y})\rangle_{\text{noise}}$

$$\langle f(\boldsymbol{y})\rangle_t=\int f(\boldsymbol{y})p(\boldsymbol{y};t)d\boldsymbol{y}=\int f(\boldsymbol{y})\langle\delta(\boldsymbol{x}(t)-\boldsymbol{y})\rangle_{\text{noise}}d\boldsymbol{y}=\langle f(\boldsymbol{x}(t))\rangle_{\text{noise}}$$

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

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

Discrétisé:

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

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

Equation de Fokker-Planck:

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

Equations de Langevin et de Fokker-Planck

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

Equation de Fokker-Planck:

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

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

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

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

$\boldsymbol{F}^k$ 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.

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

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

Equations de Langevin et de Fokker-Planck

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

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 fluctuation-dissipation $K_{ij}=\epsilon D_{ij}$

il y a un état stationnaire.: $$0=-\frac{\partial}{\partial y_i}\left(-\epsilon D_{ij}\frac{\partial V}{\partial y_j}p(\boldsymbol{y};t)-\frac{\partial}{\partial y_j}D_{ij}p(\boldsymbol{y};t)\right)$$

$$=\frac{\partial}{\partial y_i}\left(\frac{\partial}{\partial y_j}D_{ij}e^{\epsilon V}p(\boldsymbol{y};t)\right)$$

$$\rightarrow p(\boldsymbol{y})=Ae^{-\epsilon V(\boldsymbol{y})}$$

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: $p(\boldsymbol{r},\boldsymbol{v};t)$

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

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

Equation de Fokker-Planck

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

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

vérification:

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

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

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

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

Micro to meso: Projection Operators

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

$$\dot{\psi}_\alpha = \frac{\partial \psi}{\partial \boldsymbol{q}_i} \cdot \frac{d\boldsymbol{q}_i}{dt} + \frac{\partial \psi}{\partial \boldsymbol{p}_i} \cdot \frac{d\boldsymbol{p}_i}{dt} \quad = \boldsymbol{p}_i \cdot \frac{\partial \psi}{\partial \boldsymbol{q}_i} + \boldsymbol{F}_i(\Gamma) \cdot \frac{\partial \psi}{\partial \boldsymbol{p}_i} \quad = \underbrace{\left(\boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{q}_i} + \boldsymbol{F}_i(\Gamma) \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right)}_{L} \psi$$

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

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

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

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

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

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

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

Micro a macro: Projection Operators

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

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

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

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

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

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

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

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

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

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

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

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

Micro a macro: Projection Operators

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

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

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

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

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

"fluctuation-dissipation relation"

Local in time:

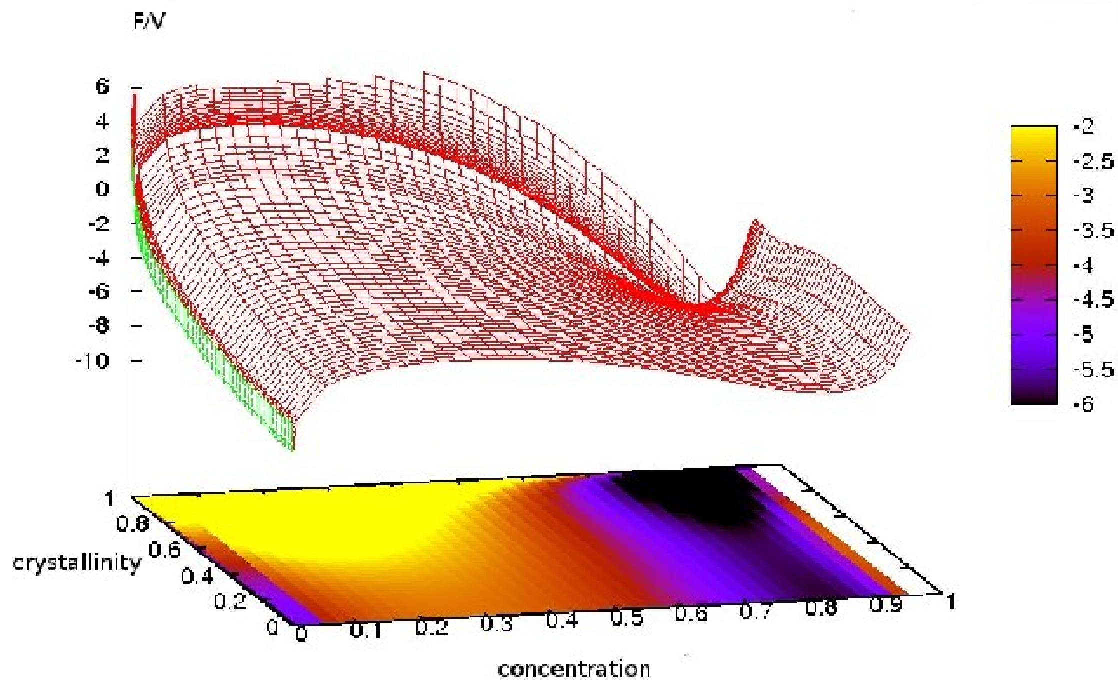
$$M_{\alpha\beta}(t)=D_{\alpha\beta}\delta(t)\Rightarrow\dot{\psi}_\alpha+\Omega_{\alpha\gamma}\psi_\gamma(t)+D_{\alpha\gamma}\psi_\gamma(t)=f_\alpha(t),\qquad\langle f_\alpha(0)f_\beta(t)\rangle=g_{\alpha\gamma}D_{\gamma\beta}\delta(t)$$

Path probabilities and Transition paths

Many physical transitions can be interpreted as “barrier crossing” which means that the beginning state and the end state are separated by configurations of higher energy.

Examples:

- phase transitions
- chemical reactions
- protein folding



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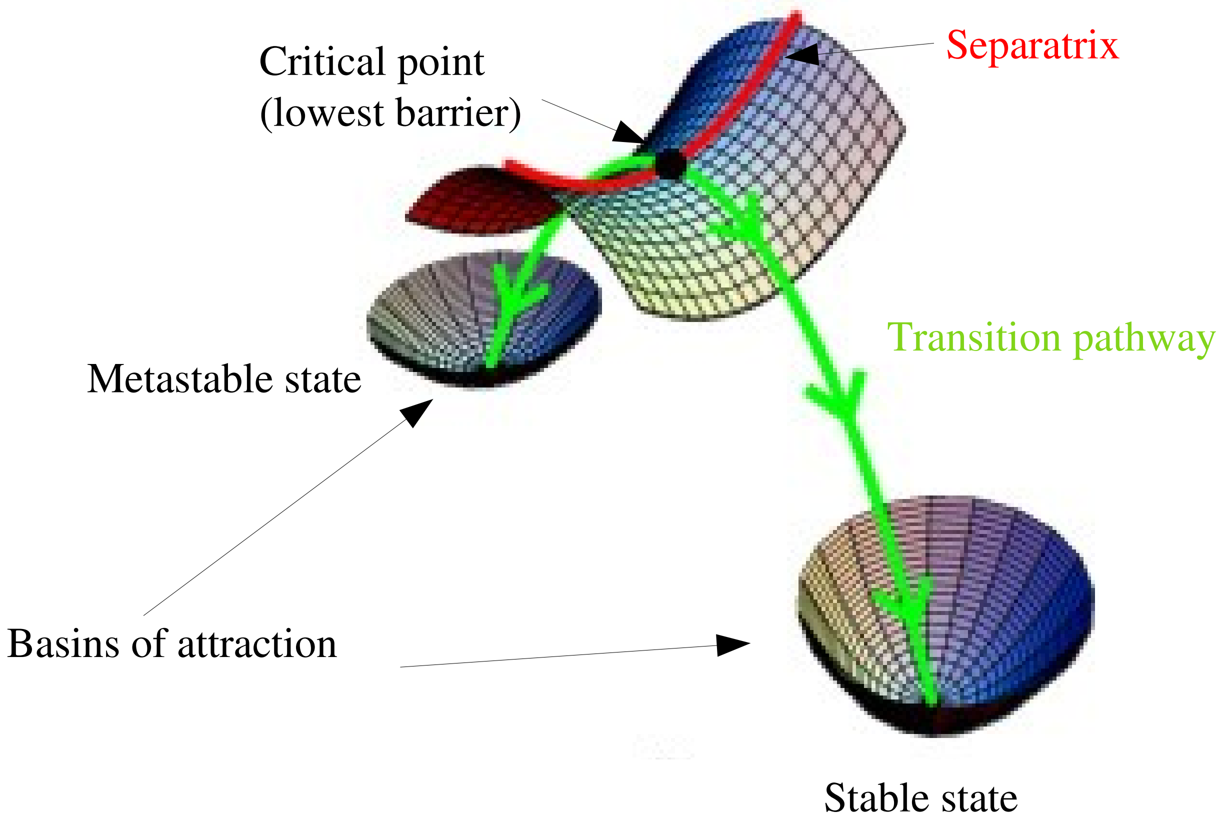

Path probabilities and Transition paths

Over-damped stochastic dynamics:

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

Noise probabilities have Gaussian statistics:

$$P(\eta_i(t)=\bar{\eta}_i) = \pi^{-1/2}\exp\left(-\frac{\bar{\eta}_i^2}{2}\right)$$

$$\dot{\boldsymbol{q}} = \boldsymbol{b}(\boldsymbol{q}) + \boldsymbol{Q}\cdot\boldsymbol{\eta}(t), \quad \langle \boldsymbol{\eta}(t)\boldsymbol{\eta}(t')\rangle = \mathbf{1}\delta(t-t')$$

$$P(\boldsymbol{\eta}(t)=\bar{\boldsymbol{\eta}}) = \pi^{-1/2} e^{-\frac{\bar{\eta}^2}{2}}$$

Discretize: $$\boldsymbol{q}(t_{k+1}) = \boldsymbol{q}(t_k) + dt\,\boldsymbol{b}(\boldsymbol{q}(t_k)) + \sqrt{dt}\,\boldsymbol{Q}\cdot\boldsymbol{\eta}(t_k), \quad \langle \boldsymbol{\eta}(t_k)\boldsymbol{\eta}(t_l)\rangle = \mathbf{1}\delta_{kl}$$

Noise needed to go from $\boldsymbol{q}(t_k) \rightarrow \boldsymbol{q}(t_{k+1})$: $$\boldsymbol{\eta}(t_k) = \sqrt{dt}\,\boldsymbol{Q}^{-1}\cdot\left(\frac{\boldsymbol{q}(t_{k+1})-\boldsymbol{q}(t_k)}{dt} - \boldsymbol{b}(\boldsymbol{q}(t_k))\right)$$

Probability that positions are $\boldsymbol{q}(t_{k+1})$:

$$P(\boldsymbol{q}(t_{k+1})) = P(\boldsymbol{q}(t_k))\,P\left(\boldsymbol{\eta}(t_k) = \sqrt{dt}\,\boldsymbol{Q}^{-1}\left(\frac{\boldsymbol{q}(t_{k+1})-\boldsymbol{q}(t_k)}{dt} - \boldsymbol{b}(\boldsymbol{q}(t_k))\right)\right)$$

$$= P(\boldsymbol{q}(t_k))\,\pi^{-1/2}\exp\left(dt\left(\dot{\boldsymbol{q}}(t_{k+1}) - \boldsymbol{b}(\boldsymbol{q}(t_k))\right)\boldsymbol{Q}_{ij}^{-2}\left(\dot{\boldsymbol{q}}(t_{k+1}) - \boldsymbol{b}(\boldsymbol{q}(t_k))\right)\right)$$

Path probabilities and Transition paths

Over-damped stochastic dynamics:

$$\dot{\boldsymbol{q}}=\boldsymbol{b}(\boldsymbol{q})+\boldsymbol{Q}\cdot\boldsymbol{\eta}(t),\quad \langle\boldsymbol{\eta}(t)\boldsymbol{\eta}(t')\rangle=\mathbf{1}\delta(t-t')$$

Path probability:

$$P(\boldsymbol{q}(t_k),\boldsymbol{q}(t_{k+1}))=P(\boldsymbol{q}(t_k))\pi^{-1/2}\exp\left(dt\left(\dot{\boldsymbol{q}}(t_k)-\boldsymbol{b}(\boldsymbol{q}(t_k))\right)\boldsymbol{Q}_{ij}^{-2}\left(\dot{\boldsymbol{q}}(t_k)-\boldsymbol{b}(\boldsymbol{q}(t_k))\right)\right)$$

$$\begin{aligned}P(\boldsymbol{q}(t_{k-1}),\boldsymbol{q}(t_k),\boldsymbol{q}(t_{k+1}))=&P(\boldsymbol{q}_i(t_{k-1}))\\ &\times\pi^{-1/2}\exp\left(dt\left(\dot{\boldsymbol{q}}(t_{k-1})-\boldsymbol{b}(\boldsymbol{q}(t_{k-1}))\right)\boldsymbol{Q}_{ij}^{-2}\left(\dot{\boldsymbol{q}}(t_{k-1})-\boldsymbol{b}(\boldsymbol{q}(t_{k-1}))\right)\right)\\ &\times\pi^{-1/2}\exp\left(dt\left(\dot{\boldsymbol{q}}(t_k)-\boldsymbol{b}(\boldsymbol{q}(t_k))\right)\boldsymbol{Q}_{ij}^{-2}\left(\dot{\boldsymbol{q}}(t_k)-\boldsymbol{b}(\boldsymbol{q}(t_k))\right)\right)\end{aligned}$$

$$P(\boldsymbol{q}(t_0)\ldots\boldsymbol{q}(t_k)\ldots\boldsymbol{q}(t_N))=P(\boldsymbol{q}_i(t_0))\pi^{-N/2}\exp\left(dt\sum_{l=0}^{N}\left(\dot{\boldsymbol{q}}_i(t_l)-b_i(\boldsymbol{q}(t_l))\right)Q_{ij}^{-2}\left(\dot{\boldsymbol{q}}_j(t_l)-b_j(\boldsymbol{q}(t_l))\right)\right)$$

$$P(\boldsymbol{q}_0,t=0;\boldsymbol{q}_f,t=T)=\int D\boldsymbol{q}(\tau)\exp\left[-\frac{1}{2}\int_0^T dt\left(\frac{1}{2}\left(\dot{\boldsymbol{q}}(t)-\boldsymbol{b}(\boldsymbol{q})\right)\boldsymbol{Q}^{-2}\left(\dot{\boldsymbol{q}}(t)-\boldsymbol{b}(\boldsymbol{q})\right)+\frac{\partial\boldsymbol{b}}{\partial\boldsymbol{q}}\right)\right]$$

Path probabilities and Transition paths

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

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

$$S_{eff} = -\int_0^T dt \underbrace{\left(\frac{1}{2}\left(\dot{\boldsymbol{q}}(t) - \boldsymbol{b}(\boldsymbol{q})\right)\boldsymbol{Q}^{-2}\left(\dot{\boldsymbol{q}}(t) - \boldsymbol{b}(\boldsymbol{q})\right) + \frac{\partial \boldsymbol{b}}{\partial \boldsymbol{q}}\right)}_{\text{Lagrangian } L}$$

Most likely path:

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

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

Weak noise approximation:

$$S_{eff} \approx -\frac{1}{2}\int_0^T dt \left(\frac{1}{2}\left(\dot{\boldsymbol{q}}(t) - \boldsymbol{b}(\boldsymbol{q})\right)\boldsymbol{Q}^{-2}\left(\dot{\boldsymbol{q}}(t) - \boldsymbol{b}(\boldsymbol{q})\right)\right)$$

Path probabilities and Transition paths

Most likely path:

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

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

Weak noise approximation: $S_{eff}\approx-\frac{1}{2}\int_0^T dt\left(\frac{1}{2}\left(\dot{\boldsymbol{q}}(t)-\boldsymbol{b}(\boldsymbol{q})\right)\boldsymbol{Q}^{-2}\left(\dot{\boldsymbol{q}}(t)-\boldsymbol{b}(\boldsymbol{q})\right)\right)$

Special case: crossing from a minimum 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***

Path probabilities and Transition paths

Gradient descent:
- start at critical point
- move infinitesimally in unstable direction
- - draw a small circle (*need a way to measure distances: i.e. a metric*)
- - calculate energy of all points on the circle (*need a way to calculate energy: i.e. a potential*)
- - move to point with lowest energy
- - repeat

$$\frac{d\boldsymbol{x}_i}{dt} = \pm K_{ij}(\boldsymbol{x}) \frac{\partial V}{\partial x_j}$$

$$\boldsymbol{x}_i(t=0) = \boldsymbol{x}_i^{\text{critical}} \pm \epsilon$$