Langevin equation: $m \frac{dv_i}{dt} = -\underline{\underline{\tilde{\gamma} v_i(t)}} + \tilde{\eta}_i(t)$ microscopic noise term

macroscopic dissipation

stochastic

$\langle \tilde{\eta}_i(t) \rangle = 0$

$\langle \tilde{\eta}_i(t) \tilde{\eta}_j(t') \rangle = \tilde{\Gamma} \delta_{ij} \delta(t-t')$

$\gamma = \tilde{\gamma}/m \;;\; \eta_i = \tilde{\eta}_i/m \;;\; \Gamma = \tilde{\Gamma}/m^2$

$$\rightarrow \begin{cases} \frac{dv_i}{dt} = -\gamma v_i(t) + \eta_i(t) & \langle \eta_i(t) \rangle = 0 \\ \langle \eta_i(t) \eta_j(t') \rangle = \Gamma \delta_{ij} \delta(t-t') \end{cases}$$

Formal integration: $v_i(t) = \exp(-\gamma t)\left[v_i(0) + \int_0^t d\tau \exp(\gamma \tau) \cdot \eta_i(\tau)\right]$

$\langle v_i(t) \rangle = v_i(0) \exp(-\gamma t)$

$\langle v_i^2(t) \rangle = v_i^2(0) \exp(-2\gamma t) + \frac{\Gamma}{2\gamma}\left[1 - \exp(-2\gamma t)\right]$

$\xrightarrow{t \to \infty} \frac{\Gamma}{2\gamma}$ thermodyn. equilibrium

$\rightarrow$ equipartition theorem

$\underline{\langle \frac{1}{2} m v_i^2(t) \rangle = T/2}$ $(k_B = 1)$

$\frac{m\Gamma}{2\gamma} = T$

$\downarrow$

$\underline{\Gamma = \frac{2\gamma}{m} T}$ $\longrightarrow$ $\boxed{\tilde{\Gamma} = 2 \tilde{\gamma} T}$ $\rightarrow$ fluctuation dissipation relation

thermal fluctuations

dissipation

$\langle (x_i(t) - x_i(0))^2 \rangle = \langle \left[\int_0^t v_i(\tau) d\tau\right]^2 \rangle =$

$= (v_i^2(0) - \Gamma/2\gamma)\left[\frac{1 - \exp(-\gamma t)}{\gamma}\right]^2 + \frac{\Gamma}{\gamma^2} t - \frac{\Gamma}{\gamma^3}(1 - \exp(-\gamma t))$

$\sim \sigma_i^2(0)\, t^2$ BALLISTIC REGIME $t \ll t_d = 1/\gamma$

$\sim \dfrac{\Gamma}{\gamma^2}\, t$ DIFFUSIVE REGIME $t \gg t_d$

$\parallel$

$2Dt \longrightarrow D = \dfrac{\Gamma}{2\gamma^2} = \dfrac{T}{\gamma m} = \dfrac{T}{\tilde{\gamma}}$

$$\boxed{D = T/\tilde{\gamma}}$$ Einstein relation

Diffusion coefficient $\underbrace{\lim_{t\to\infty} \dfrac{\langle (\vec{x}(t) - \vec{x}(0))^2 \rangle}{t}}\ = 2dD$

Langevin equation with an external conservative force

$\vec{F}(\vec{x}) = -\vec{\nabla} U(\vec{x})$

$$m\frac{d\vec{v}}{dt} = \underbrace{m\frac{d^2\vec{x}}{dt^2} = -\vec{\nabla} U(\vec{x}) - \tilde{\gamma}\frac{d\vec{x}}{dt} + \vec{\eta}(t)}_{\text{Stochastic force}}$$

Fokker-Planck equation $\longrightarrow \underbrace{p(\vec{x}, t)}_{\text{PDF in } \vec{x} \text{ at time } t}$

TRANSITION RATE

$$r(\vec{x}', \vec{x}) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \underbrace{W(\vec{x}, t \mid \vec{x}', t + \Delta t)}_{\text{conditional probability}}$$

PDF in $\vec{x}'$

MASTER EQUATION

$$\frac{\partial p(\vec{x},t)}{\partial t} = \int d^3x' \Big[\overbrace{p(\vec{x}',t)\, R(\vec{x},\vec{x}')}^{\text{"gain" term}} - \underbrace{p(\vec{x},t)\, R(\vec{x}',\vec{x})}_{\text{loss term}} \Big]$$

$R \neq 0$ for small $\vec{X}$

$\vec{X} = \vec{x}' - \vec{x}$

Taylor expand the gain term around $\vec{X} = 0$ (2^{nd} order)

$$\frac{\partial p(\vec{x},t)}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}\left(a_i(x)\, p(\vec{x},t)\right) + \frac{1}{2}\sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j}\left(b_{ij}(\vec{x})\, p(\vec{x},t)\right)$$

$a_i(\vec{x}) = \int d^3X\, R(\vec{x}',\vec{x})\, X_i \quad \vec{X} = \vec{x}' - \vec{x}$

$b_{ij}(\vec{x}) = \int d^3X\, R(\vec{x}',\vec{x})\, X_i X_j$

a_i, b_{ij}, R dependent

For a Brownian particle: $\Delta x_i = X_i$

$\vec{a} = \frac{\langle \Delta \vec{x} \rangle}{\Delta t}$ average displacement per unit time

$b_{ij} = \langle \Delta x_i \Delta x_j \rangle / \Delta t$ average squared displacement per unit time

Brownian particle subject to gravity:

uniform constant force $\vec{F}_0 = -m\vec{g}$ drift velocity

$\vec{a} = \vec{v}_0 = \vec{F}_0 / \hat{\gamma}$ (sedimentation speed) for homogeneous, isotropic medium $\rightarrow b_{ij} = 2\delta_{ij} D$

Fokker-Planck: $\underbrace{\frac{\partial p(\vec{x},t)}{\partial t} = -\vec{v}_0 \cdot \vec{\nabla} p(\vec{x},t) + D\nabla^2 p(\vec{x},t)}$

No external force: $\longrightarrow$ $\underbrace{\frac{\partial p(\vec{x},t)}{\partial t} = D\nabla^2 p(\vec{x},t)}$

Standard diffusion equation

initial condition $p(x,0) = \delta(x - x_0)$

(1 d)

$$p(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{(x-x_0)^2}{4Dt}\right)$$ solution

$$\langle (x - \langle x\rangle)^2\rangle = \langle x^2\rangle - \langle x\rangle^2 = 2Dt$$

diffusive behaviour

General F-P

$$\frac{\partial p(\vec{x},t)}{\partial t} = -\vec{\nabla}\cdot\left(\vec{a}(\vec{x},t)\, p(\vec{x},t)\right) + \frac{1}{2}\sum_{ij}\frac{\partial^2}{\partial x_i \partial x_j}\left(b_{ij}(\vec{x},t)\, p(\vec{x},t)\right)$$

$$\underbrace{\frac{\partial p}{\partial t} = -\vec{\nabla}\cdot\vec{J}(\vec{x},t)}$$ ~ conservation law (continuity equation)

$\boxed{\text{Current}}$ $J_i(\vec{x},t) = a_i(\vec{x},t)\, p(\vec{x},t) - \frac{1}{2}\sum_j \frac{\partial}{\partial x_j}\left(b_{ij}(\vec{x},t)\cdot p(\vec{x},t)\right)$

<u>Conservative</u> external force:

$\vec{a}(\vec{x},t) = \vec{F}(x)/\tilde{\gamma} = \vec{v}_0(\vec{x})$ drift velocity

$b_{ij}(\vec{x},t) = 2D\delta_{ij}$

$$\vec{F}(\vec{x}) = -\vec{\nabla} U(\vec{x}) \; ; \quad \underbrace{\frac{\partial \rho}{\partial t} = -\vec{\nabla}\cdot\vec{J}}$$

$$\vec{J}(\vec{x},t) = \underbrace{\frac{\vec{F}(\vec{x})}{\tilde{\gamma}}\rho(\vec{x},t)}_{\text{drift current}} - \underbrace{D\vec{\nabla}\rho(\vec{x},t)}_{\text{diffusive current (Fick's law)}}$$

$\boxed{\text{Stationarity condition}} \rightarrow \underbrace{\frac{\partial \rho}{\partial t} = 0}$ $(t \to \infty)$

$$\boxed{\vec{\nabla}\cdot\vec{J} = 0}$$

(Thermodyn.)
Equilibrium condition STRONGER than stationarity

NO CURRENTS ARE FLOWING $\boxed{\vec{J} = 0}$

F.P. at equilibrium $(\vec{J} = 0)$

$$\frac{\vec{\nabla}\rho^*}{\rho^*} = \frac{\vec{F}(\vec{x})}{\tilde{\gamma}D} = -\frac{\vec{\nabla}U(\vec{x})}{\tilde{\gamma}D}$$

(eq. for equilibrium PDF $\rho^*(\vec{x})$)

$$\vec{\nabla}(\ln\rho^*) = -\vec{\nabla}U/\tilde{\gamma}D \rightarrow \underline{\rho^*(\vec{x}) = A\exp\left(-\frac{U(\vec{x})}{\tilde{\gamma}D}\right)}$$

Thermal equilibrium → Boltzmann distribution

provided $\tilde{\gamma}D = k_B T = T \rightarrow \boxed{D = T/\tilde{\gamma}}$

Einstein relation