6-(2) Langevin equation & Brownian motion

$$\boxed{m \frac{dv}{dt} = F_{ext} - \alpha v + F'(t)}$$

⊙ Situation : a particle in a liquid (one dimension)

$$\begin{cases} \text{mass } m \\ \text{center of mass coordinate } x(t) \\ v \equiv \frac{dx(t)}{dt} \end{cases}$$

≡ a particle ⊕ heat reservoir
(other molecules in the liquid and the other degrees of freedom of the particle)

$F(t) = -\alpha v + F'(t)$ → force on the center of mass coordinate due to the interaction between the particle and the reservoir.

F_{ext} : external force

show the schematic diagram of $x(t)$

τ^* correlation time

$F(t) = \bar{F}(t) + F'(t)$ → rapidly fluctuating part ; $\int_t^{t+\tau'} F'(t')dt' = 0$ → purely random

τ': sufficiently long time scale

$\bar{F}(t)$ ↓ a slowly varying part which leads to the equilibrium situation

$\Rightarrow \bar{F}(t) = -\alpha \bar{v}$; $v = \bar{v} + v'$ $\begin{cases} \bar{v} : \text{slowly varying part} \\ v' : \text{rapidly fluctuating part} \end{cases}$

(Origin : Consider the situation of $F_{ext} = 0$. And $\bar{v} \neq 0$ initially.
To achieve exponentially rapid decay to $\underbrace{\bar{v}_{eq}}_{\text{equilibrium value}} = 0$,
one can have $m \frac{d\bar{v}}{dt} = -\alpha \bar{v}$.)

$\bar{F}(t) = -\alpha \bar{v}$ ~ ~~fr~~ frictional force.

α ~ frictional constant

$\Rightarrow$ energy dissipation to environment

◎ Example : calculation of the mean-square displacement $\langle x^2 \rangle$ in a time interval τ (sufficiently long time scale)

(put $F_{ext} = 0$.
initial condition: $x = 0$ at $t = 0$.

$$m \frac{dv}{dt} = -\alpha v + F'(t)$$

$\dot{x}$: $\bar{v} = \bar{v}(0)\, e^{-\frac{\alpha}{m} t} = \bar{v}(0)\, e^{-t/\tau_{relax}}$

$\tau_{relax} = m/\alpha$

$$\Rightarrow \quad m x \frac{d\dot{x}}{dt} = -\alpha x \dot{x} + x F'(t)$$

$\langle \;\ldots\; \rangle$ ensemble average.

$$\Rightarrow \left\langle m \frac{d(x\dot{x})}{dt} - m\dot{x}^2 = -\alpha x \dot{x} \right\rangle \qquad (\because \langle x F' \rangle = \langle x \rangle \underbrace{\langle F' \rangle}_{=0} = 0.$$

use $\frac{1}{2} m \langle \dot{x}^2 \rangle = \frac{1}{2} kT$

$$\Rightarrow \quad m \left\langle \frac{d}{dt}(x\dot{x}) \right\rangle = m \frac{d}{dt} \langle x \dot{x} \rangle = kT - \alpha \langle x \dot{x} \rangle$$

(see Reif p. 566)

$$\Rightarrow \langle x\dot{x} \rangle = C e^{-\gamma t} + \frac{kT}{\alpha}, \quad \gamma \equiv \frac{\alpha}{m}$$

since $x = 0$ at $t = 0$, $C = -kT/\alpha$.

$$\Rightarrow \langle x \dot{x} \rangle = \frac{kT}{\alpha}\left(1 - e^{-\gamma t}\right)$$

$$\Rightarrow \quad = \frac{1}{2} \frac{d\langle x^2 \rangle}{dt}$$

$$\langle x^2 \rangle = \frac{2kT}{\alpha}\left(t - \frac{1}{\gamma}\left(1 - e^{-\gamma t}\right)\right)$$

Study limiting cases :

$$t \ll \gamma^{-1} \Rightarrow e^{-\gamma t} = 1 - \gamma t + \frac{1}{2}\gamma^2 t^2 - \ldots$$

$$\Rightarrow \langle x^2 \rangle = \frac{kT}{m} t^2$$

~ free particle moving (without interaction with environment)

$$t \gg \gamma^{-1} \Rightarrow \langle x^2 \rangle = \frac{2kT}{\alpha} t$$

~ diffusion ; random walk.

$\Rightarrow \langle x^2 \rangle = 2Dt$

$$D = \frac{kT}{\alpha} = \frac{kT}{m}\tau_{relax} = \frac{1}{3} m \bar{v}^2 \cdot \frac{1}{m}\tau_{relax} = \frac{1}{3}\bar{v}^2 \tau_{relax} \simeq \frac{1}{3}\bar{v} l$$

Now, turn on $F_{ext} = e\mathcal{E}$. (electric field)

$$m\frac{dv}{dt} = e\mathcal{E} - \alpha v + F'(t)$$

at $t \to \infty$ (steady-state situation)

$$e\mathcal{E} - \alpha\bar{v} = 0. \quad (\because \frac{d\bar{v}}{dt} = 0)$$

$$\text{mobility} \equiv \mu \equiv \bar{v}/\mathcal{E} = e/\alpha$$

$$\mu/D = e/\alpha \cdot \left(\frac{kT}{\alpha}\right)^{-1} = \frac{e}{kT}$$

~ Einstein relation

(i) Relation between α and the fluctuating force

$$m \frac{dv}{dt} = F_{ext} + \underset{\sim}{F}$$

it comes from the interaction between the particle and heat reservoir. (see Ref Fig. 15.5.1)

α time interval τ :

$\tau \gg \tau^*$; $\tau^* \sim$ correlation time which is of the order of the mean period of fluctuations of the force $F(t)$.

In $[t, t+\tau]$, the variation of F_{ext} can be negligible.

$\tau \sim$ macroscopically short so that F_{ext} does not vary over τ,
but microscopically long

$$\Rightarrow \quad m \langle v(t+\tau) - v(t) \rangle = F_{ext}\,\tau + \int_t^{t+\tau} \langle F(t') \rangle\, dt'$$

ensemble average

Let's focus on $\langle F(t') \rangle$.

① In equilibrium, $\langle F(t') \rangle_0 = 0$

(※ $\langle \cdots \rangle_0$ means the ensemble average in equilibrium.)

$\sim$ trivial. (consider $F_{ext} = 0$ case. $\Rightarrow \langle v(t+\tau) \rangle = \langle v(t) \rangle$ in equilibrium.

② $\langle F \rangle$ is affected by the motion of the particle.

($\because$ ~~the environment~~ The internal equilibrium of environment (heat reservoir) is ~~disturbed~~ disturbed as the velocity of particle changes.)

$$\Rightarrow \langle F(t')\rangle \simeq -\beta \bar{v}(t)\int_t^{t'} dt''\ \langle F(t')F(t'')\rangle_0 , \qquad t' = t+\tau' \qquad \tau' \gg \tau^*$$

derivation

At some time t,

the particle has a velocity $v(t)$

$W_r(t)$: the probability that the particle (its center-of-mass coordinate) is in state r.

Approximation : $W_r(t) \to W_r^{(0)}$ equilibrium probability.

(i) We consider the situation where the system is very close to its equilibrium.

Or

(ii) The system is in equilibrium at t.

After τ', it deviates from the equilibrium spontaneously.

At later time $t' = t + \tau'$ $(\tau' \gg \tau^*)$,

$v(t+\tau') = v(t) + \Delta v(\tau')$

E' (energy of environment) at t' = $E'(t) + \Delta E'(\tau')$

$$\langle F(t')\rangle = \sum_r W_r(t+\tau') F_r(t')$$

$$W_r(t+\tau') \overset{?}{=} W_r(t)\,\frac{\Omega(E'+\Delta E')\cdot 1}{\Omega(E')\cdot 1} = e^{\beta\Delta E'}\,W_r(t)$$

$$\simeq (1+\beta\Delta E')\,W_r(t) \quad (\tau' \sim \text{small enough}) \qquad \beta = \frac{\partial \ln\Omega(E')}{\partial E'}$$

$$\to (1+\beta\Delta E')\,W_r^{(0)} \quad (\text{approximation})$$

$$\Rightarrow \langle F(t')\rangle = \sum_r W_r^{(0)}\,F_r(t')\,(1+\beta\Delta E')$$

$$= \langle F(t')(1+\beta\Delta E')\rangle_0 \qquad \langle\cdots\rangle_0 \sim \text{ensemble average in equilibrium.}$$

$$= \langle \beta\,\Delta E'\,F(t')\rangle_0$$

$$\Delta E' = -\underbrace{\int_t^{t'} v(t'')F(t'')\,dt''}_{\text{work done by } F \text{ on the system}} \simeq -v(t)\int_t^{t'} F(t'')\,dt''$$

variation of $v(t)$ is neglected. (τ' ~ small enough)

$$\Rightarrow \langle F(t') \rangle = -\beta \left\langle v(t) \int_t^{t'} F(t') F(t'') \, dt'' \right\rangle_0$$

$$\simeq -\beta \, \bar{v}(t) \int_t^{t'} \langle F(t') F(t'') \rangle_0 \, dt''$$

$$\Rightarrow \quad \frac{m \langle v(t+\tau) - v(t) \rangle}{\tau} = F_{ext}(t) - \beta \, \bar{v}(t) \int_t^{t+\tau} dt' \int_t^{t'} dt'' \langle F(t') F(t'') \rangle_0$$

○ Correlation function

$$\boxed{K(s) \equiv \langle F(t') F(t'+s) \rangle_0}$$

ensemble average taken in equilibrium.

$\Rightarrow$ $K(s)$ ~ independent of t'.

general
· properties :

① $K(0) = \langle F(t) F(t) \rangle > 0$.

② $s \gg \tau^*$, $K(s) \to \langle F(t) \rangle \langle F(t+s) \rangle$

$\Rightarrow$ $K(s) \to 0$ if $\langle F(t) \rangle = 0$.

③ $|K(s)| \leq K(0)$

proof $\langle [F(t) \pm F(t+s)]^2 \rangle \geq 0$

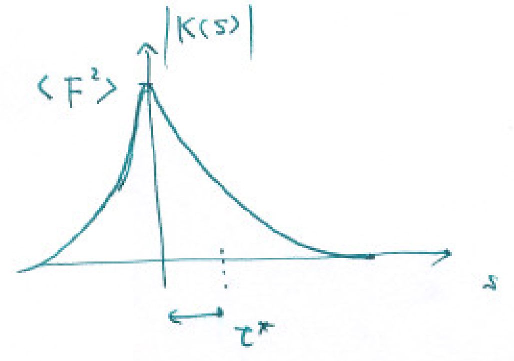
$\Rightarrow$ $2(K(0) \pm K(s)) \geq 0$

$\Rightarrow$ $-K(0) \leq K(s) \leq K(0)$

④ $K(s) = K(-s)$

(∵ $K(s) = \langle F(t) F(t+s) \rangle = \langle F(t-s) F(t) \rangle = \langle F(t) F(t-s) \rangle$
$= K(-s)$)

$\Rightarrow$



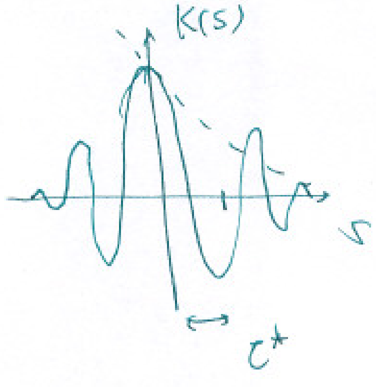
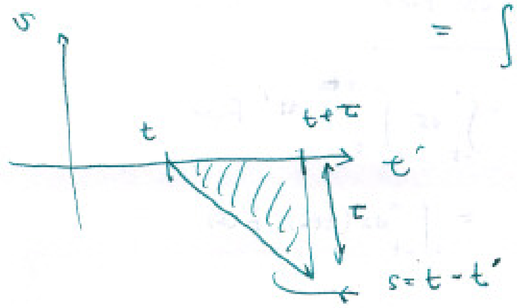


Fig : schematic shapes of $K(s)$

$$\Rightarrow \int_t^{t+\tau} dt' \int_{t-t'}^{0} ds\, K(s) = \int_{-\tau}^{0} ds \int_{t-s}^{t+\tau} dt'\, K(s)$$



$$= \int_{-\tau}^{0} ds\, K(s)\,(\tau + s)$$

$$\cong \int_{-\tau}^{0} ds\, \tau\, K(s)$$

($\because$ $K(s) \neq 0$ only for $s \lesssim \tau^*$, $\tau \gg \tau^*$.)

$$\simeq \tau \int_{-\infty}^{0} ds\, K(s)$$

$$= \frac{1}{2}\tau \int_{-\infty}^{\infty} ds\, K(s)$$

$$\Rightarrow \quad m\langle v(t+\tau) - v(t)\rangle = \tilde{F}_{ext}(t)\,\tau - \alpha \bar{v}(t)\,\tau,$$

$$\boxed{\alpha \equiv \frac{1}{2kT}\int_{-\infty}^{\infty} \langle F(0)\, F(s)\rangle_0\, ds}$$

Note : $\dfrac{d\bar{v}}{dt} = \dfrac{m\langle v(t+\tau) - v(t)\rangle}{\tau}$ ($\because$ $\langle v\rangle$ varies very slowly. ~ not changed over τ.)

$$\Rightarrow \frac{d\bar{v}}{dt} = \tilde{F}_{ext} - \alpha \bar{v}$$

if $F_{ext} = 0$, $\quad \bar{v}(t) = \bar{v}(0)\, e^{-\gamma t}$

Since $\langle v\rangle$ varies slowly, $\left|\left(\dfrac{d\bar{v}}{dt}\right)\tau\right| \ll \bar{v}$

$$\Rightarrow \gamma\tau \ll 1. \quad \Rightarrow \gamma^{-1} \gg \tau \gg \tau^*$$

* fluctuation - dissipation theorem

$$\underbrace{\alpha}_{\text{dissipation}} = \frac{1}{2kT}\int_{-\infty}^{\infty} \underbrace{\langle F(0)\, F(s)\rangle_0}_{\text{correlation of fluctuating force in equilibrium}}\, ds$$

Interaction between the system and the reservoir is ~~bigger~~ stronger

$\Rightarrow$ ($F(t)$ must be larger
α is larger since the system goes to equilibrium more rapidly.

⊙ Example of fluctuation – dissipation theorem.

electrical circuit :

$$L \frac{dI}{dt} = -RI + \underbrace{V'(t)}_{\text{fluctuating voltage.}} \quad ; \langle V'(t) \rangle = 0 \quad , \quad \langle \frac{1}{2} L I^2 \rangle = \frac{1}{2} kT.$$

(see Reif p. 590)

$$\Updownarrow$$

$$m \frac{dv}{dt} = -\alpha v + F'(t) \quad , \quad \langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} kT$$

⇒ One can immediately know the correspondence between them.

→

$$R = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle V(0) \cdot V(s) \rangle \, ds$$

$$\downarrow$$

$$\frac{1}{R} = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle I(0) \cdot I(s) \rangle \, ds$$

Generalization :

⇒

Kubo formula

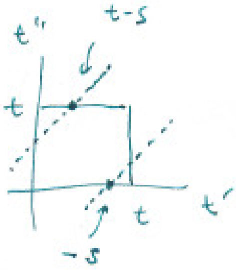
$$\underbrace{\sigma_{xx}}_{\text{conductivity}} = \frac{j_x}{E} = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle j_x(0) \, j_x(s) \rangle \, ds$$

③ Velocity correlation function and mean-square displacement (skipped)

Goal: to calculate $\langle x^2(t) \rangle$.

$x(0) = 0$ at $t = 0$.

$$x(t) = \int_0^t v(t')\,dt'$$



$$\Rightarrow \langle x^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle v(t')\, v(t'') \rangle$$

$$= \int_0^t dt' \int_0^t dt'' \langle v(0)\, v(t''-t') \rangle$$

$\downarrow$ $s = t'' - t'$

$$= \int_0^t ds \int_0^{t-s} dt' \; K_v(s) + \int_{-t}^0 ds \int_{-s}^t dt' \; K_v(s)$$

$K_v(s) = \langle v(0) v(s) \rangle$

$$= \int_0^t ds\, K_v(s)\,(t-s) + \int_{-t}^0 ds\, K_v(s)\,(t+s)$$

$\downarrow$ $s \to -s$

$$= 2\int_0^t ds\, K_v(s)\,(t-s)$$

$$m\frac{dv}{dt} = -\alpha v + F'(t)$$

$$\to \quad v(s+\tau) - v(s) = -\gamma v(s)\tau + \frac{1}{m}\int_s^{s+\tau} F'(t')\,dt'$$

$(\gamma = \alpha/m, \; \tau \gg \tau^*)$

$$\to \quad \langle v(0)\, v(s+\tau) \rangle - \langle v(0)\, v(s) \rangle = -\gamma\tau \langle v(0) v(s) \rangle + \underbrace{\frac{1}{m}\left\langle v(0) \int_s^{s+\tau} F'(t')\,dt' \right\rangle}$$

$$\simeq \frac{1}{m}\langle v(0) \rangle \left\langle \int_s^{s+\tau} F'(t')\,dt' \right\rangle = 0$$

$$\Rightarrow \quad \frac{d}{ds}\langle v(0) v(s) \rangle = -\gamma \langle v(0)\, v(s) \rangle$$

$$\Rightarrow \quad K_v(s) = \langle v^2(0) \rangle e^{-\gamma s} \quad \text{for } s > 0.$$

$$\Rightarrow \quad K_v(s) = \langle v^2(0) \rangle \; e^{-\gamma |s|} \qquad (\because \; K_v(s) = K_v(-s))$$

$$\Rightarrow \quad \langle x^2(t) \rangle = \frac{2kT}{m} \int_0^t ds\,(t-s)\, e^{-\gamma |s|} \qquad (\because \; \tfrac{1}{2}m v^2(0) = \tfrac{1}{2}kT)$$

$$= \frac{2kT}{m\gamma}\left(t - \frac{1}{\gamma}\left(1 - e^{-\gamma t}\right)\right)$$

(the same result with the previous calculation. see the note around Einstein relation.)

⊙ generalization of fluctuation – dissipation theorem

Consider an isolated system which has a parameter set $\{y_1, \cdots, y_n\}$

⇒ # of accessible state $\Omega = \Omega(y_1, y_2 \cdots, y_n)$

entropy $S = k \ln \Omega$

at equilibrium : $y_i = \tilde{y}_i$, $\left.\frac{\partial S}{\partial y_i}\right|_{y=\tilde{y}_i} = 0$ for all i.

Near equilibrium : $S(\{y_i\}) = S(\tilde{y}_1, \cdots, \tilde{y}_n) + \frac{1}{2}\sum_{ik} C_{ik} (y_i - \tilde{y}_i)(y_k - \tilde{y}_k)$

$$C_{ik} = C_{ki} = \frac{\partial^2 S}{\partial y_i \partial y_k}$$

Now, consider the time dependence of $\dot{y}_i = \frac{dy}{dt}$ and $\partial S / \partial y_i$

typically, $\dot{y}_i$, $\frac{\partial S}{\partial y_i}$ ~ rapidly fluctuating

with correlation time τ^*

at equilibrium, $\overline{\frac{\partial S}{\partial y_i}} = 0$ and $\frac{d\bar{y}_i}{dt} = 0$ for all i.

in nonequilibrium, (near equilibrium) $\frac{d\bar{y}_i}{dt} = \sum_{j=1}^{n} \alpha_{ij} \bar{Y}_j$

α_{ij} ~ friction coefficient

$\bar{Y}_j = \overline{\frac{\partial S}{\partial y_j}} = \sum_k C_{jk} (\bar{y}_k - \tilde{y}_k)$

~ "driving force"

(cf. generalized force $= \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial y}$)

This equation is similar to ~~the~~ Langevin eq. without F_{ext}.

$$\Rightarrow \alpha_{ij} = \frac{1}{k} \int_{-\infty}^{0} ds\, K_{ij}(s)$$

$$K_{ij}(s) \equiv \langle \dot{y}_i(t)\, \dot{y}_j(t+s) \rangle_0 = \langle \dot{y}_i(0)\, \dot{y}_j(s) \rangle_0$$

~ general form of ~~the~~ fluctuation – dissipation theorem derivation of generalized fluctuation - dissipation theorem

$\tau \gg \tau^*$, but τ ~ macroscopically short time interval

"coarse-grained" time derivative of $\langle y_i \rangle$

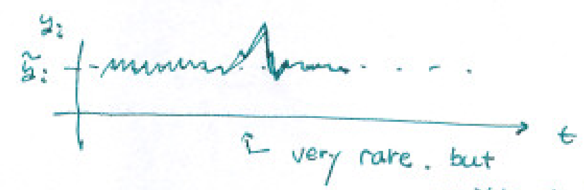
$$\frac{1}{\tau}\langle y_i(t+\tau) - y_i(t)\rangle = \frac{1}{\tau}\int_t^{t+\tau} \langle \dot{y}_i(t')\rangle dt'$$

At time t, as an approximation, the system is assumed to be in equilibrium. ← We are considering the system near equilibrium.

or,

$\Rightarrow \langle \dot{y}(t)\rangle = 0$

We can imagine spontaneous deviation from equilibrium at $t+\tau'$.



After τ' ($\tau' > \tau^*$),

the parameters are assumed to change

from $y_i(t)$ to $y_i(t+\tau') = y_i(t) + \Delta y_i(\tau')$ by small $\Delta y_i(\tau')$.

$\Rightarrow$ This causes entropy change $\Delta S(\tau')$.

$$\langle \dot{y}_i(t')\rangle = \sum_r \underbrace{W_r(t+\tau')}_{\text{probability that the system is at state } r.}(\dot{y}_i)_r$$

($t' = t+\tau$)

$(\dot{y}_i)_r$ ~ expectation value of $\dot{y}_i$ when the system is at state r.

$$\frac{W_r(t+\tau')}{W_r(t)} = \frac{\Omega(t+\tau')}{\Omega(t)} = e^{\Delta S(\tau')/k} \simeq 1 + \Delta S(\tau')/k.$$

($\because$ τ' is small enough.)

$$\Rightarrow \langle \dot{y}_i(t')\rangle = \sum_r W_r(t)\,(1+\Delta S/k)(\dot{y}_i)_r$$

$$= \langle \dot{y}_i\,[1+\tfrac{1}{k}\Delta S(\tau')]\rangle_0$$

$\langle \cdots \rangle_0$ ~ ensemble average in equilibrium.

$$= \frac{1}{k}\langle \dot{y}_i(t')\,\Delta S(\tau')\rangle_0$$

($\because$ at t, the system is in equilibrium.)

$$\Delta S(\tau') = \sum_j \frac{\partial S}{\partial y_j}\Delta y_j(\tau')$$

$\Rightarrow$

$$\langle y_i(t+\tau) - y_i(t)\rangle = \frac{1}{k}\int_t^{t+\tau} \langle \dot{y}_i(t')\,\Delta S(t'-t)\rangle_0\, dt'$$

$$= \frac{1}{k}\int_t^{t+\tau} \langle \dot{y}_i(t') \sum_j \frac{\partial S}{\partial y_j}\,\Delta y_j\,(t'-t)\rangle_0\, dt'$$

$$= \frac{1}{k}\sum_j \int_t^{t+\tau} dt' \,\langle \dot{y}_i(t') Y_j(t) \int_t^{t'} dt''\, \dot{y}_j(t'')\rangle_0$$

$$\simeq \frac{1}{k}\sum_j \bar{Y}_j(t) \int_t^{t+\tau} dt' \int_t^{t'} dt'' \,\langle \dot{y}_i(t')\,\dot{y}_j(t'')\rangle_0$$

$$s \equiv t''-t', \qquad K_{ij}(s) \equiv \langle \dot{y}_i(t)\,\dot{y}_j(t+s)\rangle_0$$

$$\Rightarrow \langle y_i(t+\tau) - y_i(t)\rangle = \frac{1}{k}\sum_j \bar{Y}_j(t) \int_{-\tau}^{0} ds \int_{t-s}^{t+\tau} dt'\, K_{ij}(s)$$

$$= \frac{1}{k}\sum_j \bar{Y}_j\, \tau \int_{-\infty}^{0} ds\, K_{ij}(s)$$

$$= \sum_j \alpha_{ij}\,\bar{Y}_j\,.$$

$$\Rightarrow \quad \alpha_{ij} = \frac{1}{k}\int_{-\infty}^{0} ds\, K_{ij}(s)\,.$$

⊙ Onsager relations

In equilibrium, $K_{ij}(s) = \langle \dot{y}_i(t)\, \dot{y}_j(t+s) \rangle_0$

~ independent of t.

$$K_{ij}(s) = \langle \dot{y}_i(t)\, \dot{y}_j(t+s) \rangle_0$$
$$= \langle \dot{y}_i(t-s)\, \dot{y}_j(t) \rangle_0$$
$$= \langle \dot{y}_j(t)\, \dot{y}_i(t-s) \rangle_0$$
$$= K_{ji}(-s)$$

· time reversal symmetry : $t \to -t$; in the presence of external magnetic field $\vec{B}$

Then, the direction of magnetic field is reversed as $t \to -t$:

$$\vec{B} \to -\vec{B}$$

($\because$ Current which produces $\vec{B}$ becomes to have the reverse direction.)

$$K_{ij}(s;\vec{B}) \longrightarrow K^{\dagger}_{ji}(s;-\vec{B})$$

(dagger $\dagger$: it represents the change of sign of ($\dot{y}_i(t)\, \dot{y}_j(t+s)$) under the time reversal.)

($\because$ $K_{ij}(s;\vec{B}) \to K^{\dagger}_{ij}(-s;-\vec{B}) = K^{\dagger}_{ji}(s;-\vec{B})$)

⇒ Onsager relation. (or Onsager reciprocal symmetry)

Example: y_i, y_j ~ both displacements or both velocities.

①

⇒ $\dot{y}_i\dot{y}_j \longrightarrow \dot{y}_i\dot{y}_j$ under time reversal

(no change of sign)

⇒ $K_{ij}(s;\vec{B}) = K_{ji}(s;-\vec{B})$

⇒ $\alpha_{ij}(\vec{B}) = \alpha_{ji}(-\vec{B})$

② y_i → displacement, y_j ~ velocity.

⇒ $\dot{y}_i\dot{y}_j \to -\dot{y}_i\dot{y}_j$ under time reversal

→ $K_{ij}(s;\vec{B}) = -K_{ji}(s;-\vec{B})$, $\alpha_{ij}(\vec{B}) = -\alpha_{ji}(-\vec{B})$