Take a small perturbation of the energy of the system.

$E(t) = E - h(t)\, A(x)$; $h(t)$: time-dependent amplitude of the perturbation

Q: What is the consequence for $\langle B(t)\rangle$ where B is any other observable

Response function $R(t-t')$

$$\langle B(t)\rangle_h = \langle B(t)\rangle_{h=0} + \int dt'\, R(t-t')\, h(t') + o(h)$$

Fluctuation-dissipation theorem:

$$\boxed{R_{BA}(t) = -\frac{1}{k_B T}\frac{\partial}{\partial t} C_{BA}(t)} \qquad (0)$$

where $C_{BA}(t) = \langle B(t)\, A(0)\rangle$

Example: colloid in an optical trap

Take $\dot{x} = -\omega x + \sqrt{2T}\eta$; $V(x) = \frac{1}{2}\omega x^2$ $(\mu = k = 1)$

In the steady state, we know that $\langle \frac{1}{2}\omega x^2\rangle = \frac{T}{2} \Rightarrow \langle x^2\rangle = \frac{T}{\omega}$

Q: If one modifies the trap in a time-dependent manner, how does the variance adapt at time t?

Perturbation: $V_h(x) = \frac{1}{2}\omega x^2 - h(t) K x^4 \Rightarrow A(x) = K x^4$

$B(x) = x^2 \Rightarrow \langle B(t, [h(s)])\rangle = ?$

2

1) $h=0 \quad C_{BA}(t-t') = K \langle x^2(t)\, x^4(t')\rangle$

$$\frac{d}{dt}\langle x^2(t)\, x^4(t')\rangle = 2\langle x\dot{x}(t)\, x^4(t')\rangle + \frac{1}{2}\, 2T\, 2 \langle x^4(t')\rangle$$

$$= -2\omega \langle x^2(t)\, x^4(t')\rangle + 0 + 2T\; 3\langle x^2\rangle^2$$

$$\frac{d}{dt}\langle x^2(t)\, x^4(t')\rangle = -2\omega \langle x^2(t) x^4(t')\rangle + 6\frac{T^3}{\omega^2}$$

$$\Rightarrow \langle x^2(t) x^4(t')\rangle = \langle x^6(t')\rangle e^{-2\omega(t-t')} + \frac{3T^3}{\omega^3}\left(1 - e^{-2\omega(t-t')}\right)$$

$\langle x^6\rangle = 5\times 3\times \langle x^2\rangle_c^3 = 15\,\frac{T^3}{\omega^3}$ (Wick theorem or $\kappa_6 = 0$)

$$\boxed{C_{BA}(t-t') = \frac{KT^3}{\omega^3}\left[12\, e^{-2\omega(t-t')} + 3\right]}$$

$$R_{BA}(t-t') = -\frac{1}{T} \times (-2\omega) \times \frac{12KT^3}{\omega^3}\, e^{-2\omega(t-t')}$$

$$\boxed{R_{BA} = \frac{24\cdot KT^2}{\omega^2}\, e^{-2\omega(t-t')}}$$

Consider a protocole such that $h(t \leq 0) = 0$

$$\langle x^2(t)\rangle = \langle x^2\rangle_{h=0} + \int_0^t ds\, h(s)\, R_{BA}(t-s$$

$$\boxed{\langle x^2(t)\rangle = \frac{T}{\omega} + \frac{24KT^2}{\omega^2}\int_0^t ds\, h(s)\, e^{-2\omega(t-s)}}$$

Check using Itō-calculus:

$$\dot{x} = -\omega x + \sqrt{2T}\,\eta + 4h(t)\,k\,x^3$$

$$\frac{d}{dt}\left(x^2 \right) = 2x\dot{x} + 2T \quad = -2\omega x^2 + \sqrt{8T}\,x\eta + 8k\,h(t)\,x^4 + 2T$$

$$\frac{d}{dt}\langle x^2\rangle = -2\omega\langle x^2\rangle + 0 + 8k\,h(t)\underbrace{\langle x^4\rangle}_{3\langle x^2\rangle^2 = 3\frac{T^2}{\omega^2} + O(h)} + 2T = -2\omega\langle x^2\rangle + 2T + 24\frac{kT^2}{\omega^2}h(t)$$

$$\frac{d}{dt}\left[\langle x^2\rangle - \frac{T}{\omega}\right] = -2\omega\left[\langle x^2\rangle - \frac{T}{\omega}\right] + 24\frac{kT^2}{\omega^2}h(t) \quad + O(h^2)$$

$$\Rightarrow \langle x^2(t)\rangle - \frac{T}{\omega} = \underbrace{\left[\langle x^2(0)\rangle - \frac{T}{\omega}\right]}_{=0} e^{-2\omega t} + \int_0^t ds\, e^{-2\omega(t-s)}\frac{24kT^2}{\omega^2}h(s)$$

q.e.d.

Comment: in practice, the FDT is a useful tool to
- test experimentally if a system is in equilibrium
- measure the temperature

4) Stochastic thermodynamics and entropy production rate

Thermodynamics is a macroscopic science, valid in the limit $N \to \infty$. As a result, many macroscopic concepts (e.g. Heat, entropy) are hard to understand.

Q: Can one use our Langevin description to get more insight into these concepts?

Yes: thanks to the work of Ken Sekimoto ("Stochastic energetics", Springer) and others.

Using the right definitions, one can reproduce at the fluctuating scale many results of thermodynamics.

4.1) Work and Heat: the 1st principle of thermodynamics

Take a potential $V(x, \lambda(t))$, where $\lambda(t)$ is a parameter that can be tuned by an external operator.

Consider the dynamics of an underdamped colloid:

$$\dot{x} = v; \quad m\dot{v} = -\gamma v - \partial_x V(x, \lambda(t)) + \sqrt{2\gamma k T}\,\eta(t)$$

Time evolution of the energy of the colloid

$$E_p = V(x, \lambda(t)) \Rightarrow \frac{d}{dt} E_p(x(t), \lambda(t)) = \partial_x E_p \cdot \dot{x} + \partial_\lambda E_p \cdot \dot{\lambda} = v\partial_x V + \partial_\lambda V \cdot \dot{\lambda}$$

$$E_k = \frac{1}{2} m v^2 \Rightarrow \frac{d}{dt} E_k(v(t)) = m v \dot{v} + \frac{\gamma k T}{m^2} \cdot m$$
$$= -\gamma v^2 - v \partial_x V(x,\lambda) + \sqrt{2\gamma k T}\, \eta(t) v + \frac{\gamma k T}{m}$$

$$\Rightarrow \frac{d}{dt} E_{tot}(x(t), v(t), \lambda(t)) = -\gamma v^2 + \frac{\gamma k T}{m} + \sqrt{2\gamma k T}\, \eta(t) v + \dot{\lambda}(t) \partial_\lambda V \quad (*)$$

Several comments are in order:

* $-\gamma v^2 = -\gamma v \cdot v$ is the power lost by the system to the bath due to the drag $\Rightarrow$ dissipation
* $\frac{\gamma k T}{m}$ is the power injected on average by thermal fluctuations
* $\sqrt{2\gamma k T}\, \eta(t) v$ is the fluctuations of this power ($\langle \eta(t) v(t) \rangle \overset{\text{Ito}}{=} 0$)
* if $V(x,\lambda) = U(x) \Rightarrow$ drops out, $f = -V'(x)$ is a conservative force. Then steady-state $\Rightarrow \frac{d}{dt}\langle E_{tot}\rangle = 0 = -\gamma \langle v^2 \rangle + \frac{\gamma k T}{m} \Leftrightarrow \frac{1}{2} m \langle v^2 \rangle = \frac{kT}{2}$

  $\Rightarrow$ equipartition is a balance between injection & dissipation of energy.
* $\dot{\lambda}\, \partial_\lambda E_p$ is the power injected by the operator into the system by changing $\lambda(t)$.

Let us integrate $(*)$ over time, along a trajectory

$$\Delta E = \int_{t_0}^{t_1} \frac{dE_{tot}}{dt} dt = \underbrace{\int_{t_0}^{t_1} \left[-\gamma v^2 + \frac{\gamma k T}{m} + \sqrt{2\gamma k T}\, \eta v \right] dt}_{Q} + \underbrace{\int_{t_0}^{t_1} dt\, \dot{\lambda}\, \partial_\lambda V}_{W}$$

ΔE is the change of internal energy

Q is the energy exchanged with the thermal bath: the HEAT

W is the energy injected by the operator into the system: the WORK

$$\boxed{\Delta E = Q + W \quad \text{is the first principle of thermodynamics.}}$$

Comment: If you do Stratonovich calculus, you use the standard chain rule to get $\frac{d}{dt} E_{tot}(x(t), v(t), \lambda(t)) = -\gamma v^2 + \sqrt{2\gamma k T}\,\eta(t)\,v + \dot{\lambda}(t)\,\partial_\lambda V$

so that $Q = \int_0^t dt\,[-\gamma v^2 + \sqrt{2\gamma k T}\,\eta(t)\,v]$ and

$$dQ = \int_t^{t+dt} \frac{dE_{tot}}{dt}\,dt = -\gamma v^2\,dt + \sqrt{2\gamma k T}\int_t^{t+dt} ds\,\eta(s)\,v(s)$$

Q: where has $\frac{\gamma k T}{m}$ gone?! Remind that the Langevin eq° really is an equation for time increments: $dv = -\underset{\uparrow}{\frac{\gamma}{m}v}\,dt + \sqrt{\frac{2\gamma k T}{m^2}}\,\underset{\uparrow}{d\eta} - \underset{\uparrow}{V'(x)}\,\frac{dt}{m}$

whose time-discretization should be specified: $v_t + \underbrace{\frac{v_{t+dt} - v_t}{2}}_{\frac{dv}{2}}$ $\quad \int_t^{t+dt} \eta(t)\,dt \quad V'\!\left(x_t + \frac{dx_t}{2}\right)$

let's compute $\langle dQ\rangle = -\gamma\langle v^2\rangle dt + \sqrt{2\gamma k T}\left\langle \int_t^{t+dt} ds\,\eta(s)\,v(s)\right\rangle$

$$\int_t^{t+dt} ds\,\eta(s)\,v(s) \overset{\text{Strat.}}{=} \int_t^{t+dt} ds\,\eta(s)\left[\tfrac{1}{2}v(t) + \tfrac{1}{2}v(t+dt)\right] = d\eta_t\left[v(t) + \frac{dv(t)}{2}\right]$$

$$\simeq d\eta_t\,v(t) + \frac{1}{2}\,d\eta_t\left[-\frac{\gamma}{m}v\,dt + \frac{\sqrt{2\gamma k T}}{m}\,d\eta_t - \frac{V'(x)}{m}dt\right]$$

$$\simeq d\eta_t\,v(t) + \frac{1}{2}\frac{\sqrt{2\gamma k T}}{m}\,d\eta^2 + o(dt)$$

$$\left\langle \int_t^{t+dt} ds\,\eta(s)\,v(s)\right\rangle = \underset{\downarrow}{0} + \frac{1}{2}\frac{\sqrt{2\gamma k T}}{m}\underbrace{\langle d\eta^2\rangle}_{dt} \neq 0 \quad \text{(very different from Itô!)}$$

$$\langle dQ \rangle = -\gamma \langle v^2 \rangle dt + \frac{\gamma k_B T}{m} dt$$

In Stratonovich calculus, the term $\sqrt{2\gamma k T}\,\eta(t)\,v(t)$ contains both the average injected power, $\frac{\gamma k T}{m} dt$, and the fluctuations.

4.2) The second principle

Entropy: Let us consider an overdamped Langevin particle:

$$v = \dot{x} = \mu f(x) + \sqrt{2\mu T}\,\eta(t) = -\mu \partial_x V + \sqrt{2T\mu}\,\eta(t) \quad (k_B = 1)$$

We adopt the Stratonovich convention so that:

- $\to$ the chain rule holds
- $\to \langle \dot{x}\,\eta(t) \rangle \neq 0$
- $\to P[\{x(t)\}] = \frac{1}{Z} e^{-\int_0^t ds \left[\frac{(\dot{x} - \mu f)^2}{4\mu T} + \frac{1}{2} f'(x(s))\right]}$

Equation of motion implies that $\dot{x} f = \gamma v^2 - \sqrt{2\gamma T}\,\eta v$ = power injected in the fluid

$\Rightarrow \dot{x} f$ is the power injected in the fluid $= \frac{dQ_f}{dt}$

$$\frac{\dot{x} f}{T} = \frac{d}{dt}\left(\frac{Q_f}{T}\right) = \frac{d}{dt} S_f \Rightarrow \text{variation of entropy of the fluid.}$$

Variation of entropy of the fluid along a trajectory: $\boxed{\Sigma = \int_0^t ds \frac{\dot{x} f}{T}}$

Σ fluctuates from trajectory to trajectory $\Rightarrow$ Q: how?

$\Rightarrow$ consider the observable $\bar{\Sigma} = \left\langle \log \frac{P[\{x(t)\}]}{P[\{x^R(t)\}]} \right\rangle_{traj}$

$x^R(t) = x(t_f - t) \Rightarrow \frac{d}{dt} x^R(t) = -\frac{dx}{dt}(t_f - t)$ & $f(x^R(t)) = f(x(t_f - t))$

$$\Rightarrow P[\{x^R\}] = \frac{1}{Z} e^{-\int_0^t ds \frac{(\dot{x}^R - \mu f(x^R))^2}{4T\mu} + \frac{1}{2}\mu f'(x^R)}$$

$$= \frac{1}{Z} e^{-\int_0^t ds \frac{(-\dot{x}(t-s) - \mu f(x(t-s)))^2}{4\mu T} + \frac{1}{2}\mu f'(x(t-s))}$$

$s \to t-s$

$$= \frac{1}{Z} e^{-\int_0^t ds \frac{(\dot{x}(s) + \mu f(x(s)))^2}{4\mu T} + \frac{1}{2}\mu f'(x(s))}$$

$$\log \frac{P[x]}{P[x^R]} = \int_0^t ds \frac{(\dot{x} + \mu f)^2}{4\mu T} - \frac{(\dot{x} - \mu f)^2}{4\mu T} = \int_0^t ds \frac{\dot{x} f}{T} = \Sigma \;!$$

The entropy produced along a path is related to its statistically irreversibility!

$$\boxed{\bar{\Sigma} = \left\langle \log \frac{P[x]}{P[x^R]} \right\rangle = \langle \Sigma \rangle}$$

is the average variation of entropy of the system.

* If $f = -V'(x)$; $\Sigma = \frac{1}{T} \int_0^t ds \left(-\frac{dx}{dt} \cdot \frac{dV}{dx}\right) = \frac{1}{T} \left[V(x(0)) - V(x(t))\right]$

In steady state, $\langle V(x(0)) \rangle = \langle V(x(t)) \rangle \Rightarrow \bar{\Sigma} = 0$

and there is no creation of entropy.

* If f is a non conservative force, Σ is the entropy created by this non equilibrium drive & $\bar{\Sigma} \neq 0$. One then defines the

entropy production rate

$$\boxed{\sigma = \lim_{t \to \infty} \frac{1}{t} \bar{\Sigma}(t) = \lim_{t \to \infty} \frac{1}{t} \left\langle \log \frac{P[x]}{P[x^R]} \right\rangle}$$

Here, $\sigma = \lim_{t\to\infty} \left\langle \frac{1}{t}\int_0^t ds\, \frac{\dot{x}f}{T} \right\rangle_{path} \underset{\substack{\text{ergodicity} \\ \text{\& steady state}}}{=} \frac{1}{T}\langle \dot{x} f \rangle_{ss}$

$\dot{x}f$ is the power dissipated by the non-conservative force f in the bath $\Rightarrow \sigma$ is proportional to the average power dissipated in steady state. ($\sigma = 0$ if $f = -V'(x)$ is a conservative force)

* The derivation above connect thermodynamic irreversibility (entropy creation) and statistical irreversibility.

* Fluctuation theorem

Σ is a fluctuating quantity. Let's compute

$$\langle e^{-\Sigma} \rangle = \int D[x(t)]\, P[x(t)]\, e^{-\log \frac{P[x(t)]}{P[x^R(t)]}}$$

$$= \int D[x(t)]\, \frac{P[x(t)]}{P[x(t)]}\, P[x^R(t)] = \int D[x(t)]\, P[x^R(t)]$$

$$D[x(t)] = \left| \frac{D[x(t)]}{D[x^R(t)]} \right| D[x^R(t)]$$

$\uparrow$ Jacobian

What is the Jacobian of the transformation $x(t) \to x^R(t)$?

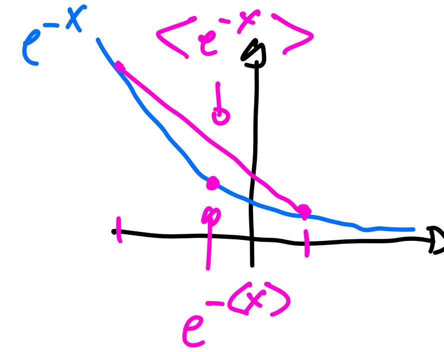
since $(x^R)^R = x$, $(\text{Jacobian})^2 = Id$

$$\Rightarrow \boxed{\langle e^{-\Sigma} \rangle = \int D[x^R]\, P[x^R(t)] = 1}$$

Fluctuation theorem

Jensen inequality : $e^{-\langle \Sigma \rangle} \leq \langle e^{-\Sigma} \rangle = 1$

Fluctuation theorem



log is an increasing function $- \langle \Sigma \rangle \leq 0$

$\Rightarrow \langle \Sigma \rangle \geq 0$

This is the second principle!