$$C_{AB}(t,t') = \langle A(t)\, B(t')\rangle = \int dx\, dx'\; A(x)\, B(x')\; P(x,t;x',t')$$
$$= \langle -|\, A\, e^{-(t-t')H}\, B\, e^{-t'H}\, |P_{\text{initial}}\rangle$$

Take t' very large $e^{-t'H}|P_{\text{initial}}\rangle = |P_s\rangle$

Since the system is in the steady state at t', $C_{AB}(t,t') = C_{AB}(t-t')$ due to time translational invariance, which can be read in

$$C_{AB}(t,t') = \langle -|\, A\, e^{-(t-t')H}\, B\, |P_s\rangle = C_{AB}(t-t')$$

$$A(x), B(x) \in \mathbb{R} \Rightarrow C_{AB} \in \mathbb{R} \Rightarrow C_{AB}^{\dagger} = C_{AB}$$

$\Rightarrow C_{AB}(t-t') = \langle P_s|\, B^{\dagger}\, e^{-(t-t')H^{\dagger}}\, A^{\dagger}\, |-\rangle$ using $\left(e^{uH}\right)^{\dagger} = \left(\sum_k \frac{u^k}{k!} H^k\right)^{\dagger} = \sum_k \frac{u^k}{k!} (H^{\dagger})^k$

Since $\langle P_s| = \langle -|\, P_s$, we get

$$C_{AB} = \langle -|\, P_s \underbrace{B\, P_s^{-1}}_{\substack{\text{commute} \\ = B P_s P_s^{-1}}} e^{-(t-t')H}\, P_s\, A\, |-\rangle = \langle -|\, B\, e^{-(t-t')H}\, A\, |P_s\rangle$$
$$= C_{BA}$$

$\Rightarrow$ Measuring B and then A or A and then B leads to the same result.

Idea for a numerical project: check this? (and its departure from equilibrium?)

3) Fluctuation dissipation theorem

Einstein relation $K(t-t') = 2\gamma k_B T\, \delta(t-t')$ (2)

has thus enforced
① the Boltzmann weight
② time-reversal symmetry

For the overdamped Langevin equation, $\dot{x} = \mu f(x) + \sqrt{2\mu kT}\,\eta$, we have 13

① $f = f_0 \Rightarrow \langle v \rangle = \mu f_0$. The mobility $\mu = \frac{\langle v \rangle}{f_0}$ measures the response of the system to a force f_0

② $f = 0 \Rightarrow \langle x^2 \rangle = 2Dt$ with $D = \mu kT$. The diffusivity characterizes the fluctuations of the system.

$D = \mu kT$ is thus a relation between fluctuations and response.

Let us now show that an equilibrium dynamics admits a much more general relation between fluctuations & response.

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 $R(t-t')$

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

Why is this true ??

$\langle B(t) \rangle$ is a functional of $h(t) \Rightarrow$ functional Taylor expansion

$$\langle B(t) \rangle_h \simeq \langle B(t) \rangle_{h=0} + \int dt' \frac{\delta \langle B(t) \rangle}{\delta h(t')} h(t') \quad \text{(functional Taylor)}$$

Morally $t = n\,dt = t_n$

$$\langle B(t_n)\rangle_h \simeq \langle B(t_n)\rangle_{h=0} + \text{“}\sum_{t_p} \frac{\partial \langle B(t_n)\rangle}{\partial h(t_p)} h(t_p)\text{''} + \mathcal{O}(h^2)$$

(Taylor expansion up to $\frac{\delta}{\delta h(n\,dt)} = \frac{1}{dt}\frac{\partial}{\partial h(t_n)}$)

Again equivalent to

“ $d\langle B\rangle = \nabla\langle B\rangle \cdot dh$ ” in a functional space

Note that $\nabla\langle B\rangle$ is independent of dh

$$R(t-t') = \frac{\delta\langle B(t)\rangle}{\delta h(t')}$$ is also independent of h.

$\Rightarrow$ Compute $R(t-t')$ once & predict $\langle B(t)\rangle_h$ for <u>any</u> small $h(t)$.

<u>Comment</u>: Since we neglect correction of order h^2, we speak about linear response.

<u>Q</u>: How can we compute $R(t-t')$? Just have to do it for a wisely chosen $h(t)$!

Take $h(t) = h_0$ for $t < t'$
$\qquad\qquad = 0$ for $t > t'$ ①

$$\langle B(t)\rangle_h = \langle B(t)\rangle_0 + \int_{-\infty}^{t'} ds\, h_0\, R(t-s) \quad ; \text{ we note } \langle\ \rangle_0 = \langle\ \rangle_{h=0}$$

$\frac{\partial}{\partial t'} \langle B(t) \rangle_h = 0 + h_0 R(t-t')$ ⇒ need to compute $\frac{\partial}{\partial t'} \langle B(t) \rangle_h$ for ①

$$\text{By definition } \langle B(t) \rangle = \langle - | B\, e^{-(t-t') H_{FP}^{\overset{h=0}{0}}} | P(t') \rangle \qquad (\Delta)$$

when $H_{FP}^{(0)}$ corresponds to the evolution after t', with $h(s > t') = 0$

What is $|P(t')\rangle$? If $t, t' \to \infty$ with $t > t'$, $|P(t')\rangle$ has relaxed to its equilibrium steady state with an energy $E - h_0 A$

$$\Rightarrow P(t') = \frac{1}{Z_{h_0}} e^{-\beta(E - h_0 A)}$$

__Small h:__ $Z_{h_0}^{-1} = \left[\int dx\, e^{-\beta(E-h_0A)}\right]^{-1} \simeq \left[\int dx\, e^{-\beta E}(1+\beta h_0 A)\right]^{-1}$

$$= \left[Z_0 + \beta h_0 \frac{Z_0}{Z_0} \int dx\, A e^{-\beta E}\right]^{-1} \quad \text{when } Z_0 = Z(h_0 = 0)$$

$$= Z_0^{-1}\left[1 + \beta h_0 \langle A \rangle_0\right]^{-1} \quad \text{with } \langle \dots \rangle_0 \Leftrightarrow \langle \dots \rangle \text{ with } h_0 = 0$$

$$\simeq Z_0^{-1}\left(1 - \beta h_0 \langle A \rangle_0\right)$$

$$\Rightarrow P(t') = Z_0^{-1}\left(1 - \beta h_0 \langle A \rangle_0\right)\left(1 + \beta h_0 A\right) e^{-\beta E}$$

$$\simeq P_0(x)\left[1 + \beta h_0 (A - \langle A \rangle_0)\right]$$

Back to $\langle B(t) \rangle$ and Eq. (Δ)

$$\langle B(t) \rangle = \langle - | B\, e^{-(t-t')H_{FP}^0} \left[1 + \beta h_0 (A - \langle A \rangle_0)\right] | P_0 \rangle$$

$$= \underbrace{\langle - | B\, e^{-(t-t')H_{FP}^0} | P_0 \rangle}_{\langle B(t) \rangle_0} + \beta h_0 \Big\{ \langle - | B\, e^{-(t-t')H_{FP}^0} A | P_0 \rangle$$

$$- \langle A \rangle_0 \underbrace{\langle - | B\, \underbrace{e^{-(t-t')H_{FP}^0} | P_0 \rangle}_{|P_0\rangle}}_{\langle B \rangle_0} \Big\}$$

$$\langle B(t)\rangle = \langle B(t)\rangle_0 + \beta h_0 \langle B(t)A(t')\rangle_0 - \beta h_0 \underbrace{\langle B(t)\rangle_0 \langle A(t')\rangle_0}_{= \langle B\rangle\langle A\rangle \text{ steady state}}$$

$$\frac{\partial}{\partial t'}\Big\downarrow$$

$$h_0 R(t-t') = \beta h_0 \frac{\partial}{\partial t'} \langle B(t)A(t')\rangle = \frac{1}{k_B T} h_0 \frac{\partial}{\partial t'} C_{BA}(t-t') = -\frac{h_0}{k_B T}\frac{\partial}{\partial t} C_{BA}(t-t')$$

Fluctuation-dissipation theorem:

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

Remarkably: This holds for any pairs of observables A & B

$\Rightarrow$ can be used to measure $k_B T$!

Comment: (i) In many non equilibrium systems, people have measured that, for some A & B, $R_{BA} \propto -\frac{\partial}{\partial t} C_{BA}$ and used that to define some effective temperature through

$$R_{BA}(t) = -\frac{1}{k_B T_{eff}}\frac{\partial}{\partial t} C_{BA}(t)$$

In general, T_{eff} is different for different choices of A & B $\Rightarrow$ not universal!

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

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

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 $\kappa_6 = 0$)

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

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

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

Conside 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:

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

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

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

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

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

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

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

$$E_K = \frac{1}{2} m v^2 \Rightarrow \frac{d}{dt} E_K(v(t)) = m v \dot{v} + \frac{\gamma k T}{m^2} \cdot m$$

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

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

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

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