VI Linear response theory - Intermezzo

We have met a number of fluctuation-dissipation-like relations. This can be explained by the linear response formalism, that starts from a microscopic (Hamiltonian) description, while Langevin (and hence Fokker-Planck) was phenomenological → linear response is general.

1°) Linear response and Onsager's intuition

In 1931, Onsager wrote that "as far as the average behavior is concerned, it does not matter whether a state was the result of a spontaneous fluctuation, or an imposed constraint": the dynamics of the decay (regression) to equilibrium is the same. This is a cornerstone of modern stat. phys., a facet of the fluctuation-dissipation theorem, shown in 1951 by Callen & Welton. What this means is: for an observable

$$\langle A(t)\rangle_{non\text{-}eq} - \langle A\rangle_{eq} \propto \langle \delta A(t)\, \delta A(0)\rangle_{eq} \quad , \quad \delta A = A(t) - \langle A\rangle_{eq}$$

$$\Rightarrow \left.\frac{\langle \delta A(t)\rangle}{\langle \delta A(0)\rangle}\right|_{non\text{-}eq} = \frac{\langle \delta A(t)\, \delta A(0)\rangle_{eq}}{\langle \delta A(0)\, \delta A(0)\rangle_{eq}}$$

work with shifted obsv.

This intuition is correct, can be proven by linear response analysis.

We will consider the following situation: a reference Hamiltonian $\mathcal{H}_0(\Gamma)$, where Γ denotes a point in phase-space (e.g. $\Gamma \equiv (\vec{r}^{\,N}, \vec{p}^{\,N})$) is perturbed by an external field f that couples to some observable $A(\Gamma)$. The perturbed Hamiltonian is $\boxed{\mathcal{H}_1(\Gamma) = \mathcal{H}_0(\Gamma) - f\, A(\Gamma)}$

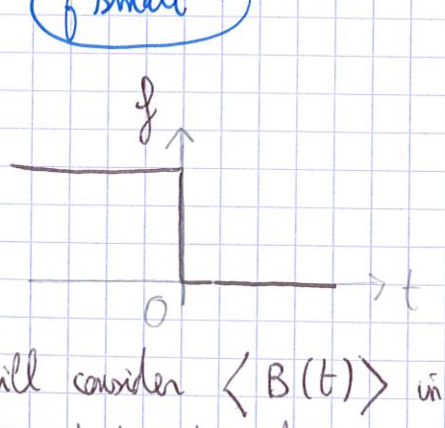
f "small"

e.g.

magn. field ← $B \times M$ in magnetic system — magnetization (total)

electric field ← $E \times P$ in electric " — electric dipole (")

Force $\times\, x$ in mechanical system

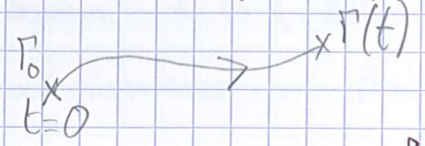


At $t=0$, the field is switched off, so that $\langle B\rangle$ will evolve from $\langle B\rangle_1$ to $\langle B\rangle_0$

2 ≠ equilibria with ≠ Hamiltonians

We will consider $\langle B(t)\rangle$ in the following sense:
B does not depend explicitly on time, only on the position in phase space, Γ.
$B(t)$ means $B(\Gamma(t))$, where the point in phase space, $\Gamma(t)$, can depend on time.
For $t>0$, the dynamics is ruled by Hamiltonian $\mathcal{H}_0$, and the density in phase space, $\rho(\Gamma, t)$, obeys Liouville equation. At $t=0$, we have $\rho(\Gamma, 0) = \frac{1}{Z_1} e^{-\beta \mathcal{H}_1(\Gamma)} = \rho_1(\Gamma)$

while for $t \to \infty$, $\rho(\Gamma, t) \to \frac{1}{Z_0} e^{-\beta \mathcal{H}_0(\Gamma)}$. We have 2 ways to express $\langle B(t) \rangle$, the observed time-dependent value:



$$\langle B(t) \rangle = \int d\Gamma \; B(\Gamma) \, \rho(\Gamma, t)$$

$$= \int d\Gamma_0 \; B(\Gamma(t)) \, \rho_1(\Gamma_0) \qquad \rho_1(\Gamma_0) = \frac{1}{Z_1} e^{-\beta \mathcal{H}_1(\Gamma)} = \rho(\Gamma_0, t=0)$$

where $\Gamma(t)$ is the trajectory s.t. $\Gamma(0) = \Gamma_0$.

The connexion between the 2 formulas follows from Liouville theorem: $|d\Gamma(t)| = |d\Gamma_0|$, and there is a bijection between the initial condition Γ_0, and the trajectory $\Gamma(t)$, plus: $\rho(\Gamma(t), t) = \rho(\Gamma_0, 0)$ since Liouville reads $\frac{D}{Dt} \rho(\Gamma(t)) = 0$.

$$\langle B(t) \rangle = \langle B(\Gamma(t)) \rangle_1$$

$$= \frac{\int d\Gamma_0 \; B(\Gamma(t)) \, e^{-\beta(\mathcal{H}_0 + \Delta\mathcal{H})(\Gamma_0)}}{\underbrace{\int d\Gamma_0 \; e^{-\beta(\mathcal{H}_0 + \Delta\mathcal{H})}}_{= Z_1}} \qquad \begin{aligned} &\mathcal{H}_1 = \mathcal{H}_0 + \Delta\mathcal{H} \\ &\Delta\mathcal{H} = - f \cdot A \\ &d\Gamma = d\vec{r}^{\,N} d\vec{p}^{\,N} \end{aligned}$$

$$\simeq \frac{\int d\Gamma_0 \; B(\Gamma(t)) \, e^{-\beta\mathcal{H}_0} (1 - \beta \Delta\mathcal{H})}{\int d\Gamma_0 \; e^{-\beta\mathcal{H}_0} (1 - \beta \Delta\mathcal{H})} \; ; \qquad \langle B(\Gamma(t)) \rangle_0 = \langle B \rangle_0$$

$$\simeq \frac{Z_0 \left(\langle B \rangle_0 - \beta \langle B(\Gamma(t)) \, \Delta\mathcal{H}(\Gamma_0) \rangle \right)}{Z_0 \left(1 - \beta \langle \Delta\mathcal{H} \rangle_0 \right)}$$

$$\simeq \left(\langle B \rangle_0 - \beta \langle B(t) \, \Delta\mathcal{H}(0) \rangle_0 \right) \left(1 + \beta \langle \Delta\mathcal{H} \rangle_0 \right)$$

$$\simeq \langle B \rangle_0 + \beta f \langle B(t) A(0) \rangle_0 - \beta f \langle B \rangle_0 \langle A \rangle_0 + \mathcal{O}(f^2)$$

$$\langle \delta B(t) \rangle \equiv \langle B(t) \rangle - \langle B \rangle_0 = \beta f \langle \delta B(t) \, A(0) \rangle_0 = \beta f \langle \delta B(t) \, \delta A(0) \rangle_0$$

since $A = \langle A \rangle_0 + \delta A$

$$\langle \delta B(t) A(0) \rangle_0 = \langle \delta B(t) \delta A(0) \rangle_0 + \overbrace{\langle \delta B \rangle_0}^{0} \langle A \rangle_0$$

Hence $$\frac{\langle \delta A(t) \rangle}{\langle \delta A(0) \rangle} = \frac{\langle \delta A(t) \delta A(0) \rangle_0}{\langle \delta A(0) \delta A(0) \rangle_0}$$

and Onsager's intuition (the regression "hypothesis"), is thus shown.

2° Response functions and the fluctuation-dissipation theorem

Instead of a step function for the external field $f(t)$, like above, we may consider a more general time dependence for the protocol $f(t)$. How does $\langle B(t) \rangle$ respond?

On grounds of linearity (small $f(t)$):

$$\langle \delta B(t) \rangle = \int_{-\infty}^{+\infty} \chi(t, t') \, f(t') \, dt' \; ; \qquad \chi \equiv \text{response function} \; // \; \text{susceptibility}$$

Here, we are applying a small perturbation to an equilibrium system, and χ is a property of the reference, unperturbed system (as is $\langle \delta B(t) \delta A(0) \rangle_{eq}$)

Thus $\chi(t,t') = \chi(t-t')$: time translational invariance. Besides:

Causality: $\chi(t) = 0, \quad t < 0$

How can we find $\chi(t)$? We note that it does not depend on the protocol, and hence, it can be obtained from the "step down" worked out in 1a). Then

$$\langle \delta B(t) \rangle = \beta f \langle \delta B(t) \delta A(0) \rangle_0 \qquad \tau = t-t'$$

$$= \int_{-\infty}^{t} \chi(t-t') f(t') dt' = f \int_{-\infty}^{0} \chi(t-t') dt' = f \int_{t}^{\infty} \chi(\tau) d\tau$$

$$\Rightarrow \chi(\tau) = -\beta \frac{d}{d\tau} \underbrace{\langle \delta B(\tau) \delta A(0) \rangle_0}_{= \langle \delta B(\tau) A(0) \rangle_0}, \quad \tau > 0$$

$$= 0 \qquad \tau < 0$$

Since χ measures the response of B to a field that is coupled to A, we use χ_{BA}

Fluct-Dissipat theorem

$$\chi_{BA}(t) = -\beta \frac{d}{dt} \langle \delta B(t) A(0) \rangle_0 = -\beta \frac{d}{dt} \langle \delta B(t) \delta A(0) \rangle_0$$

We recover Onsager's intuition: the system's response to an external field $f(t)$ that puts it out of equilibrium, is governed by an equilibrium correlation function, $\langle \ \rangle_0$

We also get $\boxed{\text{the fluctuation-response connexion}}$, in the static response case.

Here $f(t) = f, \ \forall t$. Thus $\langle B(t) \rangle = \langle B \rangle_1$, t independent

$$\langle \delta B \rangle_1 = \int_{-\infty}^{t} \chi(t-t') f \, dt' = f \underbrace{\int_0^{\infty} \chi(\tau) d\tau}_{\chi_{stat}, \text{ static susceptibility}}$$

$$= f \int_0^{\infty} \left[-\beta \frac{d}{dt} \langle \delta B(t) A(0) \rangle_0 \right]$$

$$= -\beta f \left[\overbrace{\langle \delta B(\infty) A(0) \rangle_0}^{\text{assumed } 0} - \langle \delta B(0) A(0) \rangle_0 \right]$$

$$= \beta f \langle \delta B(0) A(0) \rangle_0$$

The best known illustration is the fluct-response in a magnetic system; take $A = B =$ magnetization M, and f is the external magnetic field B_{ext}, B_{ext} small ($\to 0$)

$$\boxed{kT \chi_{stat} = kT \frac{\langle M \rangle_1}{B_{ext}} = \langle (\delta M) M \rangle_0 = \langle (\delta M)^2 \rangle_0 = \langle M^2 \rangle_0 - \langle M \rangle_0^2}$$

Note that this holds not only at 0 magnetic field, but also at non 0:

$$kT \chi_{stat} \equiv kT \frac{\partial \langle M \rangle}{\partial B_{ext}} = kT \frac{\langle M \rangle_{B+B_{ext}} - \langle M \rangle_B}{B_{ext}} = \langle (\delta M)^2 \rangle_0$$

Hamiltonian with field B.

3°) Symmetry of the correlation functions

The FDT features equilibrium correlation functions, that exhibit ≠t levels of symmetry. The first level stems from fact that the system is then in a steady state (time translational invariance) while the second level is deeper, and a signature of the reversibility of the underlying microscopic dynamics (time reversal symmetry)

a) Two levels of symmetry

We consider two observables $A(\Gamma)$ and $B(\Gamma)$ where again Γ is a point in phase space $(\vec{r}^{\,N}, \vec{p}^{\,N})$. $A(t) \equiv A(\Gamma(t))$. Because of time translational invariance

$$C_{AB}(\tau) = \langle A(t+\tau)\, B(t) \rangle_{eq} \quad \text{, does not depend on } t$$

$$= \langle A(\tau)\, B(0) \rangle_{eq} \quad \text{with } t = 0$$

$$= \langle A(0)\, B(-\tau) \rangle_{eq} \quad \text{with } t = -\tau$$

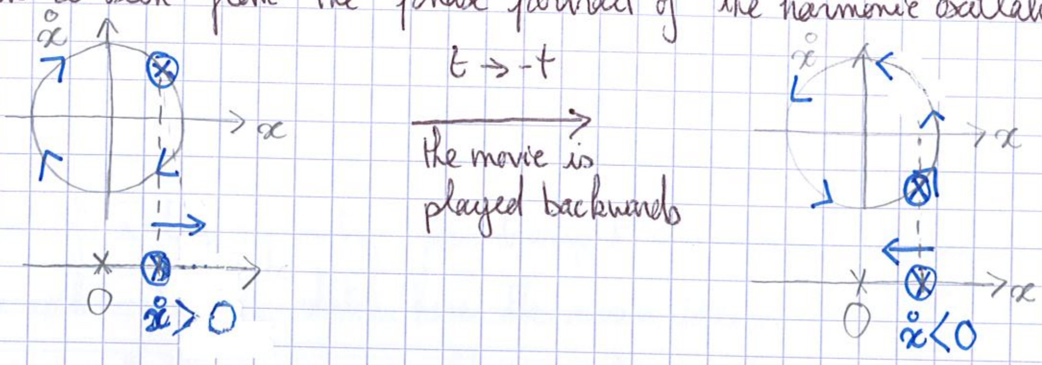
$$\boxed{C_{AB}(\tau) = C_{BA}(-\tau)} \quad \text{which means } C_{AA}(\tau) = C_{AA}(-\tau)$$

autocorrelation funct at equil are even in time

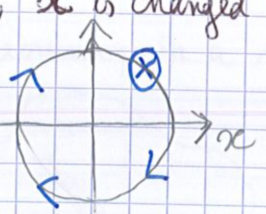
Yet, there is a more subtle level of symmetry, stemming from the reversibility of the microscopic dynamics (time reversal symmetry). Indeed, as follows from Hamilton's equations of motion, with t-reversal symmetric dynamics, then

a system with $\begin{cases} \text{time } t \\ \text{positions } \vec{r}(t) \\ \text{momenta } \vec{p}(t) \end{cases}$ has same dynamics as system with $\begin{cases} \text{time } -t \\ \text{positions } \vec{r}(-t) \\ \text{momenta } -\vec{p}(-t) \end{cases}$

This can be seen from the phase portrait of the harmonic oscillator $\begin{cases} \ddot{x} + \omega^2 x = 0 \\ p = \dot{x} \end{cases}$



Finally, $\dot{x}$ is changed into $-\dot{x}$



and we are back to the original dynamics. The two operations of playing backwards and inverting momenta cancel each other.

Same dynamics means same correlation functions, but we have to pay attention to the type of observable: for instance, an observable A that depends only on the positions is unchanged under time-reversal: $\varepsilon_A = +1$. On the other hand, an observable A that is proportional to momenta will change sign: $\varepsilon_A = -1$. Of course, an arbitrary observable may not have a well defined symmetry under t-reversal (no signature ε can be defined), but those observables who do have a well defined signature have interesting symmetry properties, that reflect on the correlation function:

$$C_{AB}(t) = \langle A(t)\, B(0)\rangle_{eq}$$

$$= \varepsilon_A\, \varepsilon_B \langle A(-t)\, B(0)\rangle_{eq} \quad \text{, under} \quad \begin{array}{l} t \to -t \\ \vec{r} \to \vec{r} \\ \vec{p} \to -\vec{p} \end{array} \text{, same dynamics same correlations}$$

$$C_{AB}(t) = \varepsilon_A\, \varepsilon_B\, C_{AB}(-t)$$

Since stationarity implies $C_{AB}(t) = C_{BA}(-t)$:

$$C_{AB}(t) = \varepsilon_A\, \varepsilon_B\, C_{BA}(t) \qquad \text{(no summation over repeated indices)}$$

If the 2 observables have the same symmetry under t-reversal:

$$C_{AB}(t) = C_{BA}(t)$$

3°| f) Towards Onsager reciprocity relations

Combining the previous constraint on the correlation function $C_{AB}(t)$ to the F.D.T. we get

$$\chi_{BA}(t) = -\beta \frac{d}{dt}\langle \delta B(t)\, A(0)\rangle = -\beta \frac{d}{dt}\langle B(t)\, A(0)\rangle$$

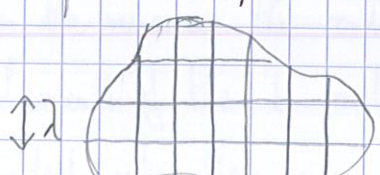
$$= -\beta \frac{d}{dt} C_{BA}(t) \qquad \text{and} \qquad C_{BA}(t) = \varepsilon_A\, \varepsilon_B\, C_{AB}(t)$$

$$= -\beta \frac{d}{dt} C_{AB}(t)\, \varepsilon_A\, \varepsilon_B$$

$$\boxed{\chi_{BA}(t) = \varepsilon_A\, \varepsilon_B\, \chi_{AB}(t)}$$

This is an important symmetry, stating the equality of cross-susceptibilities, at the root of a deep symmetry for transport coefficients. Showing this requires a bit more work. We only sketch here the main ideas.

There is no g^{al} theory of non-equilibrium system, and we assume that we are close to equilibrium, in a macroscopic system. The system is decomposed into boxes



of mesoscopic size λ (linear dimension); within each box, the system is at equilibrium, described by a set of extensive variables $A_1, A_2, \dots$ (like energy, number of molecules, mean velocity etc.). We define ↳ conserved quantities

$F_i = \frac{\partial S}{\partial A_i}$ as a thermodynamic force where $S(A_1, A_2, \dots)$ is the (equilibrium) entropy

The thermodynamic forces are not the same in neighboring boxes, which creates gradients, and then fluxes.

For instance, with $S(U, V, N)$,

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\Rightarrow F_U = \frac{1}{T} \; ; \; F_N = -\frac{\mu}{T} \; \dots$$

the gradients $(\vec{\nabla} T, \vec{\nabla}\mu, \vec{\nabla} P)$ in the system create currents $\vec{J}_i$, associated to the variables A_i (energy current, particle current, ...). Because we are by assumption close to equilibrium, there is a linear relationship between the $\vec{\nabla} F_i$, called the affinities, and the currents

$$\boxed{\vec{J}_i = \sum_j L_{ij} \vec{\nabla} F_j}$$

Each current depends on the conjugate affinity $\vec{J}_i \Leftrightarrow \vec{\nabla} F_i$, but also on crossed affinities $(\vec{\nabla} F_j, j \neq i)$. The matrices $\overleftrightarrow{L}_{ij}$ are related to the χ_{ij}, and enjoy the same symmetry:

$$L_{ij} = \varepsilon_i \varepsilon_j L_{ji} \quad \rightarrow \text{Onsager reciprocity relations (Nobel 1968)}$$

Illustration: consider a gas of light particles, that move in a medium with fixed obstacles, randomly placed (the so-called Lorentz model) → relevant for neutrons in a nuclear reactor, light solute in a solvent of heavy molecules, or for electrons in a semi-conductor. Here, the energy of the light particles is conserved (elastic collision with the fixed obstacles), but not the momentum. The number of # also is conserved $\Rightarrow A_1 = U$; $A_2 = N$ and the thermodynamic forces are $\frac{1}{T}$ and $-\frac{\mu}{T}$

$$\vec{J}_N = L_{NN} \vec{\nabla}\left(-\frac{\mu}{T}\right) + L_{NE} \vec{\nabla}\left(\frac{1}{T}\right)$$
$$\vec{J}_E = L_{EN} \vec{\nabla}\left(-\frac{\mu}{T}\right) + L_{EE} \vec{\nabla}\left(\frac{1}{T}\right) \qquad L_{NE} = L_{EN}$$

Quite remarkable cross-effect: the contribution of $\vec{\nabla} T$ to the particle current is the same as the contribution of $-\vec{\nabla}\left(\frac{\mu}{T}\right)$ to the energy current. Note that the elements of the L-matrix are related to the thermal conductivity, κ. Indeed, when there is no flux of matter $(\vec{J}_N = \vec{0})$, we expect $\vec{J}_E = -\kappa \vec{\nabla} T$

$$\vec{J}_N = \vec{0} \Rightarrow \vec{\nabla}(-\mu/T) = -\left(L_{NE}/L_{NN}\right)\vec{\nabla}(1/T)$$

$$\Rightarrow \vec{J}_E = \frac{1}{T^2}\left(L_{EE}L_{NN} - L_{EN}^2\right)\frac{1}{L_{NN}}\vec{\nabla}T \Rightarrow \kappa = \frac{L_{EE}L_{NN} - L_{EN}^2}{T^2 L_{NN}}$$

Within such a description, it can be shown that the entropy production rate is

$$\sigma = \sum_i \vec{J}_i \cdot \vec{\nabla}F_i = \sum_{ij} \vec{\nabla}F_i \cdot L_{ij}\,\vec{\nabla}F_j$$

This rate has to be ≥ 0, as a consequence of the second principle.
Hence: $\overleftrightarrow{L}$ is a positive matrix. With the Lorentz model example: $L = \begin{pmatrix} L_{NN} & L_{NE} \\ L_{NE} & L_{EE} \end{pmatrix}$ is positive $\Rightarrow \det L \geq 0 \Rightarrow L_{EE}L_{NN} - L_{NE}^2 \geq 0$ ie $\kappa \geq 0$ (as it should to avoid instabilities in heat diffusion).

<u>Remark</u>: in a system with a magnetic field $\vec{B}$ and/or a rotating reference frame at angular velocity $\vec{\Omega}$, the microscopic invariance is a bit different:

$$(\vec{r}, \vec{p}, \vec{B}, \vec{\Omega}, t) \longrightarrow (\vec{r}, -\vec{p}, -\vec{B}, -\vec{\Omega}, -t)$$

and we get $L_{ij}(\vec{B}, \vec{\Omega}) = \varepsilon_i \varepsilon_j L_{ji}(-\vec{B}, -\vec{\Omega})$

These relations, that had already been noted in the XIXth century in specific cases, such as thermoelectricity and transport in electrolytes. They were long considered as a 4^{th} law of thermodynamics.

4° Back to Langevin / Fokker-Planck description

The connexion between fluctuation and dissipation is present at various levels in the Langevin / Fokker-Planck framework: in relations between coefficients, such as $D = \mu k T$, but also in the dynamics itself, that should be compatible with FDT. Here, we will need another property of equilibrium correlation functions, resulting from <u>time translational invariance</u>:

$$\frac{d}{dt}\langle A(t)\,B(t+\tau)\rangle_{eq} = 0 = \langle \dot{A}(t)\,B(t+\tau)\rangle_{eq} + \langle A(t)\,\dot{B}(t+\tau)\rangle_{eq}$$

$$\Rightarrow \langle \dot{A}(t)\,B(0)\rangle_{eq} = -\langle A(t)\,\dot{B}(0)\rangle_{eq}$$

$$= \langle \dot{A}(t+\tau)\,B(\tau)\rangle_{eq}$$

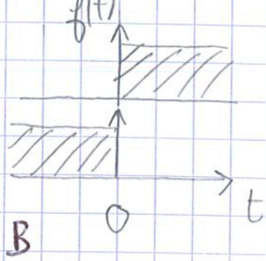
$$= -\langle A(t+\tau)\,\dot{B}(\tau)\rangle_{eq}$$

In g^{al}, there are 3 classes of response functions

→ pulse: $f(t) = f\,\delta(t)$; $\langle \delta A(t)\rangle = \chi_{A\cdot}(t)$

→ step: $f(t) = f\,\theta(t)$, $\langle \delta A(t)\rangle = \int_0^t \chi_{A\cdot}(t-t')\,dt'$

→ after effect: $f(t) = f\,\theta(-t)$, $\langle \delta A(t)\rangle = \int_t^\infty \chi_{A\cdot}(\tau)\,d\tau$



We write $\chi_{A\cdot}$ rather than χ_{AB} because we do not need here to specify B

a) We look at a step response, with an external force that couples to one particle only (tagged p, say number 1): $f(t) = f\theta(t)$

$$\Delta \mathcal{H} = -f x_1 \theta(t) \quad ; \quad x_1 \equiv \text{abscissa of the tagged particle.}$$

$$\langle v_{1x}(t)\rangle - \underbrace{\langle v_{1x}\rangle_{eq}}_{0} = \int_{-\infty}^{t} \chi_{vx}(t-t') f(t')dt' = f\int_0^t \chi_{vx}(t-t')dt' = f\int_0^t \chi_{vx}(\tau)d\tau$$

FDT tells us that

$$\chi_{vx}(t) = -\beta \frac{d}{dt}\langle v(t)x(0)\rangle_{eq} \overset{\text{TTI}}{=} \beta\langle v(t)\dot{x}(0)\rangle_{eq} = \beta\langle v(t)v(0)\rangle_{eq}$$

Thus $\langle v_{1x}(t)\rangle = f\beta\int_0^t \langle v(t')v(0)\rangle_{eq} dt'$

$$\xrightarrow[t\to\infty]{} \mu f \quad \text{where } \mu \text{ is the mobility} \Rightarrow \mu = \beta\int_0^\infty \langle v(\tau)v(0)\rangle_{eq} d\tau$$

Finally, we invoke fact that

$$D = \int_0^\infty \langle v(\tau)v(0)\rangle_{eq}\, d\tau \quad \text{is in general the diffusion coefficient.}$$

Indeed, for an arbitrary microscopic dynamics:

$$\lim_{t\to\infty} \frac{d}{dt}\langle x^2\rangle = 2D \quad \text{and} \quad \frac{d\langle x^2\rangle}{dt} = 2\langle x(t)v(t)\rangle_{eq}$$

and we take an arbitrary initial condition $x(t_0) = x_0$

$$\Rightarrow \frac{d}{dt}\langle x^2\rangle = 2\left\langle v(t)\left[x_0 + \int_{t_0}^t v(t')dt'\right]\right\rangle$$

$$= 2x_0\langle v(t)\rangle + \underbrace{2\int_{t_0}^t \langle v(t)v(t')\rangle dt'}_{2\int_0^{t-t_0}\langle v(\tau)v(0)\rangle d\tau} \qquad \tau = t-t'$$

$$\xrightarrow[t\to\infty]{} 2\int_0^\infty \langle v(\tau)v(0)\rangle d\tau$$

Gathering results, we get $D = \mu kT$, as obtained from the Langevin eq (Einstein's argument)

Rk: we have $\chi_{vx}(t) = \beta\langle v(t)v(0)\rangle_{eq}$

and $\chi_{xv}(t) = -\beta\frac{d}{dt}\langle x(t)v(0)\rangle_{eq} = -\beta\langle\dot{x}(t)v(0)\rangle_{eq} = -\chi_{vx}(t)$

and we recover the symmetry $\chi_{AB}(t) = \varepsilon_A\varepsilon_B\chi_{BA}(t)$ with $\varepsilon_x = 1$, $\varepsilon_v = -1$

b) Linear response analysis of a Fokker-Planck equation

If we perform a linear response analysis directly at the Fokker-Planck level, do we recover the FDT? Take the Kramers equation, in an external potential $\mathcal{U}(x)$, such that the equilibrium distribution $P_{eq}(x,v) = \frac{1}{Z}\exp\left(-\beta\mathcal{U}(x) - \frac{mv^2}{2kT}\right)$; $\beta = \frac{1}{kT}$

(ie normalizable, ie $Z < +\infty$, where $Z = \int dx\, dv\, e^{-\beta\mathcal{U}} e^{-\beta m v^2/2}$.

In addition to force $-\mathcal{U}'(x)$, we apply a small external force $f(t)$.

We thus have the F-P equation:

$$\partial_t P(x,v,t) = \mathcal{L}_{FP} P(x,v,t) - \frac{f(t)}{m}\partial_v P(x,v,t)$$

$$\mathcal{L}_{FP} P = \left(-v\partial_x + \frac{U'(x)}{m}\right)P + \gamma\partial_v\left[vP + \frac{kT}{m}\partial_v P\right]$$

The force $f(t)$ acts since $t=-\infty$, but is small so that $P \simeq P_{eq}$:

$$P(x,v,t) = P_{eq}(x,v) + \delta P(x,v,t) \quad \text{and} \quad \mathcal{L}_{FP} P_{eq} = 0 \; ; \; \partial_t P_{eq} = 0$$

$$\Rightarrow \partial_t \delta p = \mathcal{L}_{FP}\delta p - \frac{f}{m}\partial_v\left[P_{eq} + \delta p\right] \simeq \mathcal{L}_{FP}\delta p - \frac{f}{m}\partial_v P_{eq}$$ to linear order in perturbation

If $\mathcal{L}_{FP}$ would be a scalar, we would solve this by the variation of the constant method, as for Langevin ($\dot{v} = -\gamma v + R(t)$). Here, the method transposes, with a formal solution:

$$\delta p(x,v,t) = -\frac{1}{m}\int_{-\infty}^{t} e^{\mathcal{L}_{FP}(t-t')} f(t')\,\partial_v P_{eq}(x,v)\, dt' \quad , \; t \geq 0$$

From this, we can compute how an arbitrary observable $A(x,v)$ is affected by the perturbation $f(t)$: $\quad \delta A = A - \langle A\rangle_{eq}$

$$\langle \delta A(t)\rangle = \int dx\,dv\; A(x,v)\,\delta p(x,v,t)$$
$$= -\frac{1}{m}\int_{-\infty}^{t}\int dx\,dv\; A(x,v)\, f(t')\, e^{\mathcal{L}_{FP}(t-t')}\,\partial_v P_{eq}(x,v)$$

This is to be compared to

$$\langle \delta A(t)\rangle = \int_{-\infty}^{t} \chi_{Ax}(t-t')\, f(t')\, dt'$$

$$\Rightarrow \chi_{Ax}(\tau) = -\frac{1}{m}\int dx\,dv\; A(x,v)\, e^{\mathcal{L}_{FP}\tau}\,\overbrace{\partial_v P_{eq}(x,v)}^{-\beta m v P_{eq}}$$
$$= \beta \int dx\,dv\; A(x,v)\, e^{\mathcal{L}_{FP}\tau}\, v P_{eq}(x,v) \quad (*) \quad ; \; \tau \geq 0$$

To see that this exactly $\langle A(\tau) v(0)\rangle_{eq}$, we need to consider a generic correlation funct

$$\langle A(\tau) B(0)\rangle_{eq} = \int dx\,dv\,dx'\,dv'\; A(x,v)\, B(x',v')\, \underbrace{P_2(x',v',0\,;x,v,t)}_{P(x,v,t|x',v',0)\,P_{eq}(x',v')}$$

and we use

$$P(x,v,t|x',v',0) = \underbrace{e^{\mathcal{L}_{FP} t}}_{\text{propagation in time}}\,\underbrace{\delta(x-x')\,\delta(v-v')}_{\text{initial condition}}$$

$$\Rightarrow \langle A(\tau)B(0)\rangle_{eq} = \int dx\,dv\,dx'\,dv'\; A(x,v)\, e^{\mathcal{L}_{FP}\tau}\, B(x',v')\,\delta(x-x')\,\delta(v-v')\, P_{eq}(x',v')$$
$$= \int dx\,dv\; A(x,v)\, e^{\mathcal{L}_{FP}\tau}\, B(x,v)\, P_{eq}(x,v)$$

Thus, from $(*)$ above:

$$\chi_{Ax}(\tau) = \beta\,\langle A(\tau)\, v(0)\rangle_{eq} \qquad \text{since } B(x,v) = v \text{ in } (*)$$

On the other hand, the fluctuation-dissipation theorem yields (for $\tau \geq 0$)

$$\chi_{Ax}(\tau) = -\beta\frac{d}{dt}\langle A(\tau)\,x(0)\rangle_{eq} \overset{TTI}{=} \beta\langle A(\tau)\,\dot{x}(0)\rangle_{eq} = \beta\langle A(\tau)\, v(0)\rangle_{eq}$$

↳ consistent! No surprise.

5) Causality and Kramers - Kronig relations

The principle of causality, ie $\chi(t) = 0$ for $t \leq 0$ has mathematical consequences that constrain the Fourier transform of $\chi(t)$, and that are physically insightful. We define the Laplace transform

$$\hat{\chi}(z) = \int_0^{\infty} \chi(t)\, e^{izt}\, dt$$

The function $t \to \chi(t)$ is bounded for $t \to \infty$, because the response to a finite perturbation has to be finite. Since $t > 0$ in the integral, $\hat{\chi}(z)$ is analytic in the upper ½ plane ($\mathrm{Im}\, z > 0$). $\hat{\chi}(z)$ may have poles, and branch cuts, but for $\mathrm{Im}\, z \leq 0$ only. Analyticity brings a wealth of relations, eg using Cauchy formula. In particular, defining, for $\omega \in \mathbb{R}$

$$\lim_{\varepsilon \to 0^+} \hat{\chi}(\omega + i\varepsilon) = \underbrace{\hat{\chi}'(\omega)}_{\mathrm{Re}(\hat{\chi}(\omega^+))} + i\, \underbrace{\hat{\chi}''(\omega)}_{\mathrm{Im}(\hat{\chi}(\omega^+))}$$

$\varepsilon \to 0^+$ rather than $\varepsilon = 0$ is a precaution we take (not always necessary)

we get the Kramers - Kronig relations

$$\boxed{\begin{aligned} \hat{\chi}'(\omega) &= \mathcal{P} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi''(\omega')}{\omega' - \omega} \\ \hat{\chi}''(\omega) &= -\mathcal{P} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi'(\omega')}{\omega' - \omega} \end{aligned}}$$

where $\mathcal{P}$ denotes the Cauchy principal value: $\mathcal{P}\int_{-\infty}^{+\infty} = \int_{-\infty}^{\omega - \varepsilon} + \int_{\omega + \varepsilon}^{\infty}$ and $\varepsilon \to 0^+$

and thus, when we know $\hat{\chi}'(\omega)$, we also know $\hat{\chi}''(\omega)$, and conversely.
If $\chi(t)$ is the response of some B to a force $f(t)$ coupled to A, ie we have $\chi_{BA}(t)$, and we take for simplicity $\langle B \rangle_{eq} = 0$:

$$\langle B(t) \rangle = \int_{-\infty}^{t} \chi_{BA}(t-t')\, f(t')\, dt' = \int_{-\infty}^{+\infty} \chi_{BA}(t-t')\, f(t')\, dt' \quad \left\} \begin{array}{l} \text{since} \\ \chi(\tau) = 0 \\ \text{for } \tau \leq 0 \end{array} \right.$$

Taking Fourier Transform:

$$\langle \hat{B}(\omega) \rangle = \hat{\chi}_{BA}(\omega)\, \hat{f}(\omega) \; ; \quad \hat{\chi}_{BA}(\omega) = \hat{\chi}'(\omega) + i\, \hat{\chi}''(\omega)$$

$\hat{\chi}'(\omega)$: in-phase response (elastic-like)

$\hat{\chi}''(\omega)$: out-of-phase response (viscous-like)

and it can be shown that indeed, $\hat{\chi}''(\omega)$ controls dissipation: consider a sinusoidal excitation $f(t) = \mathrm{Re}\left[f_0\, e^{-i\omega t} \right]$, f_0 real

$$\langle B(t) \rangle = \mathrm{Re}\left[\hat{\chi}_{BA}(\omega)\, f_0\, e^{-i\omega t} \right] = f_0 \chi'(\omega) \cos(\omega t) + f_0\, \chi''(\omega) \sin(\omega t)$$

The dissipated power is

$$P_{diss}(t) = f(t) \left\langle \frac{dB}{dt} \right\rangle = f_0 (\cos \omega t) \left[-f_0\, \chi'(\omega)\, \omega \sin \omega t + f_0\, \chi''(\omega)\, \omega \cos(\omega t) \right]$$

Averaging over time yields

$$\overline{P_{diss}} = \frac{1}{2}\omega f_0^2 \hat{\chi}''(\omega) \quad : \hat{\chi}''(\omega) \text{ controls dissipation}$$

Besides, $\hat{\chi}''(\omega)$ is a convenient object to reexpress the fluctuation-dissipation theorem, that is quite often expressed in Fourier space (in terms of ω) rather than in time. We have shown that

$$\chi(\tau) = -\beta\left(\frac{d}{d\tau}\mathcal{C}(\tau)\right)\theta(\tau) \text{ where eg } \underset{\chi_{BA}}{\overset{\chi}{\downarrow}} \text{ and } \underset{\mathcal{C}_{BA}}{\overset{\mathcal{C}}{\downarrow}}(\tau) = \langle B(\tau)A(0)\rangle_{eq}$$

We then take the Fourier Transform:

$$\begin{aligned}
\hat{\chi}(\omega) &= \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\chi(t) \\
&= -\beta\int_0^\infty dt\, e^{i\omega t}\frac{d\mathcal{C}}{dt} \\
&= -\beta\left[e^{i\omega t}\mathcal{C}(t)\right]_0^\infty + \beta\int_0^\infty dt\, \mathcal{C}(t)\, i\omega\, e^{i\omega t} \qquad \text{(by parts)} \\
&= \beta\,\mathcal{C}(0) + i\omega\beta\int_0^\infty \mathcal{C}(t)\, e^{i\omega t}\, dt
\end{aligned}$$

Taking the imaginary part:

$$\hat{\chi}''(\omega) = 0 + \omega\beta\int_0^\infty \mathcal{C}(t)\cos(\omega t)\,dt$$

and we assume that the observables A and B forming $\mathcal{C}$ have same parity under $t \to -t$, so that $\mathcal{C}(t) = \mathcal{C}(-t)$, as is the case of an autocorrelation function:

$$\begin{aligned}
\hat{\chi}''(\omega) &= \omega\beta\,\frac{1}{2}\int_{-\infty}^{+\infty}\mathcal{C}(t)\cos(\omega t)\,dt \\
&= \frac{1}{2}\omega\beta\underbrace{\int_{-\infty}^{+\infty}\mathcal{C}(t)\,e^{i\omega t}\,dt}_{\hat{\mathcal{C}}(\omega)}
\end{aligned}$$

$$\Rightarrow \hat{\chi}''(\omega) = \frac{\omega\,\hat{\mathcal{C}}(\omega)}{2kT} \quad ; \text{ often used Fourier version of FDT}$$

once more connects dissipation $\Leftrightarrow \hat{\chi}''$, to fluct. ($\hat{\mathcal{C}}(\omega)$).

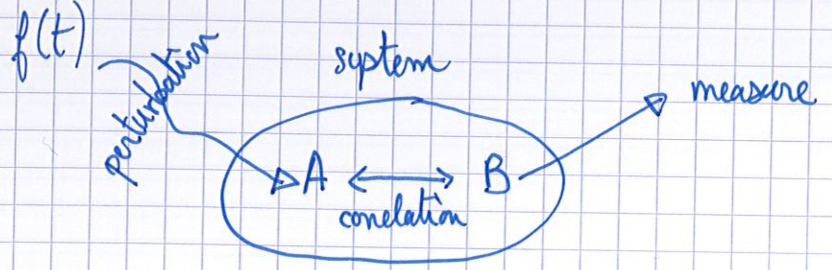
One can measure separately $\hat{\mathcal{C}}(\omega)$ and $\hat{\chi}''(\omega)$, and compute the so-called fluctuation-dissipation ratio $\frac{\omega\hat{\mathcal{C}}(\omega)}{2\hat{\chi}''(\omega)}\frac{1}{kT}$: if it is not unity, we face a non-equilibrium dynamics. In this case, one sometimes refers to the fluct-diss. ratio as $T_{eff}(\omega)/T$, where $T_{eff}(\omega)$ is an effective temperature (somewhat controversial).

It may surprise that $\chi''(\omega)$ alone appears in the ω-dependent FDT, but one should not forget Kramers-Kronig, implying that from χ'' alone, one can get $\hat{\chi}'$ (and thus $\hat{\chi}(\omega) = \hat{\chi}' + i\hat{\chi}''$). There is a redundancy of information between $\hat{\chi}'(\omega)$ and $\hat{\chi}''(\omega)$.

Recommended reading: Chaikin-Lubensky (Principles of Cond Matt Φ), ch 7 (and part 7.2).

6) Summary

We considered a system close to equilibrium, ie weakly perturbed by a force $f(t)$, that couples (in the Hamiltonian) to observable A.



$$\langle \delta B(t) \rangle \equiv \langle B(t) \rangle - \langle B \rangle_{eq} = \int_{-\infty}^{t} \chi_{BA}(t-t')\, f(t')\, dt'$$

$$\chi_{BA}(t) = -\beta \frac{d}{dt} \langle B(t) A(0) \rangle_{eq} \qquad \text{for } t > 0$$

$$= 0 \qquad \text{for } t \leq 0$$