

4 Lesson 4

4.1 Stochastic Processes

4.1.1 Relation between γ and the mobility μ

Where $\gamma^{-1} = \mu$

Let's look on a stochastic process $\vec{v}(t)$. Let's define a (1D) relation

$$r(t) = \int_0^t v(t') dt' \quad (4.1)$$

This is well defined (thanks to Ito calculus). We, therefore, can write the correlation

$$\langle r^2(t) \rangle = \int_0^t \int_0^{t''} \underbrace{\langle v(t') v(t'') \rangle}_{\text{new correlation } K_{vv}(t', t'')} \quad (4.2)$$

such that

$$K_{\xi\xi}(t, t') = \underbrace{\langle \xi(t) \xi(t') \rangle}_{\tau^*} \quad (4.3)$$

and we can:

Anticipate the result

$$t \gg \tau, \quad \langle r^2(t) \rangle = 6Dt. \quad (4.4)$$

Note that the correlation time of the velocity, $K_{vv}(t', t'') = \tau = \frac{m}{\gamma}$ is different than $\tau^* \rightarrow 0$.

Show that (as in the last week)

$$v(t) = v(0) e^{-t/\tau} + e^{-t/\tau} \frac{1}{m} \int_0^t dt' e^{t'/\tau} \xi(t') \quad (4.5)$$

such that the correlation

$$\langle v(t+s) v(t) \rangle \simeq v^2(0) e^{-(2t+s)/\tau} + e^{-(2t+s)/\tau} \frac{1}{m^2} C_{\xi\xi} \int_0^{t+s} dt' \int_0^t dt'' e^{(t'+t'')/\tau} \delta(t' - t'') \quad (4.6)$$

using $K_{\xi\xi}(t, t') = C_{\xi\xi} \delta(t - t')$. Therefore

$$\langle v(t+s) v(t) \rangle \xrightarrow{t \gg \tau} \frac{k_B T}{m} e^{|s|/\tau}, \quad (4.7)$$

where

$$\begin{cases} C_{\xi\xi} = 2k_B T \gamma & (D = 1) \\ \tau = \frac{m}{\gamma} \end{cases}. \quad (4.8)$$

Hence

$$\langle r^2(t) \rangle \xrightarrow{t \rightarrow \infty} t \int_{-\infty}^{\infty} ds \langle v(t'+s) v(t') \rangle \equiv t C_{vv} = 2Dt \quad (4.9)$$

and when we plug $C_{vv} = 2 \frac{k_B T}{m} \tau$, we get the Einstein relation:

$$D = \frac{k_B T}{\gamma} \quad (4.10)$$

and

$$C_{vv} = \int_{-\infty}^{\infty} ds \langle v(s) v(0) \rangle = 2 \frac{k_B T}{\gamma} \quad (4.11)$$

4.1.2 Correlation Functions

Following the previous discussion, we have three correlation functions:

1. The Noise Correlation Function

$$\frac{1}{\mu} = \gamma = \frac{1}{2k_B T} \int_{-\infty}^{\infty} ds \langle \xi(s) \xi(0) \rangle \quad (4.12)$$

which describes the white noise;

2. The Velocity Correlation Function

$$\mu = \frac{1}{2k_B T} \int_{-\infty}^{\infty} ds \langle v(s) v(0) \rangle \quad (4.13)$$

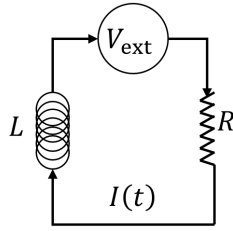
which is derived from the noise, but has different correlation argument;

3. The Diffusion

$$D = \int_{-\infty}^{\infty} ds \langle v(s) v(0) \rangle \quad (4.14)$$

4.1.3 Nyquist theorem — Kubo formula

Let's look on the following circuit:



which is described by the simple formula

$$L \frac{dI}{dt} = \underbrace{V_{\text{ext}}}_{\text{"gravity"}} - RI(t) + \underbrace{V'(t)}_{\text{underlying stochastic process}} \quad (4.15)$$

such that the noise is *thermal*:

$$\langle I \rangle = \frac{1}{R} V_{\text{ext}} \quad (4.16)$$

and the resistance of the stochastic process¹ abides

$$R = \frac{1}{2k_{\text{B}}T} \int_{-\infty}^{\infty} ds \langle V'(t+s) V'(t) \rangle = \frac{C_{VV}(0)}{2k_{\text{B}}T} \quad (4.17)$$

Hence, we can write a correlation function

$$C_{VV}(\omega) = \int_{-\infty}^{\infty} ds e^{i\omega s} \langle V'(s) V'(0) \rangle \simeq 2k_{\text{B}}T R. \quad (4.18)$$

This is the NYQUIST-JOHNSON theorem².

We can also write it in terms of the conductance:

$$\frac{1}{R} = G = \frac{1}{2k_{\text{B}}T} \int_{-\infty}^{\infty} ds \langle I(t+s) I(t) \rangle \quad (4.19)$$

It is usually more convenient to write it in terms of the conductivity σ , where $G = \sigma L^{d-2}$ (using $R = \rho \frac{L}{S}$):

$$G = \frac{1}{2k_{\text{B}}T} \int_{-\infty}^{\infty} ds \langle j(s) j(0) \rangle. \quad (4.20)$$

This is the KUBO formula³.

Corollary. *Any time we have some “viscosity”, we must seek the noise.*

Remark. When we have several sources of noise (classical), each characterized by its own viscosity η_i , then we can add all of them linearly $H = \sum_i \eta_i$ (The Mathison rule). In quantum case it is not true: due to entanglement we cannot separate them (this is the quantum mesoscopic physics).

4.2 Fluctuation-Dissipation Theorem (FDT) – Linear Response

Idea & objective: Formalize all the previous results.

4.2.1 Basic Idea

Each time we have a system out of equilibrium we can express its properties (viscosity, etc.) using the properties of the system in equilibrium (correlation function). This result is attributed to CALLEN & WELTON (PR, 1951)⁴.

The basic idea behind (ONSAGER regression hypothesis, 1930): If you take a system out of equilibrium, in order to return back to equilibrium there will be fluctuations. However, there isn't any difference between those fluctuations and the fluctuations *at equilibrium*.

The derivation of CALLEN & WELTON is quantum mechanical, but it ought not to be so.

¹The equipartition assumption we use is due to the kinetic term in the Hamiltonian, $\frac{1}{2}L \langle I^2 \rangle = \frac{1}{2}k_{\text{B}}T$, similarly to the mechanical $\frac{1}{2}m \langle v^2 \rangle = \frac{1}{2}k_{\text{B}}T$.

²This is true only in the classical case; in the quantum case the formulae break, since $T \rightarrow 0$.

³In the quantum case, we have the same formula without the $\frac{1}{2k_{\text{B}}T}$ factor, after deriving the KUBO formula using another source of noise (not thermal).

⁴Before that, EINSTEIN (1905), NYQUIST (1928).

4.2.2 Classical description

1. Hamiltonian Mechanics. Let there be a system S and microscopic states (point in phase space) $\{p_1, p_2 \dots p_n\} \cup \{q_1, q_2 \dots q\} \equiv (p, q)$.

At $t = 0$ we have $(p(0), q(0))$. The state of S at time t is completely determined by initial conditions $+ \mathcal{H}(p(0), q(0))$, where we have defined the time evolution $\mathcal{T}_t : (p(t), q(t)) = \mathcal{T}_t(p(0), q(0))$. We also assume statistical mechanics: the microstates of S at equilibrium are distributed with

$$P(p, q) = \frac{1}{Q} e^{-\beta \mathcal{H}(p, q)}, \quad Q = \int dp dq e^{-\beta \mathcal{H}(p, q)} \quad (4.21)$$

2. Time Setup. $t \rightarrow -\infty$.

S is perturbed \rightarrow new equilibrium at $t = 0$ characterized by $\mathcal{H}'(p, q)$. At $t = 0$ turn off the perturbation $\mathcal{H}(p, q)$. Relaxation: physical variable $A(p, q)$.

3. Linear response: Perturbation is weak enough such that

$$\mathcal{H}' = \mathcal{H} + \Delta \mathcal{H} \quad (4.22)$$

where

$$\Delta \mathcal{H} = -fA \quad (4.23)$$

and f is the perturbing field. With this definition,

$$f = \frac{\partial F}{\partial A} \quad (4.24)$$

and F is the free energy.

Let's solve. At $t = 0$

$$P'(p, q) = \frac{1}{Q'} e^{-\beta \mathcal{H}'(p, q)}, \quad (4.25)$$

and the relaxation

$$\langle A \rangle = \frac{1}{Q'} \int dp dq e^{-\beta \mathcal{H}'(p, q)} A(p, q). \quad (4.26)$$

At $t > 0$, we have $f \rightarrow 0$ and the system S evolves with \mathcal{H} . Therefore

$$\langle A(t) \rangle = \frac{1}{Q'} \int dp dq e^{-\beta \mathcal{H}'(p, q)} A(\mathcal{T}_t(p, q)). \quad (4.27)$$

Now we expand to the 1st order (because f is small)

$$\langle A(t) \rangle \simeq \frac{\int dp dq e^{-\beta \mathcal{H}} (1 - \beta \Delta \mathcal{H}) A(\mathcal{T}_t(p, q))}{\int dp dq e^{-\beta \mathcal{H}} (1 - \beta \Delta \mathcal{H})}. \quad (4.28)$$

After some algebra,

$$\begin{aligned} \langle A(t) \rangle \simeq & \frac{\int dp dq e^{-\beta \mathcal{H}} A(\mathcal{T}_t(p, q))}{\int dp dq e^{-\beta \mathcal{H}}} + \beta f \frac{\int dp dq e^{-\beta \mathcal{H}} A(p, q) A(\mathcal{T}_t(p, q))}{\int dp dq e^{-\beta \mathcal{H}}} \\ & - \beta f \frac{\int dp dq e^{-\beta \mathcal{H}} A(p, q)}{\int dp dq e^{-\beta \mathcal{H}}} \frac{\int dp dq e^{-\beta \mathcal{H}} A(\mathcal{T}_t(p, q))}{\int dp dq e^{-\beta \mathcal{H}}}. \end{aligned} \quad (4.29)$$

This is equivalent to

$$\langle A(t) \rangle \simeq \langle A(t) \rangle_0 + \beta f \left(\langle A(0) A(t) \rangle_0 - \langle A \rangle_0^2 \right) \quad (4.30)$$

where $\langle \cdot \rangle_0$ is equilibrium w.r.t. \mathcal{H} . The last term in the equation is because equilibrium at 0 is equal to equilibrium at t .

Let us define $\delta A(t) = A(t) - \langle A \rangle_0$. We get

$$\Delta A = \langle A(t) \rangle - \langle A(t) \rangle_0 = \beta f \langle \delta A(0) \delta A(t) \rangle_0. \quad (4.31)$$

This is another form of the Fluctuation Dissipation Theorem.

4.2.3 Generalize

Let's take some perturbation $f(t)$ (not constant). Using the same calculation, we'd get

$$\Delta A(t) = \int dt' \chi(t, t') f(t') \quad (4.32)$$

Therefore, the relaxation at time t is related to all the relaxations (possible equilibrium correlations) at all the times prior to t . But, we cannot drive the system with times $t' > t$ (causality). Therefore

$$\chi(t, t') = 0 \quad @ \quad t' > t \quad (4.33)$$