1 Linear Response and the Fluctuation-Dissipation Theorem

1.1 Linear Response Theory

Let's assume our system is perturbed by some external, t-dependent field. The perturbed Hamiltonian H becomes

$$H(t) = H_0 + \lambda H'(t) \tag{1}$$

where λ is a parameter determining the strength of the perturbation.

Linear response means: weak perturbation (small λ) $\Rightarrow$ response of system proportional to perturbation strength λ, i.e. the response is linear.

perturbation: typically (but not always) $H'(t)$ can be factorized into a purely external, time-dependent field $f(t)$, and a system variable A depending on coordinates and momenta, $\Gamma = (R, P) = (\{\mathbf{r}_i\}, \{\mathbf{p}_i\})$ but independent of time:

$$H'(t) = -A(\Gamma) f(t) \tag{2}$$

example: harmonic electric field acting on charged particles

$$A = \sum_i x_i\,, \qquad f(t) = qE\cos\omega t \quad \longrightarrow \quad H'(t) = \cos\omega t \sum_i qEx_i \tag{3}$$

response: response has to be measured, namely by observing a system variable $B = B(\Gamma)$, such as the density $\rho(\mathbf{r}; R) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, the current, etc. In thermal equilibrium B would have the (canonical ensemble) average value

$$\langle B\rangle_{NVT} = \int d\Gamma\, \rho_0(\Gamma)\, B(\Gamma) = \int d\Gamma\, \frac{e^{-\beta H_0}}{Q}\, B(\Gamma) \tag{4}$$

where ρ_0 is the canonical distribution and Q the partition function. Under the perturbation $H'(t)$, the average of B becomes

$$\langle B\rangle_{\rho(t)} = \int d\Gamma\, \rho(\Gamma, t)\, B(\Gamma) \tag{5}$$

where $\rho(\Gamma, t)$ is not the distribution in thermal equibrium anymore, but the distribution evolving in time due to the perturbation $H'(t)$.

The calculation of the response of B boils down to the calculation of $\rho(\Gamma, t)$. Remembering the chapter about the Liouville formulation and introducing Poisson brackets

$$\{X, Y\} \equiv \frac{\partial X}{\partial R}\frac{\partial Y}{\partial P} - \frac{\partial X}{\partial P}\frac{\partial Y}{\partial R} \tag{6}$$

$\rho(\Gamma, t) = \rho(t)$ obeys the following 1.order differential equation

$$\frac{d\rho(t)}{dt} = iL\rho(t) = \dot{R}\frac{\partial\rho(t)}{\partial R} + \dot{P}\frac{\partial\rho(t)}{\partial P} \tag{7}$$

$$= -\{H(t), \rho(t)\} = -\{H_0 + \lambda H'(t), \rho(t)\} \tag{8}$$

where we have used the Hamiltonian formulation of the classical equations of motion. Every differential equation needs an initial condition: we assume that the perturbation is switched on adiabaticaly, $f(t) \to f(t)e^{\varepsilon t}$, with $\varepsilon > 0$ being arbitrarily small. Hence $f(t \to -\infty) \to 0$, the system is in equilibrium for $t \to -\infty$: $\rho(-\infty) = \rho_0 = \frac{e^{-\beta H_0}}{Q}$.

Plug in the form for $H'(t)$:

$$\frac{d\rho(t)}{dt} = -\{H_0, \rho(t)\} + \lambda f(t)\{A, \rho(t)\} = iL_0\rho(t) + \lambda f(t)\{A, \rho(t)\} \tag{9}$$

To 1st order, the change from ρ_0 to $\rho(t)$ must be linear in the perturbation, so it makes sense to define $\Delta\rho(t)$ by

$$\rho(t) = \rho_0 + \lambda\Delta\rho(t) \tag{10}$$

Using $\frac{d\rho_0}{dt} = 0$, $\{H_0, \rho_0\} = 0$ and dividing by λ, Eq. (9) becomes

$$\frac{d\Delta\rho(t)}{dt} = iL_0\Delta\rho(t) + f(t)\{A, \rho_0\} + \mathrm{O}(\lambda)\,, \qquad \Delta\rho(-\infty) = 0 \tag{11}$$

The linear response treatment means that the higher order correction term $\mathrm{O}(\lambda)$ is neglected.

The formal solution of this equation of the form $\Delta\dot{\rho} = iL_0\Delta\rho + b(t)$ can be obtain by means of the retarded (causal) Green's function $G(t) = \Theta(-t)e^{iL_0t}$ (see book by Economou):

$$\Delta\rho(t) = \int_{-\infty}^{t} ds e^{iL_0(t-s)}b(s)$$

proof: plug this solution into the equation… q.e.d.
Remember from the chapter about the Liouville formalism that e^{iL_0t} is the time-evolution operator of the (unperturbed!) system.

The solution of eq. (11) is

$$\Delta\rho(t) = \int_{-\infty}^{t} ds e^{iL_0(t-s)}\{A, \rho_0\}f(s) \tag{12}$$

Now that we know $\rho(t) = \rho_0 + \Delta\rho(t)$, we can calculate $\langle B\rangle_{\rho(t)}$ where in the following we abbreviate $\langle . \rangle_{NVT} \equiv \langle . \rangle_0$

$$\langle B\rangle_{\rho(t)} = \int d\Gamma\,[\rho_0 + \lambda\Delta\rho(t)]\,B = \langle B\rangle_0 + \lambda\int d\Gamma\,\Delta\rho(t)\,B \tag{13}$$

$$\equiv B_0 + \lambda\Delta B(t) \tag{14}$$

$$\Delta B(t) = \int_{-\infty}^{t} ds f(s)\int d\Gamma\, e^{iL_0(t-s)}\{A, \rho_0\}B \equiv \int_{-\infty}^{t} ds f(s)\chi(t-s) \tag{15}$$

$$\text{with} \quad \chi(t) = \int d\Gamma\, e^{iL_0t}\{A, \rho_0\}B = \int d\Gamma\,\{A(t), \rho_0\}B \quad = \quad \text{response function} \tag{16}$$

(where e^{iL_0t} acts on A). Note that the s-integral in line (15) is *not* a convolution integral as the upper boundary is not ∞.

The response function $\chi(t)$ is independent of the external field $f(t)$ and in fact can be cast into the form of an *equilibrium average*: use $\int d\Gamma \{A, B\}C = \int d\Gamma\, A\{B, C\}$ to get

$$\begin{aligned} \chi(t) &= \int d\Gamma\, e^{iL_0t}\{A, \rho_0\}B = \int d\Gamma\, \{A(t), \rho_0\}B && (17) \\ &= \int d\Gamma\, \{B, A(t)\}\rho_0 = -\langle\{A(t), B\}\rangle_0 = -\langle\{A, B(-t)\}\rangle_0 && (18) \end{aligned}$$

(a variable B without time argument is evaluated at $t = 0$, $B \equiv B(0)$). Note the difference to the definition of the correlation function between A and B

$$c_{AB}(\tau) = \langle A(\tau)B\rangle_0 \qquad (19)$$

We can keep on manipulating χ into yet another form: using the definition of the Poisson bracket (6) and $\rho_0 = e^{-\beta H_0}/Q$

$$\begin{aligned} \{A(t), \rho_0\} &= \frac{\partial A(t)}{\partial R}\frac{\partial \rho_0}{\partial P} - \frac{\partial A(t)}{\partial P}\frac{\partial \rho_0}{\partial R} && (20) \\ &= -\beta\rho_0[\frac{\partial A(t)}{\partial R}\frac{\partial H_0}{\partial P} - \frac{\partial A(t)}{\partial P}\frac{\partial H_0}{\partial R}] = -\beta\rho_0\{A(t), H_0\} = -\beta\rho_0\dot{A}(t) && (21) \end{aligned}$$

Hence we get

$$\chi(t) = \beta\langle\dot{A}(t)B\rangle_0 = -\beta\langle A(t)\dot{B}\rangle_0 \qquad (22)$$

where the 2nd equality can be shown analogously.

Remark: Without going through the derivation we give the generalization to coordinate dependent perturbations coupling to a system variable $A(\mathbf{r})$ (like e.g. the density operator $\rho(\mathbf{r})$):

$$\begin{aligned} H'(t) &= -\int d^3r\, A(\mathbf{r})f(\mathbf{r}, t) && (23) \\ \Delta B(t) &= \int_{-\infty}^{t} ds \int d^3r'\, \chi(\mathbf{r}, \mathbf{r}'; t - s)f(\mathbf{r}', s) && (24) \end{aligned}$$

For a homogeneous system, $\chi(\mathbf{r}, \mathbf{r}'; t-s) = \chi(\mathbf{r}-\mathbf{r}'; t-s)$. Then the r' integral is simply a convolution integral, therefore the right hand side of line (24 becomes a simple produkt in k-space.

Remark: Let's take a break and think: linear response theory assumes that a small perturbation leads to a small change in the system, proportional to the perturbation. On the other hand, we have molecular chaos (Liapunov instability): a small change e.g. in the initial condition, hence also a small external perturbation, leads to trajectories which are exponentially diverging from the unperturbed trajectories. *Why does linear response theory work?* One reason is that the response function $\chi(t)$ decays quickly in time. But even if it does not (which is the case for perturbations with long wavelength), linear response turns out to work: different exponentially diverging trajectories can still give the same response $\Delta B(t)$. Of course, in the end only comparison with experiment can tell.

1.2 Fluctuation-Dissipation Theorem

Now we are going to proof an important theorem of physics: the fluctuation-dissipation theorem is an exact relation between the time-dependent correlation function $c_{AB}(t)$ between two variables A and B and the response function χ_{AB}, i.e. between the (thermal, but also quantum) *fluctuations* of two variables of a system in equilibrium (no external force), and the time-dependent response of variable B if a weak external field f is applied which couples to variable A (see eq.(2)). That c_{AB} and χ_{AB} are related, is not a trivial physical matter, but mathematically the proof is straightforward.

Since every perturbing field $f(t)$ is a superposition (Fouriertransform) of plane waves, we restrict ourselves to plane waves (but don't forget to adiabatically switch on):

$$f(t) = f_0\, e^{-i\omega t+\varepsilon t} = f_0\, e^{-i(\omega+i\varepsilon)t} \tag{25}$$

The integral expression (15) for the response becomes an algebraic expression

$$\Delta B(t) = \chi(\omega) f_0\, e^{-i\omega t} \tag{26}$$

with the Laplace transform (=half a Fourier tranform) of the response function

$$\chi(\omega) = \lim_{\varepsilon\to 0+} \int_0^\infty dt\, \chi(t)\, e^{i(\omega+i\varepsilon)t} \equiv \chi'(\omega) + i\chi''(\omega) \tag{27}$$

In order to calculate the Laplace tranformation, we keep ε finite to obtain the analytic continuation of $\chi(\omega)$ to the complex frequency $z = \omega + i\varepsilon$ (keeping ε around helps us find the integration contour around poles later). We use the Poisson-free form (22) of $\chi(t)$:

$$\begin{aligned}
\chi(z) &= \beta \int_0^\infty dt\, \langle \dot{A}(t)B\rangle_0 e^{izt} = \beta \int_0^\infty dt\, [\frac{d}{dt}\langle A(t)B\rangle_0] e^{izt} && (28)\\
&= \beta\langle A(t)B\rangle_0 \underbrace{e^{izt}}_{e^{iz\infty}=0} \Big|_0^\infty - \beta\int_0^\infty dt\, \langle A(t)B\rangle_0 \frac{d}{dt} e^{izt} && (29)\\
&= \beta\langle AB\rangle_0 - iz\beta \underbrace{\int_0^\infty dt\, \langle A(t)B\rangle_0 e^{izt}}_{=\tilde{C}_{AB}(z)} && (30)
\end{aligned}$$

Clearly, there is a relation between response and the correlation function $C_{AB}(t) = \langle A(t)B\rangle_0$. Its Laplace transform $\tilde{C}_{AB}(z)$ can be also obtained from the Fourier transform ("power spectrum" / "spectral function") $C_{AB}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} C_{AB}(t)$ via a Kramers-Kronig relation:

$$\begin{aligned}
\tilde{C}_{AB}(z) &= \int_0^\infty dt\, e^{izt}\, C_{AB}(t) = \int_0^\infty dt\, e^{izt} \int_{-\infty}^{\infty} d\omega'\, e^{-i\omega' t} C_{AB}(\omega') && (31)\\
&= i\int_{-\infty}^{\infty} d\omega'\, \frac{C_{AB}(\omega')}{z-\omega'} && (32)
\end{aligned}$$

ε has done its part to determine which way to go around the pole in the integration: let $\varepsilon \to 0+$, such that $z \to \omega$ and use $\frac{1}{x+i\varepsilon} = P\frac{1}{x} - i\pi\delta(x)$ (where P indicates the principal value integral). Taking the real part of $\tilde{C}_{AB}(z)$,

$$\Re e\, \tilde{C}_{AB}(\omega) = \pi C_{AB}(\omega) \tag{33}$$

Finally, we take the imaginary part of eq. (30) (with ε set to 0)

$$\Im m\, \chi_{AB}(\omega) = \chi''_{AB}(\omega) = \beta \underbrace{\Im m\langle AB\rangle_0}_{=0} + \omega\beta\Re e\, \tilde{C}_{AB}(\omega) = \omega\beta\pi C_{AB}(\omega) \qquad (34)$$

where we now added subscripts AB to χ. This is the famous fluctuation-dissipation theorem (classical version):

$$\boxed{\underbrace{\chi''_{AB}(\omega)}_{\leftrightarrow \text{ dissipation}} = \frac{\pi\omega}{k_B T} \underbrace{C_{AB}(\omega)}_{\text{fluctuation}}}$$

$\chi''_{AB}(\omega)$ is the imaginary part of the response function that describes what happens to B when the system is driven out of equilibrium by A. So what does χ'' have to do with dissipation? It can be shown that the imaginary part of the response function is indeed related to dissipation: $\omega\chi''_{AB}(\omega)$ is proportional to the energy absorbed by the system from the applied harmonic perturbation of frequency ω.

example: diffusion — mobility

In this example we derive a relation between thermal diffusion and mobility under an external force. Instead of simply writing down the fluctuation-dissipation theorem for specific A and B we derive the relation from scratch:

We consider a system of many particles, with one tagged particle of coordinate $\mathbf{r}_i \equiv \mathbf{r}$. Let the perturbation be $H'(t) = xf(t) = xf\,\Theta(t)$. That is, at $t = 0$, a constant force f parallel to the x-axis is switched on which acts on the tagged particle. Hence $A = x$. We are interested in the response of the velocity in x-direction of the tagged particle, hence $B = v_x$:

$$\begin{aligned} \Delta v_x(t) &= \int_{-\infty}^{t} ds\, \chi_{v_x x}(t-s) f\Theta(s) = \beta \int_0^t ds\, \langle v_x(t-s)\dot{x}\rangle_0 f = \beta f \int_0^t ds\, \langle v_x(t-s) v_x\rangle_0 \\ &= \beta f \int_0^t ds'\, \langle v_x(s') v_x\rangle_0 \end{aligned} \qquad (35)$$

The *velocity response* is simply given by the force times an integral over the *velocity auto-correlation function.*

After sufficiently long time the system reaches a steady state where the tagged particle drifts with a constant velocity proportional (linear response!) to the force f – it cannot keep on accelerating like a free particle because the surrounding particles effectively act like a friction force. The proportionality constant between drift velocity and force is called *mobility* μ:

$$\lim_{t\to\infty} \Delta v_x(t) = f\,\mu$$

On the other hand, if we let $t \to \infty$ in eq. (35), we get the Green-Kubo relation for the diffusion constant

$$\lim_{t\to\infty} \int_0^t ds'\, \langle v_x(s') v_x\rangle_0 = D$$

Hence we obtain a simple relation between the diffusion constant and the mobility

$$\mu = \frac{1}{k_B T}\, D$$

Remark: The above discussion assumed equilibrium statistical mechanics and (linear) response out of equilibrium. Therefore the fluctuation-dissipation theorem is not valid for *glasses* which are "dynamically frozen" systems, i.e. not frozen like ice but certain modes become infinitely slow, preventing the system from ever reaching equilibrium (glass does not flow, don't believe the myth about old church windows).

References

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J. P. Hansen and I. R. McDonald: "Theory of Simple Liquids"

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