Contents

Chapter 1

Linear Response theory

1.1 Plan of the chapter

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1.2 General situation in linear response

Let us start with a very generic situation of a system that produces a time dependent signal $S(t)$. Suppose that, when the system is left unperturbed, the signal is identically zero. We now feed into the system a time dependent (input) signal $F(t)$ and we are interested in the response of the system in terms of the output signal $S(t)$. In order to go on with an analytical treatment we need to assume that the system under consideration obeys the following properties:

Causality The system responds only *after* the external perturbation F has been switched on. In other words if $F(t) = 0$ for $t < t_1$, then $S(t) = 0$ for $t < t_1$.

Linearity If $F(t)$ leads to the response $S(t)$, then $\lambda F(t)$ leads to $\lambda S(t)$. Moreover, if from $F(t) = f_1(t)$ one has $S(t) = s_1(t)$ and from $F(t) = f_2(t)$ $S(t) = s_2(t)$ then, from $F(t) = f_1(t) + f_2(t)$ one gets the response $S(t) = s_1(t) + s_2(t)$. We can summarize this property in the more compact form

$$F(t) = \lambda_1 f_1(t) + \lambda_2 f_2(t) \to S(t) = \lambda_1 s_1(t) + \lambda_2 s_2(t). \tag{1.1}$$

Stationarity If $F(t) = f(t)$ leads to $S(t) = s(t)$ then $F(t) = f(t-t_1)$ gives rise to $S(t) = s(t-t_1)$.

This property comes from the hypothesis that the Hamiltonian governing the dynamics of the unperturbed system does not depend esplicitly on time (conservative system).

It turns out that the most general relationship between $F(t)$ and $S(t)$ that satisfies all the above properties can be written as

$$S(t) = \int_{-\infty}^{t} \chi(t-t')F(t')dt' \tag{1.2}$$

where $\chi(t)$ is some function of time, called *response function.* The above expression can also be written as

$$S(t) = \int_{-\infty}^{\infty} \chi(t-t')F(t')dt' \quad \text{where} \quad \chi(t-t') = 0, \quad \text{if} \quad t < t'. \tag{1.3}$$

The fact that $\chi(t,t') = \chi(t-t')$ is given by the stationarity property (homogeneity in time).Note that by the simple change of variables $t - t' = t''$ one gets

$$S(t) = \int_{\mathbb{R}} \chi(t-t')F(t')dt' = \int_{\mathbb{R}} \chi(t')F(t-t')dt'. \tag{1.4}$$

1.2.1 Typical behaviours of the response function

Clearly the behaviour of the output signal $S(t)$ is governed by the form of the response function χ. Let us consider some typical cases one encounters in physics.

Instantaneous response with no memory

In this case $\chi(t) = A\delta(t)$ and

$$S(t) = \int_{\mathbb{R}} \chi(t-t')F(t')dt' = \int_{\mathbb{R}} A\delta(t-t')F(t')dt' = AF(t). \tag{1.5}$$

In other words the response exists only when the perturbation is on.

Delayed response with no oscillation

Suppose $\chi(t)$ is a function that increases from zero and then decays very fast to the starting value (something like $\exp(-t^2/2\sigma^2)$) . In this case $S(t)$ is related to the behaviour of F at times just sligthly before t, i.e. $S(t)$ has some memory of the previous values of $F(t)$.

Exercise. Suppose $F(t) = -Bt$ and $\chi(t) = A\exp(-t^2/2\sigma^2)$. Find the output function $S(t)$.

1.2.2 Examples of the response χ for a given perturbation $F(t)$

Response to a delta function

Suppose $F(t) = A\delta(t - t_0)$. Then

$$S(t) = \int_{\mathbb{R}} \chi(t-t')F(t')dt' = \int_{\mathbb{R}} A\chi(t-t')\delta(t'-t_0)dt' = A\chi(t-t_0). \tag{1.6}$$

Since from causality $\chi(t - t_0) = 0$ for $t < t_0$, the signal turns on after t reaches the value t_0. For the special case $F(t) = \delta(t)$, $S(t) = \chi(t)$, i.e. the response function $\chi(t)$ is the output signal of the system due to a delta input at $t = 0$.

Response to an oscillatory input with a single frequency

Suppose

$$F(t) = A\cos(\omega t + \phi) = \frac{1}{2}\left[Ae^{-i\omega t} + A^* e^{i\omega t}\right]. \tag{1.7}$$

i.e. a typical monocromatic harmonic perturbation one encounters in studying interaction between matter and electromagnetic field. In this case

$$\begin{aligned}
S(t) &= \int_{\mathbb{R}} \chi(t')F(t-t')dt' \\
&= \int_{\mathbb{R}} \chi(t')A\cos(\omega(t-t')+\phi)dt' \\
&= \int_{\mathbb{R}} \chi(t')A\cos(\omega t+\phi-\omega t')dt' \\
&= \int_{\mathbb{R}} \chi(t')A\left(\cos(\omega t+\phi)\cos(\omega t') + \sin(\omega t+\phi)\sin(\omega t')\right)dt' \\
&= A\left(\cos(\omega t+\phi)\int_{\mathbb{R}} \chi(t')\cos(\omega t')dt' + \sin(\omega t+\phi)\int_{\mathbb{R}} \chi(t')\sin(\omega t')dt'\right).
\end{aligned}$$

It is then convenient to define the following response function with respect to the frequecy ω:

$$Re\tilde{\chi}(\omega) = \int_{\mathbb{R}} \chi(t')\cos(\omega t')dt' \tag{1.8}$$

$$Im\tilde{\chi}(\omega) = \int_{\mathbb{R}} \chi(t')\sin(\omega t')dt'. \tag{1.9}$$

We then have

$$S(t) = A\left[\cos(\omega t+\phi)Re\tilde{\chi}(\omega) + \sin(\omega t+\phi)Im\tilde{\chi}(\omega)\right] \tag{1.10}$$

Note that the first term is phase with the input signal while the second is out of phase by $\pi/2$.

Response to a constant input

Suppose $F(t) = A$, i.e. a constant perturbation. Then

$$S(t) = \int_{\mathbb{R}} \chi(t')F(t-t')dt' = A\int_{\mathbb{R}} \chi(t')dt' = ARe\tilde{\chi}(0). \tag{1.11}$$

The output signal is steady and proportional to the input one. Note that one may thinks to this perturbation as a special case of harmonic perturbation with $\omega = 0$

Response to a steady input abruptly turned off: relaxation process

Suppose that

$$F(t) = \begin{cases} A & t < 0 \\ 0 & t \geq 0 \end{cases} \tag{1.12}$$

For $t < 0$, since the perturbation is on, the result must coincide with the case of a constant perturbation:

$$S(t) = ARe\tilde{\chi}(0) \quad \text{for} \quad t < 0. \tag{1.13}$$

We now consider the case $t \geq 0$. In this region

$$S(t) = A\int_t^{\infty} \chi(t')dt' \tag{1.14}$$

and $\chi(t)$ describes how the output signal goes to zero when the perturbation is turned off. In particular one can define the *relaxation function* $R(t)$ as the output signal of the system for positive times given that a constant perturbation of unit amplitude has been turned off at $t = 0$:

$$R(t) = \int_t^{\infty} \chi(t')dt' \tag{1.15}$$

Assuming that $\chi(t) \to 0$ when $t \to \infty$ we have

$$\boxed{\dot{R}(t) = -\chi(t).} \tag{1.16}$$

1.2.3 Behaviour of the response function at large times

In many cases of interest, when $F(t)$ is switched off, the system might undergo a transient response but $S(t)$ will eventually goes back to its unperturbed value ($S(t) = 0$ in most cases). This corresponds to assume that $\chi(t) \to 0$ as $t \to \infty$. This behaviour is associated with a certain type of stability of the system that is responding. Alternative behaviours correspond to some kind of instability or at least metastability. For example, suppose that at large times $\chi(t) \propto \sin \omega t$. Then after beign perturbed by a delta function the system will response with an harmonic signal for all times. As anothe example suppose that $\chi(t) \to A$ as $t \to \infty$. Then a small perturbation can cause the system to respond with a non zero signal for all times. One is usually interested in situations in which $\chi(t) \to 0$ as $t \to \infty$.

1.2.4 Frequency-domain representation

Because of the linearity property the response is expressed as a convolution integral. It is then often convenient to work in the Fourier space by defining the Fourier transform of the output signal

$$\tilde{S}(\omega) = \frac{1}{2\pi} \int e^{i\omega t} S(t)dt. \tag{1.17}$$

By applying the Fourier transform to the convolution integral we get

$$\tilde{S}(\omega) = \tilde{\chi}(\omega)\tilde{F}(\omega), \tag{1.18}$$

where $\tilde{F}(\omega)$ is the Fourier transform of the perturbation $F(t)$ and

$$\tilde{\chi}(\omega) = \frac{1}{2\pi} \int e^{i\omega t} \chi(t)dt. \tag{1.19}$$

We can also define the real and imaginary part of $\tilde{\chi}(\omega)$ as

$$Re\tilde{\chi}(\omega) = \frac{1}{2\pi} \int \chi(t)\cos(\omega t)dt \tag{1.20}$$
$$Im\tilde{\chi}(\omega) = \frac{1}{2\pi} \int \chi(t)\sin(\omega t)dt. \tag{1.21}$$

$Re\tilde{\chi}(\omega)$ and $Im\tilde{\chi}(\omega)$ are respectively *even* and *odd* functions of the frequency ω:

$$Re\tilde{\chi}(\omega) = Re\tilde{\chi}(-\omega) \tag{1.22}$$
$$Im\tilde{\chi}(\omega) = -Im\tilde{\chi}(-\omega) \tag{1.23}$$

giving

$$\tilde{\chi}(-\omega) = \tilde{\chi}^*(\omega). \tag{1.24}$$

Clearly

$$Re\tilde{\chi}(\omega) = \frac{1}{2}\left[\tilde{\chi}(\omega) + \tilde{\chi}^*(\omega)\right] = \frac{1}{2}\left[\tilde{\chi}(\omega) + \tilde{\chi}(-\omega)\right] \tag{1.25}$$

$$Im\tilde{\chi}(\omega) = \frac{1}{2i}\left[\tilde{\chi}(\omega) - \tilde{\chi}^*(\omega)\right] = \frac{1}{2i}\left[\tilde{\chi}(\omega) - \tilde{\chi}(-\omega)\right]. \tag{1.26}$$

In particular we can identity

$$\chi''(t) = \frac{1}{2\pi}\int_{\mathbb{R}} Im\tilde{\chi}(\omega)e^{-i\omega t}d\omega$$

$$Im\tilde{\chi}(\omega) = \int_{\mathbb{R}} \chi''(t)e^{i\omega t}dt. \tag{1.27}$$

1.2.5 Laplace transform

An important consequence of the causality principle is that we can extend the definition to the complex plane by defining the Laplace transform $\tilde{\chi}(z)$ of $\chi(t)$ when $z = \omega + i\eta$ is located in the upper complex plane, $Imz > 0$. Indeed the integral giving $\tilde{\chi}(z)$:

$$\boxed{\tilde{\chi}(z) = \int_0^\infty \chi(t)e^{izt}dt \qquad Imz > 0} \tag{1.28}$$

is uniformly absolutely convergent and hence analytic in the upper complex plane. Moreover, since $S(t)$ and $F(t)$ are real also the response function is real giving

$$\tilde{\chi}^*(\omega + i\eta) = \tilde{\chi}(-\omega + i\eta). \tag{1.29}$$

A more precise definition of the Laplace transform consider the explixit expression of the response function

$$\chi(t - t') = 2i\Theta(t - t')\chi''(t - t'), \tag{1.30}$$

where $\Theta(t)$ is the Heaviside function and the factor $2i$ is for the moment arbitrary. In this case one defines

$$\tilde{\chi}(z) = \int_{-\infty}^\infty \chi(t)e^{izt}dt = 2i\int_0^\infty \chi''(t)e^{izt}dt. \tag{1.31}$$

The function $\chi''(t)$ is bounded as $t \to \infty$ because a perturbation at time $t = 0$ will only give rise to a finite response $S(t)$ at later times. From eq. (1.30) inserted in the Laplace transform + the Fourier transform of $\chi''(t)$ one gets

$$\tilde{\chi}(z) = 2i\int_0^\infty dte^{izt}\int_{\mathbb{R}} \frac{d\omega}{2\pi} Im\tilde{\chi}(\omega)e^{-i\omega t}. \tag{1.32}$$

Performing the integration over t one gets the so called *spectral representantion of* $\tilde{\chi}(z)$*:*

$$\boxed{\tilde{\chi}(z) = \frac{1}{\pi}\int_{\mathbb{R}} \frac{Im\tilde{\chi}(\omega)}{\omega - z}d\omega} \tag{1.33}$$

This representation shows that the function $\tilde{\chi}(z)$ has singularities only on the real axes.

1.2.6 Dissipation

If there is dissipation in the system and the external perturbation is switched off, the output $S(t)$ will reach its original unperturbed value (i.e the one before the onset of the perturbation). In other words if $F(t) = 0$ for $t \geq t_1$ then

$$S(t) = \int_{t_0}^{t_1} dt'\ \chi(t - t')F(t') \to 0 \quad \text{as} \quad t \to \infty \tag{1.34}$$

This imply $\lim_{t\to\infty}\chi(t) = 0$. One can then assumes that the approach to the unperturbed stable state is sufficiently rapid to have the integrability condition

$$\int_0^\infty |\chi(t)|dt < \infty \tag{1.35}$$

satisfied.

1.2.7 Kramers-Kronig relations

These realations are consequences of the causality principle and the fact that $\chi(t)$ is a real valued function. They can be stated as a theorem:

Theorem 1.2.1. If

$$\int_0^\infty |\chi(t)|dt < \infty \tag{1.36}$$

and $|\tilde{\chi}(z)| \leq \frac{M}{|z|}$ in the upper complex plane $\{z = \omega + i\eta | \eta > 0\}$, then the real and imaginary parts of $\tilde{\chi}(z)$ are related by the following relations (1927)

$$Re\,(\tilde{\chi}(\omega_0)) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{Im\,(\tilde{\chi}(\omega))}{\omega-\omega_0}d\omega \tag{1.37}$$

$$Im\,(\tilde{\chi}(\omega_0)) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{Re\,(\tilde{\chi}(\omega))}{\omega-\omega_0}d\omega \tag{1.38}$$

$$\tag{1.39}$$

where $\mathcal{P}\int$ denotes the principal part of the integral

$$\mathcal{P}\int_{-\infty}^{\infty}\frac{f(\omega)}{\omega-\omega_0} = \lim_{R\to\infty}\lim_{\epsilon\to 0}\left(\int_{-R}^{\omega_0-\epsilon}\frac{f(\omega)}{\omega-\omega_0}d\omega + \int_{\omega_0+\epsilon}^{R}\frac{f(\omega)}{\omega-\omega_0}d\omega\right). \tag{1.40}$$

To proof the above result let us consider the integral

$$\tilde{\chi}(z) = \int_0^\infty e^{izt}\chi(t)dt, \tag{1.41}$$

the real frequency ω_0 and the contour in the upper complex plane C_R with radius R. Since $\tilde{\chi}(z)$ is holomorphic on the upper plane the Cauchy theorem states

$$\int_C \frac{\tilde{\chi}(z)}{z-\omega_0}dz = 0 \tag{1.42}$$

We now split the integral along the circuit $C = C_R \bigcup C_L^{(1)} \bigcup C_\epsilon \bigcup C_L^{(2)}$

$$\int_{C_R}\frac{\tilde{\chi}(z)}{z-\omega_0}dz + \int_{C_\epsilon}\frac{\tilde{\chi}(z)}{z-\omega_0}dz + \int_{-R}^{\omega_0-\epsilon}\frac{\tilde{\chi}(z)}{z-\omega_0}dz + \int_{\omega_0+\epsilon}^{R}\frac{\tilde{\chi}(z)}{z-\omega_0}dz = 0 \tag{1.43}$$

In the limit $R\to\infty$ the first integral goes to zero under the hyphotesis $|\tilde{\chi}(z)| < \frac{M}{|z|} = \frac{M}{R}$ with $z \in C_R$. Indeed by using the inequality $|a-b| \geq |a| - |b|$ we have

$$\begin{aligned}\lim_{R\to\infty}\left|\int_{C_R}\frac{\tilde{\chi}(z)}{z-\omega_0}\right|dz &\leq \lim_{R\to\infty}\frac{M}{R}\int_{C_R}\frac{1}{|z-\omega_0|}dz \\ &\leq \lim_{R\to\infty}\frac{M}{R}\int_{C_R}\frac{1}{R-\omega_0}dz \\ &= \lim_{R\to\infty}\frac{M}{R}\frac{\pi R}{R-\omega_0} \\ &= 0.\end{aligned} \tag{1.44}$$

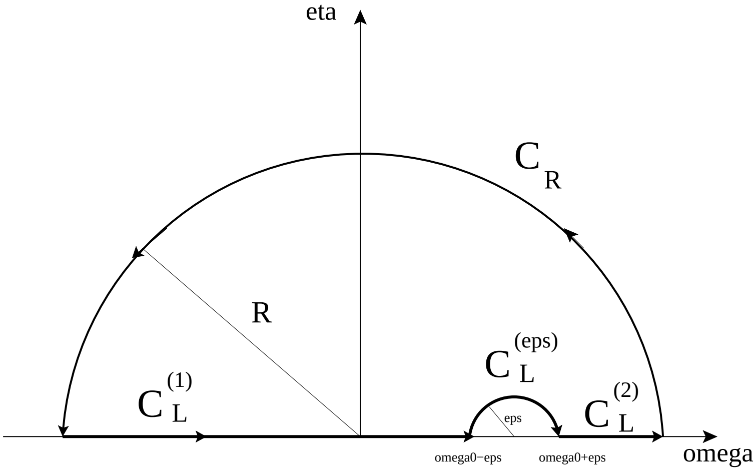

Figure 1.1: The path $C = C_R \bigcup C_L^{(1)} \bigcup C_\epsilon \bigcup C_L^{(2)}$ on the upper hals of the complex plane with a pole in $\omega_0 \in \mathbb{R}$

After having taken the $R \to \infty$ limit the starting equality becomes

$$\int_{C_\epsilon} \frac{\tilde{\chi}(z)}{z-\omega_0} dz + \int_{-\infty}^{\omega_0-\epsilon} \frac{\tilde{\chi}(\omega)}{\omega-\omega_0} d\omega + \int_{\omega_0+\epsilon}^{\infty} \frac{\tilde{\chi}(\omega)}{\omega-\omega_0} d\omega = 0 \tag{1.45}$$

The first integral can be computed by first performing the change of variables $z - \omega_0 \to z$ and $z = \epsilon e^{i\varphi}$, $dz = i\epsilon e^{i\varphi} d\varphi$, $\varphi \in [\pi, 0]$. In the limit $\epsilon \to 0$ one gets

$$\begin{aligned} & \lim_{\epsilon \to 0} \int_{C_\epsilon} \frac{\tilde{\chi}(z)}{z-\omega_0} dz \\ = \; & i \lim_{\epsilon \to 0} \int_{\pi}^{0} \tilde{\chi}(\omega_0 + \epsilon e^{i\varphi}) d\varphi \\ = \; & -i \lim_{\epsilon \to 0} \int_{0}^{\pi} \tilde{\chi}(\omega_0 + \epsilon e^{i\varphi}) d\varphi \\ = \; & -i\pi \tilde{\chi}(\omega_0). \end{aligned} \tag{1.46}$$

The last two integrals are obtained in the limit $\epsilon \to 0$ giving follows

$$\lim_{\epsilon \to 0} \left(\int_{-\infty}^{\omega_0-\epsilon} \frac{\tilde{\chi}(\omega)}{\omega-\omega_0} d\omega + \int_{\omega_0+\epsilon}^{\infty} \frac{\tilde{\chi}(\omega)}{\omega-\omega_0} d\omega \right) \equiv \mathcal{P} \int \frac{\tilde{\chi}(\omega)}{\omega-\omega_0} d\omega \tag{1.47}$$

From the above calculations we finally obtain

$$\mathcal{P} \int \frac{\tilde{\chi}(\omega)}{\omega-\omega_0} d\omega = i\pi \tilde{\chi}(\omega_0). \tag{1.48}$$

Since $\tilde{\chi}(\omega_0) = Re\tilde{\chi}(\omega_0) + iIm\tilde{\chi}(\omega_0)$ we get the relations.

From the K.K. relations it turns out that it is only necessary to find either $Re\tilde{\chi}(\omega)$ or $Im\tilde{\chi}(\omega)$ to determine the full response function. Indeed, considering as ω_0 a generic ω and $z = \omega' + \eta$ we have

$$\begin{aligned} \tilde{\chi}(\omega) &= Re\tilde{\chi}(\omega) + iIm\tilde{\chi}(\omega) \\ &= \frac{1}{\pi} \mathcal{P} \int \frac{\tilde{\chi}(\omega')}{\omega'-\omega} d\omega' + iIm\tilde{\chi}(\omega) \\ &= \frac{1}{\pi} \mathcal{P} \int \frac{\tilde{\chi}(\omega')}{\omega'-\omega} d\omega' + i\frac{\pi}{\pi} \int Im\tilde{\chi}(\omega')\delta(\omega'-\omega) d\omega'. \end{aligned} \tag{1.49}$$

On the other hand the following identity (in the distributionale sense) holds

$$\lim_{\eta\to 0}\frac{1}{\omega'-\omega\mp i\eta}=\mathcal{P}\int\left(\frac{1}{\omega'-\omega}\right)\pm i\pi\delta(\omega'-\omega) \tag{1.50}$$

and we finally get

$$\boxed{\tilde{\chi}(\omega)\lim_{\eta\to 0}\int\frac{d\omega'}{\pi}\frac{Im\tilde{\chi}(\omega')}{\omega'-\omega-i\eta}}. \tag{1.51}$$

In the other hand

$$\begin{aligned} S(t) &= \frac{1}{2\pi}\int d\omega e^{i\omega t}\tilde{S}(\omega) \\ &= \frac{1}{2\pi}\int d\omega e^{i\omega t}\tilde{\chi}(\omega)\tilde{F}(\omega) \\ &= \lim_{\eta\to 0}\frac{2}{(2\pi)^2}\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\frac{e^{i\omega(t-t')}}{\omega'-\omega-i\eta}Im\tilde{\chi}(\omega')F(t') \end{aligned} \tag{1.52}$$

Performing the change of variable $\omega''=\omega-\omega'$ and considering the identity

$$\Theta(t-t')=-\lim_{\eta\to 0}\int_{-\infty}^{\infty}\frac{d\omega}{(2\pi i)}\frac{e^{i\omega(t-t')}}{\omega+i\eta} \tag{1.53}$$

we get back

$$S(t)=2i\int_{-\infty}^{t}\chi''(t-t')F(t')dt' \tag{1.54}$$

with

$$\boxed{\chi''(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}Im\tilde{\chi}(\omega)} \tag{1.55}$$

1.2.8 Dissipation and absorption power spectra given an harmonic external perturbation

We now show that the imaginary part of the Fourier transform of the response function is related to the energy dissipation of the perturbed system into the medium and hence to the absorption power spectrum. Given an external perturbation (generalized force) F its contribution to the total Hamiltonian of the system is $-FS$ where S is the observable conjugate to the external perturbation F. The infinitesimal work done by the perturbation on the system to change the variable S into $S+dS$ is then simply $dW=-FdS$. If we consider the rate of this work (or istantaneous power) we then have

$$P(t)\equiv\frac{dW}{dt}=-F(t)\dot{S}(t) \tag{1.56}$$

In an time interval $[0,T]$ the average total absorbed power is then

$$\bar{P}_{abs}=\frac{1}{T}\int_0^T F(t)\frac{dS}{dt}dt=-\frac{1}{T}\int_0^T\dot{F}(t)S(t)dt, \tag{1.57}$$

where lest equality has been obtained by integration by parts and considering negligible the contributions of $S(t)F(t)$ at the extreme times $[0,T]$. This is partculary true for large enough T or when $F(0)=F(T)=0$ (periodic perturbation). We now consider an harmonic monocromatic perturbation of the form

$$F(t)=ReF(\omega)e^{-i\omega t}=\frac{1}{2}\left[F(\omega)e^{-i\omega t}+F^*(\omega)e^{i\omega t}\right] \tag{1.58}$$

In this case we have

$$\bar{P}_{abs} = \frac{1}{T}\int_0^T \frac{dt}{2}\left[-i\omega\left(F(\omega)e^{-i\omega t} - F^*(\omega)e^{i\omega t}\right)\right] S(t)dt. \tag{1.59}$$

We now assume

$$S(t) = ReS(\omega)e^{-i\omega t} = \frac{1}{2}\left[S(\omega)e^{-i\omega t} + S^*(\omega)e^{i\omega t}\right] \tag{1.60}$$

and since $\tilde{S}(\omega) = \tilde{\chi}(\omega)\tilde{F}(\omega)$ we get

$$\begin{aligned} S(t) &= \tilde{F}(\omega)\tilde{\chi}(\omega)e^{-i\omega t} + \tilde{F}^*(\omega)\tilde{\chi}^*(\omega)e^{i\omega t} \\ &= \tilde{F}(\omega)\tilde{\chi}(\omega)e^{-i\omega t} + \tilde{F}^*(\omega)\tilde{\chi}(-\omega)e^{i\omega t} \end{aligned} \tag{1.61}$$

We then have

$$\begin{aligned} \bar{P}_{abs} &= \frac{1}{T}\int_0^T \frac{dt}{2}\left[-i\omega\left(\tilde{F}(\omega)e^{-i\omega t} - \tilde{F}^*(\omega)e^{i\omega t}\right)\right]\times \\ &\times \frac{1}{2}\left[\tilde{F}(\omega)\tilde{\chi}(\omega)e^{-i\omega t} + \tilde{F}^*(\omega)\tilde{\chi}(-\omega)e^{i\omega t}\right] dt \end{aligned} \tag{1.62}$$

We now consider as T the period $T = \frac{2\pi}{\omega}$. In this way, since

$$\frac{1}{T}\int_0^T e^{i\omega t}e^{-i\omega t}dt = 1, \qquad \frac{1}{T}\int_0^T e^{-i\omega t}e^{-i\omega t}dt = 0 \tag{1.63}$$

we finally obtain

$$\begin{aligned} \bar{P}_{abs} &= \frac{i\omega}{4}|F(\omega)|^2\left[\tilde{\chi}(\omega) - \tilde{\chi}(-\omega)\right] \\ &= \frac{\omega}{2}F(\omega)|^2 Im\tilde{\chi}(\omega) \end{aligned} \tag{1.64}$$

The result

$$\boxed{\bar{P}_{abs} = \frac{\omega}{2}F(\omega)|^2 Im\tilde{\chi}(\omega)} \tag{1.65}$$

tells us that the imaginary part of the response function in frequency domain is proportional to the averaged energy dissipation of the system on the medium. Moreover, since at equilibrium the energy dissipation is positive, it turns out that $\omega Im\tilde{\chi}(\omega)$ is a non negative function.

1.2.9 Dissipation and absorption power spectra:general formula

The results just described can be obtained through a more general argument. We know that the rate at which work is done on the system by an external force $F(t)$ is $P(t) = dW/dt = F(t)\dot{S}(t)$ where $S(t)$ is the output signal (observable). On the other hand

$$S(t) = \int_{\mathbb{R}} \chi(t-t')F(t')dt' \tag{1.66}$$

giving

$$P(t) = -F(t)\frac{d}{dt}\int_{-\infty}^{\infty} \chi(t-t')F(t')dt'. \tag{1.67}$$

We know express $F(t)$ and $\chi(t-t')$ as inverse Fourier transform in the rhs of the abvove equation. This gives

$$\begin{aligned} P(t) &= -\frac{1}{2\pi}\int_{\mathbb{R}} d\omega e^{-i\omega t}\tilde{F}(\omega)\frac{d}{dt}\frac{1}{2\pi}\int_{\mathbb{R}} d\omega' e^{-i\omega' t}\tilde{\chi}(\omega')\tilde{F}(\omega') \\ &= \frac{i}{(2\pi)^2}\int_{\mathbb{R}} d\omega \int_{\mathbb{R}} d\omega'\omega' e^{-i(\omega+\omega')t}\tilde{F}(\omega)\tilde{\chi}(\omega')\tilde{F}(\omega') \end{aligned} \tag{1.68}$$

To compute the total energy dissipated into the medium by the perturbed system in the time interval $[-T, T]$ we have to compute

$$\boxed{P_{abs} = \int_{-T}^{T} dt \frac{i}{(2\pi)^2} \int_{\mathbb{R}} d\omega \int_{\mathbb{R}} d\omega' \omega' e^{-i(\omega+\omega')t} \tilde{F}(\omega)\tilde{\chi}(\omega')\tilde{F}(\omega')} \tag{1.69}$$

Let us consider the following special cases

Delta fuction perturbation In this case $F(t) = F_0\delta(t)$ giving $\tilde{F}(\omega) = F_0$. Inserting in eq. (1.68) gives

$$P(t) = \frac{i}{(2\pi)^2} \int_{\mathbb{R}} d\omega \int_{\mathbb{R}} d\omega' \omega' e^{-i(\omega+\omega')t} F_0^2 \tilde{\chi}(\omega') \tag{1.70}$$

an the totale energy absorbed in to the medium is

$$P_{abs} = \int_{-\infty}^{\infty} P(t)dt = \int_{-\infty}^{\infty} \frac{i}{(2\pi)} \int_{\mathbb{R}} d\omega\omega F_0^2 \tilde{\chi}(\omega) \tag{1.71}$$

On the other hand, since the total energy absorbed must be a real quantity we have to consider the imaginary term of the integral giving

$$P_{abs} = \int_{-\infty}^{\infty} P(t)dt = -\int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{\mathbb{R}} d\omega\omega F_0^2 Im\tilde{\chi}(\omega) \tag{1.72}$$

Oscillating force In this case

$$F(t) = F_0 \cos\omega_0 t = \frac{1}{2}\left(F_0 e^{i\omega t} + F_0 e^{-i\omega t}\right) \tag{1.73}$$

an we easily get back the result (1.65) obtained in the previous section. (see Exercises)

1.2.10 Response in a forced damped harmonic oscillator

A very instructive system in which all the above considerations can be made explicit is the *damped harmonic oscillator* with an applied external force $f(t)$

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{f(t)}{m} = F(t) \tag{1.74}$$

where γ is the damping constant and $\omega_0 = \sqrt{k/m}$ is the natural frequency of the oscillator. It is important to stress that, because of the viscous term $\gamma\dot{x}$ the above equation cannot be obtained by a classical conservative Hamiltonian. As a matter of fact the $\gamma\dot{x}$ term breaks the time reversal invariance of the Newton equations. The reason is that the real microscopic Hamiltonian is the one that takes into account the harmonic oscillator *and* all the fluid degrees of freedom in which the oscillator moves. The term $\gamma\dot{x}$ is related just a phenomenological description of the interactions between the oscillator and the fluid particles (Stokes law).

The full study of this system can be performed in several steps (see Exercises):

- Find the full solution of eq. (1.215) and discuss the regimes $\omega_0^2 > \gamma^2/4$ and $\omega_0^2 < \gamma^2/4$
- Compute the response function $\tilde{\chi}(\omega)$ of the system. Study the Imaginary and Real part as a function of ω and discuss the limits $\gamma << 1$, $\omega \to 0$, $\omega \to \infty$.
- Look at the particular case of an harmonic force $f(t) = f_0 \cos\omega t$.

1.3 Linear Response theory in Statistical mechanics

The problem we would like to investigate in this section is the following. Suppose we have a system in thermal equilibrium and then suppose to switch on at a given time a weak external field. How does this system respond to the external perturbation ? For example one would like to know how much current is induced in an ionic solution by an electric field or how much magnetization produces a magnetic system under the influence of an external magnetic field. If the perturbation is weak we can hope to treat the problem with then linear response theory described above, although in this case, the observables have to considered in a statistical way. Of course there are many experimental protocols in which this problem can be discussed. For example one can think to start with a equilibrum system and then at a given time switch on an external field. Another possibility is to look at the relaxation dyanmics of the system after the external field has been switched off (*regression problem*). Another possibility is to consider the response of the system with respect to an applied field that varies periodically in time. In all these cases that will be considered later, it is necesary to go beyond the equilibrium statistical mechanics considering the time evolution of the system. If, on the other hand, the applied field is kept constant for a very long time so that the system can reach an equilibrium state in presence of the field, the problem can be studied within equilibrium statistical mechanics. In quantum mechanics this situation corresponds essentially to the time-independent perturbation theory.

1.4 Static Linear Response

Let us start with the equilibrium linear response. Since there are complications when dealing with quantum statistical systems, we will mainly consider the classical treatment of the problem although, when possible, we will partially discuss also the quantum case. Let us then consider a classical statistical mechanics system described by an Hamiltonian $\mathcal{H}_o(X)$ where X represents a possible microscopic state of the system with N degrees of freedom. For example in a simple model of paramagnetyc system on a lattice the Hamiltonian may be given by

$$\mathcal{H}_o = -\sum_{i<j}^{N} J_{ij}\sigma_i \cdot \sigma_j \tag{1.75}$$

where σ_i is the spin at site i. The thermal equilibrium of the system is then given by the probability density

$$\rho_o(X) = \frac{1}{Q} e^{-\beta\mathcal{H}_o(X)}. \qquad Q = Tr e^{-\beta\mathcal{H}_o(X)} \tag{1.76}$$

where Tr means the sum over all microscopic states: for a continuum Tr is replaced by $\int dX$ while for a discrete space $Tr \to \sum_X$. From now on averages taken over the umperturbed distribution $\rho_{eq}(X)$ are denoted by $\langle\cdot\rangle$. In our specific example a possible observable is the total magnetization

$$M(X) = \sum_{i=1}^{N} \sigma_i(X) \tag{1.77}$$

and its macroscopic quantity at equilibrium is given by the thermal average

$$\langle M\rangle_{eq} \equiv \langle M\rangle \equiv \frac{1}{Q} Tr\left\{\rho_{eq}(X)M(X)\right\} \equiv \frac{1}{Q} Tr\left\{M(X)e^{-\beta\mathcal{H}_o(X)}\right\}. \tag{1.78}$$

We now consider a constant small perturbation F that has been swtiched on for sufficiently long time that the system is at a new thermal equilibrium. Now since the perturbed Hamiltonian is $\mathcal{H}(X;F) = \mathcal{H}_o(X) - A(X)F$, the statistical properties of the system are described by the probability distribution

$$\rho(X;F) = \frac{1}{Q(F)} e^{-\beta\mathcal{H}_o(X)+\beta A(X)F}, \qquad Q(F) = Tr e^{-\beta\mathcal{H}_o(X)+\beta A(X)F}. \tag{1.79}$$

Regarding our example the external perturbation can be a magnetic field h and the conjugate variable the total magnetization $M(X)$. In classical statistical physics one can easily expand the perturbed system about the unperturbed one by simply expanding the exponential factor as follows:

$$\begin{aligned} e^{-\beta\mathcal{H}_o(X)+\beta A(X)F} &= \left\{1+\beta A(X)F+O(F^2)\right\}e^{-\beta\mathcal{H}_o(X)} \\ Q(F) &= Q\left\{1+\beta\langle A\rangle F+O(F^2)\right\}. \end{aligned} \tag{1.80}$$

This gives for the perturbed distribution function

$$\begin{aligned} \rho(X;F) &= \{1+\beta\left[A(X)-\langle A\rangle\right]F\}\rho_o(X)+O(F^2) \\ &= (1-\beta\langle A\rangle F+\beta F A(X))\,\rho_o \end{aligned} \tag{1.81}$$

Note that the above expressions contain the unperturbed equilibrium average $\langle A\rangle$. If we now ask for the average of an arbitrary observable $B_F(X)$ we obtain:

$$\langle B\rangle_F = Tr\rho(X;F)B(X) = \langle B\rangle + \beta F(\langle BA\rangle - \langle A\rangle\langle B\rangle \tag{1.82}$$

If for simplicity we consider $\langle A\rangle = 0$ we get

$$\langle B\rangle_F = \langle B\rangle + \chi_{AB}F + O(F^2) \tag{1.83}$$

where the coefficient χ_{AB} is given by

$$\chi_{AB} = \beta\langle AB\rangle. \tag{1.84}$$

If in our example we choose B to be equal to the total magnetization (i.e. $A = B = M$) then χ_{MM} is a kind of magnetic susceptibility. Sometimes one writes $\Delta B(X) \equiv B(X)\langle B\rangle$ and (1.82) becomes

$$\langle \Delta B\rangle_F = \beta F(\langle BA\rangle - \langle A\rangle\langle B\rangle = F\chi_{AB} \tag{1.85}$$

1.4.1 Quantum systems

The main problem in the quantum mechanical treatment is that the expansion of the exponential used in the classical case:

$$e^{\beta A(X)F} \sim \left(1+\beta A(X)F+O(F^2)\right) \tag{1.86}$$

cannot be used blindly if $\hat{H}$ and $\hat{A}$ are operators that do not commute. In this case one has to perform an operator expansion of the perturbed distribution function. One way consists in starting with the Laplace transform in β of the perturbed distribution function

$$\int_0^\beta d\beta e^{-\beta(\hat{H}_0-\hat{A}F)}e^{-z\beta} = \frac{1}{z+\hat{H}_0-\hat{A}F} \tag{1.87}$$

and use the operator identity

$$\frac{1}{z+\hat{H}_0-\hat{A}F} = \frac{1}{z+\hat{H}_0} + \frac{1}{z+\hat{H}_0}\hat{A}F\frac{1}{z+\hat{H}_0-\hat{A}F} \tag{1.88}$$

that at first order becomes

$$\frac{1}{z+\hat{H}_0-\hat{A}F} = \frac{1}{z+\hat{H}_0} + \frac{1}{z+\hat{H}_0}\hat{A}F\frac{1}{z+\hat{H}_0} + O(F^2) \tag{1.89}$$

If we now invert the Laplace transform we obtain (see Exercises)

$$e^{-\beta\hat{H}_0+\beta\hat{A}F} = e^{-\beta\hat{H}_0} + \int_0^\beta d\lambda e^{-\lambda\hat{H}_0}\hat{A}Fe^{-(\beta-\lambda)\hat{H}_0} + O(F^2) \tag{1.90}$$

In the Heisenberg representation

$$e^{-\lambda \hat{H}_0} \hat{A} e^{\lambda \hat{H}_0} = \hat{A}(ih\lambda) \tag{1.91}$$

giving

$$e^{-\beta \hat{H}_0 + \beta \hat{A} F} = e^{-\beta \hat{H}_0} + \int_0^\beta d\lambda \hat{A}(ih\lambda) F e^{-\beta \hat{H}_0} + O(F^2). \tag{1.92}$$

If we define the *Kubo transform* as

$$\boxed{\tilde{A}_K(\beta) \equiv \frac{1}{\beta} \int_0^\beta d\lambda \hat{A}(ih\lambda)} \tag{1.93}$$

we then have

$$e^{-\beta \hat{H}_0 + \beta \hat{A} F} = e^{-\beta \hat{H}_0} \left(1 + \beta F \tilde{A}_K(\beta) + O(F^2)\right). \tag{1.94}$$

In the case $\langle \hat{A} \rangle = 0$ it is easy to show that

$$Q(F) = Q + O(F^2) \tag{1.95}$$

and finally

$$\chi_{AB} = \beta \langle B \tilde{A}_K \rangle \tag{1.96}$$

In other words the quantum version of the static linear response theory is similar in form to the classical one except that the observable A is replaced by the Kubo transform $\tilde{A}_K(\beta)$.

1.5 Dynamic linear response

In order to study non equilibrium response we need to look at the dynamical evolution of the system. In this case we suppose that the system is described by N degrees of freedom and $2N$ canonically conjugate variables: N positions $q_i(t)$ and N moments $p_i(t)$,, $i = 1, \cdots N$. To simplify equations we will use the shorthand

$$\{q_i(t), p_i(t)\} = [q(t), p(t)]. \tag{1.97}$$

For simplicity we assume that the time evolution of these variables are governed by a time-independent Hamiltonian $\mathcal{H}(q, p)$ through the Hamilton equation

$$\begin{aligned} \dot{q} &= \frac{\partial \mathcal{H}}{\partial p} \\ \dot{p} &= -\frac{\partial \mathcal{H}}{\partial q}. \end{aligned} \tag{1.98}$$

The time evolution from $t = 0$ is given by the flow map

$$[q(0), p(0)] \equiv [q, p] \to [q(t), p(t)] \equiv [q', p'] \tag{1.99}$$

Note that from the Liouville's theorem

$$dqdp = dq'dp'. \tag{1.100}$$

The time dependent density probability distribution $\rho(q, p, t)$ in the system phase space (space Γ_N of $6N$ dimensions) can be defined as

$$\rho(q, p, t)d\Gamma \equiv \rho(q, p, t)dqdp \tag{1.101}$$

i.e. as the probability of finding a microscopic state with (q, p) within the infinitesimal ($6N$-dimensional) volume of the phase space. Since $\rho(q, p, t)$ is a probability density we must require

$$\rho(q, p, t) \geq 0, \qquad \int \rho(q, p, t)dqdp = 1. \tag{1.102}$$

The conservation of probability means that $\rho(q, p, t)$ is constant along the trajectory in phase space, i.e.

$$\rho(q(t), p(t), t) = \rho(q, p, t = 0). \tag{1.103}$$

This conservation law can be written in differential form as

$$0 = \frac{d}{dt}\rho(q(t), p(t), t) = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q}\dot{q} + \frac{\partial \rho}{\partial p}\dot{p} = \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} \tag{1.104}$$

where the Poisson bracket of two dynamical variables is defined as

$$\{A, B\} \equiv \frac{\partial A}{\partial q}\frac{\partial B}{\partial p} - \frac{\partial A}{\partial p}\frac{\partial B}{\partial q} = \sum_{i=1}^{N}\left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i}\right) \tag{1.105}$$

and the partial derivative $\partial/\partial t$ is taken at a fixed point in phase space. Note that a generic dynamical variable $A(t) \equiv A\left(q(t), p(t)\right)$ does not depend esplicitly on time: its time dependence is reflected by the time evolution of the phase space coordinates $(q(t), p(t))$. The *classical Liouvillian* $\mathcal{L}$ is defined by its action on dynamical variables $A(t) \equiv (q(t), p(t))$, $A(0) \equiv (q(0), p(0))$

$$\boxed{\dot{A}(t) \equiv \frac{dA}{dt} = i\mathcal{L}A,} \tag{1.106}$$

where

$$\mathcal{L}\cdot \equiv i\{\mathcal{H},\cdot\} \quad (1.107)$$

Its formal solution is given by

$$A(t) = e^{i\mathcal{L}t}A(0) = e^{i\mathcal{L}t}A(q(0),p(0)) \quad (1.108)$$

In this respect also the density distribution satisfies a Liouvill's equation

$$\boxed{\frac{\partial\rho}{\partial t} = -\{\rho,\mathcal{H}\} = -i\mathcal{L}\rho} \quad (1.109)$$

with formal solution

$$\rho(q,p,t) = e^{-i\mathcal{L}t}\rho(q,p,0) \quad (1.110)$$

Since

$$e^{-i\mathcal{L}t} = \sum \frac{(-t)^n}{n!}(i\mathcal{L})^n \quad (1.111)$$

one gets

$$\rho(q,p,t) = \sum \frac{(-t)^n}{n!}(i\mathcal{L})^n\rho(q,p,0) = \sum \frac{(-t)^n}{n!}\frac{\partial}{\partial t^n}\rho(q,p,0). \quad (1.112)$$

Note that the formal solution corresponds to the Taylor expansion of the *explicit* time dependence of $\rho(q,p,t)$ with respect ot the initial condition $\rho(q,p,0)$.

Clearly the observable $A(t)$ is a fluctuating variable and is not sperimentally accesible. The quantity that can be observed is instead its value averaged with respect to the probability density $(\rho(q,p,t)$ describing the macroscopic state of the system. If the system evolves with time there are, as in quantum mechanics, at least two ways to follow the ensemble average of the observable A.

Lagrangian or Heisenberg picture One can compute the average value of the observable $A(t)$ at time t by following A as it changes along a single trajectory in phase space. This time evolution is given by (1.108). The average $\langle A(t)\rangle \equiv \langle A(q(t),p(t))\rangle$ can be computed by summing the values of $A(t)$ with a weight proportional to the probability of starting from each initial point phase (q,p). This probability is taken from an initial distribution function $\rho(q,p,0)$ Formally

$$\boxed{\langle A\rangle(t) = \int A(q(t),p(t))\rho(q,p,t=0)dqdp \int dqdp\rho(q,p,t=0)e^{i\mathcal{L}t}A(q(0),p(0)).} \quad (1.113)$$

This picture is similar to the Heisenberg picture of quantum mechanics. Another analogy is with the classical theory of fluid mechanics. Indeed one can imagine that the phase space point is the center of an infinitesimal volume $d\Gamma$ which changes shape (and volume for a compressible fluid) with time as the phase point follows its trajectory. The probability of each differential volume, $d\Gamma\rho(\Gamma,0)$ remains constants but the value of the dynamical observable A changes *implicitly* with time.

Eulerian or Schrodinger picture In this case $\langle A\rangle(t)$ can be computed by sitting at a particular point in the phase space and calculating the density of ensemble points as a function of time. This will give us the time-dependent probability density $\rho(q,p,t)$.

The average of A is now computed by summing up the values of $A(q,p)$ weighted by the current value of the distribution function *at that place* in phase space. Keeping the analogy with fluid mechanics the observable takes on a fixed value $A(q,p)$ for all time, while mass points with different probability flow through the box. Since $\rho(q,p,t)$ evolves with time by following eq. (1.110). We then have

$$\boxed{\langle A\rangle(t) = \int A(q(0),p(0))\rho(q(0),p(0),t)dqdp = \int A(q(0),p(0))e^{-i\mathcal{L}t}\rho(q(0),p(0),0).} \quad (1.114)$$

This is analogous to the Schrodinger picture in quantum mechanics and to the Eulerian picture in hydrodynamics (the velocity is observed to change with time at a given fixed point of the space). It is easy to show that the two pictures are equivalent (see Exercise).

Since the two pictures are equivalent the decision of choosing one of the two depends on the problem to investigate. Actually, as in quantum mechanics, one can use other equivalent pictures known as *intermediate* or *interaction* in which the probability density is computed at a given intermediate time t_i with $0 < t_i < t$.

1.5.1 Perturbed system

The aim is to find an explicit formula for the response function $\chi_{AB}(t)$ of a system given in term of the output observable $\langle B \rangle(t)$, under the effect of an external perturbation $F(t)$ coupled to another observable of the system A. We will see that the A and B are not necessary different. Once one has got the response function $\langle B \rangle(t)$ at first order in the perturbation the identification with the linear response formula

$$\langle B \rangle(t) = \int_{t_0}^{t} \chi_{AB}(t-t')F(t')dt' \tag{1.115}$$

will give the microscopic expression of $\chi_{AB}(t)$. We will assume that the perturbed Hamiltonian is of the form

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_I(t) = \mathcal{H}_0 - AF(t) \tag{1.116}$$

where:

- $\mathcal{H}_0$ is the unperturbed Hamiltonian;
- $F(t)$ is the time dependent external field;
- A is the dynamical variable conjugate to F.

For example one can think F as an external electric field $F(t) = E(t)$ and $A(q) = \sum_{i=1}^{N} Q_i \vec{r}_i$.

Given the perturbation $\mathcal{H}_I(t)$ the Liouville operator can be decomposed as follows:

There are many protocols one think of in order to study the dynamical response of a statistical mechanical system due to external perturbation. For example one can think of looking at the response of the system after the external field has been swtiched on, or one can suppose to look at the relaxation dynamics of the system starting from a perturbed state after the external field has been switched off.

1.5.2 Regression protocol

Let us first consider the case in which, after achieving a short-lived nonequilibrium steady state (say between $-\infty$ and $t = 0$) due to a constant perturbation, the system is allowed to relax back to equilibrium. This process is known as *regression.* The situation is described in terms of the Hamiltonian

$$\mathcal{H}(q,p) = \begin{cases} \mathcal{H}_0(q,p) - A(q,p)F & t < 0 \\ \mathcal{H}_0(q,p) & t > 0 \end{cases} \tag{1.117}$$

We are interested in measurements of, say the observable B, for $t > 0$ as it relaxes to equilibrium. Clearly, for $t < 0$ the distribution $\rho(q,p)$ does not depend on time since the perturbation is constant. On the other hand it is the equilibrium distribution for the *perturbed* Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$. On the other hand, for $t > 0$ the probability distribution $\rho(q,p,t)$ is no longer time-independent but it evolves with respect to the unperturbed Hamiltonian $\mathcal{H}_0$. In order to evaluate the time-dependence of the average of B it is convenient to work in the Lagrangian (Heisenberg) picture

$$\langle B\rangle(t) = \int B(q(t), p(t))\rho(q, p, t = 0)dqdp. \tag{1.118}$$

where

$$\rho(q, p, t = 0) = \frac{e^{-\beta(\mathcal{H}_0 + \mathcal{H}_I)}}{Tr\{e^{-\beta(\mathcal{H}_0 + \mathcal{H}_I)}\}} \tag{1.119}$$

In this case we have

$$\langle B(0)\rangle = \frac{Tr\left\{e^{-\beta(\mathcal{H}_0 + \mathcal{H}_I)}B(q, p)\right\}}{Tr\left\{e^{-\beta(\mathcal{H}_0 + \mathcal{H}_I)}\right\}}. \tag{1.120}$$

For $t \geq 0$ we let $(q(t), p(t)$ for each member of the ensemble to evolve under the Hamiltonian, now $\mathcal{H}_0$, from its value $(q(0), p(0))$. Hence

$$\langle B(t)\rangle = \frac{Tr\left\{e^{-\beta(\mathcal{H}_0 + \mathcal{H}_I)}B(q(t), p(t))\right\}}{Tr\left\{e^{-\beta(\mathcal{H}_0 + \mathcal{H}_I)}\right\}}. \tag{1.121}$$

We now expand the exponential to first order in $\mathcal{H}_I$ (F is small !!)

$$\begin{aligned}
\langle B(t)\rangle &\simeq \frac{Tr\left\{e^{-\beta\mathcal{H}_0}\left(1 - \beta\mathcal{H}_I\right)B(q(t), p(t))\right\}}{Tr\left\{e^{-\beta\mathcal{H}_0}\left(1 + \mathcal{H}_I\right)\right\}} \\
&= \frac{Tr\left\{e^{-\beta\mathcal{H}_0}B(q(t), p(t))\right\} - \beta Tr\left\{e^{-\beta\mathcal{H}_0}\mathcal{H}_I B(q(t), p(t))\right\}}{Tr\left\{e^{-\beta\mathcal{H}_0}\right\} - \beta Tr\left\{e^{-\beta\mathcal{H}_0}\mathcal{H}_I\right\}} \\
&= \frac{Tr\left\{e^{-\beta\mathcal{H}_0}B(q(t), p(t))\right\}}{Tr\left\{e^{-\beta\mathcal{H}_0}\right\}\left(1 - \beta\frac{Tr\left\{e^{-\beta\mathcal{H}_0}\mathcal{H}_I\right\}}{Tr\left\{e^{-\beta\mathcal{H}_0}\right\}}\right)} - \beta\frac{Tr\left\{e^{-\beta\mathcal{H}_0}\mathcal{H}_I B(q(t), p(t))\right\}}{Tr\left\{e^{-\beta\mathcal{H}_0}\right\}\left(1 - \beta\frac{Tr\left\{e^{-\beta\mathcal{H}_0}\mathcal{H}_I\right\}}{Tr\left\{e^{-\beta\mathcal{H}_0}\right\}}\right)} \\
&= \frac{\langle B(t)\rangle_0}{1 - \beta\langle\mathcal{H}_I\rangle_0} - \beta\frac{\langle\mathcal{H}_I B(t)\rangle_0}{1 - \beta\langle\mathcal{H}_I\rangle_0},
\end{aligned} \tag{1.122}$$

where in the last line we have written for simplicity $B(q(t), p(t)) \rightarrow B(t)$ and $\langle\cdot\rangle_0$ denotes the average over the ensemble for a system for which no perturbation was applied, i.e. $\rho_0 = e^{-\beta\mathcal{H}_0}/Tre^{-\beta\mathcal{H}_0}$. By using the standard approximation

$$\frac{1}{1 - x} \sim 1 + x \tag{1.123}$$

we finally get

$$\langle B(t)\rangle \simeq \langle B\rangle_0 - \beta\left[\langle H_I B(t)\rangle_0 - \langle B\rangle_0\langle H_I\rangle_0\right] + O(H_I)^2 \tag{1.124}$$

Finally, by inserting the explicit form of the perturbation term $\mathcal{H}_I$, writing $\Delta B(t) \equiv B(t) - \langle B\rangle_0$ and noticing that $A\left(q(0), p(0)\right)$ is equivalent to $A(0)$

$$\mathcal{H}_I = -FA(q, p) = -FA(q(0), p(0)) = -FA(0), \tag{1.125}$$

giving for the change in the measurement $\langle\Delta B(t)\rangle \equiv \langle B(t)\rangle - \langle B\rangle_0$

$$\langle\Delta B(t)\rangle = \beta F\left[\langle A(0)B(t)\rangle_0 - \langle A(0)\rangle_0\langle B(t)\rangle_0\right]. \tag{1.126}$$

If we now define the connected (or central) average as $\langle XY\rangle_c \equiv \langle XY\rangle - \langle X\rangle\ langleY\rangle$ we have

$$\boxed{\langle\Delta B(t)\rangle = \beta F\langle A(0)B(t)\rangle_{0c}} \tag{1.127}$$

The function $\langle A(0)B(t)\rangle_{0c}$ is the connected *equilibrium time correlation function* of B and A also known as *Kubo function* $C_{AB}(t)$

$$C_{AB}(t) \equiv \langle B(t)A(0)\rangle_{0c}. \tag{1.128}$$

We can now relate the above result with the definition of the response function. Indeed, from the linear response theory we have

$$\langle \Delta B(t) \rangle = \int_{-\infty}^{t} \chi_{AB}(t-t')F(t')dt' \tag{1.129}$$

In the case treated above, by following the protocol given in (**??**) so that $F(t') = F\Theta(-t')$ we have

$$\langle \Delta B(t) \rangle = F \int_{-\infty}^{0} \chi_{AB}(t-t')dt' = F \int_{t}^{\infty} \chi_{AB}(t')dt' \tag{1.130}$$

If we now compare (1.130) with the time derivative of (1.127) we get

$$R(t) \equiv \frac{d}{dt}\langle \Delta B(t) \rangle = \beta F \dot{C}_{AB}(t) = \begin{cases} -F\chi_{AB}(t) & t > 0 \\ 0 & t < 0 \end{cases} \tag{1.131}$$

In other words

$$\boxed{\chi_{AB}(t) = -\beta\Theta(t)\dot{C}_{AB}(t)} \tag{1.132}$$

Eq. (1.132) is the classical *Kubo expression.* Note that, because of time translation invariance at equilibrium we can write (see Exercises)

$$\dot{C}_{AB}(t) = \langle \dot{B}(t)A(0)\rangle_{0c} = -\langle B(t)\dot{A}(0)\rangle_{0c} \tag{1.133}$$

giving

$$\langle \Delta B(t) \rangle = \int_{0}^{\infty} \chi_{AB}(t')F(t-t')dt' = \beta \int_{-\infty}^{\infty} \langle B(t')\dot{A}(0)\rangle_{0c}\Theta(t')F(t-t')dt' \tag{1.134}$$

that in Fourier space becomes

$$\langle \Delta \tilde{B}(\omega) \rangle = \beta \tilde{F}(\omega) \int_{0}^{\infty} e^{i\omega t}\langle B(t)\dot{A}(0)\rangle_{0c}dt \tag{1.135}$$

where ω should be understood as $\lim_{\eta\to 0}(\omega + i\eta)$.

1.5.3 Onsager regression

If we consider $B = A$ in eq. (1.127) we obtain the relation

$$\boxed{\langle \Delta A(t) \rangle = \beta F \langle A(0)A(t)\rangle_{0c} = \beta F \langle \delta A(0)\delta A(t)\rangle_{0}} \tag{1.136}$$

One can interpret eq. (1.136) as follows: At equilibrium the variable $A(t)$ fluctuates in time with *spontaneous microscopic fluctuations* $\delta A(t)$ around its average value $\langle A(t)\rangle_0$. Its time evolution is ruled by the microscopic laws that, for classical systems are given by

$$\delta A(t) = \delta A(q, p; t) = \delta A(q(t), p(t)). \tag{1.137}$$

Unless A is an integral of motion (as for example the energy), $A(t)$ will look as a random variable even in an equilibrium system. While the equilibrium average $\langle \delta A\rangle_0 = 0$, it is interesting to look at the equilibrium correlations between fluctuations at different times. The correlation between $\delta A(t)$ and an istantaneous fluctuations at time zero is given by

$$C_{AA}(t) = \langle \delta A(0)\delta A(t)\rangle_0 \tag{1.138}$$

namely, in the Lagrangian picture

$$C_{AA}(t) = \int \delta A(q(0), p(0)\delta A(q(t), p(t))\rho(q, p, t = 0)dqdp \tag{1.139}$$

In general at small times these fluctuations are correlated and in particular

$$\lim_{t\to 0} C_{AA}(t) = \langle \delta A(0)^2 \rangle_0. \tag{1.140}$$

However at large times $\delta A(t)$ will be uncorrelated to $\delta A(0)$. Thus

$$\lim_{t\to\infty} C_{AA}(t) = \langle \delta A(0) \rangle_0 \langle \delta A(t) \rangle_0 \tag{1.141}$$

and since $\langle \delta A \rangle_0 = 0$ we get

$$\lim_{t\to\infty} C_{AA}(t) = 0, \tag{1.142}$$

This decay of correlations with increasing time is the *regression of spontaneous fluctuations.* In general the decay to zero is (possibly with some oscillations) exponential

$$C_{AA}(t) \simeq C_{AA}(0) e^{-|t|/\tau_A} \tag{1.143}$$

where τ_A is the *relaxation time* of the observable A. On the other hand the relation

$$\chi_{AA}(t) = -\beta \frac{d}{dt} C_{AA}(t) \tag{1.144}$$

has been obtained as the result of a relaxation process of the system *after an external perturbation* F has been switched off. This suggets that the system can be brougth out of equilibrium either by a small perturbation F, or by a spontaneous thermal fluctuation δA but, in both cases, the return to equilibrium is governed by the equilibrium fluctuations. This is the *Onsager's regression law* that was stated by Onsager as follows (Onsager 1931): *If a system is, at time t_0, out of equilibrium, it is impossible to know if this off-equilibrium state is the result of an external perturbation or of a spontanoues fluctuation. The relaxation of the system back to equilibrium will be the same for the two cases (assuming that the original deviation from equilibrium is small enough).*

1.5.4 Fluctuation-dissipation theorem

By recalling that $\chi''(t)$ is the odd part of χ: $\chi''(t) = \frac{1}{2}[\chi(t) - \chi(-t)]$ and is defined as $\chi(t) = 2i\Theta(t)\chi''(t)$, using eq. (1.132) we have

$$\chi''_{AB}(t) = \frac{i}{2} \beta \dot{C}_{AB}(t) \tag{1.145}$$

which, under Fourier transform gives

$$Im\tilde{\chi}_{AB}(\omega) = \frac{1}{2} \beta \omega \tilde{C}_{AB}(\omega). \tag{1.146}$$

On the other hand we have see that $Im\tilde{\chi}(\omega)$ is linked to energy dissipation per unit of time through

$$P(\omega) = \frac{\omega}{2} Im\tilde{\chi}(\omega) |\tilde{F}(\omega)|^2 \tag{1.147}$$

Hence

$$\boxed{P_{AB}(\omega) = \frac{\beta}{4} \omega^2 |\tilde{F}(\omega)|^2 \tilde{C}_{AB}(\omega)} \tag{1.148}$$

i.e. the energy dissipation is linked to equilibrium fluctuations described by the correlation function (or ots Fourier transform) $C(t)$.

1.5.5 Application of the FDT: electrical conduttivity

Let us consider a system of charge carriers each with charge Q and mass m in one-dimensional conductor and take as dynamical variables

$$A = Q\sum_i x_i, \qquad B = \dot{A} = Q\sum_i \dot{x}_i = j\Omega \tag{1.149}$$

where x_i is the position of the i-esim carrier, j the current density and Ω the volume of the one-dimensional conductor. The external perturbation is produced by a time dependent electrical field $E(t)$ and the perturbation term in the total Hamiltonian is given by

$$\mathcal{H}_I = -AF(t) = -QE(t)\sum_i x_i. \tag{1.150}$$

Hence, from eq. (1.135) we get

$$\begin{aligned}\langle \Delta\tilde{B}(\omega)\rangle &= \Omega\langle\tilde{\Delta}j(\omega)\rangle = \beta\Omega^2\tilde{E}(\omega)\int_0^\infty e^{i\omega t}\langle j(t')j(0)\rangle_c|_{E=0}dt \\ &= \beta Q^2\tilde{E}(\omega)\int_0^\infty e^{i\omega t}\sum_{i,k}\langle \dot{x}_i(t)\dot{x}_k(0)\rangle_c|_{E=0}dt\end{aligned} \tag{1.151}$$

Since the average equilibrium current density ($E = 0$) vanishes, we can replace Δj by j and omit the lowercase c. The above equation can be seen as the time dependent Ohm law $\langle\tilde{j}(\omega)\rangle = \tilde{\sigma}_{el}(\omega)\tilde{E}(\omega)$ with

$$\boxed{\tilde{\sigma}_{el}(\omega) = \beta\Omega\int_0^\infty e^{i\omega t}\langle j(t)j(0)\rangle|_{E=0}dt} \tag{1.152}$$

In other words the electrical conductivity $\tilde{\sigma}_{el}(\omega)$ is given by the Furier transform of the time-autocorrelation of the current density in the absence of an external electric field. If one assumes that the correlations between velocities of different particles is zero and that the velocity auto-correlation function of a given particle decays exponentially fast to zero (with a time scale of the order of the collision time τ_c) we have

$$\langle \dot{x}_i(t)\dot{x}_k(0)\rangle_{E=0} = \delta_{ik}\frac{1}{\beta m}e^{-|t|/\tau_c} \tag{1.153}$$

and inserting in (1.151) one gets

$$\tilde{\sigma}_{el}(\omega) = \frac{nQ^2\tau_c}{m(1 - i\omega\tau_c)} \tag{1.154}$$

where $n = N/\Omega$ is the density of carriers.

In the zero frequency limit $\omega = 0$ one gets the static conductivity σ_{el}

$$\sigma_{el} = \beta\Omega\int_0^\infty \langle j(t)j(0)\rangle_{E=0}dt. \tag{1.155}$$

Note that it may be necessary to include a factor $\exp(\eta t)$ in the above expression to have a convergent integral. The above equation is a typical *Kubo formula* that furnishes a transport coefficient (in this case σ_{el}) in terms of the integral of a equilibrium time correlation function.

1.6 Quantum linear regression theory

The main problem one encounters in computing the response function of a quantum system relaxing back to its equilibrium is similar to the one we cited in the case of static response, namely the impossibility of expanding the exponential of two operators that in general do not commute.

On the other hand, since we are considering regression we can, as in the classical case, follow the static procedure we described for quantum systems. In regression the quantum system is initially described by the perturbed density operator

$$\hat{\rho}_F = \frac{1}{\hat{Q}_F} e^{-\beta(\hat{H}_0+\hat{H}_1)} \tag{1.156}$$

Note that $\hat{H}_1$ describes the initial condition ($t = 0$). For time $t > 0$ the observable A is described by an Hermitian operator $\hat{A}$ that evolves following $\hat{H}_0$ ($F = 0$). Hence we can write

$$\hat{A}_I(t) = e^{i\hat{H}_0 t} \hat{A} e^{-i\hat{H}_0 t}. \tag{1.157}$$

we then have

$$\langle \hat{A}_I(t) \rangle_F = Tr \left\{ \hat{A}_I(t) \hat{\rho}_F(t=0) \right\} \tag{1.158}$$

On the other hand, from the static perturbation theory we had

$$e^{-\beta(\hat{H}_0+\hat{H}_1)} = e^{-\beta\hat{H}_0} + \int_0^\beta d\lambda e^{-\lambda\hat{H}_0} \hat{H}_1 e^{-(\beta-\lambda)\hat{H}_0} + O(F^2) \tag{1.159}$$

and since

$$e^{-\lambda\hat{H}_0} \hat{H}_1 e^{\lambda)\hat{H}_0} = \hat{H}_1(ih\lambda) \tag{1.160}$$

we have

$$e^{-\beta(\hat{H}_0+\hat{H}_1)} = e^{-\beta\hat{H}_0} + \int_0^\beta d\lambda \hat{H}_1(ih\lambda) e^{-\beta\hat{H}_0} + O(F^2). \tag{1.161}$$

The average of the observable B described by the hermitian operator $\hat{B}$ is then given by

$$\langle \hat{B}(t) \rangle - \langle \hat{B} \rangle = F \int_0^\beta d\lambda \left[\langle \hat{A}(ih\lambda) \hat{B}(t) \rangle_0 - \langle \hat{A}(ih\lambda) \rangle_0 \langle \hat{B}(t) \rangle_0 \right] \tag{1.162}$$

1.7 A different perturbation protocol

In computing the response function we have considered the protocol in which the system is for $-\infty < t < t_0$ in a perturbed equilibrium situation with the presence of a constant external field and then, at $t = t_0$, F is abruptly switched off and one looks to the relaxation dynamics of the system back to the unperturbed equilibrium state. It is also possible to consider the protocol in which the system that was in the past ($-\infty < t < t_0$) at its unperturned equilibrium state is for $t > t_0$ subjected to a time dependent external perturbation $F(t)$. The simplest case is the one where the external field is an Heaviside function of time

$$F(t) = \begin{cases} F & t > t_0 \\ 0 & t \leq t_0 \end{cases} \tag{1.163}$$

In this case unlike the regression process for $t > t_0$ the system evolves under the influence of the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$ with $\hat{H}_1 = -F\hat{A}$ and in this case it is more convenient to work within the Schrodinger or Eulerian representation where one has to compute the time dependence of the perturbed operator density $\hat{\rho}_F(t)$. This is known to satisfy the Liouville-von Neumann equation

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -i\mathcal{L}\hat{\rho}(t) \tag{1.164}$$

The aim is now to compute, up to first order in F, the solution of equation (1.164) with the initial condition

$$\hat{\rho}(t_0) = \rho_0 \tag{1.165}$$

where $\hat{\rho}_0$ is the unpertubed equilibrium density operator (or function if classical). We firs split the Liouville operator and the density distribution as follows

$$\begin{aligned} \mathcal{L} &= \mathcal{L}_0 + \mathcal{L}_1 &(1.166)\\ \hat{\rho}(t) &= \hat{\rho}_0 + \delta\hat{\rho}(t) &(1.167)\end{aligned}$$

By inserting these relations into eq. (1.164) one obtains

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -i\mathcal{L}_1\hat{\rho}_0 - i\mathcal{L}_0\delta\hat{\rho}(t) - i\mathcal{L}_1\delta\hat{\rho}(t), \tag{1.168}$$

and since the last term is of order $O(F^2)$ we get

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -i\mathcal{L}_1\hat{\rho}_0 - i\mathcal{L}_0\delta\hat{\rho}(t) \tag{1.169}$$

$$\delta\hat{\rho}(t_0) = 0. \tag{1.170}$$

We now look for a solution of the Cauchy problem (1.170) of the form

$$\delta\hat{\rho}(t) = e^{-i\mathcal{L}_0 t} g(t) \tag{1.171}$$

This gives

$$\frac{dg}{dt} = -ie^{i\mathcal{L}_0 t}\mathcal{L}_1\hat{\rho}_0 \tag{1.172}$$

$$g(t_0) = 0. \tag{1.173}$$

whose formal solution is

$$g(t) = -i\int_{t_0}^{t} e^{i\mathcal{L}_0 t'}\mathcal{L}_1\hat{\rho}_0 dt' \tag{1.174}$$

and finally

$$\boxed{\delta\hat{\rho}(t) - i\int_{t_0}^{t} e^{i\mathcal{L}_0 (t-t')}\mathcal{L}_1\hat{\rho}_0 dt'} \tag{1.175}$$

For an observable B we then have

$$\langle\hat{B}(t)\rangle_F = Tr\left\{\hat{\rho}(t)\hat{B}(t_0)\right\} = \langle\hat{B}\rangle_0 + Tr\left\{\delta\hat{\rho}(t)\hat{B}(t_0)\right\} \tag{1.176}$$

or

$$\boxed{\langle\Delta\hat{B}(t)\rangle_F = Tr\left\{\delta\hat{\rho}(t)\hat{B}(t_0)\right\}.} \tag{1.177}$$

N.B. So far the computation has been quite general but now, if we want to compute more explicitly the term $\delta\hat{\rho}(t)$, we need to distinguish between classical and quantum systems. In particular we should consider

$$\mathcal{L}_1\hat{\rho}_0 = -i\{H_1, \rho_0\} \qquad \text{classical} \tag{1.178}$$

and

$$\mathcal{L}_1\hat{\rho}_0 = \frac{1}{\hbar}[\hat{H}_1, \hat{\rho}_0] \qquad \text{quantum} \tag{1.179}$$

From now on we will focus on the quantum case leaving the classical one as an exercise (see Exercises). Hence

$$\delta\hat{\rho}(t) = \frac{i}{\hbar}\int_{t_0}^{t} F(t')e^{-i\mathcal{L}_0(t-t')}[\hat{A}, \hat{\rho}_0]dt' \tag{1.180}$$

Note that in the above formula $\hat{A}$ is written in the Schrodinger representation and does not depend on time. Moreover the operator $\mathcal{L}_I$ acts only on $\hat{A}$ and not on $\hat{\rho}_0$ since $[\hat{\rho}_0, \hat{H}_0] = 0$. We then have

$$\delta\hat{\rho}(t) = \frac{i}{\hbar}\int_{t_0}^{t} F(t')[\hat{A}_I(t'-t), \hat{\rho}_0]dt' \tag{1.181}$$

where

$$\hat{A}_I(t) = e^{i\mathcal{L}_0 t}\hat{A} = e^{i\mathcal{H}_0 t/\hbar}\hat{A}e^{-i\mathcal{H}_0 t/\hbar} \tag{1.182}$$

If we now take the limit $t_0 \to \infty$ we get

$$\delta\hat{\rho}(t) = \frac{i}{\hbar}\int_{-\infty}^{t} F(t')[\hat{A}_I(t'-t), \hat{\rho}_0]dt' \tag{1.183}$$

Extending to the average of $\hat{B}(t)$ we get

$$\langle\Delta\hat{B}(t)\rangle = Tr\{\delta\hat{\rho}(t)\hat{B}\} = \frac{i}{\hbar}\int_{-\infty}^{t} F(t')Tr\left([\hat{A}_I(t'-t), \hat{\rho}_0]\hat{B}\right)dt' \tag{1.184}$$

Since the trace is invariant for ciclic permutation of the operators we can also write

$$\boxed{\langle\Delta\hat{B}(t)\rangle = \frac{i}{\hbar}\int_{-\infty}^{t} F(t')\langle[\hat{B}_I(t'-t), \hat{A}\rangle_0 dt'} \tag{1.185}$$

Finally, since

$$\langle\Delta\hat{B}(t)\rangle = \int_{-\infty}^{\infty} \chi_{AB}(t)F(t')dt' \tag{1.186}$$

$$\boxed{\chi_{AB}(t) = \frac{i}{\hbar}\Theta(t)\langle[\hat{B}_I(t), \hat{A}\rangle_0} \tag{1.187}$$

Equation (1.187) is the so called *Kubo formula* and is written in terms of operators. Note that, since $\chi(t) = 2i\Theta(t)\chi''(t)$, we can also write

$$\boxed{\chi''_{AB}(t) = \frac{1}{2\hbar}\langle[\hat{B}_I(t), \hat{A}\rangle_0} \tag{1.188}$$

Kubo formula in matrix form

When one has to deals with specific cases, it is more appropriate to write eq. (1.187) in terms of a complete set of eigenvectors (bases) . In this respect let us recall that in quantum statistics, if we denote by $\{|n\rangle\}$ a complete set of eigenvectors of the unperturbed Hamiltonian $\hat{H}_0$ with eigenvalues E_n, the unperturbed density operator $\hat{\rho}_0$ is written as

$$\hat{\rho}_0 = \sum_n |n\rangle\langle n|w_n \tag{1.189}$$

where w_n is the probability for the eigenstate $|n\rangle$ to occur at equilibrium. In the canonical ensemble these are given by

$$w_n = \frac{1}{Z}e^{-\beta E_n}. \tag{1.190}$$

Clearly

$$\langle k|\hat{\rho}_0|k\rangle = \sum_n \langle k|n\rangle\langle n|k\rangle w_n = w_k \tag{1.191}$$

and

$$Tr\hat{\rho}_0 = \sum_k \langle k|\hat{\rho}_0|k\rangle = \sum_k w_k = 1 \tag{1.192}$$

Moreover, since

$$\begin{aligned}\langle k|\hat{B}\hat{\rho}_0|k\rangle &= \langle k|B\sum_n |n\rangle\langle n|w_n|k\rangle \\ &= \sum_l \langle k|B|l\rangle\langle l|\sum_n |n\rangle\langle n|w_n|k\rangle \\ &= \sum_l \langle k|B|l\rangle \sum_n w_n\langle l|n\rangle\langle n|k\rangle \\ &= \sum_{ln} w_n\langle k|B|l\rangle\delta_{ln}\delta_{nk} \\ &= w_k\langle k|B|k\rangle, \end{aligned} \tag{1.193}$$

the equilibrium average of a given observable, described by the hermitian operator $\hat{B}$, is given by

$$\begin{aligned}\langle\hat{B}\rangle_0 &= Tr\{\hat{B}\hat{\rho}_0\} \\ &= \sum_k \langle k|\hat{B}\hat{\rho}_0|k\rangle = \sum_k w_k\langle k|\hat{B}|k\rangle. \end{aligned} \tag{1.194}$$

To our porpuses it is also useful to represents the time correlation function of two operators at equilibrium with respect to the energy eigenvectors. This is given by

$$\begin{aligned}\langle\hat{A}(t_1)\hat{B}(t_2)\rangle_0 &= \sum_n w_n\langle n|A(t_1)B(t_2)|n\rangle \\ &= \sum_{nl} w_n\langle n|A(t_1)|l\rangle\langle l|B(t_2)|n\rangle \\ &= \sum_{nl} w_n\langle n|e^{i\hat{H}_0 t_1/\hbar}A(0)e^{-i\hat{H}_0 t_1/\hbar}|l\rangle\langle l|e^{i\hat{H}_0 t_2/\hbar}B(0)e^{-i\hat{H}_0 t_2/\hbar}|n\rangle \\ &= \sum_{nl} w_n\langle n|A(0)|l\rangle\langle l|B(0)|n\rangle e^{\frac{i}{\hbar}(E_n-E_l)(t_2-t_1)}. \end{aligned} \tag{1.195}$$

Given the relations obtained above the Kubo formula on the energy eigenstates of the umpertubed Hamiltonian becomes

$$\begin{aligned}\chi_{AB}(t) &= \frac{i}{\hbar}\Theta(t)Tr\left(\hat{\rho}_0[\hat{B}_I(t),\hat{A}]\right) \\ &= \frac{i}{\hbar}\Theta(t)\sum_n\langle n|[\hat{B}_I(t),\hat{A}]|n\rangle w_n \end{aligned} \tag{1.196}$$

and performing the manipulation presented above we get

$$\chi_{AB}(t) = \frac{i}{\hbar}\Theta(t)\sum_{nl} w_n\left(B_{nl}A_{ln}e^{i\omega_{nl}t} - A_{nl}B_{ln}e^{i\omega_{ln}t}\right) \tag{1.197}$$

where $A_{nl} = \langle n|A|l\rangle$ and $\omega_{nl} = (E_n - E_l)/\hbar$. By inverting the indices of the second term in the rhd we get

$$\chi_{AB}(t) = \frac{i}{\hbar}\Theta(t)\sum_{nl}(w_n - w_l)B_{nl}A_{ln}e^{i\omega_{nl}t} \tag{1.198}$$

For a finite quantum system (bounded) the spectrum of $\hat{H}_0$ is discrete and $\chi_{AB}(t)$ is a sum (numerable) of periodic functions.

1.7.1 Classical systems

For the classical case see the list of Exercises at the end of the chapter.

1.7.2 Generalization to non uniform systems

In principle the external field can be non homogeneous, i.e. $F = F(\vec{r}, t)$. In this case the perturbation is given by

$$\mathcal{H}_1(t) = -\int F(\vec{r}, t)A(\vec{r})d\vec{r} \tag{1.199}$$

and the response $S(t)$ is both time retarded and *non local* spatially. In the linear approximation the off-equilibrium average of a given dynamical variable $B(q, p)$ is then given by

$$\langle B(\vec{r}, t)\rangle = \int_{\mathbb{R}^3} d\vec{r} \int_{\mathbb{R}} dt' \chi_{AB}(\vec{r}, t; \vec{r}', t')F(\vec{r}', t'), \tag{1.200}$$

where the response function $\chi_{AB}(\vec{r}, t; \vec{r}', t')$ is in general a function of $\vec{r}, \vec{r}', t$ and t'. By performing a calculation similar to the one presented in previous sections (but just more cumbersome) one finally obtaines the Kubo formula generalized to non homogeneous external perturbation

$$\boxed{\chi(\vec{r}, t; \vec{r}', t') = \frac{i}{\hbar}\Theta(t - t')\langle[\hat{B}(\vec{r}, t), \hat{A}(\vec{r}', t')\rangle_0} \tag{1.201}$$

If the unperturbed system is invariant by spatial traslation, the response functon $\chi_{AB}(\vec{r}, t; \vec{r}', t')$ does depends only on $\vec{r} - \vec{r}'$.

1.7.3 Generalization to non uniform systems and to multiple coupling

Since we are within a linear approximation, the perturabtion term of the full Hamiltonian, $\hat{H}_1(t)$, can be generalized to a linear combination of external fields each coupled to a given observable of the system:

$$\begin{aligned} \hat{H}_1(t) &= -\int d\vec{r}\hat{\mathbf{A}}(\vec{r}) \cdot \mathbf{F}(\tilde{\mathbf{r}}, \mathbf{t}) \\ &= -\sum_{i=1}^{N} \int d\vec{r}\hat{A}_i(\vec{r})F_i(\vec{r}, t) \end{aligned} \tag{1.202}$$

Since the theory is linear everything is additive and we have

$$\langle \hat{A}_i(\vec{r}, t)\rangle = 2i \int_{-\infty}^{t} dt' \int d\vec{r}\chi''_{A_iA_j}(\vec{r}, \vec{r}', t - t')F_j(\vec{r}', t') \tag{1.203}$$

where

$$\boxed{\chi''_{A_iA_j}(\vec{r}, \vec{r}', t - t') = \frac{1}{2\hbar}\langle[\hat{A}_i(\vec{r}, t), \hat{A}_j(\vec{r}, t')]\rangle_0.} \tag{1.204}$$

Let us now consider the correlation function

$$C_{A_iA_j}(\vec{r} - \vec{r}', \tau) = \langle \hat{A}_i(\vec{r}, \tau)\hat{A}_i(\vec{r}', 0)\rangle \tag{1.205}$$

where we have implicitly assumed $\langle \hat{A}_i(\vec{r}, 0)\rangle_0 = 0$ and $\tau = t - t'$. We now Fourier transform in the spatial coordinates giving

$$\begin{aligned} \tilde{C}_{A_iA_j}(\vec{k}, \tau) &= \int d(\vec{r} - \vec{r}')e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')}\langle \hat{A}_i(\vec{r}, \tau)\hat{A}_j(\vec{r}', 0)\rangle_0 \\ &= \frac{1}{V}\int\int d\vec{r}d\vec{r}' e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')}\langle \hat{A}_i(\vec{r}, \tau)\hat{A}_j(\vec{r}', 0)\rangle_0 \\ &= \frac{1}{V}\langle \hat{A}_i(-\vec{k}, \tau)\hat{A}_j(\vec{k})\rangle_0 \\ &= \frac{1}{V}\langle \hat{A}_i^*(\vec{k}, \tau)\hat{A}_j(\vec{k})\rangle_0 \end{aligned} \tag{1.206}$$

where we have used

$$\hat{A}_j(\vec{k}) = \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \hat{A}_j(\vec{r}). \tag{1.207}$$

On the other hand it is easy to show (see list of Exercises) that

$$\begin{aligned}\langle \hat{A}_j(\vec{k},0)\hat{A}_i(\vec{k},\tau)\rangle_0 &= \langle \hat{A}_i(\vec{k},\tau - i\hbar\beta)\hat{A}_j(\vec{k},0)\rangle_0 \\ &= e^{-i\beta\hbar(\partial/\partial\tau)}\langle \hat{A}_i(\vec{k},\tau)\hat{A}_j(\vec{k},0)\rangle_0,\end{aligned} \tag{1.208}$$

where

$$\hat{A}_i(-i\hbar\beta) \equiv e^{\beta\hat{H}_0}\hat{A}_i e^{-\beta\hat{H}_0}. \tag{1.209}$$

We finally have

$$\chi''_{A_iA_j}(\vec{k},\tau) = \frac{1}{2\hbar}\left(1 - e^{-i\beta\hbar(\partial/\partial\tau)}\right)\tilde{C}_{A_iA_j}(\vec{k},\tau) \tag{1.210}$$

Hence, by taking the Fourier transform with respect to t we finally get

$$\chi''_{A_iA_j}(\vec{k},\omega) = \frac{1}{2\hbar}\left(1 - e^{-i\beta\hbar\omega}\right)\tilde{S}_{A_iA_j}(\vec{k},\omega) \tag{1.211}$$

where

$$\tilde{S}_{A_iA_j}(\vec{k},\omega) = \int_{\mathbb{R}} \langle A_i(\vec{k},\tau)A_j(\vec{k},0)\rangle_0 e^{i\omega t} dt \tag{1.212}$$

is the spectral density matrix.

Exercises

0. Given the external perturbation $F(t) = -Bt$ and the response function $\chi(\tau) = A\exp(-\tau^2/2\sigma^2)$, compute the output signal $S(t)$.

1. Starting from the general expression

$$\boxed{P_{abs} = \int_{-T}^{T} dt \frac{i}{(2\pi)^2} \int_{\mathbb{R}} d\omega \int_{\mathbb{R}} d\omega' \omega' e^{-i(\omega+\omega')t} \tilde{F}(\omega)\tilde{\chi}(\omega')\tilde{F}(\omega')} \tag{1.213}$$

compute P_{abs} for an external perturbation of the form

$$F(t) = F_0 \cos\omega_0 t = \frac{1}{2}\left(F_0 e^{i\omega t} + F_0 e^{-i\omega t}\right) \tag{1.214}$$

2. A very instructive system in which all the above considerations can be made explicit is the *damped harmonic oscillator* with an applied external force $f(t)$

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{f(t)}{m} = F(t) \tag{1.215}$$

where γ is the damping constant and $\omega_0 = \sqrt{k/m}$ is the natural frequency of the oscillator. It is important to stress that, because of the viscous term $\gamma\dot{x}$ the above equation cannot be obtained by a classical conservative Hamiltonian. As a matter of fact the $\gamma\dot{x}$ term breaks the time reversal invariance of the Newton equations. The reason is that the real microscopic Hamiltonian is the one that takes into account the harmonic oscillator *and* all the fluid degrees of freedom in which the oscillator moves. The term $\gamma\dot{x}$ is related just a phenomenological description of the interactions between the oscillator and the fluid particles (Stokes law).

The full study of this system can be performed in several steps (see Exercises):

- Find the full solution of eq. (1.215) and discuss the regimes $\omega_0^2 > \gamma^2/4$ and $\omega_0^2 < \gamma^2/4$
- Compute the response function $\tilde{\chi}(\omega)$ of the system. Study the Imaginary and Real part as a function of ω and discuss the limits $\gamma << 1$, $\omega \to 0$, $\omega \to \infty$.
- Look at the particular case of an harmonic force $f(t) = f_0 \cos\omega t$.

3. The exponential of an operator $\hat{O}$ is defined by its Taylor expansion

$$e^{\hat{O}} = \sum_0^\infty \frac{1}{n!}\hat{O}^n \tag{1.216}$$

This look similar to the Taylor expansion of a scalar function. However one hat to be carefull in dealing with operators. For example, in general, for two operators $\hat{A}$ and $\hat{B}$ one has

$$e^{\hat{A}}e^{\hat{B}} \neq e^{\hat{B}}e^{\hat{A}} \tag{1.217}$$

and

$$e^{\hat{A}+\hat{B}} \neq e^{\hat{A}}e^{\hat{B}} \tag{1.218}$$

this is however true if $[\hat{A},\hat{B}] = 0$ i.e. when the two opearators commute. To compute $\exp(\hat{A}+\hat{B})$ in general it is convenient to consider the new operator

$$\hat{O} = e^{\lambda(\hat{A}+\hat{B})}e^{-\lambda\hat{A}} \tag{1.219}$$

- Show that

$$\frac{d\hat{O}}{d\lambda} = e^{\lambda(\hat{A}+\hat{B})}\hat{B}e^{-\lambda\hat{A}} \tag{1.220}$$

- Verify that

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} + \int_0^1 d\lambda e^{\lambda(\hat{A}+\hat{B})}\hat{B}e^{(1-\lambda)\hat{A}} \tag{1.221}$$

- As an application of the above identity show that for $F << 1$

$$e^{\hat{A}+F\hat{B}} = e^{\hat{A}} + F\int_0^1 d\lambda e^{\lambda\hat{A}}\hat{B}e^{(1-\lambda)\hat{A}} + O(F^2) \tag{1.222}$$

- Compute within the same approximation $Tr\left[e^{\hat{A}+F\hat{B}}\right]$

4. Show that the Lagrangian (1.223)

$$\boxed{\langle A\rangle(t) = \int A(q(t),p(t))\rho(q,p,t=0)dqdp.} \tag{1.223}$$

and Eulerian (1.224)

$$\boxed{\langle A\rangle(t) = \int A(q(0),p(0))\rho(q(0),p(0),t)dqdp} \tag{1.224}$$

This can be done by using the Liouville equation and performing succesive integrations by parts, or equivalently by successive iterations of the property

$$\int dqdp\rho(q,p,0)i\mathcal{L}A(q,p) = -\int dqdpA(q,p)i\mathcal{L}\rho(q,p,0). \tag{1.225}$$

5. Show that, because of the time translational invariance at equilibrium, the following identity holds

$$\dot{C}_{AB}(t) = \langle\dot{B}(t)A(0)\rangle_0 = -\langle B(t)\dot{A}(0)\rangle_0 \tag{1.226}$$

where we have assumed for simplcity that $\langle A(0)\rangle_0 = 0$ and the lower case $_c$ has been removed by the definition of the correlation function.

6. In the notes we have shown that, by using the protocol in which the perturbation is switched on at $t = t_0$, the response function of a quantum system is given by the Kubo formula

$$\boxed{\chi_{AB}(t) = \frac{i}{\hbar}\Theta(t)\langle[\hat{B}_I(t),\hat{A}\rangle_0.} \tag{1.227}$$

Show that for a classical system the Kub0 formula is given by

$$\boxed{\chi_{AB}(t) = \Theta(t)\langle\{B(t),A\}\rangle_0 = \beta\Theta(t)\langle B(t)\dot{A}\rangle_0.} \tag{1.228}$$

7. Given two operators $\hat{A}_i(\vec{r},t)$ and $\hat{A}_j(\vec{r}',t')$ the correlation function at equilibrium is given by

$$C_{A_iA_j}(\vec{r},\vec{r}',t,t') = \langle\hat{A}_i(\vec{r},t)\hat{A}_j(\vec{r}',t')\rangle_0 Tr\{\hat{\rho}_0\hat{A}_i(\vec{r},t)\hat{A}_j(\vec{r}',t')\} \tag{1.229}$$

On the other hand , since the system is in thermodynamic equilibrium, the correllation functions do not depend separately on t and t' but only on $t - t' = \tau$. If we now introduce the Fourier transform in t of the operators

$$\hat{A}(\vec{r},\omega) = \int_{\mathbb{R}} \hat{A}(\vec{r},t)e^{i\omega t}dt \tag{1.230}$$

since the correlation function depends only on $t - t'$ we have

$$\langle \hat{A}_i(\vec{r}, \omega)\hat{A}_j(\vec{r}', \omega')\rangle_0 = 2\pi\delta(\omega + \omega')C_{A_iA_j}(\vec{r}, \omega; \vec{r}') \tag{1.231}$$

or

$$C_{A_iA_j}(\vec{r}, \omega; \vec{r}') = \int_{\mathbb{R}} C_{A_iA_j}(\vec{r}, t; \vec{r}', 0)e^{i\omega t}dt \tag{1.232}$$

If in addition the system is traslational invariant in space it is convenient to introduce the spatial Fourier transfor of the operator $\hat{A}(\vec{r}, t)$

$$\hat{A}(\vec{k}, t) = \int_{\mathbb{R}^3} \hat{A}(\vec{r}, t)e^{-i\vec{k}\cdot\vec{r}}d\vec{r}. \tag{1.233}$$

In order to compute the Fourier transform of the correlation function $C_{A_iA_j}$ we can use the invariance property with respect to space translation that allows to write

$$C_{A_iA_j}(\vec{r}, t) = \langle A_i(\vec{r} + \vec{r}', t)A_j(\vec{r}', 0)\rangle_0 \tag{1.234}$$

The Fourier transform can be then computed by introducing the identity $\frac{1}{V}\int d\vec{r}' = 1$:

$$\int C_{A_iA_j}(\vec{r}, t)e^{-i\vec{k}\cdot\vec{r}}d\vec{r} = \frac{1}{V}\langle A_i(\vec{k}, t)A_j(-\vec{k}, 0)\rangle_0 \tag{1.235}$$

The spatial and temporal Fourier transform of the correlation function is defined as

$$\boxed{C_{A_iA_j}(\vec{k}, \omega) = \frac{1}{V}\int_{\mathbb{R}} \langle A_i(\vec{k}, t)A_j(-\vec{k}, 0)\rangle_0 e^{i\omega t}dt.} \tag{1.236}$$

Show that the following general properties of the autocorrelation function $\langle A(\vec{k}, t)A(-\vec{k}, 0)\rangle_0$ at equilibrium holds:

1. Stationarity
$$\langle A(\vec{k}, t)A(-\vec{k}, 0)\rangle_0 = \langle A(\vec{k}, 0)A(-\vec{k}, -t)\rangle_0 \tag{1.237}$$
2. Complex conjugate
$$\langle A(\vec{k}, t)A(-\vec{k}, 0)\rangle_0^* = \langle A(\vec{k}, 0)A(-\vec{k}, t)\rangle_0 \tag{1.238}$$

$$\langle A(\vec{k}, 0)A(-\vec{k}, t)\rangle_0 = \langle A(-\vec{k}, t - i\hbar\beta)A(-\vec{k}, 0)\rangle_0 \tag{1.239}$$

8. Consider a classical system of charged particles with a Hamiltonian $H_0(q, p)$. Turning on an external field $\mathbf{E}(t)$ leads to the Hamiltonian $H = H_0(q, p) - e\sum_i \mathbf{q}_i\mathbf{E}(t)$.

(a) Show that the solution of Liouville's equation to first order in $\mathbf{E}(t)$ is

$$\rho(q, p, t) = e^{-\beta H_0(q,p)}\left[1 + \beta e\sum_i \int_{-\infty}^{t} \dot{\mathbf{q}}_i(t')\cdot\mathbf{E}(t')\right]. \tag{1.240}$$

(b) In terms of the current density $\mathbf{j}(\mathbf{r}, t) = e\sum_i \dot{\mathbf{q}}_i\delta^3(\mathbf{r} - \mathbf{q}_i)$ show that for $\mathbf{E} = \mathbf{E}(\omega)e^{i\omega t}$ the linear response is given by

$$\langle j_\mu(t)\rangle = \sigma_{\mu\nu}(\omega)E_\nu(\omega)e^{i\omega t}, \tag{1.241}$$

where μ and ν are vector components and

$$\sigma_{\mu\nu}(\omega) = \beta\int_0^\infty e^{-i\omega\tau}\langle j_\mu(0, 0)j_\nu(\mathbf{r}, -\tau)\rangle_0 d\tau d^3r \tag{1.242}$$

where $\langle\cdots\rangle_0$ ia an average of the $\mathbf{E} = 0$ system.

c Rewrite (b) for $\mathbf{j}(\mathbf{r},t)$ in presence of a position dependent $\mathbf{E}(\mathbf{r},t)$. Integrating $\mathbf{j}(\mathbf{r},t)$ over a cross section perpendicular to $\mathbf{E}(\mathbf{r},t)$ yields the current $I(t)$. Show that the resistance $R(\omega)$ satisfies

$$R^{-1}(\omega) = \beta \int_0^\infty e^{-i\omega\tau} \langle I(0) I(\tau) \rangle_0 d\tau. \tag{1.243}$$