09. Linear Response and Equilibrium Dynamics

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Abstract
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Linear response and equilibrium dynamics

- Linear response and equilibrium dynamics
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Many-body system perturbed by radiation field

Quantum many-body system in thermal equilibrium.

Hamiltonian: $\mathcal{H}_0$.

Density operator: $\rho_0 = Z_0^{-1} e^{-\beta \mathcal{H}_0}$ with $\beta = 1/k_B T$, $Z_0 = \text{Tr}[e^{-\beta \mathcal{H}_0}]$.

Dynamical variable: $A$ (describing some attribute of system).

Heisenberg equation of motion: $\frac{dA}{dt} = \frac{i}{\hbar} [\mathcal{H}_0, A]$.

Time evolution: $A(t) = e^{i\mathcal{H}_0 t/\hbar} A e^{-i\mathcal{H}_0 t/\hbar}$ (formal solution).

Stationarity, $[\rho_0, \mathcal{H}_0] = 0$, implies time-independent expectation values:

\[ \langle A(t) \rangle_0 = \frac{1}{Z_0} \text{Tr} \left[ e^{-\beta \mathcal{H}_0} e^{i\mathcal{H}_0 t/\hbar} A e^{-i\mathcal{H}_0 t/\hbar} \right] = \frac{1}{Z_0} \text{Tr} \left[ e^{-\beta \mathcal{H}_0} A \right] = \text{const}. \]

Time-dependent quantities do exist in thermal equilibrium!

Dynamic correlation function: $\langle A(t)A(0) \rangle_0 = \frac{1}{Z_0} \text{Tr} \left[ e^{-\beta \mathcal{H}_0} e^{i\mathcal{H}_0 t/\hbar} A e^{-i\mathcal{H}_0 t/\hbar} A \right]$.

In an experiment the system is necessarily perturbed:

\[ \mathcal{H}(t) = \mathcal{H}_0 - b(t)B, \]

where $b(t)$ is some kind of radiation field (c-number) and $B$ is the dynamical system variable (operator) to which the field couples.

Examples:

<table>
<thead>
<tr>
<th>$b(t)$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic field</td>
<td>magnetization</td>
</tr>
<tr>
<td>electric field</td>
<td>electric polarization</td>
</tr>
<tr>
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</table>
Linear response

Radiation field $b(t)$ perturbs equilibrium state of the system $\mathcal{H}_0$ via coupling to dynamical variable $B$.

System response to perturbation measured as expectation value of dynamical variable $A$.

Linear response to weak perturbations is predominant under most circumstances (away from criticality).

Response function $\tilde{\chi}_{AB}(t)$ (definition):

$$\langle A(t) \rangle - \langle A \rangle_0 = \int_{-\infty}^{\infty} dt' \tilde{\chi}_{AB}(t-t')b(t').$$

- Linearity: $\tilde{\chi}_{AB}(t)$ is independent of $b(t)$.
- Hermiticity: $\tilde{\chi}_{AB}(t)$ is a real function.
- Causality: $\tilde{\chi}_{AB}(t) = 0$ for $t < 0$.
- Smoothness: $|\tilde{\chi}_{AB}(t)| < \infty$.
- Analyticity: $\tilde{\chi}_{AB}(t) \to 0$ for $t \to \infty$.

Generalized susceptibility (via Fourier transform):

$$\chi_{AB}(\zeta) = \int_{-\infty}^{+\infty} dt e^{i\zeta t} \tilde{\chi}_{AB}(t) \quad (\text{analytic for } \Im\{\zeta\} > 0).$$

Complex function of real frequency:

$$\chi_{AB}(\omega) = \lim_{\epsilon \to 0} \chi_{AB}(\omega + i\epsilon) = \chi'_{AB}(\omega) + i\chi''_{AB}(\omega).$$

Linear response in frequency domain means no mixing of frequencies:

$$\alpha(\omega) = \chi_{AB}(\omega)\beta(\omega),$$

where

$$\tilde{\chi}_{AB}(t) = \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{2\pi} \chi_{AB}(\omega), \quad b(t) = \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{2\pi} \beta(\omega),$$

$$\langle A(t) \rangle - \langle A \rangle_0 = \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{2\pi} \alpha(\omega).$$
Interaction representation for time evolution of $\mathcal{H}(t) = \mathcal{H}_0 - b(t)B$:

\[
\frac{dA}{dt} = \frac{i}{\hbar}[\mathcal{H}_0, A] \quad \Rightarrow \quad A(t) = e^{i\mathcal{H}_0 t/\hbar}A e^{-i\mathcal{H}_0 t/\hbar},
\]

\[
\frac{dB}{dt} = \frac{i}{\hbar}[\mathcal{H}_0, B] \quad \Rightarrow \quad B(t) = e^{i\mathcal{H}_0 t/\hbar}B e^{-i\mathcal{H}_0 t/\hbar},
\]

\[
\frac{d\rho}{dt} = -\frac{i}{\hbar}[-b(t)B, \rho] \quad \Rightarrow \quad \rho(t) = \rho_0 + \frac{i}{\hbar} \int_{-\infty}^{t} dt' b(t') [B(t'), \rho(t')].
\]

Set $\rho(t) = \rho_0 + \rho_1(t)$ with $\rho_0 = Z_0^{-1} e^{-\beta \mathcal{H}_0}$.

Full response: $\langle A(t) \rangle - \langle A \rangle_0 = \text{Tr}\{\rho_1(t)A(t)\}$

Leading correction to $\rho_0$: $\rho_1(t) \simeq \frac{i}{\hbar} \int_{-\infty}^{t} dt' b(t') [B(t'), \rho_0]$.

Linear response:

\[
\langle A(t) \rangle - \langle A \rangle_0 = \frac{i}{\hbar} \int_{-\infty}^{t} dt' b(t') \text{Tr}\{[B(t'), \rho_0]A(t)\}
\]

\[
= \frac{i}{\hbar} \int_{-\infty}^{t} dt' b(t') \text{Tr}\{\rho_0[A(t), B(t')]\}
\]

\[
= \frac{i}{\hbar} \int_{-\infty}^{t} dt' b(t') \langle[A(t), B(t')]\rangle_0.
\]

Compare with definition of response function in [nl26].

**Kubo formula:**

\[
\tilde{\chi}_{AB}(t - t') = \frac{i}{\hbar} \theta(t - t') \langle[A(t), B(t')]\rangle_0.
\]

- Causality requirement is ensured by step function $\theta(t - t')$.
- Hermitian $A, B$ imply Hermitian $i[A, B]$. Hence $\tilde{\chi}(t)$ is real.
- Linear response depends only on equilibrium quantities.
- Response function only depends on time difference $t - t'$.

The Kubo formula establishes a general link between

- the dynamical properties of a many-body system at equilibrium,
- the dynamical response of that system to experimental probes.
Symmetry properties

Response function for Hermitian $A$ is real and vanishes for $t < 0$:

$$\tilde{\chi}_{AA}(t) = \frac{i}{\hbar} \theta(t) \langle [A(t), A] \rangle = \tilde{\chi}'_{AA}(t) + i\tilde{\chi}''_{AA}(t).$$

Reactive part is real and symmetric:

$$\tilde{\chi}'_{AA}(t) = \frac{1}{2} [\tilde{\chi}_{AA}(t) + \tilde{\chi}_{AA}(-t)] = \frac{i}{2\hbar} \text{sgn}(t) \langle [A(t), A] \rangle.$$  

Dissipative part is imaginary and antisymmetric:

$$\tilde{\chi}''_{AA}(t) = \frac{1}{2i} [\tilde{\chi}_{AA}(t) - \tilde{\chi}_{AA}(-t)] = \frac{1}{2\hbar} \langle [A(t), A] \rangle.$$  

Response function is determined by its reactive or dissipative part alone:

$$\tilde{\chi}_{AA}(t) = 2\theta(t)\tilde{\chi}'_{AA}(t) = 2i\theta(t)\tilde{\chi}''_{AA}(t).$$

Generalized susceptibility is complex:

$$\chi_{AA}(\omega) = \chi'_{AA}(\omega) + i\chi''_{AA}(\omega).$$

Real part is symmetric:

$$\chi'_{AA}(\omega) = \frac{1}{2} [\chi_{AA}(\omega) + \chi_{AA}(-\omega)] = \chi'_{AA}(-\omega).$$

Imaginary part is antisymmetric:

$$\chi''_{AA}(\omega) = \frac{1}{2i} [\chi_{AA}(\omega) - \chi_{AA}(-\omega)] = -\chi''_{AA}(-\omega).$$
Kramers-Kronig dispersion relations

Use analyticity of $\chi_{AA}(\zeta)$ for $\Im\{\zeta\} > 0$.

Cauchy integral: $\chi_{AA}(\zeta) = \frac{1}{2\pi i} \int_{c} d\zeta' \frac{\chi_{AA}(\zeta')}{\zeta' - \zeta}$.

Integral converges for $\zeta' = \omega' + i\epsilon'$, $\epsilon' \to 0$.
Integral along semi-circle vanishes for $R \to \infty$:
Sum rule implies $\chi_{AA}(\zeta) \lesssim |\zeta|^{-1}$ for $|\zeta| \to \infty$.

$\Rightarrow \chi_{AA}(\zeta) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} d\omega' \frac{\chi_{AA}(\omega')}{\omega' - \zeta}$.

Set $\zeta = \omega + i\epsilon$ and use $\lim_{\epsilon \to 0} \frac{1}{\omega' - \omega \mp i\epsilon} = P \frac{1}{\omega' - \omega} \pm i\pi \delta(\omega' - \omega)$.

$\chi_{AA}(\omega) = \lim_{\epsilon \to 0} \chi_{AA}(\omega + i\epsilon) = \lim_{\epsilon \to 0} \frac{1}{2\pi i} \int_{-\infty}^{+\infty} d\omega' \frac{\chi_{AA}(\omega')}{\omega' - \omega - i\epsilon}$

$= \frac{1}{2\pi i} P \int_{-\infty}^{+\infty} d\omega' \frac{\chi_{AA}(\omega')}{\omega' - \omega} + \frac{1}{2} \int_{-\infty}^{+\infty} d\omega' \chi_{AA}(\omega') \delta(\omega' - \omega)$.

$\Rightarrow \chi_{AA}(\omega) = \chi'_{AA}(\omega) + i\chi''_{AA}(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \frac{\chi_{AA}(\omega')}{\omega' - \omega}$.

Consider real and imaginary parts of this relation separately:

$\chi'_{AA}(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \frac{\chi''_{AA}(\omega')}{\omega' - \omega}, \quad \chi''_{AA}(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} d\omega' \frac{\chi'_{AA}(\omega')}{\omega' - \omega}$.

The Kramers-Kronig relations are a consequence of the causality property of the response function.
Causality property of response function.

The Kramers-Kronig dispersion relations
\[
\chi''_{AA}(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\chi''_{AA}(\omega')}{\omega' - \omega}, \quad \chi'_{AA}(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\chi'_{AA}(\omega')}{\omega' - \omega}
\]

between the reactive part $\chi'_{AA}(\omega)$ and the dissipative part $\chi''_{AA}(\omega)$ of the generalized susceptibility $\chi_{AA}(\omega)$ are a direct consequence of the causality property of the response function $\tilde{\chi}_{AA}(t)$. Show that $\chi_{AA}(\zeta)$ for $\Im(\zeta) > 0$ can be expressed in terms of $\chi''_{AA}(\omega)$ as follows:
\[
\chi_{AA}(\zeta) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{\chi''_{AA}(\omega)}{\omega - \zeta}.
\]

Solution:
Energy transfer

Hamiltonian of system and interaction with radiation field:

\[ H(t) = H_0 + H_1(t) = H_0 - a(t)A. \]

Interaction between system and radiation field involves energy transfer. Rate at which average energy of system changes:

\[ \frac{d}{dt} \langle H_0 \rangle = \frac{1}{i\hbar} \langle [H_0, H(t)] \rangle = -\frac{1}{i\hbar} a(t) \langle [H_0, A(t)] \rangle. \]

Calculate linear response \( \langle [H_0, A(t)] \rangle - \langle [H_0, A] \rangle_0 \).

Application of Kubo formula [nln27]:

\[ \langle [H_0, A(t)] \rangle = \frac{i}{\hbar} \int_{-\infty}^{t} dt' a(t') \langle [H_0, A(t)] \rangle_0. \]

\[ \Rightarrow \frac{d}{dt} \langle H_0 \rangle = -\frac{1}{\hbar^2} \int_{-\infty}^{t} dt' a(t') \langle [H_0, A(t')] \rangle_0 \]

\[ = \frac{i}{\hbar} \int_{-\infty}^{t} dt' a(t') \frac{\partial}{\partial t} \langle [A(t), A(t')] \rangle_0 \]

\[ = \int_{-\infty}^{+\infty} dt' a(t) a(t') \frac{\partial}{\partial t} \tilde{\chi}_{AA}(t - t') \]

with response function

\[ \tilde{\chi}_{AA}(t - t') = \frac{i}{\hbar} \theta(t - t') \langle [A(t), A(t')] \rangle_0. \]

The time-averaged energy transfer depends only on the absorptive part, \( \chi''_{AA}(\omega) \), of the generalized susceptibility as demonstrated in [nex64] for a monochromatic perturbation.

\[ ^1 \text{We have } \langle [H_0, A] \rangle_0 = \text{Tr} \{ e^{-\beta H_0} H_0 A - e^{-\beta H_0} A H_0 \} / Z_0 = 0 \text{ in thermal equilibrium.} \]
Reactive and absorptive parts of linear response.

In the framework of linear response theory for \( H = H_0 - a(t)A \), the rate of energy transfer between the system and the radiation field is

\[
\frac{d}{dt} \langle H_0 \rangle = \int_{-\infty}^{\infty} dt' a(t)a(t') \left( \frac{\partial}{\partial t} \tilde{\chi}_{AA}(t - t') \right),
\]

where

\[
\tilde{\chi}_{AA}(t - t') = \frac{1}{\hbar} \theta(t - t') \langle [A(t), A(t')] \rangle_0
\]

is the Kubo formula for the response function (see [nln38].)

(a) Evaluate this expression for a monochromatic perturbation,

\[
a(t) = \frac{1}{2} a_m (e^{i\omega_0 t} + e^{-i\omega_0 t})
\]

and express it in terms of the reactive part, \( \chi'_AA(\omega) \), and the absorptive (dissipative) part, \( \chi''AA(\omega) \), of the generalized susceptibility \( \chi_{AA}(\omega) \) as defined in [nln26].

(b) Show that the time-averaged energy transfer depends only on the absorptive part of \( \chi_{AA}(\omega) \):

\[
\frac{d}{dt} \langle H_0 \rangle = \frac{1}{2} a_m^2 \omega_0 \chi''AA(\omega_0).
\]

Solution:
Fluctuation-dissipation theorem

Three dynamical quantities in time domain:

\[ \chi''_{AA}(t) \doteq \frac{1}{2\hbar} \langle [A(t), A]_\to \rangle \quad \text{response function (dissipative part)}, \]

\[ \Phi_{AA}(t) \doteq \frac{1}{2} \langle [A(t), A]_+ - \langle A \rangle \rangle^2 \quad \text{fluctuation function}, \]

\[ S_{AA}(t) \doteq \langle A(t)A \rangle - \langle A \rangle^2 \quad \text{correlation function}. \]

Relations:

\[ \chi''_{AA}(t) = \frac{1}{2\hbar} \left[ S_{AA}(t) - S_{AA}(-t) \right], \quad \Phi_{AA}(t) = \frac{1}{2} \left[ S_{AA}(t) + S_{AA}(-t) \right]. \]

Transformation properties under time reversal (for real \( t \)):

- \( \chi''_{AA}(-t) = -\chi''_{AA}(t) = [\chi''_{AA}(t)]^* \) imaginary and antisymmetric,
- \( \Phi_{AA}(-t) = \Phi_{AA}(t) = [\Phi_{AA}(t)]^* \) real and symmetric,
- \( S_{AA}(-t) = S_{AA}(t - \hbar \beta) = [S_{AA}(t)]^* \) complex.\(^2\)

To make the last symmetry relation more transparent we write

\[ \langle A(-t)A \rangle = \text{Tr} \left[ e^{-\beta \hbar \omega} e^{-i\hbar \omega t/\hbar} A e^{i\hbar \omega t/\hbar} A \right] = \text{Tr} \left[ e^{-\beta \hbar \omega} e^{i\hbar \omega (t - \hbar \beta)/\hbar} A e^{-i\hbar \omega (t - \hbar \beta)/\hbar} A \right] = \langle A(t - \beta/h)A \rangle. \]

The imaginary part of the correlation function vanishes if

- if \( \beta = 0 \) i.e. at infinite temperature,
- if \( \hbar = 0 \) i.e. for classical systems.

\(^1\)using \([\_\_\_]\) for commutators and \([\_\_\_\_]_+\) for anti-commutators.

\(^2\)with symmetric real part and antisymmetric imaginary part.
Three dynamical quantities in frequency domain:

\[ \chi''_{AA}(\omega) \doteq \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \tilde{\chi}'_{AA}(t) \quad \text{dissipation function}, \]

\[ \Phi_{AA}(\omega) \doteq \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \tilde{\Phi}_{AA}(t) \quad \text{spectral density}, \]

\[ S_{AA}(\omega) \doteq \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \tilde{S}_{AA}(t) \quad \text{structure function}. \]

Symmetry properties:

- \( \chi''_{AA}(-\omega) = -\chi''_{AA}(\omega) \) real and antisymmetric,
- \( \Phi_{AA}(-\omega) = \Phi_{AA}(\omega) \) real and symmetric,
- \( S_{AA}(-\omega) = e^{-\beta h\omega} S_{AA}(\omega) \) real and satisfying detailed balance.

Relations:

\[ \chi''_{AA}(\omega) = \frac{1}{2\hbar} \left( 1 - e^{-\beta h\omega} \right) S_{AA}(\omega), \quad \Phi_{AA}(\omega) = \frac{1}{2} \left( 1 + e^{-\beta h\omega} \right) S_{AA}(\omega). \]

Fluctuation-dissipation relation (general quantum version):

\[ \Phi_{AA}(\omega) = \hbar \coth \left( \frac{1}{2} \beta h\omega \right) \chi''_{AA}(\omega). \]

Dissipation effects from an interaction with a weak external force as encoded in \( \chi''_{AA}(\omega) \) are determined by natural fluctuations existing in thermal equilibrium as encoded in \( \Phi_{AA}(\omega) \).

Classical limit (no zero-point fluctuations):

\[ \Phi_{AA}(\omega)_{cl} \xrightarrow{\hbar \to 0} \frac{2k_BT}{\omega} \chi''_{AA}(\omega). \]

Classical fluctuations of any frequency related to static susceptibility:

\[ \langle (A - \langle A \rangle)^2 \rangle = \tilde{\phi}_{AA}(t = 0) = \lim_{t \to 0} \int_{-\infty}^{+\infty} \frac{dw}{2\pi} e^{-i\omega t} \Phi_{AA}(\omega) \]

\[ = k_BT \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega^{-1} \chi''_{AA}(\omega) = k_BT \lim_{\omega' \to 0} \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega \frac{\chi''_{AA}(\omega)}{\omega - \omega'} \]

\[ = k_BT \chi'_{AA}(\omega' = 0) = k_BT \chi_{AA}(\omega' = 0) = k_BT \chi_{AA}. \]
Moment Expansion

Correlation function and structure function:

\[
\tilde{S}_{AA}(t) = \langle A(t)A \rangle - \langle A \rangle^2 = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} S_{AA}(\omega) = \sum_{n=0}^{\infty} \tilde{M}_n \frac{(-it)^n}{n!}.
\]

Frequency moments: use \( \dot{\tilde{S}}_{AA}(t) = \langle \dot{A}(t)A \rangle = (-i/\hbar) \langle [A(t), \mathcal{H}]A \rangle \).

\[
\tilde{M}_n(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \omega^n S_{AA}(\omega) = i^n \left[ \frac{d^n}{dt^n} \tilde{S}_{AA}(t) \right]_{t=0} = \hbar^{-n} \langle [[[A, \mathcal{H}], \mathcal{H}], \cdots, \mathcal{H}]A \rangle.
\]

High-temperature limit \( T \to \infty \):

\[
\tilde{M}_{2k+1} = 0, \quad \tilde{M}_{2k} = \hbar^{-2k} \langle [[[A, \mathcal{H}], \cdots, \mathcal{H}], [A, \mathcal{H}], \cdots, \mathcal{H}]A \rangle.
\]

Classical limit \( \hbar \to 0 \): use \( \dot{\tilde{S}}_{AA}(t) = \langle \dot{A}(t)A \rangle = \langle \{A(t), \mathcal{H}\}A \rangle \).

\[
\tilde{M}_{2k+1} = 0, \quad \tilde{M}_{2k} = (-1)^k \langle \{\cdots\{A, \mathcal{H}\}, \cdots, \mathcal{H}\}A \rangle.
\]

Fluctuation function:

\[
\tilde{\Phi}_{AA}(t) = \frac{1}{2} \langle [A(t), A]_+ \rangle - \langle A \rangle^2 = \sum_{k=0}^{\infty} \tilde{M}_{2k} \frac{(-it)^{2k}}{(2k)!},
\]

\[
\tilde{M}_{2k} = \frac{1}{2\hbar^{2k}} \langle [[[A, \mathcal{H}], \mathcal{H}], \cdots, \mathcal{H}]A \rangle.
\]

Dissipation function:

\[
\tilde{\chi}''_{AA}(t) = \frac{1}{2\hbar} [A(t), A] = \hbar^{-1} \sum_{k=0}^{\infty} \tilde{M}_{2k+1} \frac{(-it)^{2k+1}}{(2k+1)!},
\]

\[
\tilde{M}_{2k+1} = \frac{1}{2\hbar^{2k+1}} \langle [[[A, \mathcal{H}], \cdots, \mathcal{H}, A]_+ \rangle.
\]

Moment expansion not guaranteed to converge.
Convergence problem may be circumnavigated by recursion method.
Spectral representation of dynamical quantities.

Consider a quantum Hamiltonian system with known eigenvalues and eigenvectors,

\[ H|n⟩ = E_n|n⟩, \quad n = 0, 1, \ldots, \]

in thermal equilibrium at temperature \( T \). Express (a) the structure function \( S_{AA}(\omega) \), (b) the spectral density \( Φ_{AA}(\omega) \), (c) the dissipation function \( χ'_{AA}(\omega) \), and (d) the generalized susceptibility \( χ_{AA}(\omega + i\epsilon) \), all defined in [nln39], in terms of the temperature parameter \( \beta = 1/k_B T \), the energy levels \( E_n \), and the matrix elements \( ⟨n|A|m⟩ \). For simplicity assume that \( ⟨A⟩ = Z^{-1} \text{Tr}[e^{-βH}A] = 0 \).

The last result reads

\[ χ_{AA}(\omega + i\epsilon) = \frac{1}{Z} \sum_{m,n} \left( e^{-βE_m} - e^{-βE_n} \right) \frac{|⟨n|A|m⟩|^2}{\hbar\omega - (E_m - E_n) + i\epsilon}. \]

Solution:
The classical relaxator is defined by the equation of motion,

\[ \dot{x} + \frac{1}{\tau_0} x = a(t), \tag{1} \]

where \( \tau_0 \) represents a relaxation time and \( a(t) \) a weak periodic perturbation. The (linear) response function is extracted from the relation

\[ \langle x(t) \rangle - \langle x \rangle_0 = \int_{-\infty}^{t} dt' \tilde{\chi}_{xx}(t-t')a(t'), \tag{2} \]

where \( x(t) \) is the solution of (1).

(a) Solve (1) formally as in [nex53] and compare the result with (2) to show that the response function must be

\[ \tilde{\chi}_{xx}(t) = e^{-t/\tau_0} \theta(t). \tag{3} \]

(b) Calculate the generalized susceptibility \( \chi_{xx}(\omega) \) via Fourier analysis of (1) as in [nex119]. Show that the Fourier transform of (3) yields the same result, namely

\[ \chi_{xx}(\omega) = \frac{\tau_0}{1 - i\omega \tau_0}. \tag{4} \]

(c) Extract from \( \chi_{xx}(\omega) \) its reactive part \( \chi'_{xx}(\omega) \) and its dissipative part \( \chi''_{xx}(\omega) \) as prescribed in [nln30] and verify their symmetry properties.

(d) Use the (classical) fluctuation-dissipation theorem from [nln39] to infer the spectral density \( \Phi_{xx}(\omega) \) from the dissipation function \( \chi''_{xx}(\omega) \).

(e) Retrieve from the generalized susceptibility (4) the response function (3) via inverse Fourier transform carried out as a contour integral.

(f) Retrieve \( \chi'_{xx}(\omega) \) from \( \chi''_{xx}(\omega) \) and vice versa via a numerical principal-value integration of the Kramers-Kronig relations as stated in [nln37]. Use \( \tau = 1 \) and consider the interval \(-2 \leq \omega \leq 2\). Plot the curves obtained via integration for comparison with the analytic expressions. Integrate over the intervals \(-\infty < \omega' < \omega - \epsilon \) and \( \omega + \epsilon < \omega' < +\infty \) with \( 0 < \epsilon \ll 1 \).

**Solution:**
Dielectric Relaxation in Liquid Water

- H$_2$O molecules have permanent electric dipole moment (polar molecules.)
- Alignment of dipole moments with external electric field $E$ is energetically favorable.
- Alignment tendency is counteracted by thermal fluctuations.
- Turning $E$ on/off initiates relaxation process toward equilibrium.

- $P(t)$: instantaneous electric polarization (average dipole moment)
- $\chi_0$: static dielectric susceptibility
- $\tau_0$: characteristic relaxation time
- $E(t)$: oscillating electric field
- $\frac{d}{dt} P(t) = -\frac{1}{\tau_0} [P(t) - \chi_0 E(t)]:$ dielectric relaxation process
- $\langle P \rangle = \chi_0 E$: static (linear) response
- $\chi_{PP}(\omega) = \frac{\chi_0}{\tau_0} \chi_{xx}(\omega):$ link to classical relaxator [nex66]
- $\langle P(t)P \rangle - \langle P \rangle^2 = k_B T \chi_0 e^{-t/\tau_0}:$ correlation fct. (from fluc.-diss. rel.)
- $\langle P^2 \rangle \approx \frac{1}{3} np_0^2 = k_B T \chi_0:$ zero-field limit
- $n$: number density of molecules
- $p_0$: permanent molecular electric dipole moment
- $\chi_0(T) = \frac{np_0^2}{3 k_B T}:$ $T$-dependence of dielectric susceptibility
Linear response of classical oscillator.

The classical oscillator is defined by the equation of motion,

\[ m\ddot{x} + \gamma \dot{x} + m\omega_0^2 x = a(t), \]  

where \( \gamma \) is the attenuation coefficient, \( m\omega_0^2 \) the spring constant, and \( a(t) \) a weak periodic perturbation. The (linear) response function is defined by the relation

\[ \langle x(t) \rangle - \langle x \rangle_0 = \int_{-\infty}^{t} dt' \tilde{\chi}_{xx}(t-t')a(t'), \]

where \( x(t) \) is the solution of (1).

(a) Calculate the generalized susceptibility \( \chi_{xx}(\omega) \) as well as its reactive part \( \chi'_{xx}(\omega) \) and its dissipative part \( \chi''_{xx}(\omega) \).

(b) Use the (classical) fluctuation-dissipation theorem to infer the spectral density \( \Phi_{xx}(\omega) \) from the dissipation function \( \chi''_{xx}(\omega) \).

Solution:
Dynamic Structure Factor

Inelastic scattering of particles (electrons, neutrons, photons,...) involves momentum transfer, $\hbar \mathbf{q} = \hbar \mathbf{k}_f - \hbar \mathbf{k}_i$, and energy transfer, $\hbar \omega = E_f - E_i$, between scattered particles and collective excitations in the system.

Scattering cross section is proportional to dynamic structure factor:

$$\frac{d^2 \sigma}{d\omega d\Omega} \propto S_{AA}(\mathbf{q}, \omega).$$

Target system: $\mathcal{H}_0 |\lambda\rangle = E_\lambda |\lambda\rangle$.

Interaction with scattering radiation: $A(\mathbf{q}, t) = \int d^3 r \ e^{i \mathbf{k}_f \cdot \mathbf{r}} V(\mathbf{r}, t) e^{i \mathbf{k}_i \cdot \mathbf{r}}$.

Scattering events produce transitions $|\lambda\rangle \rightarrow |\lambda'\rangle$ in target system.

Transition rates: $T(\mathbf{q}, \omega) = |\langle \lambda| A(\mathbf{q}) |\lambda'\rangle|^2 \delta(\hbar \omega - E_{\lambda'} + E_\lambda) \delta_{\mathbf{q} - \mathbf{k}_{\lambda'} + \mathbf{k}_\lambda + \mathbf{Q}}$.

Dynamic structure factor: $S_{AA}(\mathbf{q}, \omega) = \frac{2 \pi}{Z} \sum_{\lambda, \lambda'} e^{-\beta E_\lambda} T(\mathbf{q}, \omega)$.

Electron scattering (Coulomb interaction with target charge density):

$$V(\mathbf{r}, t) = \frac{e \rho(\mathbf{R}, t)}{|\mathbf{r} - \mathbf{R}|} \Rightarrow S_{\rho \rho}(\mathbf{q}, \omega) = \int_{-\infty}^{+\infty} dt \ e^{i \omega t} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle.$$

Nuclear neutron scattering (contact interaction with target particle density):

$$V(\mathbf{r}, t) = a \delta(\mathbf{r} - \mathbf{R}) n(\mathbf{R}, t) \Rightarrow S_{nn}(\mathbf{q}, \omega) = \int_{-\infty}^{+\infty} dt \ e^{i \omega t} \langle n(\mathbf{q}, t) n(-\mathbf{q}, 0) \rangle.$$

Magnetic neutron scattering (interaction with target magnetisation):

$$V(\mathbf{r}, t) = S_\mu(\mathbf{r}) V_{\mu \nu}(\mathbf{r} - \mathbf{R}) M_\nu(\mathbf{R}, t) \Rightarrow S_{\mu \nu}(\mathbf{q}, \omega) = \int_{-\infty}^{+\infty} dt \ e^{i \omega t} \langle M_\mu(\mathbf{q}, t) M_\nu(-\mathbf{q}, 0) \rangle.$$

Light scattering (interaction with inhomogeneities in dielectric function):

$$\epsilon(\mathbf{r}, t) \Rightarrow S_{\epsilon \epsilon}(\mathbf{q}, \omega) = \int_{-\infty}^{+\infty} dt \ e^{i \omega t} \langle \epsilon(\mathbf{q}, t) \epsilon(-\mathbf{q}, 0) \rangle.$$
Scattering from Free Atoms \[\text{[nlh93]}\]

Consider a dilute gas of atoms with mass \(M\). Interaction between gas atoms limited to (rare) collisions.

Hamiltonian: \(\mathcal{H} = \frac{p^2}{2M}\) (dominated by kinetic energy).

Contact interaction between gas atom at position \(\mathbf{R}(t)\) and scattering radiation (see [nlh89]) defines dynamical variable relevant for scattering process:

\[
A(\mathbf{q}, t) = \int d^3 r \ e^{i\mathbf{q} \cdot \mathbf{r}} \delta(\mathbf{r} - \mathbf{R}(t)) = e^{i\mathbf{q} \cdot \mathbf{R}(t)}. \tag{1}
\]

Equation of motion (setting \(\hbar \equiv 1\)):

\[
\frac{i}{\hbar} \frac{\partial A}{\partial t} = [A, \mathcal{H}] = \frac{1}{2M} \left[ e^{i\mathbf{q} \cdot \mathbf{R}}, p^2 \right] = -A \frac{1}{2M} (2\mathbf{q} \cdot \mathbf{p} + q^2). \tag{2}
\]

Formal solution:

\[
A(\mathbf{q}, t) = e^{i\mathbf{q} \cdot \mathbf{R}(0)} \exp \left( \frac{it(2\mathbf{q} \cdot \mathbf{p} + q^2)}{2M} \right). \tag{3}
\]

Correlation function: \(\tilde{S}_{AA}(\mathbf{q}, t) \doteq \langle A^\dagger(\mathbf{q}, t)A(\mathbf{q}, 0) \rangle\).

\[
\Rightarrow \quad \tilde{S}_{AA}(\mathbf{q}, t) = e^{-itq^2/2M} \left\langle \exp \left( -it\mathbf{q} \cdot \mathbf{p}/M \right) \right\rangle \nonumber
\]

\[
= e^{-itq^2/2M} \frac{1}{Z} \int d^3 p \ e^{-\beta p^2/2M} e^{-it\mathbf{q} \cdot \mathbf{p}/M} \nonumber
\]

\[
= e^{-itq^2/2M} \frac{1}{Z} \int d^3 p \ \exp \left( \frac{(\sqrt{\beta} \mathbf{p} + it\mathbf{q}/\sqrt{\beta})^2}{2M} \right) e^{-q^2t^2/2M\beta} \nonumber
\]

\[
= \exp \left( -\frac{q^2(t^2/\beta + it)}{2M} \right). \tag{4}
\]

Third line: Gaussian integral is unaffected by a constant shift in \(\mathbf{p}\).

Note symmetry property from [nlh39]: \(\tilde{S}_{AA}(\mathbf{q}, -t) = \tilde{S}_{AA}(\mathbf{q}, t - i\beta)\).

---

\(^1\) Use \([\mathbf{R}, \mathbf{p}] = 1, [A, \mathbf{p}] = -\mathbf{q}A, [A, p^2] = [A, \mathbf{p}] \cdot \mathbf{p} + \mathbf{p} \cdot [A, \mathbf{p}] = -A\mathbf{q} \cdot \mathbf{p} - \mathbf{p} \cdot \mathbf{q}A, A\mathbf{q} \cdot \mathbf{p} - \mathbf{p} \cdot \mathbf{q}A = -Aq^2, \Rightarrow [\mathbf{A}, p^2] = -A(2\mathbf{q} \cdot \mathbf{p} + q^2)\).
Dynamic structure factor via Fourier transform:

\[ S_{AA}(\mathbf{q}, \omega) = \int_{-\infty}^{+\infty} dt \, e^{\omega t} \tilde{S}_{AA}(\mathbf{q}, t) \]

\[ = \sqrt{2\pi M \beta q^2} \exp \left( -\frac{M \beta}{2q^2} \left[ \omega - \frac{q^2}{2M} \right]^2 \right). \quad (5) \]

- Scattering is isotropic, only dependent on magnitude of \( q \).
- Maximum intensity occurs when energy transfer \( \omega \) and momentum transfer \( q \) reflect energy momentum relation, \( \omega = \frac{q^2}{2M} \), of free, non-relativistic gas particle.
- Lineshape broadens with increasing temperature and/or decreasing mass of gas atoms.
- Note detailed-balance condition from [nlh39]:

\[ S_{AA}(\mathbf{q}, -\omega) = e^{-\beta \omega} S_{AA}(\mathbf{q}, \omega). \]

- In the limit \( M \to \infty \) at fixed temperature, the atoms slow down and come to rest. The scattering becomes elastic in nature, still isotropic and with zero energy transfer:

\[ S_{AA}(\mathbf{q}, \omega) \xrightarrow{M \to \infty} 2\pi \delta(\omega). \]
Scattering from Atoms Bound to Lattice

Consider array of atoms harmonically bound to sites of rigid lattice. We set \( h = 1 \) and atomic mass \( M = 1 \):

Hamiltonian: \( \mathcal{H} = \frac{1}{2}(p^2 + \omega_0^2 a^2) = \omega_0 \left( a^\dagger a + \frac{1}{2} \right) \).

Displacement of atom from equilibrium position: \( u(t) = \frac{1}{\sqrt{2\omega_0}}(ae^{-i\omega_0 t} + a^\dagger e^{i\omega_0 t}) \).

Dynamical variable: \( A(q, t) = e^{iqu(t)} \).

Correlation function: \( \tilde{S}_{AA}(q, t) \equiv \langle A^\dagger(q, 0)A(q, -t) \rangle \).

Use Baker-Hausdorff expansion: \( e^{A}e^{B} = \exp \left( A + B + \frac{1}{2}[A, B] + \ldots \right) \).

\[ \Rightarrow \quad \tilde{S}_{AA}(q, t) = \langle e^{-iqu}e^{iqu(-t)} \rangle = \langle e^{iq[u(-t)-u]} \rangle e^{2[iu(-t)]/2} = e^{-q^2[(u(-t)-u)^2]/2} = e^{-q^2[(u^2) - (uu(-t))]/2}. \] (1)

Boson distribution: \( \langle a^\dagger a \rangle = n_B = \frac{1}{e^{\beta \omega_0/2} - 1} \quad \Rightarrow \quad \langle aa^\dagger \rangle = 1 + n_B \).

Debye-Waller factor: \( W = \frac{1}{2}q^2\langle u^2 \rangle = \frac{q^2}{4\omega_0} \coth \frac{\beta \omega_0}{2} \quad \Rightarrow \quad e^{-q^2\langle u^2 \rangle} = e^{-2W} \).

\[ \langle uu(-t) \rangle = \frac{1}{2\omega_0} \left[ \langle a^\dagger a \rangle e^{i\omega_0 t} + \langle aa^\dagger \rangle e^{-i\omega_0 t} \right] = \frac{1}{4\omega_0} \coth \frac{\beta \omega_0}{2} \left[ e^{i\omega_0 t + \beta \omega_0/2} + e^{i\omega_0 t - \beta \omega_0/2} \right]. \] (2)

Use \( e^y(s+1/s/2) = \sum_{n=-\infty}^{+\infty} s^n I_n(y) \) with \( y = \frac{q^2}{2\omega_0} \coth \frac{\beta \omega_0}{2}, s = e^{-\omega_0 t + \beta \omega_0/2} \).

\[ \tilde{S}_{AA}(q, t) = e^{-2W} \sum_{n=-\infty}^{+\infty} I_n \left( \frac{q^2}{2\omega_0} \coth \frac{\beta \omega_0}{2} \right) \exp \left( \frac{1}{2} \beta n\omega_0 - i\omega_0 t \right). \] (3)

\[ S_{AA}(q, \omega) = e^{\beta \omega/2 - 2W} \sum_{n=-\infty}^{+\infty} I_n \left( \frac{q^2}{2\omega_0} \coth \frac{\beta \omega_0}{2} \right) \delta(\omega - n\omega_0). \] (4)

---

1 We consider component of displacement parallel to \( q = k_f - k_i \) only.

2 Use also \( \langle e^{A} \rangle = e^{\langle A^2 \rangle/2} \) for linear combinations of boson operators.

3 \( I_n(y) \) are modified Bessel functions of the first kind. Note that \( I_{-n}(y) = I_n(y) \).
Scattering from Harmonic Crystal

Atoms of mass $M$ are harmonically coupled via a bilinear form in displacement coordinates. Spatial Fourier transform produces normal modes: noninteracting collective excitations (phonons) representing oscillating patterns of specific wave vectors $k$ and excitation energies determined by a characteristic dispersion relation $\epsilon(k)$.

$$\mathcal{H} = \sum_l \frac{p_l^2}{2M} + \frac{1}{2} \sum_{l,l'} \mathbf{u}_l \cdot D_{ll'} \cdot \mathbf{u}_{l'} = \sum_k \epsilon(k)a_k^\dagger a_k.$$  

Correlation function:

$$\tilde{S}(q,t) = \langle e^{-iq \cdot u_l} e^{iq \cdot u_{l'}(-t)} \rangle$$

$$= \exp \left( -\frac{1}{2} \langle [\mathbf{q} \cdot \mathbf{u}_l]^2 \rangle - \frac{1}{2} \langle [\mathbf{q} \cdot \mathbf{u}_{l'}(-t)]^2 \rangle + \langle [\mathbf{q} \cdot \mathbf{u}_l][\mathbf{q} \cdot \mathbf{u}_{l'}(-t)] \rangle \right)$$

Debye-Waller factor from $\frac{1}{2} \langle [\mathbf{q} \cdot \mathbf{u}_l]^2 \rangle = \frac{1}{2} \langle [\mathbf{q} \cdot \mathbf{u}_{l'}(-t)]^2 \rangle = W$.

Expansion into $m$-phonon processes:

$$\exp \left( \langle [\mathbf{q} \cdot \mathbf{u}_l][\mathbf{q} \cdot \mathbf{u}_{l'}(-t)] \rangle \right) = \sum_{m=0}^\infty \frac{1}{m!} \langle [\mathbf{q} \cdot \mathbf{u}_l][\mathbf{q} \cdot \mathbf{u}_{l'}(-t)] \rangle^m.$$  

Dynamic structure factor:

$$S(q,\omega) = e^{-2W} \frac{1}{N} \sum_{l,l'} e^{i\mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_{l'})} \int_{-\infty}^{+\infty} dt e^{i\omega t} \exp \left( \langle [\mathbf{q} \cdot \mathbf{u}_l][\mathbf{q} \cdot \mathbf{u}_{l'}(-t)] \rangle \right).$$

$m = 0$: Bragg scattering

$$S(q,\omega)_0 \propto e^{-2W} \delta(\omega) \sum_G \delta_{q,G}; \quad G: \text{reciprocal lattice vector.}$$

$m = 1$: 1-phonon contributions

$$S(q,\omega)_1 \propto e^{-2W} \frac{[\mathbf{q} \cdot \mathbf{e}(k)]^2}{2M\epsilon(k)} \left( [1 + n_B(\mathbf{q})] \delta(\omega - \epsilon(q)) + n_B(\mathbf{q}) \delta(\omega + \epsilon(q)) \right).$$

Harmonicity leaves phonon peaks sharp. Thermal fluctuations only affect intensity via Debye-Waller factor.

1. Use $\langle e^A e^B \rangle = e^{(A^2 + 2AB + B^2)/2}$ for operators $A,B$ that are linear in $u_l,p_l$.

2. Calculate $\langle [\mathbf{q} \cdot \mathbf{u}_0][\mathbf{q} \cdot \mathbf{u}_R(-t)] \rangle$ with $\mathbf{u}_R \propto \sum_k (2M\epsilon(k))^{-1/2} (a_k + a_k^\dagger) e^{ik \cdot \mathbf{R}} \mathbf{e}(k)$ and $a_k(t) = a_k e^{-i\omega(k)t}$. 


Magnetic Resonance or Scattering

Magnetic probe: \( \mathcal{H}_1(t) = -\mathbf{M} \cdot \mathbf{h}(t) \). We set \( \hbar = 1 \) throughout.

Linear response: \( \langle M_\mu(\mathbf{r}, t) \rangle - \langle M_\mu \rangle_{\text{eq}} = \sum_\nu \int d^3r' \int dt \tilde{\chi}_{\mu\nu}(\mathbf{r} - \mathbf{r}', t - t') h_\nu(\mathbf{r}', t') \).

Response function: \( \tilde{\chi}_{\mu\nu}(\mathbf{r}, t) = i \theta(t) \langle [M_\mu(\mathbf{r}, t), M_\nu(0, 0)] \rangle = i \theta(t) [S^\mu_{1+}(t), S^\nu_1] \).

Generalized susceptibility: \( \chi_{\mu\nu}(q, \omega) = \sum_\mathbf{r} e^{i q \cdot \mathbf{r}} \int_{-\infty}^{+\infty} dt e^{i \omega t} \tilde{\chi}_{\mu\nu}(\mathbf{r}, t) \).

Correlation function: \( \tilde{S}_{\mu\nu}(\mathbf{r}, t) = \langle S^\mu_{1+}(t), S^\nu_1 \rangle \).

Dynamic structure factor: \( S_{\mu\nu}(q, \omega) = \sum_\mathbf{r} e^{i q \cdot \mathbf{r}} \int_{-\infty}^{+\infty} dt e^{i \omega t} \tilde{S}_{\mu\nu}(\mathbf{r}, t) \).

Relation from [nl39]: \( S_{\mu\nu}(q, \omega) = \frac{2 \chi''_{\mu\nu}(q, \omega)}{1 - e^{-\beta \omega}} \).

Experimental techniques:

- Ferromagnetic resonance, EPR.
  - Long wavelengths (long compared to lattice spacing) probed.
  - Relevant quantity: \( \chi''_{\mu\nu}(q \simeq 0, \omega) \).

- Inelastic neutron scattering.
  - Interaction with magnetic dipole moment of neutron.
  - Momentum transfer \( q \) and energy transfer \( \omega \) of neutrons well matched with energy-momentum relations \( \epsilon(q) \) of typical collective magnetic excitations.
  - Scattering cross section: \( \frac{d^2\sigma}{d\omega d\Omega} \propto S_{\mu\nu}(q, \omega) \).

- Nuclear magnetic resonance, NMR.
  - Localized probe (nuclear magnetic moment) interacts with electronic magnetism in immediate vicinity.
  - Spin-lattice relaxation rate: \( \frac{1}{T_1} \propto \sum_\mathbf{q} S_{\mu\nu}(q, \omega_N) \).
  - Nuclear Larmor frequency \( \omega_N \) is very small compared to typical electronic magnetic excitations.