$$+\frac{i}{\hbar}\langle\Psi_0|e^{-i\hat{H}_0 t/\hbar}e^{i\hat{H}_0 t/\hbar}\hat{Q}_i e^{-i\hat{H}_0 t/\hbar}\hat{Q}_j(t')e^{i\hat{H}_0 t_0/\hbar}|\Psi_0\rangle\Big\}\times\Theta(t-t')$$

$$=\frac{i}{\hbar}\langle[\hat{Q}_i(t),\hat{Q}_j(t')]\rangle\,\Theta(t-t')$$

where $\langle\cdots\rangle$ is taken in the state $|\tilde{\Psi}_0\rangle = e^{i\hat{H}_0 t_0/\hbar}|\Psi_0\rangle$ and where $t'>t_0$ by assumption. We may take $t_0\to-\infty$. Thus we have obtained the important result

$$\chi_{ij}(t-t') = \frac{i}{\hbar}\langle[\hat{Q}_i(t),\hat{Q}_j(t')]\rangle\,\Theta(t-t')$$

The average $\langle\cdots\rangle$ may also be taken with respect to a Gibbs-weighted distribution of initial states, for the case when $T>0$.

- **Lecture 12** (Feb. 11) **Spectral representation:**

Inserting a resolution of the identity $\hat{I}=\sum_n |n\rangle\langle n|$, where $\hat{H}_0|n\rangle = E_n|n\rangle$, we have the **spectral representation** of the response function,

$$\hat{\chi}_{ij}(\omega+i\epsilon) = \frac{i}{\hbar}\int_0^\infty dt\,\langle[\hat{Q}_i(t),\hat{Q}_j(0)]\rangle\,e^{i\omega t}e^{-\epsilon t}$$

$$\left(P_m=\frac{e^{-\beta E_m}}{Z}\right)\qquad = \frac{1}{\hbar}\sum_{m,n}P_m\left\{\frac{\langle m|\hat{Q}_j|n\rangle\langle n|\hat{Q}_i|m\rangle}{\omega-\omega_m+\omega_n+i\epsilon}-\frac{\langle m|\hat{Q}_i|n\rangle\langle n|\hat{Q}_j|m\rangle}{\omega+\omega_m-\omega_n+i\epsilon}\right\}$$

where $\omega_m\equiv(E_m-E_0)/\hbar$ is the m^{th} excitation frequency. This is often called the **retarded response function**, because of the $\Theta(t-t')$ factor in $\chi_{ij}(t-t')$. Note that $\hat{\chi}_{ij}(-\omega)=\hat{\chi}^*_{ij}(\omega)$, which follows since $\chi_{ij}(t-t')\in\mathbb{R}$.

A related object of interest is the **time-ordered response function**,

$$\chi^T_{ij}(t-t') = \frac{i}{\hbar}\langle \hat{T}\,\hat{Q}_i(t)\,\hat{Q}_j(t')\rangle$$

$$= \frac{i}{\hbar}\langle \hat{Q}_i(t)\,\hat{Q}_j(t')\rangle\,\Theta(t-t') + \frac{i}{\hbar}\langle \hat{Q}_j(t')\,\hat{Q}_i(t)\rangle\,\Theta(t'-t)$$

The spectral representation of $\chi^T_{ij}(t-t')$ looks very similar to that for $\chi_{ij}(t-t') \equiv \chi^R_{ij}(t-t')$:

$$\hat{\chi}^T_{ij}(\omega+i\epsilon) = \frac{1}{\hbar}\sum_{m,n} P_m \left\{ \frac{\langle m|\hat{Q}_j|n\rangle\langle n|\hat{Q}_i|m\rangle}{\omega-\omega_m+\omega_n-i\epsilon} - \frac{\langle m|\hat{Q}_i|n\rangle\langle n|\hat{Q}_j|m\rangle}{\omega+\omega_m-\omega_n+i\epsilon}\right\}$$

N.B.

The difference relative to $\hat{\chi}^R_{ij}(t-t')$ is shown in red. Look closely or you might miss it! It is the time-ordered response function which is computed using diagrammatic perturbation theory. But one can retrieve $\hat{\chi}^R_{ij}(\omega)$ from $\hat{\chi}^T_{ij}(\omega)$ from the relations

$$\hat{\chi}'^R_{ij}(\omega) = \frac{\hat{\chi}'^T_{ij}(\omega)}{1+e^{-\beta\hbar\omega}} + \frac{\hat{\chi}'^T_{ji}(\omega)}{e^{\beta\hbar\omega}+1}$$

$$\hat{\chi}''^R_{ij}(\omega) = \frac{\hat{\chi}''^T_{ij}(\omega)}{1+e^{-\beta\hbar\omega}} - \frac{\hat{\chi}''^T_{ji}(\omega)}{e^{\beta\hbar\omega}+1}$$

For the diagonal responses, with $i=j$,

$$\hat{\chi}'^R_{jj}(\omega) = \hat{\chi}'^T_{jj}(\omega) \quad , \quad \hat{\chi}''^R_{jj}(\omega) = \hat{\chi}''^T_{jj}(\omega)\tanh\left(\tfrac{1}{2}\beta\hbar\omega\right)$$

Spectral densities :

Define the real and imaginary parts of

$$\langle m|\hat{Q}_i|n\rangle\langle n|\hat{Q}_j|m\rangle \equiv A_{mn}(ij) + i\,B_{mn}(ij)$$

Now define the **spectral densities**

$$\begin{Bmatrix} \rho^A_{ij}(\omega) \\ \rho^B_{ij}(\omega) \end{Bmatrix} = \hbar^{-1}\sum_{m,n} P_m \begin{Bmatrix} A_{mn}(ij) \\ B_{mn}(ij) \end{Bmatrix} \delta(\omega - \omega_n + \omega_m)$$

which satisfy

$$\rho^A_{ij}(\omega) = \rho^A_{ji}(\omega) \quad , \quad \rho^A_{ij}(-\omega) = e^{-\beta\hbar\omega}\rho^A_{ij}(\omega)$$

$$\rho^B_{ij}(\omega) = -\rho^B_{ji}(\omega) \quad , \quad \rho^B_{ij}(-\omega) = -\,e^{-\beta\hbar\omega}\rho^B_{ij}(\omega)$$

The response functions may now be written in terms of the spectral densities, viz.

$$\hat{\chi}'_{ij}(\omega) = P\int_{-\infty}^{\infty} d\nu \, \frac{2\nu}{\nu^2-\omega^2}\,\rho^A_{ij}(\nu) - \pi\left(1-e^{-\beta\hbar\omega}\right)\rho^B_{ij}(\nu)$$

$$\hat{\chi}''_{ij}(\omega) = P\int_{-\infty}^{\infty} d\nu \, \frac{2\nu}{\nu^2-\omega^2}\,\rho^B_{ij}(\nu) + \pi\left(1-e^{-\beta\hbar\omega}\right)\rho^A_{ij}(\omega)$$

Energy dissipation :

Rate at which work is done by external fields :

$$P(t) = \frac{d}{dt}\langle\Psi(t)|H_0|\Psi(t)\rangle = \sum_i \phi_i(t)\,\frac{d\langle\hat{Q}_i(t)\rangle}{dt}$$

Total energy dissipated:

$$W = \int_{-\infty}^{\infty} dt\, P(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} M_{ij}(\omega)\, \hat{\phi}_i^*(\omega)\, \hat{\phi}_j(\omega)$$

where

$$M_{ij}(\omega) = \frac{\omega}{2i}\left\{ \hat{\chi}_{ij}(\omega) - \hat{\chi}_{ji}(-\omega) \right\}$$
$$= \pi\omega\left(1 - e^{-\beta\hbar\omega}\right)\left\{ \hat{\rho}^A_{ij}(\omega) + i\hat{\rho}^B_{ij}(\omega) \right\}$$

Note $M(\omega) = M^\dagger(\omega)$, so $M(\omega)$ has real eigenvalues.

Correlation functions: The correlation function

$$S_{ij}(t-t') \equiv \frac{1}{2\pi}\langle \hat{Q}_i(t)\hat{Q}_j(t')\rangle$$

has the spectral representation

$$\hat{S}_{ij}(\omega) = \hbar\rho^A_{ij}(\omega) + i\hbar\rho^B_{ij}(\omega)$$
$$= \sum_{m,n} P_m \langle m|\hat{Q}_j|n\rangle\langle n|\hat{Q}_i|m\rangle\, \delta(\omega - \omega_n + \omega_m)$$

We have that $\quad P_m = P_n e^{+\beta(E_n - E_m)} = P_n e^{\beta\hbar(\omega_n - \omega_m)} = P_n e^{\beta\hbar\omega}$

$$\hat{S}_{ij}(-\omega) = e^{-\beta\hbar\omega} S^*_{ij}(\omega) \quad , \quad \hat{S}_{ji}(\omega) = S^*_{ij}(\omega)$$

and

$$M_{ij}(\omega) = \frac{\pi\omega}{\hbar}\left(1 - e^{-\beta\hbar\omega}\right)\hat{S}_{ij}(\omega)$$

a result known as the **fluctuation-dissipation theorem.**

Time-reversal:

$\eta_i = \pm 1$

$$\hat{T}\hat{Q}_i\hat{T}^{-1} = \eta_i \hat{Q}_i \quad \Rightarrow \quad \hat{S}_{ij}(\omega) = \eta_i \eta_j \hat{S}_{ji}(\omega) = \eta_i \eta_j \hat{S}^*_{ij}(\omega)$$

Continuous systems:

$$S_{ij}(\vec{x}-\vec{x}', t-t') \equiv \frac{1}{2\pi} \langle \hat{Q}_i(\vec{x},t)\, \hat{Q}_j(\vec{x}',t') \rangle$$

$$\hat{S}_{ij}(\vec{q},\omega) = \int_{-\infty}^{\infty} dt \int d^3x\, e^{-i\vec{q}\cdot\vec{x}} e^{i\omega t} S_{ij}(\vec{x},t)$$

$$= \frac{1}{2\pi V} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \hat{Q}_i(\vec{q},t)\, \hat{Q}_j(-\vec{q},t) \rangle$$

where we assume translational invariance.

Example: density response and correlation

The perturbing Hamiltonian is taken to be

$$\hat{H}_1(t) = -\int d^3x\, \hat{n}(\vec{x})\, \phi(\vec{x},t)$$

where $n(\vec{x}) = \sum_{i=1}^{N} \delta(\vec{x}-\vec{x}_i)$ in the ordinary canonical ensemble. The response $\delta n \equiv n - n_0$, where $n_0 = \langle \Psi_0 | n | \Psi_0 \rangle$, is given by

$$\langle \delta n(\vec{x},t) \rangle = \int dt' \int d^3x'\, \chi(\vec{x}-\vec{x}', t-t')\, \phi(\vec{x}',t')$$

$$\langle \delta \hat{n}(\vec{q},\omega) \rangle = \hat{\chi}(\vec{q},\omega)\, \hat{\phi}(\vec{q},\omega)$$

$\hat{n}_{\vec{q}} = \sum_i e^{-i\vec{q}\cdot\vec{x}_i}$

$\Rightarrow \hat{n}^{\dagger}_{\vec{q}} = \hat{n}_{-\vec{q}}$

with

$$\chi(\vec{q},\omega) = \frac{1}{\hbar V} \sum_{m,n} P_m \left\{ \frac{|\langle m|\hat{n}_{\vec{q}}|n\rangle|^2}{\omega - \omega_m + \omega_n + i\epsilon} - \frac{|\langle m|\hat{n}_{\vec{q}}|n\rangle|^2}{\omega + \omega_m - \omega_n + i\epsilon} \right\}$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty} d\nu\, S(\vec{q},\nu)\left\{\frac{1}{\omega+\nu+i\epsilon} - \frac{1}{\omega-\nu+i\epsilon}\right\}$$

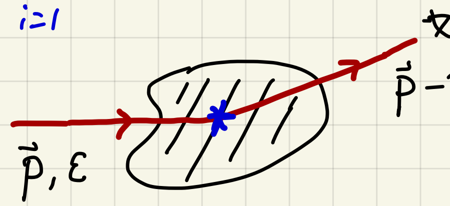
and

in magnet, $\hat{S}^z_{\vec{q}} = \sum_i e^{-i\vec{q}\cdot\vec{x}_i}\sigma^z_i$

$$S(\vec{q},\omega) = \frac{1}{V}\sum_m P_m \left|\langle m|\hat{n}_{\vec{q}}|n\rangle\right|^2 \delta(\omega - \omega_n + \omega_m)$$

The quantity $S(\vec{q},\omega)$ is the **dynamic structure factor.** Note that $\hat{n}_{\vec{q}} = \sum_{i=1}^{\tilde{N}} e^{-i\vec{q}\cdot\vec{x}_i}$ and hence $\hat{n}^\dagger_{\vec{q}} = \hat{n}_{-\vec{q}}$.

Scattering :



$\vec{p}, \varepsilon$

$\vec{p}-\hbar\vec{q}\,,\ \varepsilon - \hbar\omega_n + \hbar\omega_m = \varepsilon - \hbar\omega$

The scattering intensity is, by FGR,

$$I(\vec{q},\omega) = \frac{2\pi}{\hbar}\sum_{m,n} P_m \left|\langle m,\vec{p}\,|\hat{H}_1|\,n,\vec{p}-\hbar\vec{q}\rangle\right|^2 \delta(\omega-\omega_n+\omega_m)$$

$$= \frac{2\pi}{\hbar}\,|\hat{\phi}(\vec{q})|^2\, S(\vec{q},\omega)$$

form factor

In neutron scattering, for example, the neutron is "on shell", meaning $\varepsilon(\vec{p}) = \vec{p}^{\,2}/2m_n$. Thus

$$\varepsilon(\vec{p}-\hbar\vec{q}) = \frac{(\vec{p}-\hbar\vec{q})^2}{2m_n} = \varepsilon(\vec{p}) - \hbar\omega = \frac{\vec{p}^{\,2}}{2m_n} - \hbar\omega$$

and so

$$\hbar\omega = \frac{\hbar\vec{q}\cdot\vec{p}}{m_n} - \frac{\hbar^2\vec{q}^{\,2}}{2m_n}$$

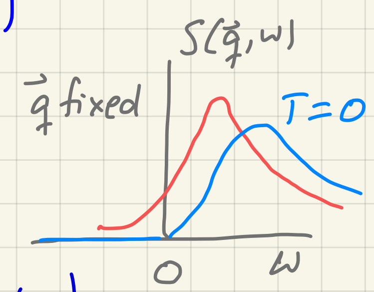
which says that at fixed momentum transfer $\hbar\vec{q}$, the frequency can be adjusted by varying the incident momentum $\vec{p}$.

Another case of interest: foreign object (e.g., impurity) moving at fixed velocity $\vec{V}$. Then

$$\hat{\phi}(\vec{q},\omega) = \int dt \int d^3x \, e^{i(\omega t - \vec{q}\cdot\vec{x})} \phi(\vec{x}-\vec{V}t) = 2\pi\,\delta(\omega - \vec{q}\cdot\vec{V})\,\hat{\phi}(\vec{q})$$

and

$$\langle \delta\hat{n}(\vec{q},\omega)\rangle = 2\pi\,\delta(\omega - \vec{V}\cdot\vec{q})\,\hat{\chi}(\vec{q},\omega)\,\hat{\phi}(\vec{q})$$



Sum rules:

From

$$S(\vec{q},\omega) = \frac{1}{V}\sum_m P_m \left|\langle m|\hat{n}_{\vec{q}}|n\rangle\right|^2 \delta(\omega - \omega_n + \omega_m)$$

we obtain the first moment

$$\begin{aligned}
\int_{-\infty}^{\infty} d\omega\, \omega\, S(\vec{q},\omega) &= \frac{1}{V}\sum_{m,n} P_m \left|\langle m|\hat{n}_{\vec{q}}|n\rangle\right|^2 (\omega_n - \omega_m) \\
&= \frac{1}{\hbar V}\sum_{m,n} P_m \langle m|\hat{n}_{\vec{q}}|n\rangle\langle n|[\hat{H},\hat{n}^\dagger_{\vec{q}}]|m\rangle \\
&= \frac{1}{\hbar V}\langle \hat{n}_{\vec{q}}[\hat{H},\hat{n}^\dagger_{\vec{q}}]\rangle = \frac{1}{2\hbar V}\langle [\hat{n}_{\vec{q}},[\hat{H},\hat{n}^\dagger_{\vec{q}}]]\rangle
\end{aligned}$$

where the last equality follows by inversion symmetry $(\vec{q}\to-\vec{q})$. If the Hamiltonian is of the form

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\vec{\nabla}_i^2 + U(\vec{x}_1,\dots,\vec{x}_N)$$

then with $\hat{n}^\dagger_{\vec{q}} = \sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{x}_i}$ we find

$$[\hat{H}, \hat{n}^\dagger_{\vec q}] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\left[\vec\nabla_i^2, e^{i\vec q\cdot\vec x_i}\right] = \frac{\hbar^2}{2im}\vec q\cdot\sum_{i=1}^{N}\left(\vec\nabla_i e^{i\vec q\cdot\vec x_i} + e^{i\vec q\cdot\vec x_i}\vec\nabla_i\right)$$

$$[\hat n_{\vec q}, [H, \hat n^\dagger_{\vec q}]] = \frac{\hbar^2}{2im}\vec q\cdot\sum_{i,j}\left[e^{-i\vec q\cdot\vec x_j}, \vec\nabla_i e^{i\vec q\cdot\vec x_i} + e^{i\vec q\cdot\vec x_i}\vec\nabla_i\right] = \frac{N\hbar^2\vec q^{\,2}}{m}$$

We have just derived the **f-sum rule**,

$$\int_{-\infty}^{\infty} d\omega\, \omega\, S(\vec q,\omega) = \frac{n\hbar\vec q^{\,2}}{2m}$$

In general, the r^{th} moment of $S(\vec q,\omega)$ at fixed $\vec q$ is

$$\int_{-\infty}^{\infty} d\omega\, \omega^r S(\vec q,\omega) = \frac{1}{\hbar V}\langle \hat n_{\vec q}\underbrace{[\hat H,[\hat H,\cdots[\hat H}_{r\text{ times}}, \hat n^\dagger_{\vec q}]\cdots]\rangle$$

Moments with $r\neq 1$ depend on the potential. The $n=0$ moment is

$$S(\vec q) \equiv \int_{-\infty}^{\infty} d\omega\, S(\vec q,\omega) = \frac{1}{\hbar V}\langle \hat n^\dagger_{\vec q}\hat n_{\vec q}\rangle$$
$$= \frac{1}{\hbar}\int d^3x\,\langle n(\vec x)n(0)\rangle e^{-i\vec q\cdot\vec x}$$

This is the **static structure factor**, the Fourier transform of the density-density correlation function.

Compressibility sum rule: The isothermal compressibility is

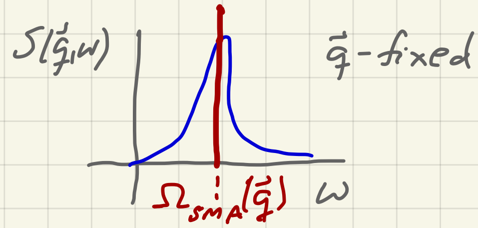
$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T = n^{-2}\frac{\partial n}{\partial\mu}\bigg|_T$$

$$\langle\delta n\rangle = \hat\chi(0,0)\,\delta\mu \implies \kappa_T = \frac{2}{\hbar}n^{-2}\lim_{\vec q\to 0}\int_{-\infty}^{\infty} d\omega\,\omega^{-1}S(\vec q,\omega)$$

Single mode approximation :

For each $\vec{q}$, $S(\vec{q},\omega)$ is a distribution in ω. The approximation

$$S(\vec{q},\omega) \approx S_{SMA}(\vec{q})\,\delta(\omega - \Omega_{SMA}(\vec{q}))$$



which presumes that all the oscillator strength $|\langle m|\hat{n}_{\vec{q}}|n\rangle|^2$ is saturated by a single transition (hence, at $T=0$, by a single mode) is known as the single mode approximation. If the SMA is exact, then $S_{SMA}(\vec{q}) = S(\vec{q})$ is the static structure factor. Within the SMA, we have

$$\Omega_{SMA}(\vec{q}) = \int_{-\infty}^{\infty} d\omega\, \omega\, S(\vec{q},\omega) \Big/ \int_{-\infty}^{\infty} d\omega\, S(\vec{q},\omega) = \frac{n\hbar\vec{q}^{\,2}}{2m\,S(\vec{q})}$$

But then we also should have

$$\Omega^2_{SMA}(\vec{q}) = \int_{-\infty}^{\infty} d\omega\, \omega\, S(\vec{q},\omega) \Big/ \int_{-\infty}^{\infty} d\omega\, \omega^{-1} S(\vec{q},\omega) = \frac{n\vec{q}^{\,2}}{m\,\hat{\chi}(\vec{q})}$$

Thus if the SMA is valid we must have

$$\frac{\hbar^2}{4}\, m n\, \vec{q}^{\,2}\, \hat{\chi}(\vec{q}) = \left[S(\vec{q})\right]^2$$

Of course this is certainly not true in general.

SMA says $\hat{n}_{\vec{q}}|G\rangle$ is an eigenstate. (Not really true.)