

G25.2651: Statistical Mechanics

Notes for Lecture 23

I. QUANTUM LINEAR RESPONSE THEORY

Consider again the Hamiltonian for a system coupled to a time-dependent field

$$H = H_0 - BF_e(t)$$

We wish to solve the quantum Liouville equation

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]$$

in the linear regime where $F_e(t)$ is small.

A. Perturbative solution of the Liouville equation

As in the classical case, we assume a solution of the form

$$\rho(t) = \rho_0(H_0) + \Delta\rho(t)$$

where

$$[H_0, \rho_0] = 0 \quad \Rightarrow \quad \frac{\partial \rho_0}{\partial t} = 0$$

and we will assume

$$\rho_0(H_0) = \frac{e^{-\beta H_0}}{Q(N, V, T)}$$

Substituting into the Liouville equation and working to first order in small quantities, we find

$$\frac{\partial \Delta\rho}{\partial t} = \frac{1}{i\hbar} [H_0, \Delta\rho] - \frac{1}{i\hbar} [B, \rho_0] F_e(t)$$

which is a first order inhomogeneous equation that can be solved by using an integrating factor:

$$\Delta\rho(t) = -\frac{1}{i\hbar} \int_{-\infty}^t ds e^{-iH_0(t-s)/\hbar} [B, \rho_0] e^{iH_0(t-s)/\hbar} F_e(s)$$

(Note that we have chosen the origin in time to be $t = -\infty$, which is an arbitrary choice.)

For an observable A , the expectation value is

$$\langle A(t) \rangle = \text{Tr}(\rho A) = \langle A \rangle_0 + \text{Tr}(\Delta\rho(t)A)$$

when the solution for $\Delta\rho$ is substituted in, this becomes

$$\begin{aligned} \langle A(t) \rangle &= \langle A \rangle_0 - \frac{1}{i\hbar} \int_{-\infty}^t ds \text{Tr} \left[A e^{-iH_0(t-s)/\hbar} [B, \rho_0] e^{iH_0(t-s)/\hbar} \right] F_e(s) \\ &= \langle A \rangle_0 - \frac{1}{i\hbar} \int_{-\infty}^t ds \text{Tr} \left[e^{iH_0(t-s)/\hbar} A e^{-iH_0(t-s)/\hbar} [B, \rho_0] \right] F_e(s) \\ &= \langle A \rangle_0 - \frac{1}{i\hbar} ds \text{Tr} [A(t-s)[B, \rho_0]] F_e(s) \end{aligned}$$

where the cyclic property of the trace has been used and the Heisenberg evolution for A has been substituted in. Expanding the commutator gives

$$\begin{aligned}\langle A(t) \rangle &= \langle A \rangle_0 - \frac{1}{i\hbar} \int_{-\infty}^t ds \operatorname{Tr} [A(t-s)B\rho_0 - A(t-s)\rho_0 B] F_e(s) \\ &= \langle A \rangle_0 - \frac{1}{i\hbar} \int_{-\infty}^t ds \operatorname{Tr} [\rho_0 (A(t-s)B - BA(t-s))] F_e(s) \\ &= \langle A \rangle_0 - \frac{1}{i\hbar} \int_{-\infty}^t ds F_e(s) \langle [A(t-s), B(0)]_0 \rangle\end{aligned}$$

where the cyclic property of the trace has been used again. Define a function

$$\Phi_{AB}(t) = \frac{i}{\hbar} \langle [A(t), B(0)]_0 \rangle$$

called the *after effect function*. It is essentially the antisymmetric quantum time correlation function, which involves the commutator between $A(t)$ and $B(0)$. Then the linear response result can be written as

$$\langle A(t) \rangle = \langle A \rangle_0 + \int_{-\infty}^t ds F_e(s) \Phi_{AB}(t-s)$$

which is the starting point for the theory of quantum transport coefficients. If we choose to measure the operator B , then we find

$$\langle B(t) \rangle = \langle B \rangle_0 + \int_{-\infty}^t ds F_e(s) \Phi_{BB}(t-s)$$

B. Relation to spectra

Suppose that $F_e(t)$ is a monochromatic field

$$F_e(t) = F_\omega e^{i\omega t} e^{\epsilon t}$$

where the parameter ϵ insures that field goes to 0 at $t = -\infty$. We will take $\epsilon \rightarrow 0^+$ at the end of the calculation. The expectation value of B then becomes

$$\begin{aligned}\langle B(t) \rangle &= \langle B \rangle_0 + \int_{-\infty}^t ds \Phi_{BB}(t-s) F_\omega e^{i\omega s} e^{\epsilon s} \\ &= \langle B \rangle_0 + F_\omega e^{(i\omega + \epsilon)t} \int_0^\infty d\tau \Phi_{BB}(\tau) e^{-i(\omega - i\epsilon)\tau}\end{aligned}$$

where the change of integration variables $\tau = t - s$ has been made.

Define a frequency-dependent susceptibility by

$$\chi_{BB}(\omega - i\epsilon) = \int_0^\infty d\tau \Phi_{BB}(\tau) e^{-i(\omega - i\epsilon)\tau}$$

then

$$\langle B(t) \rangle = \langle B \rangle_0 + F_\omega e^{i\omega t} e^{\epsilon t} \chi_{BB}(\omega - i\epsilon)$$

If we let $z = \omega - i\epsilon$, then we see immediately that

$$\chi_{BB}(z) = \int_0^\infty d\tau \Phi_{BB}(\tau) e^{-iz\tau}$$

i.e., the susceptibility is just the Laplace transform of the after effect function or the time correlation function.

Recall that

$$\Phi_{AB}(t) = \frac{i}{\hbar} \langle [A(t), B(0)] \rangle_0 = \frac{i}{\hbar} \langle [e^{iH_0 t/\hbar} A e^{-iH_0 t/\hbar}, B] \rangle_0$$

Under time reversal, we have

$$\begin{aligned} \Phi_{AB}(-t) &= \frac{i}{\hbar} \langle [e^{-iH_0 t/\hbar} A e^{iH_0 t/\hbar}, B] \rangle_0 \\ &= \frac{i}{\hbar} \langle (e^{-iH_0 t/\hbar} A e^{iH_0 t/\hbar} B - B e^{-iH_0 t/\hbar} A e^{iH_0 t/\hbar}) \rangle_0 \\ &= \frac{i}{\hbar} \langle (A e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar} - e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar} A) \rangle_0 \\ &= \frac{i}{\hbar} \langle (AB(t) - B(t)A) \rangle_0 \\ &= -\frac{i}{\hbar} \langle [B(t), A] \rangle_0 = -\Phi_{BA}(t) \end{aligned}$$

Thus,

$$\Phi_{AB}(-t) = -\Phi_{BA}(t)$$

and if $A = B$, then

$$\Phi_{BB}(-t) = -\Phi_{BB}(t)$$

Therefore

$$\begin{aligned} \chi_{BB}(\omega) &= \lim_{\epsilon \rightarrow 0^+} \int_0^\infty dt e^{-i(\omega - i\epsilon)t} \Phi_{BB}(t) \\ &= \lim_{\epsilon \rightarrow 0^+} \int_0^\infty dt e^{-\epsilon t} [\Phi_{BB}(t) \cos \omega t - i\Phi_{BB}(t) \sin \omega t] \\ &= \text{Re}(\chi_{BB}(\omega)) - i\text{Im}(\chi_{BB}(\omega)) \end{aligned}$$

From the properties of $\Phi_{BB}(t)$ it follows that

$$\begin{aligned} \text{Re}(\chi_{BB}(\omega)) &= \text{Re}(\chi_{BB}(-\omega)) \\ \text{Im}(\chi_{BB}(\omega)) &= -\text{Im}(\chi_{BB}(-\omega)) \end{aligned}$$

so that $\text{Im}(\chi_{BB}(\omega))$ is positive for $\omega > 0$ and negative for $\omega < 0$. It is a straightforward matter, now, to show that the energy difference $Q(\omega)$ derived in the lecture from the Fermi golden rule is related to the susceptibility by

$$Q(\omega) = 2\omega |F_\omega|^2 \text{Im}(\chi_{BB}(\omega))$$

C. Kubo transform expression for the time correlation function (Optional)

We shall derive the following expression for the quantum time correlation function

$$\Phi_{AB}(t) = \int_0^\beta d\lambda \langle \dot{B}(-i\hbar\lambda) A(t) \rangle_0$$

known as a Kubo transform relation. Since \dot{B} is given by the Heisenberg equation:

$$\dot{B} = \frac{1}{i\hbar} [B, H_0]$$

it follows that

$$\dot{B}(t) = -\frac{1}{i\hbar} e^{iH_0 t/\hbar} [H_0, B(0)] e^{-iH_0 t/\hbar}$$

Evaluating the expression at $t = -i\hbar\lambda$ gives

$$\dot{B}(-i\hbar\lambda) = e^{\lambda H_0} \frac{1}{i\hbar} [B(0), H_0] e^{-\lambda H_0}$$

Thus,

$$\Phi_{AB}(t) = \int_0^\beta d\lambda \langle e^{\lambda H_0} \left(\frac{1}{i\hbar} [B(0), H_0] \right) e^{-\lambda H_0} A(t) \rangle_0$$

By performing the trace in the basis of eigenvectors of H_0 , we obtain

$$\begin{aligned} \Phi_{AB}(t) &= \frac{1}{Q} \int_0^\beta d\lambda \sum_n \langle n | e^{\lambda H_0} \left(\frac{1}{i\hbar} [B(0), H_0] e^{-\lambda H_0} A(t) | n \rangle e^{-\beta E_n} \right. \\ &= \frac{1}{Q} \int_0^\beta d\lambda \sum_{m,n} \langle n | e^{\lambda H_0} \left(\frac{1}{i\hbar} [B(0), H_0] e^{-\lambda H_0} | m \rangle \langle m | A(t) | n \rangle e^{-\beta E_n} \right. \\ &= \frac{1}{Q} \int_0^\beta d\lambda \sum_{m,n} e^{\lambda E_n} e^{-\lambda E_m} \frac{1}{i\hbar} \langle n | [B(0), H_0] | m \rangle \langle m | A(t) | n \rangle e^{-\beta E_n} \\ &= \frac{1}{Q} \sum_{m,n} e^{-\beta E_n} \frac{e^{\beta(E_n - E_m)} - 1}{(E_n - E_m)} \frac{1}{i\hbar} \langle n | [B(0), H_0] | m \rangle \langle m | A(t) | n \rangle e^{-\beta E_n} \end{aligned}$$

But

$$\langle n | [B(0), H_0] | m \rangle = \langle n | B(0) H_0 - H_0 B(0) | m \rangle = (E_m - E_n) \langle n | B(0) | m \rangle$$

Therefore,

$$\begin{aligned} \Phi_{AB}(t) &= -\frac{1}{i\hbar Q} \sum_{m,n} (e^{-\beta E_n} - e^{-\beta E_m}) \langle n | B(0) | m \rangle \langle m | A(t) | n \rangle \\ &= -\frac{1}{i\hbar Q} \left[\sum_{m,n} e^{-\beta E_m} \langle m | A(t) | n \rangle \langle n | B(0) | m \rangle - \sum_{m,n} e^{-\beta E_n} \langle n | B(0) | m \rangle \langle m | A(t) | n \rangle \right] \\ &= \frac{i}{\hbar} \langle [A(t), B(0)] \rangle_0 \end{aligned}$$

which proves the relation. The classical limit can be deduced easily from the Kubo transform relation:

$$\Phi_{AB}(t) \longrightarrow \beta \langle \dot{B}(0) A(t) \rangle_0$$

Note further, by using the cyclic properties of the trace, that

$$\langle \dot{B}(-i\hbar\lambda) B(t) \rangle_0 = -\frac{d}{dt} \langle B(-i\hbar\lambda) B(t) \rangle_0$$

D. The Onsager fluctuation regression theorem (Optional)

Suppose that $F_e(t)$ is of the form

$$F_e(t) = F_0 e^{\epsilon t} \theta(-t)$$

which adiabatically induces a fluctuation in the system for $t < 0$ and the lets the system evolve in time according to the unperturbed Hamiltonian for $t > 0$. How will the induced fluctuation evolve in time? Combining the kubo transform relation with the linear response result for $\langle B(t) \rangle$, we find that

$$\begin{aligned}
\langle B(t) \rangle &= \int_{-\infty}^0 ds e^{\epsilon s} \int_0^\beta d\lambda \langle \dot{B}(-i\hbar\lambda) B(t-s) \rangle_0 \\
&= -e^{\epsilon t} \int_0^\beta d\lambda \int_t^\infty du e^{-\epsilon u} \frac{d}{du} \langle B(-i\hbar\lambda) B(u) \rangle_0
\end{aligned}$$

where the change of variables $u = t - s$ has been made. Taking the limit $\epsilon \rightarrow 0$, and performing the integral over u , we find

$$\langle B(t) \rangle = - \int_0^\beta d\lambda [\langle B(-i\hbar\lambda) B(\infty) \rangle_0 - \langle B(-i\hbar\lambda) B(t) \rangle_0]$$

Since we assumed that $\langle B \rangle_0 = 0$, we have $\langle B(-i\hbar\lambda) B(\infty) \rangle_0 = \langle B(-i\hbar\lambda) \rangle_0 \langle B(\infty) \rangle_0 = 0$. Thus, dividing by $\langle B(0) \rangle$, we find

$$\frac{\langle B(t) \rangle}{\langle B(0) \rangle} = \frac{\int_0^\beta d\lambda B(-i\hbar\lambda) B(t)_0}{\int_0^\beta d\lambda B(-i\hbar\lambda) B(0)_0} \xrightarrow{\hbar \rightarrow 0} \frac{\langle B(0) B(t) \rangle_0}{\langle B(0)^2 \rangle_0}$$

Thus at long times in the classical limit, the fluctuations decay to 0, indicating a complete *regression* or suppression of the induced fluctuation:

$$\frac{\langle B(t) \rangle}{\langle B(0) \rangle} \rightarrow 0$$