G25.2651: Statistical Mechanics

Notes for Lecture 18

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

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

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

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

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

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

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

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

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

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

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 $\epsilon \to 0^+$ 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

$$\Phi_{AB}(t) = \frac{i}{\hbar}\langle[A(t), B(0)]\rangle_0 = \frac{i}{\hbar}\langle[e^{iH_0t/\hbar}Ae^{-iH_0t\hbar}, B]\rangle_0$$

Under time reversal, we have

$$\begin{aligned}
\Phi_{AB}(-t) &= \frac{i}{\hbar}\langle\left[e^{-iH_0t/\hbar}Ae^{iH_0t/\hbar}, B\right]\rangle_0 \\
&= \frac{i}{\hbar}\langle\left(e^{-iH_0t/\hbar}Ae^{iH_0t/\hbar}B - Be^{-iH_0t/\hbar}Ae^{iH_0t/\hbar}\right)\rangle_0 \\
&= \frac{i}{\hbar}\langle\left(Ae^{iH_0t/\hbar}Be^{-iH_0t/\hbar} - e^{iH_0t/\hbar}Be^{-iH_0t/\hbar}A\right)\rangle_0 \\
&= \frac{i}{\hbar}\langle(AB(t) - B(t)A)\rangle_0 \\
&= -\frac{i}{\hbar}\langle[B(t), A]\rangle = -\Phi_{BA}(t)
\end{aligned}$$

Thus,

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

and if $A = B$, then

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

Therefore

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

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

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

so that $\mathrm{Im}(\chi_{BB}(\omega))$ 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

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

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

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

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,

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

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 cylic 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

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

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

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

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

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

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

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