

In equilibrium quantum statistical mechanics, define the density operator to be

$$\hat{\rho}(\beta) = e^{-\beta \hat{H}}, \quad \beta = \frac{1}{k_B T}$$

Recall EOM for general  $\hat{\rho}$ :

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

(in the grand canonical ensemble, replace  $\hat{H} \rightarrow \hat{H} - \mu \hat{N}$ )  
↑  
chemical potential

The partition function, in terms of the density operator is

$$Z(\beta) = \text{Tr}[\hat{\rho}(\beta)] \equiv \text{Tr} e^{-\beta \hat{H}}$$

All thermodynamic quantities follow from the partition function. The ensemble average of an operator,  $\hat{A}$  is defined as:

$$\langle A \rangle_{\beta} = \frac{1}{Z(\beta)} \text{Tr}[\hat{A} e^{-\beta \hat{H}}] = \frac{1}{Z(\beta)} \text{Tr}[\hat{A} \hat{\rho}]$$

Similarly, the thermal quantum correlation function of two operators  $\hat{A}$  and  $\hat{B}$  is:

$$\langle \hat{A} \hat{B} \rangle_{\beta} = \frac{1}{Z(\beta)} \text{Tr}[\hat{A} \hat{B} \hat{\rho}(\beta)]$$

### Kubo - Martin - Schwinger relations

For any Schrödinger operator,  $\hat{A}$ , one can define a time dependent Heisenberg operator,  $\hat{A}(t)$  defined as:

$$\hat{A}(t) = e^{i\hat{H}t} \hat{A} e^{-i\hat{H}t}$$

The correlation of two Heisenberg operators is called the thermal quantum time correlation function, and is defined as:

$$\langle \hat{A}(t) \hat{B}(t) \rangle_{\beta} = \frac{1}{Z(\beta)} \text{Tr}[\hat{A}(t) \hat{B}(t) \hat{\rho}(\beta)]$$

Note  $\langle A(t) B(t) \rangle_\beta \neq \langle B(t) A(t) \rangle_\beta$  :

Classical TCFs do obey  $\langle AB \rangle_\beta = \langle BA \rangle_\beta$ .

$$\begin{aligned}
 \langle \hat{A}(t) \hat{B}(t) \rangle_\beta &= \frac{1}{Z(\beta)} \text{Tr} [\hat{A}(t) \hat{B}(t) \hat{\rho}(\beta)] \\
 &= \frac{1}{Z(\beta)} \text{Tr} [\hat{A}(t) e^{i\hat{H}t} \hat{B} e^{-i\hat{H}t} e^{-\beta\hat{H}}] \\
 &= \frac{1}{Z(\beta)} \text{Tr} [\hat{A}(t) e^{-\beta\hat{H}} e^{+\beta\hat{H}} e^{i\hat{H}t} \hat{B} e^{-i\hat{H}t} e^{-\beta\hat{H}}] \\
 &= \frac{1}{Z(\beta)} \text{Tr} [\hat{A}(t) \hat{\rho}(\beta) e^{i(-i\beta+t)\hat{H}} \hat{B} e^{-i(-i\beta+t)\hat{H}}] \\
 &= \frac{1}{Z(\beta)} \text{Tr} [\hat{A}(t) \hat{\rho}(\beta) \hat{B}(t-i\beta)] \\
 &= \frac{1}{Z(\beta)} \text{Tr} [\hat{B}(t-i\beta) \hat{A}(t) \hat{\rho}(\beta)] \equiv \text{Tr} [\hat{B}(t) \hat{A}(t+i\beta) \hat{\rho}(\beta)]
 \end{aligned}$$

(follow same steps).

Note that the Heisenberg picture is modified in the sense that the time argument is complex

If the two operators are the same,  $\hat{A} = \hat{B}$ , but evaluated at different times, we have:

$$\langle \hat{A}(t) \hat{A}(t') \rangle_\beta = \langle \hat{A}(t'-i\beta) \hat{A}(t) \rangle_\beta = \langle \hat{A}(t') \hat{A}(t+i\beta) \rangle_\beta.$$

The goal of equilibrium thermal quantum statistics is to be able to evaluate thermal averages and quantum TCFs. In the presence of interactions, the Hilbert space is very complicated — summing over all states is difficult. Can get around this difficulty by following the Matsubara Formalism (also called imaginary time formalism).

The idea is to introduce a “modified” interaction picture by splitting up the total Hamiltonian into a free part and an interaction part:

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

(In the grand canonical ensemble treat the  $-\mu\hat{N}$  term as part of the free Hamiltonian.)

Then split up the density matrix:

$$\rho(\beta) = e^{-\beta\hat{H}} = \underbrace{e^{-\beta\hat{H}_0}}_{\hat{\rho}_0(\beta)} \underbrace{e^{\beta\hat{H}_0} e^{-\beta\hat{H}}}_{\hat{S}(\beta)}$$

(Free part)      (Interaction part)

Note that if  $\hat{H}_0$  commutes with  $\hat{H}'$ , then  $\hat{S}(\beta) = e^{\beta\hat{H}_0} e^{-\beta\hat{H}_0} e^{-\beta\hat{H}'} = e^{-\beta\hat{H}'}$   
 $\hat{S}(\beta) = \hat{\rho}_0^{-1}(\beta) \hat{\rho}(\beta)$

We can then see how the density matrices depend on  $\beta$ :

$$\frac{\partial \hat{\rho}_0(\beta)}{\partial \beta} = \frac{\partial}{\partial \beta} e^{-\beta\hat{H}_0} = -\hat{H}_0 e^{-\beta\hat{H}_0} = -\hat{H}_0 \rho_0(\beta)$$

$$\frac{\partial \hat{\rho}(\beta)}{\partial \beta} = \frac{\partial}{\partial \beta} e^{-\beta\hat{H}} = -\hat{H} \hat{\rho}(\beta) = -(\hat{H}_0 + \hat{H}') \rho(\beta)$$

$$\begin{aligned} \frac{\partial \hat{S}(\beta)}{\partial \beta} &= \frac{\partial}{\partial \beta} (e^{\beta\hat{H}_0} e^{-\beta\hat{H}}) = +\hat{H}_0 e^{\beta\hat{H}_0} e^{-\beta\hat{H}} - e^{\beta\hat{H}_0} \hat{H} e^{-\beta\hat{H}} \\ &= e^{\beta\hat{H}_0} (\hat{H}_0 - \hat{H}) e^{-\beta\hat{H}} \\ &= \underbrace{e^{\beta\hat{H}_0} (-\hat{H}')}_{\equiv -\hat{H}'_I(\beta)} \underbrace{e^{-\beta\hat{H}_0} e^{\beta\hat{H}_0} e^{-\beta\hat{H}}}_{\hat{S}(\beta)} = -\hat{H}'_I(\beta) \hat{S}(\beta) \end{aligned}$$

If we interpret  $\rho(\beta) = e^{-\beta\hat{H}}$  as the time evolution operator in the negative imaginary direction,  $t = -i\beta$ ,  $\hat{S}$ , is the time evolution operator,  $\hat{U}_I$  in the interaction picture; note similarity with its equation of motion,

$$i\hbar \frac{d\hat{U}_I}{dt} = \hat{H}'_I \hat{U}_I$$

Having introduced  $-\hat{H}'_I(\beta) = e^{\beta\hat{H}_0} \hat{H}' e^{-\beta\hat{H}_0}$ , we can define the operators in the modified interaction picture as:

$$A_I(\beta) = e^{\beta\hat{H}_0} \hat{A} e^{-\beta\hat{H}_0} \equiv \rho_0^{-1}(\beta) \hat{A} \rho_0(\beta)$$

Cautionary note: The transformation for real  $\beta$  or (negative) imaginary  $t$  is not unitary — must be careful with dealing with such operators.