Phys 726 - Lecture 19

Quantum Statistical Mechanics

* We've focussed so far on the ground-state properties of interacting systems
  - → consider what happens in systems with constant temperature rather than fixed energy
  - → in thermal equilibrium, each eigenstate is Boltzmann-occupied, according to its eigenenergy
* We've also focussed on systems with a fixed number of particles
  - → consider what happens if the system is in contact with an external particle reservoir
  - → the Hamiltonian is now augmented by a term $\hat{H} \to \hat{H} - \mu \hat{N}$ where μ is the chemical potential

* Compute finite-temperature properties by constructing the partition function

→ partition function $Z = \mathrm{tr}\, e^{-\beta \hat{H}}$

$\beta = \frac{1}{k_B T}$ "inverse temperature"

trace over all states in the Hilbert space with fixed N

→ Grand partition function $\mathcal{Z} = \mathrm{tr}\, e^{-\beta(\hat{H} - \mu \hat{N})}$

unrestricted trace

chemical potential.

EXAMPLE: A one-site Hubbard model

$$\hat{H} = U \hat{n}_\uparrow \hat{n}_\downarrow = U c_\uparrow^\dagger c_\uparrow c_\downarrow^\dagger c_\downarrow$$

has eigenstates

$|0\rangle \; \} \; N=0$

$|\uparrow\rangle, \; |\downarrow\rangle \; \} \; N=1$

$|\uparrow\downarrow\rangle \; \} \; N=2$

The partition function in each number sector is

$$Z_{N=0} = \mathrm{tr}\, e^{-\beta \hat{H}} = \langle 0 | e^{-\beta \hat{H}} | 0 \rangle = 1$$

$$Z_{N=1} = \langle \uparrow | e^{-\beta \hat{H}} | \uparrow \rangle + \langle \downarrow | e^{-\beta \hat{H}} | \downarrow \rangle = 1 + 1 = 2$$

$$Z_{N=2} = \langle \uparrow\downarrow | e^{-\beta \hat{H}} | \uparrow\downarrow \rangle = e^{-\beta U}$$

The grand partition function is

$$\mathcal{Z} = \mathrm{tr}\, e^{-\beta(\hat{H} - \mu \hat{N})} = \sum_N Z_N e^{+\beta \mu N}$$

$$= \langle 0 | e^{-\beta(\hat{H} - \mu \hat{N})} | 0 \rangle$$

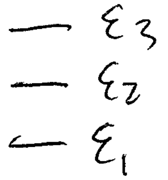
$$+ \langle \uparrow | e^{-\beta(\hat{H} - \mu \hat{N})} | \uparrow \rangle + \langle \downarrow | e^{-\beta(\hat{H} - \mu \hat{N})} | \downarrow \rangle$$

$$+ \langle \uparrow\downarrow | e^{-\beta(\hat{H} - \mu \hat{N})} | \uparrow\downarrow \rangle$$

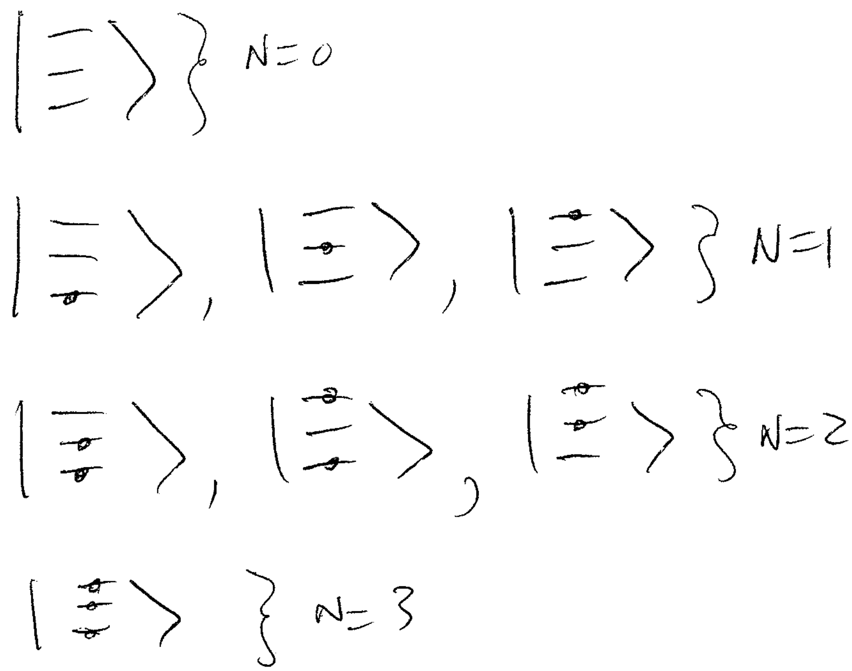
$$= 1 + e^{+\beta \mu} + e^{+\beta \mu} + e^{-\beta U + 2\beta \mu}$$

$$= 1 + 2 e^{\beta \mu} + e^{-\beta U + 2\beta \mu}$$

EXAMPLE: Spinless fermions in three energy levels.



$$\hat{H} = \sum_{n=1}^{3} \varepsilon_n c_n^\dagger c_n$$



partition functions

$$Z_{N=0} = 1$$

$$Z_{N=1} = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_3}$$

$$Z_{N=2} = e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} + e^{-\beta(\varepsilon_2+\varepsilon_3)}$$

$$Z_{N=3} = e^{-\beta(\varepsilon_1+\varepsilon_2+\varepsilon_3)}$$

grand partition function

$$\mathcal{Z} = \sum_N Z_N e^{+\beta\mu N} = 1 + (e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_3})e^{\beta\mu}$$

$$+ (e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_1+\varepsilon_3)} + e^{-\beta(\varepsilon_2+\varepsilon_3)})e^{2\beta\mu}$$

$$+ e^{-\beta(\varepsilon_1+\varepsilon_2+\varepsilon_3)} e^{3\beta\mu}$$

Thermodynamic Functions

* We understand the energy of a state

$$E(S,V,N)$$

to depend on the entropy, volume, and particle number

→ leads to the differential

$$dE = T\,dS - P\,dV + \mu\,dN,$$

which describes small changes to E in response to changes dS, dV, dN.

→ the complementary intensive variables are recovered by differentiation

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

→ In a non-degenerate quantum ground state,

$$S = 0 \quad \text{and} \quad \mu = \left(\frac{\partial E}{\partial N}\right)_V$$

Legendre transformation

* Define the Helmholtz free energy

$$F = E - TS$$

→ it has a differential

$$dF = dE - d(TS)$$

$$= T\cancel{dS} - PdV + \mu dN - \cancel{T}dS - SdT$$

$$= -SdT - PdV + \mu dN$$

→ must view $F = F(T, V, N)$ as a function of temperature rather than entropy

→ We identify $F = -\frac{1}{\beta} \log Z_N$

$$= -\frac{1}{\beta} \log \operatorname{tr} e^{-\beta \hat{H}}$$

→ partial derivatives

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{\partial}{\partial T}\left(k_B T \log \mathrm{tr}\, e^{-\hat{H}/k_B T}\right)_{V,N}$$

$$E = \frac{\partial(\beta F)}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(\log \mathrm{tr}\, e^{-\beta \hat{H}}\right)$$

$$= \frac{\mathrm{tr}\, \hat{H} e^{-\beta \hat{H}}}{\mathrm{tr}\, e^{-\beta \hat{H}}} = \langle \hat{H} \rangle$$

thermal + quantum average

* We can go a step further to construct the Grand Potential

$$\Omega = F - \mu N$$

→ differential

$$d\Omega = dF - \mu dN - d\mu \cdot N$$

$$= -SdT - PdV + \cancel{\mu dN} - \cancel{\mu dN} - Nd\mu$$

$$= -SdT - PdV - Nd\mu$$

→ The idependent variables are now

$$\Omega = \Omega(T, V, \mu)$$

and

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}, \quad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}$$

$$\text{and} \quad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{TV}$$

→ We identify

$$\Omega = -\frac{1}{\beta} \log \operatorname{tr} e^{-\beta(\hat{H} - \mu \hat{N})}$$

<u>EXAMPLE</u>: Back to the one-site Hubbard model

$$Z = 1 + 2e^{\beta\mu} + e^{-\beta U + 2\beta\mu}$$

$$\Omega = -\frac{1}{\beta}\log\left(1 + 2e^{\beta\mu} + e^{-\beta U + 2\beta\mu}\right)$$

The number of particles is

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{TV}$$

$$= \frac{2e^{\beta\mu} + 2e^{-\beta U + 2\beta\mu}}{1 + 2e^{\beta\mu} + e^{-\beta U + 2\beta\mu}}$$

<u>EXERCISE</u> ① Sketch this as a function of $\beta\mu$ for βU small and large.

② What result do you get in the limit $U \equiv 0$?

③ Compute $\langle \hat{H} - \mu\hat{N} \rangle = \frac{\partial(\beta\Omega)}{\partial\beta}$.

<u>EXERCISE</u>: Think about the one-site Hubbard model in an external field

$$\hat{H} = U\hat{n}_\uparrow \hat{n}_\downarrow - \vec{B}\cdot\frac{1}{2}c^\dagger\vec{\sigma}c$$

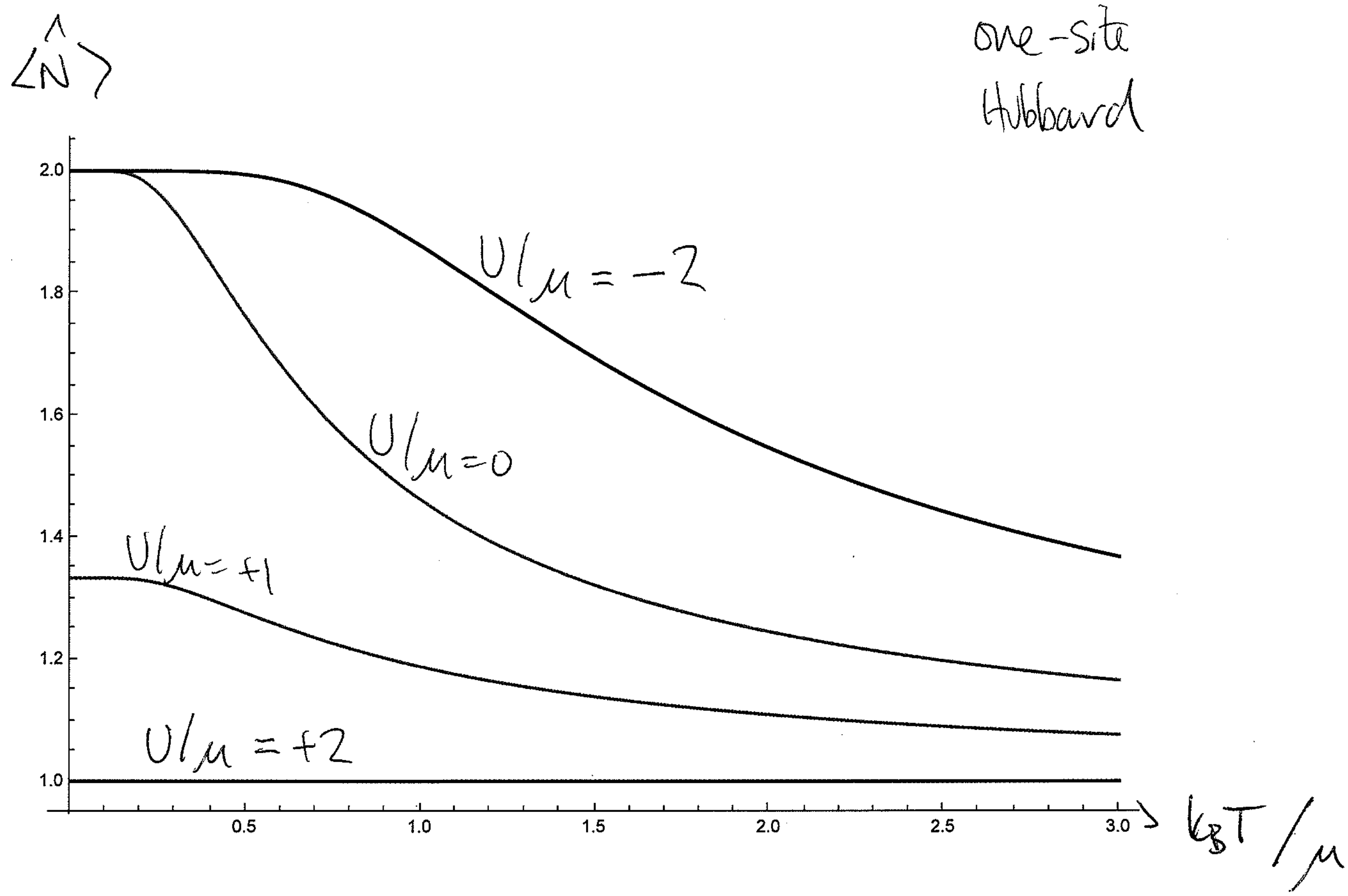
① Specialize to $\vec{B} = B\vec{e}_z$ and compute the grand partition function.

② Relate the magnetization $\langle \frac{1}{2}c^\dagger\sigma^z c\rangle = M$ to a derivative of Ω.

③ Compute the susceptibility $\chi = \frac{\partial M}{\partial B}$

and comment on its behavior in the various limits for μ and U. (Hint: the behavior is quite different when there is one-electron on average versus zero or two.)

one-site Hubbard



one-site
Hubbard