Physics 847
Spring 2010

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Syllabus:

Quantum Statistics:
- Fermions
- Bosons
Examples:
  - Electron gas
  - Neutron star
  - White dwarf
  - Photon gas
  - Phonon gas
  - Bose-Einstein condensation
  - Cases with internal degrees of freedom
Interacting systems:
  - Ising model — magnetic phase transitions
  - Order—disorder transitions
Liquids/liquid-gas phase transitions
Monte Carlo and other numerical methods
(outline only)
Heisenberg model.
Introduction to critical phenomena,
critical exponents, etc. (if there is time)
Magnetic phase transition
Superconducting, superfluid phase transitions

Requirements:
1 MT (~25%)
1 Final (~40%)
Homework (~35%)
Can omit one homework

Text: Pathria, course notes
Quantum Statistics: Analog of the density matrix

Let's first assume a fixed number \( N \) of particles, with Hamiltonian \( H \) which we assume is time-independent for the moment.

Let us introduce a complete set of states \( \{|m\rangle\} \) which are orthonormal, such that

\[
\langle m|n \rangle = \delta_{mn}
\]

Assume that our system at time \( t \) has a wave-function

\[
|\Psi(t)\rangle
\]

which can be expanded in the manner

\[
|\Psi(t)\rangle = \sum_n a_n(t) |m\rangle \quad \text{(always possible since the \( |m\rangle \)'s are complete)}.
\]

Schrödinger equation takes the form

\[
H|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle
\]

or

\[
H \sum_n a_n |m\rangle = i\hbar \sum_n \hat{a}_n |m\rangle
\]

since the \( |m\rangle \)'s are time-independent.

Now let left multiply by \( \langle m| \) to get

\[
\sum_n a_n H_{mn} = i\hbar \delta_{nm}
\]

Schrödinger equation in some
particular configuration. 

Now introduce ensemble of $N$ identically prepared systems. Let

$$
S_{mn}(t) = \frac{1}{N} \sum_{k=1}^{N} a_{m}^{k}(t) [a_{n}^{*}(t)]^{k}
$$

\[ = \langle a_{m} a_{n}^{*} \rangle \text{ ensemble average}
\]

Will show this is a lot like the classical density function.

For example, the average of a quantity $\Theta$, according to quantum mechanics, is

$$
\langle \langle \psi | \Theta | \psi \rangle \rangle \equiv \langle \Theta \rangle
$$

where the second bracket denotes an ensemble average.

Rewrite this as follows:

$$
\langle \Theta \rangle \equiv \langle \Theta \rangle
$$

First, $\langle \psi | \psi \rangle = \sum_{m} a_{m}^{*} a_{m}$

So $\langle \psi | \Theta | \psi \rangle = \sum_{mn} a_{n}^{*} a_{m} \Theta \langle n | \Theta | m \rangle$

$$
= \sum_{mn} a_{n}^{*} a_{m} \Theta_{nm}
$$

$$
\langle \langle \psi | \Theta | \psi \rangle \rangle = \sum_{mn} \langle a_{n}^{*} a_{m} \rangle \Theta_{nm} = \sum_{mn} S_{mn}(t) \Theta_{nm}
$$
\[ \sum_{mn} \langle m | \rho | n \rangle \langle n | \Theta | m \rangle = \sum_{m} \langle m | \rho \Theta | m \rangle = \text{Tr}(\rho \Theta) = \langle \Theta \rangle = \text{Tr}(\Theta \rho) \]

\[ \rho = \text{density matrix} \]

Equation: Equation of motion of \( \rho \):

We have \[ i \hbar \dot{\rho}_{mn} = i \hbar \left[ \langle a_m a_n^* \rangle + \langle a_m^* a_n \rangle \right] \]

But \[ i \hbar \dot{a}_m = \sum_p H_{mp} a_p \]

so \[ -i \hbar \dot{a}_m = \sum_p H^*_{mp} a_p^* = \sum_p H_{pn} a_p^* \]

or \[ i \hbar \dot{a}_m = -\sum_p H_{pn} a_p^* \]

So we have

\[ i \hbar \dot{\rho}_{mn} = \sum_p H_{mp} \langle a_p a_n^* \rangle - \sum_p H_{pn} \langle a_m a_p^* \rangle \]

\[ = \sum_p (H_{mp} \rho_{pn} - \rho_{mp} H_{pn}) \]

\[ = \sum_p (H \rho - \rho H)_{pn} \]

or \[ i \hbar \dot{\rho} = H \rho - \rho H = [H, \rho] \]
Analogous to Liouville's equation from last quarter

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

where

\[ [A,B] \text{ means } \]

\[ [A,B] \equiv \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \]

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**Stationary ensemble:** \( \dot{\rho} = 0 \)

or \([\rho, H] = 0 \)

**Example:**

(i) Canonical ensemble:

\( \rho = C e^{-\frac{H}{k_B T}} \)

(ii) Microcanonical ensemble:

\( \rho = 0 \)

More interpretation: choose \( \theta \) to define \( \rho \)

Some more properties of \( \rho \):

(i). \( Tr \rho = 1 \)

Proof:

\[ \rho_{mn} = \langle a_m^* a_n \rangle \]
\[ \text{Tr} \rho = \sum_m s_{mm} = \sum_m \langle \lambda_m^2 \rangle = \sum_m \langle \lambda_m^2 \rangle \]

But \[ \langle \psi | \psi \rangle = 1 = \sum_{mn} a^*_m a_n \langle m | n \rangle \delta_{mn} \]

\[ = \sum_m \lambda_m^2 \quad \text{So} \quad \text{Tr} \rho = 1 \]

Evidently \( p_{mn}(t) \) is probability that a system at time \( t \) is found to be in state \( |N \rangle \).

**Note:** (if \( H \) is still diagonal in the basis \( n \))

Some examples of ensembles \( \rho \) in various ensembles.

1. **Microcanonical Ensemble.** Here we assume that any state \( |N \rangle \) is as likely as any other, at a given energy \( E \):

\[ s_{mn} = \frac{1}{N} \sum_{i=1}^{N} \langle a_m a^*_n \rangle = \frac{1}{N} \sum_{i=1}^{N} \left( \text{Tr} \rho \right) = 1 \]

Here we are assuming that the states \( |m \rangle \) are eigenstates of \( H \), i.e.,

\( H|m \rangle = E_m |m \rangle \)

\[ = 0 \quad \text{otherwise}, \quad \frac{1}{2} \delta_{mn} \]

\( \Gamma = \# \text{of states between } E \text{ and } E + \frac{1}{2} \Delta \)
This is known as the postulate of equal a priori probabilities.

How about \( \rho_{nm} \)? (\( n \neq m \))

This is: 
\[
\frac{1}{N} \sum_{k=1}^{N} \langle a_n a_m^* \rangle
\]
\[
= \frac{1}{N} \sum_{k=1}^{N} \langle \hat{H}_n \hat{H}_m \rangle e^{i(\Theta_n - \Theta_m)} \mathcal{M}
\]

("postulate of random phases")

That is, we assume that the relative phase of any two components is zero, i.e., \( \rho_{nm} = 0 \) for \( n \neq m \).

So in short, the density matrix in the microcanonical ensemble is

\[ \rho_{nm} = \delta_{nm} \rho_n \]

where

\[ \rho_n = \frac{1}{\Gamma} e^{-\frac{1}{2} \Gamma} \]

\[ 0 < \rho_n < e^{-\frac{1}{2} \Gamma} \]

Properties in microcanonical ensemble:

\[ S = k_B \ln \Gamma \]

Can now get everything as previously in the classical case.
"Pure" case: \( \beta = 1 \), \( \varphi = \varphi_0 \)

Microcanonical ensemble:

\[
\varphi = \frac{1}{N} \begin{pmatrix}
0 & 0 & \cdots & 0 \\
0 & 0 & \cdots & 0 \\
\vdots & \ddots & \ddots & \vdots \\
0 & \cdots & 0 & 0
\end{pmatrix}
\]

where states in the same block are all within \( \Delta \) of the same energy \( E \).

Canonical ensemble: In representation where \( H \) is diagonal

\[
\rho_{n n'} = \frac{e^{-\beta E_n}}{\sum_{n} e^{-\beta E_n}}
\]

Also, \( \rho_{n n'} = \frac{1}{N} \sum_{k=1}^{N} a_n^k a_n^{* k} \) = 0 by assumption (random phase assumption)

So

\[
\rho_{n n'} = \delta_{n n'} \frac{e^{-\beta E_n}}{\sum_{n} e^{-\beta E_n}}
\]

\[
e^{-\beta E_n} = \langle n | e^{-\beta H} | n \rangle
\]

\[
\sum_{n} e^{-\beta E_n} = Tr e^{-\beta H}
\]

Since \( e^{-\beta H} \) is diagonal in energy representation we have

\[
\rho = \frac{1}{Q_N(V, \mathbb{T})} e^{-\beta H}
\]

where \( Q_N(V, \mathbb{T}) = Tr e^{-\beta H} \) in any representation

So \( \langle \hat{\Theta} \rangle = \frac{Tr e^{-\beta H}}{Tr e^{-\beta H}} = Tr(\hat{\Theta}) = Tr(\Theta) \)
Grand canonical ensemble

\[ S = \frac{\mathcal{N} \, e^{-\beta(H - \mu N)}}{\operatorname{Tr} e^{-\beta(H - \mu N)}} \]

where \( H, N \) are taken as operators in state \( \mathcal{N} \).

\[ \mathcal{N} \] is the number of particles in state \( \mathcal{N} \).

\[ \mathcal{O} = \frac{\operatorname{Tr}(\mathcal{O} \rho)}{\operatorname{Tr} \, e^{-\beta(H - \mu N)}} = \frac{\operatorname{Tr} \, e^{-\beta(H - \mu N)} \mathcal{O} \operatorname{Tr} e^{-\beta(H - \mu N)}}{\operatorname{Tr} e^{-\beta(H - \mu N)}} \]

I will give examples of all this.

Note, by the way, that

\[ \operatorname{Tr}(\mathcal{O} \rho) \neq \text{is independent of choice of basis} \]

For example, in a different basis,

\[ \mathcal{O} \rightarrow R^T OR \]

\[ \operatorname{Tr} \mathcal{O} \rightarrow \operatorname{Tr}(R^T OR) = \operatorname{Tr}(OR^T O) = \operatorname{Tr} \mathcal{O} \]

(Skip this)
Ideal gases: Bose and Fermi gases

First consider a particle in a box (assume spinless for now)

\[ H = -\frac{\hbar^2}{2m} \nabla^2 = \frac{p^2}{2m} \quad \hat{p} = -i\hbar \nabla \]

Consider \( H |\psi\rangle = \varepsilon |\psi\rangle \)

\[ \psi(x) = C e^{i\mathbf{k} \cdot \mathbf{x}} \quad \text{where } C = \text{normalization constant} \]

Corresponding energy is

\[ \varepsilon_{\mathbf{k}} = \varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad k^2 = k_x^2 + k_y^2 + k_z^2 \]

Normalization? Assume we are in a large box of vol \( V \) with periodic b.c.

\[ \int |\psi(x)|^2 d^3x = 1 = |C|^2 \cdot V \quad V = L^3 \]

\[ |C| = \frac{1}{\sqrt{V}} \quad \text{Take } C \text{ real. } C = \frac{1}{\sqrt{V}} \]

Allowed values of \( \mathbf{k} \):

\[ \psi(x + L, y, z) = \psi(x) \]

How to treat statistical mechanics of this system? (Either Bosons or Fermions)
\[ e^{i \vec{k} \cdot (\vec{x} + \vec{L} \vec{x})} = e^{i \vec{k} \cdot \vec{x}} \]
\[ e^{i \vec{k} \cdot \vec{x}} = 1 \quad e^{i \vec{k} \cdot \vec{L} \vec{x}} = 1 \]

\[ k_x = \frac{2 \pi}{L} p_x \quad p_x = 0, \pm 1, \pm 2, \ldots \]

and in general \[ \vec{k} = \frac{2 \pi}{L} (p_x, p_y, p_z) \]

\[ p_x, p_y, p_z = 0, \pm 1, \pm 2, \ldots \]

Note: there is one allowed point in \( k \) space for every \( \frac{1}{(2\pi/L)^3} \) of volume of \( k \) space.

So density of points in \( k \) space is \( \frac{1}{(2\pi/L)^3} = \frac{L^3}{(2\pi)^3} \)

Now: \( N \) particle system

Total energy \( E = \sum_{\vec{k}} n_{\vec{k}} E_{\vec{k}} \)

\[ \vec{k} = \frac{2 \pi}{L} (p_x, p_y, p_z) \]

\( n_{\vec{k}} \) = occupation of state \( \vec{k} \).

Two types of particles: Bosons and Fermions

Bosons: \( n_{\vec{k}} = 0, 1, 2, \ldots \)

Fermions: \( n_{\vec{k}} = 0 \) and \( 1 \) only

How to treat this system statistical-mechanically?
Easiest method: grand canonical ensemble

\[ Z(\mu, V, T) = \sum_{\text{states}} e^{-\beta (E - \mu N)} \]

\[ = \sum_{\text{states}} e^{-\beta \left( \sum_k n_k (E_k - \mu) \right)} \]

\[ = \prod_k e^{-\beta (E_k - \mu) n_k} \]

Case 0: Fermions \( n_k = 0, 1 \)

\[ Z = \sum_{n_k=0,1} \prod_k e^{-\beta (E_k - \mu) n_k} \]

\[ = \prod_k \left[ 1 + e^{-\beta (E_k - \mu)} \right] \]

and \( \Omega = -PV = \mu N - k_B T \ln Z \)

\[ \Omega = -k_B T \sum_k \ln \left( 1 + e^{-\beta (E_k - \mu)} \right) \]
Bosons:

\[
2 = \prod_k \frac{\sum_{n_k=0,1,2,\ldots} \prod_k e^{-\beta (E_k - \mu) n_k}}{\prod_k (1 + e^{-\beta (E_k - \mu)} + e^{-2\beta (E_k - \mu)} + e^{-3\beta (E_k - \mu)} + \ldots)}
\]

\[
= \prod_k \frac{1}{1 - e^{-\beta (E_k - \mu)}}
\]

\[
\Omega = -k_B T \ln 2 = +k_B T \sum_k \ln (1 - e^{-\beta (E_k - \mu)})
\]

or, in general

\[
\Omega = +k_B T \sum_k \ln (1 + e^{-\beta (E_k - \mu)})
\]

for Fermions

We now introduce spin degeneracy \( g \)

\[
g = \text{even } 2S + 1 \quad \text{where } S = \text{spin of particle}
\]

\( S = \) half-integer for Fermions

\( S = \) integer for Bosons

So in general

\[
\Omega = +g k_B T \sum_k \ln (1 + e^{-\beta (E_k - \mu)})
\]

Thermodynamics

\[
\bar{N} = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{V,T}
\]

\[
= g \sum_k \frac{1}{\overline{\left( n_k \right)}}
\]

\[
= g \sum_k \frac{1}{e^{\beta (E_k - \mu)} + 1}
\]
Could interpret \( \langle \eta_k \rangle = \frac{1}{e^{\beta(E_k - \mu)} + 1} \) as

average occupation no. of state \( k \).

Why is this reasonable?

Prob. of \( \eta_k \)

Case (a). Prob. of having \( \eta_k \) excitations

in state \( k \) is proportional to \( e^{-\beta(E_k - \mu)\eta_k} \)

so

\[
\langle \eta_k \rangle = \frac{\sum \eta_k e^{-\beta(E_k - \mu)\eta_k}}{\sum \eta_k} = \frac{\sum \eta_k}{\sum \eta_k} = \frac{1}{e^{\beta(E_k - \mu)} + 1}
\]

where sum runs from 0 to 1 for fermions or 0 to \( \infty \) for bosons.

Fermions:

\[
\langle \eta_k \rangle = \frac{e^{-\beta(E_k - \mu)}}{[1 + e^{-\beta(E_k - \mu)}]} = \frac{1}{e^{\beta(E_k - \mu)} + 1}
\]

Bosons:

\[
\sum_{\eta_k = 0}^{\infty} e^{-\beta(E_k - \mu)\eta_k} = \frac{1}{1 - e^{-\beta(E_k - \mu)}}
\]

\[
\sum_{\eta_k = 0}^{\infty} \eta_k e^{-\beta(E_k - \mu)\eta_k} = -\frac{d}{dx} \sum_{\eta_k = 0}^{\infty} e^{-\eta_k x} \quad x = \beta(E_k - \mu)
\]

So the ratio is

\[
\frac{e^{-x}}{1 - e^{-x}} = \frac{1}{e^{\beta(E_k - \mu)} - 1}
\]

g. e. d.
More details of ideal gases:

(i). Fermi system

We have

\[ \Omega = -k_B T g \sum_k \ln \left(1 + e^{-\beta (E_k - \mu)} \right) \]

for \( g = \text{even} \# \)

How to do the sum?

We have that density \( \rho \) of points in \( k \) space is

\[ \frac{1}{(2\pi)^d} = \frac{1}{(2\pi)^d} \quad \text{in } d \quad \text{dimensions} \]

So \( \sum_k \rightarrow \int \frac{d^d k}{(2\pi)^d} \quad \text{in } d \quad \text{dimensions} \)

\[ \Omega = -k_B T g \int \frac{d^d k}{(2\pi)^d} \ln \left(1 + e^{-\beta (E_k - \mu)} \right) \]

Let \( d = 3 \), \( \varepsilon_k = \frac{\hbar^2 k^2}{2m} \)

\[ P/N = \Omega = -k_B T \frac{V}{(2\pi)^3} \cdot 4\pi \int \frac{d^2 k}{(2\pi)^3} \ln \left(1 + e^{-\beta (\frac{\hbar^2 k^2}{2m} - \mu)} \right) \]

\[ P = \frac{k_B T}{2\pi^2} \int_0^\infty d^2 k \ln \left(1 + e^{-\beta (\frac{\hbar^2 k^2}{2m} - \mu)} \right) \]

Can also get number of particles from

\[ \bar{N} = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{V,T} = g \sum_k \frac{1}{e^{\beta (E_k - \mu)} + 1} \]
\[ = \frac{g V}{(2\pi)^3} \int_0^{\infty} \frac{d^3k}{e^{\beta(E_k - \mu)} + 1} \]

where \( \beta k = \frac{k_B T}{2m} \)

\[ = \frac{g V}{2\pi^2} \int_0^{\infty} \frac{k^2 dk}{e^{\beta(E_k - \mu)} + 1} \quad \Rightarrow \quad \mu \left( \frac{N}{V}, T \right) \]

Can be rewritten in many other ways.

**Internal energy:**

that we have \( U - TS + PV = N\mu \)

Evolution relation

or \( U = N\mu + TS - PV \)

\[ = -\Omega - T \left( \frac{\partial \Omega}{\partial T} \right)_{N, \mu} - \mu \left( \frac{\partial \Omega}{\partial \mu} \right)_{N, T} \]

\[ \left( \frac{\partial \Omega}{\partial T} \right)_{N, \mu} = -g k_B \sum_k \ln \left( 1 + \frac{e^{-\beta(E_k - \mu)}}{k_B T} \right) \]

\[ - k_B T \sum_k \frac{e^{-\beta(E_k - \mu)}}{1 + e^{-\beta(E_k - \mu)}} \]

So \( U = -k_B T g \sum_k \ln \left( 1 + \frac{e^{-\beta(E_k - \mu)}}{k_B T} \right) \]

\[ + g k_B T \sum_k \ln \left( 1 + \frac{e^{-\beta(E_k - \mu)}}{k_B T} \right) \]

\[ + g \sum_k \frac{E_k}{e^{\beta(E_k - \mu)} + 1} + \mu \sum_k \frac{g}{e^{\beta(E_k - \mu)} + 1} \]

\[ = g \sum_k \frac{E_k}{1 + e^{\beta(E_k - \mu)}} = g \sum_k \frac{E_k \langle n_k \rangle}{1 + e^{\beta(E_k - \mu)}} \]
\[ \langle n \rangle = g \frac{V}{2\pi^2} \int_0^\infty \frac{\varepsilon_k}{e^{\beta(\varepsilon_k - \mu)} + 1} k^2 dk \]

But we also have

\[ U = g \frac{V}{2\pi^2} \frac{\hbar^2}{2m} \int_0^\infty \frac{k^4 dk}{e^{\beta(\varepsilon_k - \mu)} + 1} \]

\[ \Omega = -PV = -\frac{V k_B T}{2\pi^2} \int_0^\infty k^2 \ln \left( 1 + e^{-\beta \left( \frac{k^2}{2m} - \mu \right)} \right) dk \]

Integrate by parts

\[ = -\frac{V k_B T}{2\pi^2} g \frac{k^3}{3} \left[ \frac{-\beta \left( \frac{k^2}{2m} - \mu \right)}{e^{\beta \left( \frac{k^2}{2m} - \mu \right)}} + \right]_0^\infty \]

\[ + \frac{V k_B T}{2\pi^2} \frac{\hbar^2}{3} \int_0^\infty k^3 \frac{1}{1 + e^{-\beta \left( \frac{k^2}{2m} - \mu \right)}} \left[ -2 \beta \frac{k^2}{m} \right] dk \]

\[ = -\frac{2}{3} \frac{V k_B T}{3} \int_0^\infty \frac{k^4 dk}{1 + e^{\beta \left( \frac{k^2}{2m} - \mu \right)}} \]

\[ = -\frac{2}{3} \Omega U \]

or

\[ \bar{E} = \frac{3}{2} PV \]

Ideal Fermi gas in 3d