Theory 4. Statistical Physics. 1/9

Lecture 26.

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Last time: van der Waals eqn.
Gibbs degeneracy + phase coexistence
Classification of phase transitions

Today: Quantum statistics
Exchange symmetry + spin-statistics
Bose-Einstein distribution, Fermi-Dirac distribution
Fermi gas, Fermi energy. Bose-Einstein condensation

We now exploit the fact that stat. mech. does not need to adopt the thermodynamic limit of $N \to \infty$, but instead is also applicable for finite N. It is also important to understand non-interacting models obeying quantum statistics.

Recall quantum physics. [Mini-review]

Microstate of quantum system is its wavefunction, commonly expressed over position-space variables.

$$\Psi(\vec{q}_1, \ldots, \vec{q}_N) \equiv \langle \{\vec{q}_i\} | \Psi \rangle$$

In general, the state vector $|\Psi\rangle$ belongs to an infinite-dimensional Hilbert space & can be written via components $\langle \Lambda | \Psi \rangle$, where

$|n\rangle$ are an orthonormal basis of vectors:

$$|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle$$

The normalization condition (necessary for a probabilistic interpretation) is

$$\langle\psi|\psi\rangle = \sum_n \langle\psi|n\rangle\langle n|\psi\rangle = 1, \quad \text{with } \langle\psi|n\rangle \equiv \langle n|\psi\rangle^*$$

In position space, we need

$$\langle\psi|\psi\rangle = \int \prod_{i=1}^{N} d^d\vec{q}_i \; |\psi(\vec{q}_1,\ldots,\vec{q}_N)|^2 = 1.$$

Observables are now Hermitian matrices in Hilbert space, where functional dependence of $O(\{\vec{p}_i,\vec{q}_i\})$ on momenta + coordinates is now an operator dependence subject to the quantization condition

= non-zero commutation relation, $[p_j, q_k] \equiv p_j q_k - q_k p_j$

Typically, momentum operator in positionspace is $p_j = \frac{\hbar}{i}\frac{\partial}{\partial q_j}$. $= \frac{\hbar}{i}\delta_{j,k}$.

To evaluate operators, we now need to evaluate expectation values as inner products:

$$\langle O\rangle = \langle\psi|O|\psi\rangle \equiv \sum_{m,n}\langle\psi|m\rangle\langle m|O|n\rangle\langle n|\psi\rangle$$

Operators must be Hermitian for real-valued exp. values, $O = O^\dagger$, $\langle m|O^\dagger|n\rangle \equiv \langle n|O|m\rangle^*$.

(Need to symmetrize $\hat{p}\hat{q}$ operators for hermiticity.)

The state vector time-evolves by Hamiltonian, know as Schrödinger's eqn.

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

It is convenient to diagonalize $\hat{H}$ and this defines the energy eigenstate basis,

$\hat{H}|n\rangle = E_n |n\rangle$, with E_n as eigenvalues.

Can derive $\frac{i\hbar d}{dt} \langle n|\psi(t)\rangle = E_n \langle n|\psi(t)\rangle$

$$\Rightarrow \langle n|\psi(t)\rangle = \exp\left(-i\frac{E_n t}{\hbar}\right) \langle n|\psi(0)\rangle$$

Can also see the Hamiltonian is the generator of time evolution, $|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle$

with unitary matrix $U(t,t_0) = \exp\left[\frac{-i}{\hbar}\hat{H}(t-t_0)\right]$

and $U(t_0,t_0) = 1$.

Now, we want to construct quantum macrostates.

In classical physics, trajectories in phase space were individual microstates and then we constructed macrostates from finite regions in phase space + calculating the number of microstates.

In quantum physics, the microstates already offer a probabilistic interpretation, but measuring any ~~prob~~ property (at large) of a system will generally ascribe the system as a <u>mixed</u> state, not a pure state.

Thus, a mixed quantum state is a set of possible states $\{|\psi_\alpha\rangle\}$ with probabilities $\{p_\alpha\}$.

The corresponding ensemble average in quantum physics thus follows

$$\overline{\langle O\rangle} = \sum_\alpha p_\alpha \langle\psi_\alpha|O|\psi_\alpha\rangle$$

$$= \sum_{\alpha,m,n} p_\alpha \langle\psi_\alpha|m\rangle\langle n|\psi_\alpha\rangle\langle m|O|n\rangle$$

$$= \sum_{m,n} \langle n|\rho|m\rangle\langle m|O|n\rangle$$

$$= \mathrm{tr}(\rho O)$$

where ρ = density matrix, defined via:

$$\langle n|\rho(t)|m\rangle \equiv \sum_\alpha p_\alpha \langle n|\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|m\rangle$$

Regardless of basis choice,

$$\rho(t) = \sum_\alpha p_\alpha |\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|$$

ρ is pure state iff $\rho^2 = \rho$.

[In contrast, recall classical ensemble avgs:

$$\overline{O(\{\vec{p}_i,\vec{q}_i\})} = \sum_\alpha p_\alpha O(\mu_\alpha(t))$$

$$= \int \prod_{i=1}^N d^3\vec{p}_i\, d^3\vec{q}_i\; O(\{\vec{p}_i,\vec{q}_i\})\cdot\rho(\{\vec{p}_i,\vec{q}_i\},t)$$

with

$$\rho(\{\vec{p}_i,\vec{q}_i\},t) = \sum_\alpha p_\alpha \prod_{i=1}^N \delta^3(\vec{q}_i-\vec{q}_i(t)_\alpha)\,\delta^3(\vec{p}_i-\vec{p}_i(t)_\alpha)$$

as phase space density.]

The density matrix obeys normalization, $\langle 1\rangle = \mathrm{tr}(\rho) = 1$, Hermiticity, & positivity (all eigenvalues are positive definite).

[By Liouville's theorem, the classical density time evolved via

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} - \{H, \rho\} = 0 \ ]$$

The quantum density matrix time-evolves in energy basis via

$$i\hbar \frac{\partial}{\partial t} \langle n|\rho(t)|m\rangle = \langle n|(H\rho - \rho H)|m\rangle.$$

$$\Rightarrow \quad i\hbar \frac{\partial \rho}{\partial t} = [H, \rho], \text{ independent of basis.}$$

Equilibrium requires time-independent avgs., so $\frac{\partial \rho}{\partial t} = 0$, and so is satisfied for $\rho = \rho(H)$.

Can formulate microcanonical, canonical, & grand canonical ensembles. See Kardar, Chap. 6.5.

The density matrix is then directly related to the partition fcn.

Recall that the spin-statistics theorem states that bosons have integer spin and have symmetric wavefunctions under particle exchange while fermions have half-integer spin and have anti-symmetric wavefcns under particle exchange.

Bosons: ^{4}He (spin 0), photons (spin 1)

Fermions: proton, neutron, electron, ^{3}He (spin 1/2), ^{7}Li nuclei (spin 3/2).

Boson: $\Psi(\vec{x}_1, \vec{x}_2) = \Psi(\vec{x}_2, \vec{x}_1)$; fermions: $\Psi(\vec{x}_1, \vec{x}_2) = -\Psi(\vec{x}_2, \vec{x}_1)$

Importantly, the spin-statistics theorem is a consequence of studying 1-particle representations of the Poincaré group in 4D spacetime ($O(1,3)$ group). Aside: this is why the dimensionality of spacetime affects the possible ways particles can carry spin, leading to anyons in 2 spatial dimensions (see Blundell & Blundell, p. 347.)

Ex: Suppose a particle can have states $|0\rangle$ and $|1\rangle$. Two particles:

Classical: $|0\rangle|0\rangle$, $|0\rangle|1\rangle$, $|1\rangle|0\rangle$, $|1\rangle|1\rangle$

Indistinguishable: $|0\rangle|0\rangle$, $|1\rangle|0\rangle = |0\rangle|1\rangle$, $|1\rangle|1\rangle$

Bosons: $|0\rangle|0\rangle$, $\frac{1}{\sqrt{2}}(|1\rangle|0\rangle + |0\rangle|1\rangle)$, $|1\rangle|1\rangle$

Fermions: $\frac{1}{\sqrt{2}}(|1\rangle|0\rangle - |0\rangle|1\rangle)$

Recall: Pauli exclusion principle. Two fermions cannot occupy same quantum state: must differ by at least one quantum number eigenvalue.

Deriving occupation numbers.

Consider grand partition fcn. $\mathcal{Z}_G$, all fermions or bosons.

$$\mathcal{Z}_G = \sum_\alpha e^{\beta(\mu N_\alpha - E_\alpha)}$$

Suppose only one state to put particles & energy is E. Grand partition fcn sums over configurations, each with different number n: $\mathcal{Z}_G = \sum_n e^{n\beta(\mu - E)}$

Then, $\langle n \rangle = \dfrac{\sum_n n e^{n\beta(\mu - E)}}{\sum_n e^{n\beta(\mu-E)}} = \dfrac{-1}{\beta \mathcal{Z}} \dfrac{\partial \mathcal{Z}}{\partial E} = \dfrac{-1}{\beta} \dfrac{\partial \ln \mathcal{Z}}{\partial E}$

For fermions, sum truncates at $n=0$ + $n=1$,

$$\mathcal{Z}_F = \sum_{n=0}^{1} e^{n\beta(\mu-E)} = 1 + e^{\beta(\mu-E)},$$

$$\ln \mathcal{Z}_F = \ln\left(1 + e^{\beta(\mu-E)}\right)$$

For bosons, sum runs from 0 to ∞:

$$\mathcal{Z}_B = \sum_{n=0}^{\infty} e^{n\beta(\mu-E)} = \frac{1}{1 - e^{\beta(\mu-E)}}$$

$$\ln \mathcal{Z}_B = -\ln\left(1 - e^{\beta(\mu-E)}\right)$$

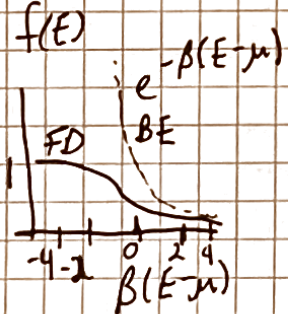
Then, $\langle n \rangle = \dfrac{-1}{\beta} \dfrac{\partial \ln \mathcal{Z}}{\partial E} = \dfrac{1}{e^{\beta(E-\mu)} \pm 1}$, with

+ for fermions and − for bosons.

When system has multiple states i each with energy cost E_i, then $\langle n_i \rangle = \dfrac{1}{e^{\beta(E_i - \mu)} \pm 1}$.

These define the Fermi-Dirac distribution fcn:

$$f_F(E) = \frac{1}{e^{\beta(E-\mu)} + 1},$$



and Bose-Einstein distribution fcn.,

$$f_B(E) = \frac{1}{e^{\beta(E-\mu)} - 1},$$

which dictate the mean occupation of a state with energy E, $f(E) = \langle n \rangle$.

Two fcns. look same for $\beta(E-\mu) \gg 1$, low density (μ small).

The key difference is when we consider the $T \to 0$ limit. Even with no interactions, the req. from exchange symmetry of quantum spin reveals qualitatively diff. behavior between fermions + bosons.

Fermions at $T=0$: Fermi gas.

Fermions occupy lowest energy state, $2S+1$ in each energy level with each particle with spin S. Will get to E_F = Fermi energy = energy of highest occupied state at $T=0$.

$$E_F = \mu(T=0) = \frac{\partial E}{\partial N} = E(N) - E(N-1) = E_F.$$

Take $T \to 0$, $\beta \to \infty$,

$$n_{\vec{k}} = \frac{1}{e^{\beta(E_{\vec{k}} - \mu)} + 1} = \theta(\mu - E_k) = \theta(E_F - E_k).$$

Now use momentum states & label mean occupation $n_{\vec{k}}$ of state w/ wave vector $\vec{k}$.

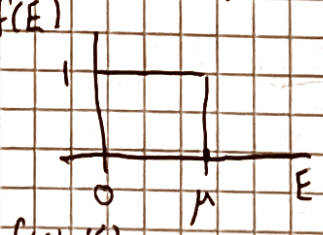
$$N = \int_0^{k_F} g(\vec{k})\, d^3k,$$

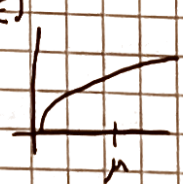
k_F = Fermi wave vector, $E_F = \frac{\hbar^2 k_F^2}{2m}$.

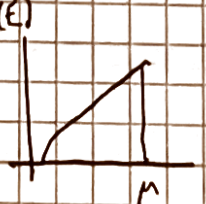
Fermi surface: set of points in $\vec{k}$ space whose energy equals chemical potential.

$$\Rightarrow N = \frac{(2S+1)}{2\pi^2} V \frac{k_F^3}{3}$$

$$\& \quad n = \frac{N}{V} \Rightarrow k_F = \left[\frac{6\pi^2 n}{2S+1}\right]^{1/3}, \quad E_F = \frac{\hbar^2}{2m}\left[\frac{6\pi^2 n}{2S+1}\right]^{2/3}$$







Responsible for semiconductors. depending on chemical potential.

Bose-Einstein condensation.

We will need the expressions for quantum ideal gas/fluid.

$$\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$N = \frac{(2S+1)V}{\lambda_{th}^3}\left[\mp Li_{3/2}(\mp z)\right]$$

$$U = \frac{3}{2} N k_B T \frac{Li_{5/2}(\mp z)}{Li_{3/2}(\mp z)}.$$

Li = dilogarithm.

$z \equiv$ fugacity $= e^{\beta\mu}$

$-$ = fermion
$+$ = boson.
See Blundell

+Blundell, $N = N_0 + N_1$ ← not in gd state
Chap. 30.

$$N_0 = \frac{1}{z^{-1}-1} = \frac{1}{e^{-\beta\mu}-1}$$

Have issue for ~~FG~~ ~~(Bose)~~

$$\frac{n\lambda_{th}^3}{2S+1} = Li_{3/2}(z)$$

$\Rightarrow$ extract $k_B T_c = \frac{2\pi\hbar^2}{m}\left(\frac{n}{\zeta(3/2)(2S+1)}\right)^{2/3}$

This dictates, for $T < T_c$,

$$n = \frac{(2S+1)\zeta(3/2)}{[\lambda_{th}(T_c)]^3} + n_1 = \frac{(2S+1)\zeta(3/2)}{[\lambda_{th}(T)]^3}$$

such that $\frac{n_0}{n} = \frac{n-n_1}{n} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$

is a macroscopic fraction of the dof. in the ground state. This is true w/o interactions!

Familiar example of Bose-Einstein condensation is liquid Helium, LHe, which acts as a superfluid for $T_c = 2.2$K, although it interacts from high molecular density. Pure BEC system is ultracold atomic gases.

Next time: Course summary.