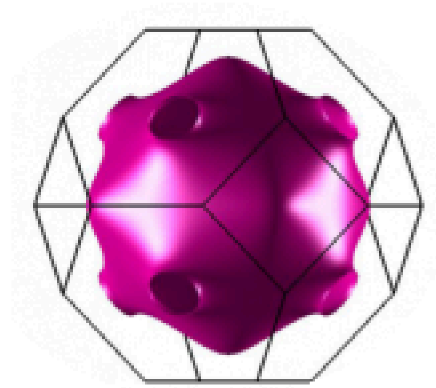
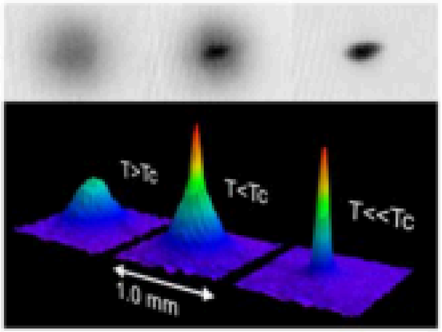
Lecture 30. *Quantum gases and condensates*

- **Quantum gas**: when quantum statistics affects observables
  - **Low-density** (low chemical potential): quasi-classical…
  - **High-density**: quantum mechanical effects start to show more significantly



Fermi surface



Bose condensate

Previous lecture

Other reminder:

$$\lambda_{\mathrm{th}} = n_{\mathrm{Q}}^{-1/3} = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}$$

The wave function of a pair of bosons is symmetric under exchange of particles, while the wave function of a pair of fermions is antisymmetric under exchange of particles.

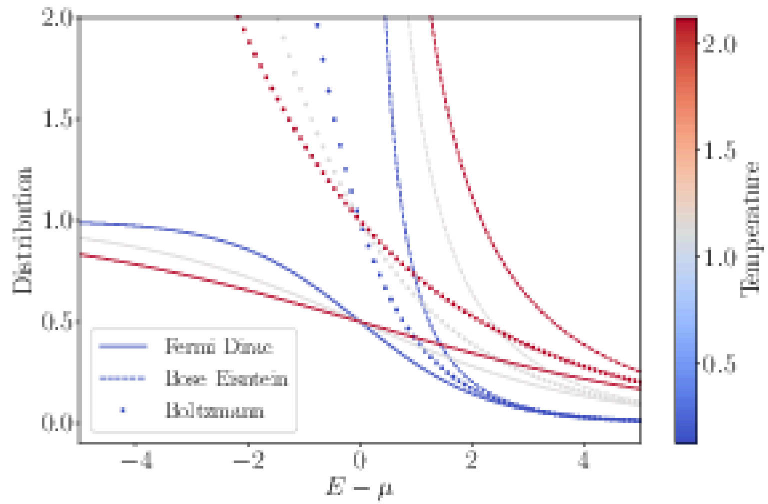
Bosons can share quantum states, while fermions cannot share quantum states.

Bosons obey Bose-Einstein statistics, given by

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

Fermions obey Fermi-Dirac statistics, given by

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



The non-interacting quantum fluid

- Particles of spin S
- Degeneracy: $2S+1$ spin states
- Grand partition function is the product of the GPF of individual particles (non-interacting)

$$\mathcal{Z} = \prod_{\boldsymbol{k}} \mathcal{Z}_{\boldsymbol{k}}^{2S+1}$$

$$\mathcal{Z}_{\boldsymbol{k}} = \left(1 \pm \mathrm{e}^{-\beta(E_{\boldsymbol{k}}-\mu)}\right)^{\pm 1}$$

Individual GPF

Fermions (+)

Bosons (-)

Notes

- Non-interacting
- Number of particles can change

$$\ln \mathcal{Z} = \pm(2S+1)\sum_{k} \ln\left(1 \pm \mathrm{e}^{-\beta(E_k-\mu)}\right)$$

Grand potential

$$\ln Z = \pm(2S+1)\sum_{k}\ln\left(1 \pm e^{-\beta(E_k-\mu)}\right)$$

$$\begin{aligned}
\Phi_{\rm G} &= -k_{\rm B}T\ln\mathcal{Z} \\
&= \mp k_{\rm B}T(2S+1)\sum_{\boldsymbol{k}}\ln(1\pm \mathrm{e}^{-\beta(E_{\boldsymbol{k}}-\mu)}) \\
&= \mp k_{\rm B}T\int_0^\infty \ln(1\pm \mathrm{e}^{-\beta(E-\mu)})\, g(E)\,\mathrm{d}E
\end{aligned}$$

$$= \mp k_{\rm B}T\frac{(2S+1)V}{(2\pi)^2}\left(\frac{2m}{2}\right)^{3/2}\int_0^\infty \ln(1\pm \mathrm{e}^{-\beta(E-\mu)})\, E^{1/2}\,\mathrm{d}E$$

Density of states

$$g(k)\,\mathrm{d}k = \frac{4\pi k^2\,\mathrm{d}k}{(2\pi/L)^3}\times(2S+1)$$

$$= \frac{(2S+1)Vk^2\,\mathrm{d}k}{2\pi^2}$$

If we have: $E = \hbar^2k^2/2m$

$$g(E)\mathrm{d}E = \frac{(2S+1)VE^{1/2}\,\mathrm{d}E}{(2\pi)^2}\left(\frac{2m}{2}\right)^{3/2}$$

$$\Phi_{\rm G} = -\frac{2}{3}\frac{(2S+1)V}{(2\pi)^2}\left(\frac{2m}{2}\right)^{3/2}\int_0^\infty \frac{E^{3/2}\,\mathrm{d}E}{\mathrm{e}^{\beta(E-\mu)}\pm 1}$$

Fermions (+)

Bosons (-)

Thermodynamics functions

Mean occupation of state with wave vector $\mathbf{k}$: $$n_{\boldsymbol{k}} = k_{\mathrm{B}}T \frac{\partial}{\partial \mu} \ln \mathcal{Z}_{\boldsymbol{k}} = \frac{1}{\mathrm{e}^{\beta(E_{\boldsymbol{k}}-\mu)} \pm 1}$$

Total number of particles: $$N = \sum_{\boldsymbol{k}} n_{\boldsymbol{k}} = \int_0^\infty \frac{g(E)\,\mathrm{d}E}{\mathrm{e}^{\beta(E-\mu)} \pm 1}$$

Internal energy: $$U = \sum_{\boldsymbol{k}} n_{\boldsymbol{k}} E_{\boldsymbol{k}} = \int_0^\infty \frac{E\,g(E)\,\mathrm{d}E}{\mathrm{e}^{\beta(E-\mu)} \pm 1}$$

Using DoS:

$$N = \left[\frac{(2S+1)V}{(2\pi)^2}\left(\frac{2m}{2}\right)^{3/2}\right]\int_0^\infty \frac{E^{1/2}\,\mathrm{d}E}{z^{-1}\mathrm{e}^{\beta E} \pm 1}$$

$$U = \left[\frac{(2S+1)V}{(2\pi)^2}\left(\frac{2m}{2}\right)^{3/2}\right]\int_0^\infty \frac{E^{3/2}\,\mathrm{d}E}{z^{-1}\mathrm{e}^{\beta E} \pm 1}.$$

Density of states

$$g(E)\,\mathrm{d}E = \frac{(2S+1)V E^{1/2}\,\mathrm{d}E}{(2\pi)^2}\left(\frac{2m}{2}\right)^{3/2}$$

Fugacity

$$z = \mathrm{e}^{\beta\mu}$$

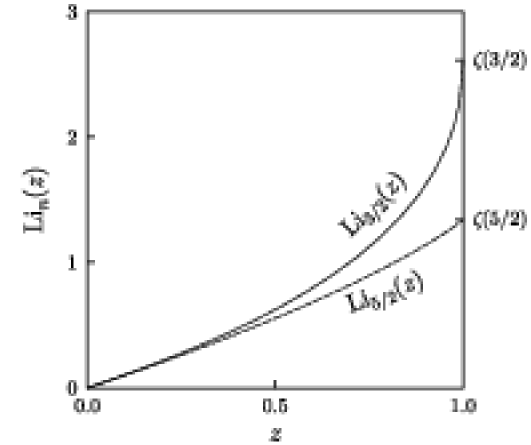
A bit of math: polylogarithm and gamma functions

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

Only depends on temperature and chemical potential

Polylogarithm function

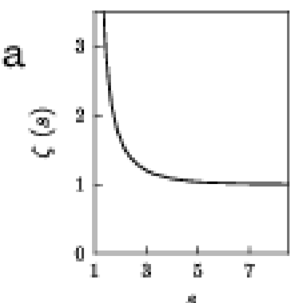
$$\mathrm{Li}_n(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^n}$$



$$\int_0^{\infty} \frac{E^{n-1}\,\mathrm{d}E}{z^{-1}e^{\beta E} \pm 1} = (k_B T)^n \Gamma(n)[\mp \mathrm{Li}_n(\mp z)]$$

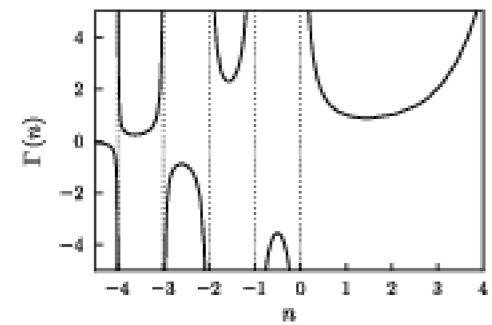
Riemann zeta function

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}$$



Gamma function

$$\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x}\,\mathrm{d}x$$



$$\Gamma(n) = (n-1)!$$

Thermodynamic potentials

Number of particles: $N = \frac{(2S+1)V}{\lambda_{\rm th}^3}[\mp \mathrm{Li}_{3/2}(\mp z)]$

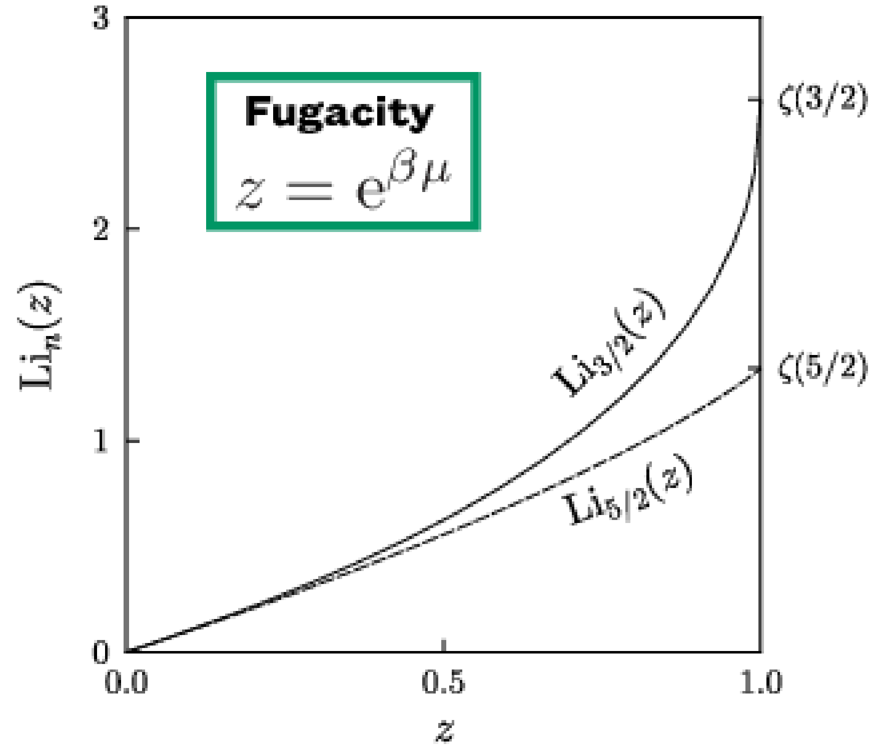
Internal energy: $U = \frac{3}{2} N k_{\rm B} T \frac{\mathrm{Li}_{5/2}(\mp z)}{\mathrm{Li}_{3/2}(\mp z)}$

Grand potential: $\Phi_{\rm G} = -N k_{\rm B} T \frac{\mathrm{Li}_{5/2}(\mp z)}{\mathrm{Li}_{3/2}(\mp z)}$

$$\Phi_{\rm G} = -\frac{2}{3} U$$

Fugacity

$$z = \mathrm{e}^{\beta\mu}$$



Application to ideal gas

$z = e^{\beta\mu} \ll 1$ since density is low!

$\longrightarrow \mathrm{Li}_n(z) \approx z$

$$N \approx \frac{(2S+1)Vz}{\lambda_{\mathrm{th}}^3}$$

$2S+1$ particles occupy λ_{th}^3/z (small volume, no overlap!)

$$U \approx \frac{3}{2}Nk_{\mathrm{B}}T$$

Equipartition result!

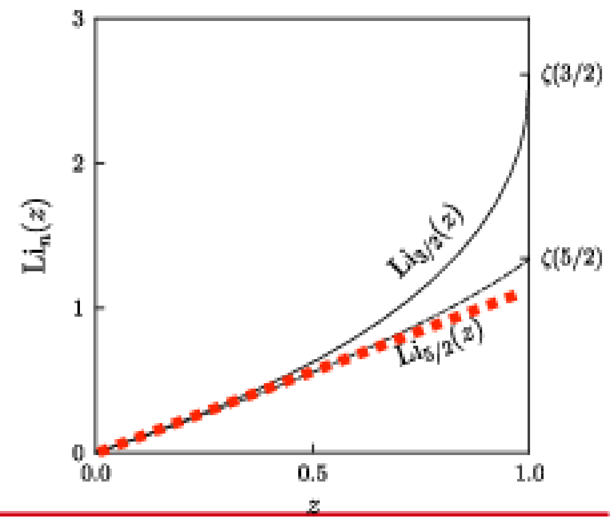
$$\Phi_{\mathrm{G}} \approx -Nk_{\mathrm{B}}T = -pV$$

As we've seen before

$$N = \frac{(2S+1)V}{\lambda_{\mathrm{th}}^3}[\mp\mathrm{Li}_{3/2}(\mp z)]$$

$$U = \frac{3}{2}Nk_{\mathrm{B}}T\frac{\mathrm{Li}_{5/2}(\mp z)}{\mathrm{Li}_{3/2}(\mp z)}$$

$$\Phi_{\mathrm{G}} = Nk_{\mathrm{B}}T\frac{\mathrm{Li}_{5/2}(\mp z)}{\mathrm{Li}_{3/2}(\mp z)}$$



The Fermi gas at $T = 0$

Fermi energy E_F

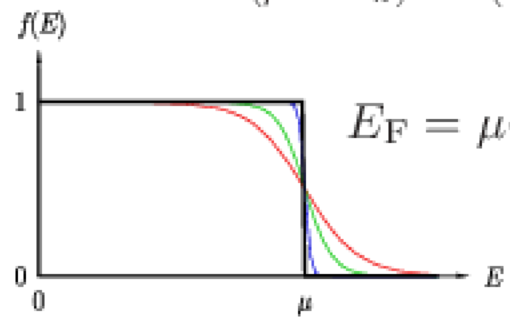
The highest occupied state at $T = 0$

- Fermion occupy lowest-energy states, one fermion per states, so $2S + 1$ in each energy level.
- Fermions will fill up the energy level until energy E_F

$$n_{\boldsymbol{k}} = \frac{1}{e^{\beta(E_{\boldsymbol{k}} - \mu)} + 1}$$

at $T = 0$

$$= \theta(\mu - E_k) = \theta(E_F - E_k)$$



$$E_F = \mu(T = 0)$$

- Number of fermions: $N = \int_0^{k_F} g(\boldsymbol{k})\,\mathrm{d}^3 k$

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

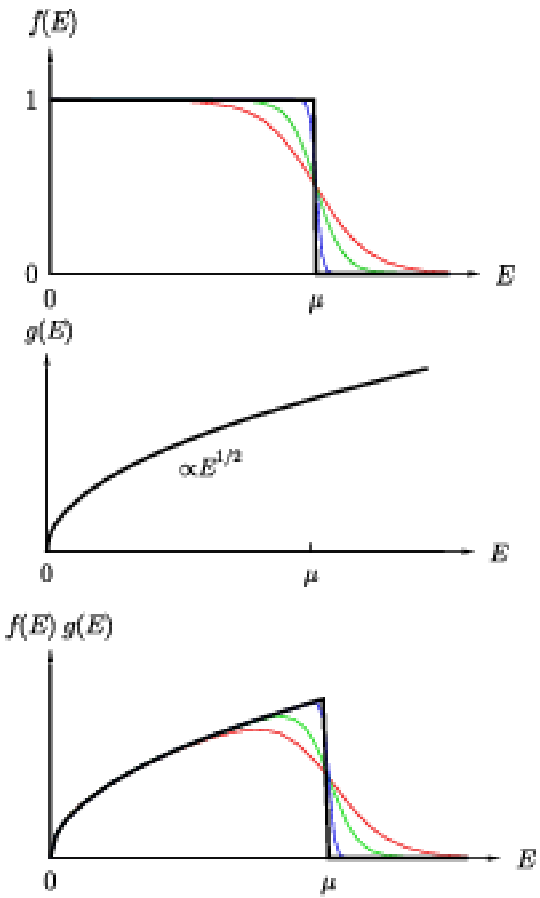
$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

Fermi wave vector

$$\rightarrow \quad k_F = \left[\frac{6\pi^2 n}{2S+1}\right]^{1/3}$$

$$\rightarrow \quad E_F = \frac{{}^2}{2m}\left[\frac{6\pi^2 n}{2S+1}\right]^{2/3}$$

$T > 0$ behavior



Metals

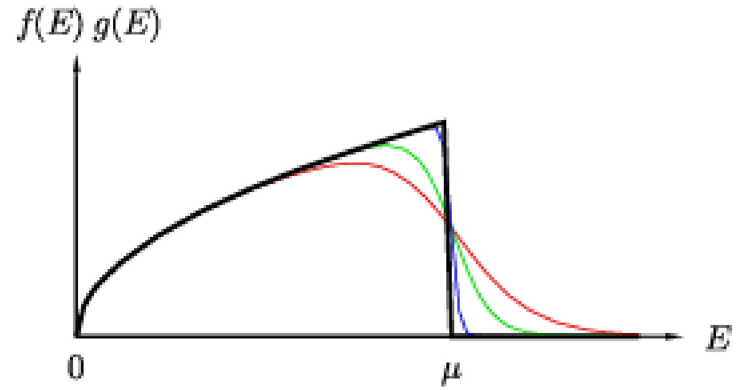
- E_F is a large number corresponding to a large Fermi temperature (E_F/k_B)
- The scale is very large compare to T and the sharp transition is found at most T
- We are, in this sense, in the degenerate limit

Average energy: $\langle E \rangle = \dfrac{\int_0^{E_F} E g(E)\,\mathrm{d}E}{\int_0^{E_F} g(E)\,\mathrm{d}E}$

$$\langle E \rangle = \tfrac{3}{5}E_F$$

Bulk modulus: $B = -V\dfrac{\partial p}{\partial V} = \dfrac{10U}{9V} = \dfrac{2}{3}nE_F$

$$p = \frac{2U}{3V}$$ Non-relativistic limit



	n ($10^{28}\,\mathrm{m}^{-3}$)	E_F (eV)	$\frac{2}{3}nE_F$ ($10^9\,\mathrm{N\,m}^{-2}$)	B ($10^9\,\mathrm{N\,m}^{-2}$)
Li	4.70	4.74	23.8	11.1
Na	2.65	3.24	9.2	6.3
K	1.40	2.12	3.2	3.1
Cu	8.47	7.00	63.3	137.8
Ag	5.86	5.49	34.3	103.6

Sommerfeld Integral: effects of finite T

$$I = \int_0^\infty \phi(E) f(E)\,\mathrm{d}E$$

$$= \int_{-\infty}^{\mu} \phi(E)\,\mathrm{d}E + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 \left(\frac{\mathrm{d}\phi}{\mathrm{d}E}\right)_{E=\mu} + \frac{7\pi^4}{360}(k_\mathrm{B}T)^4 \left(\frac{\mathrm{d}^3\phi}{\mathrm{d}E^3}\right)_{E=\mu} + \ldots$$

(proof not provided here, see Blundell and Blundell for detailed proof)

Number of particles ($S = 1/2$)

$$N = \frac{V}{2\pi^2}\left(\frac{2m}{2}\right)^{3/2}\int_0^\infty E^{1/2} f(E)\,\mathrm{d}E$$

$$= \frac{V}{3\pi^2}\left(\frac{2m}{2}\right)^{3/2}\mu^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{k_\mathrm{B}T}{\mu}\right)^2+\dots\right]$$

Chemical potential:

$$\mu(T) = \mu(0)\left[1-\frac{\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\mu(0)}\right)^2+\dots\right]$$

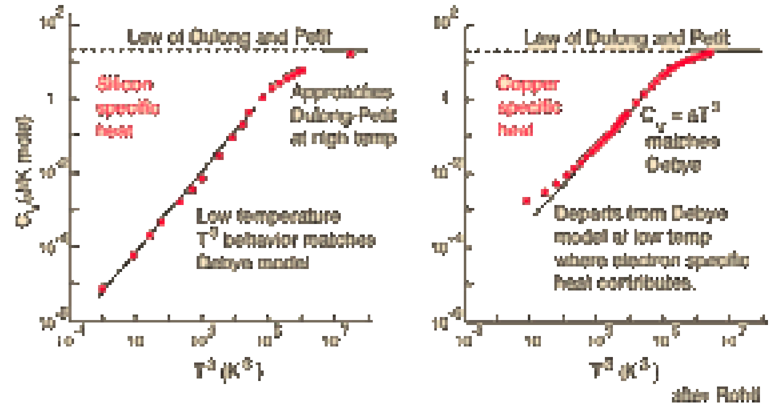
$$\mu(T) = E_F - \frac{\pi^2}{12E_F}(k_BT)^2$$

E_F and μ are almost the same but not quite!

Internal energy

$$U = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty E^{3/2} f(E)\,\mathrm{d}E$$

$$= \frac{3}{5}N\mu(0)\left[1+\frac{5\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\mu(0)}\right)^2+\ldots\right]$$

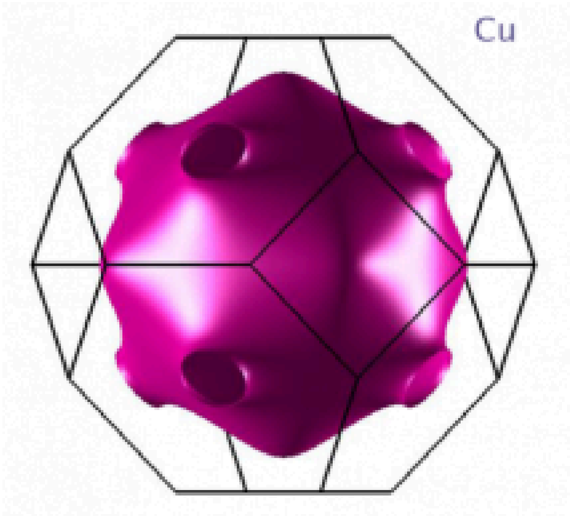


Heat capacity: $C_V = \frac{3}{2}Nk_\mathrm{B}\left(\frac{\pi^2}{3}\frac{k_\mathrm{B}T}{\mu(0)}\right) + O(T^3)$

Linear (as opposed to cubic for phonons): dominates at low T

Fermi surface

- Set of points in k-space whose energy is equal to the chemical potential



https://www2.physics.ox.ac.uk/research/quantum-matter-in-high-magnetic-fields/fermi-surfaces

The Bose gas

$$N = \frac{(2S+1)V}{\lambda_{\rm th}^3}\mathrm{Li}_{3/2}(z)$$

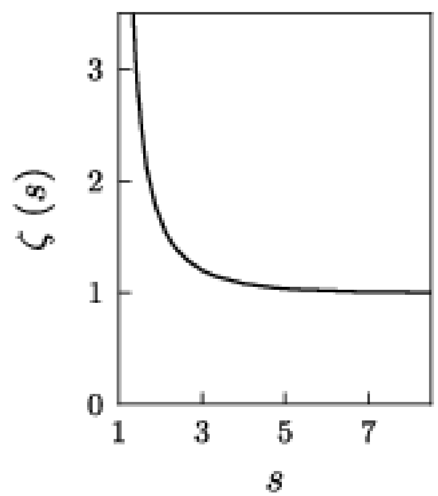
$$U = \frac{3}{2}Nk_{\rm B}T\frac{\mathrm{Li}_{5/2}(z)}{\mathrm{Li}_{3/2}(z)}$$

If $\mu = 0, z = 1$ →

$$N = \frac{(2S+1)V}{\lambda_{\rm th}^3}\zeta\left(\frac{3}{2}\right)$$

$$U = \frac{3}{2}Nk_{\rm B}T\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}$$

Riemann zeta function



$\zeta(\frac{3}{2}) = 2.612$, $\zeta(\frac{5}{2}) = 1.341$

$\zeta(\frac{5}{2})/\zeta(\frac{3}{2}) = 0.513$

This applies to systems with dispersion relation

$$E = \hbar^2 k^2/2m$$

The photon case $E = \quad kc$

$$U = \int_0^\infty \frac{E\,g(E)\,\mathrm{d}E}{z^{-1}\mathrm{e}^{\beta E} - 1} = \frac{V}{\pi^2 \quad {}^3 c^3} \int_0^\infty \frac{E^3\,\mathrm{d}E}{z^{-1}\mathrm{e}^{\beta E} - 1}$$

$$\int_0^\infty \frac{E^3\,\mathrm{d}E}{z^{-1}\mathrm{e}^{\beta E} - 1} = (k_\mathrm{B}T)^4\Gamma(4)\mathrm{Li}_4(z)$$

$$U = \frac{V\pi^2}{15\hbar^3 c^3}(k_\mathrm{B}T)^4$$

Just as in chapter 23!

(Stefan-Boltzmann)

Density of States

$$g(k)\,\mathrm{d}k = (2S+1)Vk^2\,\mathrm{d}k/(2\pi^2)$$

$$g(E)\,\mathrm{d}E = \frac{V}{\pi^2\hbar^3 c^3}E^2\,\mathrm{d}E$$

Spin 1, only two polarizations possible

A system is only in an eigenstate of spin around an axis if a rotation about the axis doesn't change the system. If travel along z: the $s_z = 0$ state is symmetric to a rotation about an axis normal to the direction of travel.

For a massless particle there is no rest frame and therefore it is impossible to find a spin eigenfunction about any axis other than along the direction of travel.

Fugacity

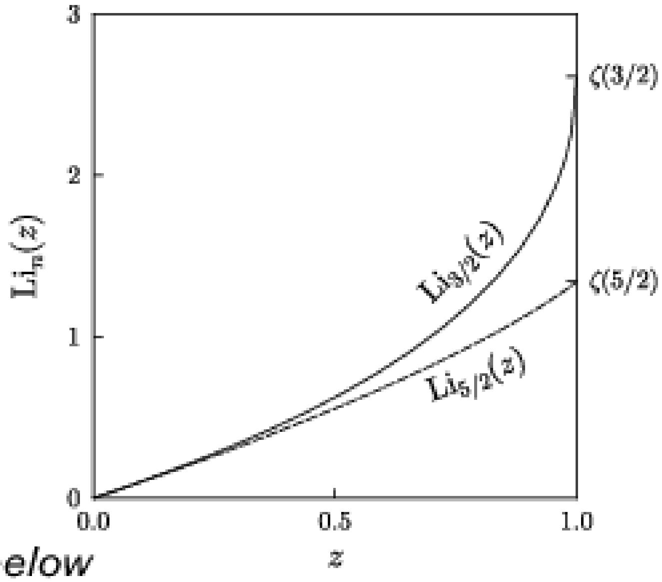
$$z = e^{\beta\mu}$$

$$E = \hbar^2 k^2/2m$$

The lowest energy is at $k = 0$, this means $\mu < 0$

The fugacity must be less than one!

$$0 < z < 1$$



Number of particles

$$N = \frac{(2S+1)V}{\lambda_{\mathrm{th}}^3}\mathrm{Li}_{3/2}(z) \longrightarrow \frac{n\lambda_{\mathrm{th}}^3}{2S+1} = \mathrm{Li}_{3/2}(z)$$

We can increase the left hand-side (increase n or decrease T)

μ increases and becomes less negative, approaching zero *from below*

But there is a limit!

If: $\frac{n\lambda_{\mathrm{th}}^3}{2S+1} > \zeta(\frac{3}{2}) = 2.612$ There is no solution!

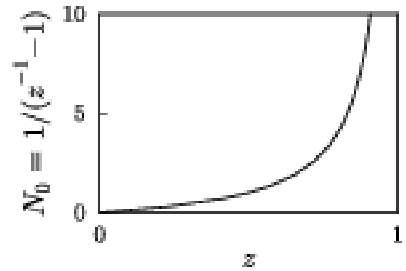
Bose-Einstein condensation

- As we get closer and close to zero energy, approaching from below, the lowest energy level becomes macroscopically occupied.
- The mathematics thus breaks down as we replaced a sum by an integral (early on!)
- It happens when we are below a temperature T_C
- Let's see how we can try to understand this.

$$k_B T_c = \frac{2\pi\hbar^2}{m}\left(\frac{n}{2.612(2S+1)}\right)^{2/3}$$

Setting up the ground state energy to zero

$$N = N_0 + N_1$$



- Total number of particles is the number of particles in the ground state + the rest.

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

- Above T_C , $z < 1$, we have N_0 bosons in the ground state, a number much less that the total number of bosons N:

$$N = N_1 = \frac{(2S+1)V}{[\lambda_{\text{th}}(T)]^3}\text{Li}_{3/2}(z)$$

- At T_C, the density of bosons is

$$n \equiv \frac{N}{V} = \frac{(2S+1)\text{Li}_{3/2}(1)}{[\lambda_{\text{th}}(T_c)]^3} = \frac{(2S+1)\zeta(\frac{3}{2})}{[\lambda_{\text{th}}(T_c)]^3}$$

- Below T_C, z is extremely close to unity and so we make the approximation $z = 1$
- The density of particles in the excited states

$$n_1 \equiv \frac{N_1}{V} = \frac{(2S+1)\text{Li}_{3/2}(1)}{[\lambda_{\text{th}}(T)]^3} = \frac{(2S+1)\zeta(\frac{3}{2})}{[\lambda_{\text{th}}(T)]^3}$$

The rest of the particles must be in the ground state

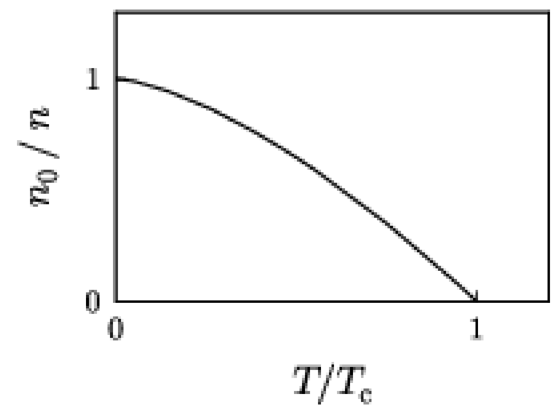
$$n \equiv \frac{N}{V} = \frac{(2S+1)\mathrm{Li}_{3/2}(1)}{[\lambda_{\mathrm{th}}(T_c)]^3} = \frac{(2S+1)\zeta(\frac{3}{2})}{[\lambda_{\mathrm{th}}(T_c)]^3}$$

$$n_1 \equiv \frac{N_1}{V} = \frac{(2S+1)\mathrm{Li}_{3/2}(1)}{[\lambda_{\mathrm{th}}(T)]^3} = \frac{(2S+1)\zeta(\frac{3}{2})}{[\lambda_{\mathrm{th}}(T)]^3}$$

$$\longrightarrow \quad \frac{n_1}{n} = \frac{[\lambda_{\mathrm{th}}(T_c)]^3}{[\lambda_{\mathrm{th}}(T)]^3} = \left(\frac{T}{T_c}\right)^{3/2}$$

Remaining particles must be in the ground state, so that:

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

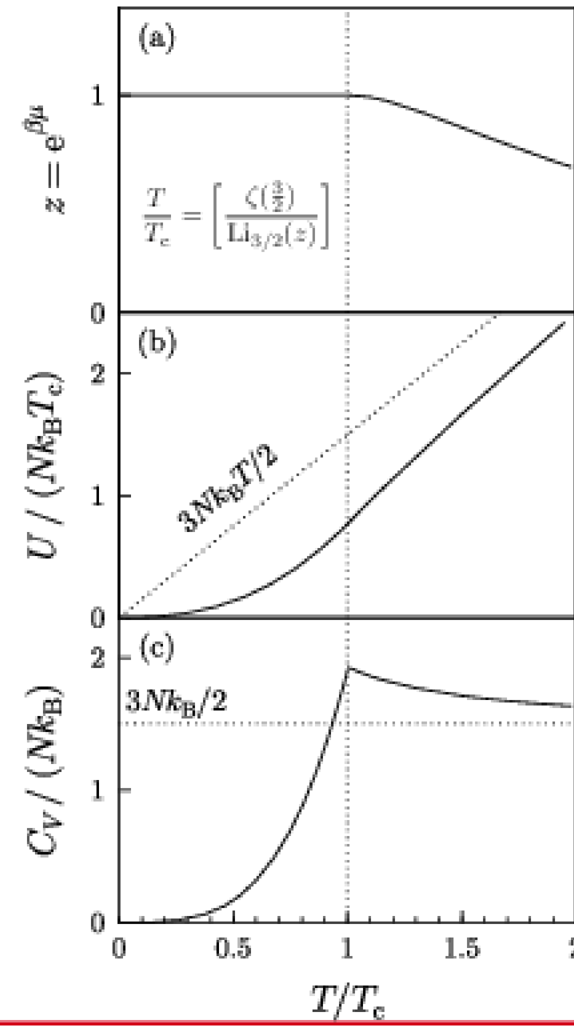


Most bosons are in the ground state below T_C! This is known as the BEC

This is not a phase transition, in fact we do no have interactions but due to the symmetry imposed to Bosons

Note that the condensation is in fact, in k-space

The fugacity rises up towards unity T goes down, and below T_c is not actually one but very close to it.



Example

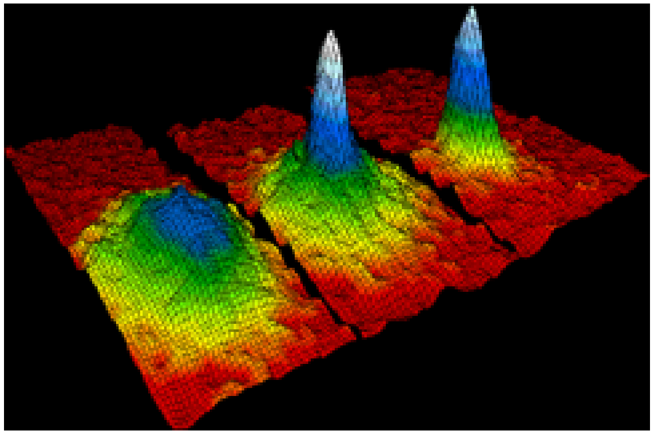
$$k_B T_c = \frac{2\pi\hbar^2}{m}\left(\frac{n}{2.612(2S+1)}\right)^{2/3}$$

Very dilute gases of alkali metal atoms (about $10^4 - 10^6$) , can be trapped and cooled using laser cooling.

These alkali atoms have a single electronic spin due to their one valence electron and this can couple with the non-zero nuclear spin. Each atom therefore has a magnetic moment and thus can be trapped inside local minima of magnetic field. The densities of these ultracold atomic gases inside the traps are very low.

The Bose-Einstein condensation temperature is therefore also very low, typically $10^{-8} - 10^{-6}$K

The low density precludes significant three-body collisions, but two-body collisions do occur, which allow the cloud of atoms to thermalize.



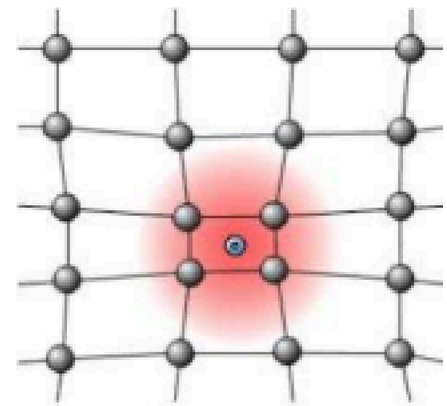
The 2001 Nobel Prize was awarded to Eric Cornell and Carl Wieman (rubidium atoms) and Wolfgang Ketterle (sodium atoms).

Another example

Electrons do not exhibit Bose-Einstein condensation because they are fermions, not bosons, but they can show other condensation effects such as superconductivity.

In a superconductor, a weak attractive interaction (which can be mediated by phonons) allows pairs of electrons to form Cooper pairs. A Cooper pair is a boson, and the Cooper pairs themselves can form a coherent state below the superconducting transition temperature.

Many common superconductors can be described in this way using the BCS theory of superconductivity, though many newly discovered superconductors, such as the high-temperature superconductors, which are ceramics, do not seem to be described by this model.



http://www.chm.bris.ac.uk/

BCS is named after its discoverers, John Bardeen, Leon Cooper, and Robert Schrieffer.

Summary

In a Fermi gas (a gas of fermions), fermions fill states up to E_{F} at absolute zero. The Pauli exclusion principle ensures that fermions only singly occupy states.

The results for a Fermi gas can be applied to the electrons in a metal. At non-zero temperature, electrons with energies within $k_{\mathrm{B}}T$ of E_{F} are important in determining the properties.

In a Bose gas, Bose- Einstein condensation can occur below a temperature given by

$$k_{\mathrm{B}}T_{\mathrm{c}} = \frac{2\pi\ ^2}{m}\left(\frac{n}{2.612(2S+1)}\right)^{2/3}$$