Chap 9

Statistical Physics

Gas of atoms

- Maxwell Velocity Distribution
- Equipartition Theorem
- Maxwell Speed Distribution

General manybody system

- Classical and Quantum Statistics
- Fermi-Dirac Statistics
- Bose-Einstein Statistics

Maxwell velocity **distribution** of ideal gas (1860)

- Velocity distribution function $f(\vec{\boldsymbol{v}})$:

  $f(\vec{\boldsymbol{v}})\, d^3v$ = the probability of finding a particle with velocity between $\vec{\boldsymbol{v}}$ and $\vec{\boldsymbol{v}} + d\vec{\boldsymbol{v}}$.

  $$\boxed{d^3v = dv_x dv_y dv_z}$$

- Since the motion along *x, y, z* are independent, we expect $f(v_x, v_y, v_z) = h(v_x)h(v_y)h(v_z)$

- Rotational invariance requires that $f(\vec{\boldsymbol{v}})$ can depend only on the magnitude of $\vec{\boldsymbol{v}}$, not it's direction: $f(\vec{\boldsymbol{v}}) = f(v)$.

- The only function of $v_x^2 + v_y^2 + v_z^2$ that has the form $h(v_x)h(v_y)h(v_z)$ is proportional to an exponential function (Weinberg, Foundations of MP)

$$f(v_x, v_y, v_z) \propto \exp[-C(v_x^2 + v_y^2 + v_z^2)]$$

(*C*>0 so that *f*(v) won't diverge)

Normalization of *f*(*v*)

- $h(v_x)\,dv_x$ is the probability that the *x* component of a molecule's velocity lies between v_x and $v_x + dv_x$.
- If we integrate $h(v_x)\,dv_x$ over all of v_x, it equals to 1

$$h(v_x) = De^{-Cv_x^2}$$

$$\int_{-\infty}^{\infty} h(v_x)dv_x = D\left(\frac{\pi}{C}\right)^{1/2} = 1$$

➡ $$D = \left(\frac{C}{\pi}\right)^{1/2}$$

➡ $$f(\vec{v}) = h(v_x)h(v_y)h(v_z)$$

$$= \left(\frac{C}{\pi}\right)^{3/2} \exp\left(-C\left|\vec{v}\right|^2\right)$$

- The mean value of v_x

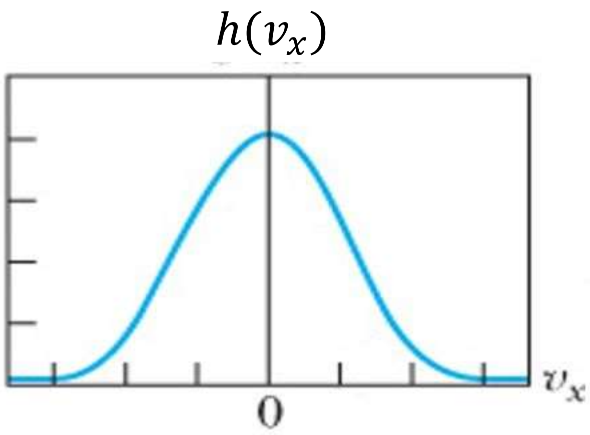
$$\overline{v_x} = \int_{-\infty}^{\infty} v_x h(v_x) dv_x = D\int_{-\infty}^{\infty} v_x \exp\left(-Cv_x^2\right) dv_x = 0$$

- The mean value of v_x^2

$$\overline{v_x^2} = D\int_{-\infty}^{\infty} v_x^2 \exp\left(-Cv_x^2\right) dv_x$$

$$= \left(\frac{C}{\pi}\right)^{1/2} \frac{\sqrt{\pi}}{2} \frac{1}{C^{3/2}} = \frac{1}{2C}$$

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \rightarrow \overline{v^2} = \frac{3}{2C}$$



- We know that $\frac{m}{2}\overline{v^2} = \frac{3}{2}kT$ $\quad \therefore C = \frac{m}{2kT}$

recall high school physics

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2/2}{kT}\right)$$

or $$f(\vec{v}) = \left(\frac{m\beta}{2\pi}\right)^{3/2} \exp\left(-\frac{\beta}{2}mv^2\right)$$

$$\boxed{\beta \equiv \frac{1}{kT}}$$

(this is mentioned in Chap 3)

Equipartition theorem 能量均分定理

In equilibrium, a mean energy of ½ kT is associated with each term of a molecular's energy. (Learn Statistical Physics for a proof.)

- In a monatomic ideal gas, each molecule has the energy

$$\bar{E} = \overline{\frac{1}{2}mv^2} = \frac{1}{2}m(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{1}{2}m\left(\frac{3kT}{m}\right) = \frac{3}{2}kT$$

This agrees with the result we cited earlier.

- In a gas of N atoms, the total internal energy is

$$U = N\bar{E} = \frac{3}{2}NkT$$

- The heat capacity at constant volume is $C_V = \frac{dU}{dT} = \frac{3}{2}Nk$
- For n mole of atoms,

$$C_V = \frac{3}{2}nN_A k = \frac{3}{2}nR = 12.5n \text{ J/K}$$

The ideal gas constant $R = N_A k$ = 8.31 J/K.

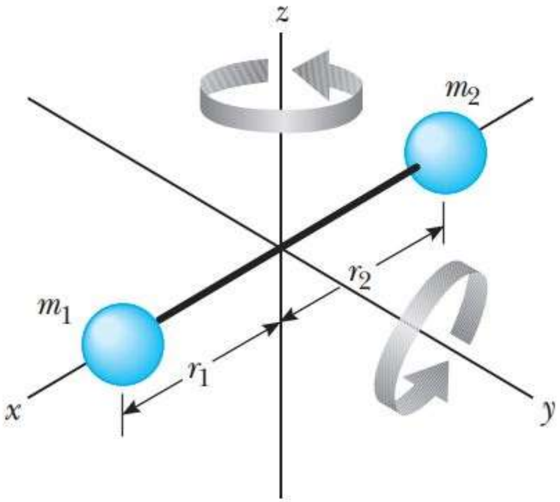
Diatomic molecule

- There are 7 energy terms (3 translational, 2 rotational, and 2 vibrational).

  Note: Vibration has 2 energy terms: kinetic energy and potential energy
- Why only 2 terms in rotational energy?

  A: The energy of a **rigid rotator is**

$$E = \frac{I_x}{2}\omega_x^2 + \frac{I_y}{2}\omega_y^2 + \frac{I_z}{2}\omega_z^2$$



- The mass of an atom is confined to a nucleus

  → I_z is much smaller than I_x and I_y, and only rotations about x and y are allowed.

Ex 9.2: Consider the gases HF and Ne, both at a (room) temperature of 300 K. Compare the average translational kinetic energy and total kinetic energy of the two types of molecules.

Solution

Ne: $K = \frac{3}{2}kT$ per atom

$K_T = \frac{3}{2}RT$ per mole

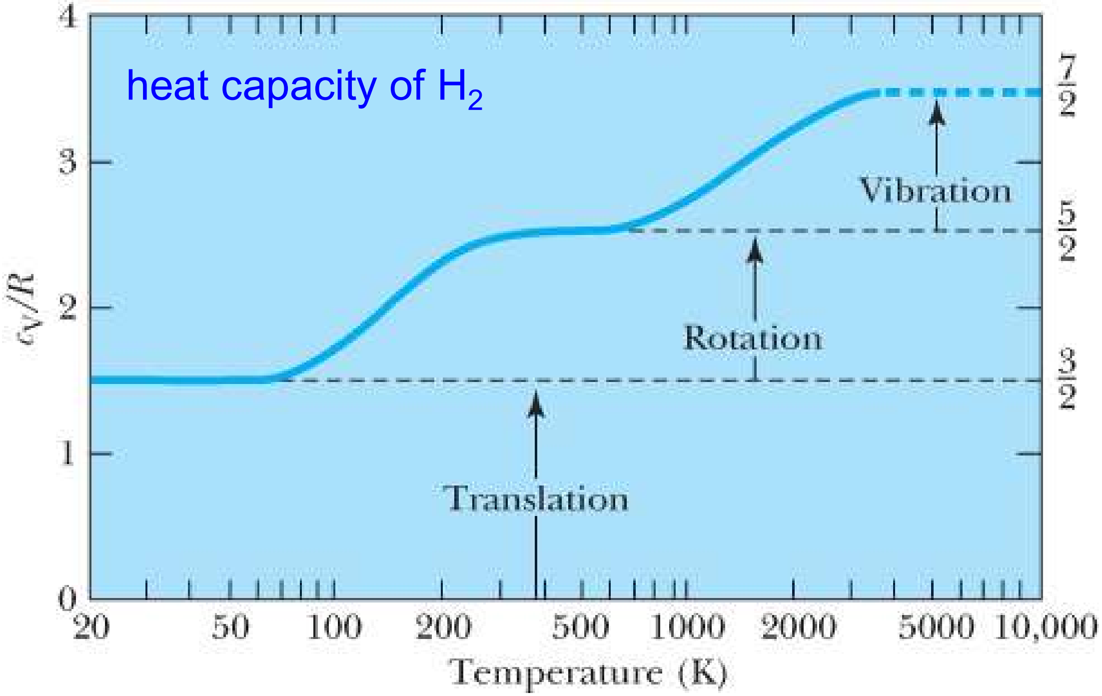
HF: $K = \frac{5}{2}kT$ per atom

$K_T = \frac{5}{2}RT$ per mole

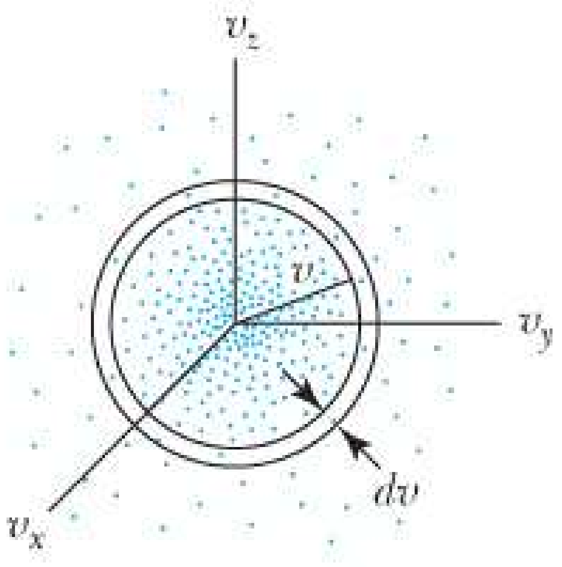
20 ºC $\boxed{kT \simeq 25\text{ meV} \simeq \frac{1}{40}\text{ eV}}$

$k = 1.381 \times 10^{-23}$ J/K

$E_{\mathrm{HF}}^{rot} \simeq 0.5\text{ meV}\ (\ell = 1);\ \mathrm{E}_{\mathrm{HF}}^{\mathrm{vib}} \simeq 0.8\text{ eV}\ (\mathrm{n} = 1)$



Maxwell speed distribution



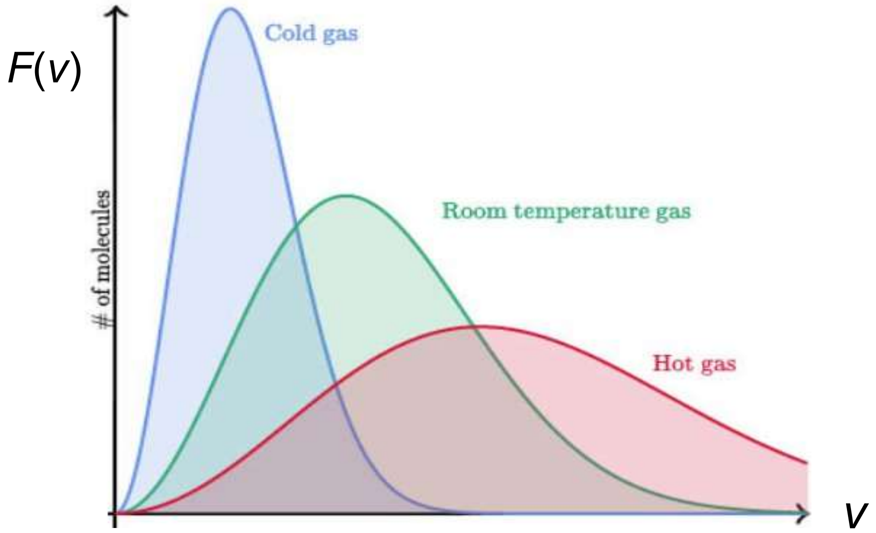
- Recall that $f(\vec{v})\, d^3v$ = the probability of finding a particle with velocity between $\vec{v}$ and $\vec{v} + d\vec{v}$.
- $F(v)\, dv$ = the probability of finding a particle with speed between v and $v + dv$.
- The volume of the spherical shell is $4\pi v^2\, dv$.

Speed distribution

$$F(v)\,dv = f(v)4\pi v^2 dv$$

Velocity distribution

➡ $$F(v) = D^{3/2}\exp\left(-\tfrac{1}{2}\beta m v^2\right)4\pi v^2$$



Three different scales

1. **Most probable speed** (peak of the speed distribution):

$$\frac{dF(v)}{dv} = 0 \quad \Rightarrow \quad v^* = \sqrt{\frac{2}{\beta m}} = \sqrt{\frac{2kT}{m}}$$

2. **Mean speed** (average of all speeds):

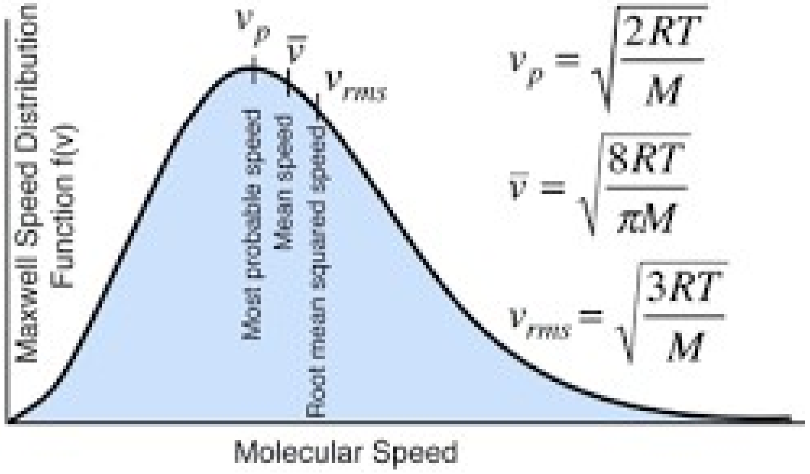
$$\bar{v} = \int_0^\infty vF(v)\, dv$$

$$= 4\pi D^{3/2}\left[2\left(\frac{1}{2}\beta m\right)^2\right]^{-1} = \frac{4}{\sqrt{2\pi}}\sqrt{\frac{kT}{m}}$$

3. **Root-mean-square speed**

$$v_{\text{rms}} = (\overline{v^2})^{1/2} = \sqrt{\frac{3kT}{m}}$$

$$F(v) = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



$$v_p = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Ex 9.3:

(same thermal energy)

Compute the mean molecular speed $\bar{v}$ in the light gas hydrogen (H_2) and the heavy gas radon (Rn), both at room temperature 293 K. (Use the longest-lived radon isotope, which has a mass of 222 u.) Compare the results.

$$\boxed{1\text{u} = 1.66 \times 10^{-27}\ \text{kg}}$$

Solution The mass of the hydrogen molecule is twice that of a hydrogen atom (neglecting the small binding energy), or 2(1.008 u) = 2.02 u. Thus the average molecular speed of hydrogen is

$$\bar{v} = \frac{4}{\sqrt{2\pi}}\sqrt{\frac{kT}{m}}$$

$$= \frac{4}{\sqrt{2\pi}}\sqrt{\frac{(1.38 \times 10^{-23}\ \text{J/K})(293\ \text{K})}{(2.02\ \text{u})(1.66 \times 10^{-27}\ \text{kg/u})}} = 1750\ \text{m/s}$$

The average molecular speed of radon is

$$\bar{v} = \frac{4}{\sqrt{2\pi}}\sqrt{\frac{kT}{m}}$$

$$= \frac{4}{\sqrt{2\pi}}\sqrt{\frac{(1.38 \times 10^{-23}\ \text{J/K})(293\ \text{K})}{(222\ \text{u})(1.66 \times 10^{-27}\ \text{kg/u})}} = 167\ \text{m/s}$$

- Maxwell Velocity Distribution
- Equipartition Theorem
- Maxwell Speed Distribution
- Classical and Quantum Statistics
- Fermi-Dirac Statistics
- Bose-Einstein Statistics

➡ Superfludity
Superconductivity …

Distribution function (for classical systems in thermal equilibrium)

- Recall that $f(\vec{v}) = D^{3/2}\exp\left(-\frac{1}{2}\beta m v^2\right) = D^{3/2}\exp(-\beta E)$

  Boltzmann showed that the factor $\exp(-\beta E)$ is universal for all classical system.

  called Boltzmann factor

- **Maxwell-Boltzmann distribution:**

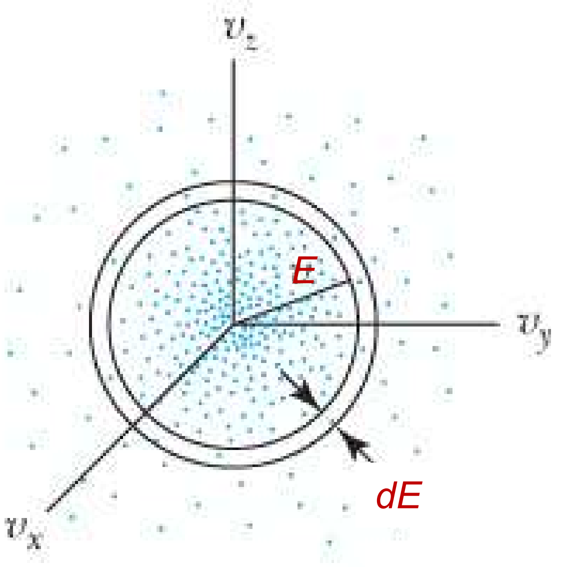
  Probability for a particle at energy-*E* state: $f(E) = A\exp(-\beta E)$

➡ Relative occupations between two states $$\frac{f_2}{f_1} = e^{-\beta(E_2 - E_1)}$$

- The distribution of particles with respect to energy:

$$f(v)4\pi v^2 dv \Leftrightarrow f(E)g(E)dE$$

$$\boxed{4\pi v^2 dv = g(E)dE}$$



For ideal gas,

$$E = \frac{mv^2}{2} \rightarrow dE = mvdv$$

➡ $$4\pi v^2 dv = \frac{4\pi}{m} v dE = \frac{4\pi}{m}\sqrt{\frac{2}{m}}E^{1/2}\mathrm{d}E$$

optional

- In classical statistical mechanics, to count the number of states, we need to calculate the volume in phase space,

$$\left(\int d^3V\right) \times 4\pi p^2 dp = V \times 2\pi(2m)^{3/2}E^{1/2}\mathrm{dE}$$

- Suppose a volume element of phase space = Δ^3

  Number of states in this shell: divide the volume by Δ^3.

- After the discovery of quantum physics, it is natural to set Δ=h

$$\Rightarrow \quad g(E) = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

- **Density of states** $g(E)$ 態密度

  The number of states within [E,E+dE] $= g(E)dE$

  The number of particles within [E,E+dE]: $n(E)$ dE = $\underbrace{F(E,T)}_{\text{Distribution function}}\ \underbrace{g(E)}_{\text{Density of states}}$ dE

Ex 9.6: Assume that the Maxwell-Boltzmann distribution is valid in a gas of atomic hydrogen. What is the relative number of atoms in the ground state and first excited state at 293 K (room temperature), 5000 K (the temperature at the surface of a star), and 10^6 K (a temperature in the interior of a star)?

Solution

$$\frac{n(E_2)}{n(E_1)} = \frac{g(E_2)}{g(E_1)} \exp[\beta(E_1 - E_2)]$$

$$g(E_1) = 2 \qquad g(E_2) = 8.$$

$$E_1 - E_2 = -10.2 \text{ eV}.$$

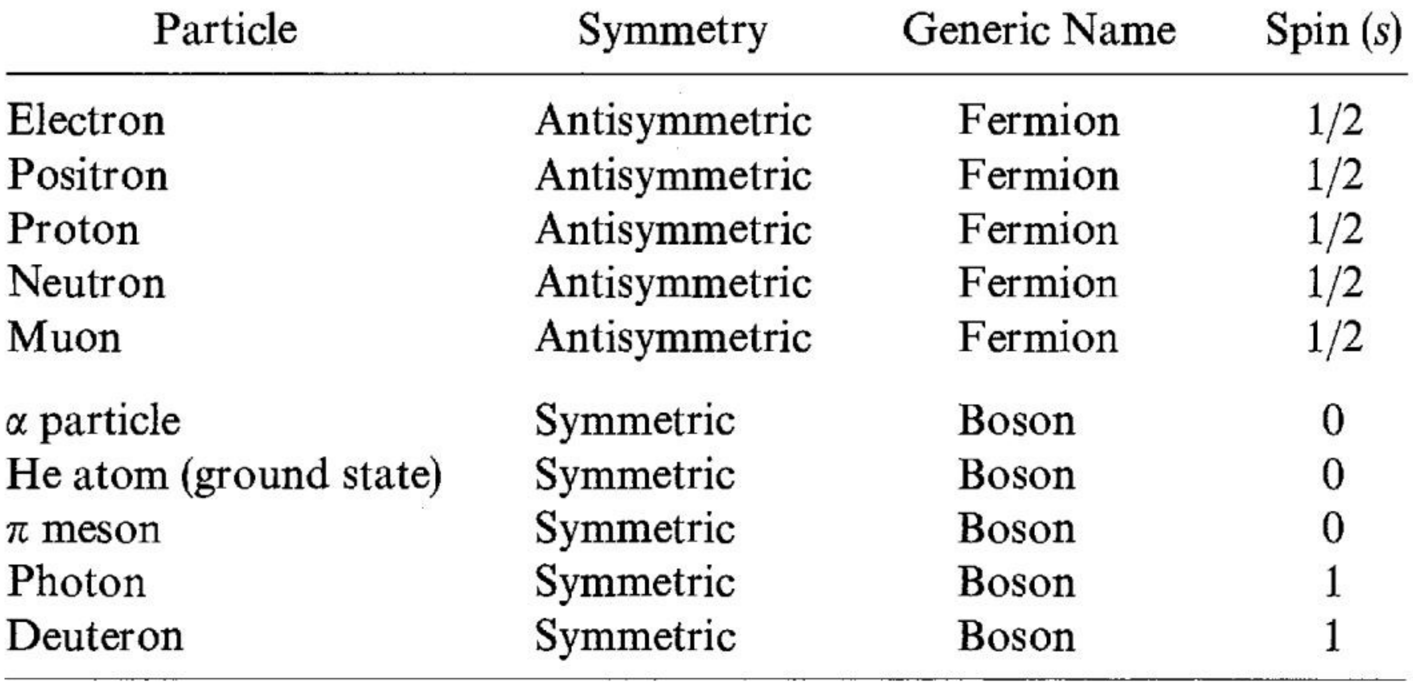
$$\frac{n(E_2)}{n(E_1)} = 4 \exp[\beta(-10.2 \text{ eV})]$$

$$= 4 \exp(-404) \approx 10^{-175} \qquad \text{for } T = 293 \text{ K}$$

$$= 4 \exp(-23.7) \approx 2 \times 10^{-10} \qquad \text{for } 5000 \text{ K}$$

$$= 4 \exp(-0.118) \approx 3.55 \qquad \text{for } 10^6 \text{ K}$$

Before studying quantum statistics, we need to know all particles belong to one of two types: **boson** or **fermion**. They have different distribution functions.



Particle	Symmetry	Generic Name	Spin (s)
Electron	Antisymmetric	Fermion	1/2
Positron	Antisymmetric	Fermion	1/2
Proton	Antisymmetric	Fermion	1/2
Neutron	Antisymmetric	Fermion	1/2
Muon	Antisymmetric	Fermion	1/2
α particle	Symmetric	Boson	0
He atom (ground state)	Symmetric	Boson	0
π meson	Symmetric	Boson	0
Photon	Symmetric	Boson	1
Deuteron	Symmetric	Boson	1

- Particles with half-integer spin are fermions;

  particles with integer spin are bosons.
- Fermions satisfy Fermi-Dirac statistics;

  bosons satisfy Bose-Einstein statics (spin-statistics theorem).

Three distribution functions for systems in thermal equilibrium

- **Maxwell-Boltzmann distribution** $(f \rightarrow F_{MB})$:

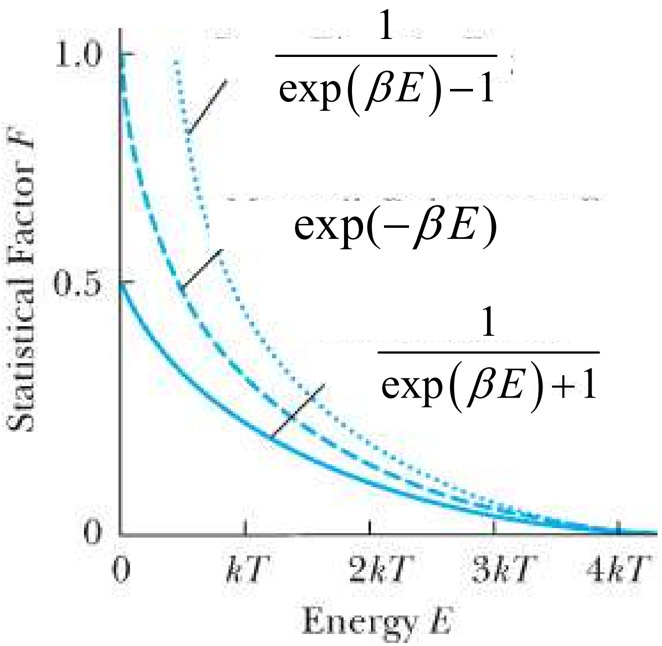
$$F_{\mathrm{MB}} = A\exp(-\beta E)$$

- **Bose-Einstein distribution** (1924):

$$F_{BE} = \frac{1}{A\exp(\beta E) - 1}$$

- **Fermi-Dirac distribution** (1926):

$$F_{FD} = \frac{1}{A\exp(\beta E) + 1}$$



Both reduce to the Maxwell-Boltzmann distribution when *E* >> *kT*

- The number of states within [*E*,*E*+*dE*] $= g(E)dE$

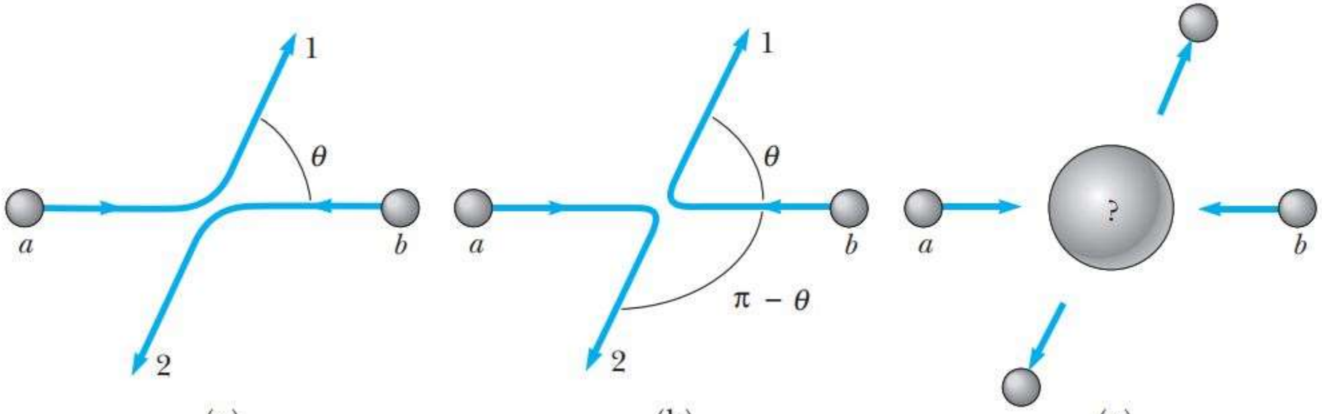
The number of particles within [*E*,*E*+*dE*]: *n*(*E*) d*E* = $\underbrace{F(E,T)}_{\text{Distribution function}}\ \underbrace{g(E)}_{\text{Density of states}}$ d*E*

To understand boson and fermion better, we need to understand the concept of **identical particles:** 全同粒子

- In a quantum world, elementary particle of the same type are ***indistinguishable*** from each other

2 particles interact with each other:

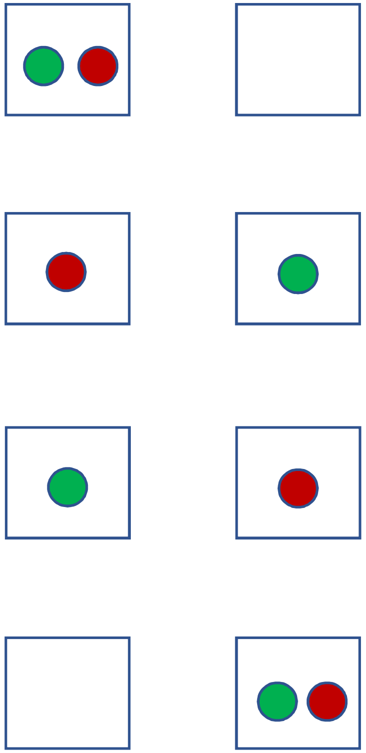
- Classical physics: frequent observations are allowed without disturbing the system. This is no longer true for a quantum system, so we cannot follow the trajectory closely.



(a) (b) (c)

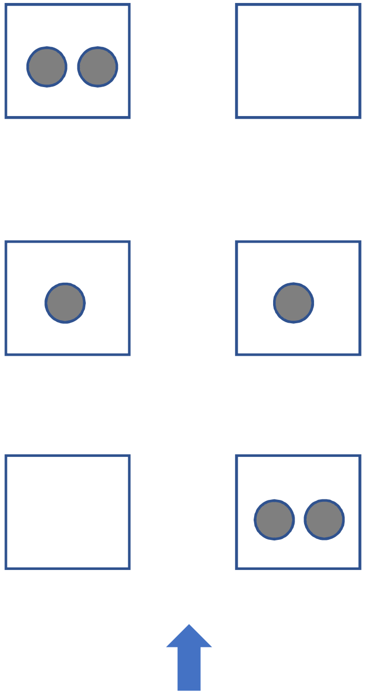
A simple statistics: Different ways to put 2 particles in 2 states

- Distinguishable particles (classical)

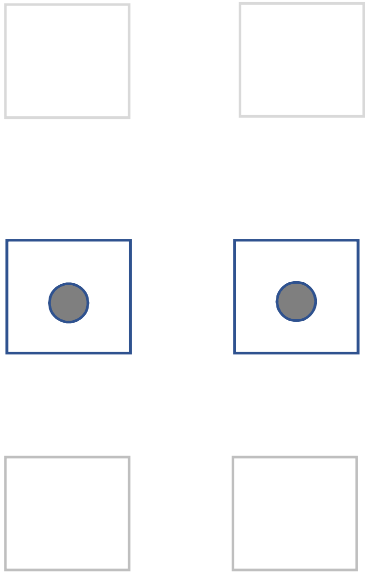


- Indistinguishable particles (quantum)

Bosons



Fermions



In 1924, Bose used this statistics, applied it to photons to derive the Planck radiation law.
He would fail if the one on the left is used.

“*He appears to have missed the fact that in asserting this new counting method, he had made a profound discovery about the atomic world, that elementary particles are indistinguishable in a new and fundamental sense*.“

(p.247 Stone, Einstein and quantum)

“I had no idea that what I had done was really novel... Somehow this was the same question that Einstein asked when I met him: How had I arrived at this method of de-riving Planck’s formula? Well, I recognized the contradictions in the attempts of Planck and Einstein, and applied statistics in my own way, *but I did not think that it was different from Boltzmann statistics.”*

In his book 'Subtle is the Lord' Pais states, *'The paper by Bose is the fourth and last of the revolutionary papers of the old quantum theory*." (the other three being by, respectively, Planck, Einstein, and Bohr)

Q: What would happen if he used distinguishable particle?

A: Rayleigh-Jeans formula

交換對稱性 **Exchange symmetry** of wave function

Two-particle wave function: $\psi(\vec{r}_1, \vec{r}_2)$

- Exchanging two indistinguishable particles:

$$|\psi(\vec{r}_2, \vec{r}_1)|^2 = |\psi(\vec{r}_1, \vec{r}_2)|^2$$

➡ $\psi(\vec{r}_2, \vec{r}_1) = \mathrm{C}\psi(\vec{r}_1, \vec{r}_2), |C| = 1$

- After exchanging twice, the system should come back to the original state

➡ $\mathrm{C}^2 = 1 \rightarrow C = \pm 1$

Therefore

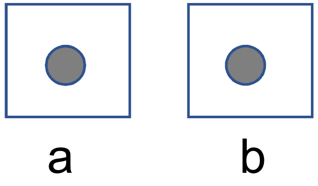
$$\text{or} \begin{cases} \psi(\vec{r}_2, \vec{r}_1) = +\psi(\vec{r}_1, \vec{r}_2) & \text{boson} \\ \psi(\vec{r}_2, \vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_2) & \text{fermion} \end{cases}$$

Wave function for 2 particles

- 2 particles in 2 different states *a* and *b*:

Distinguishable $\psi_M = \psi_a(1)\psi_b(2)$

Boson $$\psi_B = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

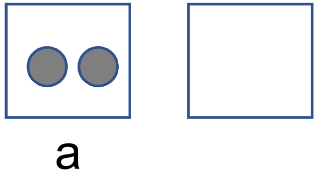


Fermion $$\psi_F = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

- Probability density for 2 particles in the same state (*b*=*a*)

Distinguishable $\psi_M^* \psi_M = \psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2)$

Boson $$\psi_B^*\psi_B = 2\psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2) = \boxed{2}\psi_M^*\psi_M$$

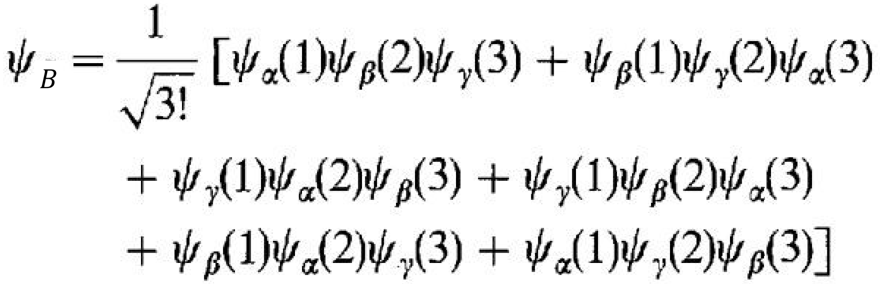


Fermion $$\psi_F = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)] = \boxed{0}$$

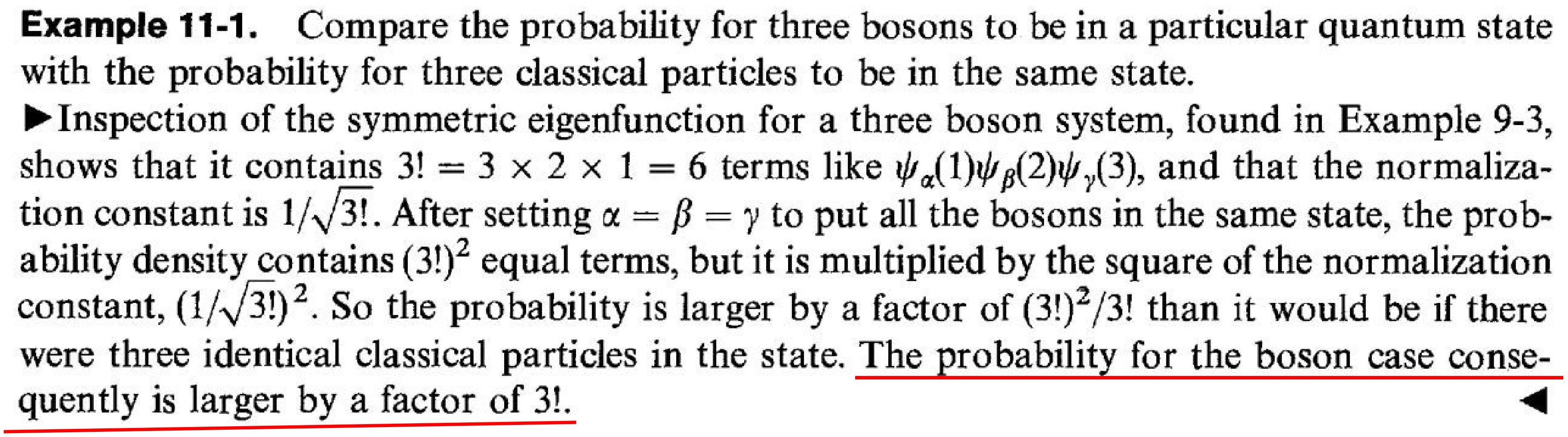
- Bosons like to stick together; fermions like to repel each other.

optional

Wave function of 3 bosons



$$\psi_B = \frac{1}{\sqrt{3!}}[\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3) + \psi_\beta(1)\psi_\gamma(2)\psi_\alpha(3) + \psi_\gamma(1)\psi_\alpha(2)\psi_\beta(3) + \psi_\gamma(1)\psi_\beta(2)\psi_\alpha(3) + \psi_\beta(1)\psi_\alpha(2)\psi_\gamma(3) + \psi_\alpha(1)\psi_\gamma(2)\psi_\beta(3)]$$



Example 11-1. Compare the probability for three bosons to be in a particular quantum state with the probability for three classical particles to be in the same state.

▶Inspection of the symmetric eigenfunction for a three boson system, found in Example 9-3, shows that it contains $3! = 3 \times 2 \times 1 = 6$ terms like $\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3)$, and that the normalization constant is $1/\sqrt{3!}$. After setting $\alpha = \beta = \gamma$ to put all the bosons in the same state, the probability density contains $(3!)^2$ equal terms, but it is multiplied by the square of the normalization constant, $(1/\sqrt{3!})^2$. So the probability is larger by a factor of $(3!)^2/3!$ than it would be if there were three identical classical particles in the state. The probability for the boson case consequently is larger by a factor of 3!. ◀

$$\psi_B^*\psi_B = 3!\,\psi_M^*\psi_M$$

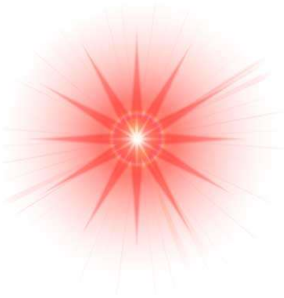
➡ Bose-Einstein condensation, laser … etc

玻色-愛因斯坦凝聚

Bosons (photon, H, ^{4}He, ^{87}Rb…)

Spin = 0, 1, 2...

- laser



- superconductor

- superfluid

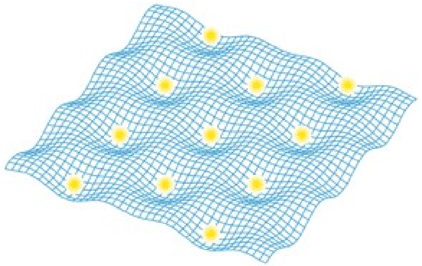
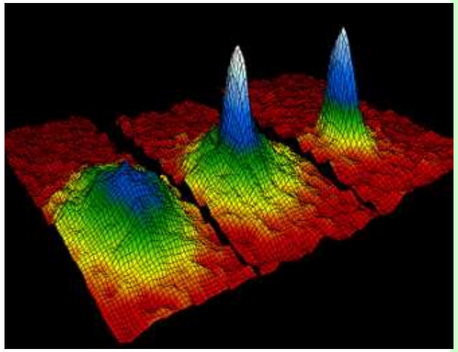


Figure 4: Dimples on the liquid helium surface caused by Wigner crystals

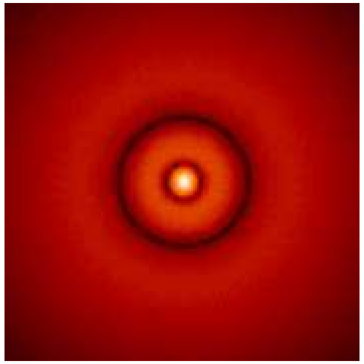
- Bose-Einstein condensation



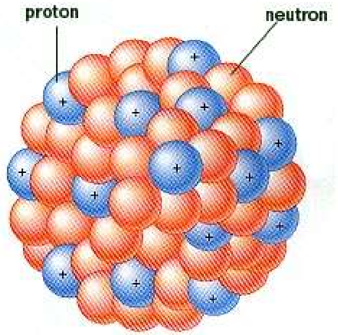
Fermions (electron, proton, neutron, ^{3}He …)

Spin = 1/2, 3/2...

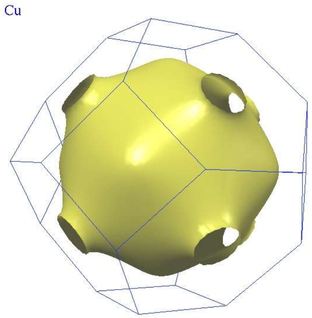
- atom



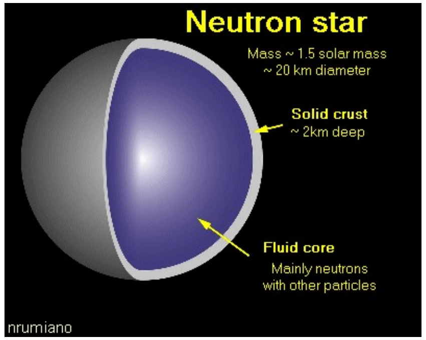
- nucleus



- solid



- neutron star



optional

Justification of the distribution laws (Eisberg and Resnick)

First, classical particles

- Suppose P_1 is the probability of finding 1 particle in some state. The probability of finding *n* particle in the same state is

$$P_n = (P_1)^n$$

- Assume that there are on average n_1 particles in state 1, n_2 particles in state 2, and $R_{1\to2}$ is the transition rate (number of transitions per sec) from state 1 to 2. In equilibrium, the transfer of particles between states 1,2 satisfies (aka detailed balance) 細節平衡

$$\bar{n}_1 R_{1\to2} = \bar{n}_2 R_{2\to1}$$

($\bar{n}$ is the avg number of *n*)

Boltzmann distribution

$$\frac{\bar{n}_1}{\bar{n}_2} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_2}{kT}}}$$

➡

$$\frac{R_{2\to1}}{R_{1\to2}} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_2}{kT}}}$$

optional

Justification of the distribution laws

- **Boson**

See the example of 3 bosons

$$P_n^{boson} = n!\,P_n = n!\,(P_1)^n$$

Q: If there are already *n* bosons in a final state, what is the probability that one more boson makes a transition to that state?

$$P_{n+1}^{boson} = (1+n)P_1 P_n^{boson}$$

Comparing to the classical case,

$$P_{n+1} = P_1 P_n$$

➡ A: The probability is enhanced by 1+*n*

That is, the transition rate is enhanced by a factor of 1+*n*. As a result,

➡
$$\begin{cases} R_{1\to 2}^{boson} = (1+\bar{n}_2)R_{1\to 2} \\ R_{2\to 1}^{boson} = (1+\bar{n}_1)R_{2\to 1} \end{cases}$$

On the other hand, for **fermion**,

$$R_{1\to 2}^{fermion} = \begin{cases} R_{1\to 2} \text{ if state-2 is empty} \\ 0 \text{ if state-2 is filled} \end{cases}$$

Therefore, on average

$$\begin{cases} R_{1\to 2}^{fermion} = (1-\bar{n}_2)R_{1\to 2} \\ R_{2\to 1}^{fermion} = (1-\bar{n}_1)R_{2\to 1} \end{cases}$$

optional

- **Boson**

Detailed balance:

$$\bar{n}_1 R_{1\to 2}^{boson} = \bar{n}_2 R_{2\to 1}^{boson}$$

➡ $$\frac{\bar{n}_1(1+\bar{n}_2)}{\bar{n}_2(1+\bar{n}_1)} = \frac{R_{2\to 1}}{R_{1\to 2}} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_2}{kT}}}$$

➡ $$\frac{\bar{n}_1}{1+\bar{n}_1} e^{\frac{E_1}{kT}} = \frac{\bar{n}_2}{1+\bar{n}_2} e^{\frac{E_2}{kT}}$$

$$\bar{n}_1 = \frac{1}{Ae^{\frac{E_1}{kT}} - 1}$$

Bose-Einstein distribution

- **Fermion**

$$\bar{n}_1 R_{1\to 2}^{fermion} = \bar{n}_2 R_{2\to 1}^{fermion}$$

➡ $$\frac{\bar{n}_1(1-\bar{n}_2)}{\bar{n}_2(1-\bar{n}_1)} = \frac{R_{2\to 1}}{R_{1\to 2}} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_2}{kT}}}$$

➡ $$\frac{\bar{n}_1}{1-\bar{n}_1} e^{\frac{E_1}{kT}} = \frac{\bar{n}_2}{1-\bar{n}_2} e^{\frac{E_2}{kT}}$$

$$\bar{n}_1 = \frac{1}{Ae^{\frac{E_1}{kT}} + 1}$$

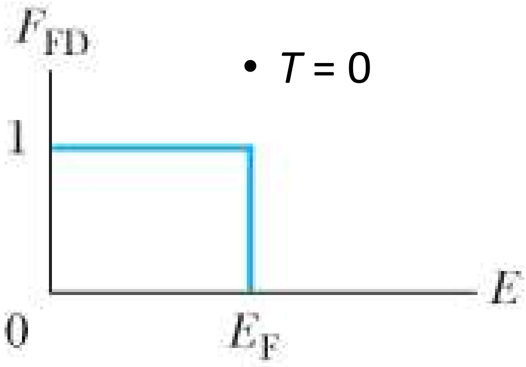
Fermi-Dirac distribution

Note: The $\bar{n}$ here corresponds to F_{BE} or F_{FD}.

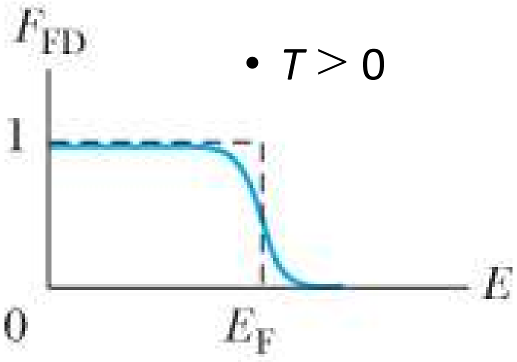
Systems of fermions

Fermi-Dirac distribution $$F_{FD} = \frac{1}{\exp\left[\beta\left(E - E_F\right)\right] + 1}$$

- E_F is called the **Fermi energy**. It is determined by the total number of particles, $N = \int dE g(E) F_{\mathrm{FD}}(E)$
- When $E = E_F \rightarrow F_{FD} = \frac{1}{2}$
- In the limit as $T \rightarrow 0$, $$F_{\mathrm{FD}} = \begin{cases} 1 & \text{for } E < E_{\mathrm{F}} \\ 0 & \text{for } E > E_{\mathrm{F}} \end{cases}$$



- $T = 0$

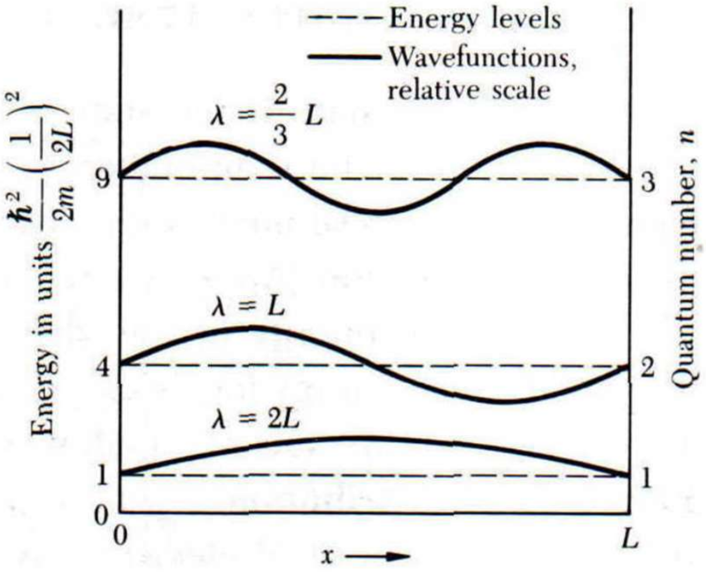


- $T > 0$

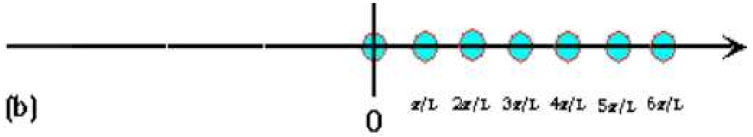
- At $T = 0$, fermions occupy the lowest energy levels available.

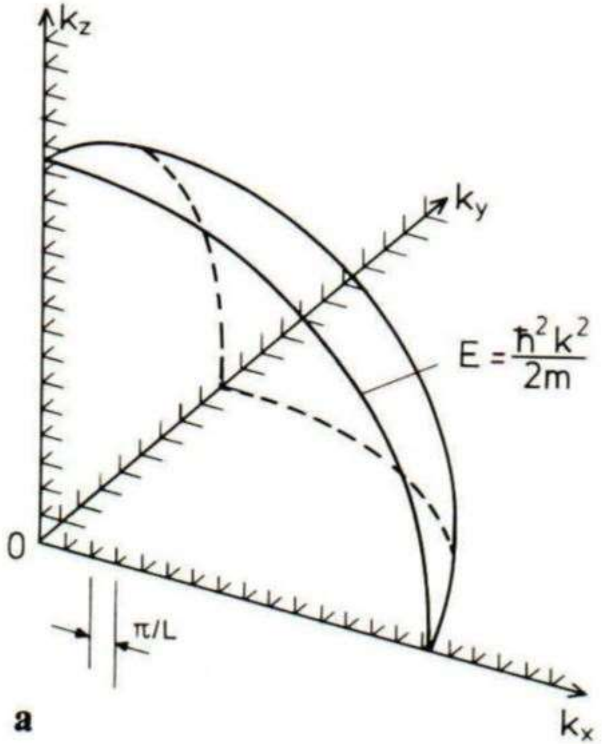
Sommerfeld model of electrons in a metal (1927):

Free electrons in an empty box (it works well!)



k = π/L, 2π/L, 3π/L…





- Standing wave

$$(k_x, k_y, k_z) = \frac{\pi}{L}\left(n_x, n_y, n_z\right) \qquad \Delta^3 k = \left(\frac{\pi}{L}\right)^3$$

- The allowed energies for electrons are

$$E = \frac{\hbar^2 |\vec{k}|^2}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

- Each *k*-point can have 2 electrons (because of spin). After filling in *N* electrons, the result is 1/8 of a spherical sea of electrons called the Fermi sphere. Its radius is called the Fermi wave vector, and the energy of the outermost electron is called the Fermi energy.

  Note: if we choose periodic BC, then it is a whole sphere.

- The number of states up to radius k_F (Fermi wave vector) is

$$N = 2\frac{1}{8}\frac{(4\pi/3)k_F^3}{\Delta^3 k} \qquad \Delta^3 k = \left(\frac{\pi}{L}\right)^3$$

- Total number of electrons (this determines the Fermi energy)

$$N = \frac{k_F^3}{3\pi^2}V \quad \Rightarrow \quad k_F = \left(3\pi^2 n\right)^{1/3}, \quad E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

- For example, for K, the electron density $n=1.4\times10^{28}$ m^{-3}, therefore

$$k_F = 0.746\ A^{-1} \qquad E_F = 3.40\times10^{-19} J = 2.12\ \text{eV}$$

Fermi temperature, Fermi velocity …

$$E_F = k_B T_F = \frac{m}{2} v_F^2$$

also, $\hbar k_F = m v_F$

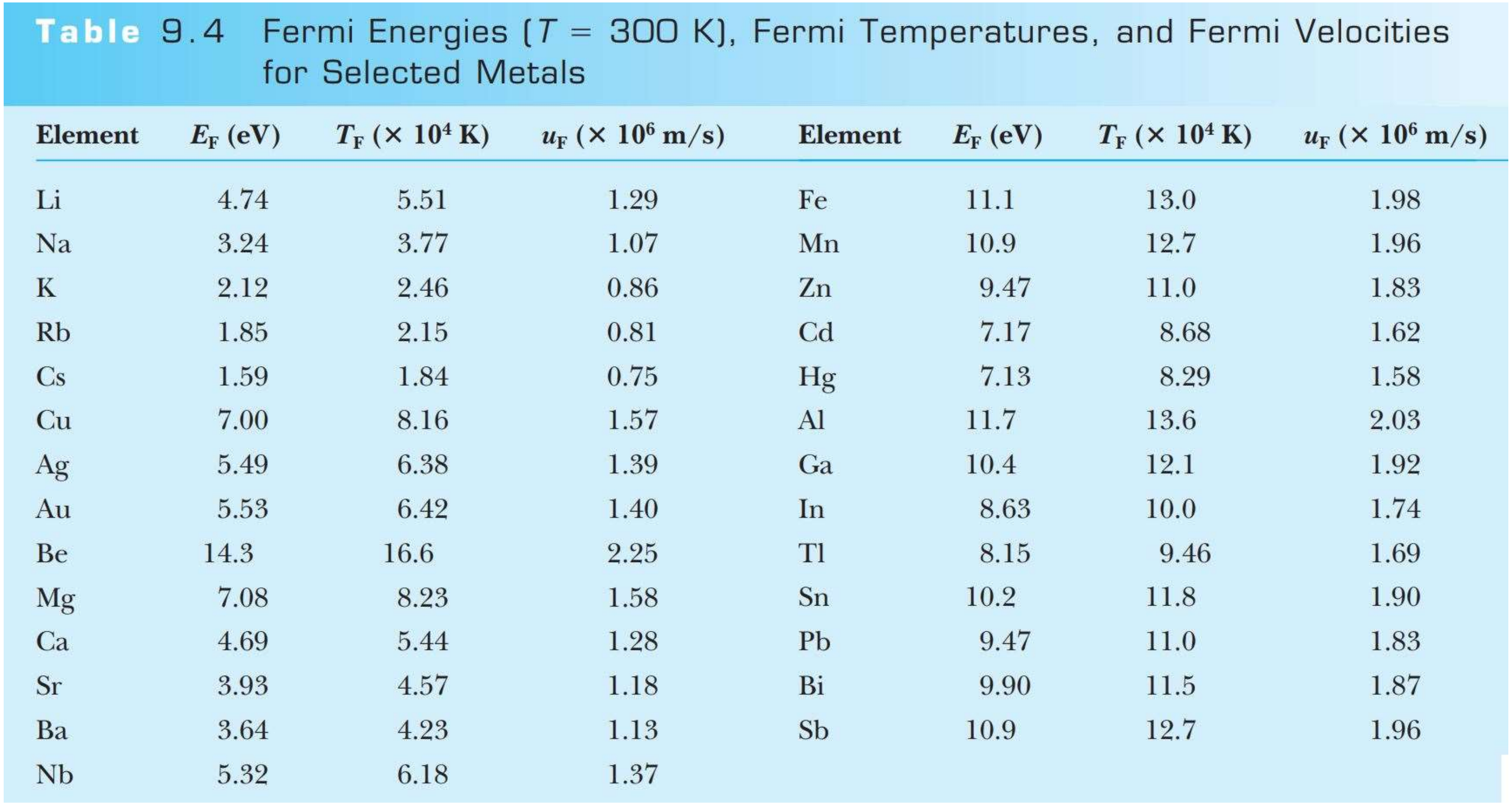
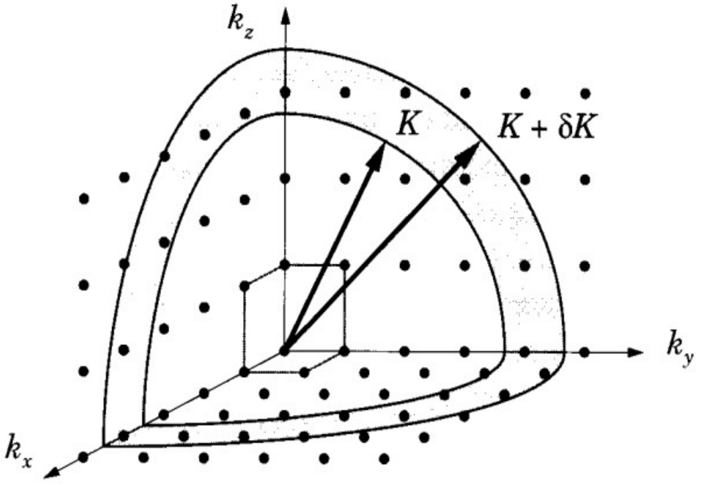


Table 9.4 Fermi Energies (T = 300 K), Fermi Temperatures, and Fermi Velocities for Selected Metals

Element	E_F (eV)	T_F (× 10^4 K)	u_F (× 10^6 m/s)	Element	E_F (eV)	T_F (× 10^4 K)	u_F (× 10^6 m/s)
Li	4.74	5.51	1.29	Fe	11.1	13.0	1.98
Na	3.24	3.77	1.07	Mn	10.9	12.7	1.96
K	2.12	2.46	0.86	Zn	9.47	11.0	1.83
Rb	1.85	2.15	0.81	Cd	7.17	8.68	1.62
Cs	1.59	1.84	0.75	Hg	7.13	8.29	1.58
Cu	7.00	8.16	1.57	Al	11.7	13.6	2.03
Ag	5.49	6.38	1.39	Ga	10.4	12.1	1.92
Au	5.53	6.42	1.40	In	8.63	10.0	1.74
Be	14.3	16.6	2.25	Tl	8.15	9.46	1.69
Mg	7.08	8.23	1.58	Sn	10.2	11.8	1.90
Ca	4.69	5.44	1.28	Pb	9.47	11.0	1.83
Sr	3.93	4.57	1.18	Bi	9.90	11.5	1.87
Ba	3.64	4.23	1.13	Sb	10.9	12.7	1.96
Nb	5.32	6.18	1.37				

- k_F is of the order of a^{-1}.
- ε_F is of the order of the atomic energy levels.

Density of states $g(\varepsilon)$



$$\Delta^3 k = \left(\frac{\pi}{L}\right)^3$$

- $g(E)dE$ is the number of states within the energy surfaces of E and $E+dE$

- For a Fermi sphere,

$$g(E)dE = \frac{2}{8}\frac{4\pi k^2 dk}{(\pi / L)^3}$$

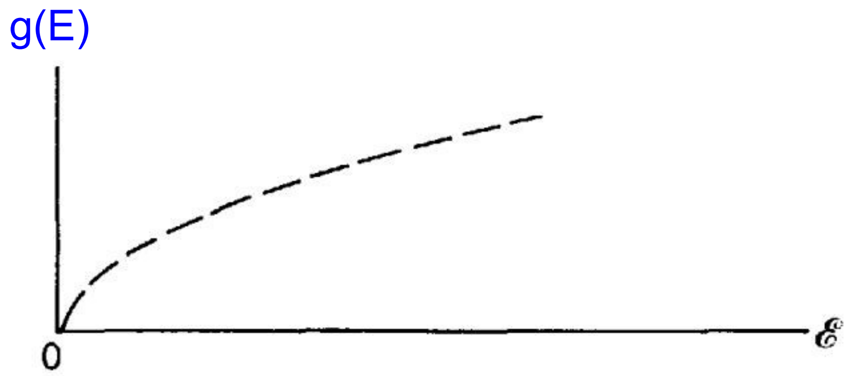
$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} \Rightarrow g(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$$

- Total number of electrons

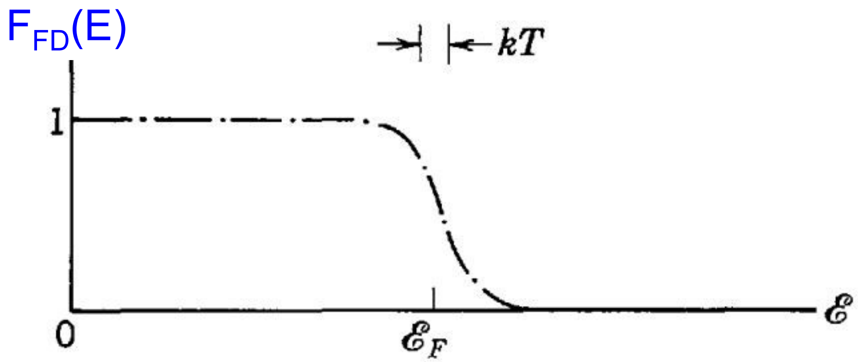
$$N = 2\sum_{\vec{k}} F_{FD}(E_k) \rightarrow 2\int \frac{d^3k}{\Delta^3 k} F_{\mathrm{FD}}(E_{\vec{k}}) = \int dE g(E) F_{\mathrm{FD}}(E)$$

- Total energy

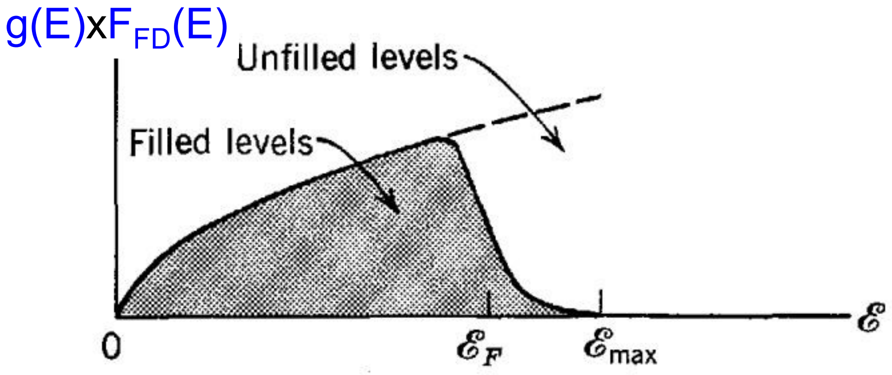
$$U(T) = 2\sum_{\vec{k}} F_{FD}(E_k)E_k \rightarrow \int dE g(E) F_{\mathrm{FD}}(E) E$$

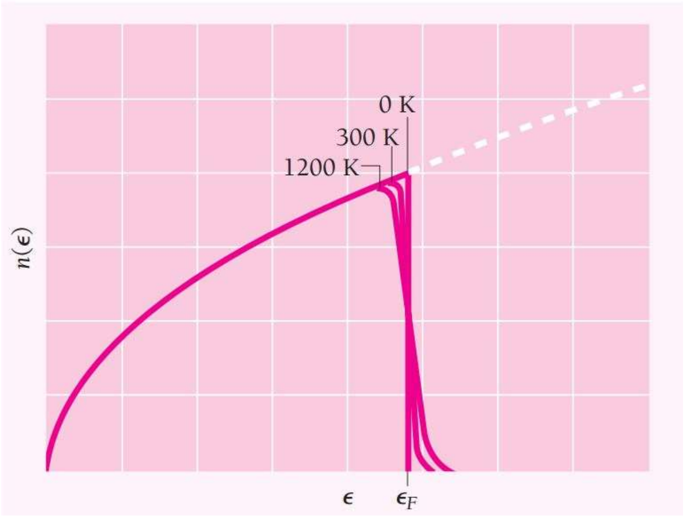


~ Hotel rooms



~ Occupation





$$N = \int dE\, g(E) F_{\mathrm{FD}}(E)$$

- At $T = 0$, $F_{FD}(E)g(E) = \begin{cases} g(E) & \text{for } E < E_\mathrm{F} \\ 0 & \text{for } E > E_\mathrm{F} \end{cases}$

- The mean electronic energy at T=0:

$$\overline{E} = \frac{1}{N}\int_0^\infty E\, F_{FD}(E)g(E)\,dE = \frac{1}{N}\int_0^{E_\mathrm{F}} E\, g(E)\,dE$$

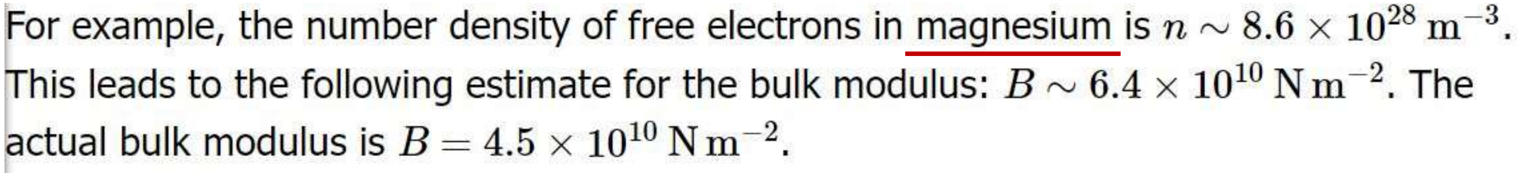
$$= \frac{1}{N}\int_0^{E_\mathrm{F}} \left(\frac{3N}{2}\right) E_\mathrm{F}^{-3/2} E^{3/2}\,dE = \frac{3}{5}E_\mathrm{F}$$

Electron degenerate pressure 電子簡併壓力

- Internal energy of the system: $U = N\overline{E} = \dfrac{3}{5}NE_F$

pressure $P = -\dfrac{\partial U}{\partial V} = \dfrac{2}{5}nE_F \quad >> nkT$

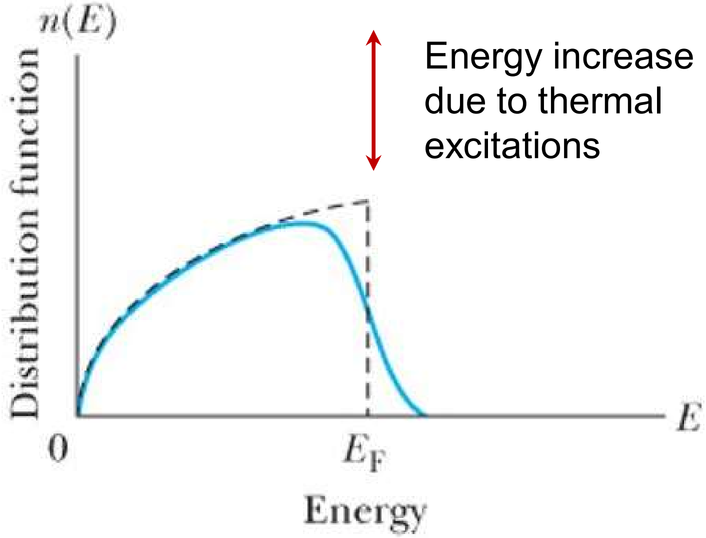
Bulk modulus
體積彈性係數
$B = -V\dfrac{\partial P}{\partial V} = \dfrac{5}{3}P = \dfrac{\hbar^2\pi^3}{9m}\left(\dfrac{3n}{\pi}\right)^{5/3}$



For example, the number density of free electrons in magnesium is $n \sim 8.6\times10^{28}\ \mathrm{m}^{-3}$. This leads to the following estimate for the bulk modulus: $B \sim 6.4\times10^{10}\ \mathrm{N\,m}^{-2}$. The actual bulk modulus is $B = 4.5\times10^{10}\ \mathrm{N\,m}^{-2}$.

- Only those electrons within about kT of E_F will be able to absorb thermal energy and jump to higher states. Therefore the fraction of electrons capable of participating in this thermal process is on the order of kT / E_F.

- In general $$U = \frac{3}{5}NE_F + \alpha\left(N\frac{kT}{E_F}\right)kT \qquad \alpha = \frac{\pi^2}{4}$$ (Kittel, Intro to SS)



Energy increase due to thermal excitations

- Electron heat capacity $$C_V = \frac{\partial U}{\partial T} = 2\alpha Nk^2\frac{T}{E_F}$$

Note: There is also a (much larger) heat capacity from lattice vibration (not included here)

Molar specific heat $$c_V = 2\alpha R\frac{T}{T_F} \ll R$$

(Thornton called it molar heat capacity)

Ex 9.8: Use the Fermi theory to compute the electronic contribution to the molar heat capacity of (a) copper and (b) silver, each at temperature $T = 293$ K. Express the results as a function of the molar gas constant R.

Solution

use $\alpha = \pi^2/4$

➡ $$c_V = 2\left(\frac{\pi^2}{4}\right)R\frac{T}{T_F} = \frac{\pi^2 RT}{2T_F}$$

➡ $T_F = 8.16 \times 10^4$ K for copper

$$c_V = \frac{\pi^2(293\text{ K})}{2(8.16 \times 10^4\text{ K})}R = 0.0177R$$

$T_F = 6.38 \times 10^4$ K for silver

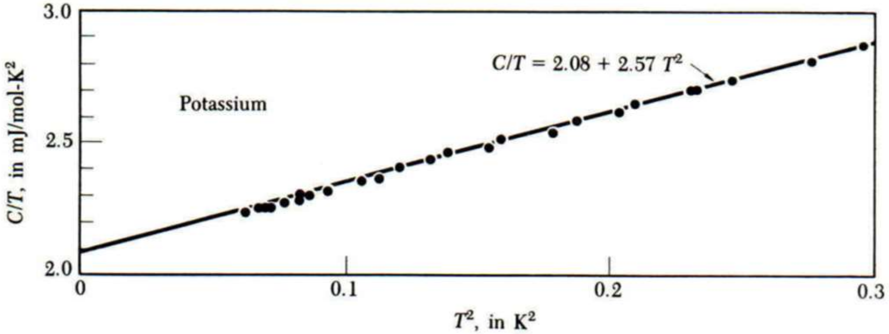
$$c_V = \frac{\pi^2(293\text{ K})}{2(6.38 \times 10^4\text{ K})}R = 0.0227R$$

In general $C = C_e + C_p$

$= \gamma T + aT^3$

Electron + lattice vibration

C_e is important only at very low T.



$$\gamma = \frac{C_e}{T}$$

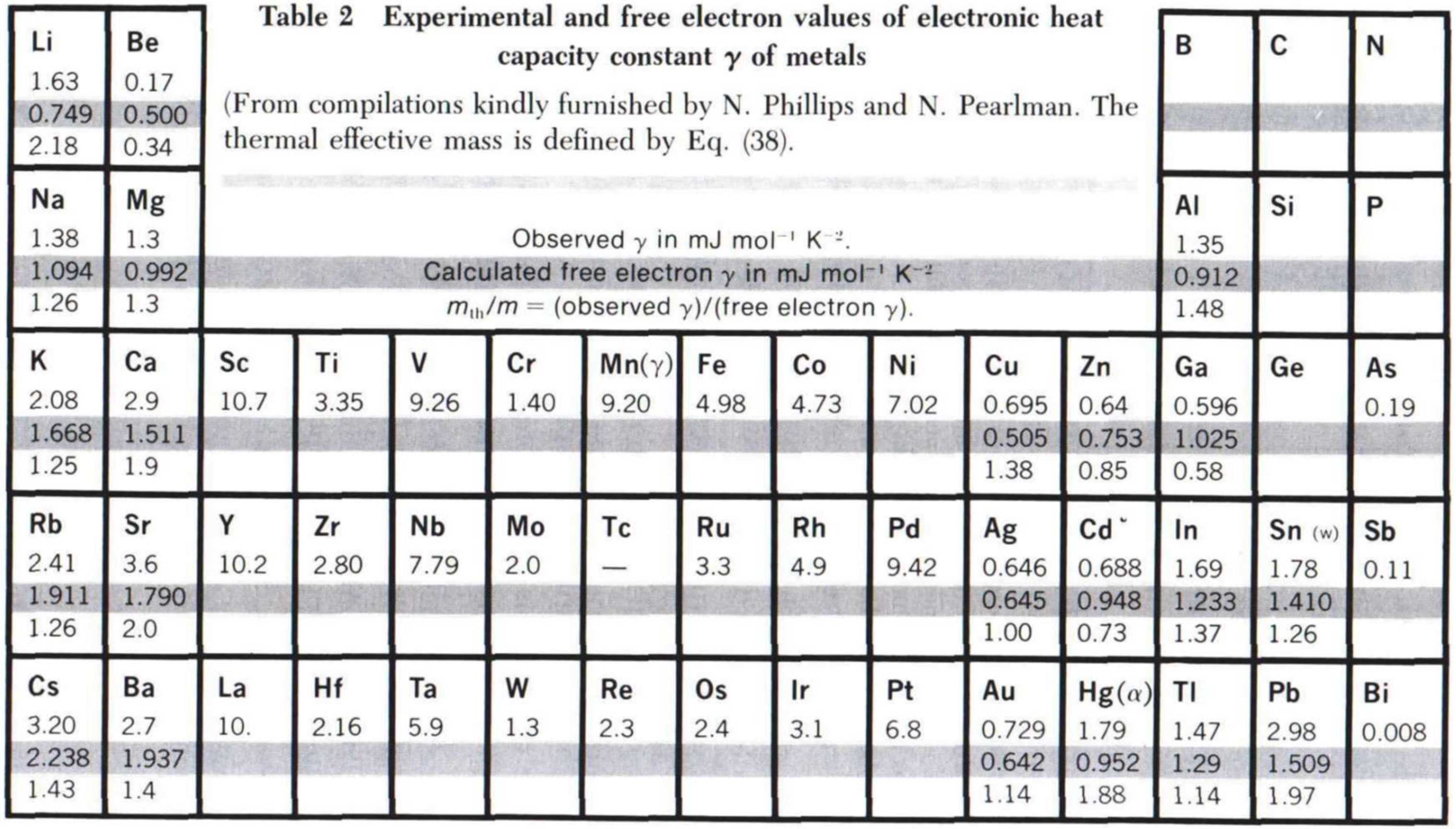


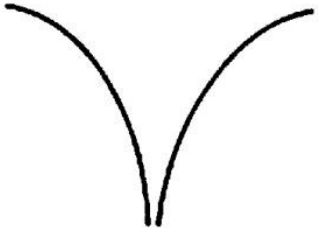
Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).

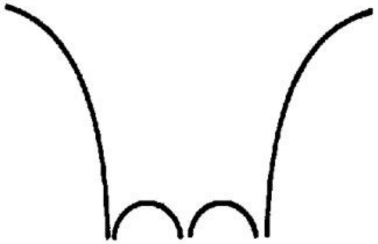
Observed γ in mJ mol⁻¹ K⁻².
Calculated free electron γ in mJ mol⁻¹ K⁻²
m_{th}/m = (observed γ)/(free electron γ).

Li 1.63 0.749 2.18	Be 0.17 0.500 0.34											B	C	N
Na 1.38 1.094 1.26	Mg 1.3 0.992 1.3											Al 1.35 0.912 1.48	Si	P
K 2.08 1.668 1.25	Ca 2.9 1.511 1.9	Sc 10.7	Ti 3.35	V 9.26	Cr 1.40	Mn(γ) 9.20	Fe 4.98	Co 4.73	Ni 7.02	Cu 0.695 0.505 1.38	Zn 0.64 0.753 0.85	Ga 0.596 1.025 0.58	Ge	As 0.19
Rb 2.41 1.911 1.26	Sr 3.6 1.790 2.0	Y 10.2	Zr 2.80	Nb 7.79	Mo 2.0	Tc —	Ru 3.3	Rh 4.9	Pd 9.42	Ag 0.646 0.645 1.00	Cd 0.688 0.948 0.73	In 1.69 1.233 1.37	Sn (w) 1.78 1.410 1.26	Sb 0.11
Cs 3.20 2.238 1.43	Ba 2.7 1.937 1.4	La 10.	Hf 2.16	Ta 5.9	W 1.3	Re 2.3	Os 2.4	Ir 3.1	Pt 6.8	Au 0.729 0.642 1.14	Hg(α) 1.79 0.952 1.88	Tl 1.47 1.29 1.14	Pb 2.98 1.509 1.97	Bi 0.008

Work function 功函數



One ion



Three ions in line

Many closely spaced ions in line

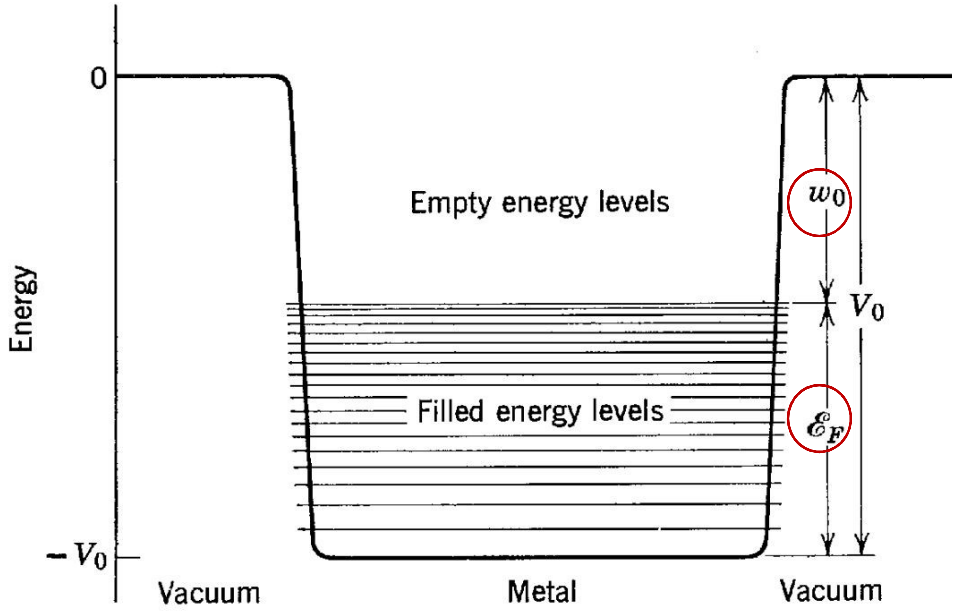
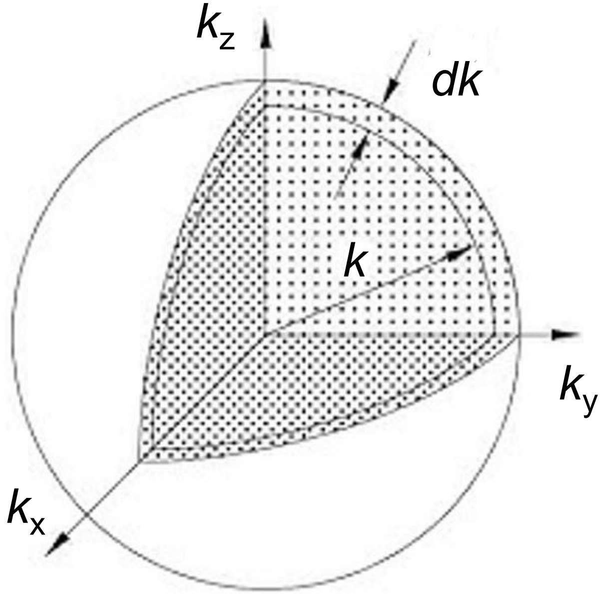


Table 11-2 Work Function and Fermi Level Energy for Some Metals

Metal	w_0 (eV)	$\mathscr{E}_F$ (eV)
Ag	4.7	5.5
Au	4.8	5.5
Ca	3.2	4.7
Cu	4.1	7.1
K	2.1	2.1
Li	2.3	4.7
Na	2.3	3.1

System of bosons

Bose-Einstein distribution $F_{BE} = \frac{1}{A\exp(\beta E) - 1},\ A \geq 1$



Case 1: Blackbody radiation (*A*=1 for photons)

- Photons in a box with side length *L*

$$(k_x, k_y, k_z) = \frac{\pi}{L}(n_x, n_y, n_z)$$

$$\Rightarrow\ E = cp = c\hbar k = c\hbar\sqrt{k_x^2 + k_y^2 + k_z^2}$$

- The number of states within "radius" *k* is

2 from 2 photon polarizations

$$N_k = \frac{2\left(\frac{1}{8}\right)\left(\frac{4}{3}\pi k^3\right)}{\left(\frac{\pi}{L}\right)^3} = \frac{L^3}{3\pi^2}k^3 \quad \text{or} \quad N_E = \frac{L^3}{3\pi^2}\frac{1}{(c\hbar)^3}E^3$$

$\Rightarrow$
- Density of states $g(E) = \frac{dN_E}{dE} = \frac{L^3}{\pi^2 (c\hbar)^3}E^2$

(This has been mentioned in Chap 3)

- Convert to distribution of energy density $u(E)$.

Energy density within the range $[E, E + dE]$:

Multiply by a factor E/L^3

$$
\begin{aligned}
u(E)dE &= \frac{E}{L^3} g(E) F_{BE}(E) dE \\
&= \frac{8\pi}{h^3c^3} \frac{E^3}{e^{E/KT}-1} dE
\end{aligned}
$$

This agrees with the one derived in Chap 3 (Here is the 3rd derivation of Planck's law.
What's the 2nd one we learned?)

optional

- Using $E = hc/\lambda$ and $dE = (hc/\lambda^2)\, d\lambda$

➡ $$u(\lambda,T)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda KT}-1}$$

- From energy density to flux density, multiplying by $c/4$ is required.

$$\ell(\lambda,T) = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/\lambda KT}-1}$$

optional

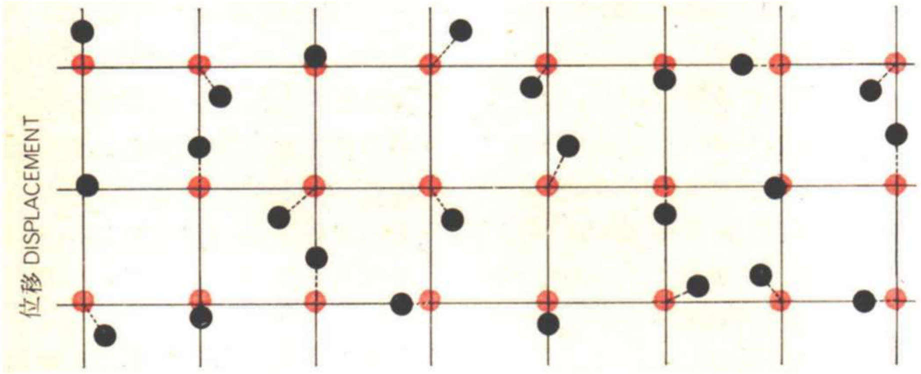
Heat capacity of solids

- Einstein model (1907)

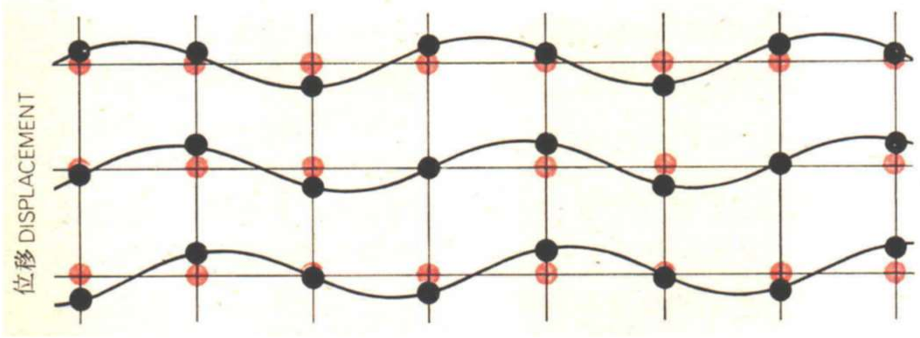
Assume that

1. each atom vibrates independently of each other, and

2. every atom has the same vibration frequency ω_0



- Debye model (1912), not discussed here



optional

Einstein model

Internal energy

$$U = 3N\left(\bar{n} + \frac{1}{2}\right)\hbar\omega_0 = 3N\frac{\hbar\omega_0}{\exp(\hbar\omega_0 / kT) - 1} + 3N\frac{\hbar\omega_0}{2}$$

$$\bar{n} = \frac{\sum n e^{-n\frac{\hbar\omega_0}{kT}}}{\sum e^{-n\frac{\hbar\omega_0}{kT}}}$$

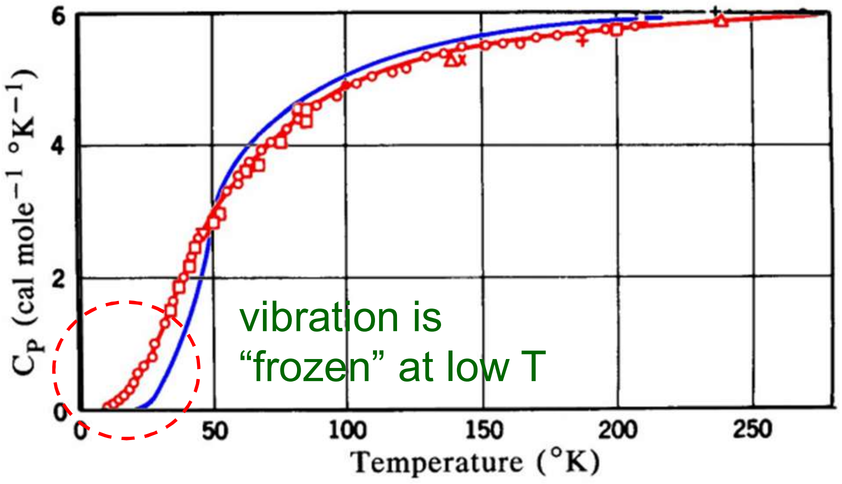
Heat capacity

$$C_V = (\partial U / \partial T)_V = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \frac{e^{\hbar\omega_0/kT}}{\left(e^{\hbar\omega_0/kT} - 1\right)^2}$$

$$\approx e^{-\hbar\omega_0/kT} \text{ as } T \to 0\,K$$

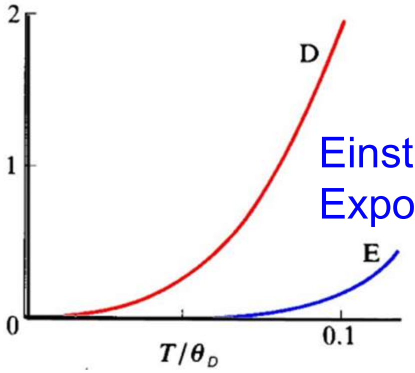
Comparison with experimental data

Heat capacity of silver



vibration is
“frozen” at low T

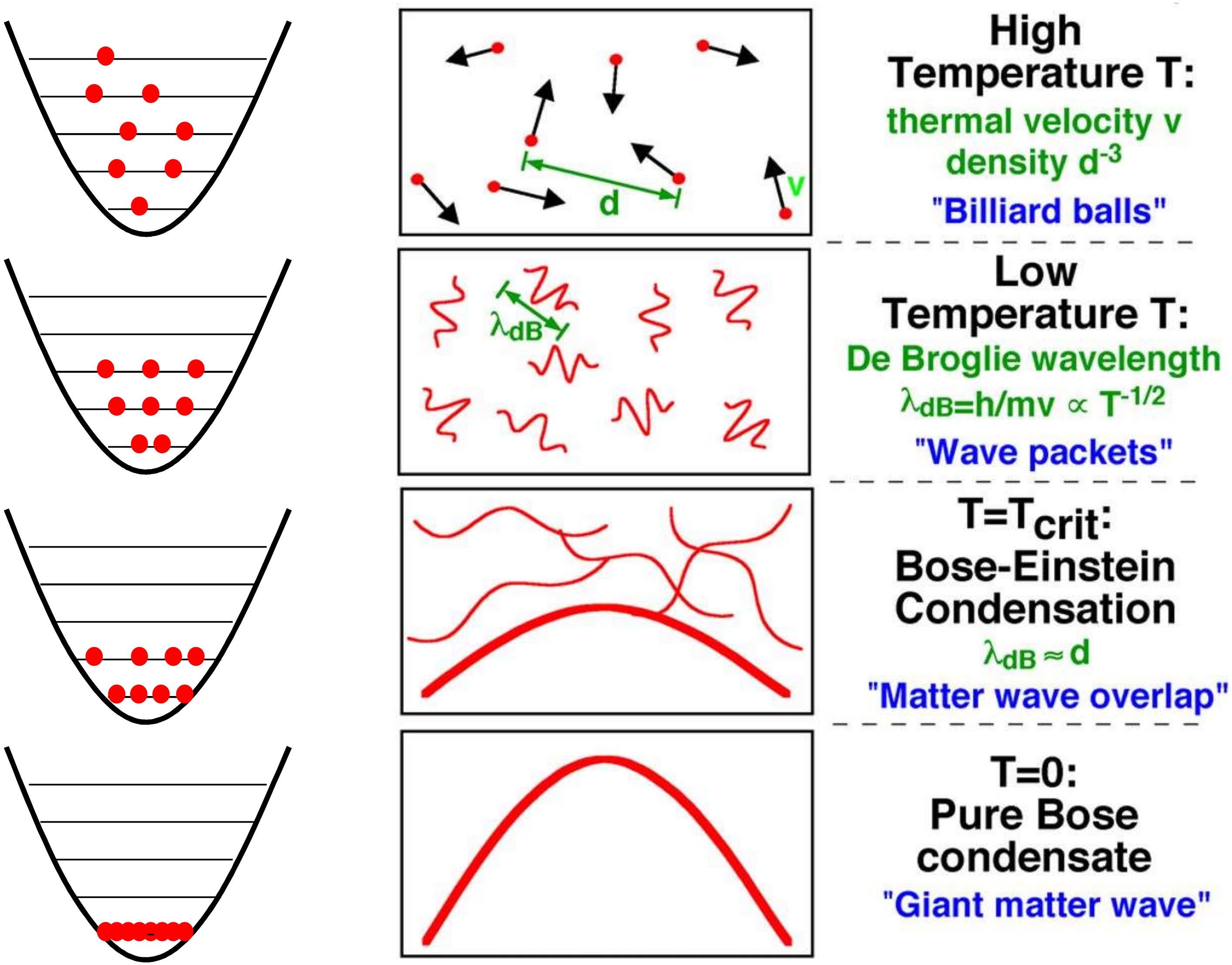
Debye model:
Debye T^3 law



Einstein model:
Exponential decay

optional

Case 2: Bose-Einstein condensation in gases



High Temperature T:
thermal velocity v
density d^{-3}
"Billiard balls"

Low Temperature T:
De Broglie wavelength
$\lambda_{dB}=h/mv \propto T^{-1/2}$
"Wave packets"

$T=T_{crit}$:
Bose-Einstein Condensation
$\lambda_{dB} \approx d$
"Matter wave overlap"

T=0:
Pure Bose condensate
"Giant matter wave"

optional

Cool a gas of ^{87}Rb atoms to about 1 mK, then used a magnetic trap to cool the gas to about 20 nK.

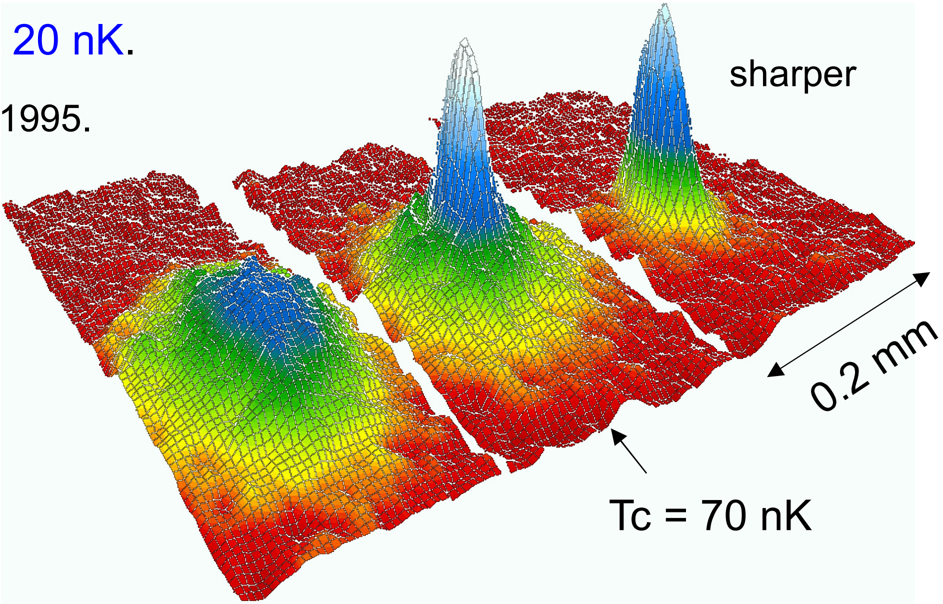
(v ~ 1 mm/s) Cornell and Wieman, Ketterle 1995.

$$v = \sqrt{\frac{3k_BT}{m}}$$

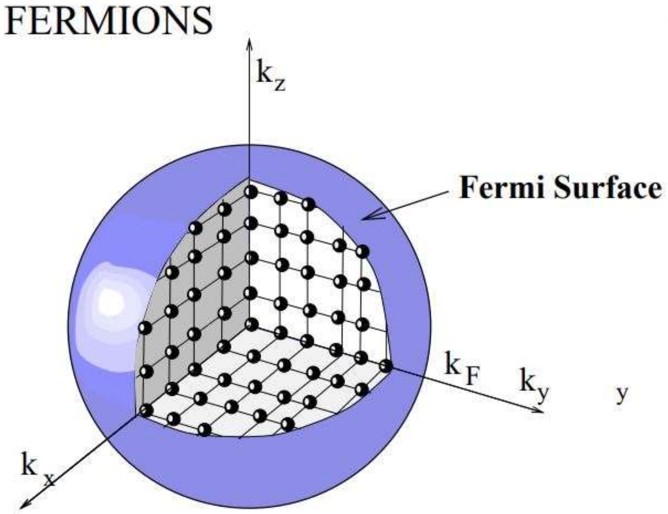
De Broglie wavelength $$\lambda_{dB} = \frac{h}{p} = \frac{h}{\sqrt{3k_BTm}}$$

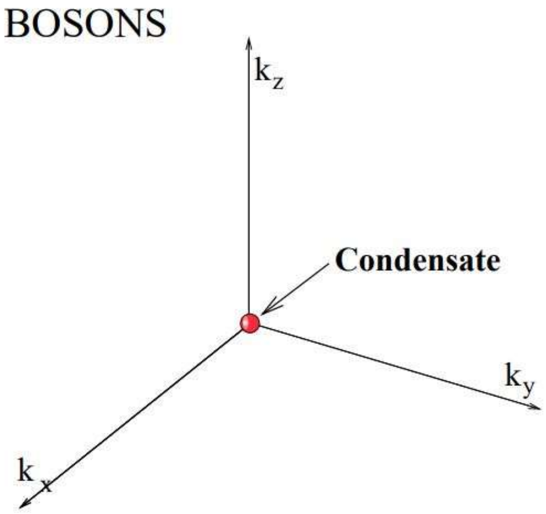
BEC: $$\lambda_{dB} > d = \frac{1}{n^{1/3}}$$

Ru atoms: $m = 1.4 \times 10^{-25}$ kg, $n \sim 2.5 \times 10^{12}$ /cm^3



The graphic shows successive snapshots in time in which the atoms condensate.

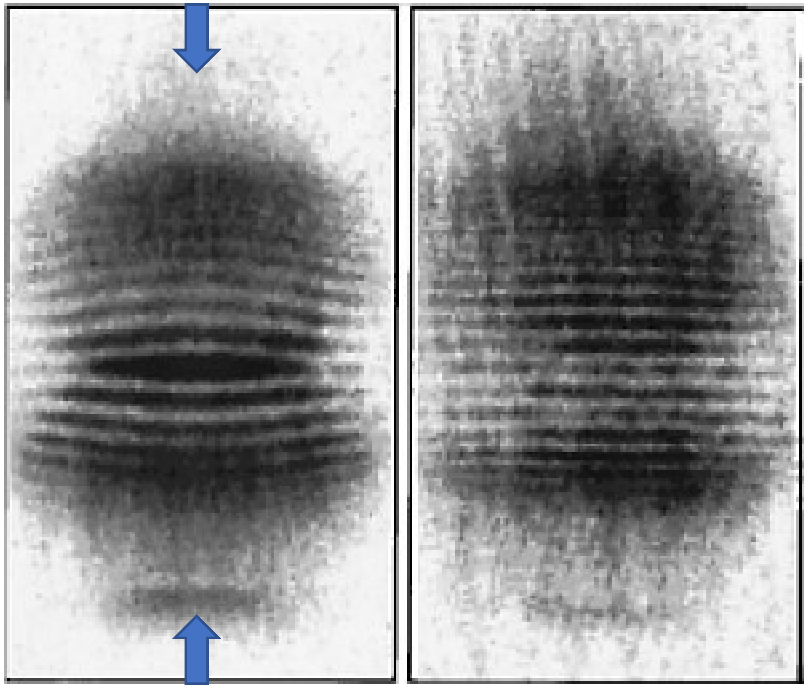




optional

Macroscopic, coherent matter wave

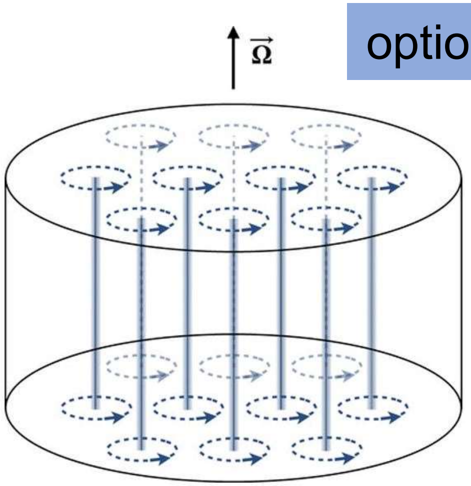
Interference between two BEC of Na atoms (1997)

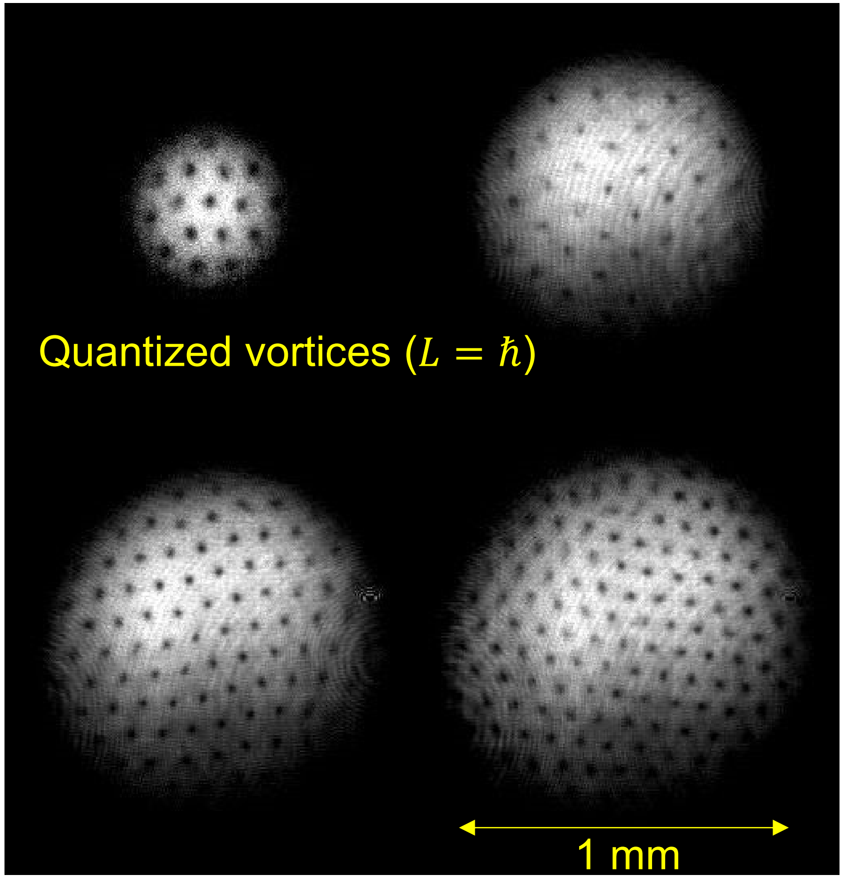


www.science.org/doi/10.1126/science.275.5300.637

The interference fringes have a spacing of 20 and 15 μm (2 different cases)

Vortex lattices in rotating Na BEC (2001)



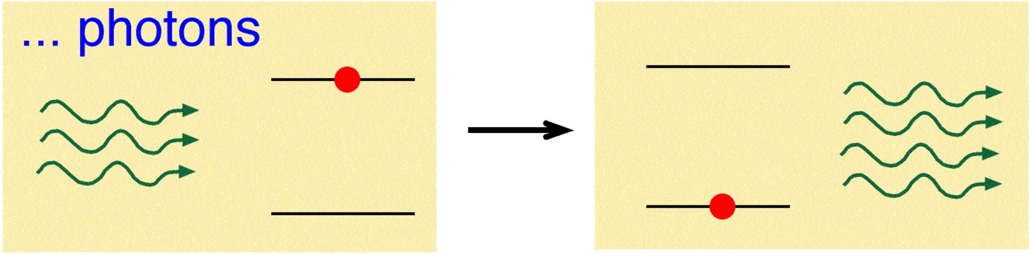


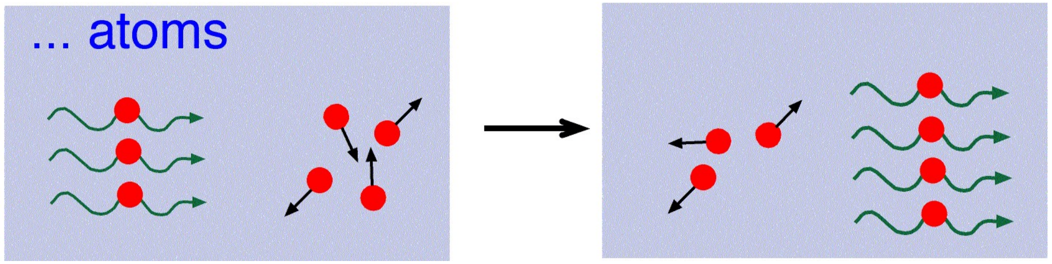
https://www.science.org/doi/10.1126/science.1060182

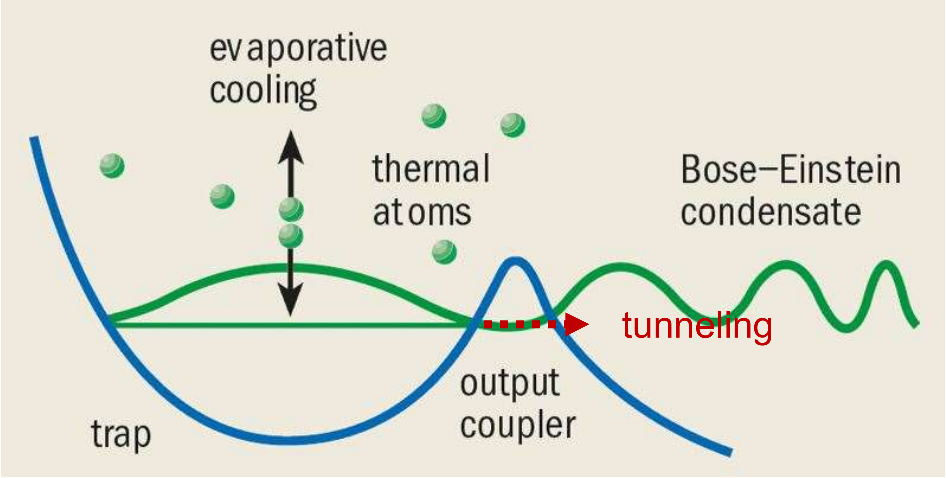
optional

Laser: condensation of photons

Atom laser: condensation of atoms (1996, CW 1999)

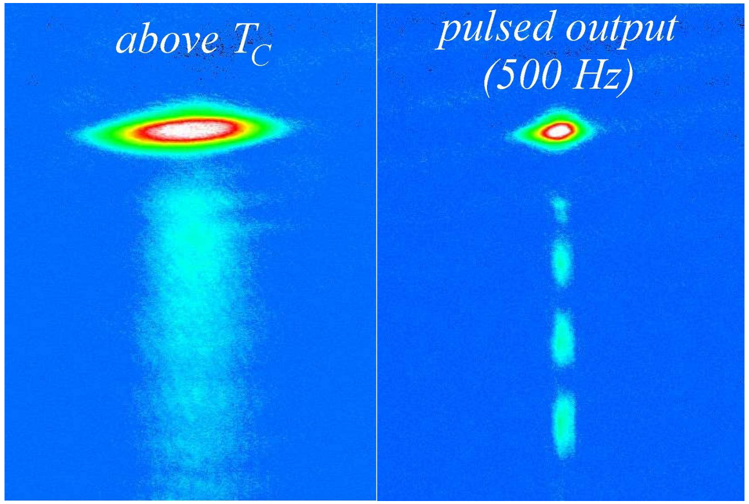






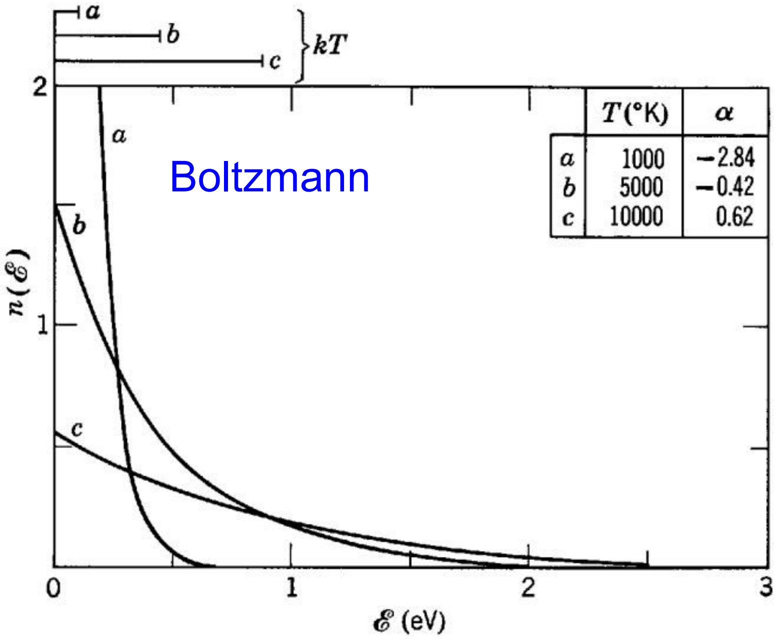
The gain medium is a thermal cloud of atoms. The extracted atoms form a beam of coherent matter wave.

Atom laser



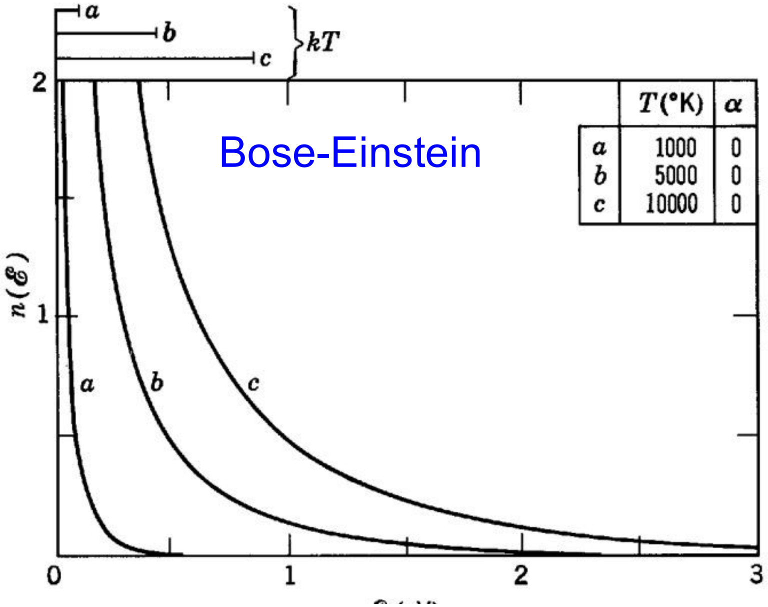
https://physicsworld.com/a/atom-lasers/

Boltzmann



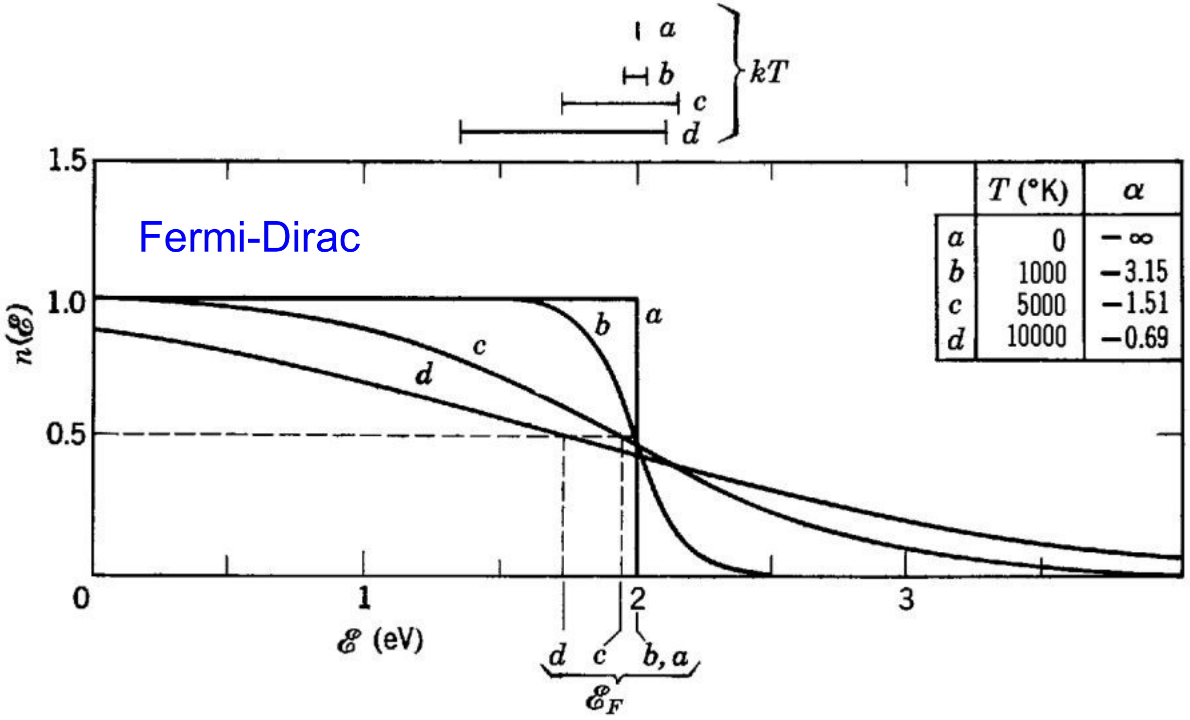
	T (°K)	α
a	1000	−2.84
b	5000	−0.42
c	10000	0.62

Bose-Einstein



	T (°K)	α
a	1000	0
b	5000	0
c	10000	0

Fermi-Dirac

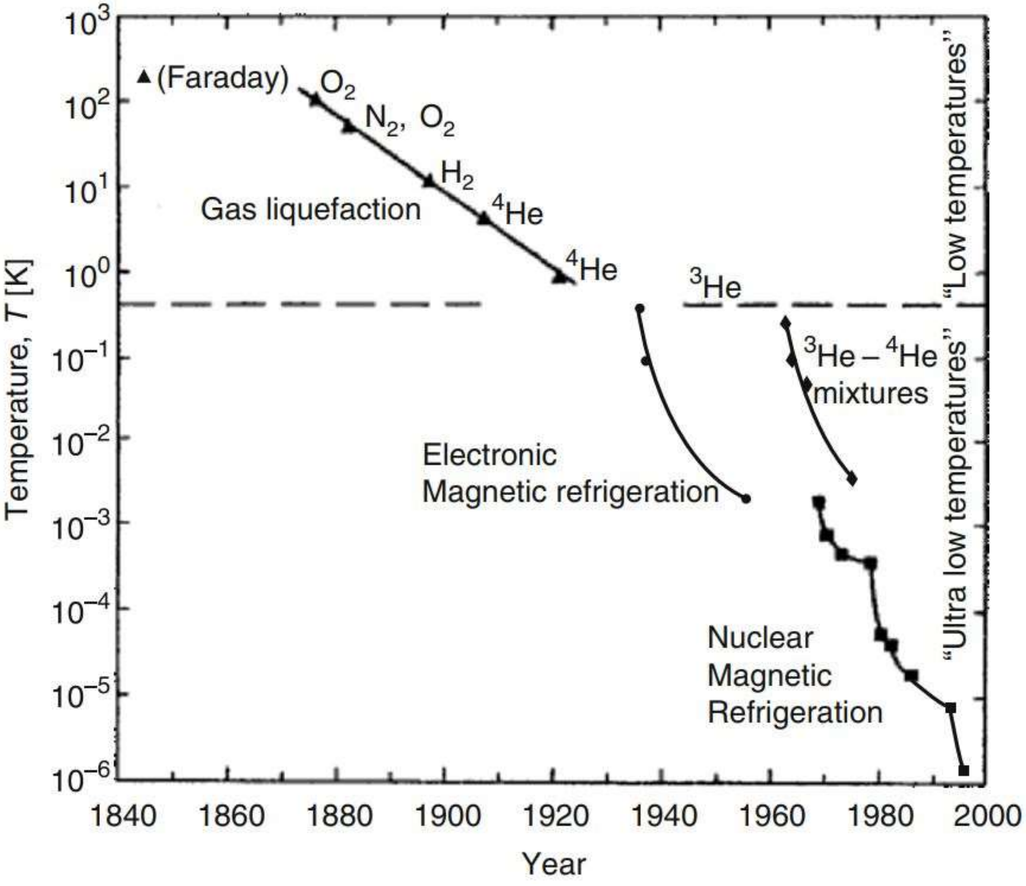


	T (°K)	α
a	0	$-\infty$
b	1000	−3.15
c	5000	−1.51
d	10000	−0.69

Case 3: Superfluid

First, a timeline of low temperature

- 1800 Charles and Gay-Lusac (from *P-T* relationship) proposed that the lowest temperature is -273 C (= 0 *K*)
- 1877 Cailletet and Pictet liquified Oxygen (-183 C or 90 *K*). Soon after, Nitrogen (77 *K*) is liquified
- 1898 Dewar liquified Hydrogen (20 *K*)
- 1908 Onnes liquified Helium (4.2 *K*)
- 1911 Onnes discovered superconductivity.

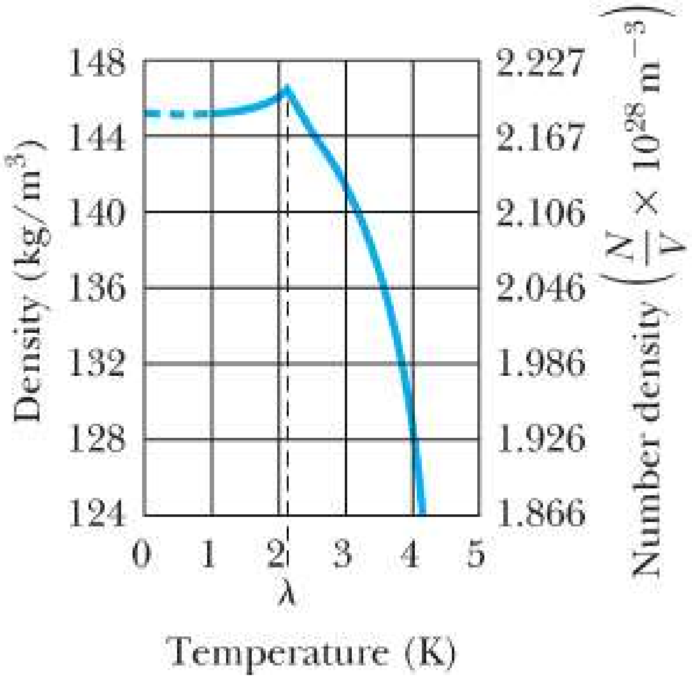


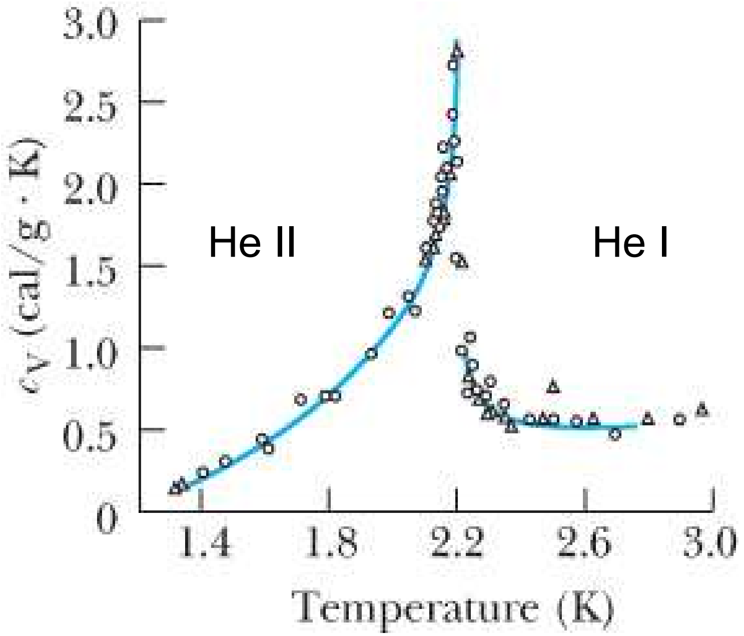
Pobell, Matter and Methods at Low Temperatures

Superfluid, a fluid with zero viscosity 黏滯度

Helium gas is liquified at 4.2 K (Onnes, 1908)

- The density of liquid helium as a function of temperature (1924).
- The specific heat of liquid helium as a function of temperature (1932).

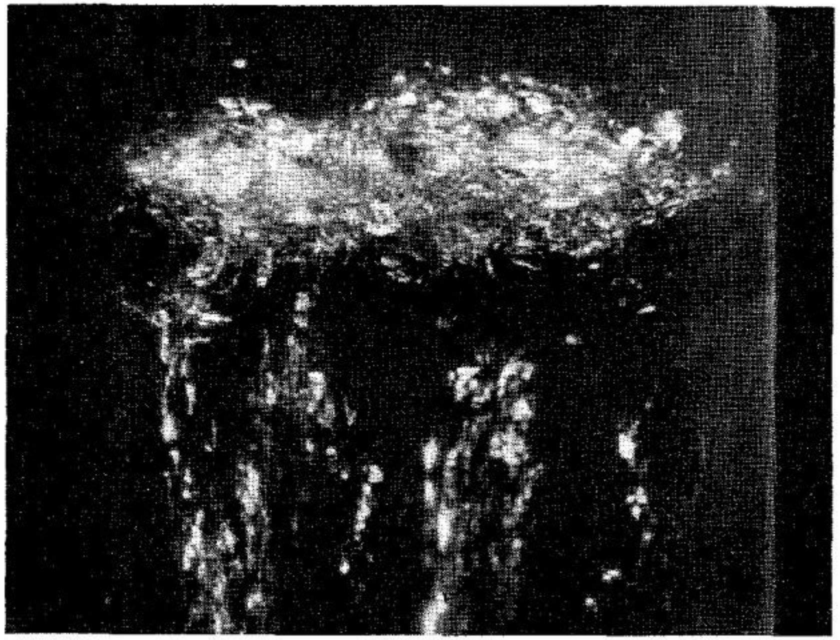




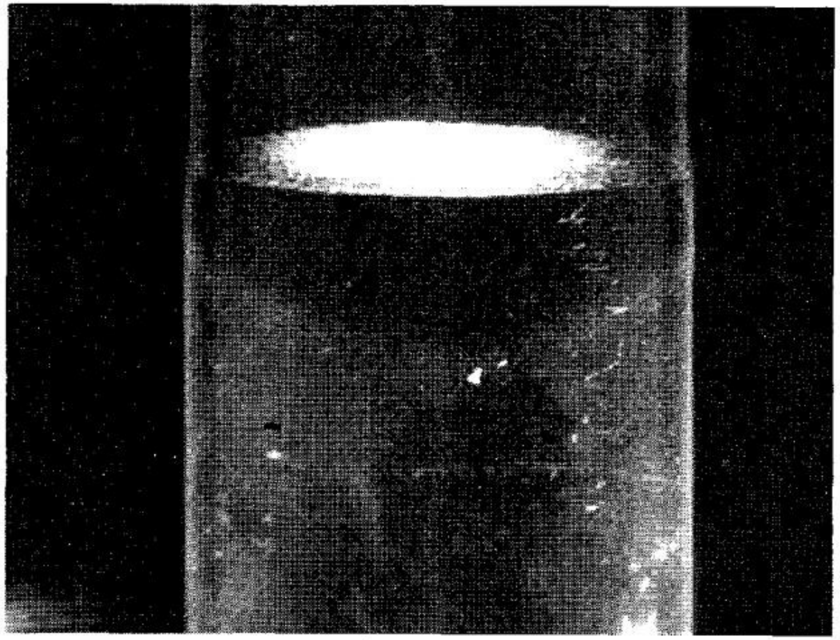
This implies a phase transition at T_c=2.17 K.

- As the temperature is reduced from 4.2 K, the liquid boils vigorously.
- At 2.17 K the boiling suddenly stops.

  This implies that the low-T phase has a very large thermal conductivity.



$T>T_c$

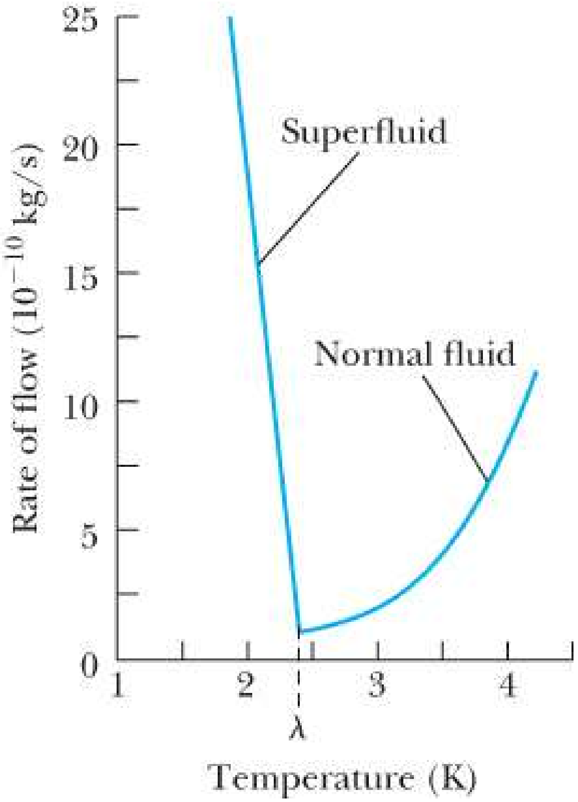


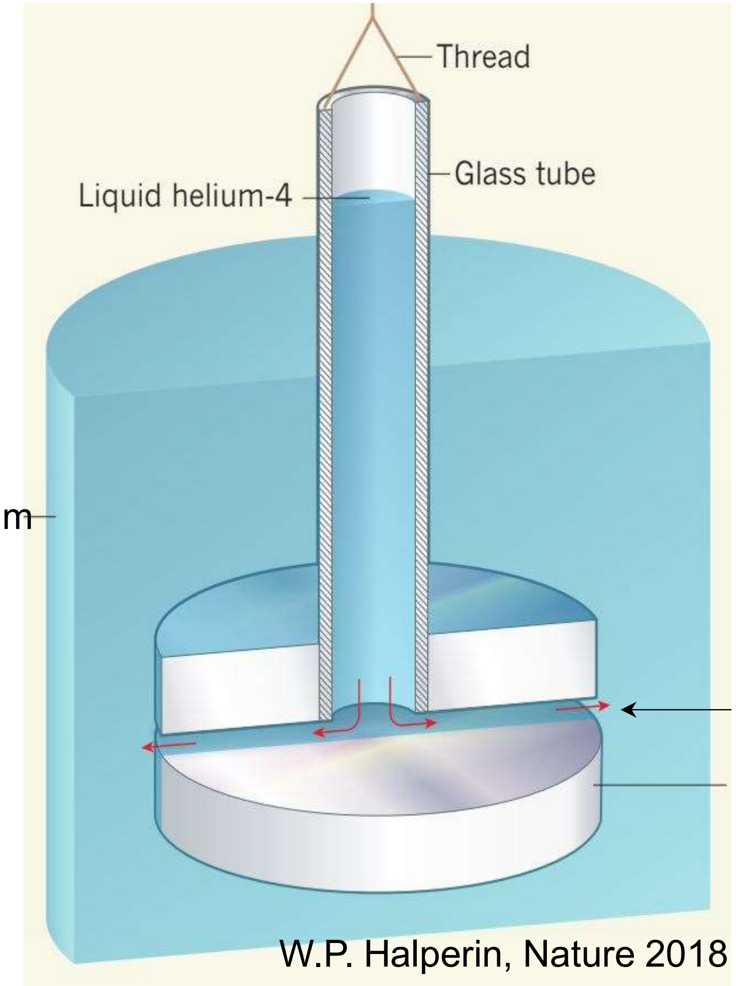
$T<T_c$

Youtube: Superfluid helium

Discovery of superfluid with zero viscosity (Kapitza, 1938) 超流體

The phase below 2.17 K is a **superfluid phase**.





Helium

a narrow gap between two glass disks.

Glass disk

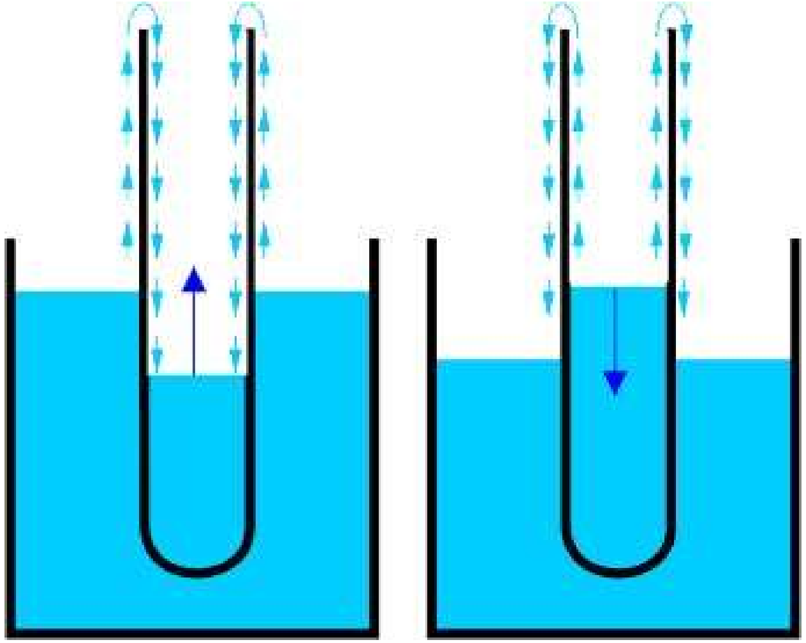
W.P. Halperin, Nature 2018

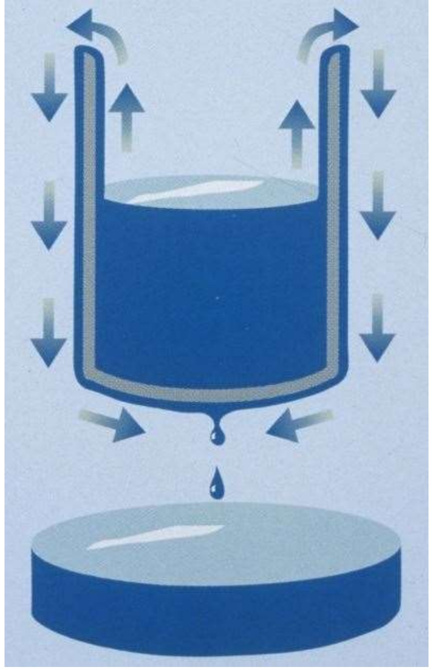
Superfluid helium is an example of **Bose-Einstein condensation**

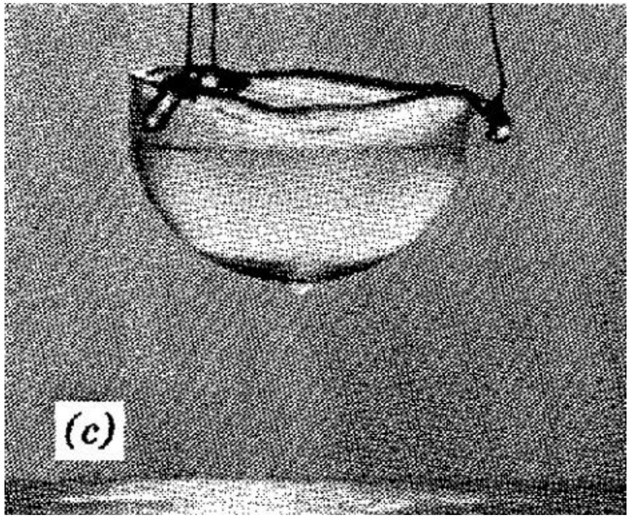
It is also a rare example of **macroscopic quantum phenomena**

蠕動

- Creeping of superfluid







Helium film covers container via

absorption of He atoms from vapor

→ superfluid film

(~ 20 nm thick, creep ~ 20 cm/s)

The Unusual Properties of Liquid Helium

Estimate the critical temperature T_c of superfluid transition

- **Density of states**

  It’s less by a factor of 2 compared to DOS of electron gas,

$$g(E) = 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2}$$

- **The number distribution** *n*(*E*)

$$F_{\mathrm{BE}}(E) g(E) = 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} \frac{E^{1/2}}{A e^{E/kT} - 1}$$

- **Normalization condition**: For *N* helium atoms,

$$N = \int_0^\infty F_{\mathrm{BE}} g(E)\, dE = 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} \boxed{\int_0^\infty \frac{E^{1/2}}{A e^{E/kT} - 1} dE}$$

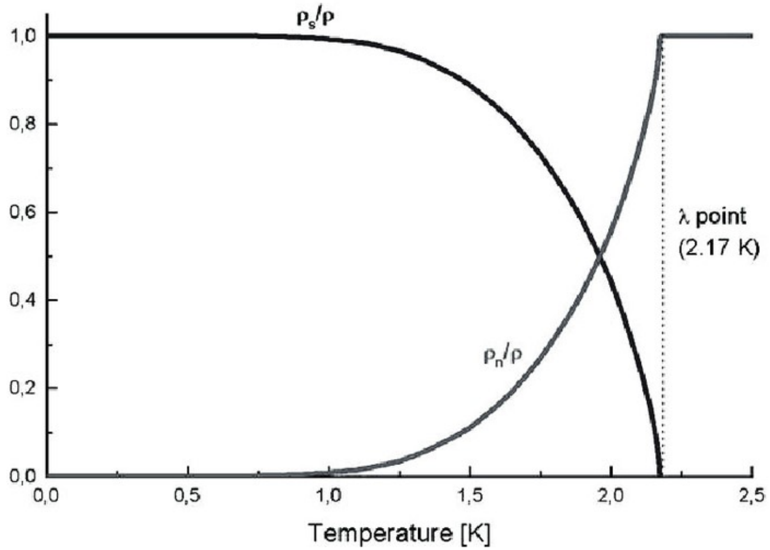
$$= 2.315 (kT)^3 \text{ if } A = 1$$

Note: $A e^{E/kT} = e^{(E-\mu)/kT}$: $A = 1 \leftrightarrow \mu = 0$

- **Two-fluid model** (London 1938)

Fraction of helium atoms in superfluid state:

$$F = 1 - \left(\frac{T}{T_c}\right)^{\alpha}$$



- Use A = 1 ← This corresponds to the maximum value of *N* (before some atoms condenses to the ground state)

$$N \le 2\pi V \left(\frac{2mkT}{h^2}\right)^{3/2} \times 2.315$$

$$\Rightarrow \quad T \ge \frac{h^2}{2mk}\left[\frac{N}{4.63\pi V}\right]^{2/3}$$

For liquid helium, $n = 2.11 \times 10^{28}$ atoms/m^3

The result gives $T \ge 3.06$ K, which is close to the actual T_c.

Ex 9.9: For a gas of nitrogen (N_2) at room temperature (293 K) and 1 atmosphere pressure, calculate the Maxwell-Boltzmann constant A and thereby show that Bose-Einstein statistics can be replaced by Maxwell-Boltzmann statistics in this case.

Solution

$$g(E) = \frac{2\pi V}{h^3}(2m)^{3/2}E^{1/2}$$

$$F_{\text{MB}} = A\exp(-E/kT)$$

→

$$N = \frac{2\pi V}{h^3}(2m)^{3/2}A\int_0^\infty E^{1/2}\exp(-E/kT)\,dE$$

$$= \frac{2\pi V}{h^3}(2m)^{3/2}A\frac{\sqrt{\pi}}{2}(kT)^{3/2}$$

$$= \frac{V}{h^3}(2\pi mkT)^{3/2}A \quad \rightarrow \quad A = \frac{h^3N}{V}(2\pi mkT)^{-3/2}$$

Under normal conditions (atmospheric pressure and room temperature) the number density of nitrogen gas is $N/V = 2.50 \times 10^{25}\ \text{m}^{-3}$. Plugging this into our result for A along with the molecular mass of N_2 and $T = 293$ K yields the value $A = 1.8 \times 10^{-7}$. Because this is much less than unity, the use of Maxwell-Boltzmann statistics is justified

Summary of the **density of states** studied so far

- Ideal gas; Electron gas (p.324)

$$g(E) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

- EM wave (photon gas, p.328; also ch 3 on blackbody radiation)

$$g(E) = \frac{8\pi V}{h^3 c^3} E^2$$

- Helium gas (p.334), similar to the first one above

$$g(E) = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

The number of states within $[E, E+dE]$ $= g(E)dE$

Case 4: Superconductivity (see Chap 10)