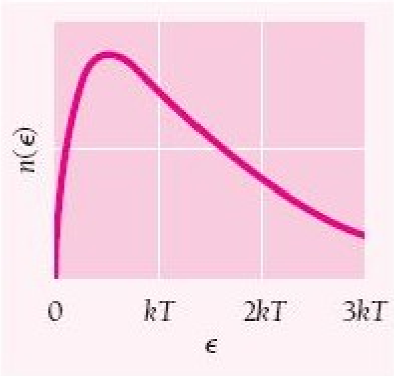
Chapter 7 Statistical Mechanics

7-1 Maxwell-Boltzmann Distribution Function $f_{MB}(E)=Ag(E)e^{-E/kT}$



For many **identical** particles which **can be distinguished in some ways**, and a number of particles in the same energy interval to occupy the same small energy in space, the average number of particles $f_{MB}(E)$ in a state of energy E is $f_{MB}(E)=Ag(E)e^{-E/kT}$, where $g(E)$ is the number of states of energy of E, T is the absolute temperature, and $k=1.381\times10^{-23}J/°K=8.617\times10^{-5}eV/°K$ is **Boltzmann's constant.**

Maxwell-Boltzmann distribution is suitable to analyze the behavior of an **ideal gas**.

Eg. Obtain the relative populations of the rotational states of a rigid diatomic molecule.

(Sol.) $E_J=J(J+1)\hbar^2/2I$, $L=\sqrt{J(J+1)}\hbar$, $L_z=M_J\hbar$, $M_J=-J, -J+1, -J+2, \ldots, 0, \ldots, J-1, J$

$\Rightarrow g(E)=2J+1$, $\therefore$ $n(E)=A(2J+1)e^{-J(J+1)\hbar^2/2IkT}$

Eg. At what temperature would one in thousand of atoms in a gas of atomic hydrogen be in the first excited energy level?

(Sol.) Ground state 1*s*: $m_s=\pm\frac{1}{2}\Rightarrow g(E_1)=2$

The first excited state 2*s*: $l=0$, $m_l=0$; 2*p*: $l=1$, $m_l=-1, 0, 1$; $m_s=\pm\frac{1}{2}\Rightarrow g(E_2)=8$

$n(E_2)/n(E_1)=1/1000=\frac{Ag(E_2)e^{-E_2/kT}}{Ag(E_1)e^{-E_2/kT}}=\frac{g(E_2)}{g(E_1)}\cdot e^{-(E_2-E_1)/kT}=8\,e^{-(E_2-E_1)/kT}/2=4\,e^{-(E_2-E_1)/kT}$

$E_2-E_1=-13.6(1/2^2-1/1^2)=10.2\text{eV}\Rightarrow T=1.4271\times10^4°K$

Energy distribution of an ideal gas: $n(E)dE=\frac{2\pi N}{(\pi kT)^{3/2}}\sqrt{E}e^{-E/kT}dE$

(Proof) Consider a phase space (x,y,z,p_x,p_y,p_z). The number of states $g(p)dp$ with momenta whose magnitudes are between p and $p+dp$ is $g(p)dp\propto4\pi p^2dp$.

Set $g(p)dp=Bp^2dp$, and $p^2=2mE\Rightarrow g(E)dE=2m^{3/2}B\sqrt{E}dE$

$\Rightarrow n(E)dE=Ag(E)e^{-E/kT}dE=2m^{3/2}AB\sqrt{E}e^{-E/kT}dE=C\sqrt{E}e^{-E/kT}dE$

$\because$ Total number of molecules $N=\int_0^\infty n(E)dE \Rightarrow C=\frac{2\pi N}{(\pi kT)^{3/2}}$

$\Rightarrow n(E)dE=\frac{2\pi N}{(\pi kT)^{3/2}}\sqrt{E}e^{-E/kT}dE$

Total energy of N gas molecules: $E=\int_0^\infty En(E)dE=\frac{3kT}{2}$

Average molecular energy: $\overline{E}=\frac{3kT}{2}=\frac{kT}{2}+\frac{kT}{2}+\frac{kT}{2}$

RMS (root-mean-square) velocity: $v_{rms}=\sqrt{\overline{v^2}}=\sqrt{\frac{3kT}{m}}$

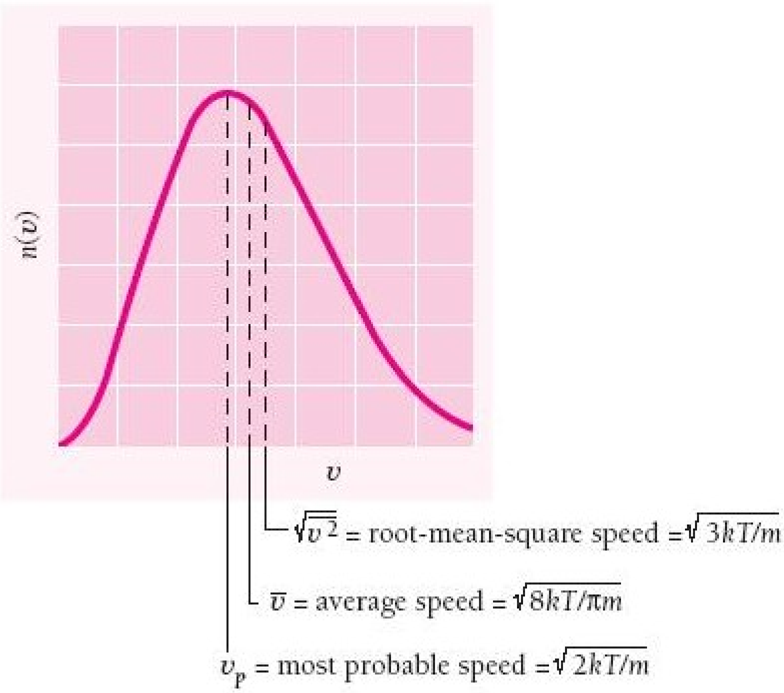
(Proof) $\overline{E}=\frac{3kT}{2}=\frac{m\overline{v^2}}{2}\Rightarrow v_{rms}=\sqrt{\overline{v^2}}=\sqrt{\frac{3kT}{m}}$

Average velocity: $\overline{v}=\sqrt{\frac{8kT}{\pi m}}$

(Proof) $E=mv^2/2$, $dE=mvdv$, $n(v)dv=\frac{\sqrt{2}\pi Nm^{3/2}}{(\pi kT)^{3/2}}v^2e^{-\frac{mv^2}{2kT}}dv\Rightarrow \overline{v}=\frac{\int_0^\infty vn(v)dv}{N}=\sqrt{\frac{8kT}{\pi m}}$

The most probable velocity: $v_p=\sqrt{\frac{2kT}{m}}$

(Proof) $dn(v)=0\Rightarrow v_p=\sqrt{\frac{2kT}{m}}$



Maxwell-Boltzmann speed distribution.

And we have $v_{rms}>\overline{v}>v_p$

7-2 Bose-Einstein Distribution Function $f_{BE}(E)=\frac{1}{e^{\alpha}e^{\frac{E}{kT}}-1}=\frac{1}{Be^{\frac{E}{kT}}-1}$

For **identical** and **indistinguishable** particles (bosons) that **do not obey Pauli's exclusion principle**, the probability that a boson occupies a state of energy E is

$$f_{BE}(E)=\frac{1}{e^{\alpha}e^{\frac{E}{kT}}-1}=\frac{1}{Be^{\frac{E}{kT}}-1}$$

Bose-Einstein distribution is suitable to analyze the effects such as **photons** in a cavity, **phonons** in a solid, **liquid He** at the low temperatures, etc.

(1) Consider a system of **distinguishable** particles 1 and 2, one of which is in state a and the other in state b.

If $a\neq b$, $\Psi_I=\Psi_a(1)\Psi_b(2)\neq\Psi_a(2)\Psi_b(1)=\Psi_{II}$; else if $a=b$, $\Psi_I=\Psi_a(1)\Psi_b(2)=\Psi_a(2)\Psi_b(1)=\Psi_{II}$

(2) Consider a system of **bosons** 1 and 2, one of which is in state a and the other in state b. Its wavefunction is $\Psi_B=[\Psi_a(1)\Psi_b(2)+\Psi_a(2)\Psi_b(1)]/\sqrt{2}$: symmetric

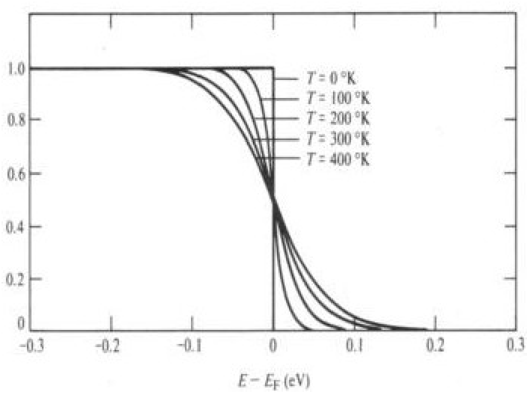
If $a=b$, $|\Psi_B|^2=2|\Psi_a(1)\Psi_a(2)|^2>|\Psi_a(1)\Psi_a(2)|^2=|\Psi_I|^2$ or $|\Psi_{II}|^2$ if $a=b$

$\therefore$ The probability that two bosons are in the same state is twice what it is for distinguishable particles.

(3) Consider a system of **fermions** 1 and 2, one of which is in state a and the other in state b. Its wavefunction is $\Psi_F=[\Psi_a(1)\Psi_b(2)-\Psi_a(2)\Psi_b(1)]/\sqrt{2}$: antisymmetric.

If $a=b$, $|\Psi_F|^2=0$. It obeys Pauli's exclusion principle.

7-3 Fermi-Dirac Distribution Function $f_{FD}(E)=\frac{1}{e^{\frac{E-E_F}{kT}}+1}$



For **identical** and **indistinguishable** particles (fermions) that **obey Pauli's exclusion principle**, the probability that a fermion occupies a state of energy E is

$$f_{FD}(E)=\frac{1}{e^{\frac{E-E_F}{kT}}+1}.$$

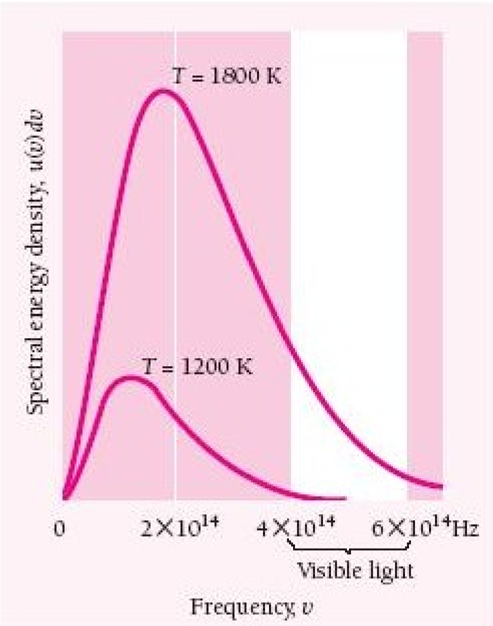
Fermi-Dirac distribution is suitable to analyze the effects of free electrons in metal, electrons in a star whose atoms have collapsed (white dwarf stars), etc.

Fermi energy (level), E_F: $f_{FD}(E_F)=0.5$

Table The Three Statistical Distribution Functions

	Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
Applies to systems of	Identical, distinguishable particles	Identical, indistinguishable particles that do not obey exclusion principle	Identical, indistinguishable particles that obey exclusion principle
Category of particles	Classical	Bosons	Fermions
Properties of particles	Any spin, particles far enough apart so wave functions do not overlap	Spin 0, 1, 2, . . . ; wave functions are symmetric to interchange of particle labels	Spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$; wave functions are antisymmetric to interchange of particle labels
Examples	Molecules of a gas	Photons in a cavity; phonons in a solid; liquid helium at low temperatures	Free electrons in a metal; electrons in a star whose atoms have collapsed (white dwarf stars)
Distribution function (number of particles in each state of energy ϵ at the temperature T)	$f_{MB}(\epsilon) = Ae^{-\epsilon/kT}$	$f_{BE}(\epsilon) = \frac{1}{e^{\alpha}e^{\epsilon/kT} - 1}$	$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1}$
Properties of distribution	No limit to number of particles per state	No limit to number of particles per state; more particles per state than f_{MB} at low energies; approaches f_{MB} at high energies	Never more than 1 particle per state; fewer particles per state than f_{MB} at low energies; approaches f_{MB} at high energies

7-4 Blackbody Radiation



Blackbody: The most efficient absorber of radiation, also the most efficient radiator. In fact, no true blackbody exists. But a hole in the wall of a hollow object is an excellent approximation.

Plank's radiation formula: $u(\nu)d\nu = \frac{8\pi h}{c^3}\cdot\frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$ is the spectral energy density of blackbody radiation.

Total energy density per unit area: $u = \int_0^\infty u(\nu)d\nu = \frac{8\pi^5 k^4}{15c^3h^3}T^4$

Stefan-Boltzmann law: $R = e\sigma T^4$, where $0 < e \leqq 1$ and $\sigma = 5.67\times10^{-8}\ W/m^2 °K^4$

Eg. At what rate does radiation escape from a hole 1cm^2 in area in the wall of a furnace whose interior is at 700°C?

(Sol.) $700°C = 973°K$, $R = 5.67\times10^{-8}\times973^4 = 50819.97\, W/m^2$

Power$=50819.97\times10^{-4}=5.081\,W$

Eg. How many photons are present in 1cm^3 of radiation in thermal equilibrium at 1000°K? What is their average energy?

(Sol.) $N = V\int_0^\infty n(\nu)d\nu = \int_0^\infty \frac{u(\nu)d\nu}{h\nu} = 2.03\times10^{10}$ photons

$\overline{E} = \int_0^\infty u(\nu)d\nu \,/\, n(\nu)d\nu = \sigma T^4/(N/V) = 3.73\times10^{-20}J = 0.233\text{eV}$

Wien's displacement law: $\lambda_{max}T = 2.898\times10^{-3}m°K$

(Proof) $du(\nu)=0 \Rightarrow du(\lambda)=0 \Rightarrow \frac{hc}{kT\lambda_{max}} = 4.965 \Rightarrow \lambda_{max}T = 2.898\times10^{-3}m°K$

Eg. The temperature of the surface of a blue star is higher than that of a red star because $\lambda_{blue} < \lambda_{red}$.

Rayleigh-Jeans formula: $u(\nu)d\nu == \frac{8\pi\nu^2 kTd\nu}{c^3}$

(Proof) When ν is very small, $e^{h\nu/kT} \approx 1 + h\nu/kT$,

$\Rightarrow u(\nu)d\nu = \frac{8\pi h}{c^3}\cdot\frac{\nu^3 d\nu}{e^{h\nu/kT}-1} \approx \frac{8\pi h}{c^3}\cdot\frac{kT\nu^3 d\nu}{h\nu} = \frac{8\pi\nu^2 kTd\nu}{c^3}$

7-5 Specific Heats of Solids

Einstein's specific heat formula: $C_v=\left(\frac{\partial E}{\partial T}\right)_V=3R\left(\frac{h\nu}{kT}\right)^2\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}$ at constant volume, where $R=N_0k=8.31\times10^3 J/Kmol\cdot{}^\circ K=1.99 Kcal/Kmol\cdot{}^\circ K$

Modern theory of specific heat of electron gas in a metal:

Define $j=2L/\lambda=2Lp/h=\frac{2L\sqrt{2mE}}{h}$, and then the number of electron states is $g(j)dj=\pi j^2dj=\frac{8\sqrt{2}\pi L^3m^{3/2}}{h^3}\sqrt{E}dE=g(E)dE$. ∴ The total number of electrons is

$$N=\int_0^{E_f}g(E)dE=\frac{16\sqrt{2}\pi Vm^{3/2}}{3h^3}E_F^{\ 3/2}\Rightarrow E_F=\frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}\propto V^{-2/3}$$

$f_{FD}(E)=\frac{1}{e^{\frac{E-E_F}{kT}}+1}$ and $n(E)dE=g(E)f_{FD}(E)dE=\frac{8\sqrt{2}\pi Vm^{3/2}\sqrt{E}dE}{h^3(e^{\frac{E-E_F}{kT}}+1)}=\frac{3NE_F^{\ -3/2}\sqrt{E}dE}{2(e^{\frac{E-E_F}{kT}}+1)}$

At $T=0^\circ K$, the average energy $\overline{E}=\int_0^{E_F}En(E)dE=3E_F/5$

A detailed calculation shows that the specific heat of electron gas in a metal is $C_{ve}=\frac{\pi^2}{2}\left(\frac{kT}{E_F}\right)R$, where E_F is dependent on materials.

Eg. The Fermi energy of silver is 5.51eV. (a) What is the average energy of the free electrons in silver at 0°K. (b) What is the velocity of electron with this energy?

(Sol.) (a) $\overline{E}=3E_F/5=3.3eV$

(b) Suppose $v<<c$, $\frac{9.11\times10^{-31}v^2}{2}=3.3\times1.61\times10^{-19}\Rightarrow v=1.0766\times10^6 m/\text{sec}$

Eg. Find the Fermi energy of copper. The density of copper is $8.94\times10^3 Kg/m^3$ and its mass is 63.5*u*.

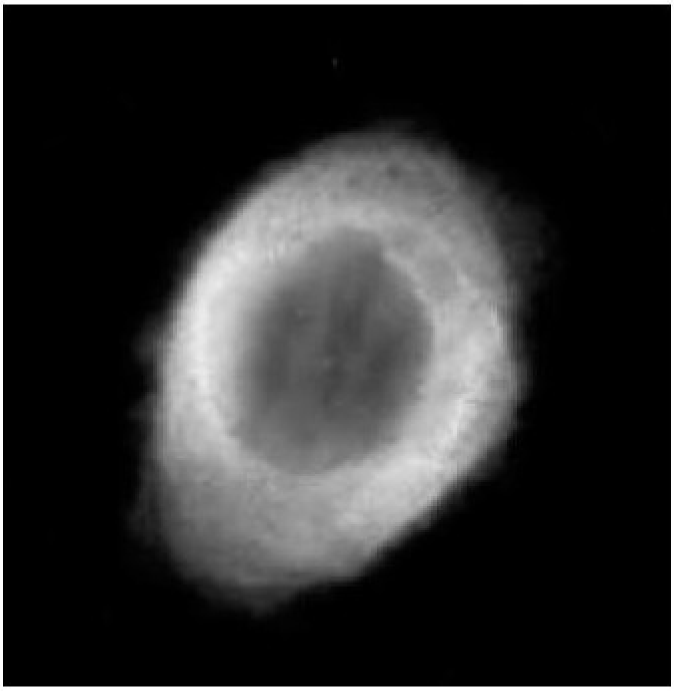
(Sol.) $N/V=8.94\times10^3/63.5\times1.66\times10^{-27}=8.48\times10^{28}\text{electrons}/m^3$

$$E_F=\frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}=1.13\times10^{-18}J=7.04eV$$

7-6 Dying Stars and the Chandrasekhar Limit

White dwarf star: After a star with original mass<8M_{sun} run out of fuel, it becomes unstable. It swells to become a red giant, and eventually throws off its outer layer. The remaining core then cools and contracts gravitationally until its atoms collapse into nuclei and electrons packed closely together. $\because$ $E_F \propto V^{-2/3}$, $\therefore$ E_F increases as the volume decreases. When $E_F > kT$, the electron form a degenerate gas. And only electrons with the highest energies can radiate by falling into the empty lower energy states. As the states lower than E_F is filled, the star becomes dimmer and dimmer. After a few billion years, a white dwarf ceases to radiate and becomes a black dwarf. And the energies of its electrons are forever locked up below the Fermi level.

The size of a white dwarf is determined by a balance between the inward gravitational pull of its atomic nuclei and the pressure of its degenerate electron gas. A typical volume of a white dwarf which has a mass of the two-thirds of the sun is about the size of the earth.

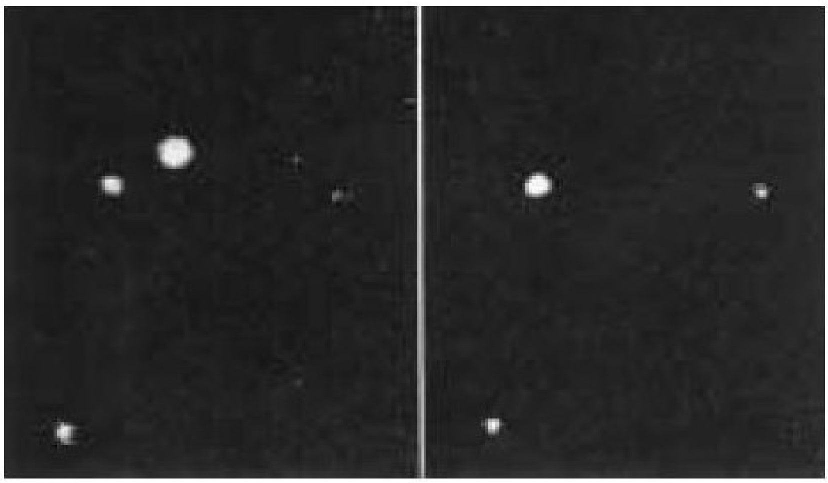


The Ring nebula in the constellation Lyra is a shell of gas moving outward from the star at its center, which is in the process of becoming a white dwarf.

Neutron star (Pulsar): After a heavier star with original mass>8M_{sun} run out of fuel, it collapses abruptly, and then to explode violently (**Supernova**). If the remnant of its mass>1.4M_{sun} but <3M_{sun}, the star contracts gravitationally and its electrons become more and more energetic. When $E_F \approx 1.1 MeV$ and the average electron energy is 0.8 MeV, an electron will react with a proton to produce a neutron. A typical radius of neutron star is about 10-15Km.

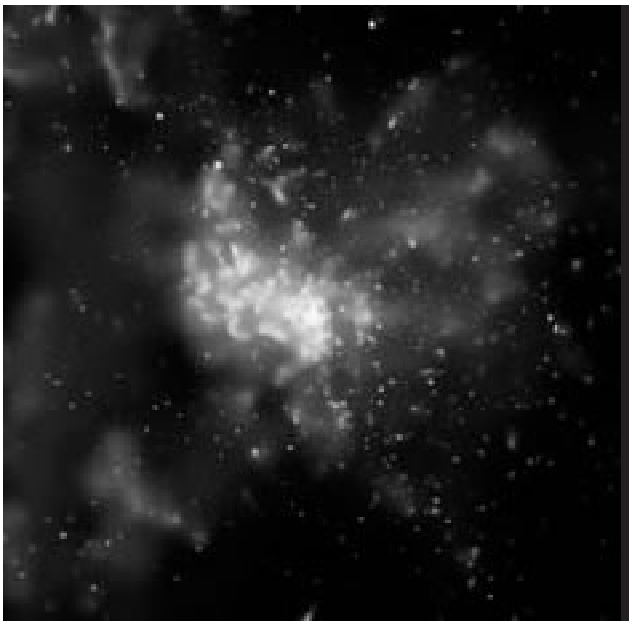
The Crab Nebula is the result of a supernova explosion that was observed in A.D. 1054. The explosion left behind a star believed to consist entirely of neutrons. Statistical mechanics is needed to understand the properties of neutron stars.

The magnetic field of a pulsar traps tails of ionized gas that radiate lights, radio waves, and X-rays. If the magnetic axis of a neutron star is not aligned with the rotational axis, an observer on the earth will receive bursts of radiation as pulsar spin.



The pulsar at the center of the Crab nebula flashes 30 times per second and is throught to be a rotating neutron star. These photographs were taken at maximum and minimum emission. The nebula itself is shown in the photograph at the start of this chapter; it is now about 10 light-years across and is still expanding.

Black hole: If the remnant of the mass of a dying star>~$3M_{sun}$, It becomes a black hole. A black hole does not seem to end up as a point in a space because of the uncertainty principle, $\triangle p \cdot \triangle x \geqq \hbar/2$.



The Chandrasekhar limit: The maximum white dwarf mass is $1.4M_{sun}$. Two observations: (1) Both the internal energy of a white dwarf and its gravitational potential energy vary with $1/R$, where R is its radius. (2) The internal energy of a white dwarf is proportional to M, but its gravitational potential energy is proportional to M^2.