

Thermodynamics and statistical mechanics

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown (for the special attention of those who are skeptics on principle). Albert Einstein

Ludwig Boltzmann, who spend much of his life studying statistical mechanics, dies in 1906 by his own hand. Paul Ehrenfest, carrying on his work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously. D.L. Goodstein, States of Matter, Dover Press, 1985)

J. Willard Gibbs, Elementary Principles in Statistical Mechanics developed with especial reference to the rational foundation of thermodynamics,
New York: Charles Scribner's Sons, London: Edward Arnold, 1902

From the preface:

The usual point of view in the study of mechanics is that where the attention is mainly directed to the changes which take place in the course of time in a given system. The principle problem is the determination of the condition of the system with respect to configuration and velocities at any required time, when its condition in these respects has been given for some one time, and the fundamental equations are those which express the changes continually taking place in the system. Inquiries of this kind are often simplified by taking into consideration conditions of the system other than those through which it actually passes or is supposed to pass, but our attention is not usually carried beyond conditions differing infinitesimally from those which are regarded as actual.

For some purposes, however, it is desirable to take a broader view of the subject. We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and

velocities at any required time, when the distribution has been given for some other time. The fundamental equation for this inquiry is that which gives the rate of change of the number of systems which fall within any infinitesimal limits of configuration and velocity.

Such inquiries have been called by Maxwell statistical. ...The laws of thermodynamics, as empirically determined, express the appropriate and probable behavior of systems of a great number of particles, or more precisely, they express the **laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probably results.** The laws of statistical mechanics apply to conservative systems of any number of degrees of freedom, and are exact....

The laws of thermodynamic may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression, ..

1. What thermodynamics is and historic overview

Deals with “bulk” properties of matter and the processes by which these properties are changed, bulk is a system that is large enough that certain fluctuations can be “treated statistically-mathematically”

Two primary divisions, statistical mechanics (frequently called statistical physics interchangeable) & macroscopic thermodynamics

There is a part of thermodynamics that predated statistical physics – statistical physics delivered the mathematical structure – underpinning, rational basis so to speak - with extending the range of thermodynamics to basically all physical phenomena

up to about 1850, classic (Newtonian) mechanical viewpoint, whole universe is a Perfect Machine that runs by strict unvarying deterministic law

Lagrange 1790 and Hamilton 1840 added computational power to Newton’s approach

Laplace: It is possible – in principle – to have a perfect knowledge of the universe, one can know – in principle – all the positions, masses and velocities of all particles in the universe, using Newton’s mechanics and all kind of forces that govern all interactions, one can calculate – in principle – the whole past of the universe and the whole future of the universe, cause and effect calculations go both ways

Wait a minute: how about modern physics? $\Delta x \cdot \Delta p_x \geq \hbar/2$

$$\Delta E \cdot \Delta t \geq \hbar/2$$

Einstein always thought quantum mechanics is incomplete, there *must* still be a cause and effect relationship to everything “God does not play dice”, i.e. quantum mechanical uncertainty is not the last word on the matter, Bohr’s reply: “It is not for you Einstein to tell god what to do.”

Quantum mechanics has been made compliant to special relativity by Dirac in 1928, but is still not compliant to general relativity, perhaps superstring theory by Eddin, Hawkin’s “theory of everything”?

One of these two theories “has to go in its present form” either current quantum mechanics or current general relativity, both of them are very likely to survive as approximations to a more general theory

after about 1850, statistical physics and better thermodynamics, driven by industrial revolution, it was necessary to have better steam engines, ... locomotives were running, but nobody really knew how

energy and entropy are central in thermodynamics

Joule 1843, demonstrate the mechanical equivalent of heat, energy of falling weight is transferred to internal energy in water as manifested by an increase of its temperature
Clausius: $S = Q/T$ gas molecules do not all travel at the same speed, there should be certain well defined distribution of speeds

Maxwell: equilibrium (most probable) speed distribution for gas molecules having speeds between v and $v+dv$ at a specific temperature, ... Maxwell relations

Boltzmann: approach to equilibrium problem, how does a gas reach at a specific temperature the most probable speed distribution? Boltzmann constant, $S = k \cdot \ln W$, Boltzmann statistics

Helmholtz, free energy and it's minimization, $F = E - TS$, $dF = -SdT - pdV + \mu dN$

Gibbs, Gibbs free energy = chemical potential - and it's minimization,
 $G = E - TS + pV$, $dG = -SdT + Vdp + \mu dN$

Einstein, 1905, explains Brownian Motion on the atom hypothesis, indicating that atoms are real

Bose & Einstein: Bose & Einstein statistics

Fermi & Dirac: Fermi & Dirac statistics

2. Statistical physics in general following 3rd year Modern Physics texts

2.1. Statistical distributions: Maxwell-Boltzmann statistics: classical particle statistics

2.2. When is Maxwell-Boltzmann statistics applicable / ideal gas

2.3. Quantum statistics (note there are two different versions for fermions and bosons)

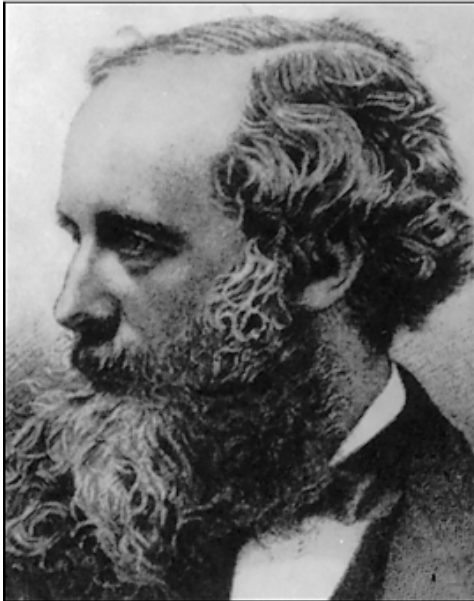
2.4. Application of Bose-Einstein statistics: Blackbody Radiation, Einstein's Theory of Specific Heat

2.5. Application of Fermi-Dirac statistics: Free electron theory of metals

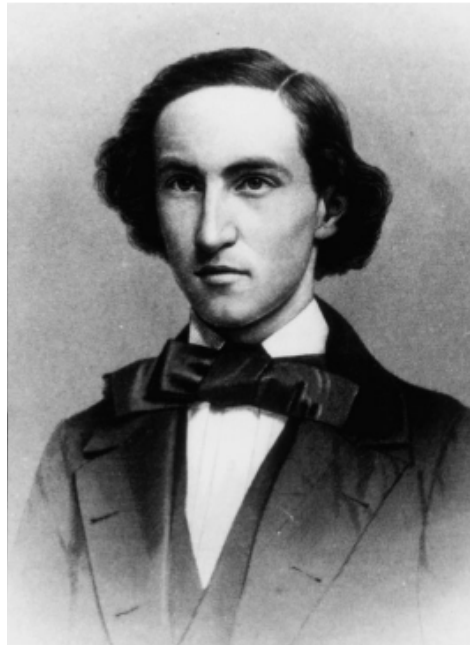


An Austrian, i.e. quasi German professor in Berkeley at the turn of the century, sticking to his guns !!!

2.1. Statistical distributions: - Maxwell-Boltzmann statistics, classical particle statistics



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Ludwig Boltzmann (1844-1908)

Josiah Willard Gibbs (1839-1903)

James Clerk Maxwell (1831-1879)

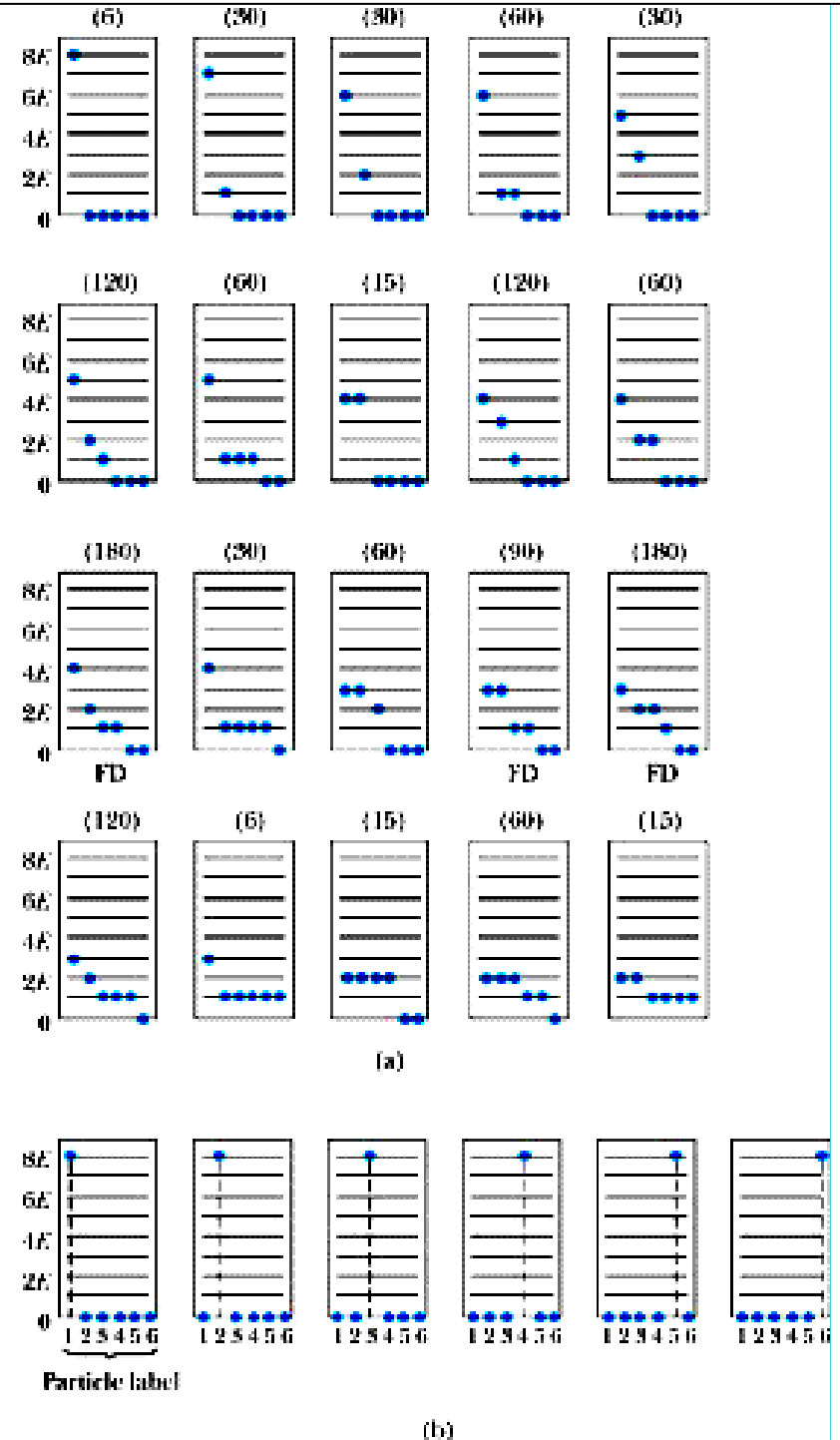
Underlying assumptions of Maxwell-Boltzmann statistics

particles are identical in terms of physical properties, but distinguishable in terms of position, path, or trajectory – i.e. classical physics particles, e.g. an ideal gas

- this is equivalent to saying the particle size is small with respect to the average distance between particles

equilibrium distribution is most probable way of distributing particles among the various allowed energy states subject to constraints of fixed particle number

Figure 10.1 (a) The 20 arrangements (states of a system) of six *indistinguishable* particles with a total energy of $8E$. (b) The decomposition of the upper left-hand arrangement of part (a) into six distinguishable states for *distinguishable* particles.



statistical approach – small system for overview

say total energy is 8E distributed between six particles, 1 E is the smallest unit of energy – indivisible unit, we are not dealing with quantum mechanics, so particles can have zero energy

each arrangement of energies of six particles is called a state, each state has a certain number of microstates, e.g. 6 microstates for one particle at 8 E and five at 0E (top left corner Fig. 10.1

GOAL: want to know probability of finding a particle with a given energy

$$\text{Number of microstates } N_{MB} = \frac{N!}{n_1!n_2!n_3!\dots}$$

N total number of states, n_i number of particles in occupied states

$6! / 5! 1! = 6$ microstates as shown in Fig. 10.1 b (bottom row)

total of 1287 states, 20 states with certain number of microstates

Basic postulate of statistical mechanics: any individual microstate is as likely as any other individual microstate (just as in a lottery)

Sum the number of particles with that energy in each of the states above, weighted by the probability of realizing that state (arrangement)

Total of 1287 microstates, 6 distinguishable microstates for state #1

Probability of finding system in this state is $6/1287$

to calculate average number of particles with E_0 ,

of such particles in each state time number of microstates divided by total number of microstates all summed up

$5 (6/1287) + 4 (30/1287) + 4 (30/1287) + 3 (60/1287) + \dots = 2.307$ (see Serway et al.)

so on average 2.307 particles have energy E_0 , the probability of finding such a particle by reaching randomly into a box with 6 particles is $2.307 / 6 = 0.385$

38.5 % probability finding a particle with E_0

25.6 % probability finding a particle with E_1

16.7 % probability finding a particle with E_2

9.78 % probability finding a particle with E_3

5.43 % probability finding a particle with E_4

2.72 % probability finding a particle with E_5

1.17 % probability finding a particle with E_6

0.388 % probability finding a particle with E_7

0.0777 % probability finding a particle with E_8

let's plot that distribution – close to exponential decrease

so now you get an inkling that playing the lottery may give you a good feeling, but incredibly high odds are against you

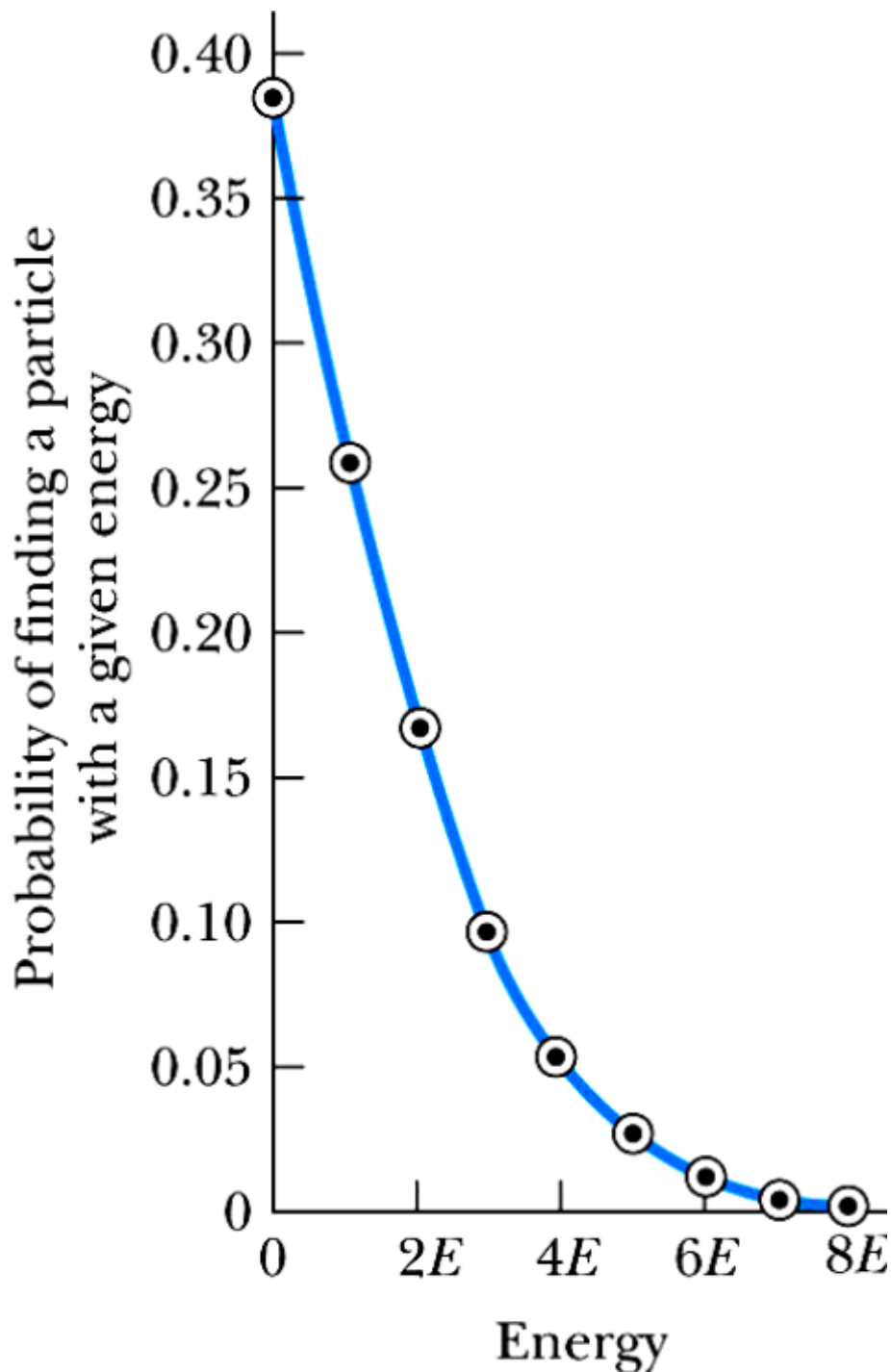
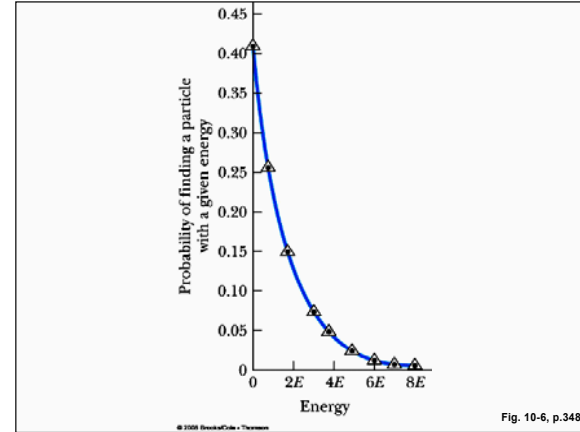


Figure 10.2 The distribution function for an assembly of six distinguishable particles with a total energy of $8E$. (looks similar to energy distribution of undistinguishable bosons who also can all be in one state, Bose-Einstein condensate)



$$f_{MB} = Ae^{-E/k_B T}$$

Maxwell-Boltzmann distribution (for classical particles)

probability of finding a particle with energy E_i , or probability that a state with energy E_i is occupied at the absolute temperature T

for E_0 in example above it would just be 0.385

number of states with same energy E_0 is called degeneracy or statistical weight. g_i

number of particles n_i with energy E_i is just statistical weight times probability that the state E_i is occupied

$$n_i = g_i f_{MB} = 0.385 \text{ times } 6 \text{ for EO particles} = 2/307$$

A is a normalization constant – determined by requirement that total number of particles (N) in system is constant

$$\text{If bosons } n_i = g_i f_{BE} \qquad \text{If fermions } n_i = g_i f_{FD}$$

For large number of particles and available energy states smooth

functions $n_i(E) = g_i(E) f_{MB}(E, T)$ where $g_i(E)$ is called density of states or the number of energy states per unit volume in the energy interval $E+dE$

Maxwell's speed distribution for an ideal gas

Good classical system, ideal gas of point particles (no internal structure and no interaction between particles)

Maxwell's equilibrium speed distribution for ideal gas, or number of molecules with speeds between v and $v + dv$

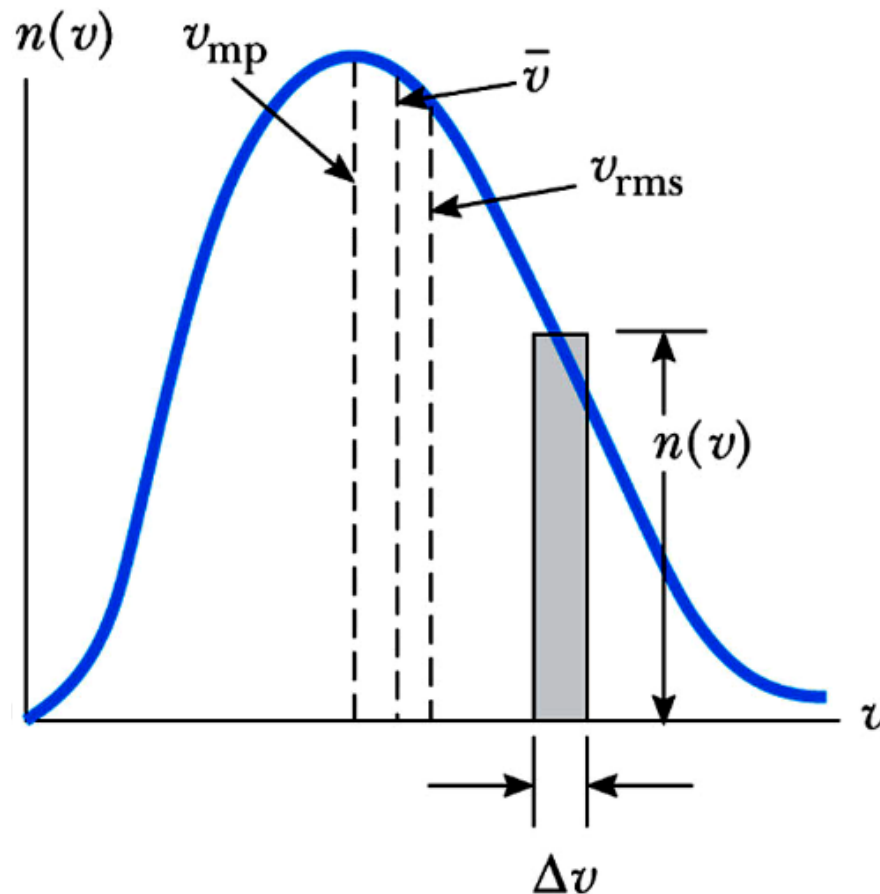


Figure 10.4. The speed distribution of gas molecules at some temperature. The number of molecules in the range Δv is equal to the area of the shaded rectangle, $n(v) \Delta v$. The most probable speed, v_{mp} , the average speed, \bar{v} , and the root mean square speed, v_{rms} , are indicated.

Maxwell's molecular energy distribution

one can derive

$$E = \frac{3}{2} NkT = \frac{3}{2} RT$$

$$\frac{E}{N} = \frac{3}{2} kT = \text{average molecular energy}$$

an ideal gas particle (i.e. classical particle that does not interact with anything) has 3 degrees of freedom, so in each one of these degrees of freedom there is just

$$\frac{1}{2} kT$$

equipartition theorem

The average energy per degree of freedom of any classical object that is a member of a system of such objects in thermal (thermodynamic) equilibrium at the absolute

temperature T is $\frac{1}{2} kT$ this is a general classical physics result !

Degrees of freedom are not limited to linear velocity components – each variable that appears squared in the formula for the energy of a particular object represents a degree of freedom – just like

$$\frac{1}{2}m\bar{v}_x^2 = \frac{1}{2}m\bar{v}_y^2 = \frac{1}{2}m\bar{v}_z^2 = \frac{1}{2}I_x\bar{\omega}_x^2 = \frac{1}{2}K(\Delta x)^2 = \frac{1}{2}kT$$

ω angular velocity, I angular momentum for a rotation

K force constant, Δx displacement in an harmonic oscillation

So a one dimensional harmonic oscillator has

$$E = \frac{1}{2}m\bar{v}_x^2 + \frac{1}{2}K(\Delta x)^2 = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

even better, equipartition theorem is even valid for non-mechanical systems such as thermal fluctuations in electrical circuits

2.2. Application of Maxwell-Boltzmann statistics: ideal gas

applicable when average distance between particles, d , is large compared with quantum uncertainty in particle position

$$\frac{\hbar}{2\sqrt{mkT}} \leq \Delta x \ll d$$

then particles are distinguishable, wave properties of particles can be neglected, some algebra

$$\left(\frac{N}{V}\right) \frac{\hbar^3}{8\sqrt{(mkT)^3}} \ll 1$$

i.e. particle concentration (density) is low, particle mass is high (classical particle), temperature is high

Are Maxwell-Boltzmann statistics valid for hydrogen gas at standard temperature and pressure (abbreviated typically STP, 273 K, 1 atmosphere) ?

Under STP 1 mol H₂ gas = $6.02 \cdot 10^{23}$ molecules occupies 22.4 liter dm³

Mass of H₂ molecule $3.34 \cdot 10^{-27}$ kg,

$h = 6.626 \cdot 10^{-34}$ Ws²

$k = 1.381 \cdot 10^{-23}$ J/K = $8.617 \cdot 10^{-5}$ eV/K

$$\left(\frac{N}{V}\right) \frac{\hbar^3}{8\sqrt{(mkT)^3}} = 8.83 \cdot 10^{-8} \ll 1 \quad \text{surprise}$$

Are Maxwell-Boltzmann statistics valid for electrons in Silver?

Silver has a density of 10.5 g/cm³ and molar weight 197.9 g. assuming one free electron per silver atom, density of free electrons is

$$\frac{10.5}{197.9} 6.02 \cdot 10^{23} \text{ electrons} / \text{m}^3 = 5.86 \cdot 10^{28} \text{ electrons} / \text{m}^3$$

mass of electron $9.109 \cdot 10^{-31}$ kg

assuming “room temperature” $T = 300$ K then $kT = 4.14 \cdot 10^{-21}$ J ≈ 25 meV

$$\left(\frac{N}{V}\right) \frac{\hbar^3}{8\sqrt{(mkT)^3}} = 4.64$$

so Maxwell-Boltzmann statistic not applicable

two reasons, small mass of electron, density of electrons in silver about 2000 times higher than density of H₂ at STP

electrons are fermions, so Fermi-Dirac statistics is applicable

OK quantum mechanical “wavicals” at high density and low temperature are non classical

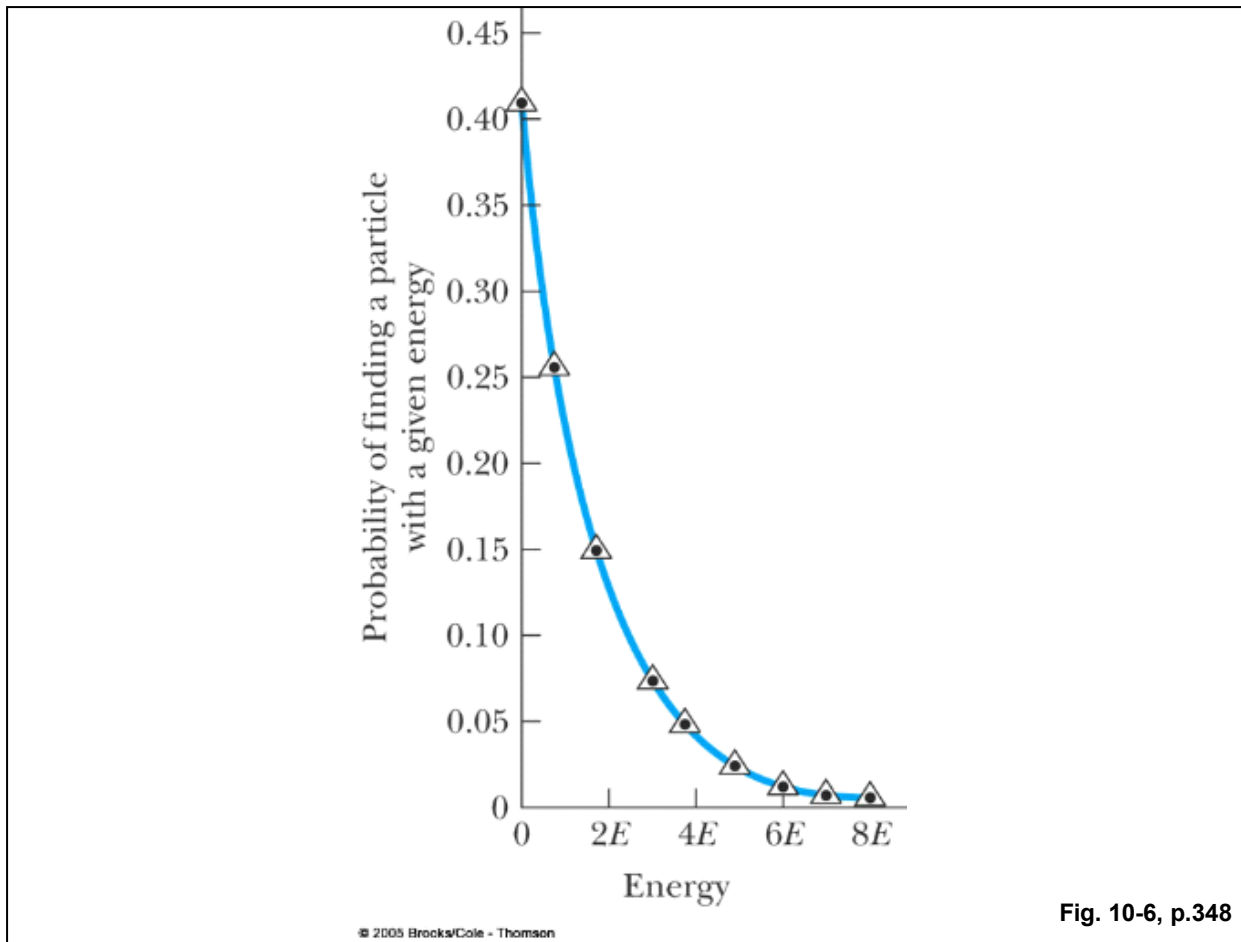


Fig. 10-6, p.348

Figure 10.6: The distribution function for six indistinguishable particles with total energy $8E$ (bosons). Looks “similar” to Maxwell-Boltzmann distribution function

Important bosons: photons – (coupling electromagnetic force between charges), phonons – the wavical of a sound wave in a solid, a quasi-particle that does not exist outside of the solid, α -particle and He atom

$$f_{BE} = (Be^{E/k_B T} - 1)^{-1} \quad \text{but} \quad f_{MB} = Ae^{-E/k_B T}$$

B = 1 for photons and phonons

for Bose-Einstein distribution function

Since particles are indistinguishable, each of the 20 states are equally likely

To calculate average number of particles with energy $E_0 = 5/20 + 4/20 + 4/20 + 3/20 + \dots = 2.45$

The probability of finding a particle with a given energy $p(E)$ is average number of particles with that E divided by total number of particles = 6

$$p(0E) = 2.45 / 6 = 0.408$$

$$p(1E) = 0.258$$

$$p(2E) = 0.150$$

$$p(3E) = 0.075$$

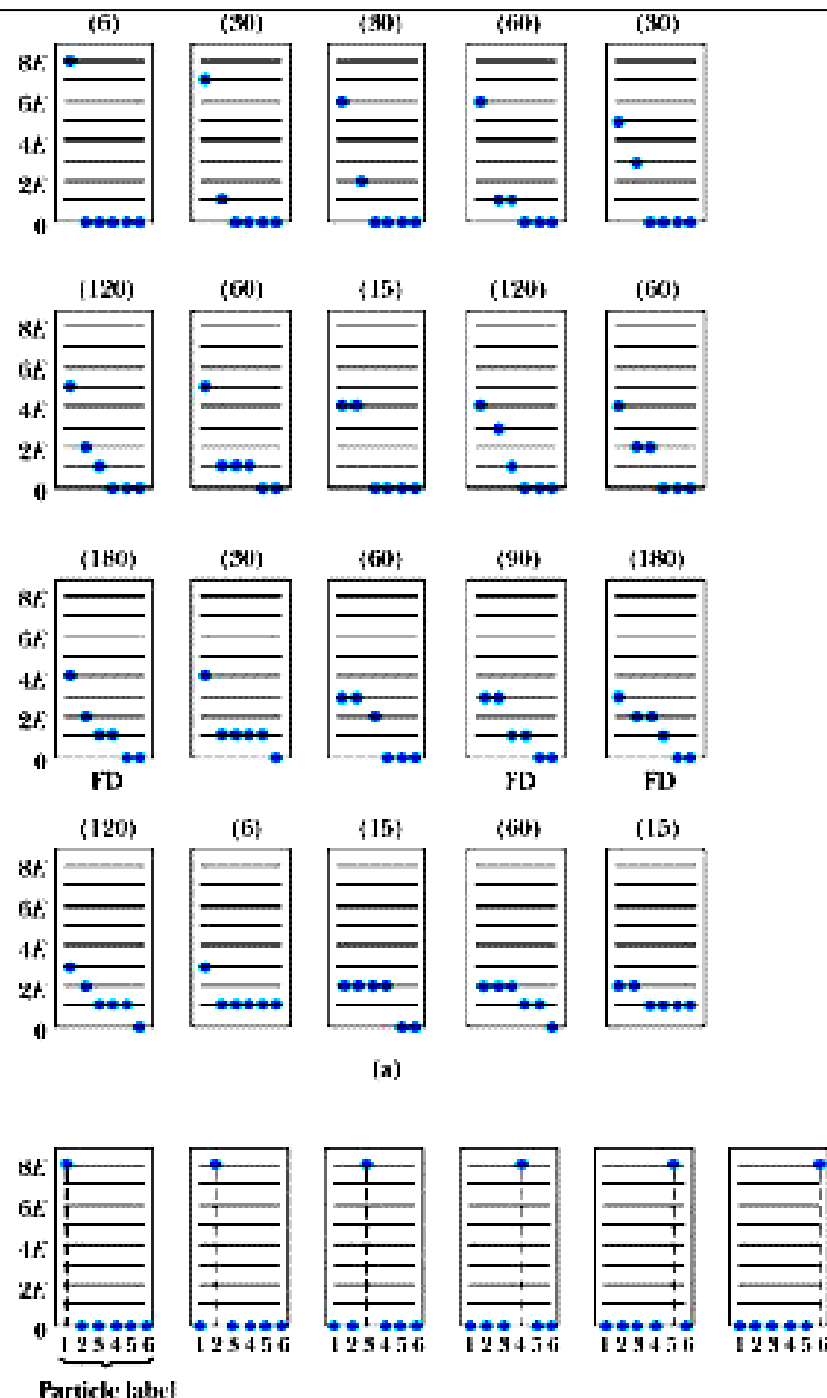
$$p(4E) = 0.050$$

$$p(5E) = 0.025$$

$$p(6E) = 0.0167$$

$$p(7E) \approx 0.00833$$

$$p(8E) \approx 0.00833 \text{ but smaller than } p(7E)$$



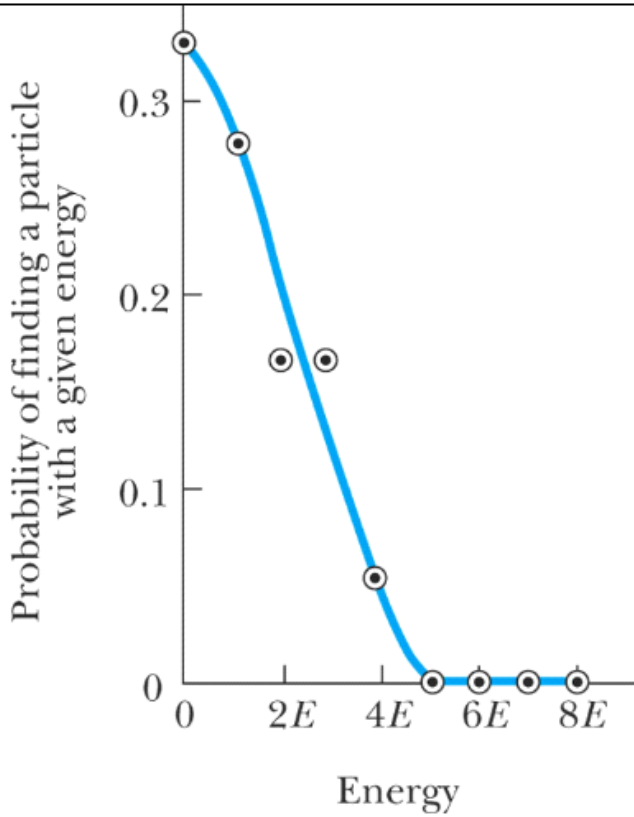


Figure 10.7: The distribution function for six indistinguishable particles with total energy $8E$ constrained so that no more than two particles occupy the same energy state (fermions).

Fermions all non-integer spin particles:
electrons, protons, neutrons, their antiparticles,
most atoms

Distinctly different shape in comparison to MB and BE distribution, there is a second inflection, the Fermi-Dirac distribution function levels off both at high and at low energy values

$$f_{BE} = (Ce^{E/k_B T} + 1)^{-1} \quad \text{but} \quad f_{MB} = Ae^{-E/k_B T}$$

In addition to particles being indistinguishable, there is at most only two in each state, one spin up one spin down, there are only three states that obey this constraint, marked as FD, each of these arrangements is equally likely, each of them has two fermions at E_0 , so average number of particles with energy $E_0 = 2/3 + 2/3 + 2/3 = 2$

The probability of finding a particle with a given energy $p(E)$ is average number of particles with that E divided by total number of particles = 6

Note non of these states has a particle with energies E_5, E_6, E_7 or E_8

$$p(0E) = 2.00 / 6 = 0.333$$

$$p(1E) = 0.278$$

$$p(2E) = 0.167$$

$$p(3E) = 0.167$$

$$p(4E) = 0.055$$

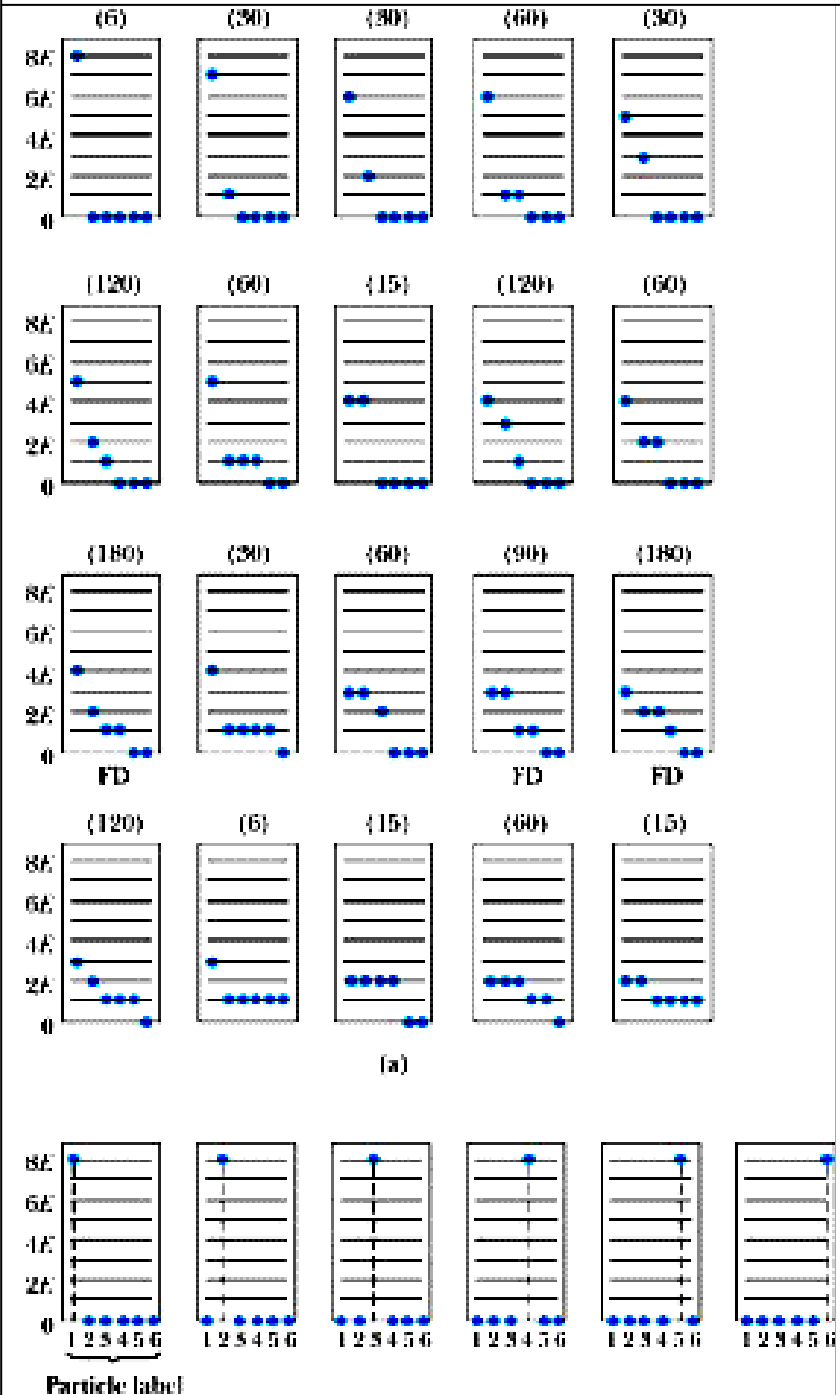
$$p(5E) = 0$$

$$p(6E) = 0$$

$$p(7E) = 0$$

$$p(8E) = 0$$

loosely speaking shells and sub-shells are filled by two fermions with opposite spin, that's it, the result is frequently atoms = matter,



(b)

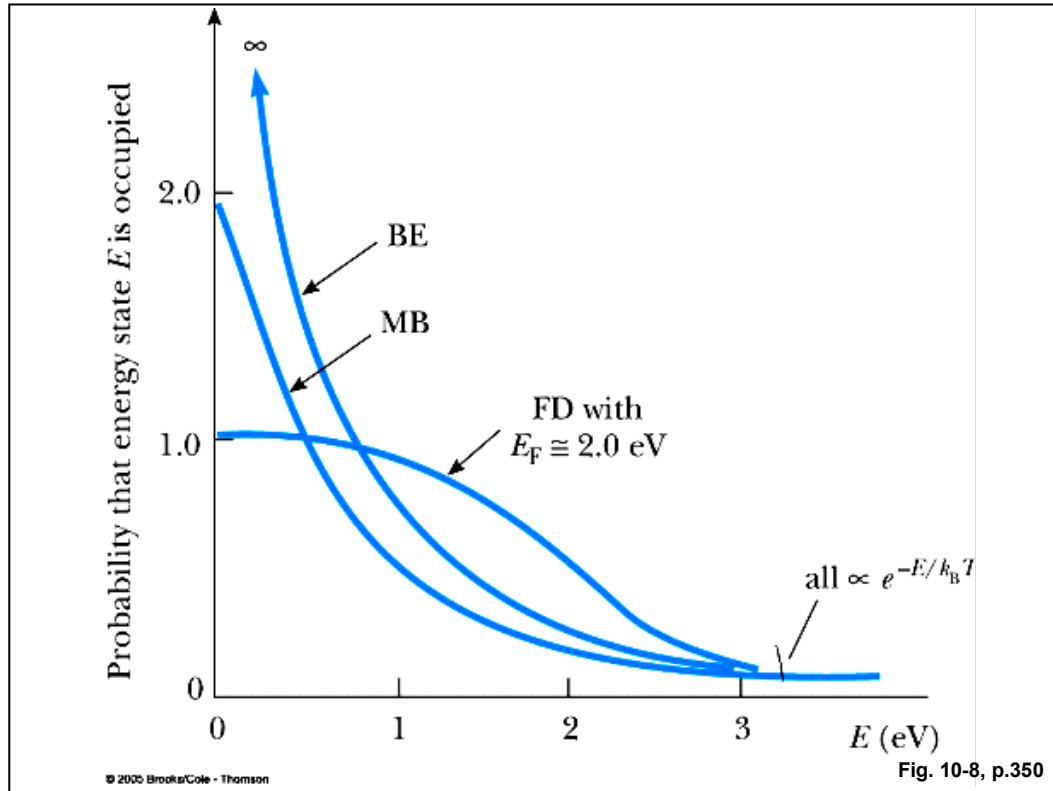


Figure 10.8: A comparison of Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distribution functions at 5000 K. For high energies (and temperatures) the two quantum distribution functions converge to the Maxwell-Boltzmann distribution function (for the same constant pre-factor) BE is always higher than MB, which is always higher than FD

Term -1 in denominator for BE distribution expresses increased likelihood of multiple occupancy of an energy state, at very very low temperatures all wavefunctions overlap and one gets one superwave-function, in a sense the distinct atoms disappear and a superatom is created, predicted by Einstein in 1924, produced by Cornell+Wieman (1995 Nobel prize)

While MB distribution is for a finite number of particles, BE distribution is for an infinite number of particles, bosons such as photons are not conserved, can be created and destroyed

Term +1 in denominator for FD distribution is consequence of Pauli's exclusion principle, for small energies FD approaches 1 (Fig, 10-8 not quite OK in this respect)

For FD distribution, since C depends strongly on temperature, defined by

$$C = e^{-E_F / k_B T} \quad \text{where } E_F \text{ is called Fermi energy}$$

$$f_{FD} = (e^{(E-E_F) / k_B T} + 1)^{-1}$$

$$\text{if } E = E_F \quad e^{(E-E_F) / k_B T} = e^0 = 1$$

this means: the probability of finding an electron with an energy equal to the Fermi energy is exactly 0.5 at any temperature !!!

E_F has a weak dependency on T, that frequently gets neglected

for $T = 0$ all states below the Fermi level (energy) are occupied, all states above the Fermi level are empty

for $T > 0$ some states below the Fermi level are empty some states above the Fermi level are occupied

the higher the T , the more states above the Fermi level are occupied

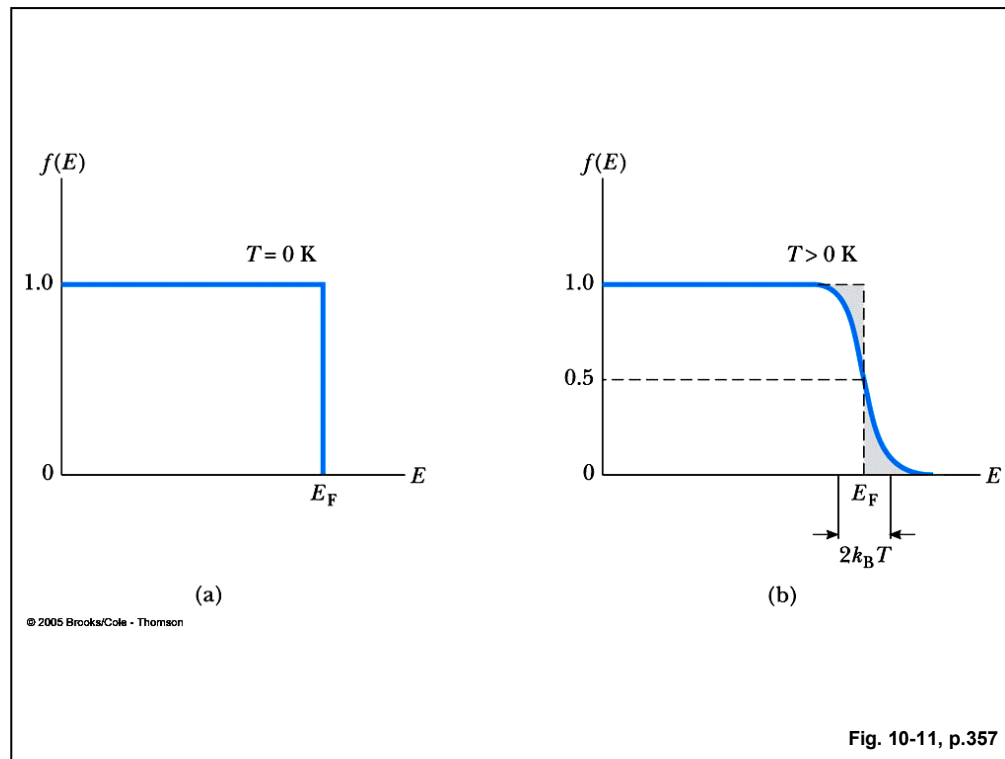
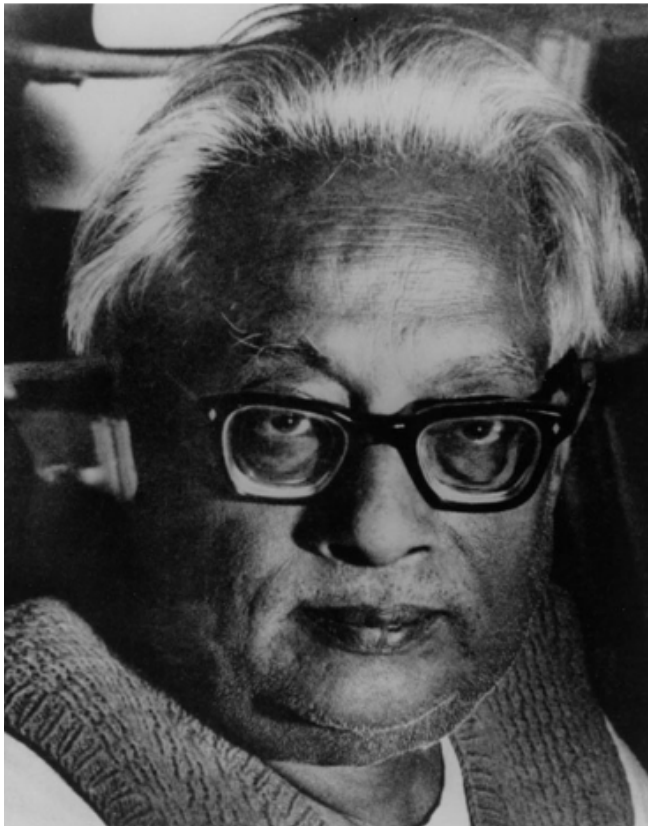
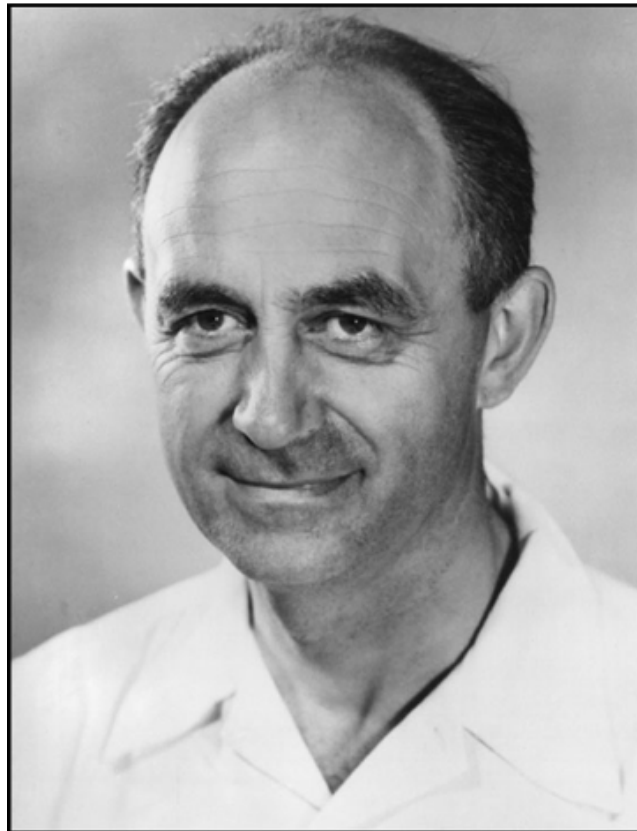


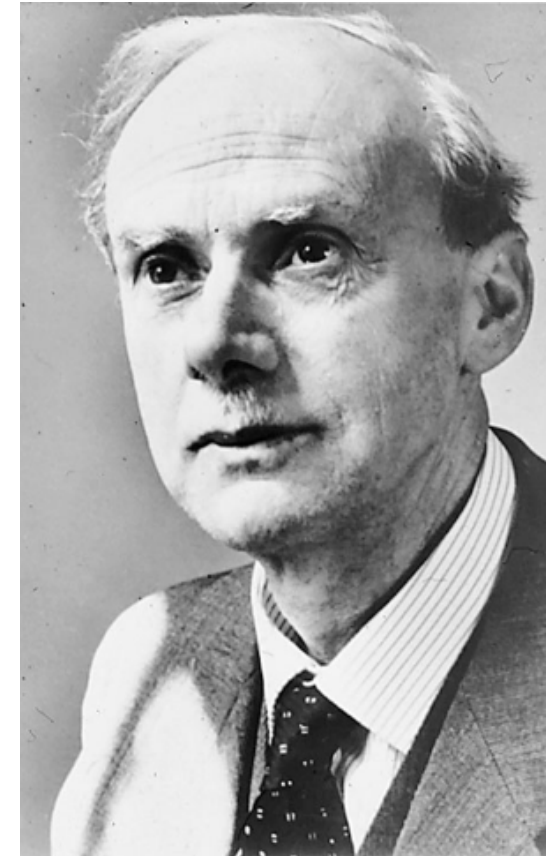
Figure 10.11: A comparison of the Fermi–Dirac distribution functions at (a) absolute zero (b) at some $T > \text{zero Kelvin}$



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Satyendranath Bose (1894-1974)

Enrico Fermi (1901-1954)

Paul Adrien Maurice Dirac (1902-1984)

note that beards and long hair went out of fashion by the time the quantum distribution functions were developed ☺

2.4.1 Application of Bose-Einstein statistics: Blackbody Radiation

energy per unit volume (in the range E to $E + dE$) of electromagnetic radiation in an enclosure heated to T , treating radiation as a gas of photons

first number of photons per unit volume with energy between E and $E + dE$:

$$n(E) dE = g(E) f_{BE}(E) dE \quad \text{constant } B \text{ in } f_{BE} \text{ for photons} = 1$$

$$g(E) \text{ is density of states (degeneracy)} \quad g(E) = \frac{8\pi E^2}{(hc)^3}$$

$$\text{energy density} \quad u(E)dE = En(E)dE = \frac{g(E)EdE}{e^{E/k_B T} - 1}$$

$$u(E)dE = En(E)dE = \frac{8\pi}{(hc)^3} \frac{E^3 dE}{e^{E/k_B T} - 1} \quad \text{converting from photon energy to frequency with } E = hf \text{ we obtain Planks curve fitting result from 1901:}$$

$$u(f, T) = \frac{8\pi}{c^3} \frac{f^3 dE}{e^{hf/k_B T} - 1}$$

total number of photons of all energies (N) per unit volume of a black body, say one cm³, at 300 K (about room temperature)

$$\frac{N}{V} = \int_0^{\infty} n(E) dE = \frac{8\pi (k_B T)^3}{(hc)^3} \int_0^{\infty} \frac{(E/k_B T)^2 (dE/k_B T)}{e^{E/k_B T} - 1}$$

$$\frac{N}{V} = 8\pi \left[\frac{8.62 \cdot 10^{-5} \text{ eV} / \text{K} \cdot 300 \text{ K}}{1.24 \cdot 10^{-4} \text{ eV cm}} \right]^3 \cdot \int_0^{\infty} \frac{z^2 dz}{e^z - 1}$$

$$\frac{N}{V} = 2.28 \cdot 10^{10} \cdot \int_0^{\infty} \frac{z^2 dz}{e^z - 1} = 5.47 \cdot 10^{10} \text{ cm}^{-3}$$

2.4.2 Application of Bose-Einstein statistics: Einstein's Theory of Specific Heat

molar specific heat $C_V = \left(\frac{dU}{dT}\right)_v$ cal = 4.184 J

to calculate internal energy following Boltzmann's ideas, we think of atoms vibrating independently while being connected by springs

use equipartition theorem, count the numbers of degrees of freedom and multiply by $\frac{1}{2} k_B T$

3 dimension, times two degrees of freedom per oscillator (kinetic energy plus potential energy) makes 6 degrees of freedom, so

U for a whole mole = $3 N_A k_B T = 3RT$ with R universal gas constant 1.99 cal/mol K

So $C_v = \left(\frac{dU}{dT}\right)_v = 3R = 5.97 \text{ cal} / \text{mol} \cdot \text{K}$ know as **Dulong-**

Petit law, it's an empirical observation that can be explained by classical statistical physics !!!

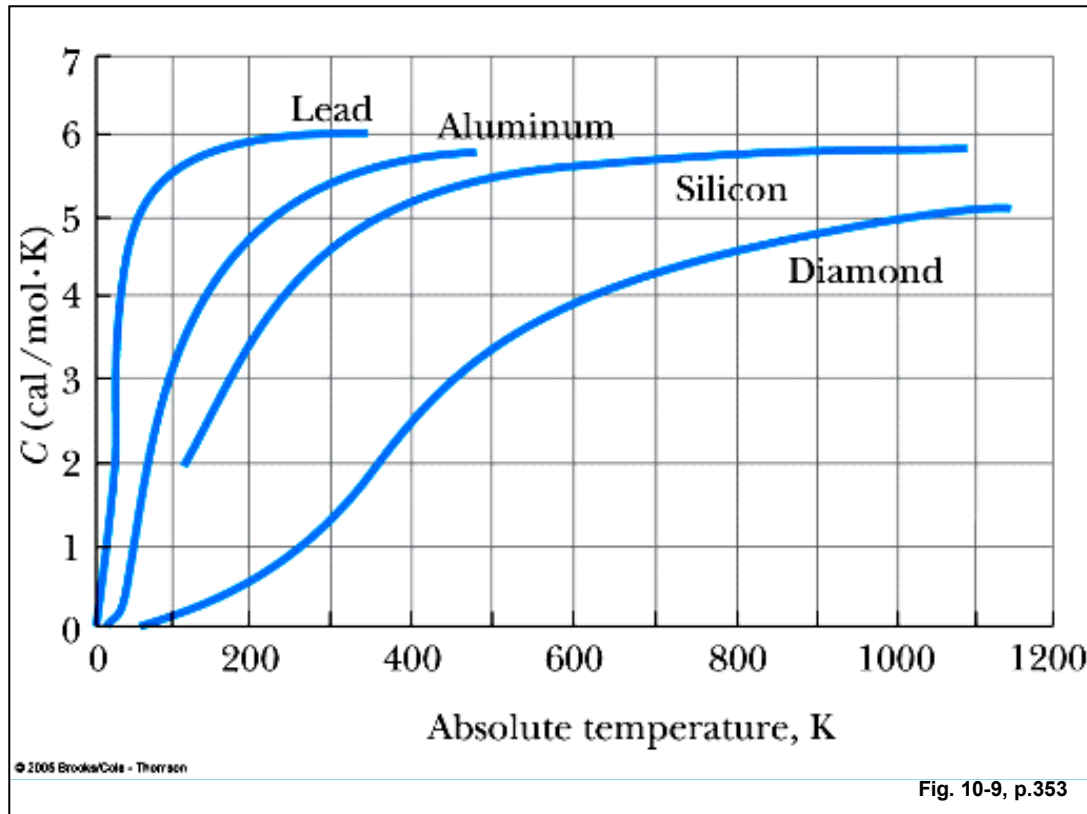


Figure 10.9: empirical observation: dependence of specific heat on temperature for several solid elements.

so again at higher temperature, larger mass, Boltzmann statistics seem to be a good approximation, but what about lower temperatures???

Some values of C_v far 300 K for boron = 3.34 carbon (as diamond) = 1.4 cal / mol K !!!!

Einstein to the rescue, 1907 : quantization of the vibration must be explicitly considered,

vibration is small, so let's treat it as being harmonic

let's take independent (not coupled) 3D quantum harmonic oscillations

Planck's result: quantized energy levels $\Delta E = hf$ apart

average energy of a 1D oscillator
$$\bar{E} = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$U = 3N_A \bar{E} = 3N_A \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$C_v = \left(\frac{dU}{dT}\right)_v = 3R \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \text{ there is one}$$

free parameter ω , which gets chosen to fit the data best

C_v goes to $3R$ for high temperatures, equivalent to high quantum numbers, where $hf \ll k_B T$, where there is imperceptibly small spacing of the energy levels with respect to the thermal energy that is available, Bohr's correspondence principle

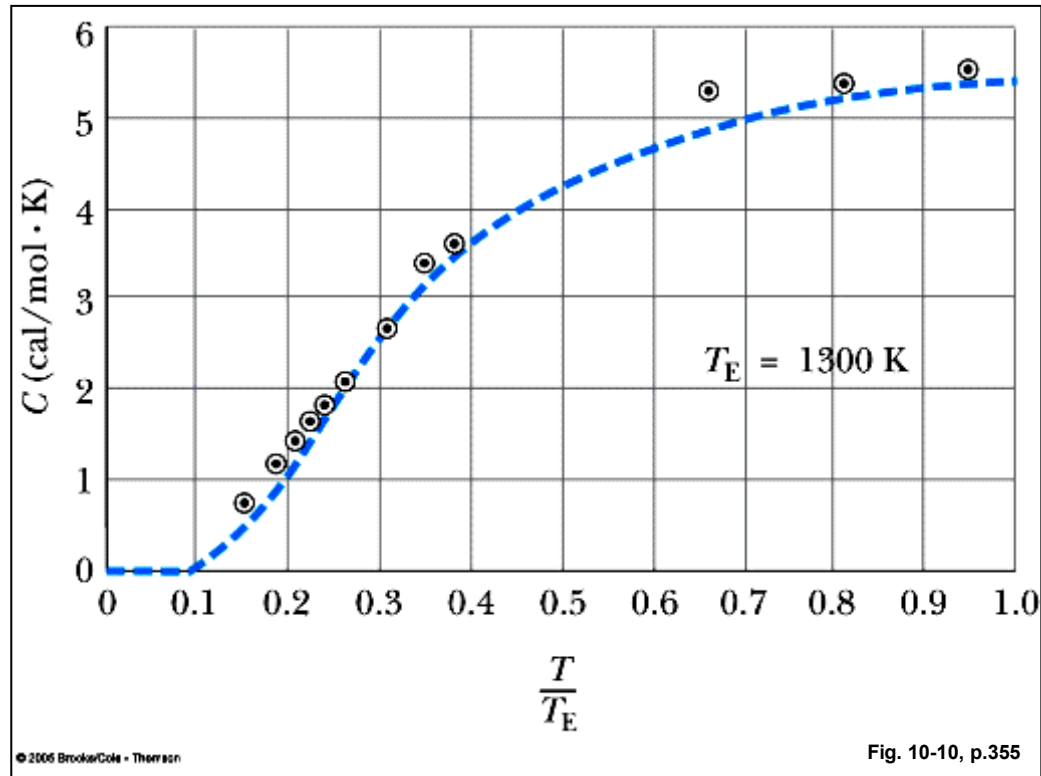


Figure 10.10: Einstein's specific heat formula fitted to Weber's experimental data for diamond. This figure is adapted from A. Einstein, *Ann. Physik.*, 4(22):180, 1907.

$$\hbar\omega = k_B T_E$$

T_E = Einstein temperature

C_v also goes to zero for low temperatures, because then the average thermal energy is equal or smaller than the spacing of the energy levels, the atoms can't absorb energy to vibrate more because there need to be integral multiples of hf to go around

even Einstein's results need sometimes improvements

$C_V \sim T^3$ for low temperatures,

this gets resolved by Peter Debye in 1912 by modeling the solid as a continuous elastic object, where internal energy is due to energy of quantized standing elastic waves (sound waves), now known as phonons, pseudo-particles that travel with the speed of sound and have quantized energy of $h f$

in a metal we have free electrons, let's treat them as a classical monatomic gas, 3 degrees of freedom, so the electron gas for one mole of electrons should contribute $\frac{3}{2} RT$ to the internal energy of a metal,

so really **Dulong-Petit law's law for metals should be $C_V = 4.5 RT$ which is not observed !!** How come the free electrons do not contribute much to C_V ?? They are Fermions, and follow Fermi-Dirac statistics with a very high characteristic temperature that is known as Fermi temperature at which this distribution approached the classical Boltzmann temperature

2.5. Application of Fermi-Dirac statistics: Free electron theory of metals

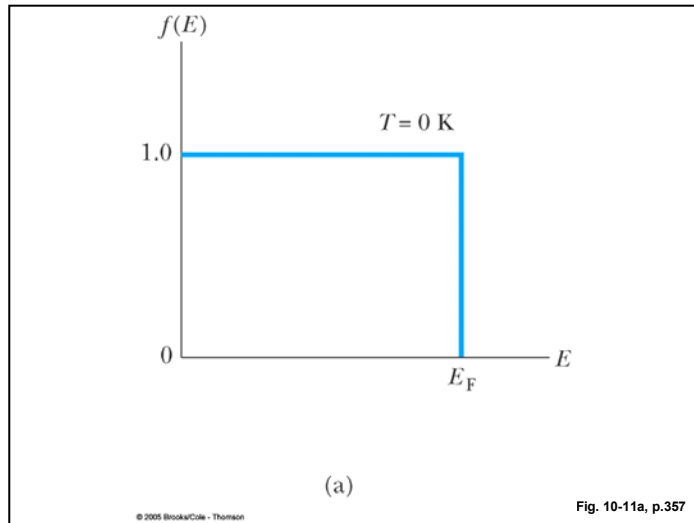


Figure 10.11a: A comparison of the Fermi-Dirac distribution functions at (a) absolute zero

$$f_{FD}(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

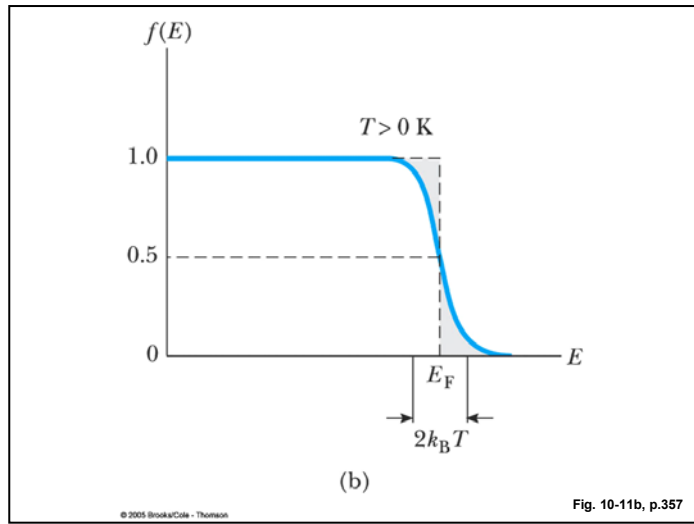


Figure 10.11b: A comparison of the Fermi-Dirac distribution functions at (b) finite temperature.

E_F is only weakly dependent on temperature, effectively independent at room temperature, so this dependency frequently ignored

E_F on the order of magnitude 5 eV, so electrons have kinetic energy up to

$$E_F = \frac{1}{2} m_e v^2$$

resolve for v and you get 10^6 m/s !!!

$n(E) dE = g(E) f_{FD}(E) dE$ density of states $g(E) = \frac{8\sqrt{2}\pi m_e^{1.5} E^{0.5}}{h^3}$

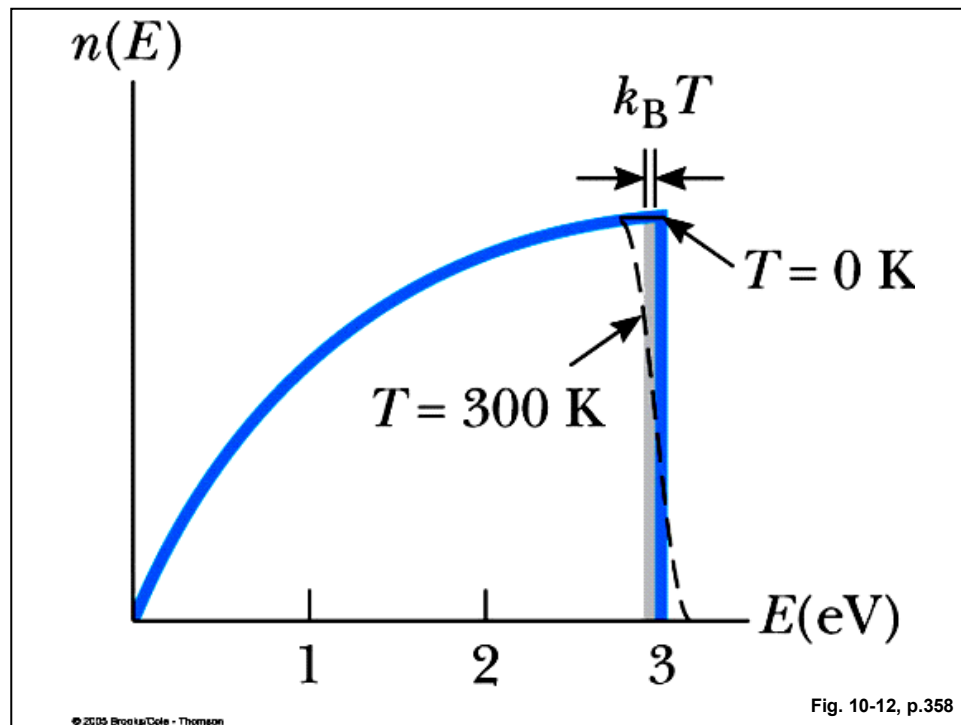


Figure 10.12: The number of electrons per unit volume with energy between E and $E + dE$. **Note that only a small fraction of the electrons (f) became thermally excited and gained $k_B T$!!!** That fraction is roughly the ratio of the area of the gray rectangle to the total area under the $n(E)$ curve !

$$f \approx \frac{3}{2} k_B T / E_F = \frac{3}{2} T / T_F$$

with $T_F =$ Fermi Temperature order of magnitude $5 \cdot 10^4$ K

since only f times N of all electrons gain energy on the order of $k_B T$

the internal energy of one mole of electron gas becomes

$$U_{ele} = \left(\frac{3}{2} \frac{T}{T_F}\right)(N_A k_B T) = \frac{3}{2} \frac{RT^2}{T_F}$$

$$C_{V_{ele}} = \left(\frac{dU_{ele}}{dT}\right) = 3R \frac{T}{T_F}$$

for 300 K and $T_F = 5 \cdot 10^4$ K

$C_{V_{ele}} = 0.018 R$ with is only about 1 % of the classically expected amount of $1.5 R$

Table 10.1 Calculated Values of Various Parameters for Metals Based on the Free Electron Theory

Metal	Electron Concentration (m⁻³)	Fermi Energy (eV)	Fermi Speed (m/s)	Fermi Temperature (K)
Li	4.70×10^{28}	4.72	1.29×10^6	5.48×10^4
Na	2.65×10^{28}	3.23	1.07×10^6	3.75×10^4
K	1.40×10^{28}	2.12	0.86×10^6	2.46×10^4
Cu	8.49×10^{28}	7.05	1.57×10^6	8.12×10^4
Ag	5.85×10^{28}	5.48	1.39×10^6	6.36×10^4
Au	5.90×10^{28}	5.53	1.39×10^6	6.41×10^4

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Table 10-1, p.359