Lecture # 10 Quantum Statistics

Pauli Exclusion applied to conductor electrons in metals.

~ 1 conducting electron / atom

$$\frac{V}{N} \sim (0.2\,nm)^3 \ll (\ell_Q \cong 4.3\,nm)^3$$

$$\varepsilon_F = \frac{(2\pi\hbar c)^2}{8\,mc^2}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

$$\cong \frac{36\,(2000\,eV\,nm)^2}{8\;\;0.5\times10^6\,eV}\left(\frac{1}{0.2\,nm}\right)^2$$

$$\cong \frac{36}{8}\times 2\times 10^{4-6+2} = \frac{36}{4} \cong \underline{10\,eV}$$

ε_F for Cu = 7 eV

Fe = 11.1 eV

so we can approximate T k << ε_F

$$T_F \equiv \frac{\varepsilon_F}{k} \cong \frac{10\,eV}{8.6\times10^{-5}\,eV/K} \cong 10^5\,K$$

hypothetical as metals liquefy and evaporate well below their temperature

rewrite density of state constant with ε_F

$$g(\varepsilon) = \underbrace{(2j+1)}_{=2} C_V \sqrt{\varepsilon}$$

$$C_V = \frac{\pi}{4h^3}(8m)^{3/2} V$$

$$\varepsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

$$\frac{V}{N} = \frac{3}{\pi}\left(\frac{h^2}{8m}\right)^{3/2}\frac{1}{\varepsilon_F^{3/2}}$$

then $$2CV = 2N\left(\frac{\pi}{4h^3}\right)(8m)^{3/2}\frac{3}{\pi}\left(\frac{h^2}{8m}\right)^{3/2}\frac{1}{\varepsilon_F^{3/2}}$$

$$= \frac{3}{2}\frac{N}{\varepsilon_F^{3/2}} \equiv g_0$$

$$g(\varepsilon) = g_0\sqrt{\varepsilon}$$

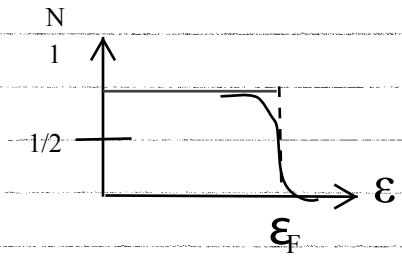
Chemical potential $\mu(T)$ is related to N as

$$N = g_0\int_0^\infty \sqrt{\varepsilon}\,\bar{n}_{FD}\,d\varepsilon$$

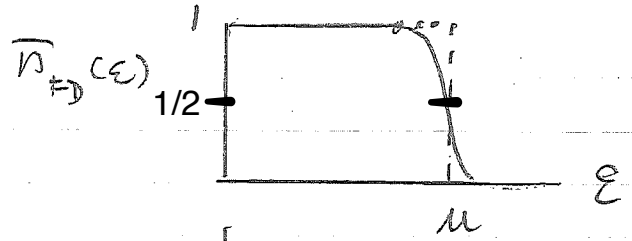
$$\bar{n}_{FD} = \left(e^{\beta(\varepsilon-\mu)}+1\right)^{-1}$$

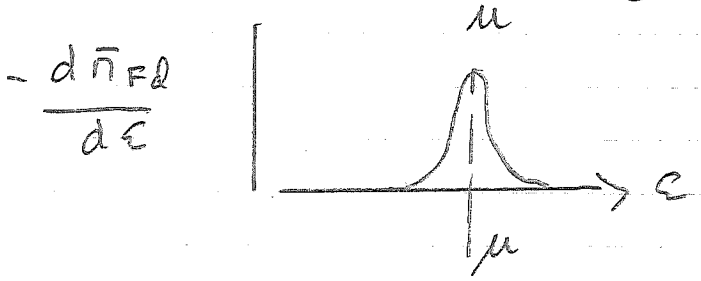
For $kT \ll \varepsilon_F$ (normal temperature)
$\beta\varepsilon_F \gg 1$

$$\boxed{\text{We can approximately solve to get } \mu(T). \text{ Sommerfeld expansion.}}$$



First integrate by parts.





sharply peaked about μ

$$N = \frac{2}{3} g_0 \, \varepsilon^{3/2} \bar{n}_{FD}(\varepsilon) \Big|_0^\infty + \frac{2}{3} g_0 \int_0^\infty \varepsilon^{3/2} \left(-\frac{d\bar{n}_{FD}}{d\varepsilon} \right) d\varepsilon$$

$$\overset{\shortparallel}{0}$$

$$-\frac{d\bar{n}_{FD}}{d\varepsilon} = \beta \frac{e^x}{(e^x+1)^2} \qquad x \equiv \beta(\varepsilon - \mu)$$

solve for ε

change variables from ε to x, then ε(x) and

Taylor expand $\varepsilon^{3/2}(x) = \left(\frac{x}{\beta} + \mu\right)^{3/2}$ about $x=0$

$$\varepsilon^{3/2}(x) \simeq \mu^{3/2} + \frac{3}{2}\frac{1}{\beta}\mu^{1/2} x + \frac{1}{2!}\left(\frac{3}{2}\right)\left(-\frac{1}{2}\right)\frac{1}{\beta^2}\mu^{-1/2} x^2$$

$$= \mu^{3/2} + \frac{3}{2}\frac{1}{\beta}\mu^{1/2} x - \frac{3}{8}\frac{1}{\beta^2}\mu^{-1/2} x^2$$

$$N = \frac{2}{3} g_0 \int_{-\mu\beta}^{\infty} \frac{e^x}{(1+e^x)^2} \varepsilon^{3/2}(x) \, dx$$

note β from dn/dε

extend to $-\infty$ since $-\frac{d\bar{n}_{FD}}{dx}$ is sharply peaked at μ

then x term is odd function of x and integrates to zero.

$$N = \frac{2}{3} g_0 \int_{-\infty}^{\infty} \frac{e^x}{(1+e^x)^2} \left[\mu^{3/2} - \frac{3}{8} \frac{1}{\beta^2} \mu^{-1/2} x^2 \right] dx$$

1st term $\frac{2}{3} g_0 \mu^{3/2} \int_{-\infty}^{\infty} \frac{e^x}{(1+e^x)^2} dx$

$$= \frac{2}{3} g_0 \mu^{3/2} \int_{-\infty}^{\infty} \left(\frac{-d\bar{n}_{FD}}{dx} \right) dx$$

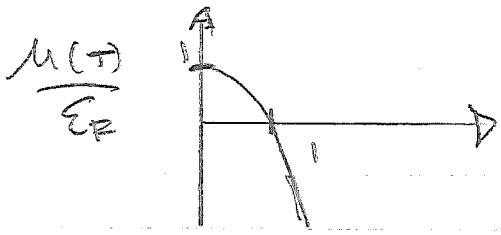
$$= \frac{2}{3} g_0 \mu^{3/2} \left[\underbrace{\bar{n}_{FD}(-\infty)}_{1} - \underbrace{\bar{n}_{FD}(\infty)}_{0} \right]$$

2nd term : $\int_{-\infty}^{\infty} \frac{x^2 e^x}{(1+e^x)^2} dx = \frac{\pi^2}{3}$ (App. B)

giving

$$N = \underbrace{\frac{2}{3} g_0}_{\frac{3}{2}\frac{N}{\varepsilon_F^{3/2}}} \left[\mu^{3/2} - \frac{3}{8} \frac{1}{\beta^2} \mu^{-1/2} \left(\frac{\pi^2}{3} \right) \right]$$

$$\boxed{\begin{aligned} \varepsilon_F^{3/2} &= \mu^{3/2} \left[1 - \frac{\pi^2}{8} \frac{1}{\beta^2} \frac{1}{\mu^2} \right] \\ \mu(\beta) &\simeq \left[1 - \frac{\pi^2}{8} \frac{1}{\beta^2} \frac{1}{\varepsilon_F^2} \right]^{2/3} \varepsilon_F \\ &\qquad \mu \simeq \varepsilon_F \end{aligned}}$$



sketch

$\mu(T)$ drops slightly below ε_F with increasing T

numerically,

$$\frac{\pi^2}{8}\frac{1}{\beta^2}\frac{1}{\varepsilon_F^2}\Bigg| \simeq \left(\frac{1/40\ eV}{10\ eV}\right)^2 = \underline{0.6\times10^{-5}}$$

$\beta = 40\ eV^{-1}$ @ room temp

$\varepsilon_F \approx 10\ eV$

So at normal temperature $\mu \cong \varepsilon_F$ is a very good approximation.

You will show thermal energy (conducting electron)

$$\frac{U}{N} = \frac{3}{5}\varepsilon_F + \frac{\pi^2}{4}\frac{(kT)^2}{\varepsilon_F}$$

increases slightly with temperature

<u>Note</u> $\frac{U}{N} \sim 10\ eV \gg \frac{1}{40}\ eV$

most of e^- energy is from exclusion principle

$\frac{1}{2}mv^2 \simeq 10\ eV$

$\frac{1}{2}\left(\frac{1}{2}\times10^6\ eV\right)\left(\frac{v}{c}\right)^2 = 10\ eV$ $\qquad \frac{v}{c} \approx 0.6\times10^{-2}$

<u>Very fast</u>

but non-relativistic

<u>Photon Gas</u> in equilibrium at temperature T
photons is not conserved. atoms in walls of container constantly absorb/emit photons. So free energy of gas depends on T, V but not N.

Free energy is minimum in equilibrium and fixed T,V

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 = \mu_\gamma \quad \text{chemical potential}$$

also in equilibrium sum of chemical potentials is constant –

$$\text{atom} \leftrightarrow \text{atom} + \gamma$$

$$\mu_{atom} = \mu_{atom} + \mu_\gamma \Rightarrow \mu_\gamma = 0$$

So $\bar{n}_\gamma = \dfrac{1}{e^{\beta\varepsilon}-1}$ where $\varepsilon = hf = \dfrac{hc}{\lambda}$

for each wavelength λ

Total energy of photons is, *photon has j=1*

$\dfrac{d^3 r\, d^3 p}{h^3}$ *in this case not 2j+1*

$$U = \frac{V}{h^3}\int_0^\infty \underbrace{D_\gamma}_{\text{multiplicity}}\, 4\pi p^2 dp \left(\frac{1}{e^{\beta\varepsilon}-1}\right)\underbrace{\varepsilon}_{\text{energy weight}}$$

massless photons have 2 polarizations so multiplicity factor $D_\gamma = 2$

with $\boxed{p = \frac{\varepsilon}{c}}$

$$U = \frac{8\pi V}{(ch)^3}\int \varepsilon^3 d\varepsilon \left(\frac{1}{e^{\beta\varepsilon}-1}\right)$$

you will calculate N in p 7.44

$$U = \frac{8\pi V}{(ch)^3}\frac{1}{\beta^4}\int_0^\infty \frac{x^3}{e^x-1}\,dx$$

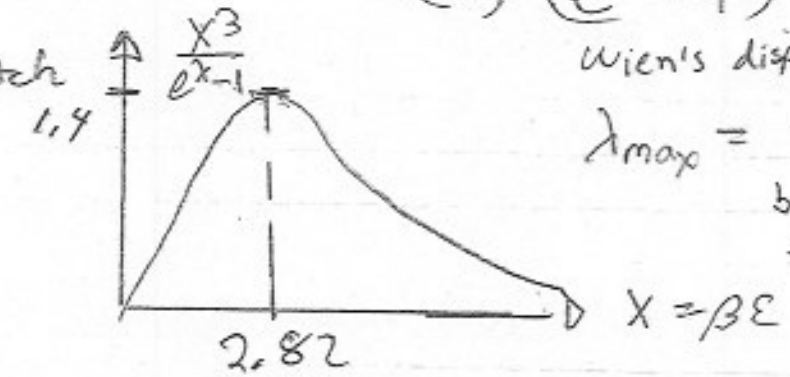
Integral in Appendix B.3b $= 3!\,\zeta(4) = 6\left(\frac{\pi^4}{90}\right) = \frac{\pi^4}{15}$

we get $\frac{U}{V} = \left(\frac{8}{15}\right)\frac{\pi^5}{(hc)^3}(kT)^4 \propto T^4$

energy spectrum

$$\frac{dU}{V\,d\varepsilon} \equiv u(\varepsilon) = \frac{8\pi}{(hc)^3}\left(\frac{\varepsilon^3}{e^{\varepsilon\beta}-1}\right)$$

sketch



Wien's displacement law

$$\lambda_{max} = \frac{b}{T}$$

$b = 2.898\times10^{-3}\ m\cdot K$
$= 2898\ \mu m\,K$

Planck Spectrum. $\boxed{\text{CMB } T = 2.73\,K}$ Peaks in far infrared

Heat Capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V = -k\left(\frac{\partial U}{\partial \beta}\right)_V$

$$C_V = \left(\frac{8}{15}\right)\frac{\pi^5}{(hc)^3}k^4(4T^3) \equiv 4aT^3$$ defines constant a

In terms of wavelength $\lambda = \frac{c}{f}$

$u(\varepsilon)d\varepsilon = u_\lambda(\lambda)\,d\lambda \qquad \varepsilon = \frac{hc}{\lambda}$

$$u_\lambda(\lambda) = u\left(\frac{hc}{\lambda}\right)\left|\frac{d\varepsilon}{d\lambda}\right| = \frac{8\pi(hc)}{\lambda^5}\frac{1}{e^x-1}$$

$x = \left(\frac{hc}{\lambda kT}\right)$

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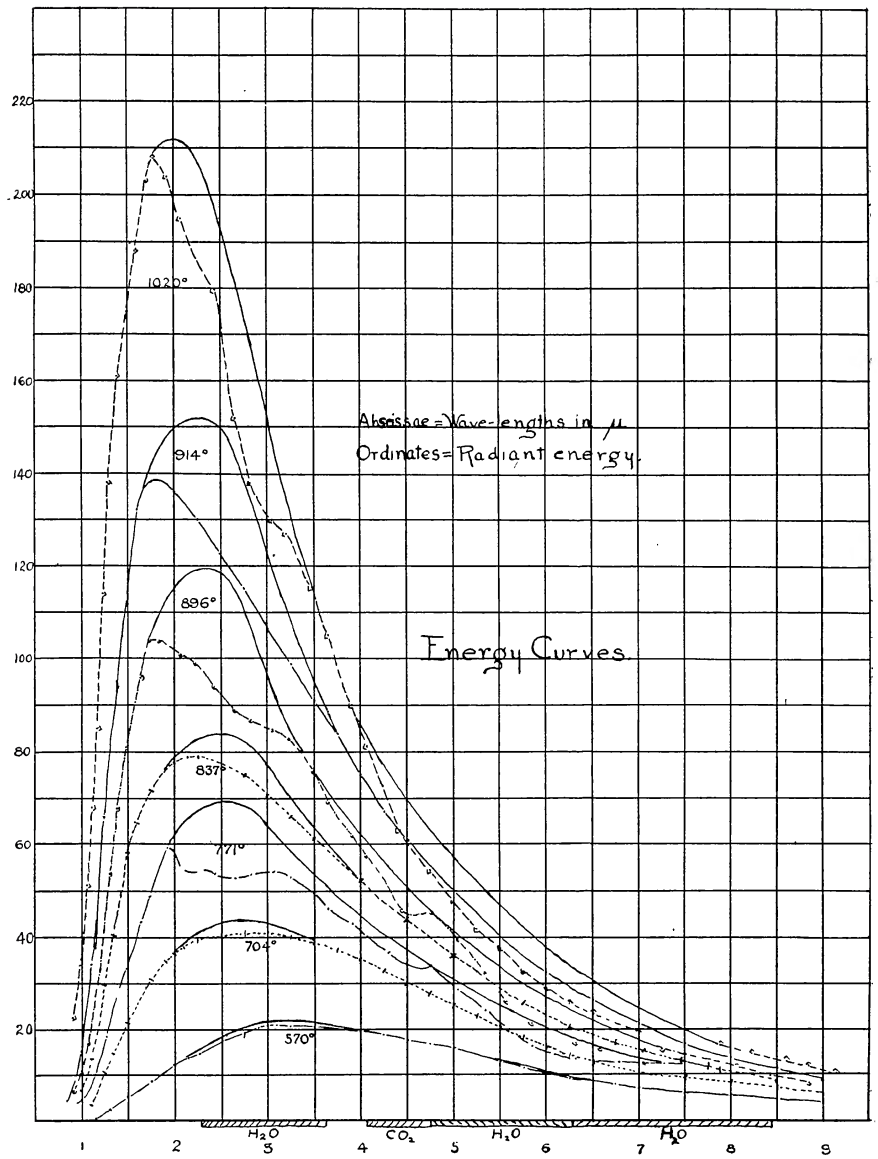

FIG. 1.

Broken lines, uncorrected or partially corrected curves.
Full lines, corrected curves, drawn to fit relation $\lambda_m T = \text{const.}$
Absorption bands indicated at bottom.

Title: The Radiation of a Black Body
Authors: Mendenhall, C. E. & Saunders, F. A.
Journal: Astrophysical Journal, vol. 13, p.25
Bibliographic Code: 1901ApJ....13...25M

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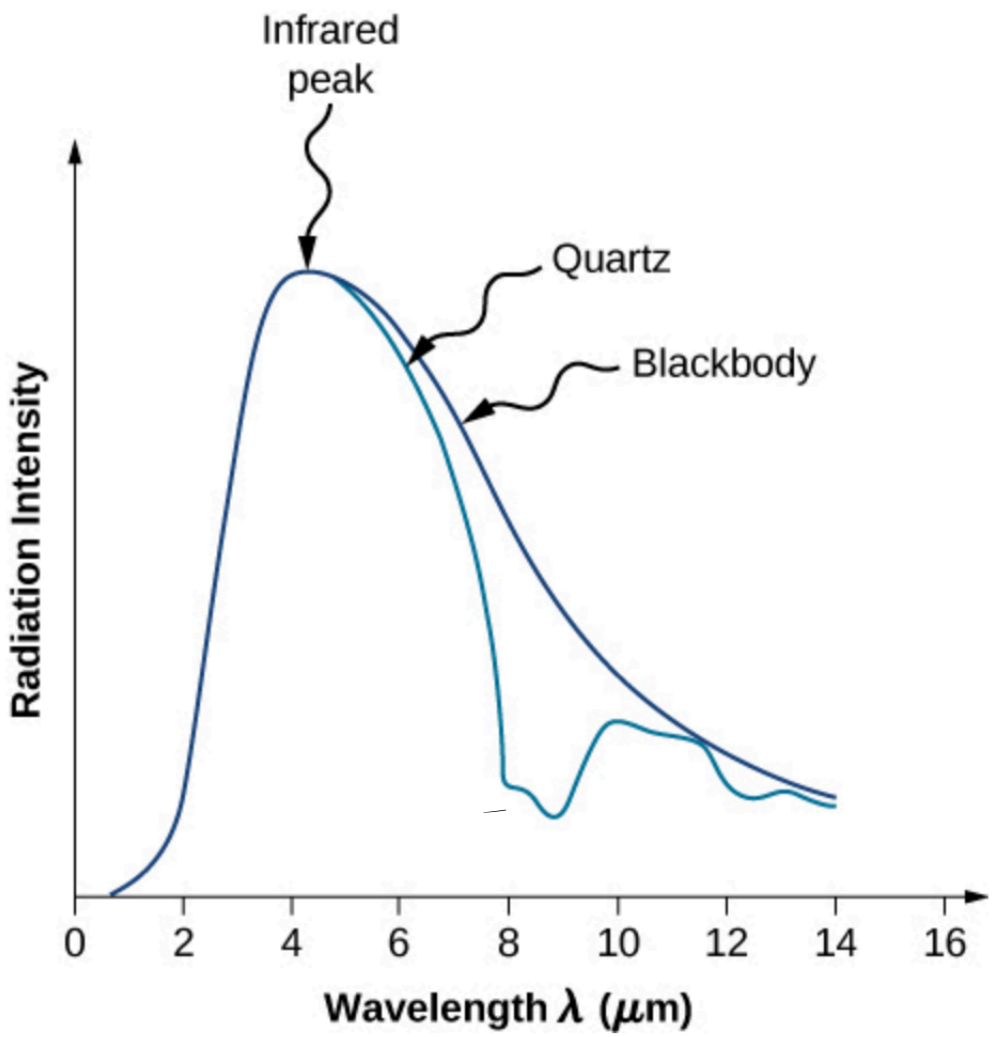
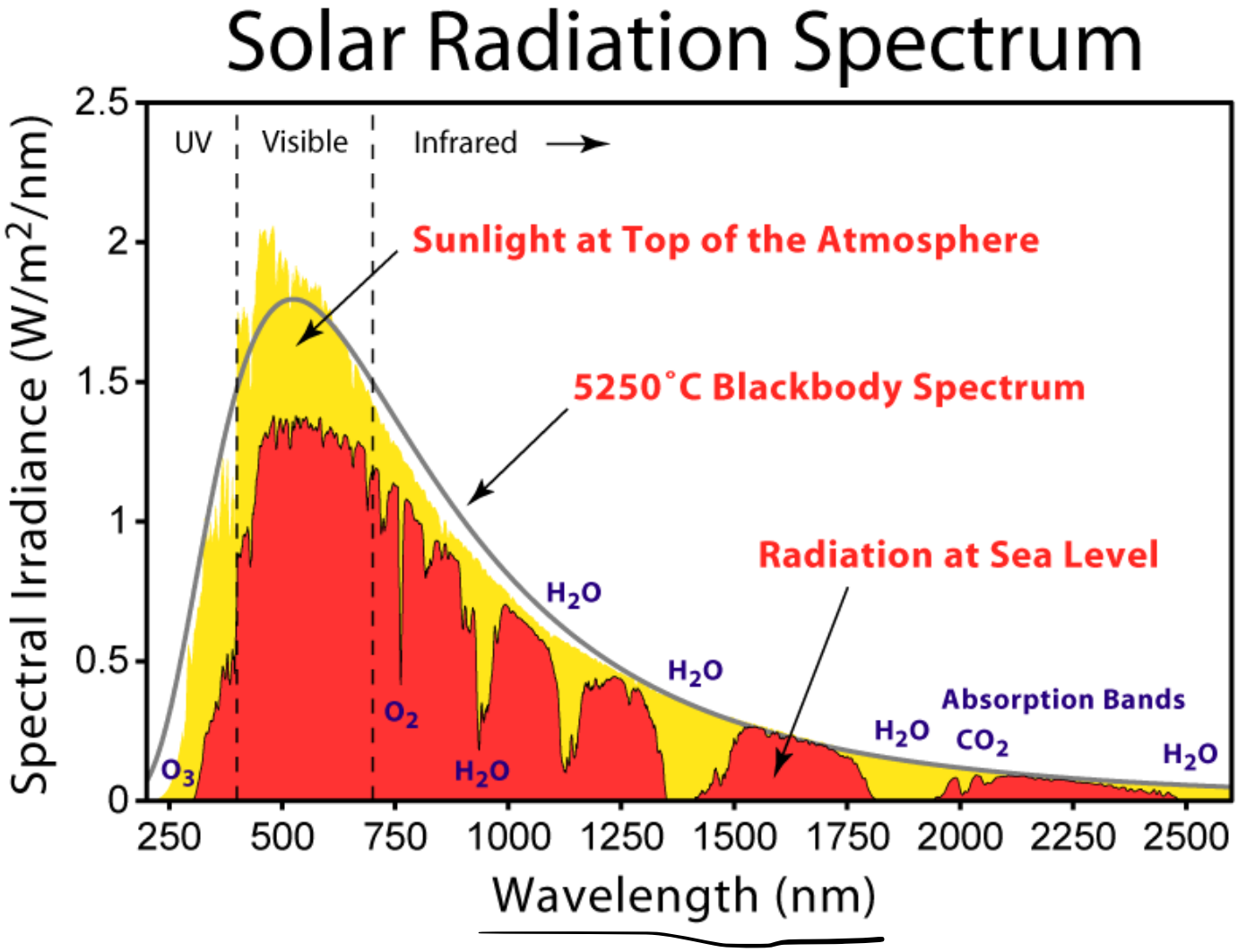
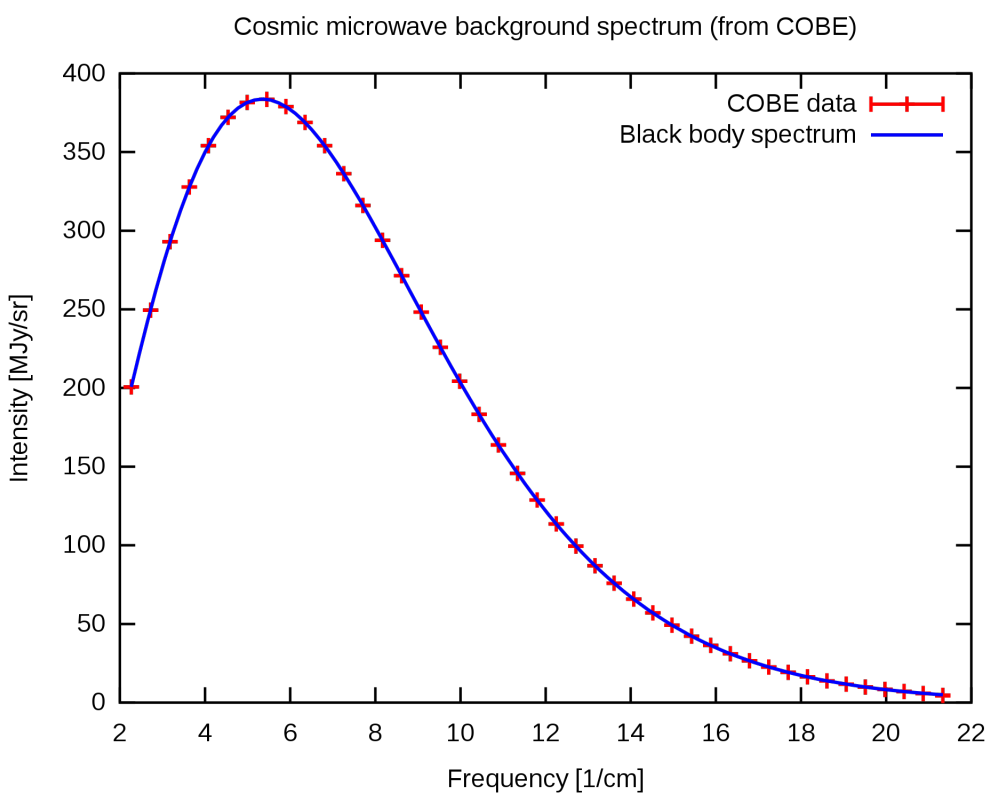


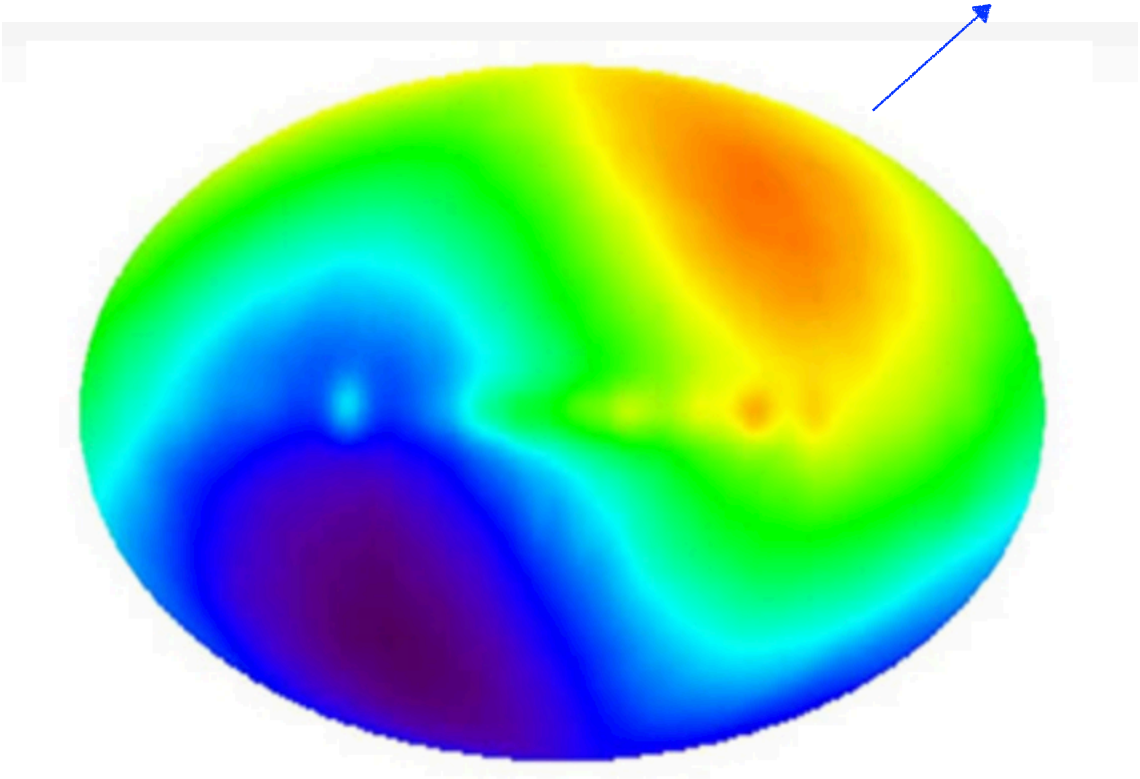
radiation from quartz surface T=600K


Solar Radiation Spectrum
UV
Visible
Infrared
Sunlight at Top of the Atmosphere
5250˚C Blackbody Spectrum
Radiation at Sea Level
H_2O
H_2O
O_2
O_3
H_2O
H_2O
Absorption Bands
CO_2
H_2O
Spectral Irradiance (W/m²/nm)
2.5
2
1.5
1
0.5
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
Wavelength (nm)



Observational error bars smaller than thickness of blue line. T_CMB = 2.7260±0.0013 K

Universe has preferred inertial reference frame



The **cosmic microwave background dipole**. The slightly (-0.0035 **Kelvin**) cooler regions are shown in blue, while (+0.0035 Kelvin) hotter regions are shown in red. The pattern is consistent with the **Local group** of **galaxies** (which includes the **Milky Way**) having a **speed** of 600 km/sec towards the centre of the red patch which lies in **constellation** Centaurus – the home of the Great Attractor.

N.B. Rather confusingly, red (hot) areas correspond to blue-shifted radiation, while blue (cool) areas correspond to red-shifted radiation.

Credit: DMR, COBE, NASA, Four-**Year** Sky Map

After removing dipole, nearly perfectly uniform, with 1/10^5 temperature fluctuations with information about big bang.

Entropy

$$S(T) = \int_0^T \frac{C_v(T')}{T'}\,dT' = \frac{4}{3}aT^3$$

$$= V\left(\frac{32\pi^5}{45}\right)\left(\frac{kT}{hc}\right)^3 k$$

Free energy (p. 7.46)

$$F = U - TS = V\left(\frac{8}{15}\right)\frac{\pi^5}{(hc)^3}(kT)^4 - V\left(\frac{32}{45}\right)\frac{\pi^5}{(hc)^3}(kT)^4$$

$$= -\frac{8}{45}\frac{V\pi^5}{(hc)^3}(kT)^4$$

We can see that

$$\boxed{\left(\frac{\partial F}{\partial T}\right) = -S}$$

From $F = -kT\ln Z$:

free energy of single photon energy (mode hf)

$$Z^{(1)} = \frac{1}{1-e^{-\beta\varepsilon}}$$

Then summing all modes to get total,

$$F = \frac{8\pi V}{h^3}\int_0^\infty p^2 dp\left[\frac{1}{\beta}\ln\left(1-e^{-\beta\varepsilon}\right)\right]$$

$\varepsilon = pc$

$$= \frac{8\pi V}{(hc)^3}\frac{1}{\beta}\int_0^\infty \varepsilon^2 \ln\left(1-e^{-\beta\varepsilon}\right)d\varepsilon$$

$$= \frac{8\pi V}{(hc)^3}\frac{1}{\beta^4}\int_0^\infty x^2\ln\left(1-e^{-x}\right)dx$$

integrate by parts –

$$dV = x^2 dx \qquad u = \ln(1-e^{-x})$$

$$V = \frac{1}{3}x^3 \qquad du = \frac{e^{-x}}{1-e^{-x}} = \left(\frac{1}{e^x-1}\right)$$

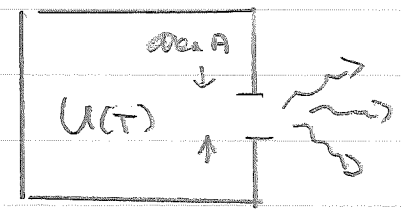
$$uV\Big|_0^\infty = 0$$

$$F = -\frac{8\pi V}{(hc)^3}\frac{1}{\beta^4}\left(\frac{1}{3}\right)\underbrace{\int_0^\infty \left(\frac{x^3}{e^x-1}\right)dx}_{3!\,\zeta(4) = 6\left(\frac{\pi^4}{90}\right)}$$

$$\boxed{F = -\left(\frac{8}{45}\right)\frac{V\pi^5}{(hc)^3}\frac{1}{\beta^4}}$$ as before

Radiative flux,

Box at temp. T with hole



Box @ T, volume V

Power radiated $\mathbb{P} \equiv$

$$\left(\frac{\text{radiated energy}}{\text{time}}\right) \propto \frac{U}{V} \cdot A \cdot (\text{speed of light} \equiv c)$$

Integration gives factor $\frac{1}{4}$. eq. 7.95

$$\mathbb{P} = \frac{1}{4} A \cdot c \cdot \frac{U(T)}{V} = A\,(\sigma T^4)$$

Stephan-Boltzmann constant

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2} = 5.67 \times 10^{-8} \left(\frac{W}{m^2 K^4}\right)$$

"Black-body" radiation cavity is perfectly "black" = absorbing & emitting equal amount of energy at temp. T.

real materials have a (T dependent) emissivity factor ε.

$$\frac{\mathbb{P}}{A} = \varepsilon \sigma T^4$$

Some emissivities of materials (near T=300K)

Polished gold/silver	0.02 - 0.03
Graphite (crystalline carbon)	0.7 - 0.8
lampblack (carbon soot)	0.96
Vantablack	0.99965
(vertically aligned carbon nanotube array)	

Greenhouse effect

Sun surface $T = 5800\,K$

peak photon $\epsilon = \frac{hc}{\lambda} = 2.82(kT)\Big|_{5800K} = 1.41\,eV$

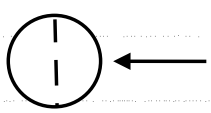
with peak $\lambda =$ 500 nm

Solar constant = radiative power at earth's distance from sun = $1370\ \frac{W}{m^2}$

at the earth's surface, ave. = $1120\ W/m^2$

Estimate T_E at equilibrium with $\epsilon = 1$ —

T earth



(Solar constant) $\pi R^2 = 4\pi R^2 \sigma T_E^4$

$T_E^{est.} = 279\,K$

this is close to, but less than, $\bar{T}_E \cong 288\,K$

difference is greenhouse effect.

BMW X6 Vantablack at Frankfurt Motor Show 2019

Apparent paradox of life. Bairlein

Change in entropy of earth is sum of life formation + other thermodynamics

$$\Delta S_E = \underset{<0}{\Delta S_{Life}} + \underset{>0}{\Delta S_{thermo}}$$

$\Delta S_{env} + \Delta S_E > 0$ second law

in equilibrium

$$\Delta S_{env} = \frac{-Q}{T_S} + \frac{Q}{T_E} = -Q\left(\frac{1}{T_E} - \frac{1}{T_S}\right) > 0$$

T of sun T of earth

So $\Delta S_E = \Delta S_{Life} + \Delta S_{thermo} > -Q\left(\frac{1}{T_E} - \frac{1}{T_S}\right)$

Baierlein Fig. 6.5 shows that this inequality holds over time period from (3.5×10^9 y – 200×10^6) year ago bacteria – dinosaurs.

From standpoint of photons, black body spectrum has constant energy/photon

$$\frac{S}{N} = 3.60k$$

Because $T_E < T_{sun}$ in equilibrium $\approx 20\times$ more photons are emitted than absorbed.
Entropy is being radiated away by photons.

N calculated in p 7.44

Heat capacity of Einstein solid

$$\Omega(N, q) \simeq \frac{(q+N)!}{q!\,N!}$$

$q, N \gg 1$

q = # energy units

N = # oscillators

= 3 (# atoms)

$$\ln \Omega = (q+N)\ln(q+N) - (q+N) - (q\ln q - q) - (N\ln N - N)$$

$\ln x! = x\ln x - x$ approx

$$= (q+N)\ln(q+N) - q\ln q - N\ln N$$

$$\frac{1}{kT} = \frac{1}{k}\frac{\partial S}{\partial U} = \frac{\partial}{\partial U}(\ln \Omega) \qquad \text{where } U = q\varepsilon \quad \varepsilon \equiv \text{energy unit}$$

$T \to \infty$ limit $(q \gg N)$

$$\ln \Omega = (q+N)\underbrace{\ln\left[q\left(1+\frac{N}{q}\right)\right]}_{\ln q + \ln(1+\frac{N}{q}) \simeq \ln q + \frac{N}{q}} - q\ln q - N\ln N$$

$$= N\ln q + N + \frac{N^2}{q} - N\ln N = N\left[\ln\left(\frac{q}{N}\right) + 1\right]$$

neglect

$$= N\ln U - N\ln \varepsilon N + 1$$

$$\frac{1}{kT} = \frac{N}{U} \qquad U = NkT \qquad \boxed{C = Nk = 3(\#\text{atoms})\,k}$$

Correct

$T \to 0$ limit $(q \ll N)$

$$\ln \Omega = (q+N)\ln\left[N\left(1+\frac{q}{N}\right)\right] - q\ln q - N\ln N$$

$$= q\ln N + \frac{q^2}{N} + q - q\ln q = q\left[\ln\frac{N}{q} + 1\right]$$

neglect

$$\frac{1}{kT} = \frac{\partial}{\partial U}\ln\Omega = \frac{\partial}{\partial U}\left[\frac{U}{\varepsilon}\left(\ln\frac{N\varepsilon}{U} + 1\right)\right] = \frac{1}{\varepsilon}\ln\left(\frac{N\varepsilon}{U}\right)$$

$$U = N\varepsilon e^{-\varepsilon/kT}$$

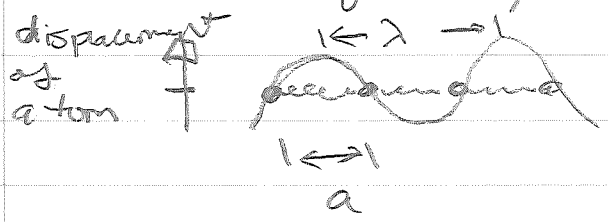
$$\boxed{C = \frac{\partial U}{\partial T} = Nk\left(\frac{\varepsilon}{kT}\right)^2 e^{-\varepsilon/kT} \xrightarrow[T\to 0]{} 0}$$

using L'Hopital's rule

Debye model of solids

Einstein model 1906. By 1912, experiments of Nernst showed disagreement at low T (~20K). That same year Debye developed improved model.

Phonons - quantized sound waves



lattice of atoms

min. wavelength $\lambda_{min} = 2a$

frequency cut off $f_{max} = \frac{c_s}{2a}$ c_s = speed of sound

Phonons are spin=1 Bosons with 3 polarization states. Phonon number is not conserved so

$$\bar{n} = \frac{1}{e^{\beta\varepsilon}-1}$$ (like for photons)

Energy of phonon gas is thus similar to that of photons except factor of 3/2 for polarization; $c \to c_s$; and frequency cut-off.

Relate cut-off f_{max} to total number of modes which is $3N$ in volume V.

$$3N = \underset{\text{polarizations}}{3} \frac{V}{h^3} \int d^3p = \frac{3V}{h^3} \int_0^{p_{max}} 4\pi p^2 dp \qquad \varepsilon = pc_s \qquad p_{max} = \frac{h f_{max}}{c_s}$$

$$= \frac{3V}{h^3} \frac{(4\pi)}{3} p_{max}^3 = \frac{V}{h^3} 4\pi \left(\frac{h f_{max}}{c_s} \right)^3$$

$$f_{max} = c_s \left(\frac{3N}{4\pi V} \right)^{1/3}$$

calculate energy U

weight by $\bar{n}(\varepsilon)$

weight by energy

$$U = \frac{3V}{h^3} \int_0^{p_{max}} 4\pi p^2 dp \left(\frac{1}{e^{\varepsilon\beta} - 1} \right) \varepsilon$$

$$= \frac{3V}{h^3} \left(\frac{1}{c_s} \right)^3 \frac{4\pi}{\beta^4} \underbrace{\int_0^{x_{max}} \frac{x^3 dx}{e^x - 1}}_{\equiv I}$$

dimensionless integral

$$x_{max} = \frac{h f_{max}}{kT} = \frac{h}{kT} c_s \left(\frac{3N}{4\pi V} \right)^{1/3} \equiv \frac{T_D}{T}$$

$$T_D = \frac{h}{2kT} c_s \left(\frac{6N}{\pi V} \right)^{1/3}$$

Then $\boxed{U = \frac{9NkT^4}{T_D^3} I}$ integral must be done numerically

Two interesting limits.

$\boxed{\text{High } T \gg T_D}$ approximate $e^x - 1 \approx x$

$$I = \int_0^{T_D/T} x^2 dx = \frac{1}{3}\left(\frac{T_D}{T}\right)^3$$

and $U = 3NkT$ correct high T limit

$\boxed{\text{low } T \ll T_D}$ $$I = \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1} \cong \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$U = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3}$$

$$C_V = \frac{12\pi^4}{5}\left(\frac{T}{T_D}\right)^3 Nk \propto T^3$$

Some Debye temperatures

material	T_D (K)
argon	93
Silicon	640
iron	467
diamond	2230

Note: $T_D \propto$ Speed of sound

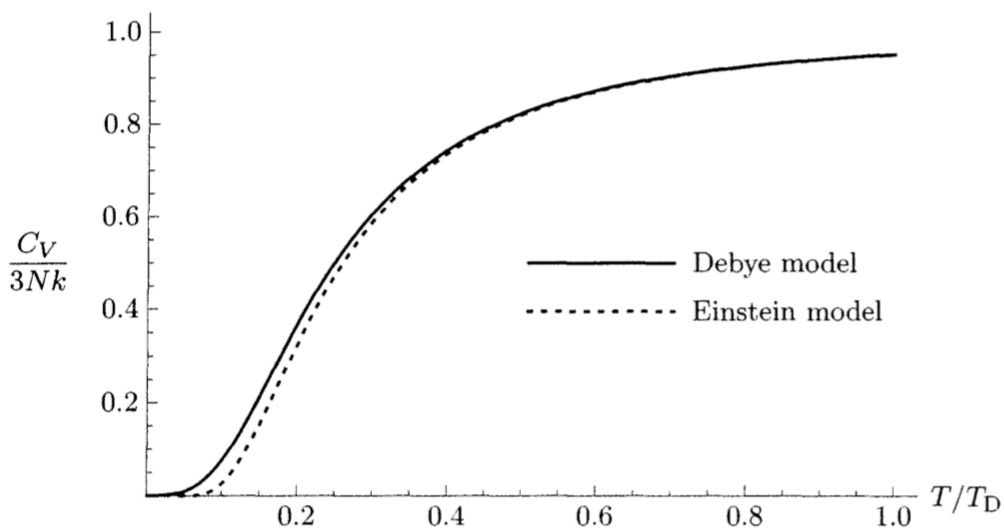


Figure 7.29. The Debye prediction for the heat capacity of a solid, with the prediction of the Einstein model plotted for comparison. The constant ϵ in the Einstein model has been chosen to obtain the best agreement with the Debye model at high temperatures. Note that the Einstein curve is much flatter than the Debye curve at low temperatures.

 from Baierlein

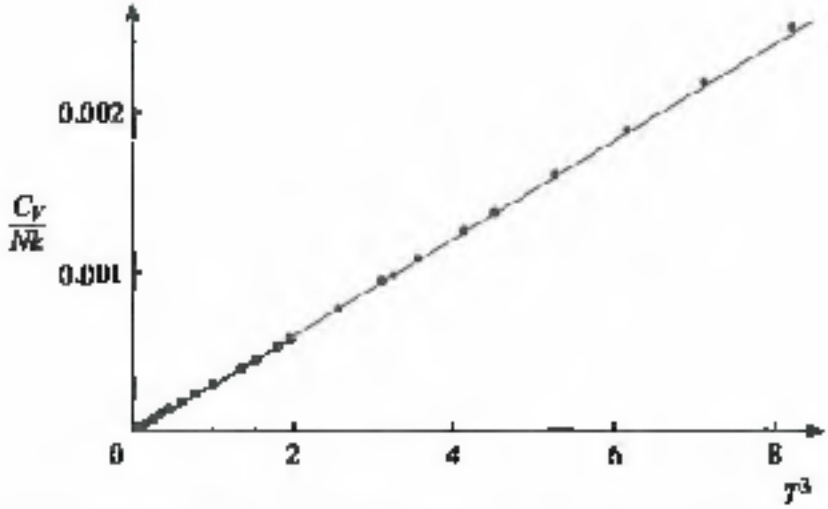


Figure 6.7 The heat capacity of solid argon at low temperatures: 0.44 K to 2.02 K. The slope of the C_V versus T^3 line is well fit with $\theta_D = 92$ K. Then the upper end of the temperature range corresponds to $T/\theta_D = 2/92 = 0.022$, and so the Debye approximation should be excellent, as indeed it is. [*Source*: Leonard Finegold and Norman E. Phillips, *Phys. Rev.* 177, 1383–91 (1969).]

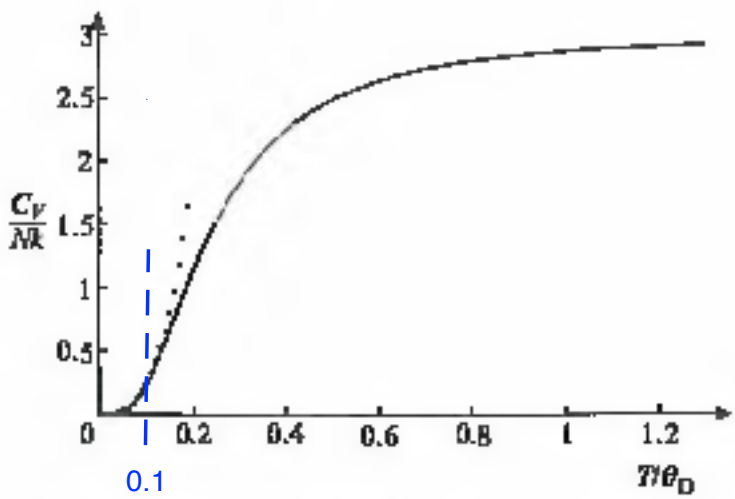


Figure 6.8 The full run of the Debye theory's heat capacity as a function of temperature. The dotted curve is a strictly T^3 curve whose third derivative at the origin agrees with the Debye theory's third derivative. Evidently the T^3 behavior is restricted to temperatures below $T \cong 0.1\theta_D$. Indeed, when $T \leq 0.1\theta_D$, the T^3 form differs from the exact value by 1 percent or less. At the other limit, the heat capacity has reached 95 percent of its asymptotic value when $T/\theta_D = 1$, specifically, $C_V/Nk = (0.952) \times 3$ at $T = \theta_D$.

When the temperature is low, specifically, when $T \lesssim 0.1\theta_D$, so that the T^3 behavior holds, then the heat capacity is substantially smaller than its classical limit. That conclusion is evident in figure 6.8, also.

Table 6.2 gives a selection of Debye temperatures. Crystals formed from the noble gases are loosely bound; so the maximum frequency ν_{max} should be small and,

Bose Einstein Condensation (BEC)

(I follow Baierlein ch 9)

History Consequence of BE statistics circa 1905

London (1938) BEC mechanism for superfluid ^4He ($j=0$) and superconductivity

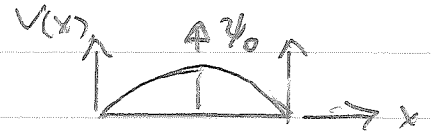
1995 gas BEC Nobel 2001

(*) rubidium @ 170×10^{-9} K Cornell, Wieman
sodium Ketterle

Theory. Energy states of particle in box

$$E = \frac{1}{2m}|\vec{p}|^2 \qquad \text{quantized } p_i = \frac{h n_i}{2L} \quad i = x, y, z$$

$$n_i = 1, 2, 3, \ldots$$



ground state energy $\varepsilon_0 = \frac{3}{2m}\left(\frac{h}{2L}\right)^2 = \frac{3h^2}{8mL^2}$

Mean number in state ε_s $\langle n_s \rangle = \dfrac{1}{e^{\beta(\varepsilon_s - \mu)} - 1}$

and $N = \sum_s \langle n_s \rangle$ total number fixed

(*) picture on homepage of course

in limit $T \to 0$ must have

$$\lim_{T\to 0} \langle n_0 \rangle = \lim_{\beta\to\infty} \frac{1}{e^{\beta(\varepsilon_0-\mu)}-1} = N$$

this implies $\mu < \varepsilon_0$. since N is large $e^{\beta(\varepsilon_0-\mu)} \approx 1$ or $\beta(\varepsilon_0-\mu) \ll 1$.
Taylor expand

$$e^{\beta(\varepsilon_0-\mu)} - 1 \approx \beta(\varepsilon_0-\mu) \quad \text{then}$$

$$\frac{1}{e^{\beta(\varepsilon_0-\mu)}-1} = N \Rightarrow \mu(T) \approx \varepsilon_0 - \frac{kT}{N}$$

which is essentially 0; see next page

For $T > 0$,

and see prob. 7.74

$$\langle n_0 \rangle + \sum_{s>0} \langle n_s \rangle = N$$

approximate $\sum_s$ as integral, with lower limit of 0 since $g(0) = 0$.

$$N_{excited} \equiv \sum_{s>0} \langle n_s \rangle = \int_0^\infty g(\varepsilon) \left[\frac{1}{e^{\beta(\varepsilon-\mu)}-1} \right] d\varepsilon$$

$$g(\varepsilon) = CV(2j+1)\sqrt{\varepsilon} \qquad j=0 \text{ for } {}^4He$$

$$C = \frac{\pi}{4} \frac{(8m)^{3/2}}{h^3} = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2}$$

Chemical potential ≈ 0 below T_c

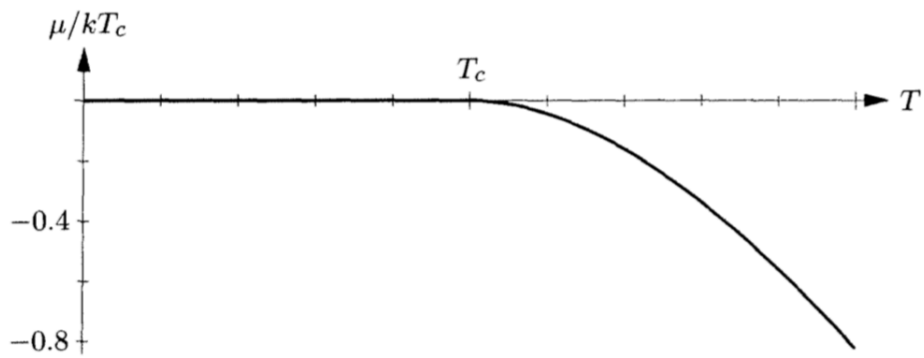


Figure 7.33. Chemical potential of an ideal Bose gas in a three-dimensional box. Below the condensation temperature, μ differs from zero by an amount that is too small to show on this scale. Above the condensation temperature μ becomes negative; the values plotted here were calculated numerically as described in Problem 7.69.

near T=0, μ(T)= ε-kT/N

For Helium-4

ε=1.5E-18 eV
T_c ≈ 3 K
ε/kT_c = 6E-15

Define critical temperature as $\mu(T_c) = 0$. Then we can do the integral.

$$I = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{3/2} V \int_0^\infty \frac{\sqrt{\varepsilon}\, d\varepsilon}{e^{\beta\varepsilon} - 1}$$

$$= \frac{V}{l_c^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}\, dx}{e^x - 1} = \frac{V}{l_c^3} \underbrace{\zeta(3/2)}_{2.612}$$

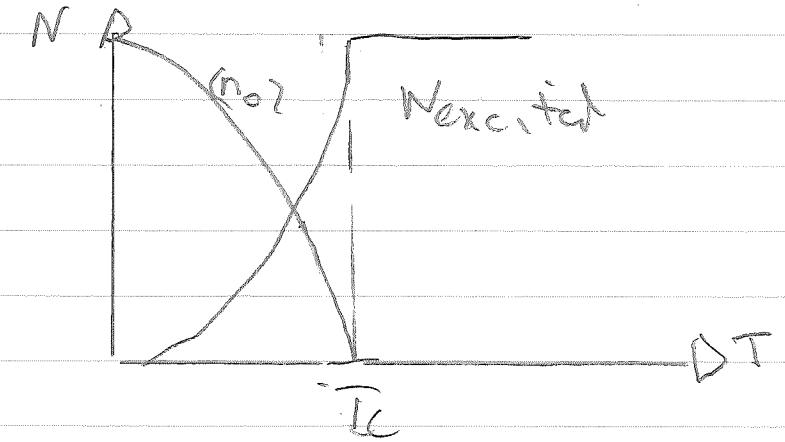
$$l_c = \left(\frac{h^2}{2\pi m k T_c}\right)^{1/2}$$ thermal de Broglie wavelength @ T_c.

Then if we can say $\langle n_0 \rangle \ll N$ for $T > T_c$, and for $T<T_c$

$$N_{excited} = N \left(\frac{T}{T_c}\right)^{3/2} \qquad T < T_c$$

and $$\langle n_0 \rangle + N \left(\frac{T}{T_c}\right)^{3/2} = N \qquad T < T_c$$

$$\langle n_0 \rangle = \left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right) N \qquad T < T_c$$



gives this picture

Experimental potential is 3D harmonic

Example p. 7.73

N spin-0 (Bosons) in 3D harmonic oscillator potential.

$$U(r) = \frac{1}{2} m\omega^2 r^2 = \frac{1}{2} m (2\pi)^2 f^2 r^2$$

P.E. not total E

Quantized energy levels are

$$\varepsilon_n = nhf + \frac{3}{2} hf \qquad n = 0, 1, 2, \ldots$$

here we can ignore groundstate energy as $hf \ll \bar{\varepsilon} \sim kT$

$$\Delta\varepsilon = hf$$

with degeneracy –

$$\mathcal{D}_n = \frac{(n+1)(n+2)}{2} \underset{n \gg 1}{\simeq} \frac{n^2}{2}$$

and $\varepsilon_n \to \varepsilon$ continuous energy

density of states is

$$g(\varepsilon) = \frac{\Delta n}{\Delta \varepsilon} = \frac{1}{hf}\left(\frac{n^2}{2}\right) = \frac{1}{2}\frac{\varepsilon^2}{(hf)^3}$$

$$n = \frac{\varepsilon}{hf}$$

$$N = \int_0^\infty g(\varepsilon)\, \bar{n}_{BE}(\varepsilon)\, d\varepsilon$$

$$= \int_0^\infty g(\varepsilon) \left[\frac{1}{e^{(\varepsilon-\mu)\beta} - 1}\right] d\varepsilon$$

Take $\mu = 0$. Correspond to T_c.

$$N = \int_0^\infty \frac{1}{2}\left(\frac{1}{hf}\right)^3 \varepsilon^2 \left(\frac{1}{e^{\beta\varepsilon}-1}\right) d\varepsilon \qquad x = \beta\varepsilon$$

$$= \frac{1}{2}\left(\frac{kT_c}{hf}\right)^3 \underbrace{\int_0^\infty x^2 \left(\frac{1}{e^x - 1}\right) dx}_{\text{Appendix B.5}}$$

$$2!\,\zeta(3)$$

Riemann-Zeta ≈ 1.2

Giving $N = 1.2\left(\frac{kT_c}{hf}\right)^3$ and then

$$\boxed{\langle N_0 \rangle = \left[1 - \left(\frac{T}{T_c}\right)^3\right]}$$

$$kT_c = hf\left(\frac{N}{1.2}\right)^{1/3}$$

scaled T_c, $t_c \equiv \frac{kT_c}{hf} = \left(\frac{N}{1.2}\right)^{1/3}$
dimensionless

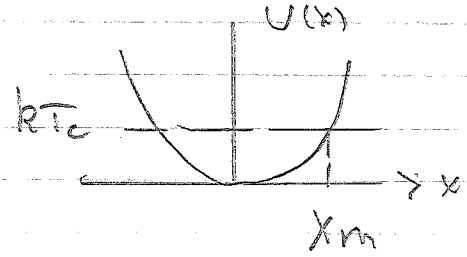
for $N = 2000$, $t_c = 11.85$

Below T_c we have Bose-Einstein condensation.

Semi-classical estimate of volume.

Turning point of 1D harmonic oscillator

$$U(x_m) = \frac{1}{2} m (2\pi f)^2 x_m^2 \simeq kT_c$$



Volume $V = x_m^3$

$$U(x_m) = 2\pi^2 \frac{m}{h^2} (hf)^2 V^{2/3} = \underline{kT_c}$$

and $N = \zeta(3) \left(\frac{kT_c}{hf}\right)^3$

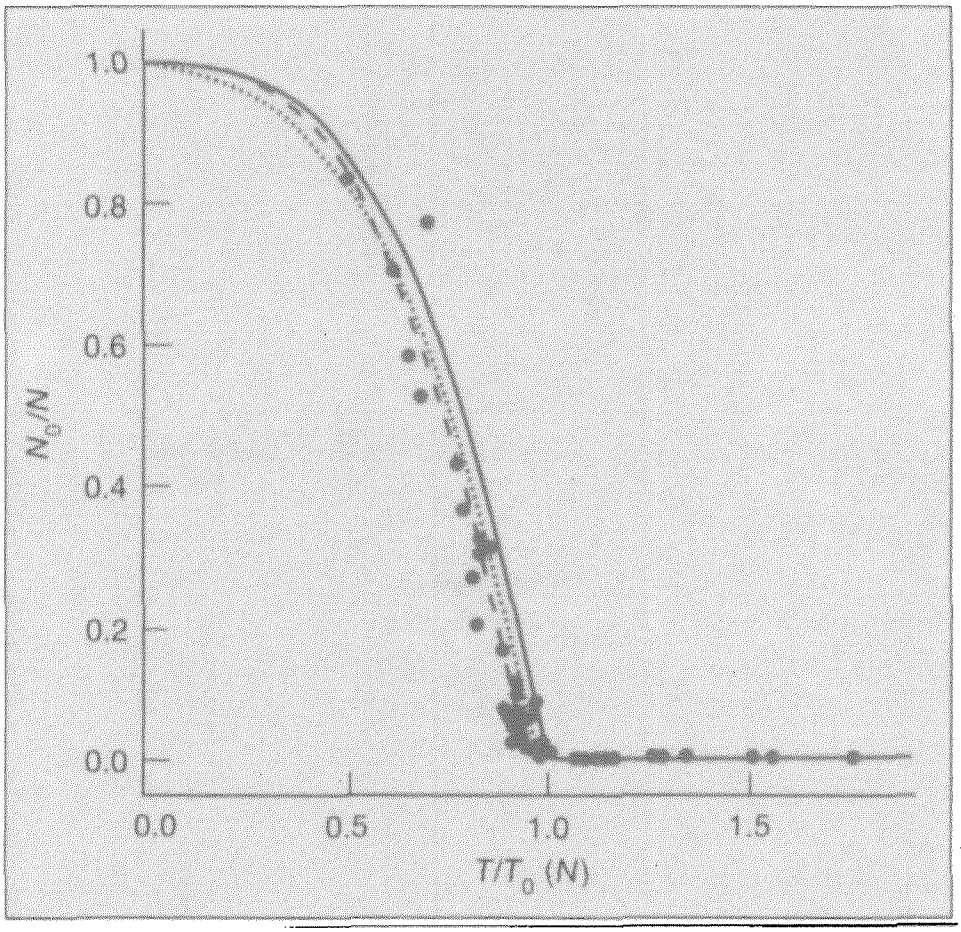
$$hf = kT_c \left(\frac{\zeta(3)}{N}\right)^{1/3}$$

So $$kT_c = 2\pi^2 \frac{m}{h^2} V^{2/3} (kT_c)^2 \left(\frac{\zeta(3)}{N}\right)^{2/3}$$

$$kT_c = \left(\frac{N}{V}\right)^{2/3} \left(\frac{h^2}{2\pi m}\right) \left[\frac{1}{(\pi\, \zeta(3))^{2/3}}\right] = 0.413$$

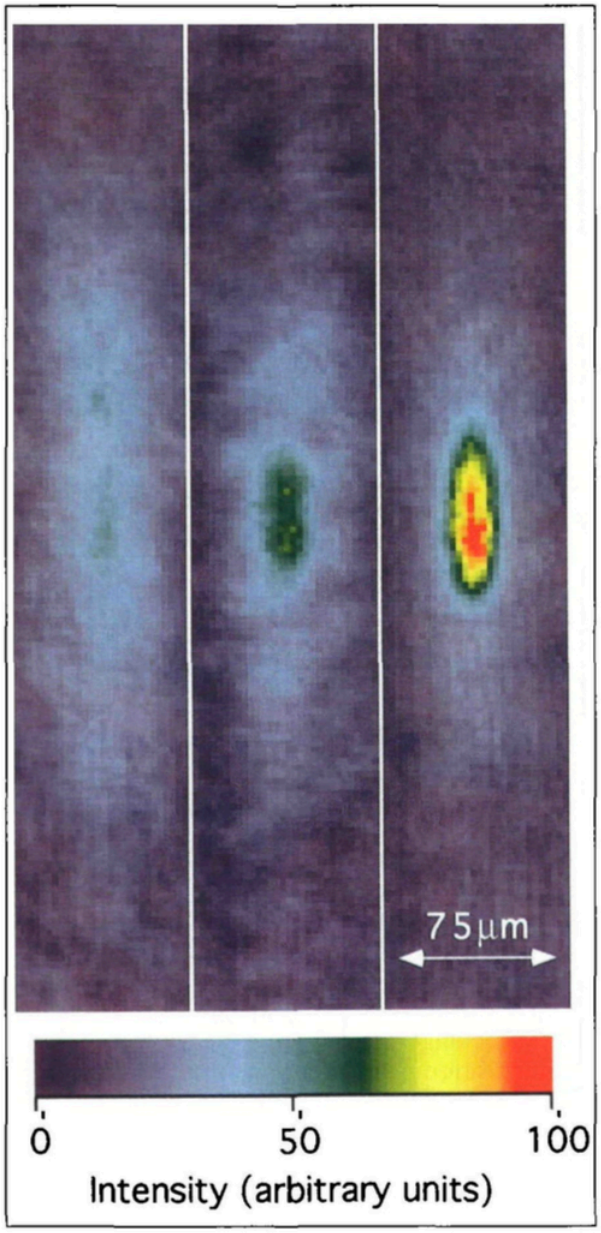
Same form as 3D Box potential with slightly different constant (0.527 box)

From ketterle-physicsworld.pdf



5 Condensate fraction, N_0/N, measured as a function of scaled temperature, T/T_0, at Boulder. T_0 is the predicted critical temperature for an ideal gas in a harmonic trap in the thermodynamic limit (many atoms). The solid curve is the predicted dependence in the thermodynamic limit, and the dotted curve includes a correction for the finite number of atoms (4000) in the condensate. To the uncertainties in the data, the measurement is consistent with the theory for non-interacting bosons. The dashed line is a best fit to the experimental data.

Physics World Bose-Einstein condensation
CHRISTOPHER TOWNSEND, WOLFGANG KETTERLE AND SANDRO STRINGARI



2 Direct and non-destructive observation of the formation of a Bose condensate by dispersive light scattering (phase-contrast imaging) at MIT. The intensity of scattered light is shown as a function of position in the trap, which is proportional to the column density of atoms along the line-of-sight. The image on the left shows the cloud cooled to just above the BEC transition temperature, and the distribution of atoms is almost classical. As the temperature is lowered through the phase transition a sharp peak of atoms begins to appear at the trap centre (middle), and further cooling increases the condensate fraction to almost 100% (right).

Physics World Bose-Einstein condensation
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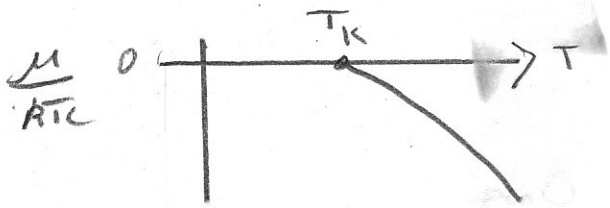
An interesting example.

Problem 7.75 gas of Spin 0 Bosons

$T \gg T_c$ can still be below 1K



$\beta(\varepsilon-\mu) \equiv x$

$x \gg 1$ limit

$$\bar{n}(\varepsilon) = \frac{1}{e^{x}-1} = e^{-x}(1-e^{-x})^{-1} \simeq e^{-x}(1+e^{-x})$$

In lecture #9 we found:

$$\beta\mu = -\ln\left(\frac{1}{C}\right) + \frac{1}{2\sqrt{2}}C \qquad C \equiv \frac{N\ell_Q^3}{V} \ll 1$$

<u>Grand free energy</u> $\Phi = U - TS - \mu N$

$$d\Phi = dU - SdT - TdS - \mu dN - Nd\mu$$

$$= (TdS - pdV + \mu dN) - SdT - TdS - \mu dN - Nd\mu$$

$$= -SdT - pdV - Nd\mu$$

$$\Phi = U - TS - \mu N = G - PV - \mu N = -PV$$

$$G = U - TS + PV \qquad G = \mu N$$

Boltzmann $Z_B = \sum_s e^{-\beta(E_s - \mu N_s)}$

$$\frac{\partial}{\partial\beta}\ln Z_B = -\bar{E} + \mu\bar{N} = -U + \mu\bar{N}$$

$$\Phi = U - TS - \mu N$$

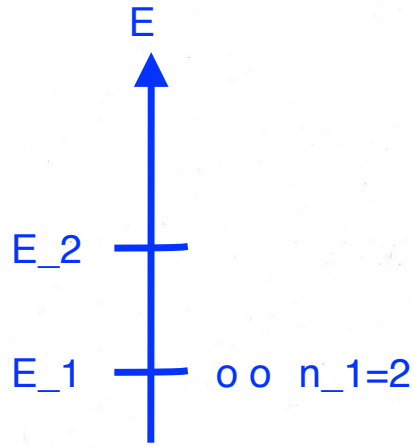
$$\left(\frac{\partial \Phi}{\partial T}\right)_{V,U} = -S = \frac{\phi + \mu N - U}{T}$$

$$-k\beta^2 \left(\frac{\partial \Phi}{\partial \beta}\right)_{V,U} = k\beta(\phi + \mu N - U)$$

$$= k\beta\phi + k\beta\left(-\frac{\partial}{\partial\beta}\ln Z_B\right)$$

$$\frac{\partial}{\partial\beta}(\phi\beta) = -\frac{\partial}{\partial\beta}(\ln Z_B)$$

$$\boxed{\phi = -\frac{1}{\beta}\ln Z_B}$$



B.E. $\quad Z_\varepsilon = \sum_n e^{-\beta(n\varepsilon - n\mu)}$ $\quad$ energy mode ε occupied by n bosons

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

each mode a separate sub-sytem

$$Z = \prod_{\text{modes}} Z_\varepsilon$$

$\boxed{\text{non-interacting approximation}}$

$$\ln Z = \sum_{\text{modes}} -\ln\left(1 - e^{-\beta(\varepsilon-\mu)}\right)$$

$$= \int_0^\infty g(\varepsilon)\,d\varepsilon\left[-\ln\left(1 - e^{-\beta(\varepsilon-\mu)}\right)\right]$$

$$\ln(1-x) \simeq -x - \tfrac{1}{2}x^2$$

$$\ln Z = \int_0^\infty g(\varepsilon)\,d\varepsilon\left[e^{-\beta(\varepsilon-\mu)} + \tfrac{1}{2}e^{-2\beta(\varepsilon-\mu)}\right]$$

$$g(\varepsilon) = \frac{2}{\sqrt{\pi}} \frac{V}{l_Q^3} \beta^{3/2} \sqrt{\varepsilon}$$

$$\ln Z = \frac{2}{\sqrt{\pi}} \frac{V}{l_Q^3} \int_0^\infty \beta^{3/2} \sqrt{\varepsilon}\, d\varepsilon \left[e^{-\beta\varepsilon} e^{\beta\mu} + \frac{1}{2} e^{-2\beta\varepsilon} e^{2\beta\mu} \right]$$

$$= \frac{2}{\sqrt{\pi}} \frac{V}{l_{Q_3}} \left[e^{\beta\mu} \underbrace{\int_0^\infty \sqrt{x} e^{-x} dx}_{\frac{\sqrt{\pi}}{2}} + \frac{1}{2} e^{2\beta\mu} \underbrace{\int_0^\infty \sqrt{x} e^{-2x} dx}_{\frac{1}{4}\sqrt{\frac{\pi}{2}}} \right]$$

$$= \frac{V}{l_Q^3} \left[e^{\beta\mu} + \frac{1}{4\sqrt{2}} e^{2\beta\mu} \right]$$

with $e^{\beta\mu} \cong c - \frac{1}{2\sqrt{2}} c^2 \qquad c \equiv \frac{N l_Q^3}{V}$

$e^{2\beta\mu} \approx c^2$

$$\ln Z = \frac{V}{l_Q^3} c \left[1 + \underbrace{\left(-\frac{1}{2\sqrt{2}} + \frac{1}{4\sqrt{2}} \right)}_{-\frac{1}{4\sqrt{2}}} c \right]$$

$$= N \left[1 - \frac{1}{4\sqrt{2}} \frac{N}{V} l_Q^3 \right]$$

$$P = \frac{1}{\beta} \frac{N}{V} \left[1 - \frac{1}{4\sqrt{2}} \frac{N}{V} l_Q^3 \right]$$

lec 10-28

Virial coefficients (chapter 1)

$$PV = \frac{N}{\beta}\left(1 + \frac{NB(T)}{V N_A} + \frac{N^2}{V^2}\frac{C(T)}{N_A^2} + \cdots\right)$$

So our prediction in semi-classical <u>non-interacting</u> approximation is

$$B(T) = -\frac{N_a}{4\sqrt{2}}\, l_Q^3$$

For Helium-4 this gives

$$B(2K) = -25 \text{ cm}^3/\text{mole}$$ Schroeder calculates

measured value $-154 \text{ cm}^3/\text{mole}$ my reading of Fig 8.2

non-interacting approximation not good enough

→ <u>Chapter 8</u> systems of interacting particles

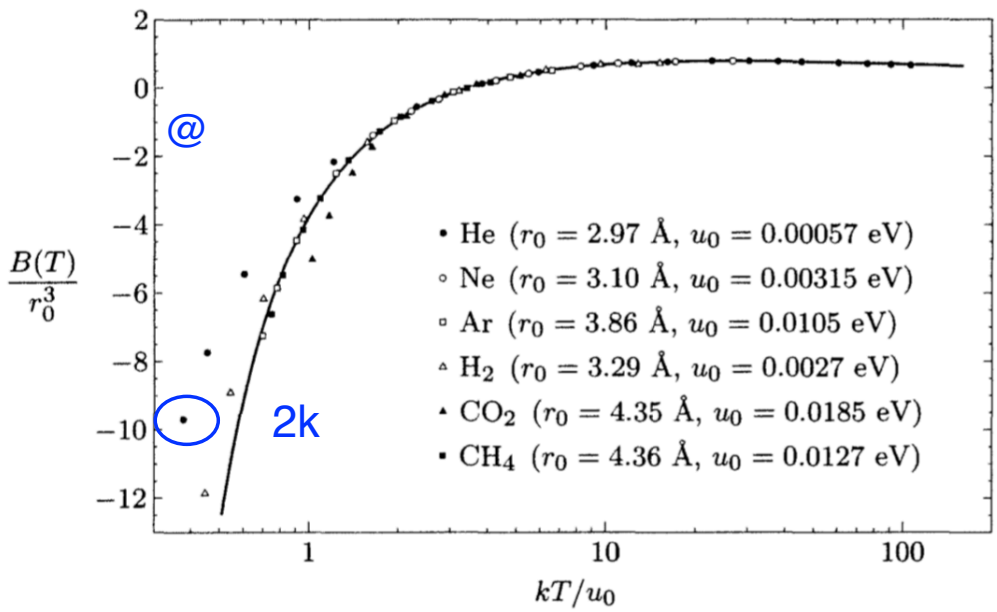


Figure 8.2. Measurements of the second virial coefficients of selected gases, compared to the prediction of equation 8.36 with $u(r)$ given by the Lennard-Jones function. Note that the horizontal axis is logarithmic. The constants r_0 and u_0 have been chosen separately for each gas to give the best fit. For carbon dioxide, the poor fit is due to the asymmetric shape of the molecules. For hydrogen and helium, the discrepancies at low temperatures are due to quantum effects. Data from J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation* (Oxford University Press, Oxford, 1980).

Quantum effects contribute to B but are not the dominant effect.

Cannot ignore interactions.