4/21/11

Key results from last lecture:

Discussed ideal gas of identical weakly-interacting fermions in context of electron gas

Looked at $T=0$ limit for which Fermi-Dirac distribution becomes simple:

$$T=0 \qquad \bar{n}_{FD}(\epsilon) = \begin{cases} 1 & \text{if } \epsilon < \mu \\ 0 & \text{if } \epsilon > \mu \end{cases}$$

Could then evaluate average energy by using quantum states of free particle in cubic box of volume $V=L^3$ with impenetrable walls

$$E(n_x,n_y,n_z) = \frac{p^2}{2m} = \frac{h^2}{2m}\left(\frac{1}{\lambda_x^2}+\frac{1}{\lambda_y^2}+\frac{1}{\lambda_z^2}\right) \qquad \lambda_i = \frac{2L}{n} \quad n \geq 1$$

$$= \frac{h^2}{8L^2 m}\left(n_x^2+n_y^2+n_z^2\right)$$

$$\langle E \rangle = 2\sum_{n_x}\sum_{n_y}\sum_{n_z} E(n_x,n_y,n_z)\, \underbrace{\bar{n}_{FD}\left[E(n_x,n_y,n_z)\right]}_{1}$$ general case

$$\cong 2\int_0^{n_{max}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\varphi \, \frac{h^2 n^2}{8mL^2} \cdot n^2 \sin\theta \cdot 1$$

$$\cong \frac{\pi h^2 n_{max}^5}{40 m L^2} = \frac{3}{5} N E_F \qquad E_F = \frac{h^2 n_{max}^2}{8L^2 m} = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3} = \text{Fermi energy}$$

$$P = -\frac{\partial \langle E \rangle}{\partial V} = \frac{2}{5}\frac{N}{V}\epsilon_F = \frac{2}{3}\frac{U}{V}$$ degeneracy pressure

$S = ?$ class question $\qquad P \simeq 4 \cdot 10^5$ atm Cu

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{10}{9}\frac{U}{V} \sim 6 \cdot 10^5 \text{ atm for Cu at } 300T$$

$$C_V \simeq \left(\frac{kT}{E_F}\right) \cdot Nk \cdot \frac{3}{2}$$ grows linearly with T, only electrons near Fermi energy can contribute

Highlights of Section 7.4: Blackbody radiation

Classical equipartition theorem applied to light in a metal box ("cavity") leads to terribly wrong prediction: Maxwell equations predict light in box described by superposition of Fourier modes: $\vec{E} = \sum E_{mnl}(t)\, e^{i(mk_x x + nk_y y + lk_z z)} + c.c.$ where each mode $E_{mnl}(t)$ satisfies harmonic oscillator, so contributes $2 \times \frac{kT}{2}$ thermal energy. But light has no limit to range of wavelengths, $\lambda_n = \frac{2L}{n}$, $n = 1, 2, \ldots, \infty$, so predict infinite amount of energy in box if light is in equilibrium, wrong!

Planck suggested this "ultraviolet catastrophe", no limit to short-wavelength modes, could be eliminated if oscillator energy was quantized in equal integer amounts

$$E_n = 0,\ \epsilon,\ 2\epsilon,\ \ldots \qquad \epsilon = hf$$

$$Z = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \cdots \qquad e^{-\beta\epsilon} < 1 \Leftrightarrow e^{\beta\epsilon} > 1, \text{ always true}$$

$$= \frac{1}{1 - e^{-\beta\epsilon}}$$

$$\bar{N} = \frac{\bar{E}}{\epsilon} = \frac{1}{\epsilon}\left(-\frac{\partial \ln Z}{\partial \beta}\right) = \frac{1}{e^{\beta\epsilon} - 1}$$

Planck distribution implies $\mu = 0$ when compared with $\bar{n}_{BE}(\epsilon)$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\epsilon}{e^{\beta\epsilon} - 1}$$

finite energy!

Planck's idea was correct. Photons have property of being absorbed and emitted by matter so number is not conserved. Equil. # of photons determined by minimum in free energy w.r.t. N

$$\boxed{\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 \Rightarrow \mu = 0}$$

$\mu = 0$ holds in other cases, e.g. matter/antimatter reactions $e^+ + \bar{e} \rightleftarrows 2\gamma$

Bose-Einstein distribution then becomes special case called Planck distribution:

$$\boxed{\bar{n}_{Pl}(\epsilon) = \frac{1}{e^{\beta\epsilon} - 1}} \qquad \epsilon \geq 0$$

For massive bosons like He^3, $\mu \neq 0$ and is determined by conservation of particles:

$$N = \sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}$$

Given Planck distribution, can repeat logic we used for electron gas, compute $\langle \mathcal{E} \rangle = U$, C_V, S, P, etc.

Photons have diff. energy dependence $E = \sqrt{p^2c^2 + m^2c^4} \approx pc$

$$\epsilon = pc = c\sqrt{p_x^2 + p_y^2 + p_z^2} = \frac{hc}{2L} n \qquad n^2 = n_x^2 + n_y^2 + n_z^2 \quad p_n = \frac{h}{\lambda_n} \quad \lambda_n = \frac{2L}{n}$$

$$U = \sum_s E_s \bar{n}_{BE}[E_s] = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \left[\left(\frac{hc}{2L}\right) n\right] \cdot \frac{1}{e^{\beta\left[\frac{hcn}{2L}\right]} - 1}$$

convert to spherical coordinates: $n_x, n_y, n_z \rightarrow n, \theta, \varphi$

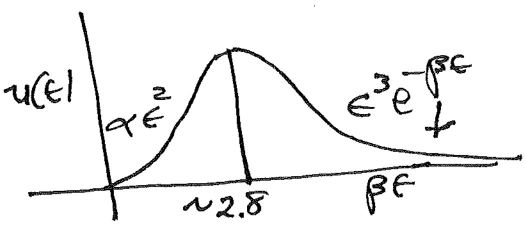
$$\mathcal{U} \cong 2 \underbrace{\int_0^\infty dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\varphi}_{\text{octant of positive triplets } (n_x, n_y, n_z)} \, n^2 \sin\theta \cdot \frac{hcn}{2L} \cdot \frac{1}{e^{\beta \frac{hcn}{2L}} - 1}$$

Standard trick is to change variable to simplify integrand

$$\epsilon = \frac{hc}{2L} n$$

Find:

$$\boxed{\frac{\mathcal{U}}{V} = \int_0^\infty \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} \, d\epsilon}$$



Can interpret $u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\beta\epsilon} - 1}$

as energy density distribution (energy per unit volume density) or Planck spectrum. This is universal form that depends only on temperature T

has max (peak) for $\beta\epsilon \simeq 2.8$, allows frequency f to be deduced from peak of spectrum, as $f \propto$ of energy.

leads to Wien's displacement law

$$\lambda_{max} = \frac{2{,}700{,}000 \text{ nm}}{T}$$

$\lambda_{max} \neq E_{max}$ because of Jacobian factor from nonlinearity $E \propto \frac{1}{\lambda}$

Examples: Sun: $T \simeq 6000K \Rightarrow \lambda_{max} \cong 500 nm$

human: $T \simeq 300K \Rightarrow \lambda_{max} \simeq 10^4 nm$, for infrared,

pit vipers can detect this

measure temp of sick person by λ_{max} in ear & canal

Get total energy of equil. photon gas by changing variables yet again: $x = \beta\epsilon$

$$\frac{U_{photon}}{V} = \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{x^3\,dx}{e^x - 1} \;\propto\; T^4 \,!$$

$$\int_0^\infty \frac{x^3\,dx}{e^x-1} = \underbrace{\Gamma(n+1)}_{6}\,\underbrace{\zeta(n+1)}_{\pi^4/90} \quad n=3 \quad = \frac{\pi^4}{15}$$

$$\frac{U_{photon}}{V} = \frac{8\pi (kT)^4}{15(hc)^3}$$

not large in practice, $T \simeq 460\,K$ for ~~digestion~~ oven $\Rightarrow$ $U/V \simeq 10^{-5} \frac{J}{m^3}$ $1m^3$ (375F $\downarrow$ 460 K)

$NkT \approx PV \approx 10^5 \frac{J}{m^3}$ much larger

$$C_{photon} = \frac{dU_{photon}}{dT} \propto T^3 V$$

$$S = \int_0^T \frac{C(T')}{T'}\,dT' \propto VT^3 \;\Rightarrow\; \text{adiabatic process for photon gas obeys } VT^3 = \text{const}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_T \propto T^4 \;\Rightarrow\; PV^{4/3} = \text{const for adiabatic}$$

consider clay arc kiln, $T \simeq 1500\,K$

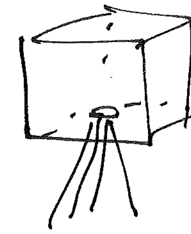
$$P = \frac{1}{3}\frac{U}{V} = \frac{8\pi^5 k^4}{15(hc)^3} \cdot T^4 \approx 10^{-3}\,Pa \quad \text{for } T = 1{,}500\,K$$

compare $P_{air} \approx 10^5\,Pa$, 10^8 bigger

in ~~stars~~ stellar cores, photon pressure can be comparable to gas pressure

$T \approx 10^{8}\,K$, $P \propto (10^4)^4$ bigger

Blackbody emission of warm opaque objects



Apply kinetic theory to equilibrium photon gas in box with hole, what is flux of energy ~~gas~~ from hole (effusion):

$$\Delta E = \underbrace{\left(A\, c \cos\theta\, \Delta t\right)}_{\Delta\tau} \cdot \left(\frac{U}{V}\right) \cdot \frac{\sin\theta\, d\theta\, d\varphi}{4\pi}$$

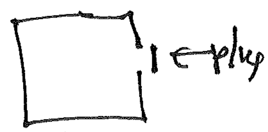
$$\frac{E}{A\Delta t} = \text{energy flux} = \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \left[\cos\theta \cdot \sin\theta \cdot \left(\frac{U}{V}\right) \frac{1}{4\pi} \cdot c\right]$$

power per area $\Rightarrow \dfrac{c}{4}\dfrac{U}{V}$ similar to $\frac{1}{4} n v$ formula w/ $v = c$

substitute $\dfrac{U}{V} = \dfrac{8\pi^5 (kT)^4}{15\,(hc)^3}$, get

$$\boxed{\text{power per unit area} = \sigma T^4, \quad \sigma = \frac{2\pi^5 k^4}{15\, h^3 c^2} \approx 6 \cdot 10^{-8}\, \frac{W}{m^2 K^4}}$$

Stefan's law of 1879, σ called Stefan-Boltzmann constant



Argument due to Kirchoff on p. 303 of Schroeder leads to conclusion that surface of warm opaque body must emit energy at same rate per unit area as flux

$$\boxed{\text{power emitted} = \sigma e A T^4}$$

e = emissivity = 1 blackbody
= 0 mirror

conclude:
- blackbody emits thermal spectrum of equil. radiation
- light isotropic
- light unpolarized
- homogeneous
- independent of material, shape

} by introducing filters of diff. kinds

Application of blackbody emission

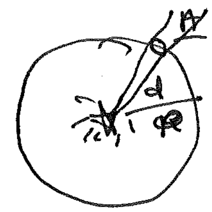
(1) radius of remote star

$$L = \text{luminosity} = \text{total power} = (4\pi R^2)\,[\sigma T^4]$$

I = light intensity measured on Earth

$$= \underbrace{\frac{\text{area sensor}}{4\pi d^2}}_{\substack{\text{fraction of emitted power} \\ \text{absorbed by sensor}}} \times (4\pi R^2)\cdot \sigma T^4$$

distance to star



Can solve for R from I, d, T; T known from Wien's law

(2) equil. temp. of planet or rock around Sun

$$(4\pi R_e^2)\,\sigma T_e^4 = (1-r)\,\frac{\pi R_e^2}{4\pi d^2_{sun\text{-}earth}}\left[4\pi R_{star}^2 \cdot \sigma \cdot T_{star}^4\right]$$

reflectivity of planet

$$\Rightarrow \quad T_e = (1-r)^{1/4}\sqrt{\frac{R_{star}}{d_{star\text{-}earth}}}\;T_{star}$$

independent of radius of planet!

calculation assumes no atmosphere, fast rotation so T constant over surface

	r	predicted	actual
Earth	30%	−16°C	15°C
Venus	75%	−40°C	470°C
Mars	12%	−56°C	−50°C
Moon	?	−2°C	125° day, −175° night

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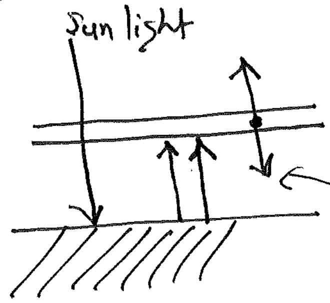
Deviation of equil. temp from prediction due to greenhouse gases H_2O, CO_2, CH_4

greenhouse is good: life couldn't otherwise exist, Earth would freeze



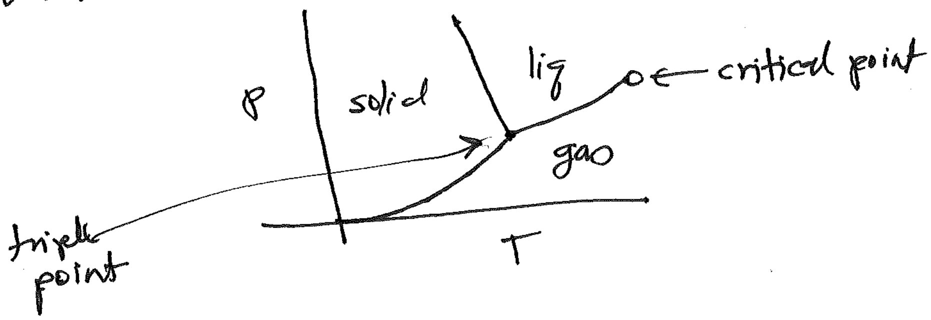
atmosphere absorbs infrared from warm ground and radiates out into space and back to ground.

so ground has to radiate twice as much power as amount from sun,

i.e. ~~power = ke~~ $2^{1/4}$ increase in T ✓

Section 5.3: Phase transition of pure substances.

when particles can interact, can get novel structure as T, P, B varied. Diff. rearrangements of same particles called <u>phases</u>



vocabulary: phase region   triple point
phase line   critical point
phase

solid → gas <u>sublimation</u>   gas → solid <u>deposition</u>

solid → liquid melting   liquid → solid <u>freezing</u>

liquid → gas vaporization   gas → liquid condensation

<u>critical point:</u> liquid-gas line ends, many remarkable properties near this point: no surface tension
high heat transport
increased solubility (remove caffeine)

<u>triple point</u>: 3 phases can coexist

(11)
4/21/17

show some slides:

H_2O phase diagram } can boil water with ice!

CO_2

iron-steel

He^3, He^4

Understanding phase boundaries via Gibb's free energy G

$$G = U - TS + PV$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$G = G(T, P, N)$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$ slope of G vs T curve gives S

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$ slope of G vs P curve gives V

$$G = N\mu$$

phase with smaller Gibbs free energy (chem. potential) is more stable and will be observed.

phase line occurs when chem. pots of two phases are equal

$$\mu_s = \mu_g \quad \text{or} \quad \mu_l = \mu_s \quad \text{or} \quad \mu_l = \mu_g$$

Example: graphite $\leftrightarrow$ diamond conversion

at atm pressure, for one mole of C atoms

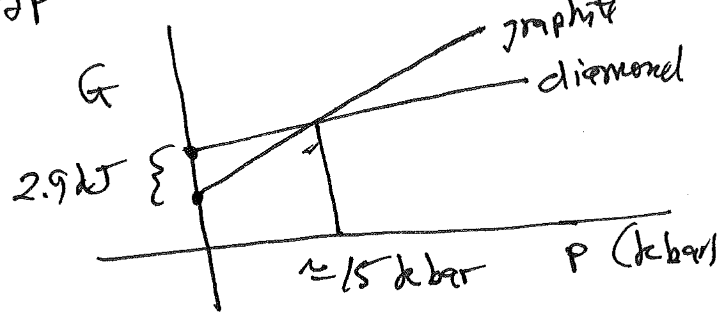
$$G_{graphite} < G_{diamond}$$

What about higher pressure?

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

$V_{graphite} > V_{diamond}$ for one mole (diamond denser)

$$\Rightarrow \quad \frac{\partial G}{\partial P}\text{ graphite} > \frac{\partial G}{\partial P}\text{ diamond}$$

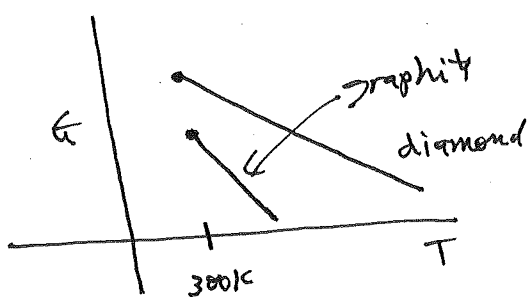


explain why diamonds form ~ 50 km underground

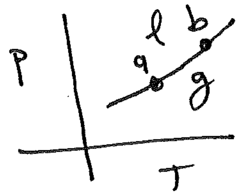
Similarly, $\quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$ $\quad$ $S_{graphite} = 5.7$ J/K $\quad$ $S_{diamond} = 2.4$ $\quad$ p. 404–405 Schroeder

$$\text{so } \left|\frac{\partial G}{\partial T}\text{ graphite}\right| > \frac{\partial G}{\partial T}\text{ diam}$$

conclude: increasing temp makes graphite more stable compared to diamond.



Clausius – Clapeyron eq. for phase boundaries



make <u>small</u> change <u>along</u> phase boundary

$$G_l^a = G_g^a$$
$$-\quad G_l^b = g_g^b$$
$$\Delta G_l = \Delta G_{gas}$$

$$dG = -SdT + VdP$$

$$-S_g dT + V_g dP = -S_l \Delta T + V_l \Delta P$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}}$$ Clausius – Clapeyron eq

often $V_g \gg V_l, V_s$ $\qquad S_g - S_l = \frac{L}{T}$

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \cong \frac{L}{T V_g}$$ $\qquad \Delta V = V_g - V_l \simeq V_g$

application: how to boil water with ice

$$\frac{\Delta P}{\Delta T} \approx \frac{L_{g-l}}{T \Delta V_{g-l}}$$

$L = 333\ J$
$V_{ice} = (917{,}000)^{-1}\ m^3 \approx 1.091 \cdot 10^{-6}\ m^3$
$V_{H_2O} = 1000 \cdot 10^{-6}\ m^3$

$$\frac{\Delta P}{\Delta T} \cong \frac{333}{273(-0.091 \cdot 10^{-6}\ m^3)} \approx -140\ \frac{bar}{K}$$

need to increase pressure by 140 bar to have ice melt at $-1^\circ C$
(<u>not</u> how ice skates work)