## Notes for today

- Reading: Today starting Ch. 3.

- Note <u>no</u> exam next week. (Originally 3 midterm exams in Howdy schedule).

- We have a midterm Oct. 29. More details on this later in the term.

**Formal structure of the thermodynamics relationships**:

$$\boldsymbol{U(S, V, N_1, N_2 \ldots)}$$

- *r* distinct particle types makes *r*+2 parameters.
- We *can* change coordinates if desired; e.g. T, P, N also serves to specify 1-component system in large-N limit.
- We also obtain *r*+2 eqns. of state (intensive quantities.):

$$T = \left(\frac{\partial U}{\partial S}\right)_{VN},\ -P = \left(\frac{\partial U}{\partial V}\right)_{SN},\ \mu = \left(\frac{\partial U}{\partial N}\right)_{SV}$$

- Having all *r*+2 eqns. of state completely determines the function $U(S, V, N_1, N_2 \ldots)$ [or $S(U, V, N_1, N_2 \ldots)$ ]; this will always work.
- However one more relation among the intensive parameters (Gibbs-Duhem) means actually *r*+1 degrees of freedom *to determine fundamental equation*.

**Formal structure of the thermodynamics relationships**:

$U(S, V, N_1, N_2 \ldots)$ vs $dU = TdS - PdV + \mu dN$:

$$\lambda U(S, V, N_1, N_2 \ldots) = U(\lambda S, \lambda V, \lambda N_1, \lambda N_2 \ldots)$$

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$$\boxed{U = TS - PV + \mu N}$$

*Euler equation*, distinct from *first law*; general property comes from extensivity behavior.

- From this result, establish that r+2 equations completely determine thermal properties.
- Similar $S(U,V,N_1,N_2 \ldots)$ relation, see text.

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Example from HW1:

$S = \alpha V^{1/4} U^{3/4}$ (Blackbody radiation)

Find $T$ & $P$ relationships?

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Means: $$dU = TdS - PdV + \mu dN$$

And: $$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

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$$SdT - VdP + Nd\mu = 0$$

Gibbs-Duhem relation

or $SdT - VdP + \sum N_i \, d\mu_i = 0$

*r*+1 degrees of freedom can see

**Formal structure of the thermodynamics relationships**:

$$SdT - VdP + \sum N_i \, d\mu_i = 0$$ Gibbs-Duhem relation

- Can integrate to find e.g. $\mu$ in terms of other parameters.

Thus 2 (or *r*+1) equations of state are sufficient.

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$$U = U(S, V, N)$$

$$\longrightarrow \quad u \equiv \frac{U}{N} = U(s, v) \qquad v \equiv \frac{V}{N} = \frac{1}{n} \qquad s \equiv \frac{S}{N}$$

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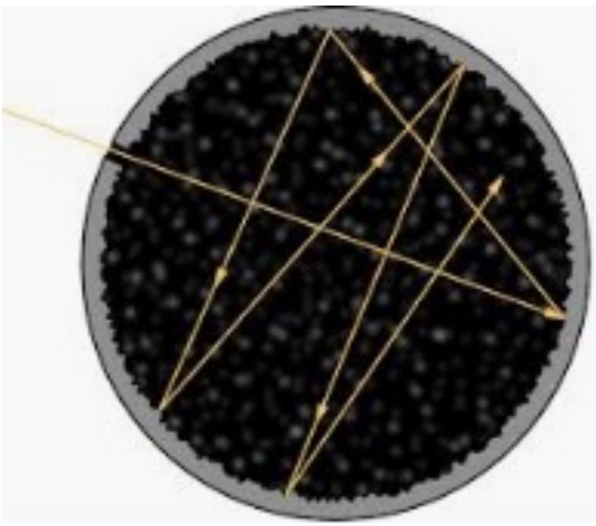
$PV = Nk_BT, U = \frac{3}{2}Nk_BT;$ find $s$?

## Blackbody Radiation



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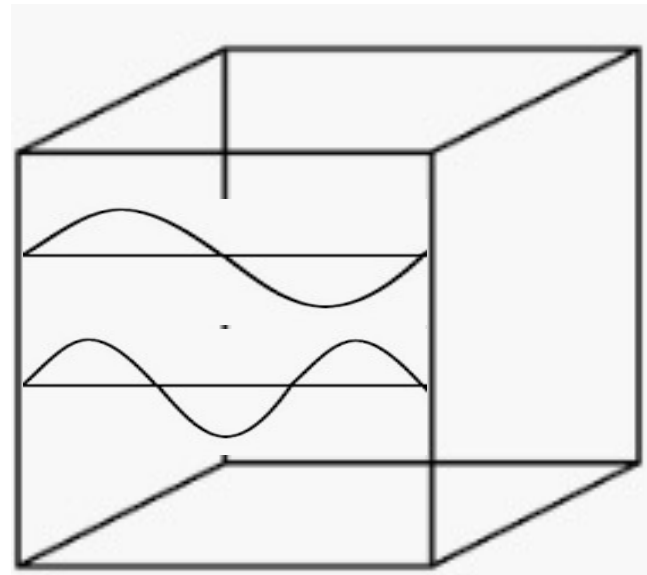


- Cavity with perfect emissivity walls
- Measure output through tiny non-perturbing aperture.

- Cavity mode, perfect conducting walls
- Each normal mode equivalent to “simple harmonic oscillator”

# Blackbody radiation, thermodynamic solution

- Experimental quantities:

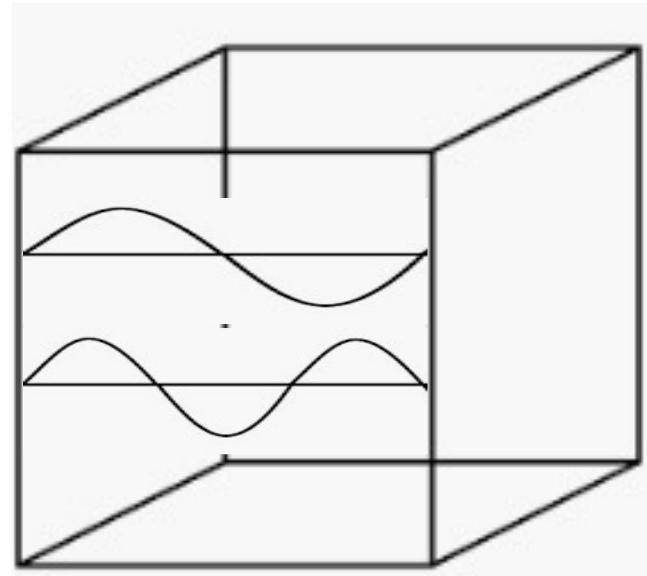
$$U = bVT^4$$

$$P = U/(3V)$$

*$I = \sigma T^4$ Stefan-Boltzmann intensity relation*

- Then can easily solve for $S = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}$, using methods we have seen.
- Also note, $S = \frac{4U}{3T}$ simpler form.
- Note $N$ is formally zero (or can treat $N$ as number of photons; $\mu = 0$ since $U$ independent of $N$).

Absorbers& emitters in walls maintain thermal equilibrium
EM standing waves equivalent to set of harmonic oscillators:



- Cavity mode, perfect conducting walls, electric field solutions

$$E_x(x,y,z) = E_0^{(x)} \cos[n\,\pi\,x/L_x]\,\sin[m\,\pi\,y/L_y]\,\sin[l\,\pi\,z/L_z]$$
$$E_y(x,y,z) = E_0^{(y)} \sin[n\,\pi\,x/L_x]\,\cos[m\,\pi\,y/L_y]\,\sin[l\,\pi\,z/L_z]$$
$$E_z(x,y,z) = E_0^{(z)} \sin[n\,\pi\,x/L_x]\,\sin[m\,\pi\,y/L_y]\,\cos[l\,\pi\,z/L_z]$$

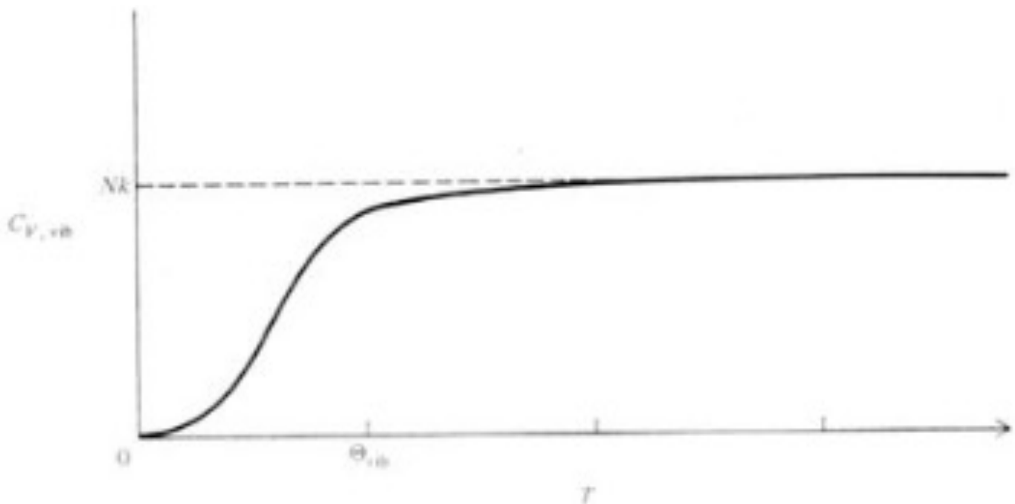
See E&M book

- 3 pre-factors must solve Maxwell equations; 2 solutions for each *n, m, l* = TE and TM standing waves.
- Possible modes fill up one octant in "wave-number space"
  (except some modes not allowed: 100, etc.)

## Counting photon states: recall harmonic oscillator result

(3N independent 1D oscillators)

$$U = N\frac{\hbar\omega}{2} + N\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$



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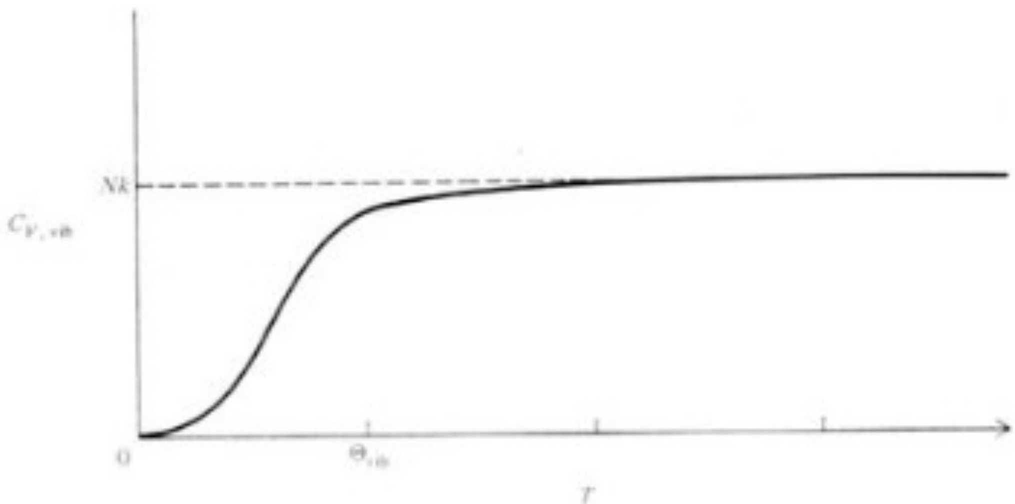



Same as Bose-Einstein occupation number (photon statistics)

$$\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \equiv \hbar\omega\langle n\rangle$$

**Photons:** Quantized cavity modes.

$$\langle n \rangle = \sum_{all\ modes} \frac{1}{(e^{\beta \varepsilon_i} - 1)}$$

$\varepsilon_i \equiv \hbar\omega_i = \hbar k_i c$

"energy per photon"

• 2 polarizations, for each cavity mode
N goes to infinity

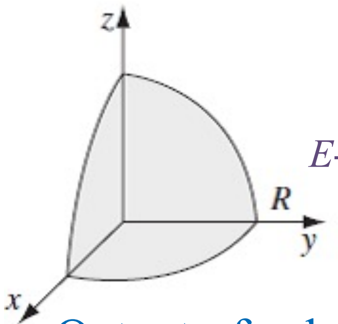
Bose distribution with photon statistics

$$U = \sum_{all\ modes} \frac{\hbar\omega_i}{(e^{\beta\hbar\omega_i} - 1)}$$

• Throwing away *infinite* amount of zero-point energy!

## State counting:

- Start with cavity modes in a box with perfectly conducting sides, dimensions $L$.




$$E_x \propto cos\left(n_x \frac{\pi}{L} x\right) sin\left(n_y \frac{\pi}{L} y\right) sin\left(n_z \frac{\pi}{L} z\right) \text{ etc.}$$

*E*-field

Cavity mode Counting: one TM + one TE per k-vector

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

"Phase space volume" $h^3/8$

Octant of sphere;
but with 8× state density.
(3D sphere radius will go to infinity)