Notes:

Exam: You can make up some points:

1. Choose 2 problems; blank exam is posted.
2. Work out the solutions from scratch on your own.
3. Turn in the problems by Thursday in class or Friday afternoon 3:30-4 PM; I will arrange be at my office or you can email if necessary. Not in my mailbox
4. You will get 60% of the made-up points back.

Homework: Problem set 8 due Tomorrow. I am looking for volunteers for problems 1 and 2 for Thursday presentation.

Reading: This week we continue with <u>chapter 16</u> (continuum systems densities of states; Debye model for vibrations). Next up, phase transformations (chapters 8-9).

Canonical ensemble Recall:

Partition function

$$Z = \sum_{states\ i} Exp[-E_i/kT]$$

$\Longrightarrow$

$$F \equiv -k_B T lnZ$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} lnZ$$

Etc ….

Last time: Z as a product for independent sub-systems, e.g.:

$$Z = \frac{1}{N!} \prod_i Z_i$$

Equipartition theorem

- Classical systems (continuum not discrete energies)
- Works in cases having separable variables.
- Requires energy quadratic in position and/or momentum: $E = cq^2$

$$Z = \frac{1}{h^{3N}} \iiint d^{3N}r\, d^{3N}p\, e^{-\beta E}$$ ← $Z = \prod_i Z_i$; includes all cross terms.

Classical partition function

systems of distinguishable particles, non-interacting.

or:

$$Z = \frac{1}{N!} \prod_i Z_i$$

systems of **indistinguishable** particles, still non-interacting case.

Result:

$$U = \frac{f}{2} kT$$

(1/2)*kT* for each "degree of freedom" *f*.

Harmonic oscillator systems (N independent 1D oscillators)

$$U_i = \frac{\overrightarrow{p_u}^2}{2m} + \frac{\kappa \vec{u}^2}{2} \quad \text{or} \quad U_i = \frac{p^2}{2m} + \frac{\kappa u^2}{2}$$

c.m. coordinates
& reduced mass

Vibrational term in product-form partition function, Z:

$$Z_{vibr} = \left(\frac{1}{h} \iint dpdue^{-\beta\left(\frac{p^2}{2m} + \frac{\kappa u^2}{2}\right)} \right)^N$$

N independent oscillators (Einstein solid approximation, ideal gas molecules, etc.) all with same $\omega = \sqrt{\kappa/m} =$ "ω_0"

$$Z_{vibr} = \left(\frac{kT}{\hbar\omega}\right)^N \qquad \langle E \rangle = NkT$$

effectively $f = 2$

Equipartition theorem:

- Classical systems (continuum not discrete energies)
- Works in cases having separable variables.
- Requires energy quadratic in position and/or momentum (or other coordinate)
- Vibrations, rotations, translational states. Rotational case in text, won't show here.

Harmonic oscillator systems (N independent 1D oscillators)

$$U_i = \frac{\overrightarrow{p_u}^2}{2m} + \frac{\kappa \vec{u}^2}{2} \quad \text{or} \quad U_i = \frac{p^2}{2m} + \frac{\kappa u^2}{2}$$

c.m. coordinates
& reduced mass

Vibrational term in product-form partition function, *Z*:

$$Z_{vibr} = \left(\frac{1}{h} \iint dp du e^{-\beta\left(\frac{p^2}{2m} + \frac{\kappa u^2}{2}\right)} \right)^N$$

$$Z_{vibr} = \left(\frac{kT}{\hbar\omega} \right)^N \qquad \langle E \rangle = NkT$$

classical-limit solution

Quantum version / general case:

$$Z_{vibr} = \prod_i Z_i = \left(\sum_{n=0}^{\infty} e^{-\beta n \hbar \omega} \right)^N$$

Harmonic oscillator systems (N independent 1D oscillators)

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$$

Quantum vibrational partition function

$$Z_{vibr} = \prod_i Z_i = \left(e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} \right)^N = e^{-\frac{\beta\hbar\omega N}{2}} \left[\frac{1}{1 - e^{-\beta\hbar\omega}} \right]^N$$

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

zero point term no effect on entropy

- Z shown with zero point motion term.
- Indistinguishable cases: we grouped $1/N!$ factor with Z_{trans} last time.
- Equivalent to "$3N + q - 1$" counting method for fixed-U case, large-N limit.
- Here, easy to extend to a distribution of <u>different</u> oscillator frequencies.

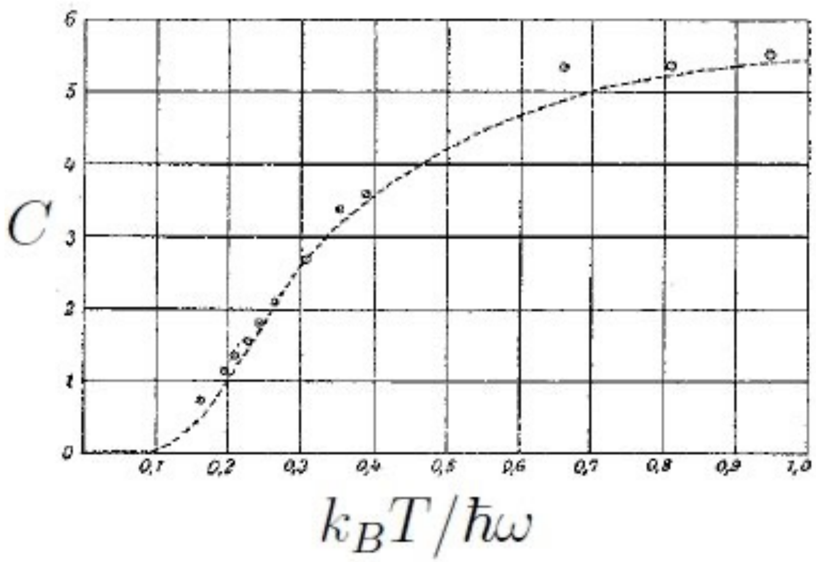
$$\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \equiv \hbar\omega \langle n \rangle$$

$\langle n \rangle$ = Bose-Einstein occupation number (photon statistics) we saw before, derived using S & U to find T.

Harmonic oscillator systems (N independent 1D oscillators)

Quantum version

$$Z_{vibr} = \prod_i Z_i = \left(e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}\right)^N = e^{-\frac{\beta\hbar\omega N}{2}} \left[\frac{1}{1 - e^{-\beta\hbar\omega}}\right]^N$$



Einstein Ann Phys 1907 [for solids; $3N$ identical oscillators. Specific heat of diamond fit to ω = 1310 K.]

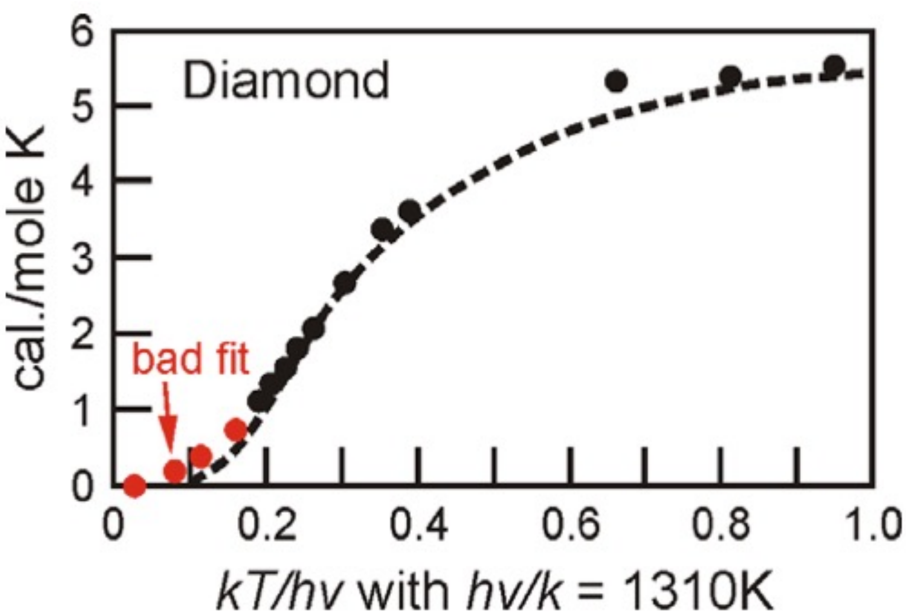
$$\langle E \rangle = \frac{\hbar\omega N}{2} + N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

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

Harmonic oscillator systems (N independent 1D oscillators)

Quantum version

$$Z_{vibr} = \prod_i Z_i = \left(e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}\right)^N = e^{-\frac{\beta\hbar\omega N}{2}} \left[\frac{1}{1 - e^{-\beta\hbar\omega}}\right]^N$$



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

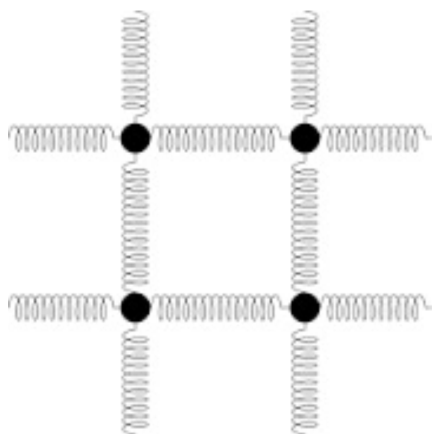
$$\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \equiv \hbar\omega\langle n \rangle$$

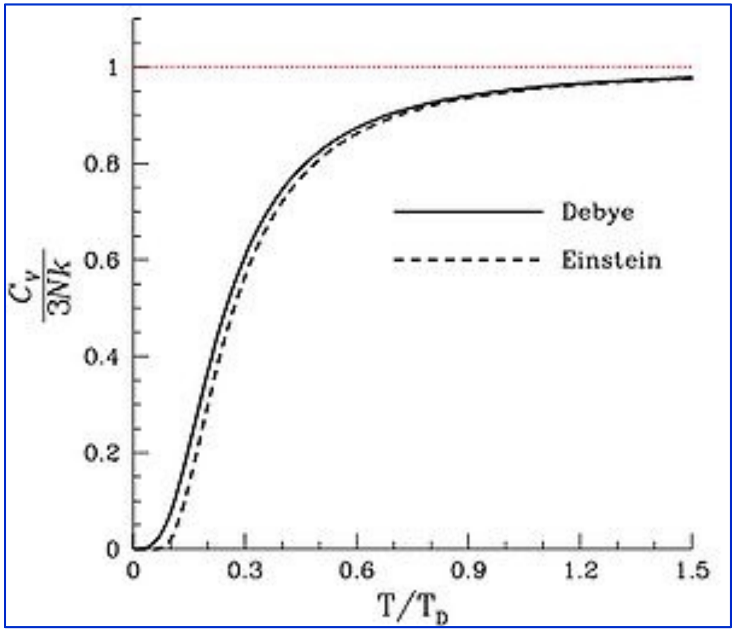
Debye model: T^3 behavior at low T agrees well with data.

<< assumes a specific distribution of vibrational frequencies (normal modes).

Phonons: **quantized lattice vibrations in crystals.**

- Liquids and non-crystal solids: have similar modes.
- **Einstein**: independent 3D oscillators, same ω_o.
- **Debye**: Phonons are normal modes in a *connected* harmonic lattice.
- Debye-theory solutions identical to sound waves , $\omega = kc$ (exact in low-frequency limit); also map onto blackbody-radiation photons.





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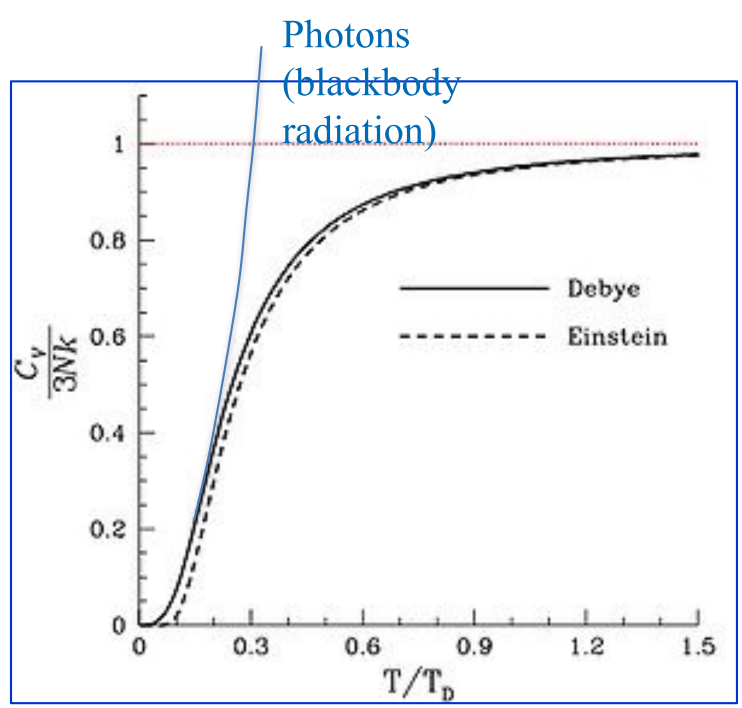
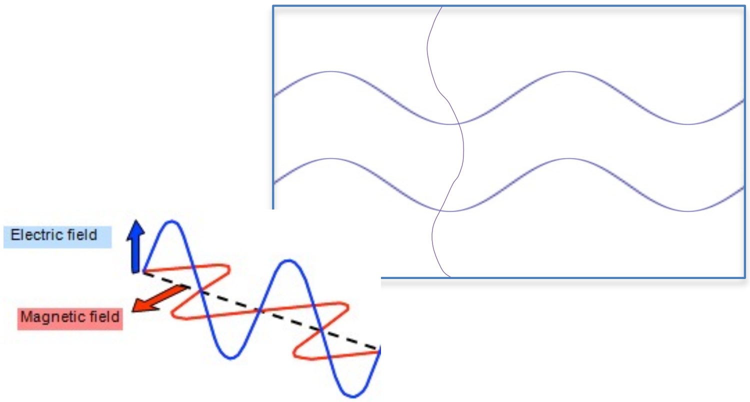
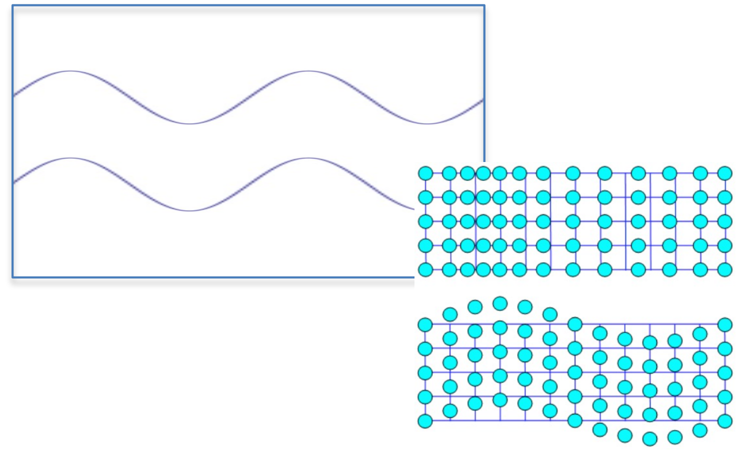
- Debye-theory solutions identical to sound waves , $\omega = kc$ (exact in low-frequency limit); also map onto blackbody-radiation photons.
- Except: mode counting requires finite number of phonon modes, and 3 polarizations, not 2.



Photons vs. Phonons:





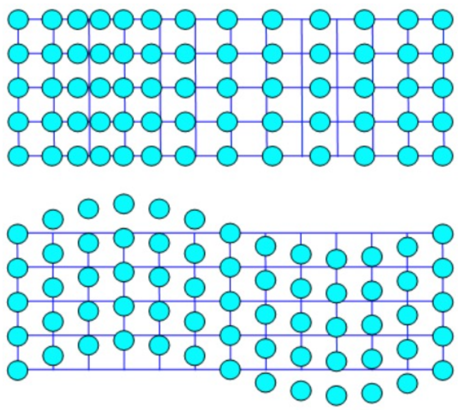
Photons:

- Cavity modes
- 2 polarizations
- $\omega = kc.$
- Extend to $\omega \to \infty$.
- $e^{-i\vec{k}\cdot\vec{r}-\omega t}$ free space solution
- Bose statistics ($\mu = 0$).
- Energies quantized, $\hbar\omega(n + \frac{1}{2})$.
- Speed of <u>light</u>: c.

Phonons:

- elastic (standing) waves
- **3 polarizations**
- $\boldsymbol{\omega \cong kc}$**, exact for low** $\boldsymbol{k}$
- **Bounded: *N* values of *k*.**
- $e^{-i\vec{k}\cdot\vec{r}-\omega t}$ [or $\sin(\vec{k}\cdot\vec{r})\sin(\omega t)$]
- Bose statistics ($\mu = 0$).
- Energies quantized, $\hbar\omega(n + \frac{1}{2})$.
- Speed of <u>sound</u>: c

Phonons & mode counting:



1) General elastic solid (isotropic case): wave equation

$$\ddot{\mathbf{u}} = \underbrace{\alpha^2 \nabla(\nabla \cdot \mathbf{u})}_{P\ wave} - \underbrace{\beta^2 \nabla \times (\nabla \times \mathbf{u})}_{S\ wave}$$

has wave solutions, $\omega = kc$.
(actually may have 2 or more frequencies)

2) Quantization of energies: won't show this; result is analogous to familiar SHO solution in quantum mechanics,

$$E = \hbar\omega(n + \tfrac{1}{2}).$$

3) Wave-vector cutoff: maximum wavenumber ~ frequency in THz range

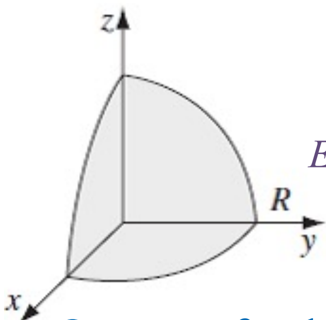
⇩

N *k*-vectors in 1D, leads to a cutoff for phonon wavenumber.

3*N* total phonon modes in general 3D crystal.

State counting: I showed this slide before for *photons*.

- 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

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

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

One k-vector per volume element; same as "Phase space volume" $h^3/8$

Consider continuum limit (large cavity, very small Δk)
Also recall $\omega = kc$

Mode counting directly in k-space (similar to number space for Einstein summation, ch. 15)

photons

$$U = \sum_{all\ modes} \frac{\hbar\omega_i}{(e^{\beta\hbar\omega_i} - 1)} \Longrightarrow 2\int_0^\infty \frac{\pi}{2}\frac{Vk^2dk}{\pi^3}\frac{\hbar kc}{(e^{\beta\hbar kc} - 1)}$$

\# modes in thin shell, thickness $dk = d\omega/c$

Density of states: for summations involving only ω (or E).

Example for energy sum:

$$U = \sum_{all\ modes} \frac{\hbar\omega_i}{(e^{\beta\hbar\omega_i} - 1)} \Longrightarrow 2\int_0^\infty \frac{\pi}{2}\frac{Vk^2dk}{\pi^3}\frac{\hbar kc}{(e^{\beta\hbar kc} - 1)}$$

modes in thin shell, thickness $dk = d\omega/c$

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photons

$$U = \sum_{all\ modes} \frac{\hbar\omega_i}{(e^{\beta\hbar\omega_i} - 1)} \Longrightarrow 2\int_0^\infty d\omega \times \left(\begin{matrix} \#states \\ in\ (\omega, \omega + d\omega) \end{matrix}\right) \times \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)}$$

$$\equiv \int_0^\infty \frac{\hbar\omega D(\omega) d\omega}{(e^{\beta\hbar\omega} - 1)}$$

$\Delta k = \frac{\pi}{L}$ -> $V_k = \left(\frac{\pi}{L}\right)^3$ for <u>octant</u>;

$= \left(\frac{2\pi}{L}\right)^3$ for <u>complete sphere</u> traveling-waves