Notes:

Homework : Set #9 due Thursday. Looking for volunteers, for problems 2, 4, 6. (note, now extended to next Tuesday.)

Next week : I have a Wednesday jury duty call. It is likely I won’t get picked to serve, but watch for an announcement before class just in case.

Also I have an unidentified HW8 paper. If you think it is yours let me know.

Formal structure of the thermodynamics relationships:

Showed before

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

- *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:

Showed before

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

- Can integrate to find e.g. μ in terms of other parameters.

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

- Nice trick when $r = 1$: per-atom (or molar) relations.

$$u \equiv \frac{U}{N} = U(s, v) \longrightarrow \boxed{du = Tds - Pdv}$$

similar result for *dS*

Phonons: Note about high-*T* limit

$$\omega_D = c\left(6\pi^2 \frac{N}{V}\right)^{1/3}$$

continuum limit

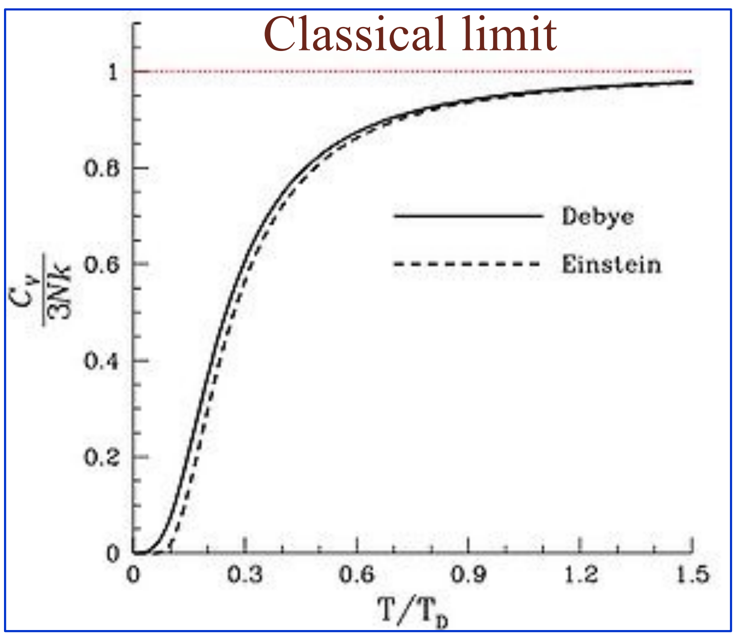
$$\langle E\rangle = \sum_{all\ modes} \frac{\hbar\omega_i}{(e^{\beta\hbar\omega_i}-1)} \Rightarrow \int_0^{\omega_D} \frac{3V\hbar\omega^3 d\omega}{2\pi^2 c^3 (e^{\beta\hbar\omega}-1)}$$

$$\langle E\rangle = \frac{V\pi^2 (kT)^4}{10(\hbar c)^3}$$

low T limit (*exact result*)
c = speed of sound (or *directional average*)

$$\text{Low-}T\ C_V = \frac{12}{5} N\pi^4 k_B \left(\frac{T}{\Theta_D}\right)^3 \qquad \Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar c}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Debye Temperature



high T: can solve integral numerically. Generally good agreement, Debye theory commonly used to model thermal behavior of solids. And reproduces expected $C = 3Nk_B$.

Copper $\Theta_D = 315$ K
Lead $\Theta_D = 88$ K
Diamond $\Theta_D = 1860$ K

Debye approximation: Commonly used as measure of phonon behavior (even when "real" behavior of crystal can be obtained)

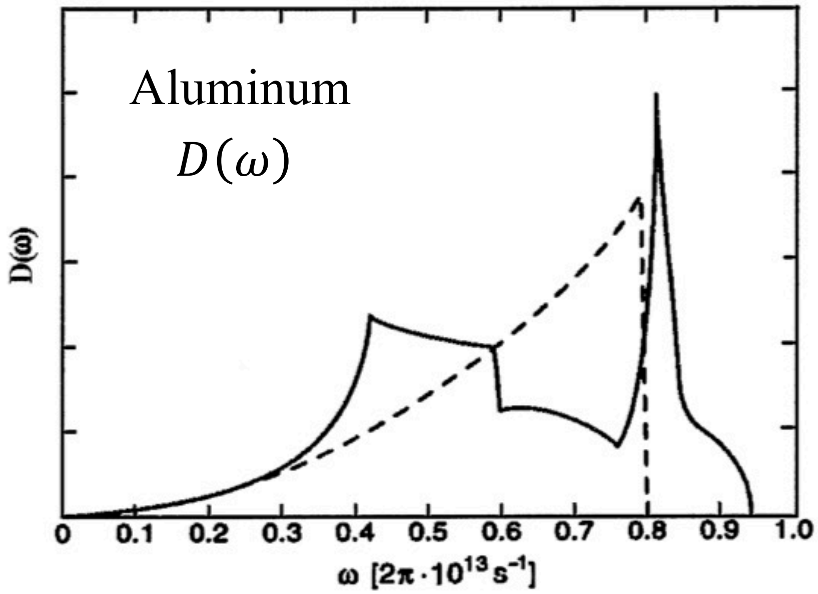
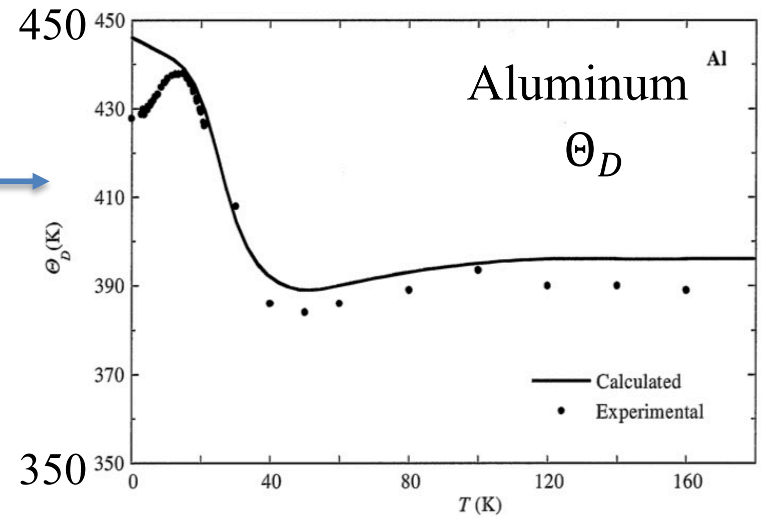
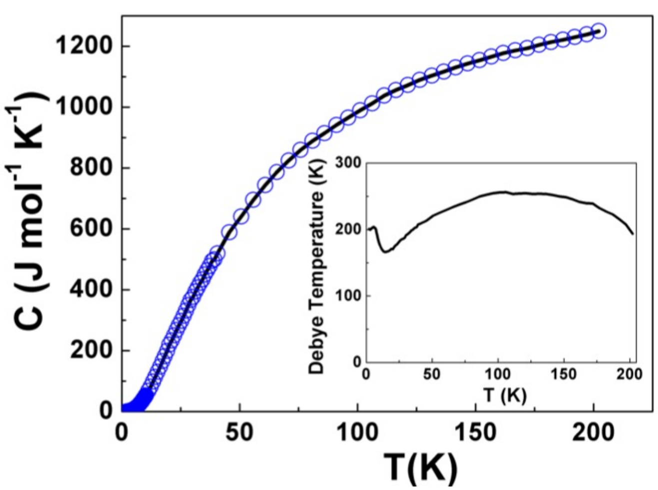
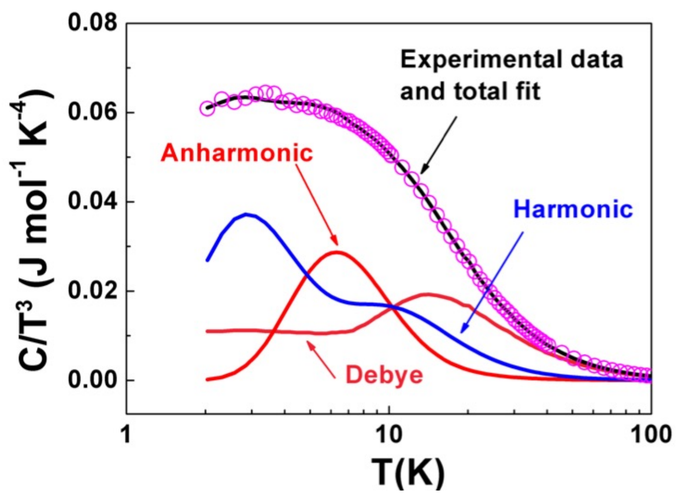


Figure 2.9. The density of frequency modes for Al at 300K (solid line) obtained by Walker [30] and that for the Debye model (dashed lines)



from "The Specific Heat of Matter at Low Temperatures" [Tari, 2003].

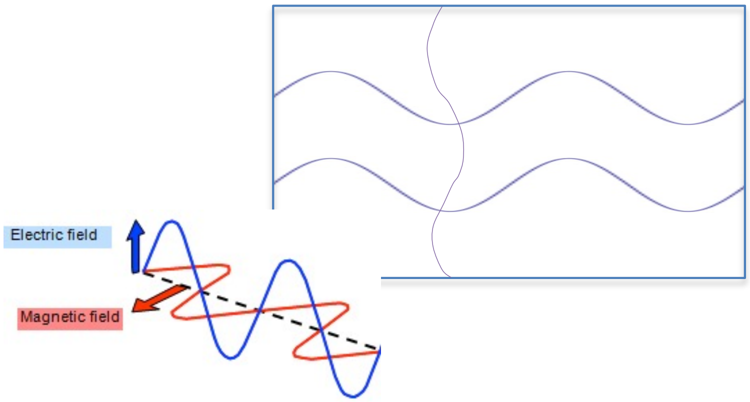


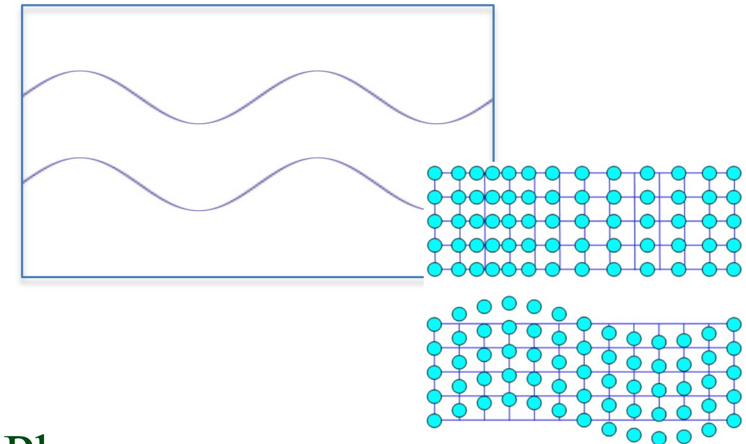


X Zheng et al. Phys. Rev. B 85, 214304 (2012) [my lab]:

<u>Specific heat</u> of thermoelectric crystal.

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 light: c.

$D(\omega) = \frac{2}{3} \times \frac{3\omega^2 V}{2\pi^2 c^3} = \frac{\omega^2 V}{\pi^2 c^3}$ exact in vacuum

Phonons:

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

$D(\omega) = \frac{3\omega^2 V}{2\pi^2 c^3}$ Debye model

Photons; summations and state variables:

$$Z = \prod_{all\ modes} Z_i = \prod_{all\ modes} \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega_i} = \prod_{all\ modes} \frac{1}{1 - e^{-\beta \hbar \omega_i}}$$

Z_i, but for *modes* not atoms or particles.
Similar for other oscillatory excitations.

$$F = -kT \ln(Z) = \sum_{all\ modes} \frac{-kT}{(1 - e^{-\beta \hbar \omega_i})}$$

can be solved using $D(\omega)$ integration, as long as cavity large enough/T not too small.

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = \left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad U = F + TS$$

Differentiate F to obtain Entropy, pressure, etc. (HW)
<u>All state variables</u> can be obtained based on a sum over modes.

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$$F = \int_0^{\infty} \frac{-kTD(\omega)d\omega}{(1-e^{-\beta\hbar\omega})} = \int_0^{\infty} \frac{-kTV\omega^2 d\omega}{\pi^2 c^3 (1-e^{-\beta\hbar\omega})}$$

(updated: what I originally displayed in class was mis-written.)

Photon result, F = const. $\times\ T^4$

From before

- State equations:

$$U = bVT^4$$
$$P = U/(3V)$$

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

P was previously quoted from experiment; now know that we can obtain it from Free energy.

- 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.

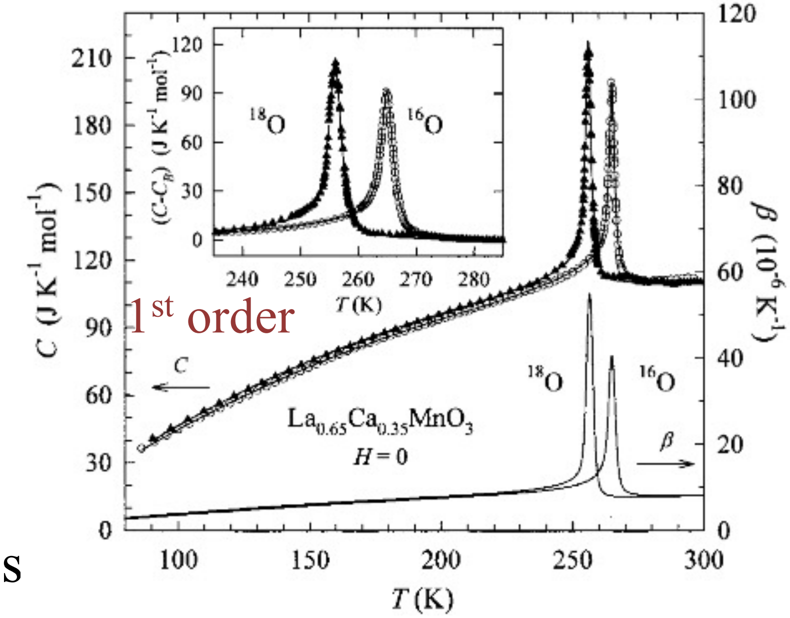
$S \cong 3.6 \langle N \rangle k_B$

- Note *N* is formally zero (or can treat *N* as number of photons; $\mu = 0$ since *U* independent of *N*).

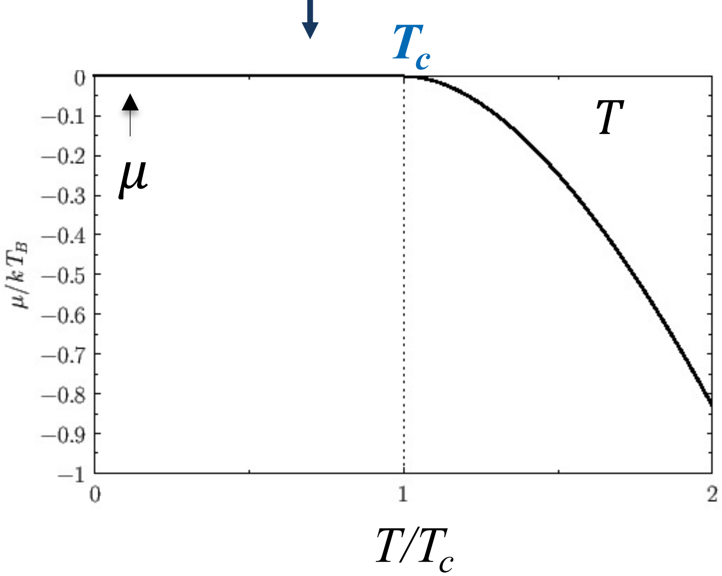
Interesting result, $PV \approx NkT$

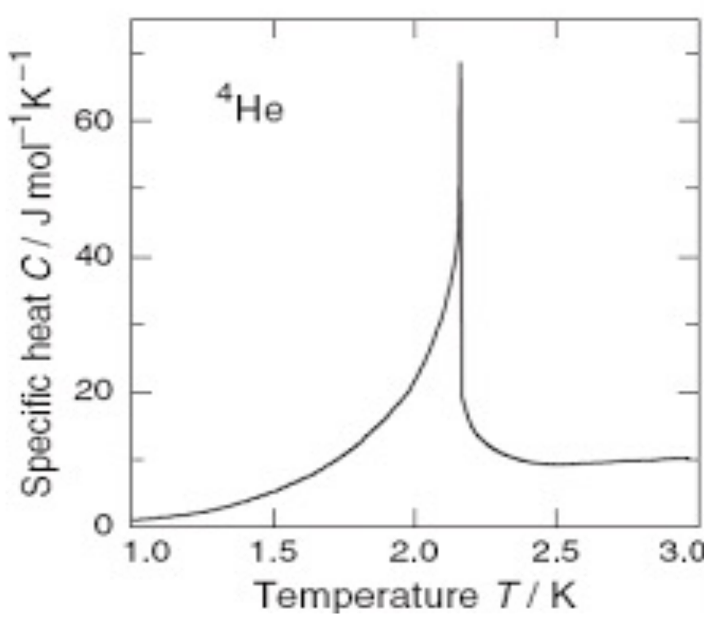
1st order phase transitions (chapter 9, also read ch. 8).

First order (discontinuous) phase transitions:
G continuous, other quantities not.
Jump in measured quantities
Hysteresis effects + Latent heat



Second order (continuous) phase transition:
G first derivative continuous
Continuous change in some measured quantities
Critical fluctuations.





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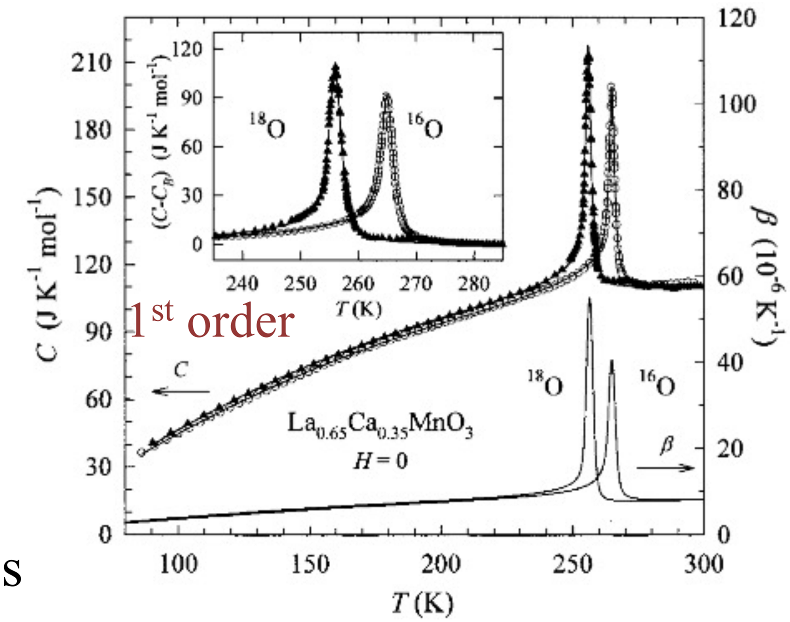

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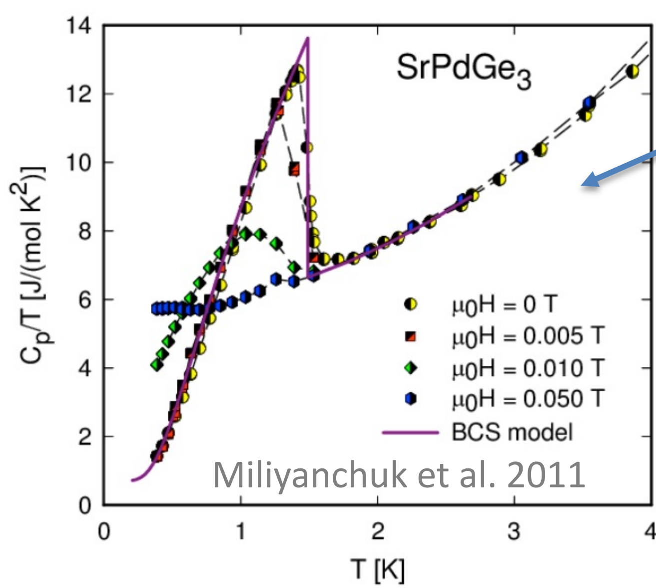
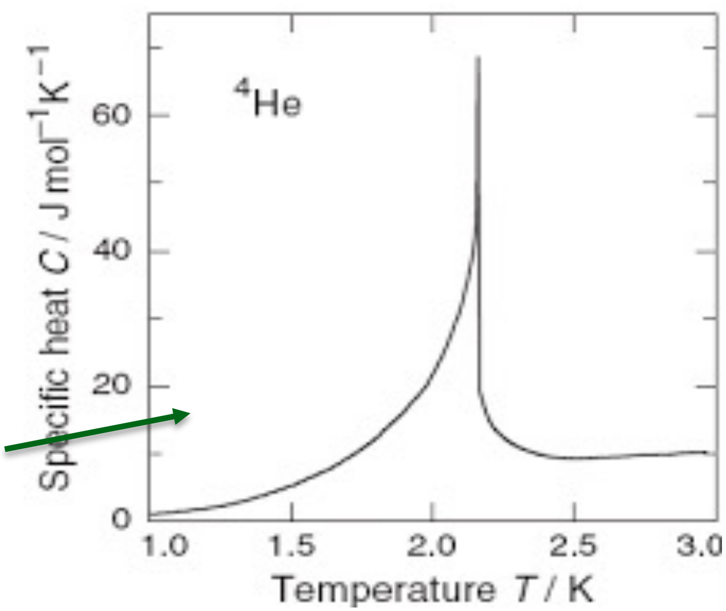


Superconductor, classic 2nd order for $H = 0$

3He, 2nd order with critical fluctuations near Tc:

$$C \propto |T - T_C|^{-\alpha}$$



1st order Transformations:

- Consider P and T to be fixed, then find equilibrium.
- Gibbs free energy minimized.
- Phase transformation due to *instability in G vs external parameters*.