



Why Statistical Mechanics?

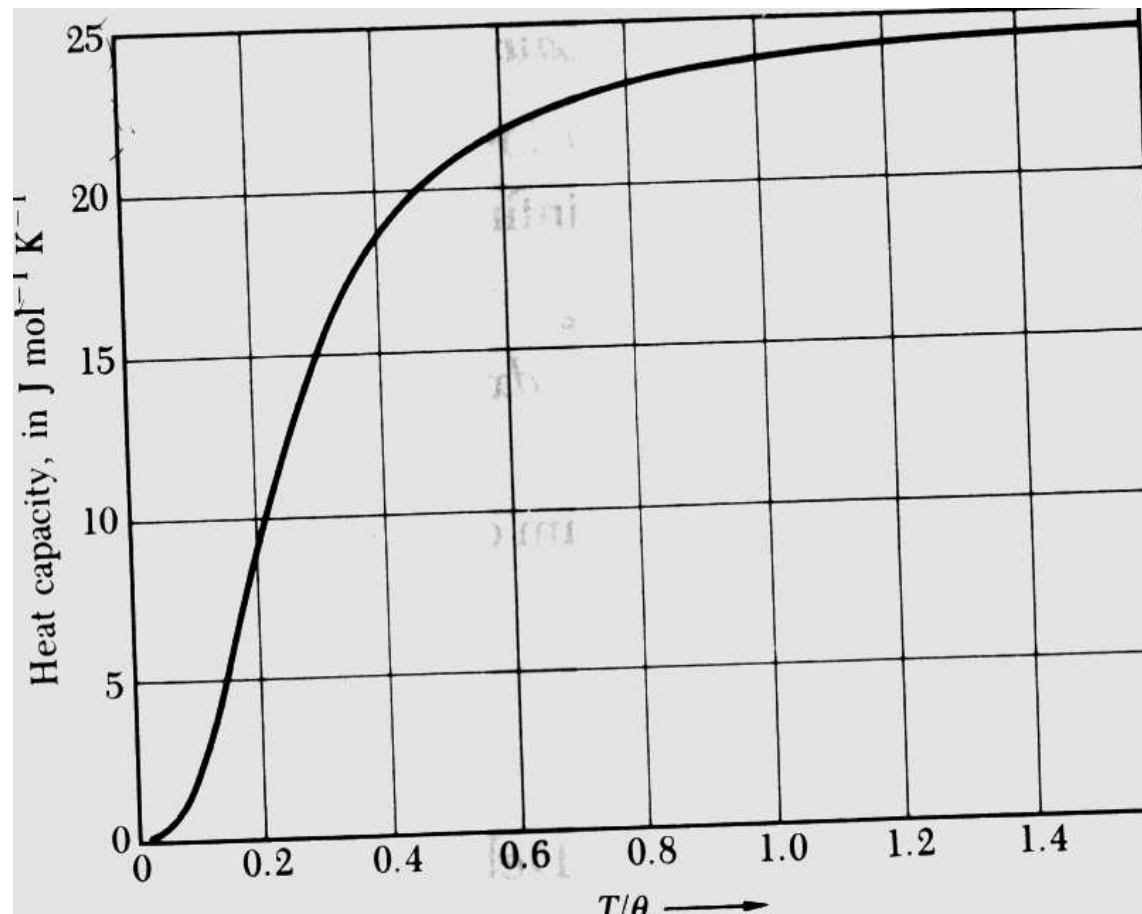


Why Statistical Mechanics?

- Material properties depend on temperature!
- Indeed, there are phase transitions (solid-liquid, ferro-para etc.)
- Conductivity of a metal decreases with T , but reverse for semiconductors...
- Can we understand this?
- More precisely, if we are AASs, how can we predict how properties will depend on temperature if we know the “microscopic Hamiltonian”
- But, first let us look at some examples...

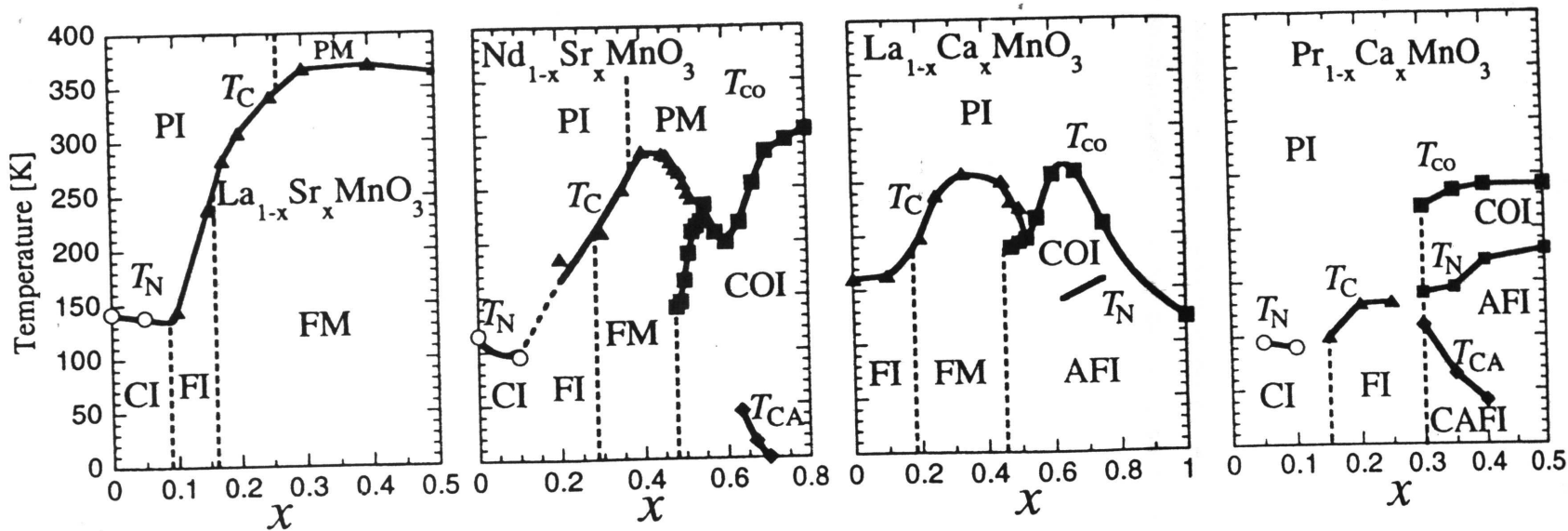
Good Ol' Specific Heat

- Why is high- T specific heat equal to $3R$? And why does it drop to zero?



(Kittel)

And the Exotic Manganites!



(Tokura

- There are Ferro-Para, Metal-Insulator, and What have you! Explain this, huh?



And, Where Do We Start?

- A material contains electrons (M) and the nuclei (N)
- The “exact” Hamiltonian is

$$H_{exc} = \sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{\alpha=1}^M -\frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 + \frac{1}{2} \sum_{\alpha=1}^N \sum_{i=1}^M -\frac{Z_{\alpha} e^2}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} \\ + \frac{1}{2} \sum_{i=1}^M \sum_{j \neq i}^M \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\alpha=1}^M \sum_{\beta \neq \alpha}^M \frac{Z_{\alpha} Z_{\beta} e^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}$$

- Goal: Determine the eigenstates $\Psi_n(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{r}_1, \dots, \mathbf{r}_M)$ that solves $H_{exc} \Psi_n = E_n \Psi_n$
- Impossible goal...and a very intelligent one!
- Need approximations...intelligent ways to solve problems under certain restrictions...



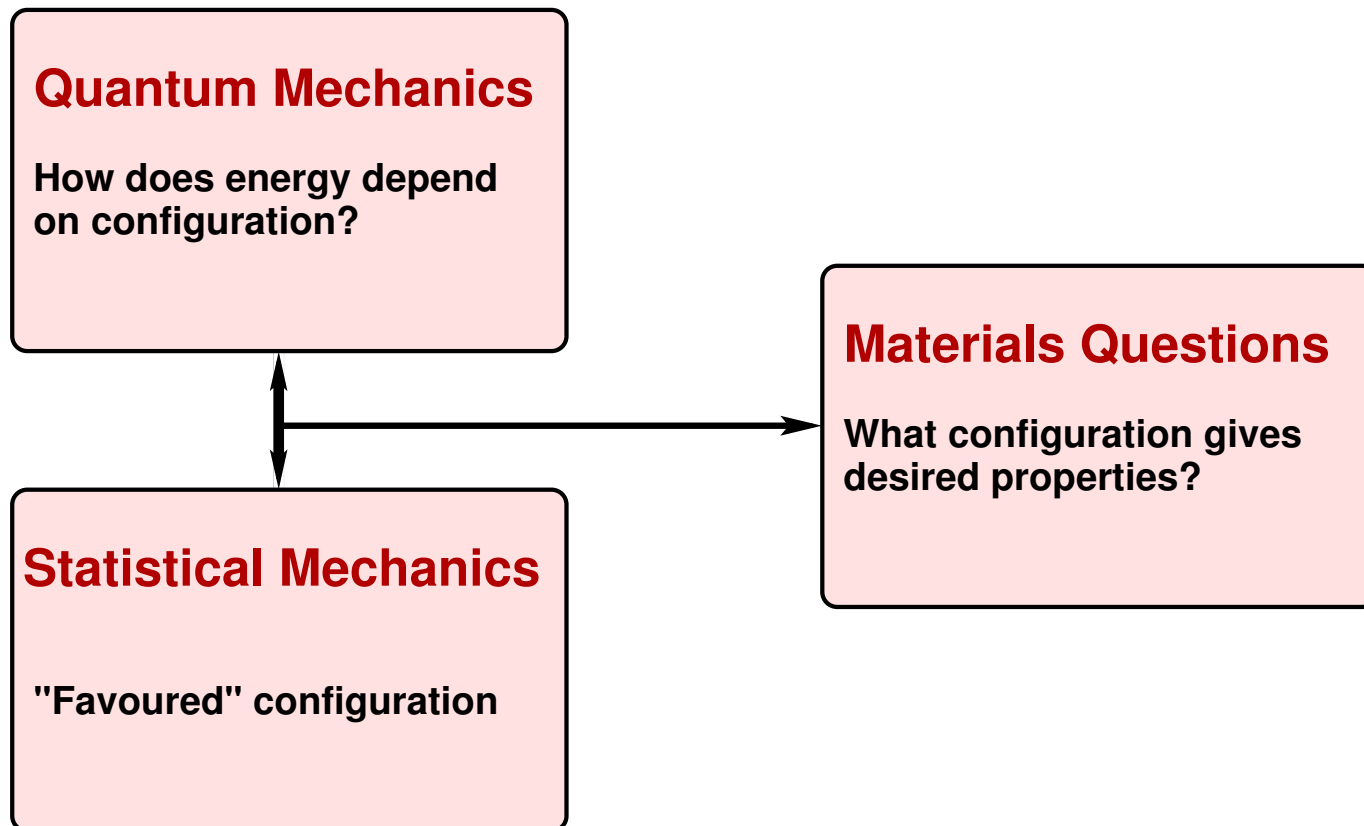
Approximations and Outcome

- Free electron picture...keep only electronic kinetic energy
- Independent electron picture...keep ions fixed, electrons feel ions, but not other electrons
- ...
- Treat full problem in QM, keeping only important terms
- Outcome: Energy as a function of CONFIGURATION
- Configuration means many things...atomic arrangement, electronic structure etc. Understand this with hydrogen molecule..
- What configuration is chosen at at given temperature?



Materials Science – The Grand Scheme

- **Material:** Atoms in a particular configuration
- **Properties:** Which atoms? What configuration?
- **The Scheme of Materials Design**





Thermodynamics

- Observations on many systems starting from steam engines to superfluids have taught us a few things...and surprisingly few common things regarding macroscopic observables
- These empirical laws have been codified as the Laws of Thermodynamics
- They seem to work pretty well...especially for “large” systems...in thermodynamic limit
- Roughly, thermodynamic limit means that $N/V \rightarrow \text{finite}$ but both N and V go to infinity
- In fact there are only few exceptions so far, but more are likely to come with “Nano-revolution”
- But, not to worry, these are not “Laws” as we shall



Laws of Thermodynamics

- **Zeroth Law: Concept of Equilibrium...** If A is in equilibrium with B , B with C , then A is in equilibrium with C (Temperature)
- **First Law: Energy is conserved in any “process” ...** “Heat” (Q) is equivalent to work (W)... $dU = dQ - dW$
- **Second Law: There is “something” called entropy S .** In any process $\int_1^2 \frac{dQ}{T} \leq S(2) - S(1)$... Isolated systems can change in only ways that increase entropy
- **Where do these laws come from? What is entropy?**



Thermodynamic Potentials

- **First Law + Second Law implies**
$$dU = TdS - PdV + \mu dN$$
- **Macroscopic observables (state) $(P, V); (T, S); (\mu, N)$**
- **Second law tells us that an isolated system goes to a state of maximum entropy...the entropy is the appropriate thermodynamic potential $S(E, V, N)$**
- **What if you keep a system at constant volume V and temperature T ? This is the Helmholtz Free Energy**
$$A(V, T, N) = U - TS$$
- **Constant pressure and temperature...Gibbs free energy**
$$G(P, T, N) = A + PV$$
- **Goal of Stat Mech....Derive thermodynamic potentials from microscopics!**