



Quantum Statistical Mechanics Primer



Why Quantum StatMech?

- Nature is really quantum mechanical...classical statmech is an approximation (and typically a good one at “high temperatures”)
- Classical problem cases:
 - Specific Heat of Solids - Why does it go down at lower temperatures?
 - Drudé’s problem: Why are the electrons not contributing to specific heat?



Quantum StatMech – Main Ideas

What is different from Classical StatMech? Mainly, Two Things

- A description in terms of quantum mechanical states (energy levels, typically) is necessary (as opposed to the classical phase space description)
- Counting has to be done carefully when there are more particles than one! Fermions and Bosons have different statistics and give rise to *completely* different physics...such distinction does not exist in classical statmech



Quantum StatMech – Main Ideas

- EAPP remains unchanged...every quantum mechanical state with the same energy is equally likely
- Entropy is $S = k_B \ln \Omega$... Ω is the number of quantum mechanical states...microcanonical ensemble can be worked out this way...
- Taking a system to have levels labeled by n with energy E_n , the partition function $Z = \sum_n e^{-\beta E_n}$...the probability of state n is $P(n) = \frac{e^{-\beta E_n}}{Z}$, and $A = -k_B T \ln Z$!
- The key thing is in counting! Bose is not Fermi! And, Fermi is not Bose!

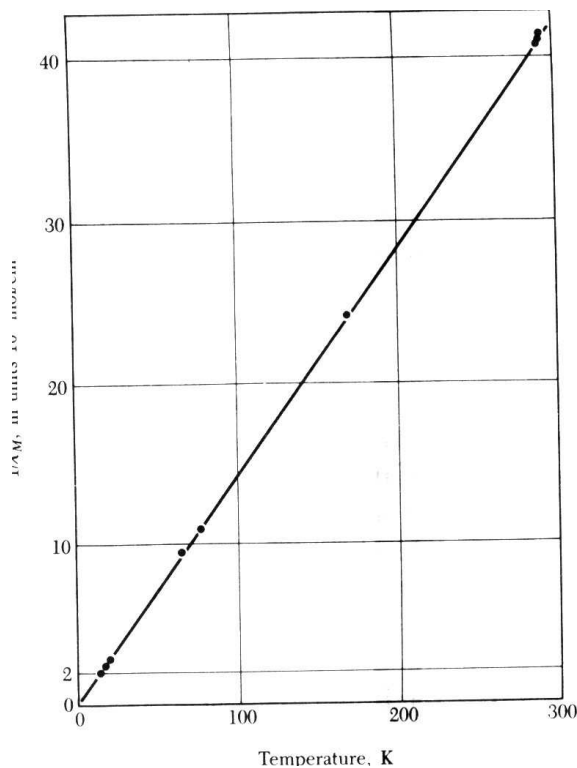


Quantum Statmech – How it works!

- Look at simple examples where counting will not be an issue
- Example: Paramagnetism
- Example: Thermal properties of solids (specific heat, thermal expansion etc.)

Paramagnetism

- On application of magnetic field B , a magnetization M appears in the material with is in the same direction as B
- $M = -\frac{\partial A}{\partial B} = \chi B$, χ is magnetic susceptibility



- Curie's Law $\chi \sim \frac{1}{T}$

(Gd salt, Kittel)

Paramagnetism

- Simplest model...Lattice containing N sites each with one unpaired s-electron (spin $\frac{1}{2}$, $\mu = \mu_b$, no net orbital angular momentum)
- Hamiltonian of the system $-\mu S_z^{tot} B$; $S_z^{tot} = \sum_i S_z^i$, S_z^i is the z -component of spin operator at site i (energy states from quantum mechanics!)
- Each site can have spin pointing along the magnetic field $S_z^i = 1$ or $S_z^i = -1$...Thus there are a total of 2^N configurations!
- Since spins at different site are independent
 $Z = \prod_{i=1}^N Z_i$, with
 $Z_i = e^{-\beta(-\mu B)} + e^{-\beta(+\mu B)} = 2 \cosh(\beta\mu B)$ and
 $Z = (2 \cosh(\beta\mu B))^N$

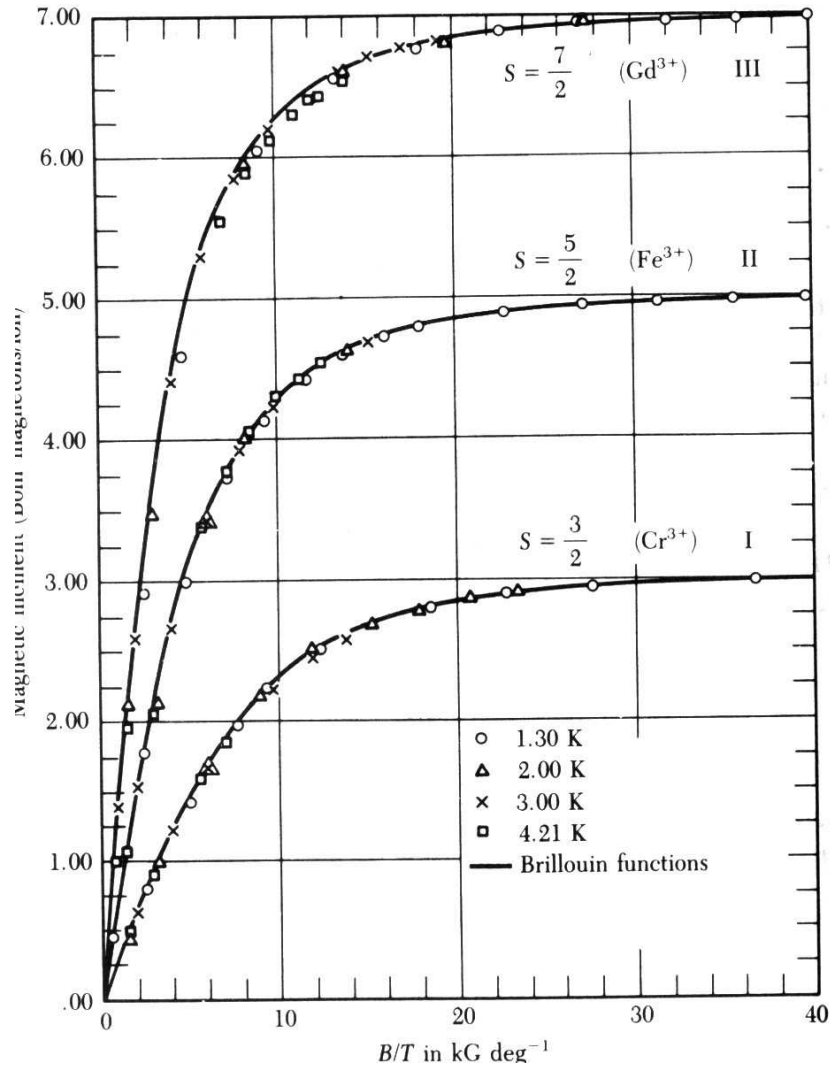


Paramagnetism

- $A = -k_B T \ln Z = -Nk_B T \ln (2 \cosh(\beta\mu B))$... **Thus**
 $M = -\frac{\partial A}{\partial B} = N\mu \tanh \beta\mu B$
- For “small” B , $M = \frac{N\mu^2}{k_B T} B$ or $\chi = \frac{N\mu^2}{k_B T}$, ...its **Curie herself!**
- Physics...spins want to align with magnetic field, but they get “kicked” around by temperature
- Most paramagnetic materials will not be spin $\frac{1}{2}$...could be larger...but same theory can be applied...and works wonders!
- Take metals, they should also obey this, right?

Paramagnetic Salts

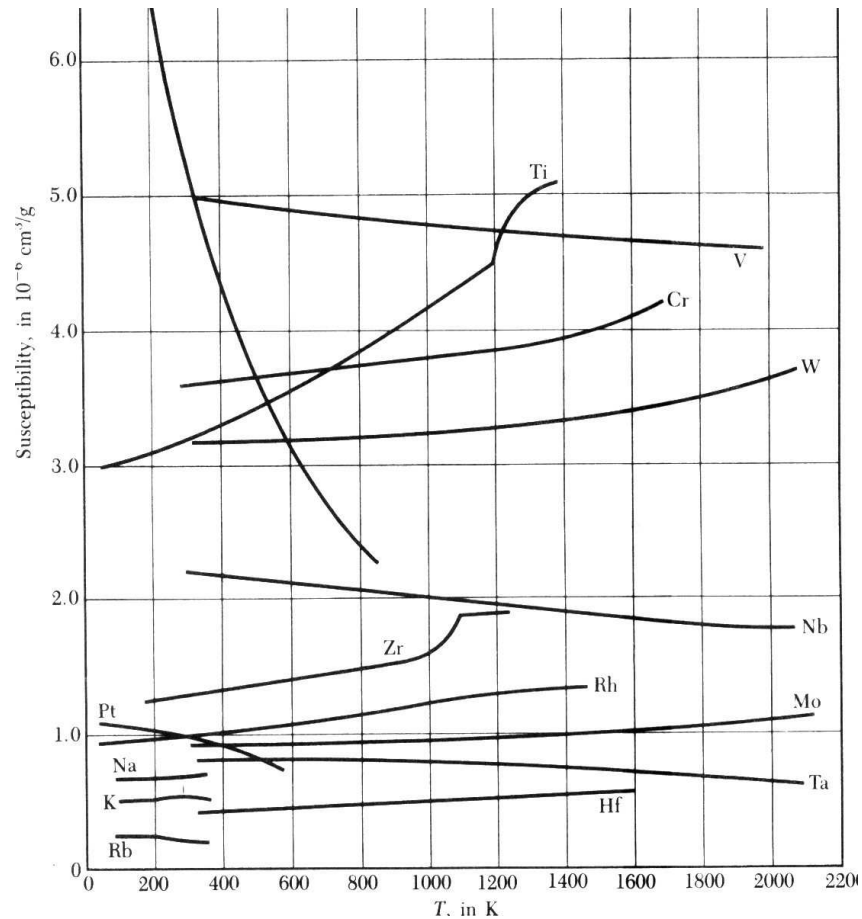
● Works wonders!



(Kittel)

And, Metals

● Works not wonders!



(Kittel)

● Why? Its Pauli, not Curie!

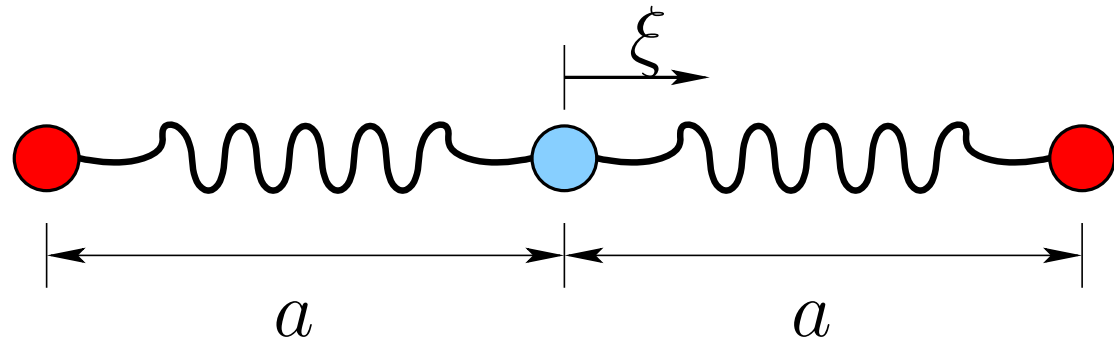


Thermal Properties of Solids

- Specific heat...why it falls with temperature?
- Whence thermal expansion?
- Strategy...compute free energy A via partition function Z ...everything else falls through
- Work in 1D, model illustrates basic ideas...

Simple 1D Model of Solid

- A chain of N atoms (mass m) interacting with their neighbors via a potential energy $\phi(|x_i - x_j|)$ (ϕ is given [how?])



- Model assumption...fix the neighboring atoms at an average distance a (which depends on temperature) and imagine the central atom to be “jiggling” described by ξ



Simple 1D Model of Solid

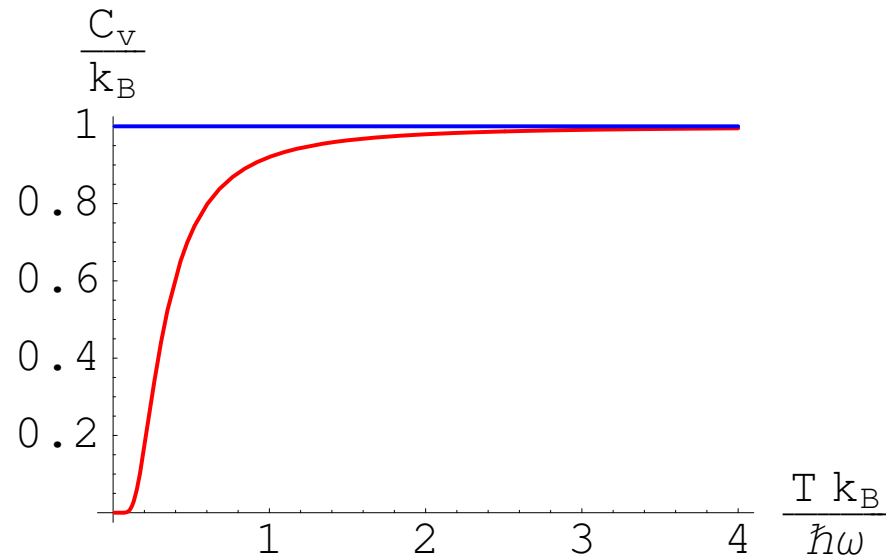
- **The potential energy of the atom**
 $= \frac{1}{2}(\phi(a - \xi) + \phi(a + \xi)) \approx \phi(a) + \frac{1}{2}\phi''(a)\xi^2$ (call $\phi''(a) = m\omega^2(a)$), note ω in general depends on a)
- **Hamiltonian of atom :**
 $H = \frac{P^2}{2m} + \frac{m\omega^2\xi^2}{2} + \phi(a)$...harmonic oscillator! There are N of them (treated independently as an approximation)...treat these quantum mechanically (energy states from quantum mechanics)
- **Energy states** $E_n = (n + \frac{1}{2})\hbar\omega(a) + \phi(a)$



1D Solid: Specific Heat

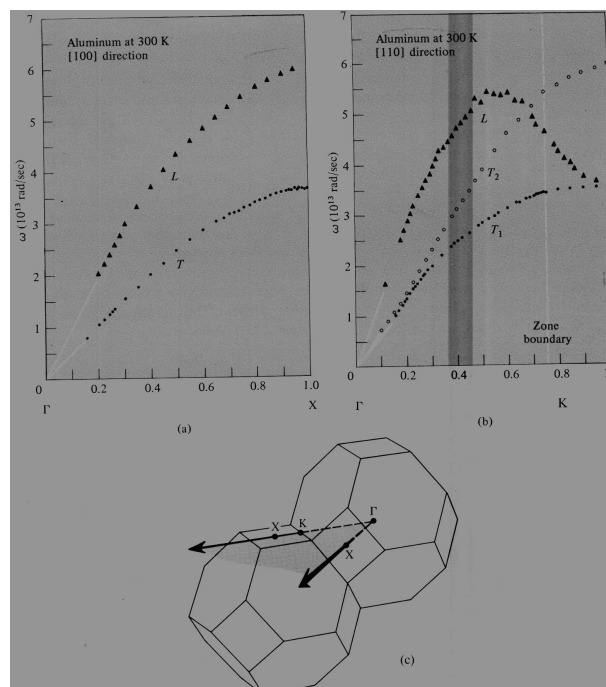
- The probability of state $n \sim e^{-\beta E_n}$, or partition function is $Z = \sum_{n=0}^{\infty} e^{-\beta E_n}$
- Sum can be evaluated easily : $Z = e^{-\beta \phi(a)} \frac{1}{2 \sinh\left(\frac{\beta \hbar \omega}{2}\right)}$
- Internal energy $U = -\frac{\partial \ln Z}{\partial \beta} = \phi(a) + \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$
- Specific Heat : $C_v = \frac{\partial U}{\partial T} = k_B \left[\left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2} \right]$
- $k_B T \gg \hbar \omega \implies C_v \rightarrow k_B \dots \text{nice!}$
- $k_B T \ll \hbar \omega \implies C_v \rightarrow \left(\frac{\hbar \omega}{k_B T} \right)^2 e^{-\frac{\hbar \omega}{k_B T}} \rightarrow 0 \dots \text{Nicer!}$

Specific Heat 1D and 3D solids



- The specific heat of an oscillator vanishes exponentially when $k_B T \ll \hbar\omega \dots$ "quantum alacrity"
- The above model was proposed by Einstein for 3D solid (just $3N$ oscillators instead of N)!
- So why do we see T^3 specific heat in insulating solids?

Specific Heat, Debye Theory



- In real solids, the phonon frequencies are not equal
- In particular long wavelength phonons (elastic waves) have very low frequency...Thus, for any given temperature there are many phonons which satisfy $k_B T \gg \hbar \omega$

Specific Heat, Debye Theory

- It can be shown that the fraction of these phonons is $\left(\frac{k_B T}{\hbar \omega_D}\right)^3$ where ω_D is the Debye frequency (corresponding temperature Θ_D)...hence T^3 specific heat

DEBYE TEMPERATURES FOR SELECTED ELEMENTS^a

ELEMENT	Θ_D (K)	ELEMENT	Θ_D (K)
Li	400	A	85
Na	150	Ne	63
K	100		
		Cu	315
Be	1000	Ag	215
Mg	318	Au	170
Ca	230		
		Zn	234
B	1250	Cd	120
Al	394	Hg	100
Ga	240		
In	129	Cr	460
Tl	96	Mo	380
		W	310
C (diamond)	1860	Mn	400
Si	625	Fe	420
Ge	360	Co	385
Sn (grey)	260	Ni	375
Sn (white)	170	Pd	275
Pb	88	Pt	230
As	285	La	132
Sb	200	Gd	152
Bi	120	Pr	74



Thermal Expansion, 1D

- Math easier at high temperatures

$$A(a, T) = -k_B T \ln Z \approx \phi(a) + k_B T \ln \left(\frac{\hbar \omega(a)}{k_B T} \right)$$

- To find equilibrium lattice parameter set

$$\frac{\partial A}{\partial a} = 0 \implies \phi'(a) + k_B T \frac{1}{\omega(a)} \frac{\partial \omega}{\partial a}$$

- Say $\phi(a) = \phi(a_0) + \frac{\phi''(a_0)}{2!} (a - a_0)^2 + \frac{\phi'''(a_0)}{3!} (a - a_0)^3$

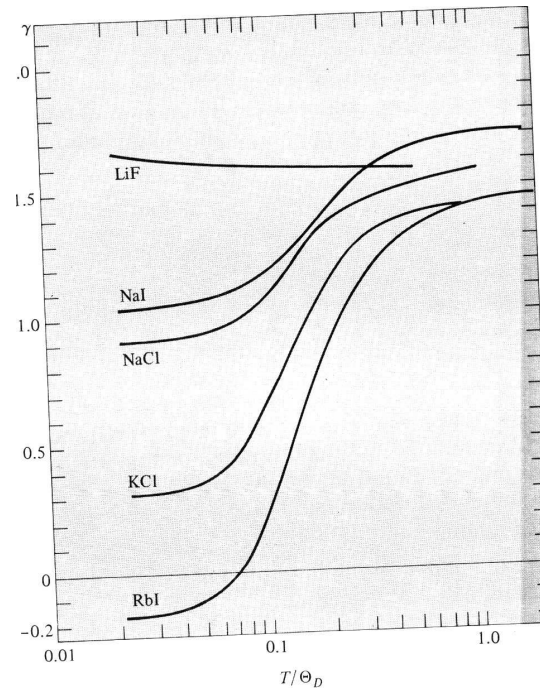
- Then $\alpha = \frac{1}{T} \frac{a - a_0}{a_0} = \frac{k_B}{a_0 \phi''(a_0)} \times -\frac{\phi'''(a_0)}{\phi''(a_0)} \dots$ note that

$$-\frac{\phi'''(a_0)}{\phi''(a_0)} = -\frac{\partial \ln \omega}{\partial a} \text{ typically } \omega \text{ decreases with increase in } a$$

- Thermal expansion is due to anharmonicity! Harmonic crystals will not expand!

Thermal Expansion in 3D Solids

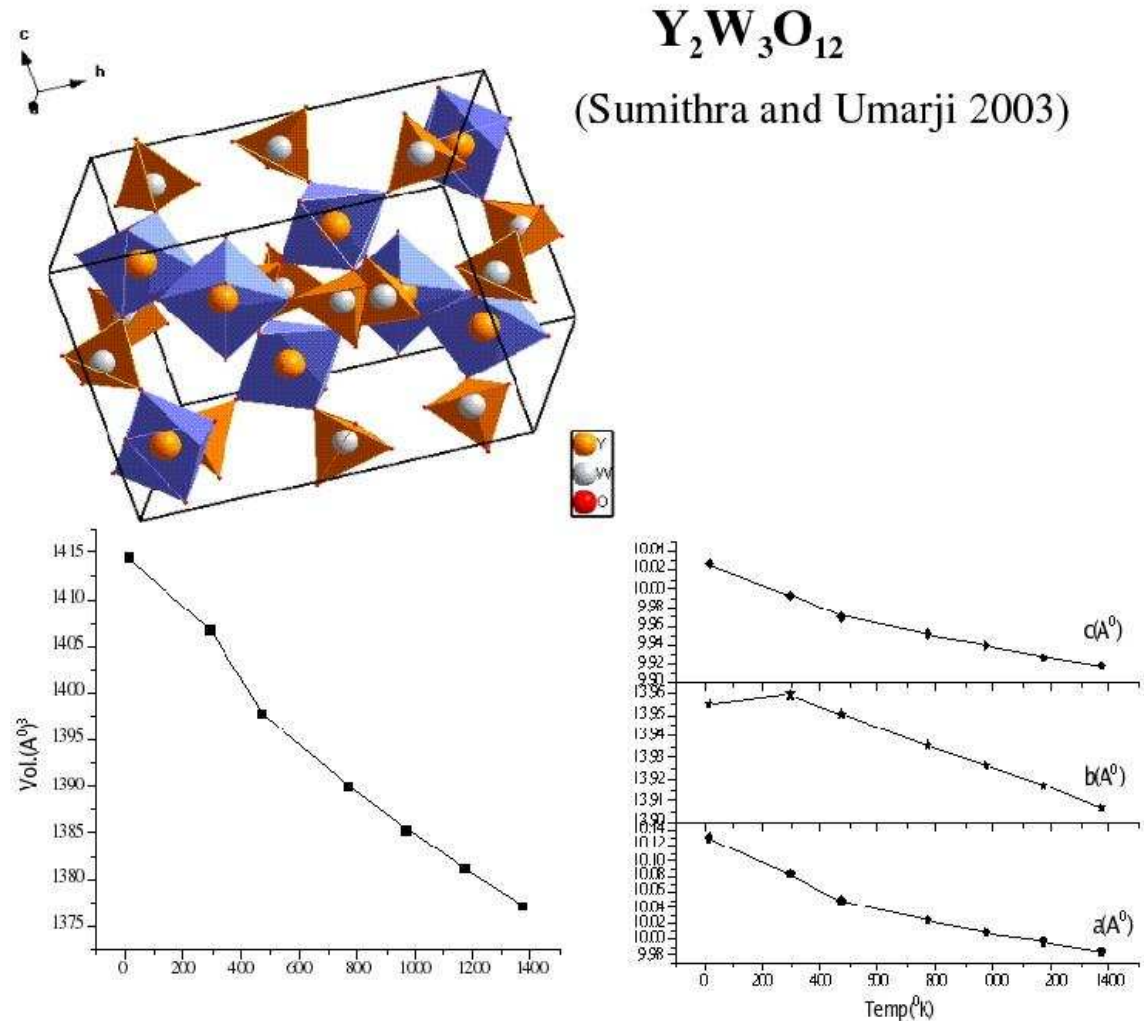
- General results $\alpha = \frac{\gamma C_v}{3B}$, $\gamma = - \sum_i \frac{\partial \ln \omega_i}{\partial V}$, i over all phonons
- Grüneisen parameter γ , roughly 2 in insulators



- Do we expect all crystals to expand on heating?

Negative Thermal Expansion!

- Crystalline materials with -ve α !! Why?





Now for some Quantum Counting!

- When there is more than one particle in a quantum system, one has to be careful regarding counting
- Identical particles are indistinguishable
- Fermions: Only one particle is allowed in a quantum state
- Bosons: Any number of particles can occupy a state
- Assume that the energy levels ε_i are solved for and the state i is g_i fold degenerate
- There are a total of N particles at temperature T ; what fraction of the g_i states at energy level i will be occupied?



Fermi-Dirac Statistics for Fermions

- **Strategy:** Find Entropy as a function of n_i (number occupying level i), then, A ; Minimize A with respect to n_i
- **Note** $\sum_i n_i = N$...this is a tough condition to enforce directly...so we will do the following trick..
- **Assume** that there are n_i particles occupying level i which is g_i fold degenerate...How many ways are there to do this?... $\frac{g_i!}{n_i!(g_i - n_i)!}$
- **The total number of ways is just the product of number of ways at each level** $\Omega = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$
- $S = k_B \ln \Omega =$
 $k_B \sum_i (g_i \ln(g_i) - n_i \ln(n_i) - (g_i - n_i) \ln(g_i - n_i))$

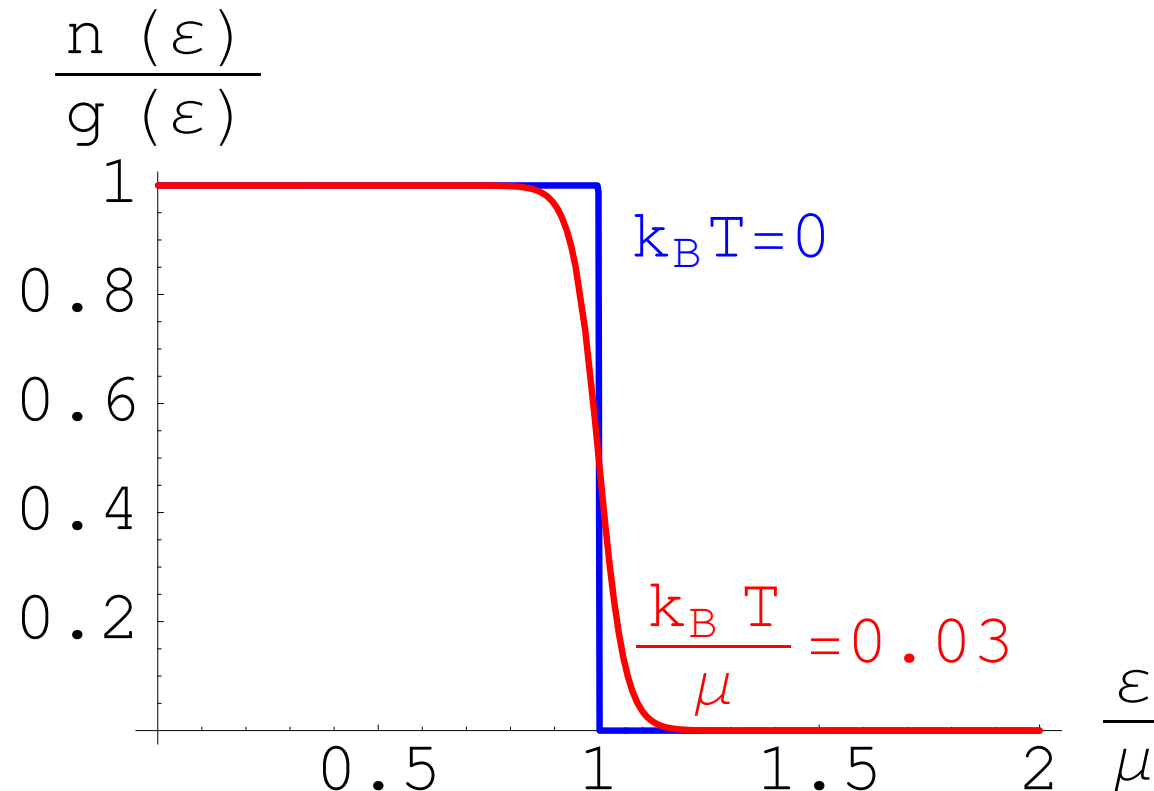


Fermi-Dirac Statistics for Fermions

- **Internal energy** $U = \sum_i n_i \varepsilon_i$
- $A = \sum_j n_j \varepsilon_j - k_B T \left(\sum_j (g_j \ln(g_j) - n_j \ln(n_j) - (g_j - n_j) \ln(g_j - n_j)) \right) - \mu(\sum_j n_j - N)$ **where μ is the chemical potential (ensure #particles is N via a Lagrange multiplier trick!)**
- $\frac{\partial A}{\partial n_i} = 0 \implies n_i = \frac{g_i}{e^{\beta(\varepsilon_i - \mu)} + 1}$ **(Fermi-Dirac)**
- **Determine μ from** $\sum_j \frac{g_j}{e^{\beta(\varepsilon_j - \mu)} + 1} = N, \mu = \mu(T, N)$
- **As $T \rightarrow 0$,** $\frac{n_i}{g_i} = 1$ ($\varepsilon_i \leq \mu$), $\frac{n_i}{g_i} = 0$ ($\varepsilon_i > \mu$)
- **Chemical potential μ at $T = 0$ is called Fermi energy ε_F , and at $T = 0$ all levels below Fermi level are fully occupied!**



Fermi-Dirac Statistics for Fermions



- In the thermodynamic limit, energy levels become very closely spaced thus $g_i \rightarrow g(\epsilon)d\epsilon$...to get

$$n(\epsilon)d\epsilon = \frac{g(\epsilon)d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}$$



Fermi-Dirac Statistics for Fermions

- Chemical potential obtained from $\int_0^\infty \frac{g(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = N$
- Internal energy $U = \int_0^\infty \frac{\varepsilon g(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1}$, etc..
- Fermi-Dirac Strategy for Fermions:
 1. Obtain density of states $g(\varepsilon)$ by solving the Quantum Mechanics problem
 2. Obtain chemical potential
 3. Use F-D distribution above to obtain required thermodynamic potentials



Free Electron Gas

- **Step 1: Obtain $g(\varepsilon) \dots g(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar}\right)^{3/2} \sqrt{\varepsilon}$**
- **Step 2: Obtain chemical potential (**
@ $T = 0, \mu = \varepsilon_F; \frac{n(\varepsilon)}{g(\varepsilon)} = 1 \ (\varepsilon \leq \varepsilon_F), \frac{n(\varepsilon)}{g(\varepsilon)} = 0 \ (\varepsilon > \varepsilon_F)$)
Thus, $\int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = N \implies \varepsilon_F = \frac{\hbar^2}{2m} \left[\frac{3\pi^2 N}{V} \right]^{2/3}$
- **Step 3: $T = 0, U = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = \frac{3}{5} N \varepsilon_F$**
- **How about specific heat $\frac{\partial U}{\partial T}$? For that we have to calculate U as a function of T ...can do this rigorously, but we will do it in an approximate way**
- **Note, for free electron gas, $g(\varepsilon_F) = \frac{3}{2} \frac{N}{\varepsilon_F}$**

Fermi Energies in Metals

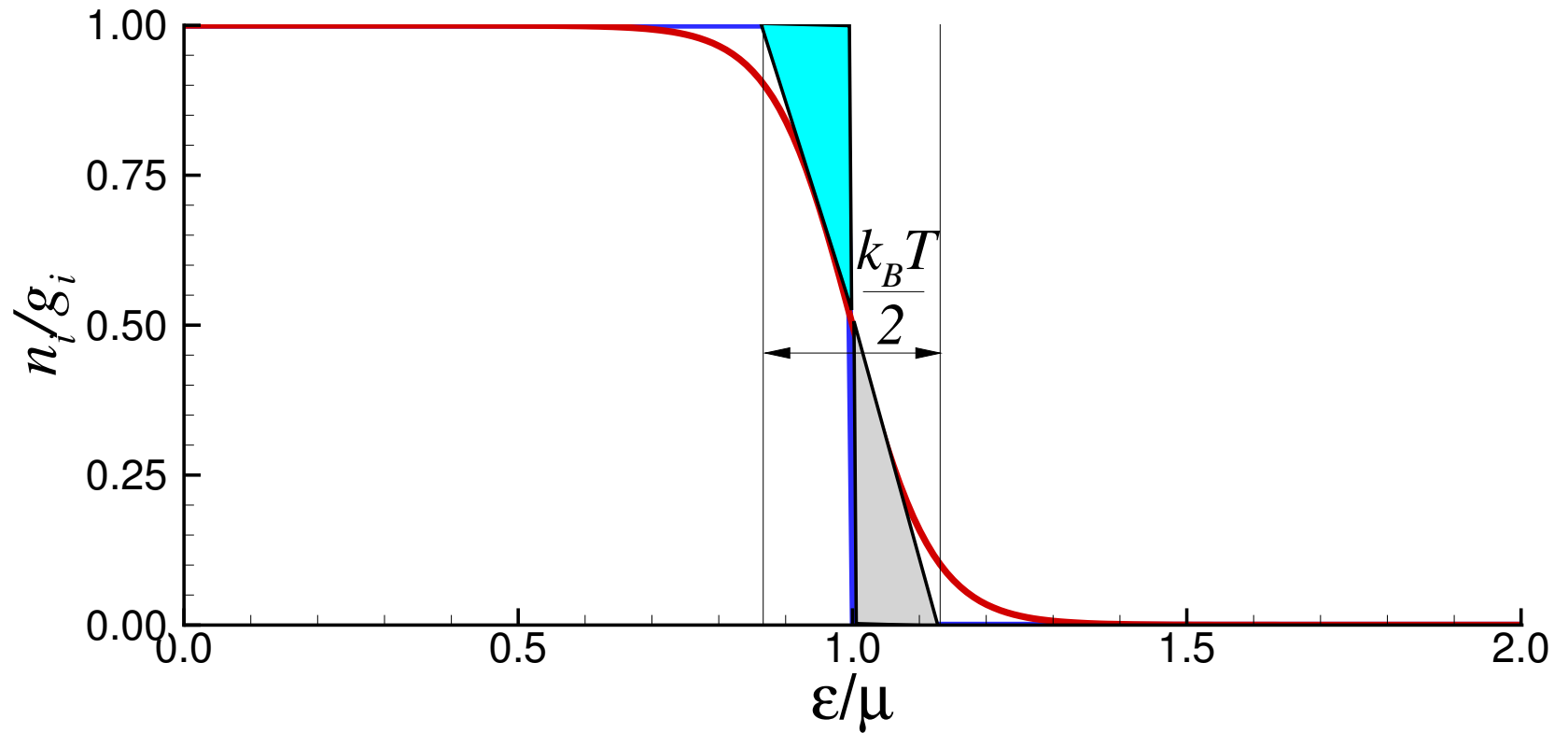
FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS^a

ELEMENT	r_s/a_0	ε_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm ⁻¹	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

^a The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 0.11 \times 10^{-28}$ grams.

- Fermi temperatures ($k_B T_F = \varepsilon_F$) are $\sim 10^5$ K,
i. e. $k_B T_{ROOM}/\varepsilon_F \sim 10^{-3}$ (key point!)

Specific Heat of Free Electron Gas



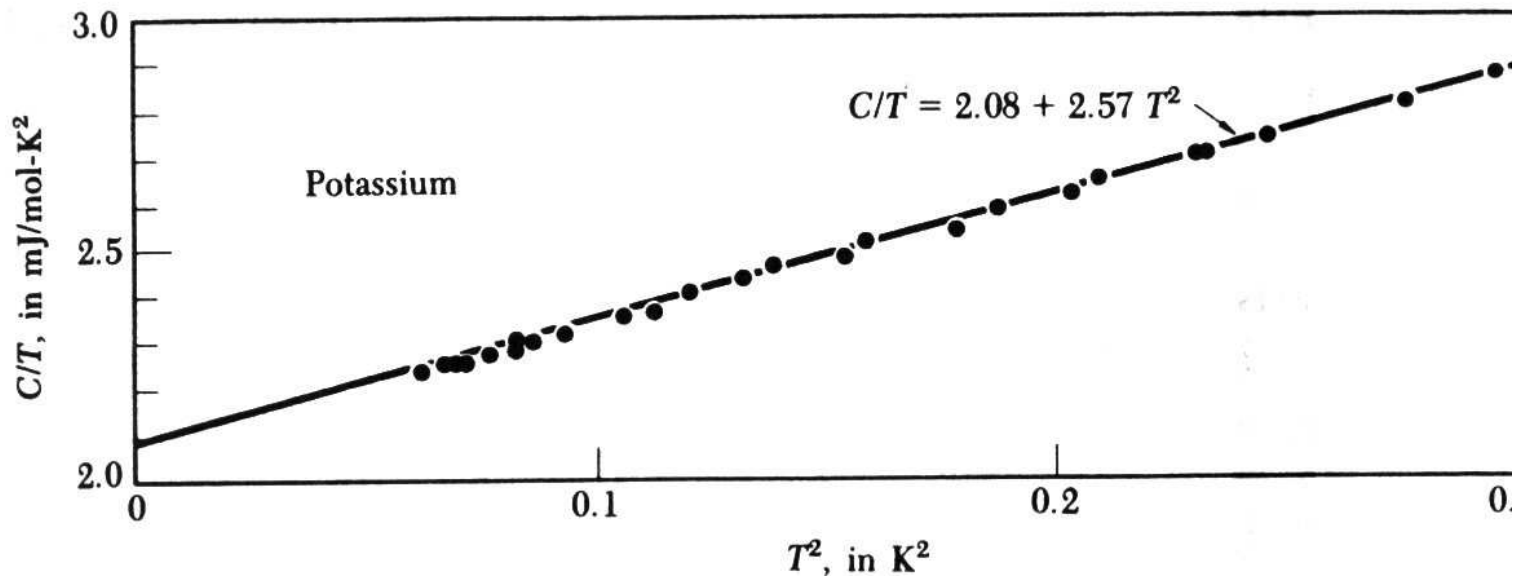
- On increasing temperatures electrons occupying states just below the Fermi level are excited to states just above the Fermi level



Specific Heat of Free Electron Gas

- Number of electrons whose states are changed
 $\sim g(\varepsilon_F) \frac{k_B T}{4}$ (average increases of energy
 $\sim \frac{k_B T}{4}$)... **Total energy increase** $\sim g(\varepsilon_F) \frac{k_B^2 T^2}{4}$
- $U(T) \approx \frac{3}{5} N \varepsilon_F \sim g(\varepsilon_F) \frac{k_B^2 T^2}{8} \implies C_V = g(\varepsilon_F) \frac{k_B^2 T}{4}$
- **Noting** $g(\varepsilon_F) = \frac{3}{2} \frac{N}{\varepsilon_F}$,
 $C_V = \frac{1}{12} \frac{T}{T_F} \left(\frac{3}{2} N \right) k_B \ll \frac{3}{2} N k_B @ T_{ROOM}$...**Drudé**
problem resolved!! Party starts again!
- **Physics:** Due to Pauli, only a fraction of electrons can participate in the thermal dance...the others continue their “worker bee” existence!

Specific Heat of Free Electron Gas



(Kittel)

- **Physics:** Due to Pauli, only a fraction of electrons can participate in the thermal dance...the others continue their “worker bee” existence!

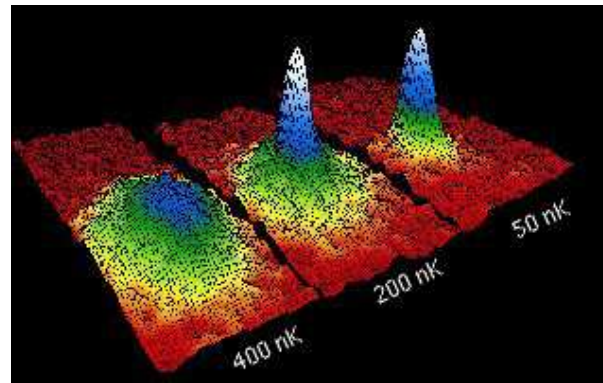


Bose-Einstein Statistics

- Many systems of interest...light, phonons, He^4 , Alkali metal atoms etc..
- Number of ways of distributing n_i particles becomes $\prod_k \frac{(g_i + n_i)!}{g_i! n_i!}$...resulting in $n_i = \frac{g_i}{e^{\beta(\varepsilon - \mu)} - 1}$ (BE Distribution)
- Strategy is same as that of FD case
 1. Obtain density of states $g(\varepsilon)$ by solving the Quantum Mechanics problem
 2. Obtain chemical potential
 3. Use B-E distribution above to obtain required thermodynamic potentials

Bose-Einstein Condensation

- A very interesting thing happens (in systems where particle number is conserved $\mu \neq 0$)...Bose-Einstein condensation
- As temperature is lowered a finite fraction of particles N occupy the lowest energy state...temperature required are 10^{-9} K!!!! This is a “new state of matter”!



(Colorado Group)



Well, Whats left to do?

- A LOT!
- Phase Transitions (Order-disorder, Magnetism, Ferroelectricity) need to consider interactions...mean field theory, renormalization group etc..
- Transport Properties (“Dynamics”)
- ...
- Many challenges remain!



Materials Science – The Grand Scheme

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

