
Introduction to non-zero temperature DFT calculations

These notes closely follow a lecture from
[MIT's 3.320](#) course notes

TEMPERATURE IN ELECTRONIC STRUCTURE CALCULATIONS

How do we include non-zero temperature on DFT?

If you look at the Kohn-Sham equation, there is no temperature in it!

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \hat{H}_{KS} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

NON-ZERO TEMPERATURE RAISES THE ENERGY ABOVE THE GROUND STATE

- Up to now we have concentrated on calculating the ground state energy.
- **When you are at non-zero temperature you have to put energy in the system to bring it above the ground state energy.**

Indeed recall that the derivative of the energy with respect to temperature is the heat capacity (which is always positive):

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V > 0$$

Raising the temperature from zero results in an energy above the ground state energy

TEMPERATURE AS A MEASURE OF EXCITATIONS

- The extra energy that you put in the system goes to excitations:
 - ❖ atomic vibrations, phonons
 - ❖ electron excitations across a gap
 - ❖ configurational excitations, defects, etc.

When you do temperature modeling, you need to select the types of excitations in which you allow energy to be pumped in for temperature.

- There is essentially no technique that allows for all possible excitations that you have in nature.
- The amount of average energy you have above the ground state is a measure of temperature.

GENERALIZED COORDINATES AND HAMILTONIAN

- In classical mechanics to derive the equation of motion, you often write the Hamiltonian (kinetic energy K + potential energy U) as follows:

$$\text{Hamiltonian: } H = U(q_i, p_i) + K(q_i, p_i)$$

generalized coordinates q_i

generalized momenta p_i

- Generalized coordinates are not just coordinates of atoms. They could e.g. be linear combinations of atomic coordinates.
- The Hamiltonian is the sum of the potential energy as a function of (q_i, p_i) and the kinetic energy as a function of (q_i, p_i) .
- In general, the kinetic energy K and potential energy U can be functions of both q_i and p_i , although normally you find that U is only a function of the generalized coordinates and K is only a function of the generalized momentum.

EQUI-PARTITION THEOREM

The equipartition theorem essentially tells us the definition of temperature

- The time average expectation value of the momentum times the derivative of the Hamiltonian with respect to that momentum is equal to kT .
- The same is true for the expectation value with the generalized coordinates.

Equipartition Theorem

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = kT \quad \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = kT$$

EQUI-PARTITION THEOREM

Equipartition Theorem

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = kT \quad \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = kT$$

Generalized
coordinate

Generalized
force

- The derivative of the Hamiltonian (energy function) with respect to a coordinate is a force. So the terms on the left of the equipartition theorem are force times a coordinate, i.e. energy.

**The equipartition theorem essentially
tells us the definition of temperature.**

QUADRATIC HAMILTONIAN

- Consider a quadratic Hamiltonian

“quadratic Hamiltonians $H = a p_i^2 + b q_i^2$

- For example, think of the kinetic energy being $mv^2/2$, and consider a harmonic quadratic potential $kx^2/2$.
- In this case, the equi-partition theorem leads to the following:

$$\langle a p_i^2 \rangle = \langle b q_i^2 \rangle = \frac{kT}{2}$$

EQUI-PARTITION THEOREM

$$\langle a p_i^2 \rangle = \langle b q_i^2 \rangle = \frac{kT}{2}$$

- The average of the squared coordinate or squared momentum is $kT/2$.
- **Every degree of freedom q_i and p_i contains a thermal energy equivalent to $kT/2$.**
- The above statement doesn't tell us anything about the stiffness of that degree of freedom. **A stiff or a soft spring will have the same thermal energy at a given T even though they will vibrate very differently:**
 - ❖ The **stiff spring** will vibrate with **small amplitude** but at **high frequency**.
 - ❖ The **soft spring** will vibrate with **higher amplitude** at **low frequency**.

EQUI-PARTITION THEOREM

Every degree of freedom contributes $kT/2$ thermal energy to the Hamiltonian (average energy)

- For n atoms (3 coordinates per atom), we have $3n$ DOF. We also have $3n$ components from the velocity, so we have a total of $6n$ degrees of freedom.
 - ❖ The thermal energy for n atoms is $6n kT/2 = 3n kT$.
- The heat capacity is then $3k$ (**Dulong & Petit law**).
- The above statement is only true when the energy depends quadratically on the coordinates – around equilibrium you are quadratic in the potential. The same is true for the velocities.

$$\langle a p_i^2 \rangle = \langle b q_i^2 \rangle = \frac{kT}{2} \quad \leftarrow \text{Only correct when energy depends quadratically on coordinates}$$

- The above calculations will not be correct if you have oscillations far from equilibrium.

QUANTUM STATISTICAL MECHANICS

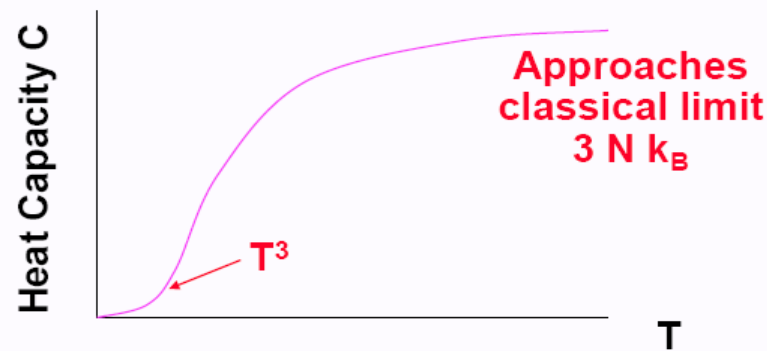
- **What we did up to now is only valid in classical mechanics!**
- The results we obtained are only true for DOF for which there is enough energy for them to be excited.
- We know from quantum statistical mechanics that **the states for degrees of freedom and the energies associated with them are quantized** -- you cannot move from the ground state continuously in excitations. For example, the first excitation from the ground state takes a finite amount of energy.
- If the temperature is not sufficiently high to get the first excitation, then the system will, essentially, not be excited in those degrees of freedom and they will not contribute to the thermal energy.
- For example, if we are at room temperature (temperature corresponding ~ 25 meV) and your first excitation is 1 eV, that degree of freedom is not going to contribute to the internal energy or the heat capacity.

QUANTIZATION OF DOF

In Quantum Statistical Mechanics DOF are quantized

Only DOF for which there is enough energy to excite them should be counted

- This is why if you plotted the heat capacity versus temperature, the heat capacity is $3k_b$ at high temperature but then it drops off at low temperatures.
- Essentially, the heat capacity coming from the atomic displacements gets frozen out since the atomic displacements are quantized



Which excitations are important to include in your model?

- You need to understand which excitations are going to be present in your model to allow for the extra energy that comes with temperature.

- What are the excitations that are relevant for the property you want to study as a function of temperature?
- How do they store the extra energy?

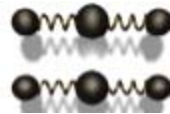
EXCITATION MECHANISMS

Here is some possible excitations mechanisms.

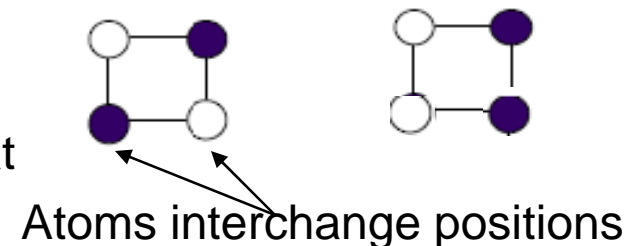
Electronic excitations. Up to now, in quantum mechanics we calculated not only the atomic ground state (you relax all the atoms) but also the electronic ground state.

At non-zero temperature, you can have electronic excitations, e.g. **electron excitations across a band gap**. If the band gap is large, it's a small number of electrons. But in a metal, there's no gap so you can have at any temperature excitations of electrons across the Fermi level.

Vibrational excitations: If you raise the temperature, the atoms start vibrating.



Configurational excitations: If you have an ordered system, atoms might start interchanging positions. Similarly, in polymers you change their conformation at elevated temperatures.



CHANGES IN MATERIALS WITH TEMPERATURE

Crystal structure changes with temperature (phase changes, surface structure change)

- Calculating the structure of materials is already a really hard problem at 0 K because **it's a global optimization problem** – you cannot solve it by local optimization, mainly by just minimizing forces on coordinates.
- To find the change of structure as a function of temperature, you not only have to find the ground state but **you have to figure out what are the entropic factors (excitations) that make free energy different from energy.**

CHANGES IN MATERIALS WITH TEMPERATURE

- Changes in chemistry as a function of temperature, e.g. oxygen content in oxides, concentration profiles towards the surface, etc.
- Many materials are open systems to the environment. An Oxide for example can exchange Oxygen to the environment. Ceramics e.g. loose Oxygen when you heat them up high enough.

Properties (e.g. thermal and electrical conductivity)
Volume (thermal expansion)

BULK MODULUS AS A FUNCTION OF TEMPERATURE

PHYSICAL REVIEW B

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First-principles calculations of the thermal expansion of metals

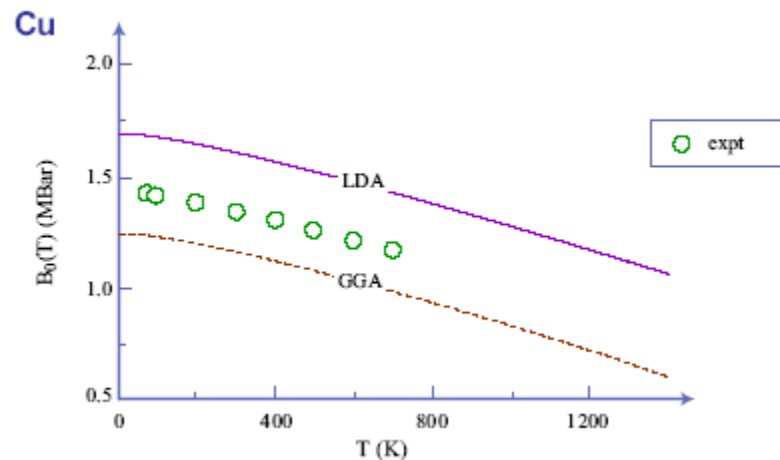
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Temperature dependence of the bulk modulus of Copper



http://prola.aps.org/pdf/PRB/v56/i13/p7767_1

Variation with temperature of the bulk modulus B_0 . At all temperatures, the LDA (solid line) overestimates B_0 and the GGA (dashed line) underestimates it; however, $\partial B_0 / \partial T$ is approximately the same for the LDA, GGA, and experimental values.

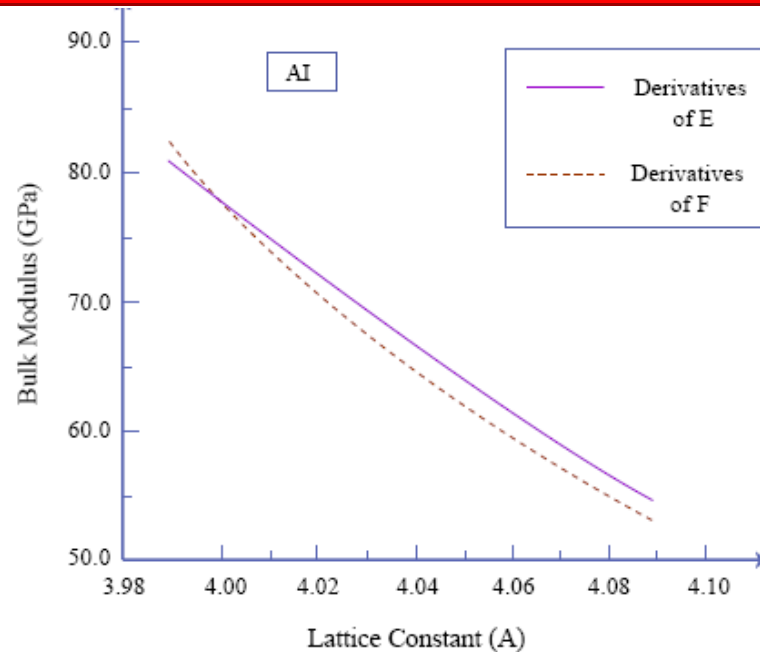
CHANGES OF BULK MODULUS WITH TEMPERATURE

- **What is the physics that makes the bulk modulus temperature dependent?**
- Using molecular dynamics is an easy way to get the temperature dependence of the bulk modulus.
- But you can do this faster. **The bulk modulus is defined as the 2nd derivative of the “free energy” with respect to volume.**

$$B=V \left. \frac{\partial^2 F}{\partial^2 V} \right|_a$$

- You evaluate this derivative **at the equilibrium lattice constant a.**
- At zero temperature, the energy is equal to the free energy so you take the 2nd derivative of the energy (not of the free energy) at the zero temperature lattice parameter.

CHANGES OF BULK MODULUS WITH TEMPERATURE



Bulk modulus artificially taken at different lattice constants.

Calculated bulk modulus as a function of lattice parameter. The dashed line is obtained from the temperature-dependent Helmholtz free energy and the solid line from the $T=0$ electronic energy.

- **In the calculation shown here we have 2 sources of error:** (1) we use energy to calculate the bulk modulus at zero temperature rather than free energy and (2) we use the zero temperature lattice parameter rather than the finite temperature lattice parameter. We need to deal with both of them.

CHANGES OF BULK MODULUS WITH TEMPERATURE

- To a good approximation, one only needs to get the lattice parameter at some T , then do 0 K calculation at that lattice parameter.
- You do this by **plotting either energy or free energy** as a function of lattice parameter.

You can also compute the curvature at different lattice parameters (and not just at the minimum). This will give you the bulk modulus as a function of the lattice parameter.

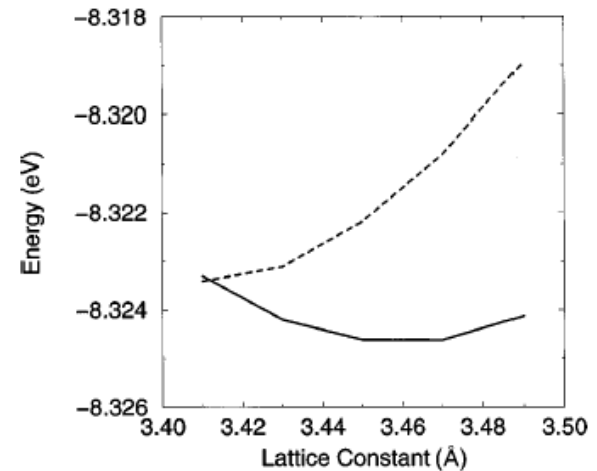
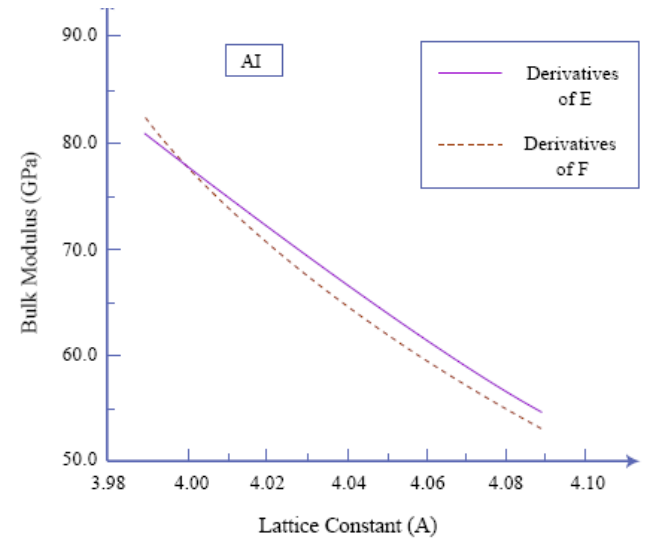


FIG. 1. Equations of state for Li. The solid curve is the Helmholtz free energy at 298 K and the dashed curve is the electronic energy (LDA) at $T=0$.

This is energy vs volume for Lithium at room temperature. The point where the two curves meet would be the 0 K equilibrium lattice constant and **the minimum of the free energy as a function of volume would be the room temperature equilibrium lattice constant.**

CHANGES OF BULK MODULUS WITH TEMPERATURE

- Here it is done in 2 ways: by taking derivatives of the energy (E) and by taking derivatives of the free energy (F).
- **At given lattice parameter, whether I take the 2nd derivative of the energy or the free energy is not a big error.**
- **The biggest error comes from the fact that we are not at the right lattice parameter, i.e.** what causes the temperature dependence of the bulk modulus is the fact that the lattice parameter changes with temperature.
- Thus we need to get the lattice parameter as a function of temperature and then calculate the curvature of the energy in that lattice parameter.



CHANGES OF BULK MODULUS WITH TEMPERATURE

- Unfortunately, if you want the lattice parameter, you'll need to know the entropy, thus the free energy.
- If you have the lattice parameter from experiments you can just compute the the bulk modulus at that lattice parameter (can do this in your HW if nothing else works!).

The physics here that drives the temperature dependence of the bulk modulus is the thermal expansion.

At what lattice parameter?

- Here are 3 different options for calculating (using LDA) the bulk modulus.
- We first compute B at the **zero temperature lattice parameter**. The LDA values are too stiff.

a and *B* Calculated at Zero temperature lattice parameter

System	<i>a</i> ₀		B (GPa)	
	Calc	Exp	Calc	Exp
Li	3.41	3.49	15.4	11.6
Na	4.11	4.23	9.0	6.8
Al	3.98	4.02	85.0	72.2

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- To compute the room temperature bulk modulus, you just compute the bulk modulus at the **experimental room temperature lattice constant**. Notice that now you are too soft.

At experimental room-temperature lattice constant

System	<i>a</i> ₀		B (GPa)	
	Exp	Calc	Calc	Exp
Li	3.52	9.4	11.6	11.6
Na	4.28	4.6	6.8	6.8
Al	4.05	64.2	72.2	72.2

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At what lattice parameter?

- You can find the **equilibrium room temperature lattice parameter of your LDA** (recall that LDA tends to overcontract), and calculate the bulk modulus there.

At LDA room- temperature minimum

System	a_0		B (GPa)	
	Calc	Exp	Calc	Exp
Li	3.48	3.52	11.5	11.6
Na	4.19	4.28	6.8	6.8
Al	4.00	4.05	75.2	72.2

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- This is much better since **you are working in a consistent solution of the Hamiltonian**. You know this is the minimum the Hamiltonian gives you, whereas at the zero-temperature lattice parameter you are actually above the real minimum and with the experimental room temperature lattice parameter you are actually below it.

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For more details of first-principles calculation of B consult

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Computing thermal expansion

Thus the thermal expansion depends on how the entropy changes with volume.

$$\alpha_V = \left(\frac{\partial S}{\partial V} \right)_T \beta_T$$

- So the critical part is calculating the entropy of the system as a function of volume.
- Computing the entropy is essentially counting the excitation the system goes into. Temperature is the average energy of these excitations.

You have to know which excitation you have to deal with and you need a model for them (equilibrate them)

- Thermal expansion is largely caused by vibrational (Fulman) entropy.

Computing thermal expansion

- Why does the entropy goes up with volume (which is what gives you thermal expansion)?
- At higher volume, force constants become weaker, hence phonon frequencies lower, hence entropy higher
- If you stretch a material, the bonds get slightly softer so the vibrational frequencies get smaller and you get more vibrations, i.e. higher entropy
- You can see this in a quantized-scheme. The space between the ground state and the first excited state is $h\nu$. So, if the frequency becomes smaller, your first excited state is closer so you excite more, you have more disorder and thus more entropy.
- Most materials have positive thermal expansion because essentially they get softer as you stretch them.

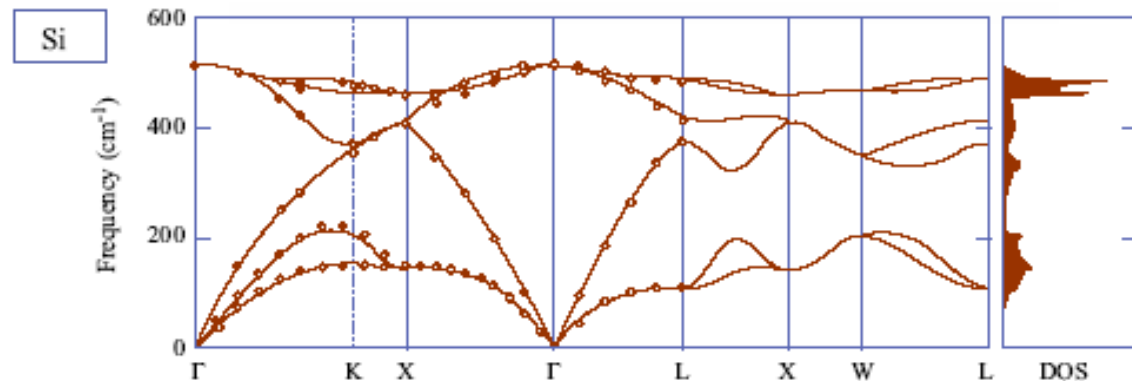
Phonon calculations

- The way you would calculate the vibrational entropy is by calculating the **Fulman density of states**. You would look at the quantized vibrations, do the statistical mechanics on them and calculate the free energy with phonons.

$$F(V, T) = E_{\text{LDA}}(V) + k_B T \sum_{\mathbf{q}j} \ln \left(2 \sinh \frac{\hbar \omega_{\mathbf{q}j}(V)}{2k_B T} \right)$$

- Here $E_{\text{LDA}}(V)$ is the energy of the static lattice at a given volume V , and $\omega_{\mathbf{q}j}(V)$ is the frequency of the j th phonon band at the point \mathbf{q} in the Brillouin zone.

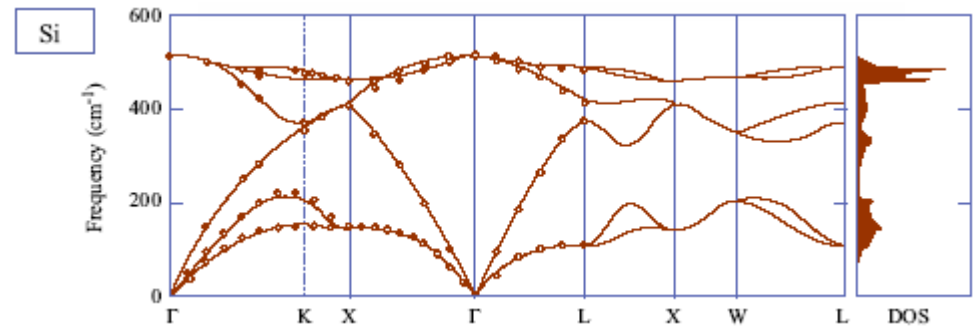
This is the phonon spectrum for Silicon



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Frozen phonon approximation, perturbation techniques

We need to get the entropy as a function of volume. This means that we need to **do the phonons at several different volumes to get the thermal expansion right.**



- Phonon calculations have become quite routine. It's typically done by **linear response techniques** where you perturb a lattice by a phonon with short wavelength so that you can calculate the energy of it.

<http://cst-www.nrl.navy.mil/~mehl/phonons/>

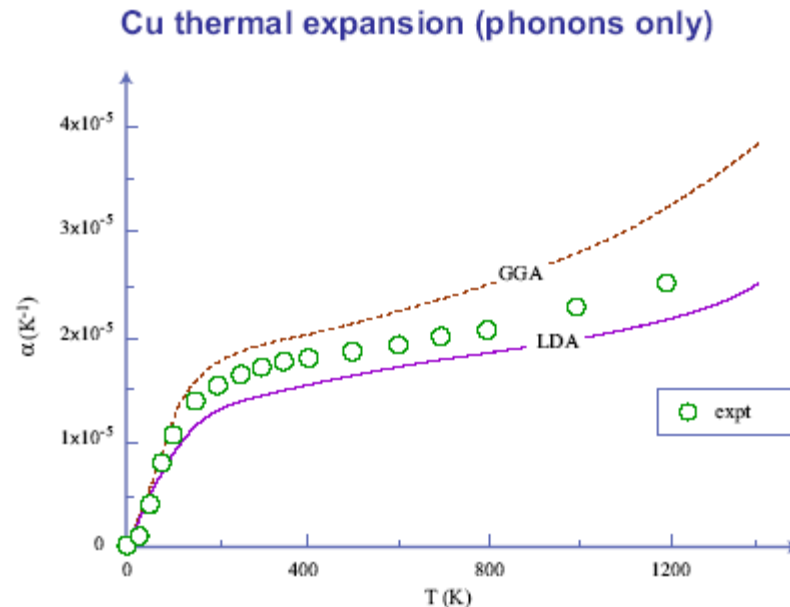
<http://stokes.byu.edu/frozsl.html>

<http://stokes.byu.edu/findsym.html>

- It's like setting up a supercell with a phonon in it (**frozen phonon approximation**). There are **perturbation techniques, linear response techniques**. Also people do this in real space by calculating force constants and setting up **force constants models for phonons**.

Computing thermal expansion with phonon calculations

- Here are the results with LDA and GGA for Copper with phonons only. The LDA and GGA numbers bracket the experimental results.
- LDA is on the stiff side and GGA on the soft side. These are very typical results for metals.



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Electronic excitations

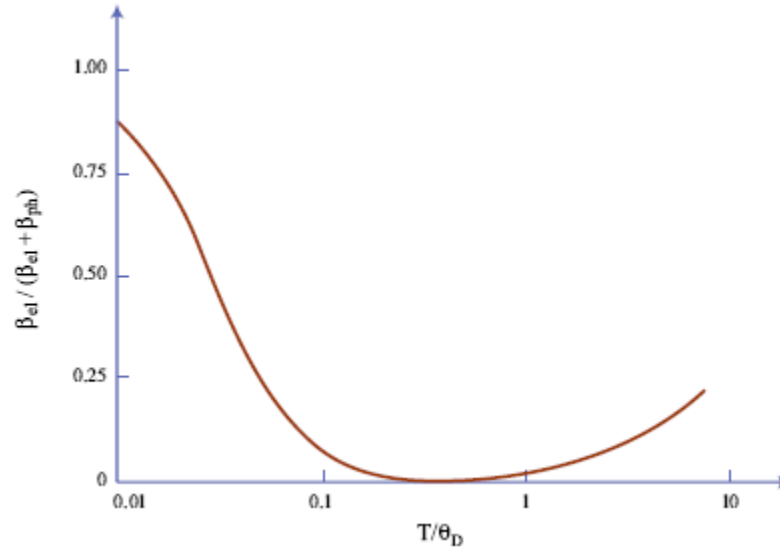
- The thermal expansion comes from how the entropy changes with volume but that's the total entropy.

$$\alpha_V = \left(\frac{\partial S}{\partial V} \right)_T \beta_T$$

- The calculations up to now only had the vibrational entropy. Other excitations that change with volume can affect your thermal expansion and this includes electronic excitations.
- Any time you are not working on an insulator, you will start getting electronic excitations which can change with volume.

Electronic versus thermal expansion

What it is shown here is (for some metal) the ratio of the electronic thermal expansion β_e to the total thermal expansion (the electronic plus the vibrational one)

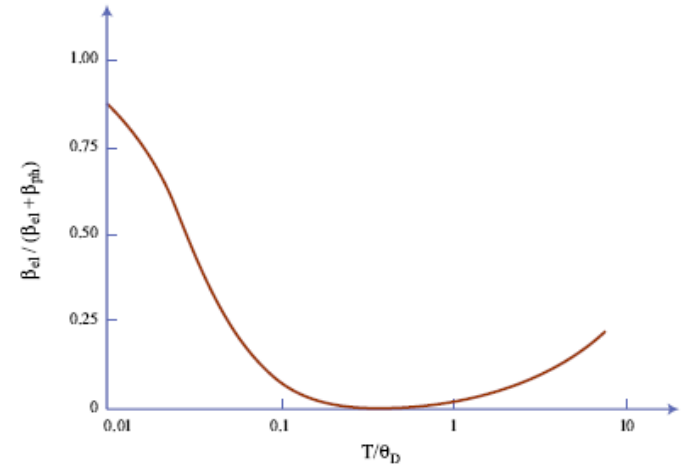


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- A reduced temperature scale (temperature in units of the Debye temperature) is used.
- The Debye temperature is the temperature scale at which the vibrations become classical (~200 to 500 K).

Electronic excitations

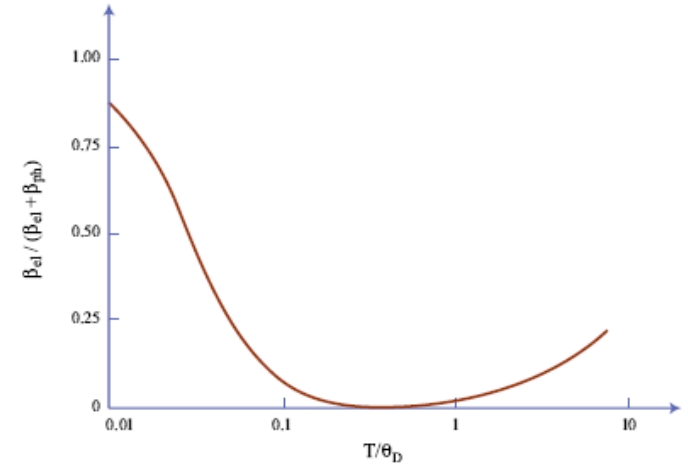
- It's only at low temperature that the electronic thermal expansion becomes important.
- When you are at low temperature, the thermal expansion is very small. You are essentially harmonic in your phonon degrees of freedom so you have almost no thermal expansion -- if you have fully harmonic vibrations, the curvature is the same everywhere, so your phonon frequency is the same everywhere, so your entropy is the same everywhere.
- So at very low temperature you have almost no phonon thermal expansion and the electronic thermal expansion plays an important (but small) role.



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Electronic excitations in oxides are important

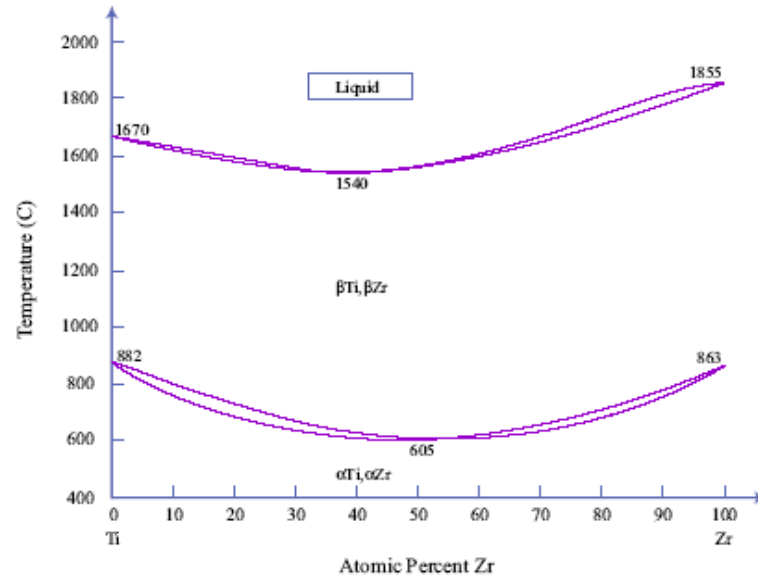
- When you are at ~ 0.5 of the Debye temperature, the electronic effect is almost meaningless.
- There are materials however where this may not be the case. In complex oxides e.g. you could start inducing valence fluctuations at elevated temperatures (even at 300-400 K). **In oxides** if you change the valence of an ion, they often change size because the orbitals are very localized. So there **you can see a substantial effect of electrons on thermal expansion.**



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HCP (low T) to BCC (high T) transitions

- Here is another example where you would need a temperature dependent study. This is the phase diagram for Titanium and Zirconium.



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- Titanium and Zirconium are both HCP at low temperature. At high temperature they are both BCC. The transition temperature for Ti is 882 C and for Zr 863 C.
- To predict such transition temperatures you need to get the subtle energy difference between HCP Ti and BCC Ti as a function of temperature. **You need to know what contributes to the entropy of these phases.**

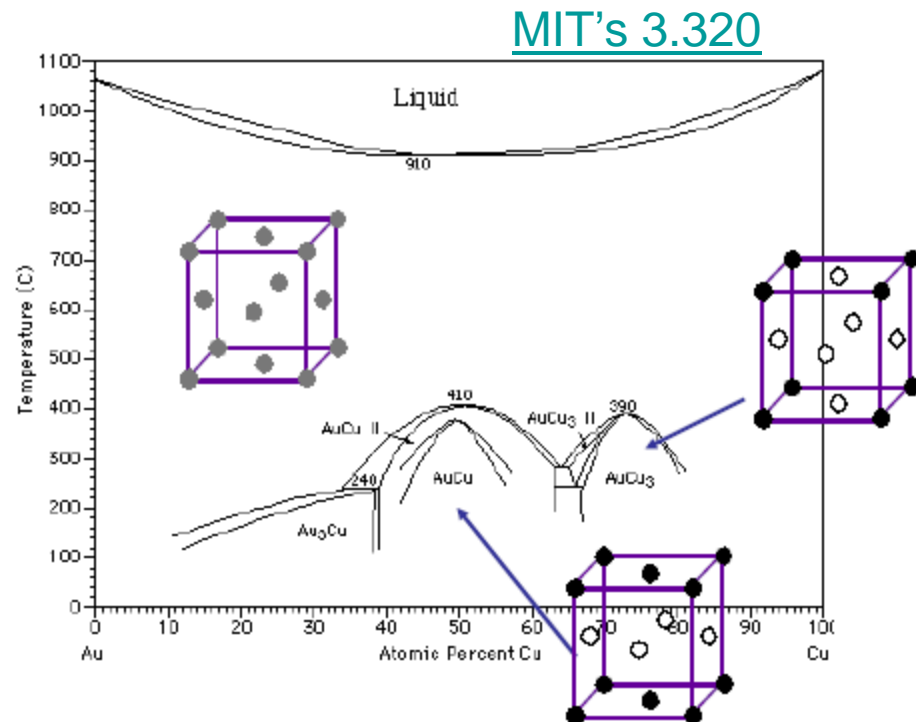
HCP (low T) to BCC (high T) transitions

- Can you get this HCP (closed packed) to BCC (less closed packed) transitions by doing ab-initio MD? In MD the atoms move according to Newton's law (essentially doing the vibrations of the atoms).
- Is this transition determined by atomic vibrations? -- since that's the only excitation mode we allow by doing dynamics of atoms with MD.
- What drives these transitions that are very common in metals is not known.
- We can argue that it is the atomic vibrations (vibrational entropy). The close packed phase tends to be stiffer and the less close packed phase tends to be softer. Softer implies lower frequencies, thus higher entropy. Higher entropy means you become favorite at high temperatures. If this argument is true, then ab-initio MD can predict this type of transition.
- We can also argue that this is driven by electronic excitations since BCC phases tend to have higher electronic entropy. So you will need to include electronic excitations with ab initio MD which is not easy to do.

Configurational entropy: Ordered compounds

- This is the Copper-Gold phase diagram. Here the phase transition is not driven by vibrations or electronic excitations. Cu and Au are FCC phases. All these compounds in between are ordered FCC compounds -- basically ordering of Cu and Au atoms on the FCC lattice.

Cu-Au phase diagram



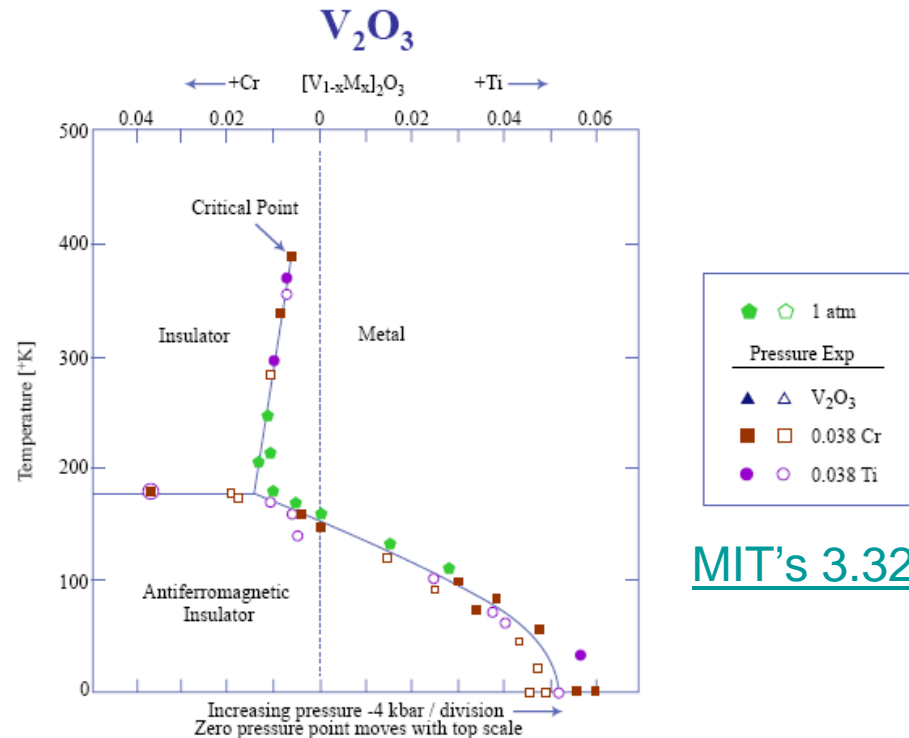
Cu and Au interchange sites on the FCC lattice. Atomic vibrations are much less important in defining the topology of this diagram.

This phase diagram is completely driven by **configurational entropy**.

So different problems with different physics are going to lead to different models for dealing with temperature

Metal insulator transitions: driven by electronic entropy

Here the system that is completely driven by electronic entropy. This is Vanadium Oxide which undergoes **metal insulator transitions**. This is its phase diagram in temperature-pressure space since there is no compositional axis (it's a stoichiometric compound)



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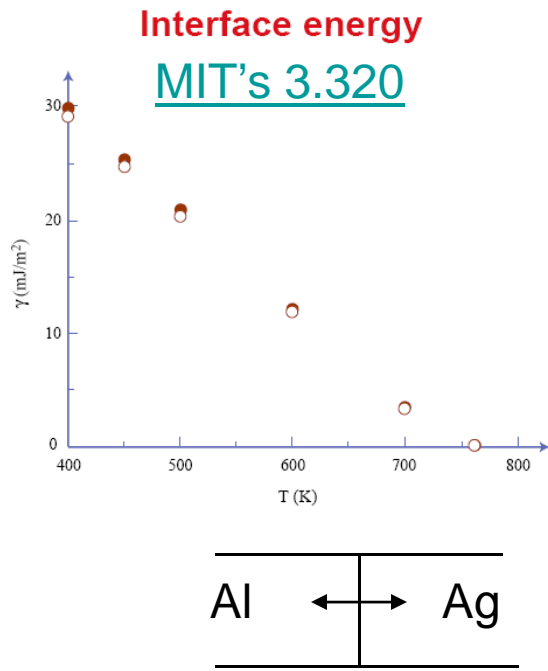
- At low T and low P, it's an antiferro-magnetic insulator. If you raise the temperature, it becomes metallic and changes structure. This is completely driven by the fact that **in the metal, the entropy of the electrons is higher than in the antiferro-magnetic insulator**. You need to use ab-initio MD that includes electronic excitations to get this right.

Interfacial energy decrease with T is purely driven by inter-diffusion

- Consider the calculation of the interface energy between Silver and Aluminum. They are both FCC metals. This is important when studying wetting and nucleation problems.
- Below we see the interfacial energy as a function of temperature. The 2 types of results are for different interface orientations -- (111) and (100). **The interfacial energy goes down with temperature.**

From where does that temperature dependence of the interfacial energy come from?

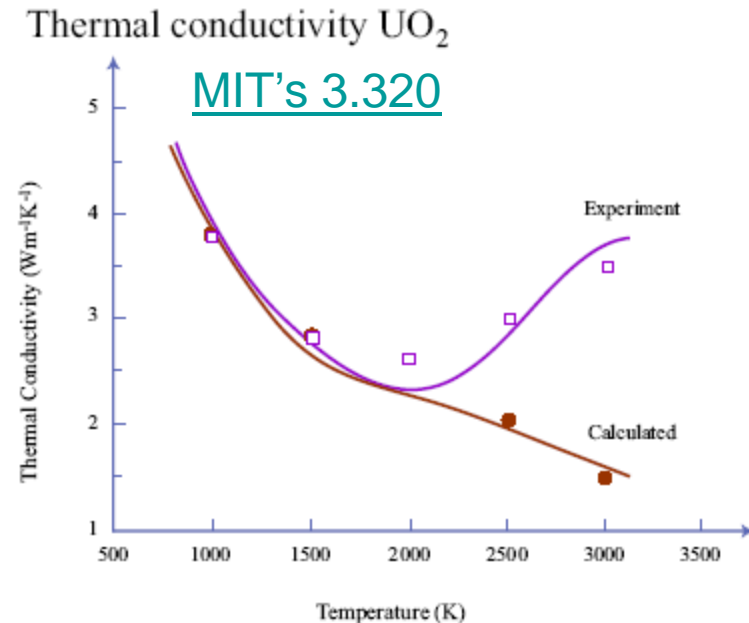
Ag and Al are immiscible at low T but **at high T, Ag and Al inter-diffuse** – the interface is getting more diffused. On the Ag side you have a lot more Al atoms and on the Al side you have a lot more Ag atoms. At ~760 K, near the interface you've reached almost perfect solubility (zero interface energy)



Electronic excitations

- The next example is about the thermal conductivity as a function of temperature of Uranium oxide.

There's a whole region of temperature with good agreement but above 2000 K the 2 curves diverge -- the physics must be changing!



- This result is calculated with MD simulation looking at energy transport through phonons. Phonons become decoherent and scatter in order to deliver their energy.

Electronic excitations

- Uranium oxide is an insulator. At high T close to 2000 K you get an electronic contribution to the thermal conductivity.
- In most materials at low temperature, the electronic thermal conductivity is small. It's largely dominated by phonons. But in a lot of materials it becomes important at high temperature.
- All this depends if you have a metal or an insulator. If you have a really big band gap insulator this will never show up because you will never have mobile electrons.

