3.320/SMA5107: Lecture 11 (3/10/05)

But, … it is only zero temperature, Professor

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Today's objective:

- Why is "Temperature" difficult
- Assess when temperature effects are important for your prediction
- When are zero-K energy calculations OK ?

It's a "Sham". There is no temperature in the Kohn-Sham equations

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

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

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

Temperature = Energy excess (above the ground state)

Quantum Mechanics gives you the ground state energy

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

When temperature increases, energy increases

Additional energy is contained in **excitations**

e.g. electron excited across the gap

atomic vibrations

Average energy above ground state can be used as measure of temperature

Total energy (and hence T) is initial condition for time-dependent Schrödinger equation.

Temperature (Formal; Classical Picture)

Classical Mechanics Generalized coordinates q_i and momenta p_i

Hamiltonian: H = U(q_i , p_i) + K(q_i , p_i)

Equipartition Theorem

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

For "quadratic Hamiltonians $H = a\,p_i^2 + b\,q_i^2$

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

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

Subtleties

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

← **Only correct when energy depends quadratically on coordinates**

In Quantum Statistical Mechanics degrees of freedom are quantized

Only degrees of freedom for which there is “enough” energy to excite them should be counted -> approach classical theory

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

Can not study “temperature” effects without

a) understanding which excitations store the extra energy

b) understand which excitations are relevant for the property which you want as function of temperature

How do materials store energy: Some types of excitations

Electronic

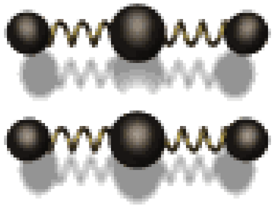
Occupation

$\Psi \longrightarrow \rotatebox{180}{Ψ}$

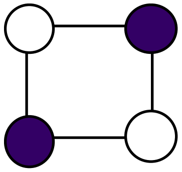
Magnetic (electron spin)

$\uparrow \longrightarrow \downarrow$

Vibrational



Configurational



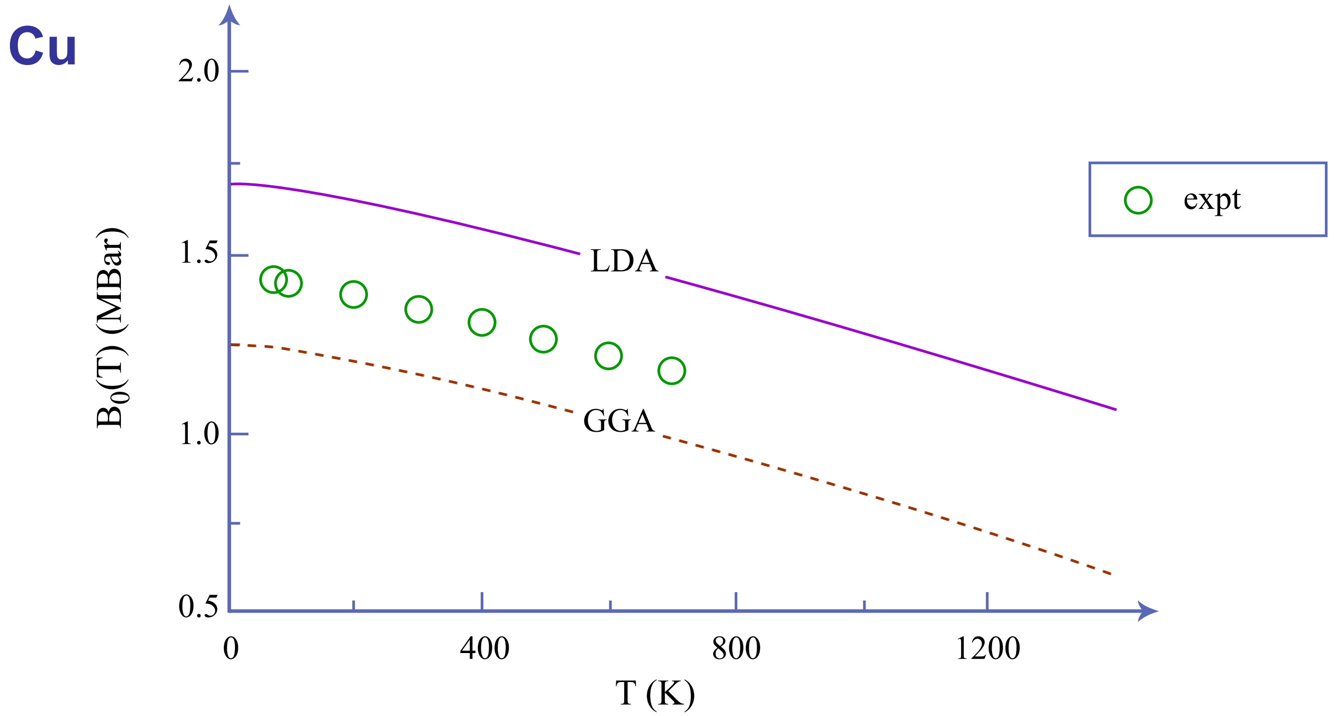
In polymers and bio-molecules, vibrational and configurational can not always be distinguished

Conformational

Changes in Materials with Temperature

- Crystal structure (phase changes, surface structure change)
- Chemistry (e.g. oxygen content in oxides, concentration profiles towards surface)
- Properties (e.g. electrical conductivity)
- Volume

Example: T-dependence of Cu bulk modulus



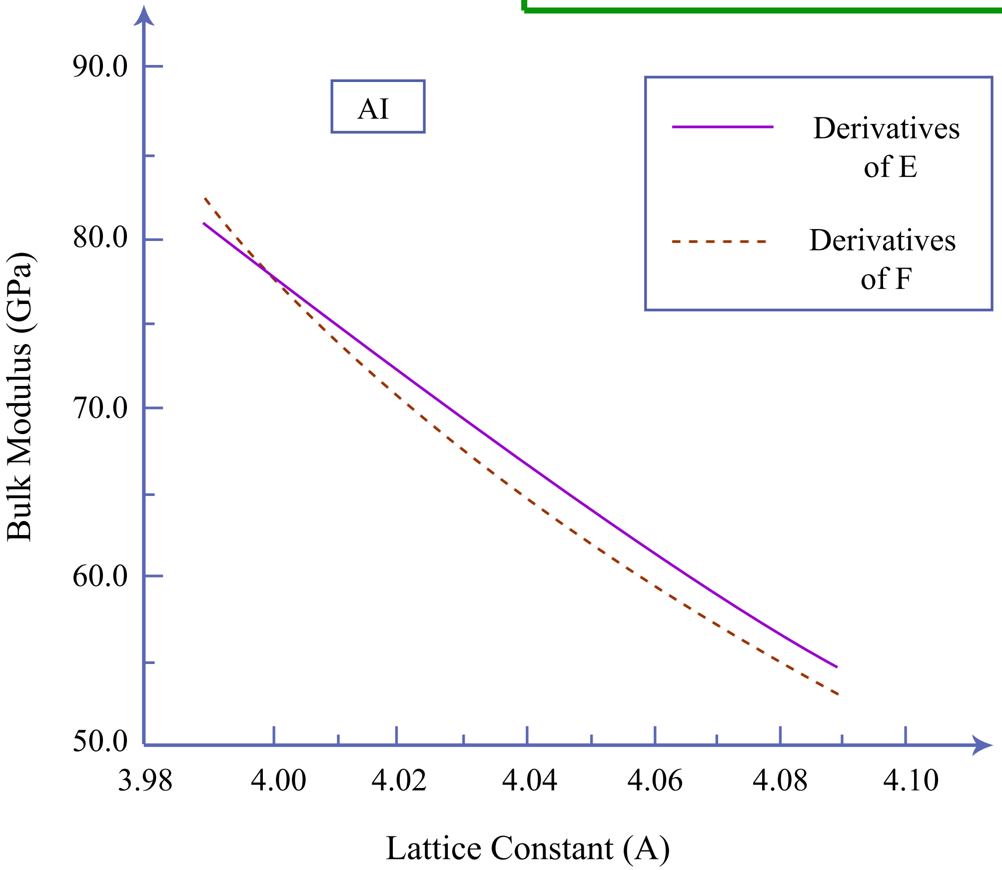
Variation with temperature of the bulk modulus B_0. At all temperatures, the LDA (solid line) overestimates B_0 and the GGA (dashed line) underestimates it; however, $\partial B_0 / \partial T$ is approximately the same for the LDA, GGA, and experimental values.

Figure by MIT OCW.

Why does bulk modulus change with T ?

Calculate at zero K $V\left(\frac{\partial^2 E}{\partial V^2}\right)_{a_0}$

Experiment at $V\left(\frac{\partial^2 F}{\partial V^2}\right)_{a}$



Al

So, to a good approximation, only need to get lattice parameter at some T, then do zero K calculation at that lattice parameter.

Figure by MIT OCW.

Source: Quong, A. and A. Liu, 1997 *Physical Review B*, **56,** 7767-7770.

At what lattice parameter ?

a and *B* Calculated at Zero temperature lattice parameter

System	a_o		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

At LDA room- temperature minimum

System	a_o		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

At experimental room-temperature lattice constant

System	a_o	B (GPa)	
	Exp	Calc	Exp
Li	3.52	9.4	11.6
Na	4.28	4.6	6.8
Al	4.05	64.2	72.2

data from Quong, A. and A. Liu, 1997: First-Principles calculations of the thermal expansion of metals. *Physical Review B*, **56,** 7767-7770.

But Materials Expand with Temperature

$$F(V,T) \;=\; E(V,T) - TS(V,T)$$

Volume dependence of the entropy causes thermal expansion

At higher volume, force constants become weaker, hence phonon frequencies lower, hence entropy higher

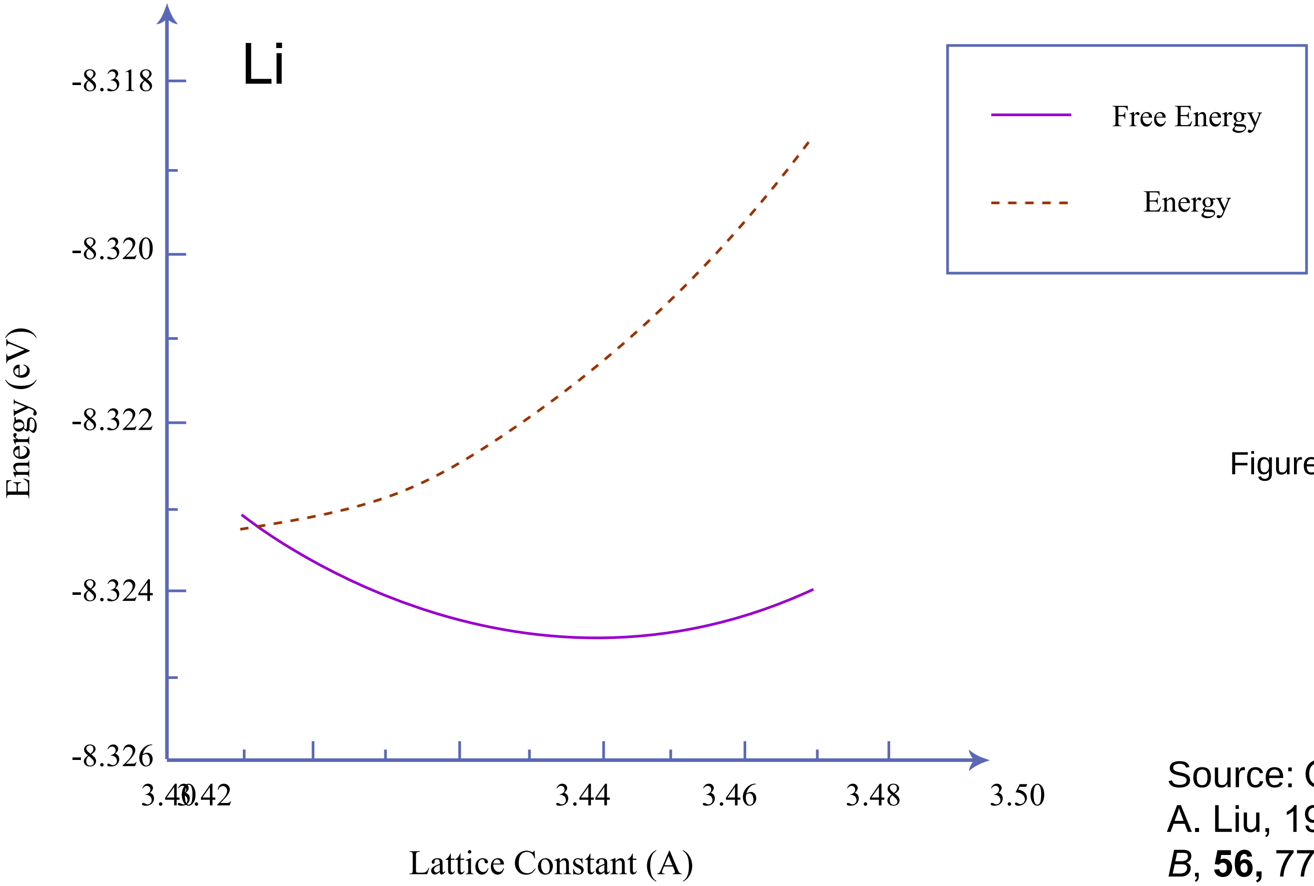


Figure by MIT OCW.

Source: Quong, A. and A. Liu, 1997 *Physical Review B*, **56,** 7767-7770.

How to calculate thermal expansion ?

Brute Force: Direct Simulation (e.g Molecular Dynamics, see later)

Calculate entropy as function of volume: $\alpha_V = \left(\frac{\partial S}{\partial V}\right)_T \beta_T$

Which entropy ? -> phonons etc.

$$F(a,T) = E_{\text{stat}}(a) + k_B T \sum_{q\lambda} \ln\left\{ 2\sinh\left(\frac{\hbar\,\omega_{q\lambda}(a)}{2k_B T} \right) \right\}$$

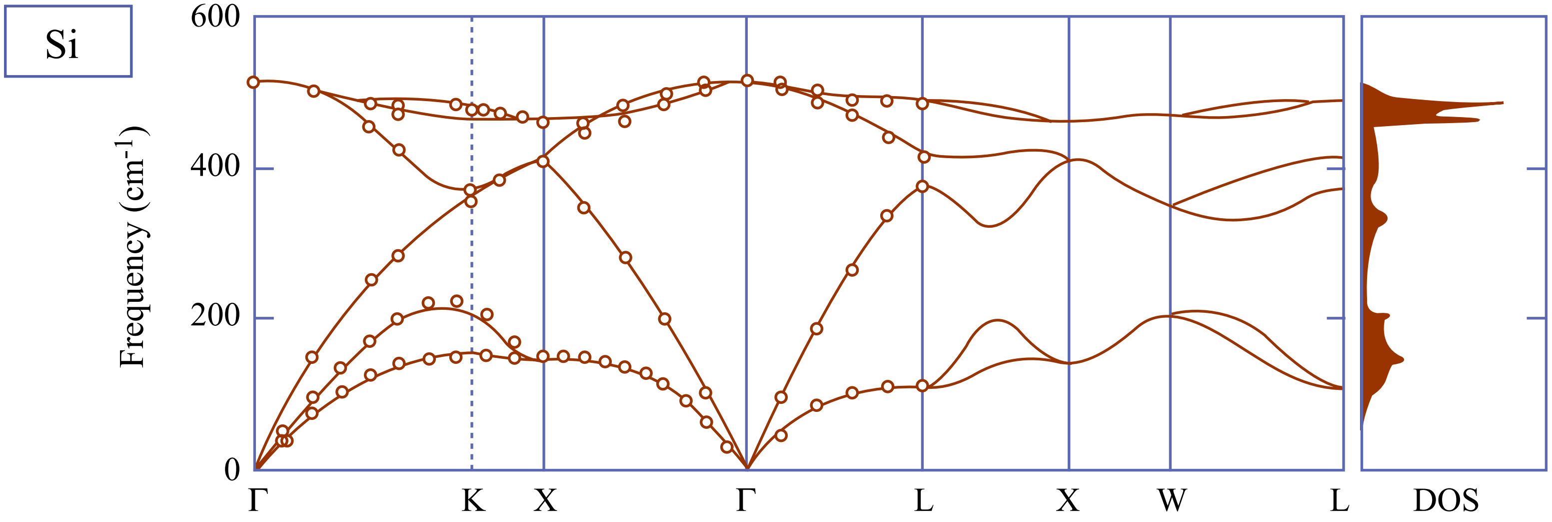


Figure by MIT OCW.

Cu thermal expansion (phonons only)

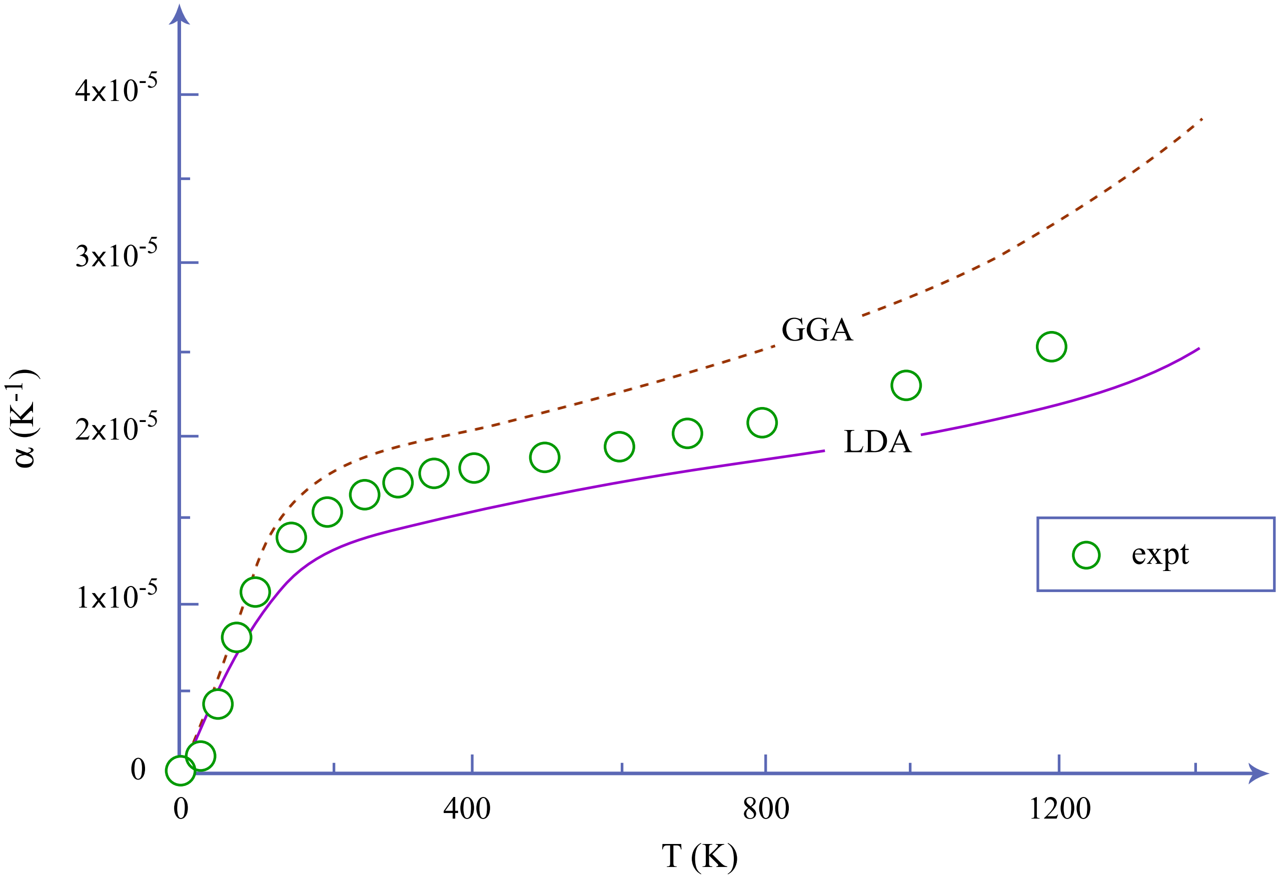
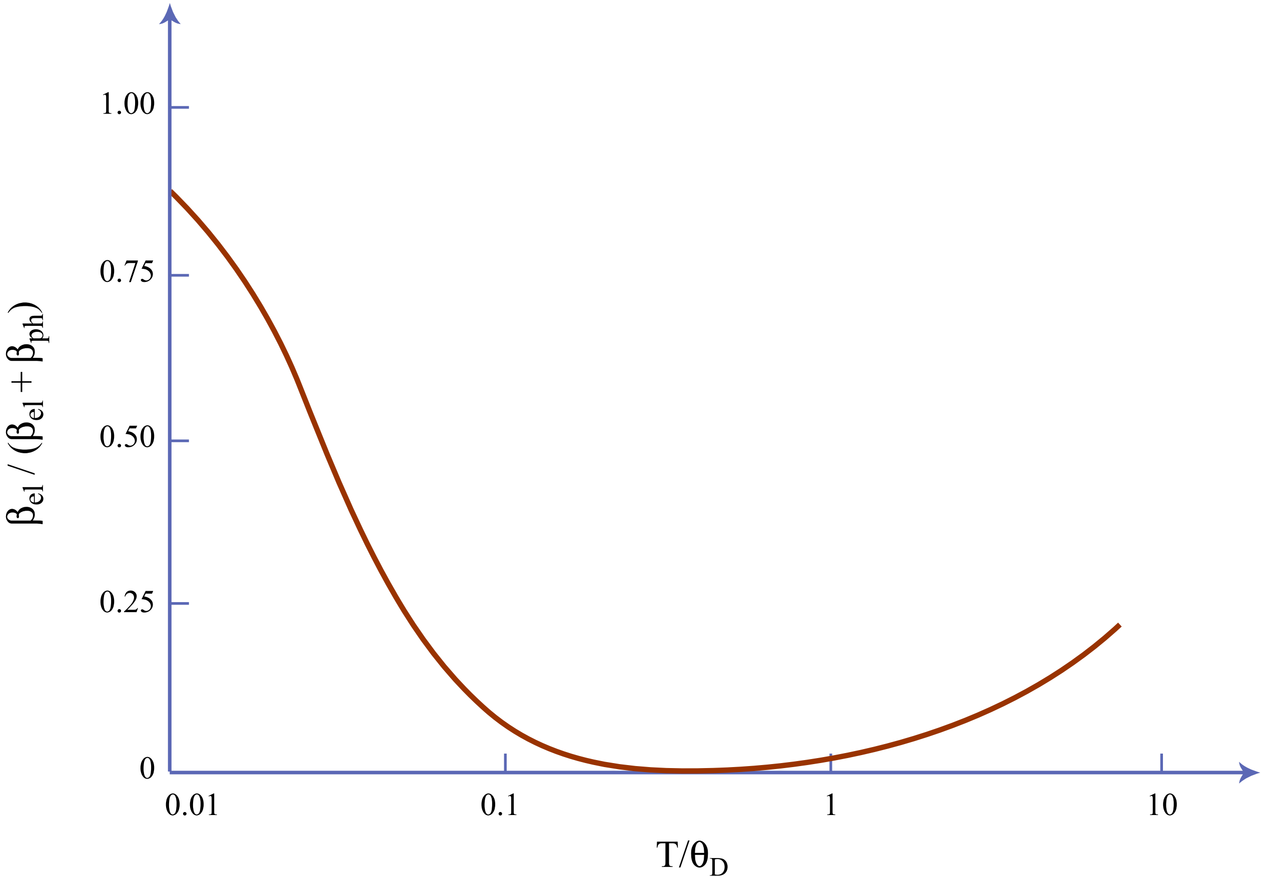


Figure by MIT OCW.

Do the electrons cause thermal expansion ?



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Why does structure change ? Phase transitions

Phase that minimizes free energy G(p,T) *or* F(V,T)

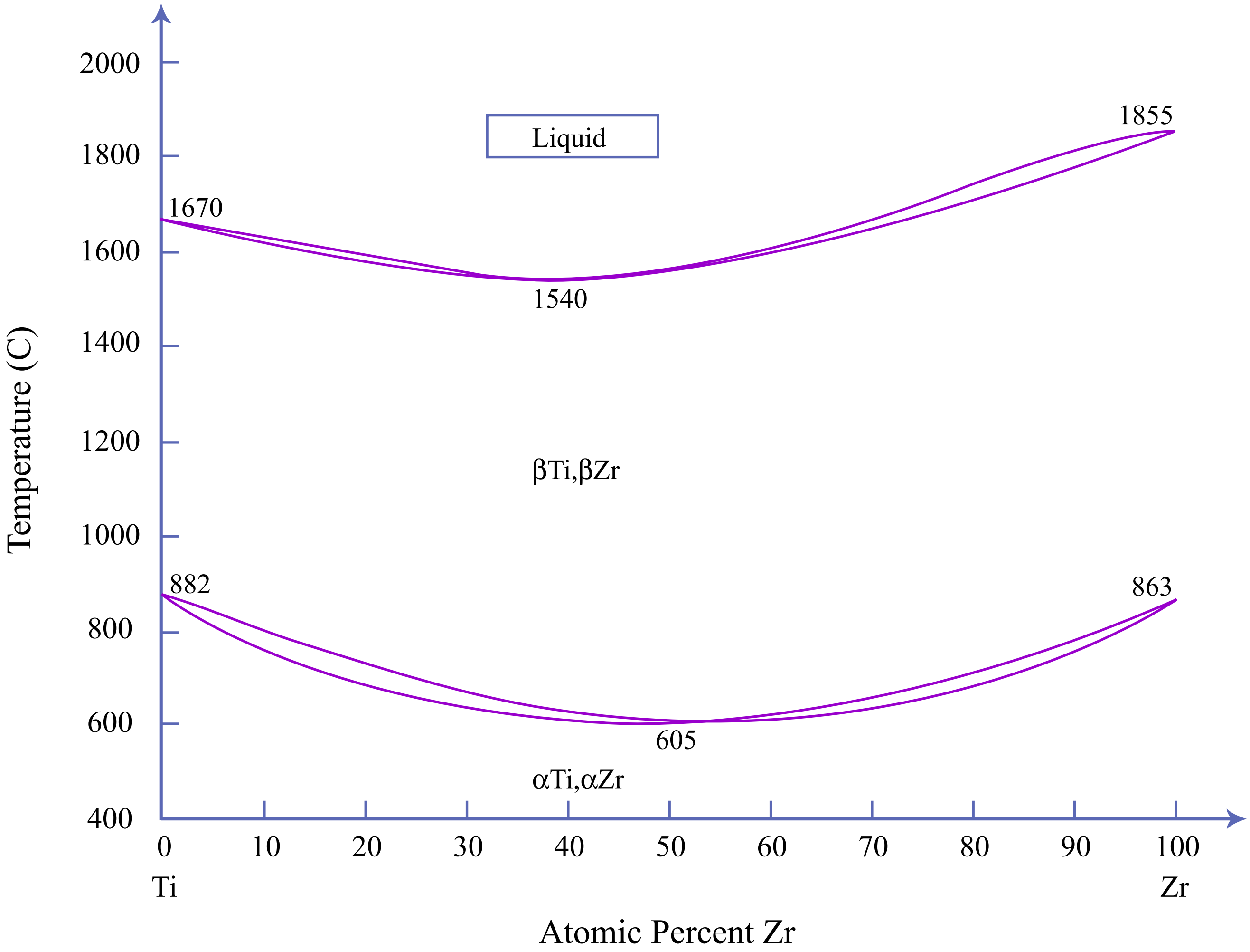
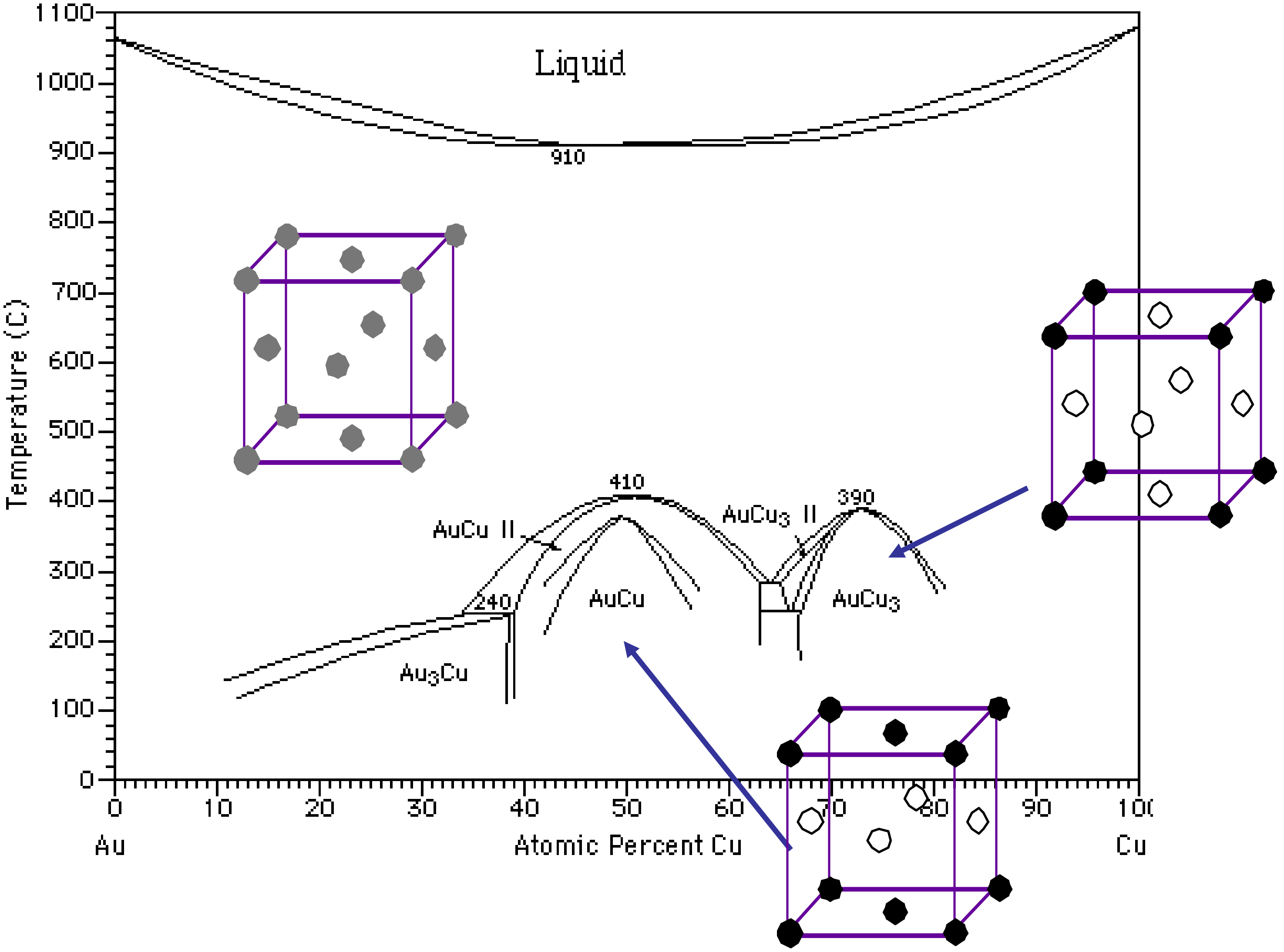


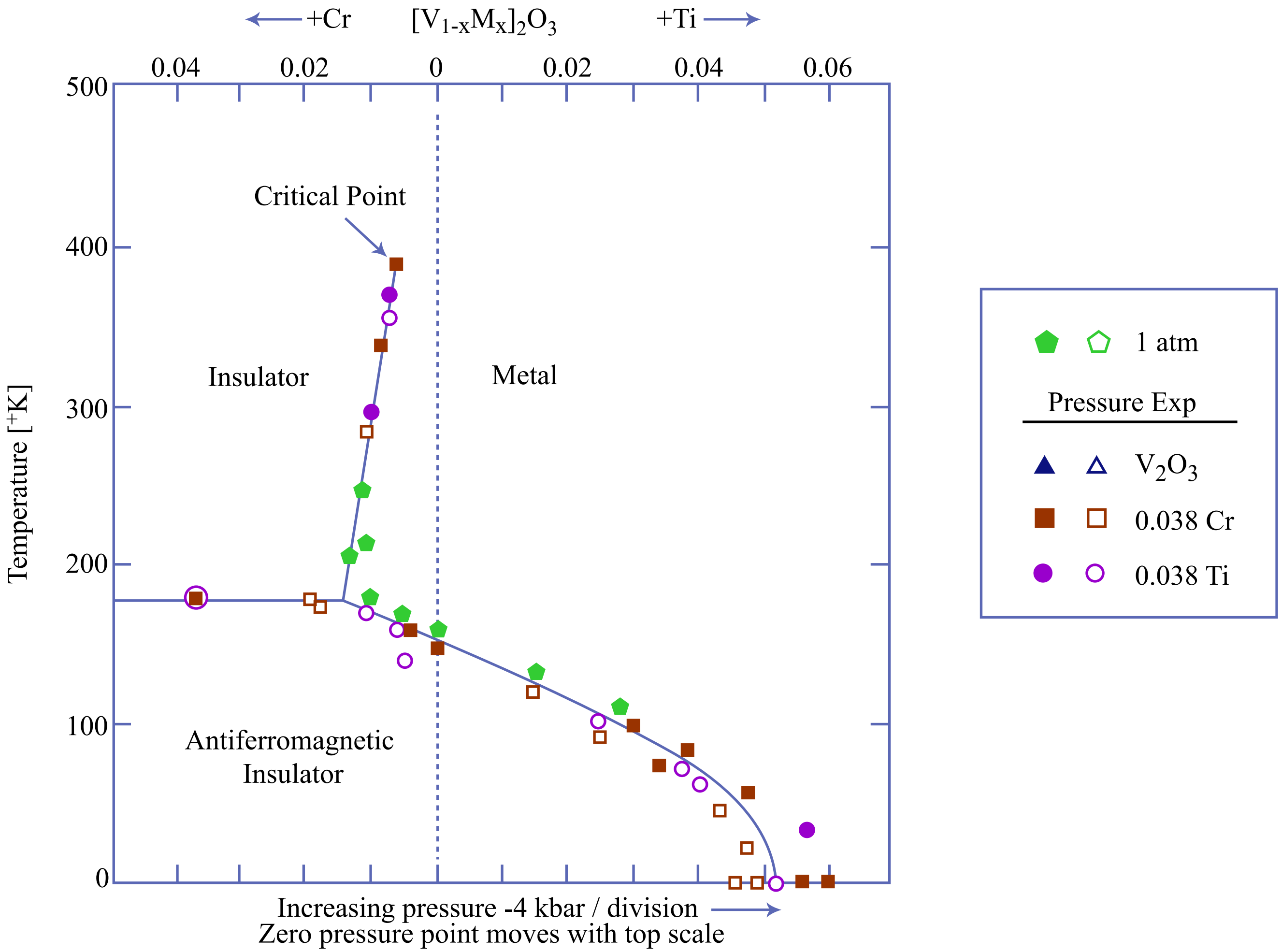
Figure by MIT OCW.

Cu-Au phase diagram



Electronic Phase Transformations

V_2O_3



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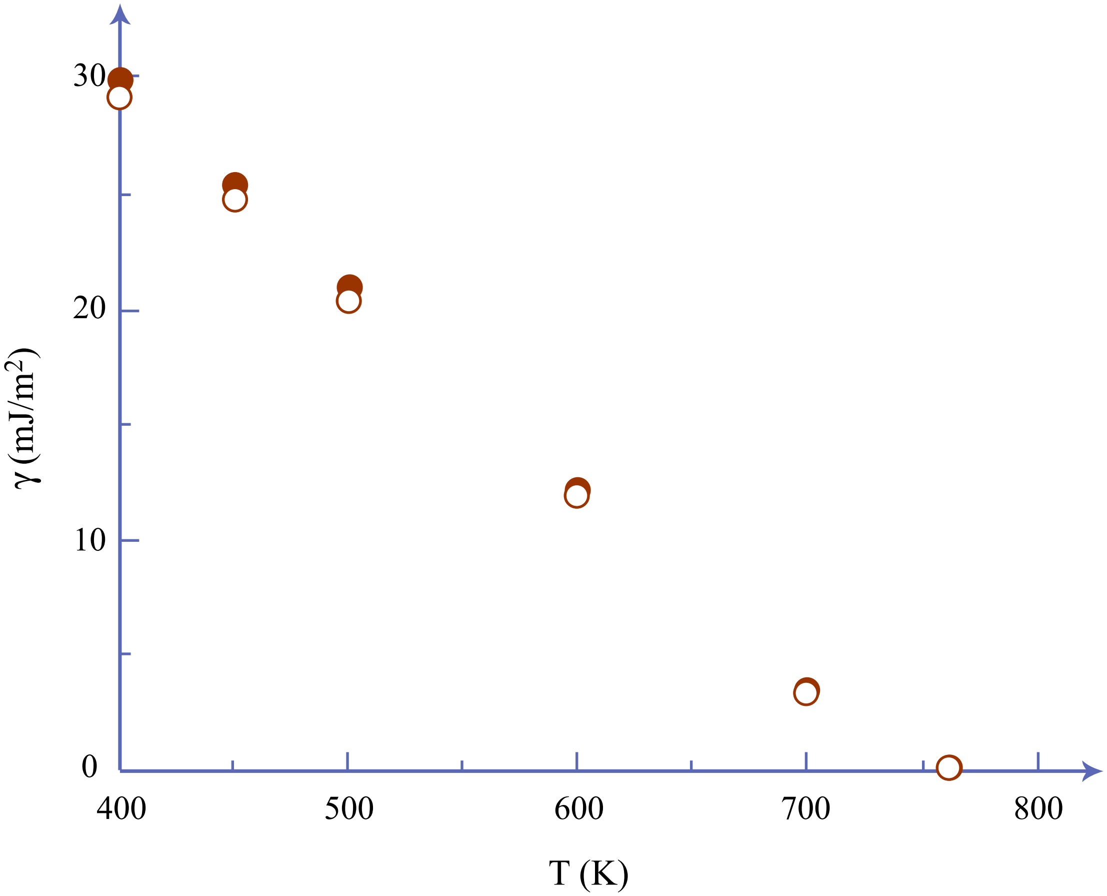
Ag-Al

Interface energy



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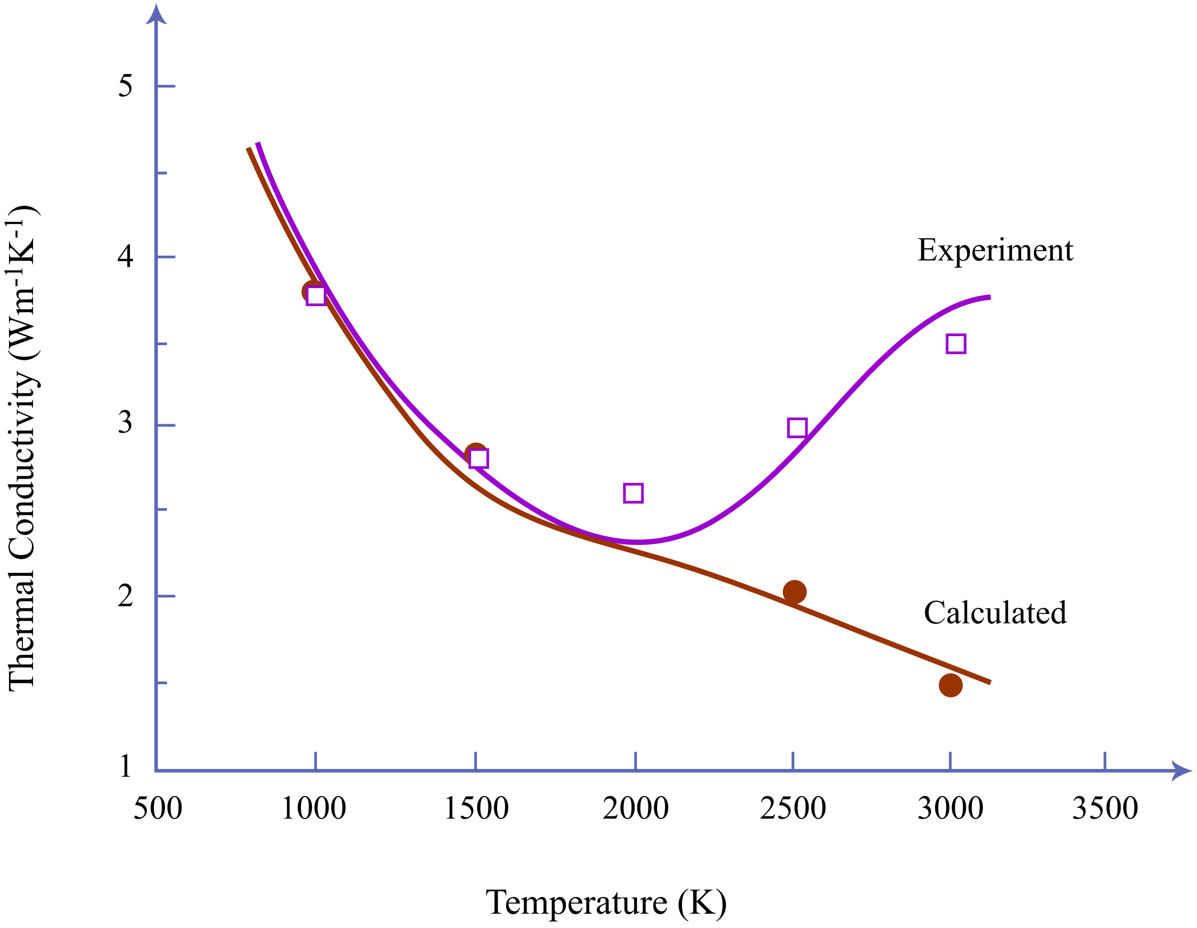
Properties

Thermal conductivity UO_2



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How to model finite temperature systems ?

Simulate Dynamics

Example: Molecular Dynamics

- Newtonian motion for atoms
- Average Kinetic energy determines temperature
- Forces can be calculated from empirical potential model or from quantum mechanics

Statistical Mechanics

- Build approximate model
- Simulation or analytical integration of thermodynamic properties

Remaining lectures focus on finite-temperature behavior and applications

Finite Temperature: Review of Stat Mech and Thermodynamics. Excitations in materials

Lab 3: Density Functional Theory II.

Molecular Dynamics I

Molecular Dynamics II

Lab 4: Molecular Dynamics

Molecular Dynamics III

Monte Carlo simulation: Application to Lattice models: sampling errors. metastability.

Lab 5: Monte Carlo

Coarse graining: Alloy Theory

Alloy Theory II, Free Energy Integration.

Modeling in industry (Chris Wolverton from Ford Motor Company)

Data Mining in Materials Science and Engineering I

Data Mining in Materials Science and Engineering II

Case studies I

Case Studies II

Molecular Dynamics

Show movie clips

Images removed for copyright reasons.
Stills from several animation clips.

Limitations of Simulation (with all degrees of freedom)

Wide disparity of time scales between different materials phenomena (e.g. vibration and atom hopping in solids).

Examples: diffusion, vapor deposition, solidification

Great for looking at phenomena

Example Atomic Vibrations versus Diffusion

Numerical integration of atomic motion requires tracking atoms at the time-scale of their vibration

for $\nu \approx 10$ THz (10^{13}/s)
take $\Delta t \approx 10^{-14}$ s (10 fs)

100,000 time steps = 1ns

Time scale of diffusion in solids

$D \approx a^2$ x jump rate
for $D \approx 10^{-14}$ cm^2/s and $a \approx 10^{-8}$ cm

jump rate = D/a^2 = 100/sec

Statistical Mechanics on Relevant Degrees of Freedom

Ergodicity *Time-average* of a property can be replaced by a suitable average over collection of possible microscopic states (= *ensemble*)

Ensemble Collection of microscopic states consistent with thermodynamic boundary conditions

$$P_i = \frac{\exp\left[-\beta\, E_i\right]}{Q} \longrightarrow$$ Probability to be in a given state i

$$Q = \sum_i \exp\left[-\beta\, E_i\right] \longrightarrow$$ Partition Function

$$F = -\beta \ln[Q] \longrightarrow$$ Free energy (Helmholtz)

$$S = -k_B \sum_i P_i \ln(P_i) \longrightarrow$$ Entropy

Example: Electronic Entropy

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\vec{r})\right]\psi_i = \varepsilon_i \psi_i$$

$$V_{KS}(\vec{r}) = \int \frac{n(\vec{r}_1)}{|\vec{r}-\vec{r}_1|}\,d\vec{r}_1 + V_{ext}(\vec{r}) + V_{XC}(\vec{r})$$

$$V_{XC}(\vec{r}) = \frac{\delta E_{XC}\left[n(\vec{r})\right]}{\delta n(\vec{r})}$$

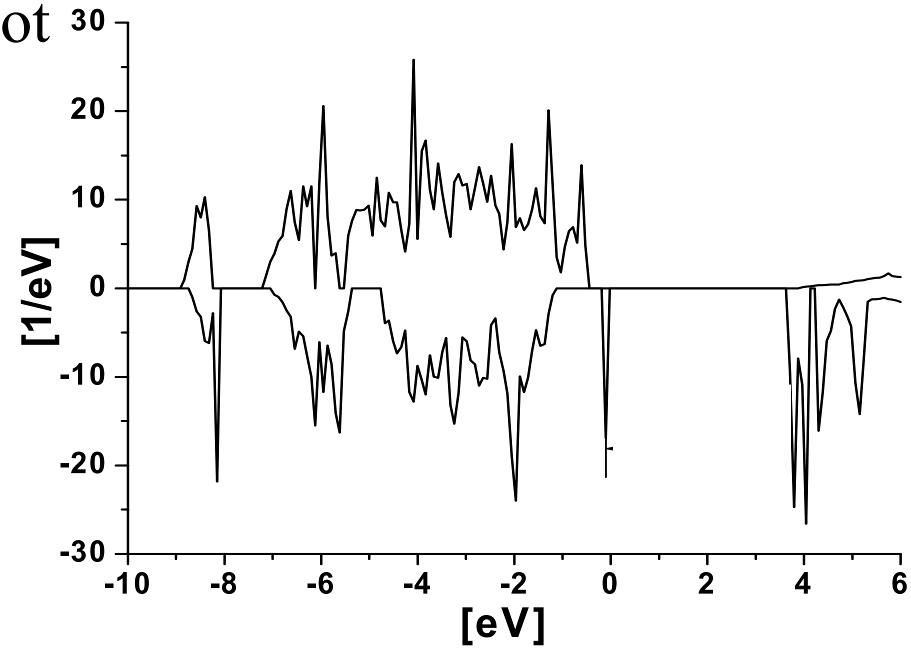
Treat as independent one-electron states (eigenstates)

Each state can be occupied or not

Electronic Entropy

Every state ε_i can be occupied or not occupied: Probability is given by Fermi Dirac distribution function

$$f_i = \frac{e^{-\beta(\varepsilon_i - \varepsilon_F)}}{1 + e^{-\beta(\varepsilon_i - \varepsilon_F)}}$$



The set of occupation numbers $\{f_i\}$ describes the electronic state of the system

$$S_{el} = -k_B \sum_i \left[f_i \ln(f_i) + (1 - f_i)\ln(1 - f_i) \right]$$

In principle, the Fermi-Dirac occupation needs to be included in the self-consistency iteration

Approximation lies in treating the Kohn-Sham eigenvalues as eigenstates of the real electron system.

T*electronic entropy

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copyright reasons.

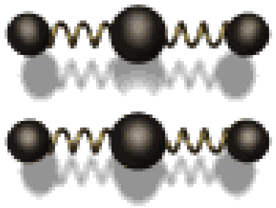
electronic energy

vibrational free energy

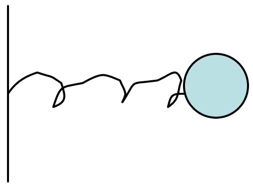
electronic free energy

Fig. 2 in Moroni et al,
Phys. Rev. Lett, 76, 2758 (1996).

Example: phonons -> vibrational entropy



One atom



$$F = k\xi_i$$

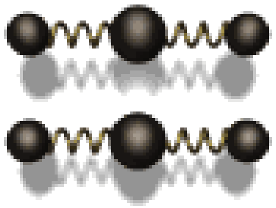
$$E = \frac{k\xi_i^{\,2}}{2}$$

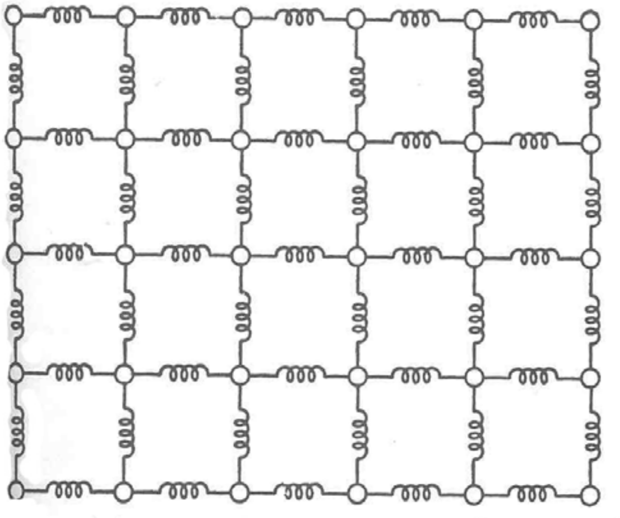
Discrete energy levels at $\varepsilon_i = \left(n + \frac{1}{2}\right) \hbar\omega_i$

Partition function: $$Q = \sum_{n=0}^{\infty} \exp\left(-\beta\left(n + \tfrac{1}{2}\right)\hbar\omega_i\right)$$

$$Q = \exp\left(\beta\hbar\omega_i / 2\right) - \exp\left(-\beta\hbar\omega_i / 2\right)$$

Example: phonons -> vibrational entropy





$$E\left(\vec{r}_1, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N\right)$$

r_i not eigenstates of the system

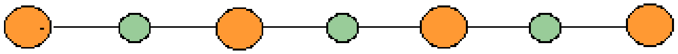
$$E\left(\vec{r}_1, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N\right) = E\left(\vec{r}_1^{\,0}, \vec{r}_2^{\,0}, \vec{r}_3^{\,0} \ldots \vec{r}_N^{\,0}\right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\frac{\partial^2 E}{\partial r_i \partial r_j}\right)\delta r_i \delta r_j + \ldots$$

go to eigenmodes -> ξ_i (amplitude A_i)

$$E\left(A_1, A_2, A_3 \ldots A_N\right) = E(A_1) + E(A_2) + E(A_3) + \ldots + E(A_N)$$

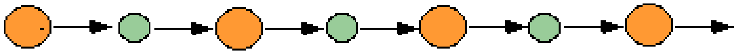
Phonon modes are linear combinations of atomic displacement such that changing their amplitude does not change the amplitude of other phonon modes (i.e. phonon modes are orthogonal)

A diatomic chain:

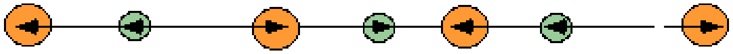


The Acoustic Modes

$k = 0$

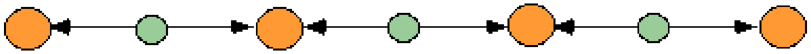


$k = \pi/a$

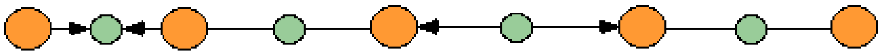


The Optic Modes

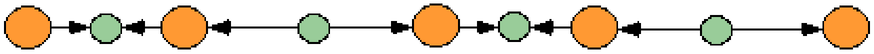
$k = 0$



$k = \pi/2a$



$k = \pi/a$



Each eigenmode is independent harmonic oscillator

$$Q = \sum_{n=0}^{\infty} \exp\left(-\beta\left(n + \tfrac{1}{2}\right)\hbar\omega_i\right)$$

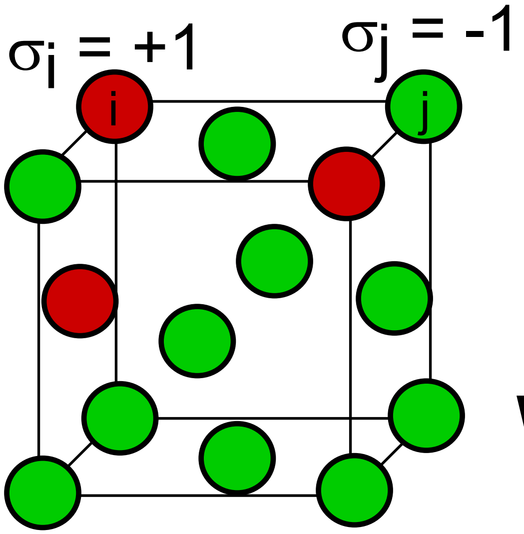
$$Q = \exp\left(\beta\hbar\omega_i / 2\right) - \exp\left(-\beta\hbar\omega_i / 2\right)$$

$$Q_{tot} = \prod_i Q_i$$

Gives free energy, entropy, heat capacity …

Good reference for phonons: *Introduction to Modern Statistical Mechanics*, by D. Chandler (section 4.3)

Configurational Degrees of Freedom



$E(\sigma_1, \sigma_2, \ldots, \sigma_N)$?

Write as expansion

$$E(\sigma_1, \sigma_2, \ldots, \sigma_N) \;=\; V_0 + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j} \sigma_i \sigma_j \sigma_k + \;\ldots$$

-> difficult to solve analytically

-> alloy theory