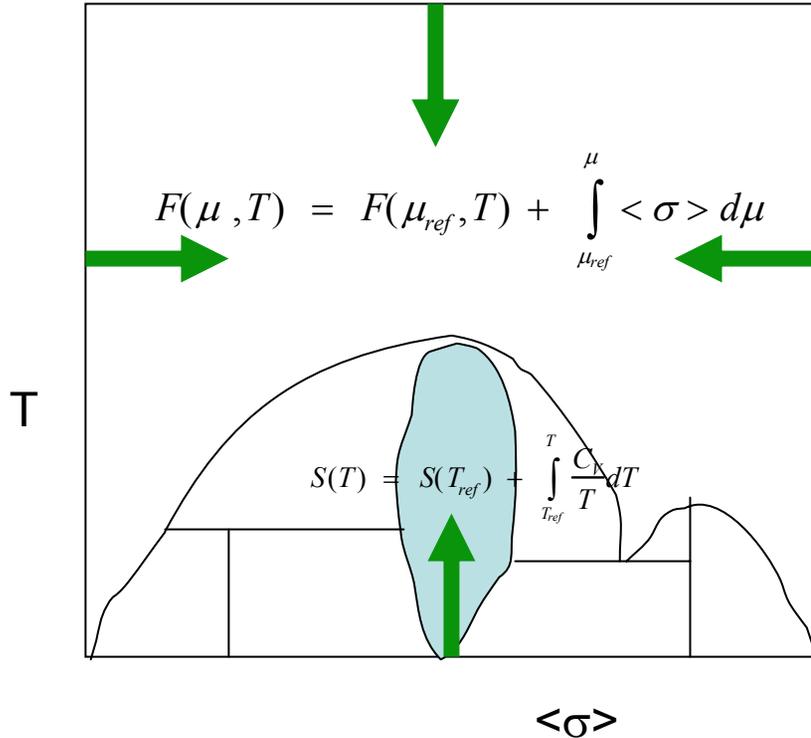


## 3.320: Lecture 19 (4/14/05)

### Free Energies and physical Coarse-graining

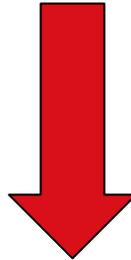


# Non-Boltzmann sampling and Umbrella sampling

## Simple Sampling

Sample randomly

$$\langle A \rangle = \frac{\sum_{v=1}^M \exp(-\beta H_v) A_v}{\sum_{v=1}^M \exp(-\beta H_v)}$$



## Importance Sampling

Sample with Boltzmann weight

$$\langle A \rangle = \sum_{v=1}^M A_v$$

## Non Boltzmann Sampling

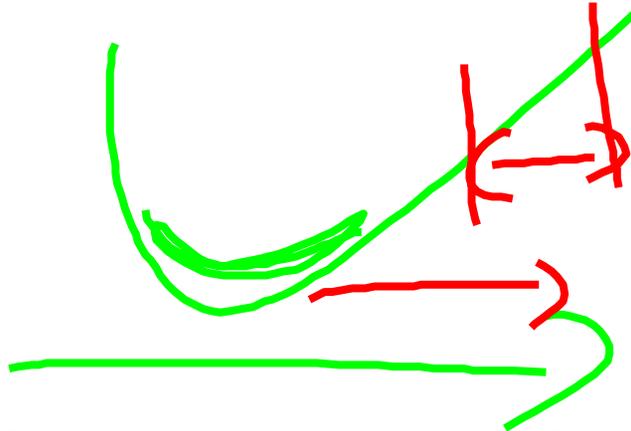
Sample with some Hamiltonian  $H^o$

$$\langle A \rangle = \frac{\sum_{v=1}^M \exp(-\beta(H_v - H_v^o)) A_v}{\sum_{v=1}^M \exp(-\beta(H_v - H_v^o))}$$

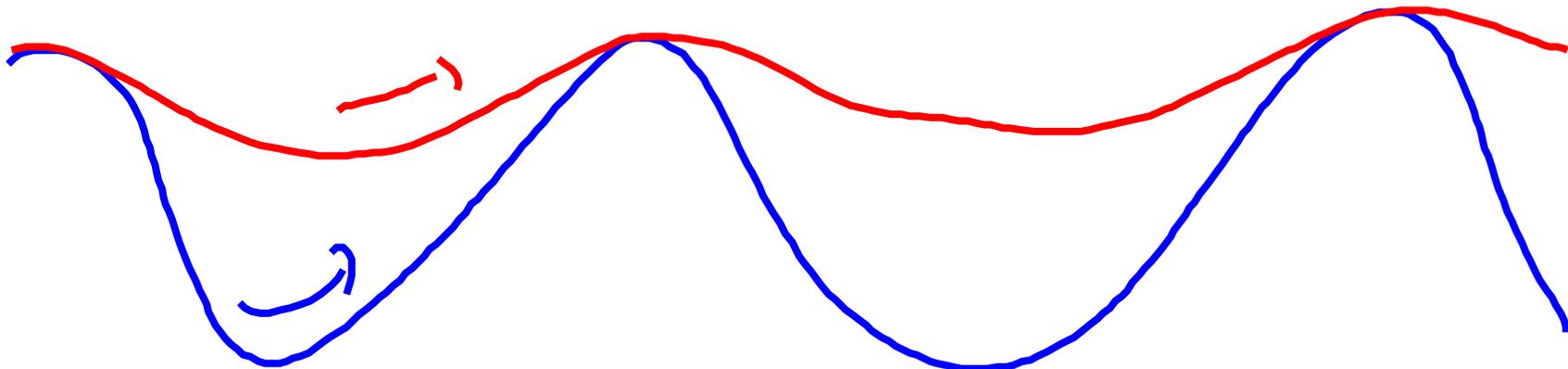
$$\Delta H = H - H^o$$

## Cases where non-Boltzmann sampling may be useful

1) To sample part of phase space relevant for a particular property



2) To sample phase space more efficiently



# Non-Metropolis Monte Carlo

$$w_{ij}^o = w_{ji}^o$$

Allow non-equal a-priori probabilities to get less possible moves that are not accepted

$$\rightarrow W_{ij}^o = f[\Delta H_{ij}]$$

In Metropolis this is symmetric

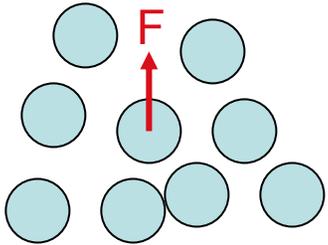
$$\rightarrow W_{ji}^o = f[\Delta H_{ji}]$$

## Detailed balance

$$P_i W_{ij}^o P_{jj} = P_j W_{ji}^o P_{ii}$$

$$\rightarrow \frac{P_{ij}}{P_{ji}} = \frac{f[\Delta H_{ij}]}{f[\Delta H_{ji}]} \exp(-\beta \Delta H_{ij})$$

## Example: Force-bias Monte Carlo



$$\delta r_i = AF_i + \delta r_i^{random}$$

The equation is annotated with red markings: a red box encloses the term  $AF_i$ , and a red arrow points to the  $\delta r_i$  term in the second part of the equation.

Go downhill faster, but requires force calculation

 Pangali et al., Chem. Phys. Lett., **55**, 413 (1978)

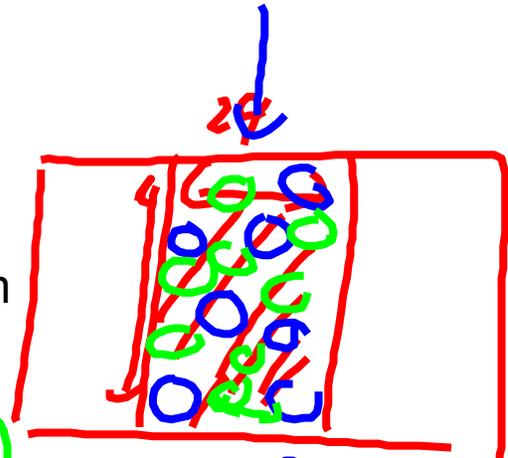
## Case Study: Studying Surface segregation in Cu-Ni

See Foiles, S. M. "Calculation of the surface segregation of Ni-Cu alloys with the use of the embedded atom method." *Physical Review B* 32, no. 12 (1985): 7685–7693.

Embedded atom for energy model

Supercells that are 24x15 to 48x25 atoms with vacuum

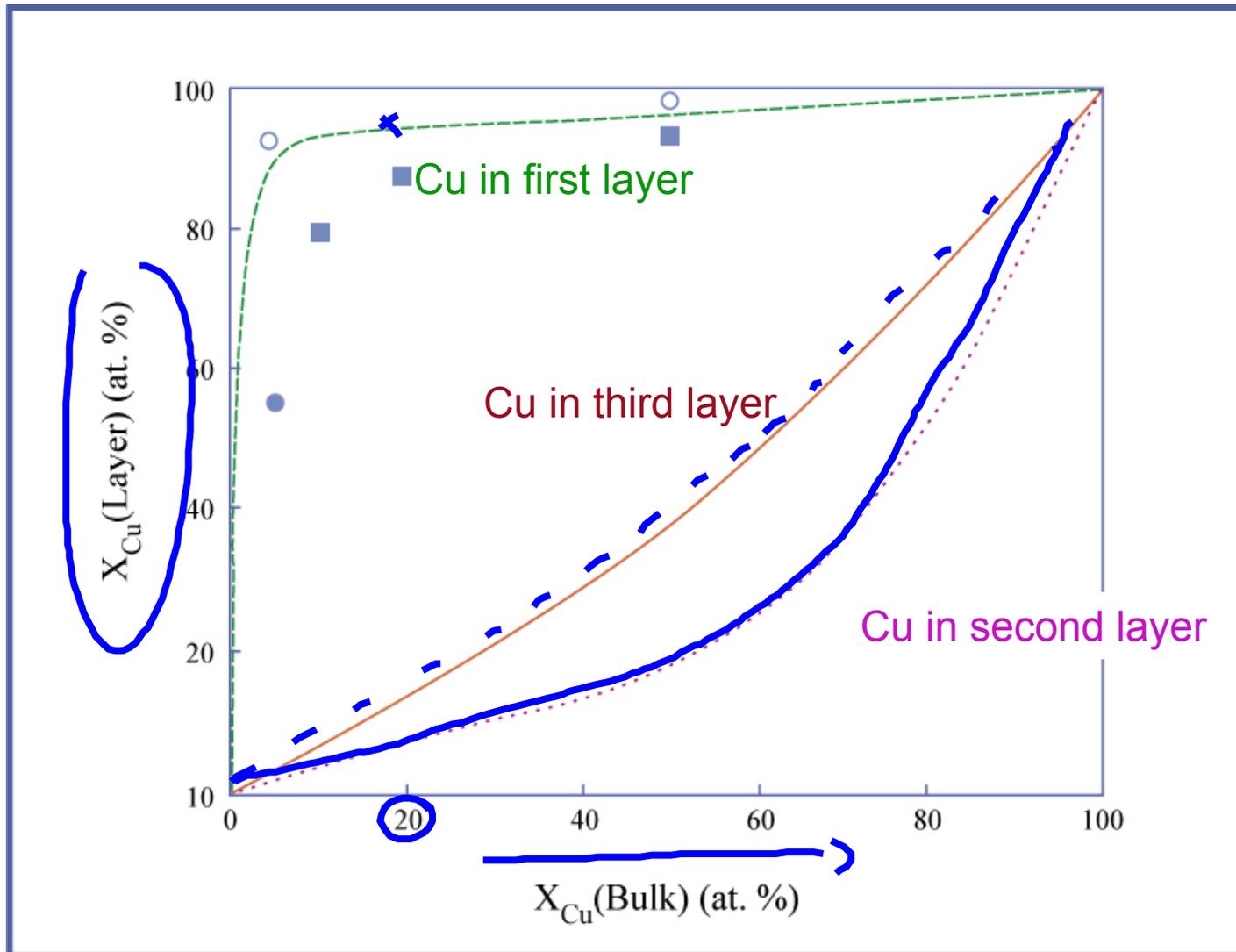
Grand canonical Hamiltonian

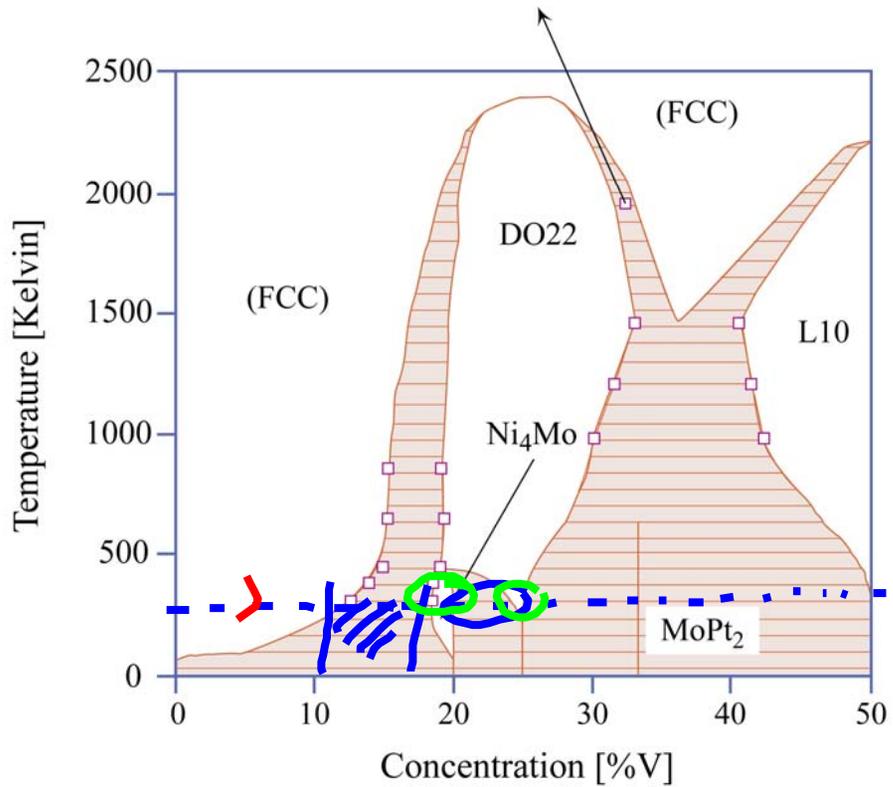


$$\mathcal{H} = E - \mu_{\text{Cu}} N_{\text{Cu}} - \mu_{\text{Ni}} N_{\text{Ni}}$$

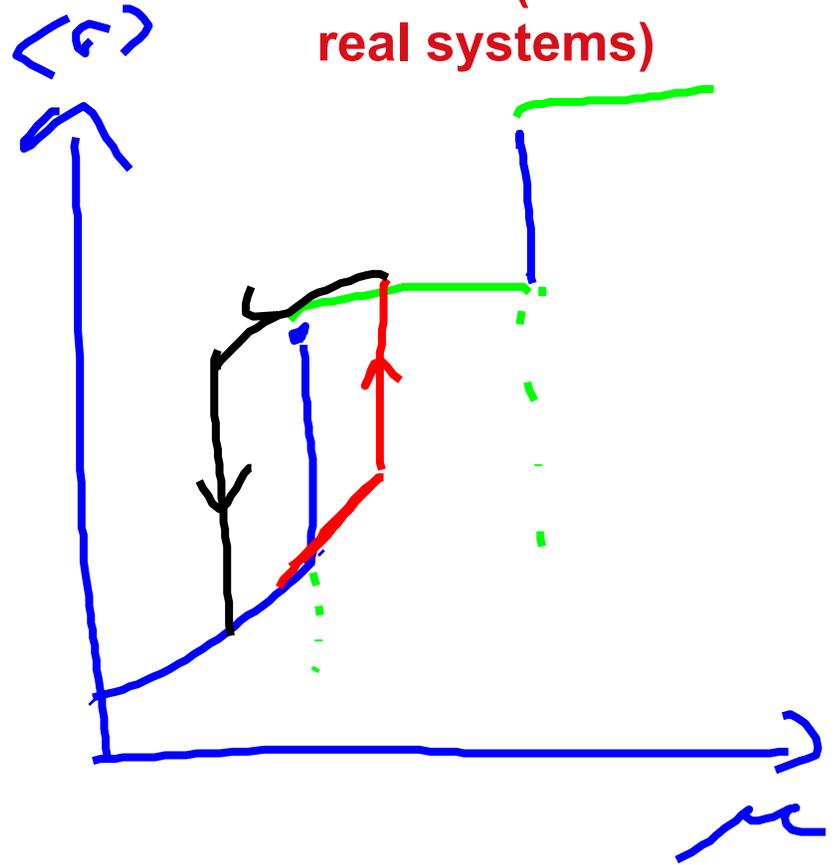
$$E - (\mu_{\text{Cu}} - \mu_{\text{Ni}}) N_{\text{Cu}}$$

# Cu distribution



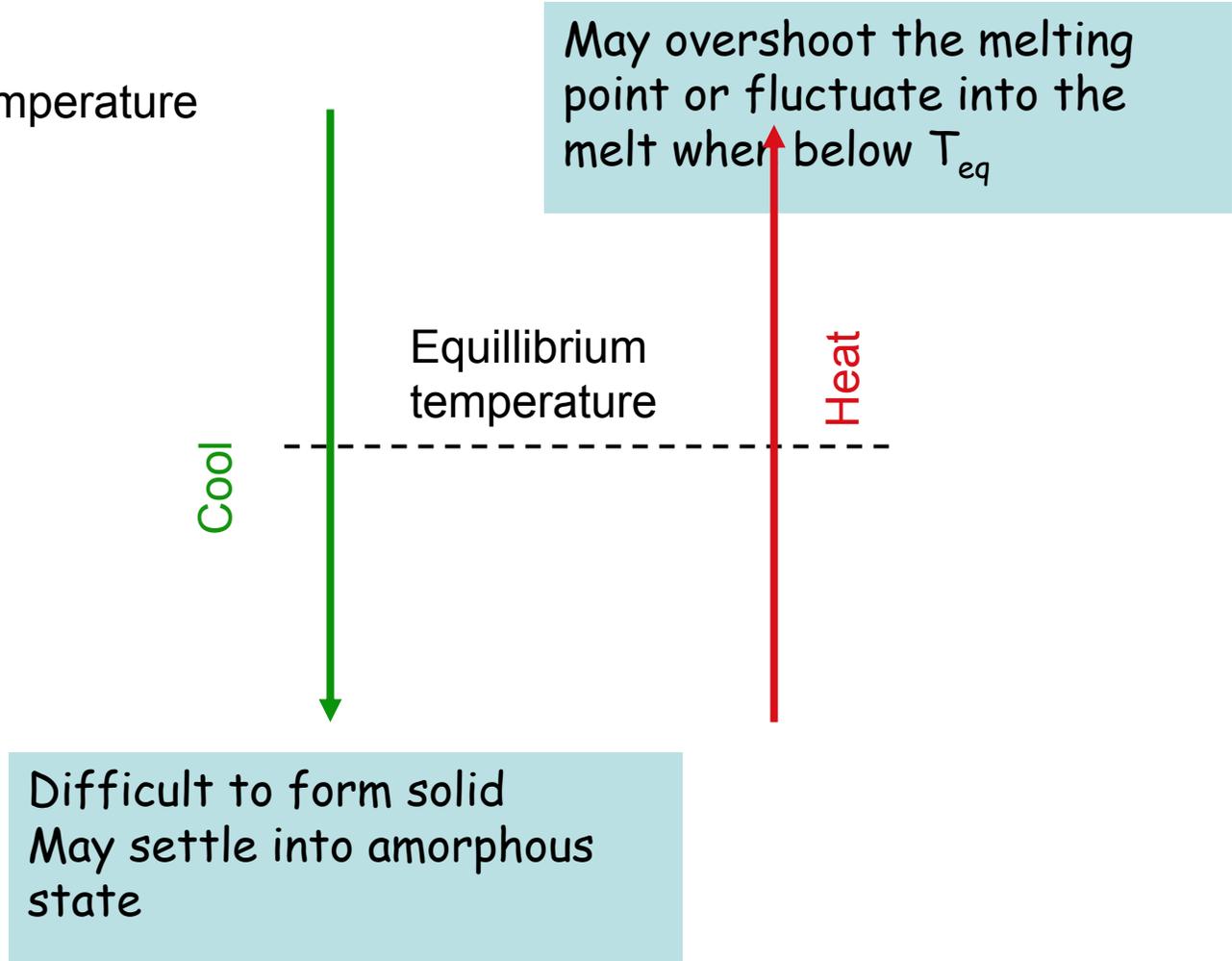


**Equilibration problems in Monte Carlo (not unlike real systems)**



## This problem is similar to problems in MD

e.g. solidification temperature



## Could get free phase transitions from free energies, but F and S are difficult to compute ...

F and S are not simple averages

$$U = \sum_{\nu} P_{\nu} E_{\nu}$$

Need relative probabilities

$$F = U - TS$$

$$S = -k_B \sum_{\nu} P_{\nu} \ln(P_{\nu})$$

Need absolute probabilities

F as an integrated quantity

$$F = \sum_{\nu} P_{\nu} [E_{\nu} + k_B T \ln(P_{\nu})]$$

$$\rightarrow F = \sum_{\nu} P_{\nu} [-k_B T \ln(Z)]$$

Quantity that needs to be integrated is flat (but unknown)

## Could we get the free energy ?

**Problem:** F is not an average. Free energy does not exist in a microstate, it is a property of the distribution function. Same for entropy

$$F = -kT \ln(Q) = -kT \ln \left[ \sum_{v \in \mathbb{E}} \exp(-\beta H_v) \right]$$

Can write F as an average, but not over the important states

$$F = -kT \ln \left[ \frac{1}{\langle \exp(\beta H_v) \rangle} \right] - kT \ln[M]$$

**Proof**

$$\begin{aligned} \langle \exp(\beta H_v) \rangle &= \sum_{v \in \mathbb{E}} \frac{\exp(-\beta H_v)}{Q} \exp(\beta H_v) \\ &= \frac{1}{Q} \sum_{v \in \mathbb{E}} 1 = \frac{M}{Q} \end{aligned}$$

## Methods to Obtain Free Energy *Differences*

- 1) Free energy integration (including  $\lambda$ -integration)
- 2) Overlapping distribution methods
- 3) Others

## Overlapping Distribution Methods

$$\underline{\Delta F} = -kT \ln \frac{Q_{II}}{Q_I} = -kT \ln \frac{\sum_{v \in E} \exp(-\beta H_v^{II})}{\sum_{v \in E} \exp(-\beta H_v^I)}$$

$\rightarrow \sum \exp(-\beta H_v^{II}) * 1 = \exp(\beta \chi_{v0}^{II}) \exp(-\beta \chi_{v0}^I)$

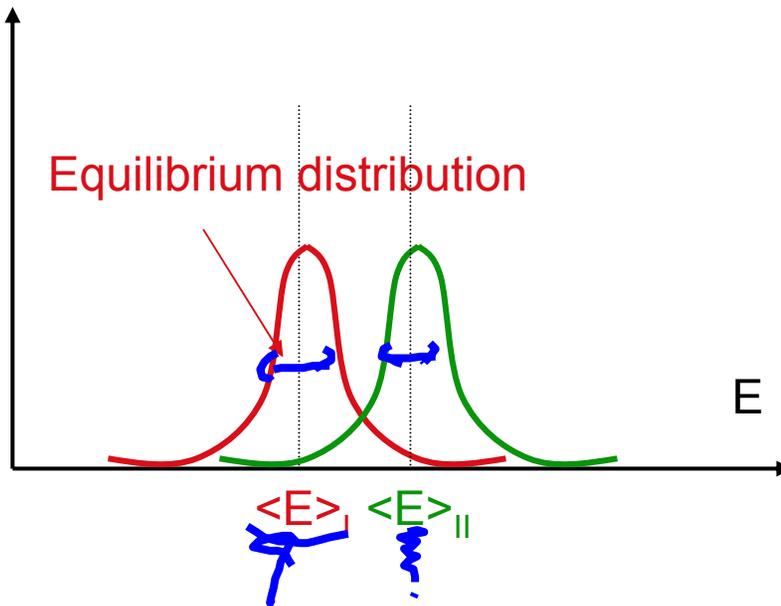
$$\Delta F = -kT \ln \left[ \sum_{v \in E} \exp(-\beta(H_v^{II} - H_v^I)) \frac{\exp(-\beta H_v^I)}{Q_I} \right]$$

$\rightarrow \beta H^I$

$$\Delta F = -kT \ln \left[ \left\langle \exp(-\beta(H_v^{II} - H_v^I)) \right\rangle_I \right]$$

Forward projecting: Using the states sampled in state I to get the free energy difference with II.

Example: free energy difference between two different temperature



Overlapping distribution methods will fail when the distributions do not overlap much. E.g. Low temperature simulation may not sample much of the excitations that would be present at high temperature

# Thermodynamic Integration: *You will be so proud you remember thermodynamics*

And now for an important message ...

$$\rightarrow A(\lambda_2) - A(\lambda_1) = \int_{\lambda_1}^{\lambda_2} \frac{\partial A}{\partial \lambda} d\lambda$$

Example: **Entropy** as function of T

$$\rightarrow S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{\partial S}{\partial T} dT = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

Can be obtained from Monte Carlo

$$\frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}$$

$$S(T) = S(T_{ref}) + \int_{T_{ref}}^T \frac{C_V}{T} dT$$

Need to find reference state in which we know entropy

Example: Ising model from T = 0

# Example: Integrate from T=0 in Ising model

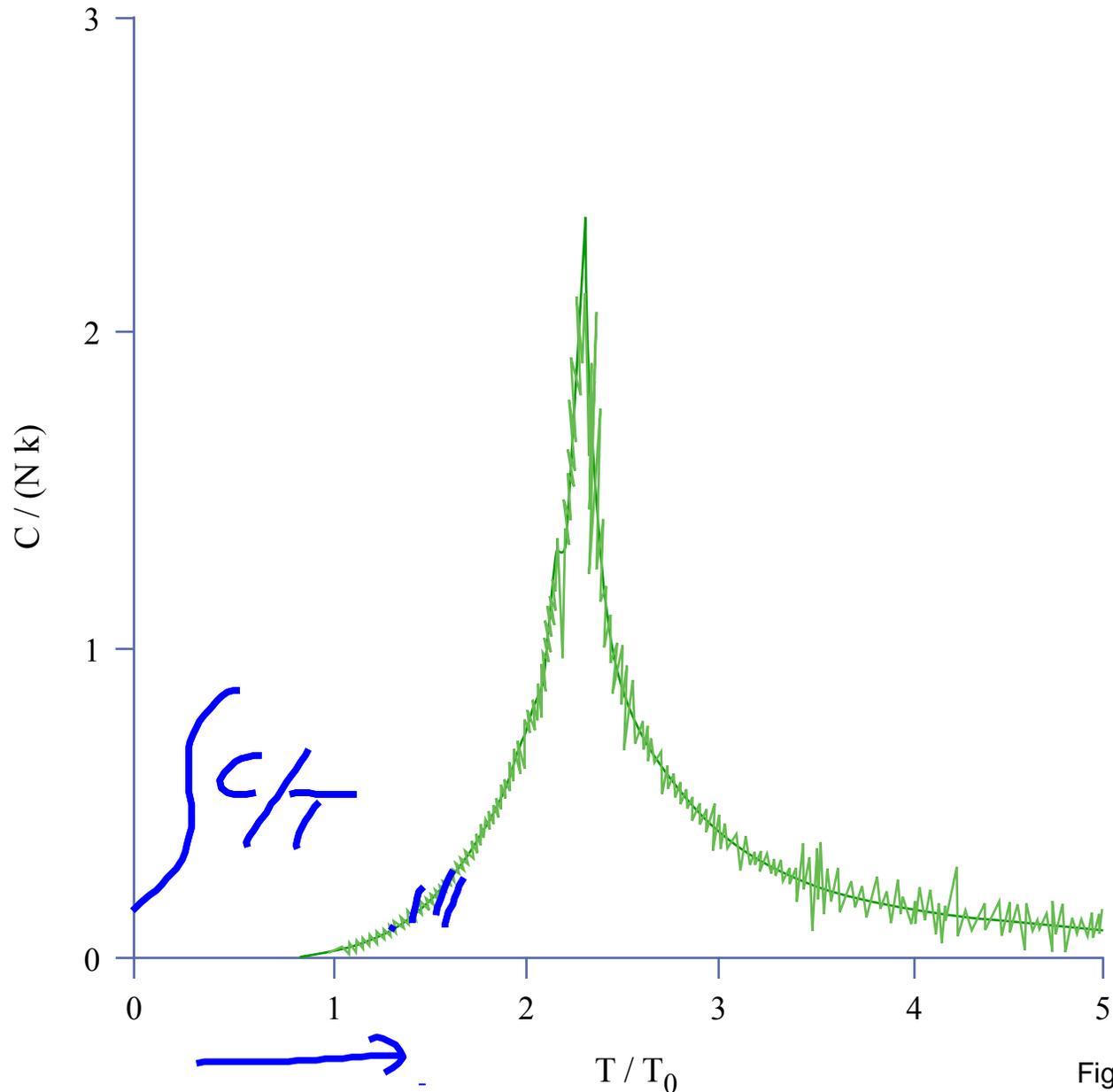


Figure by MIT OCW.

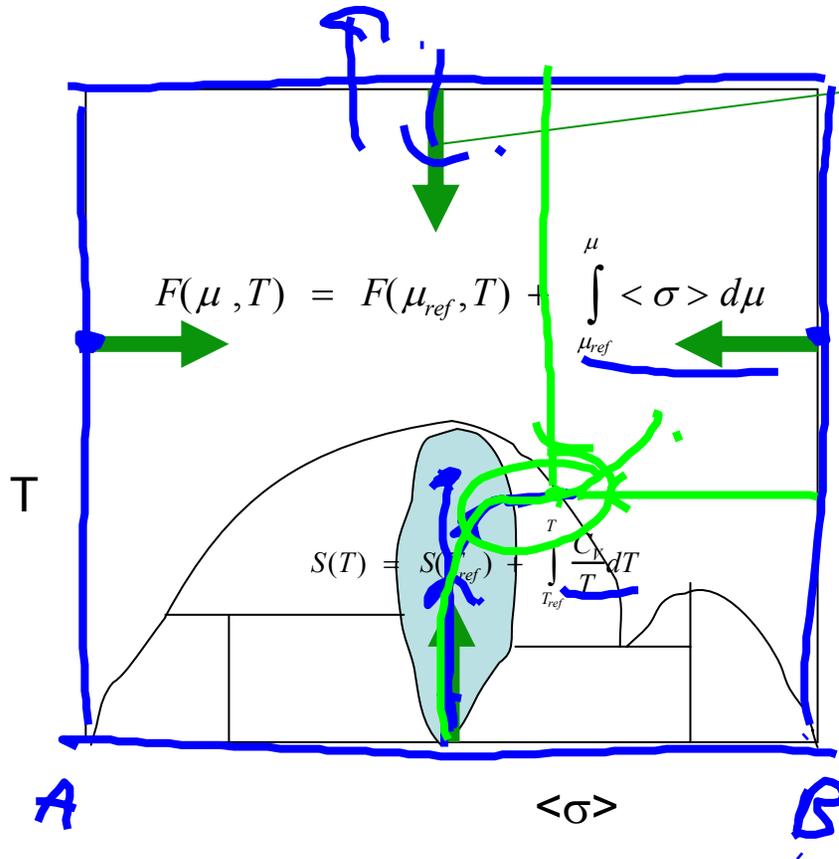
# Examples of TD integration in Ising-like Models

$$\left( \frac{\partial P/F}{\partial (1/T)} \right)$$

$$\langle \sigma \rangle =$$

$$\langle E \rangle = \frac{\partial (F/T)}{\partial (\beta/T)}$$

$$\beta F = \beta F_{ref} + \int_{\beta_{ref}}^{\beta} \langle E \rangle d\beta$$



$$C = \frac{\partial F}{\partial \mu}$$

$$C d\mu = dF$$

# Issues with Thermodynamic Integration

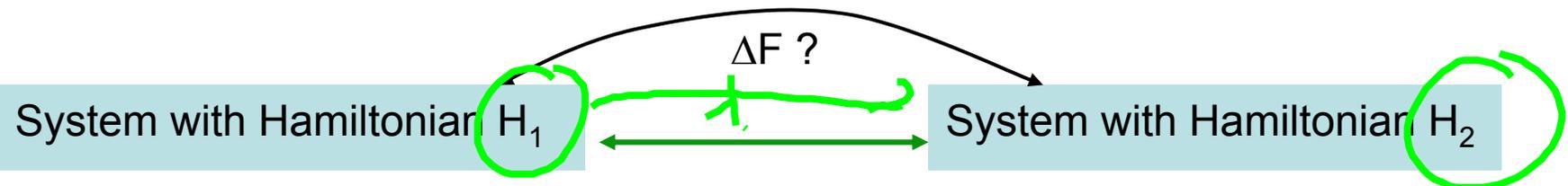
## Disadvantages

- 1) Need to have a reference state
- 2) Need to simulate along path from reference state to desired state
- 3) Error accumulates along path
- 4) Need path to be in equilibrium

## Advantages

- 5) Highly accurate
- 6) All approximations are under control and error be reduced by longer simulations.

# Why stop at integrating with physical parameters; The wonders of computations



Any parameter in Hamiltonian could be different

Turn on additional interaction

Add a particle

Change temperature

$$\frac{\partial^2 \ln Z}{\partial \lambda^2}$$

$$H(\lambda) = H_I + \lambda(H_{II} - H_I) \longrightarrow F(\lambda)$$

$$\frac{\partial(F)}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left[ -\frac{1}{\beta} \ln \sum_{v \in \Omega} \exp(-\beta H_v(\lambda)) \right]$$

$$= \left[ -\frac{1}{\beta} \frac{1}{Q} \sum_{v \in \Omega} (-\beta) \frac{\partial H_v(\lambda)}{\partial \lambda} \exp(-\beta H_v(\lambda)) \right]$$

$$= \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle$$

$$= \langle H_{II} - H_I \rangle_\lambda \longrightarrow \text{Quantity that needs to be integrated}$$

# Effect of dipole in water

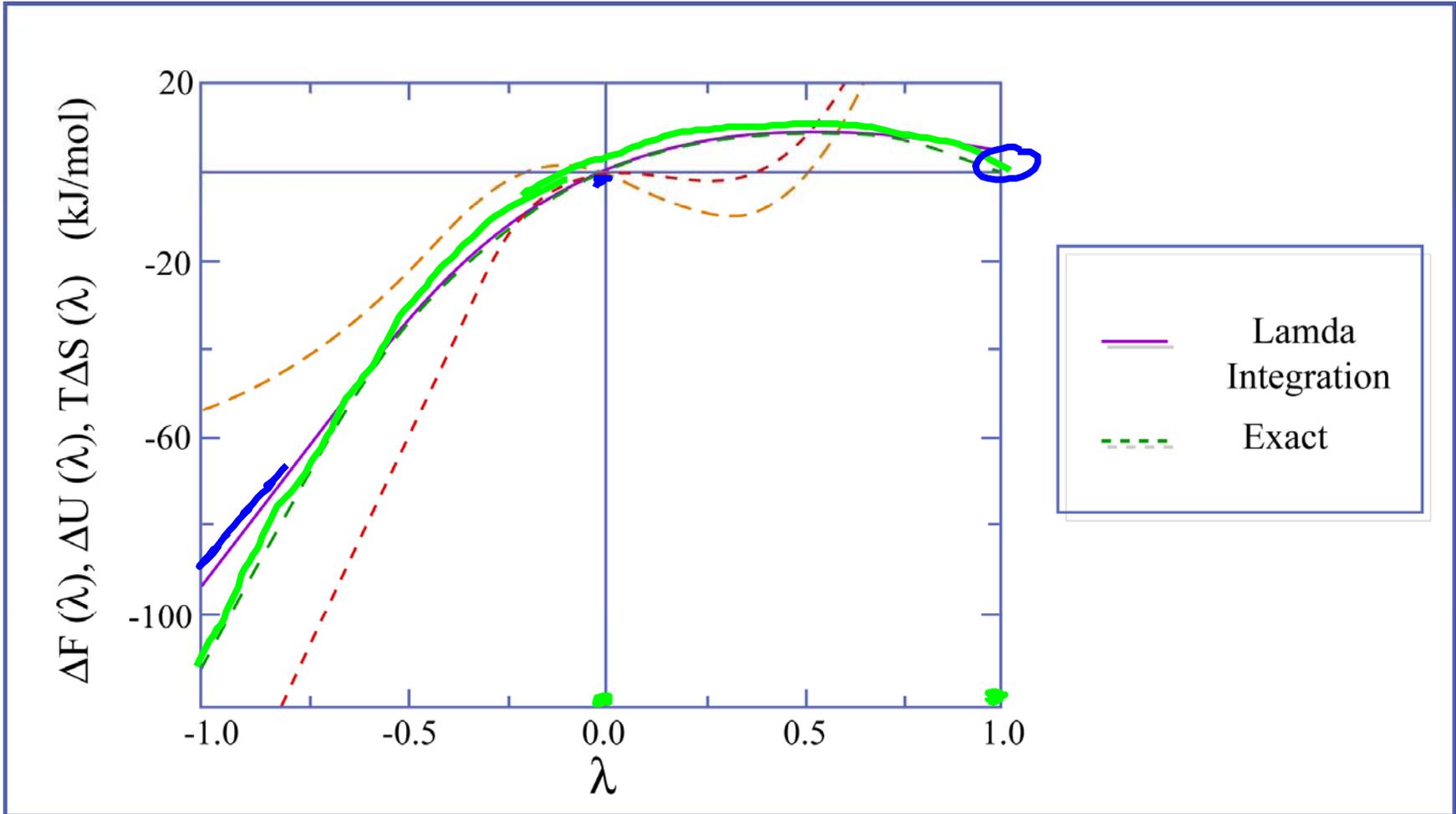
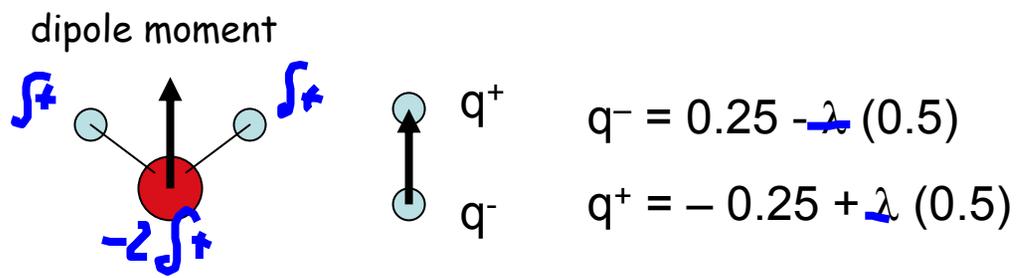
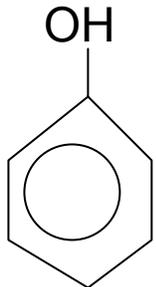


Figure by MIT OCW.

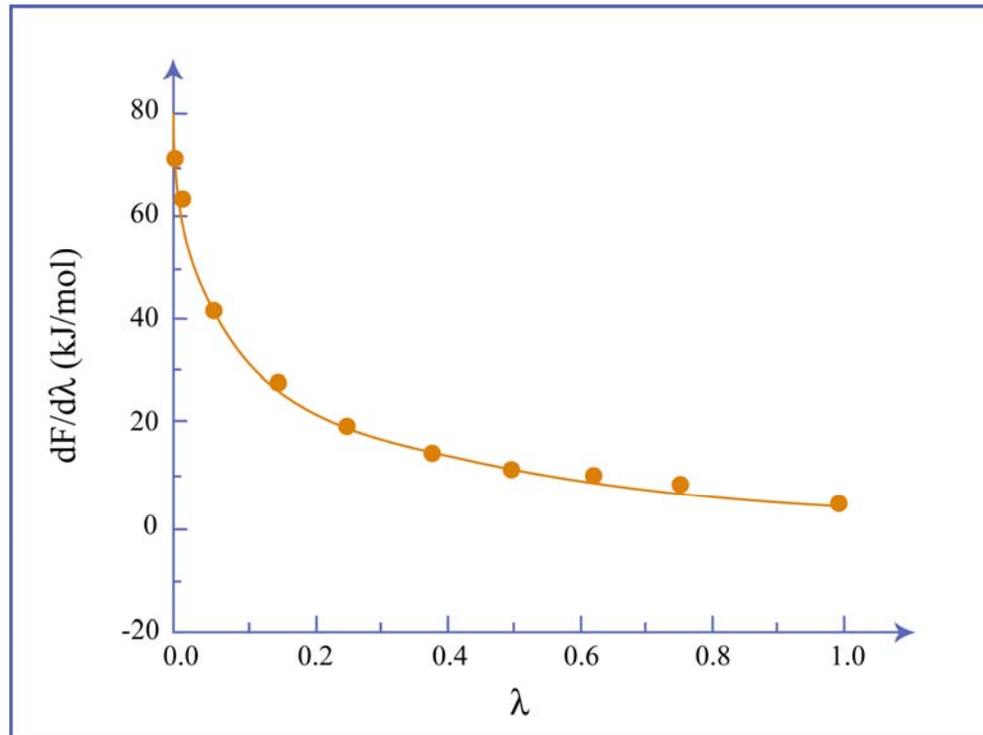
See Liu, H. et al, *J. Phys. Chem* **100**, 9485 (1996)

# Turn Lead into Gold ?

Change Hamiltonian to go from one molecule to another



- Cl chlorophenol
- CH3 methylphenol
- CN cyanophenol
- OCH3 methoxyphenol



methylphenol  $\longrightarrow$  chlorophenol

# Monte Carlo

## Advantages

- Conceptually simple
- Easy to implement
- Can Equilibrate any degree of freedom/No Dynamics needed
- Accurate Statistical Mechanics

## Disadvantages

- No Kinetic Information
- Requires many Energy Evaluations
- Stochastic nature gives noise in data
- Not easy to get entropy/free energy

## References

D. Frenkel and B. Smit, "Understanding Molecular Simulation", Academic Press.

*Fairly recent book. Very good background and theory on MD, MC and Stat Mech. Applications are mainly on molecular systems.*

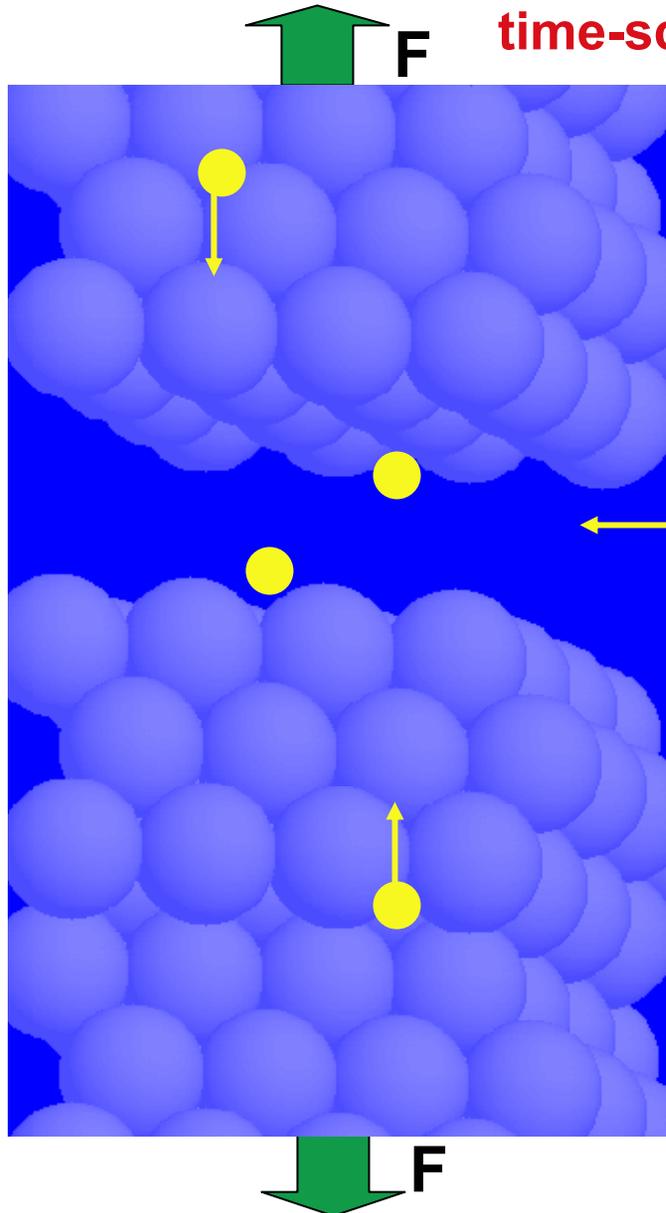
*A.R. Leach, "Molecular Modeling Principles and Applications", Chapter 7*

*M.E.J. Newman and G.T. Barkema, "Monte Carlo Methods in Statistical Physics"*

*K. Binder and D.W. Heerman, "Monte Carlo Simulation in Statistical Physics"*

**Methods with multiple time scales:  
*Coarse-grain fast one away***

# Equilibration of Chemical Composition and Structure: A slow time-scale problem

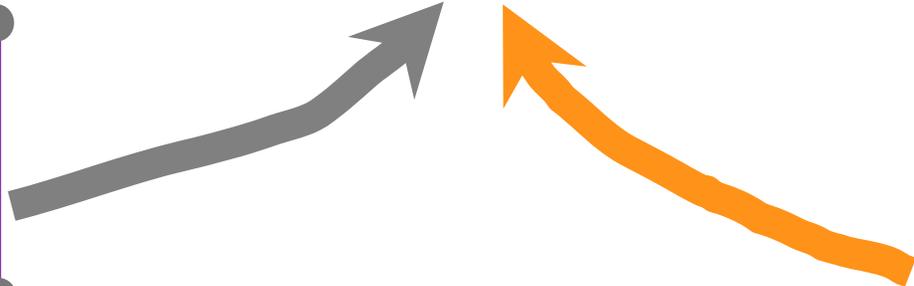
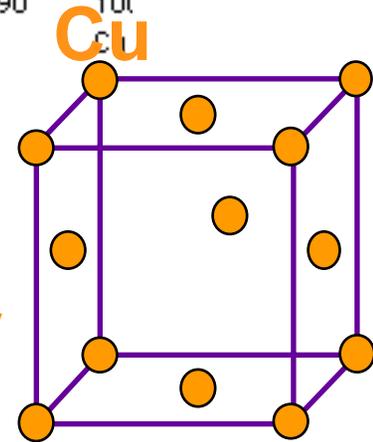
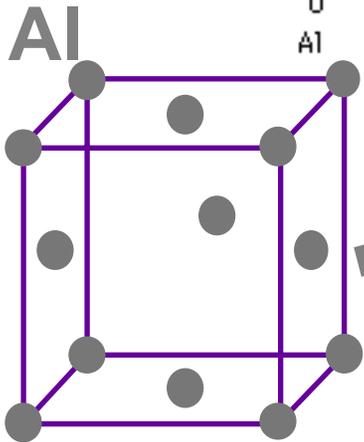
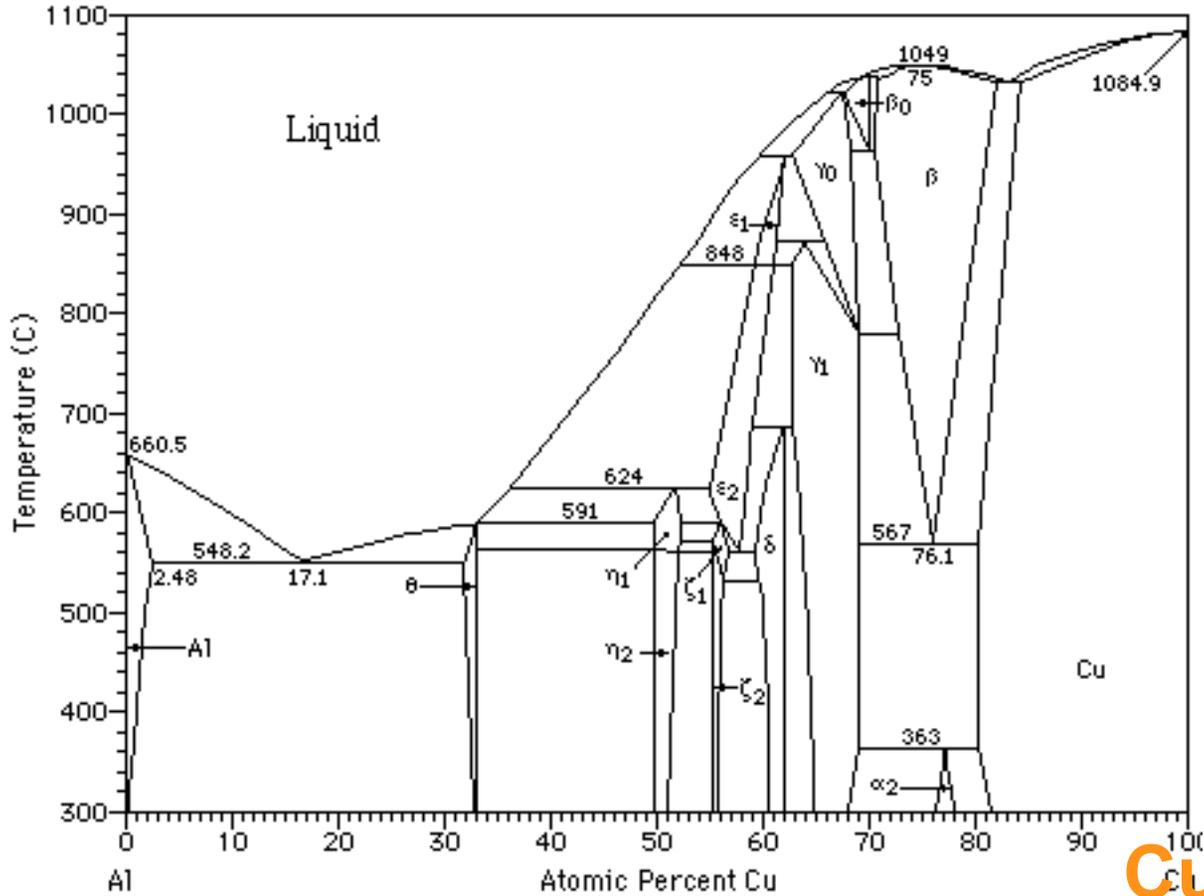


Cracking of Al with hydrogen impurities in the material

Hydrogen can flow into the opening crack and reduce the cohesion there

**Need to equilibrate both amount and arrangement of H on Al(111) for each separation**

# Case Study: First Principles Predication of Alloy Phase Stability



# Need to Equilibrate all Time Scales -> Free Energy

## Electronic

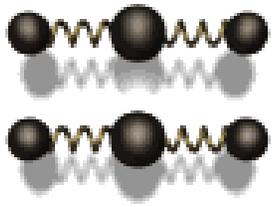
Occupation

$$\Psi \longrightarrow \hbar$$

Magnetic (electron spin)

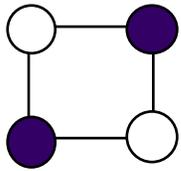


## Vibrational



**Molecular Dynamics:** can not reach configurational excitations  
**Monte Carlo:** too many energy evaluations required

## Configurational



We can use lattice models for studying mixing and ordering of atoms in crystalline materials. But why is this a good approximation ?

## Coarse-graining: The concept

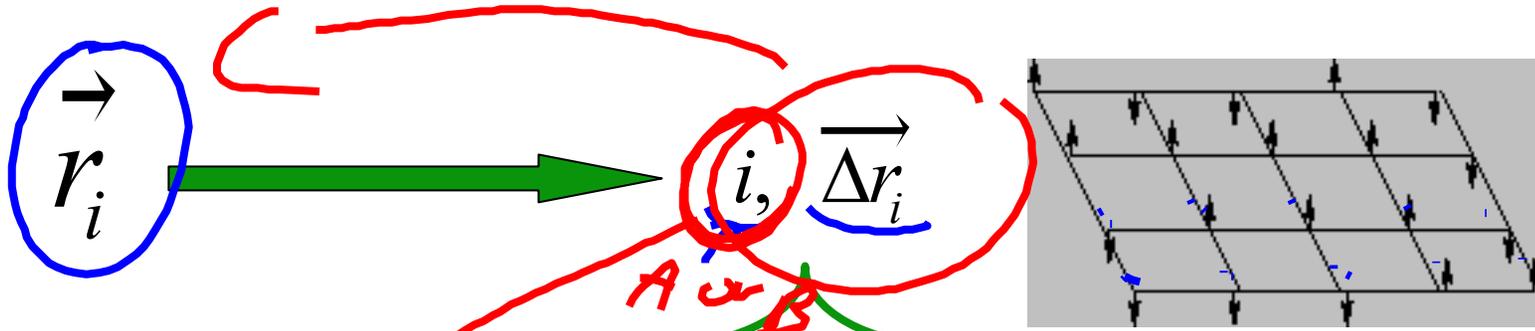
Can we integrate partition function over fast degrees of freedom to obtain an effective Hamiltonian for the slower degrees of freedom ?

e.g. **for an alloy**: Can we find an effective free energy function for the **substitutional** arrangement of an alloy that includes the entropic effect of vibrations and electronic excitations ?

**YES**

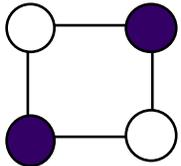
Use Monte Carlo, Molecular Dynamics, or analytical methods to integrate effect of temperature on fast degrees of freedom

# Change coordinates



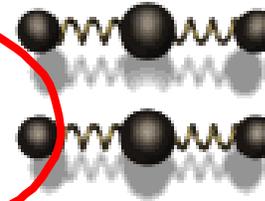
A or B

$$\{\sigma\} = \{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N\}$$



Configurational arrangement

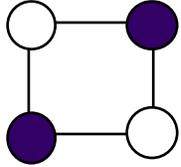
$$\{V\} = \left\{ \overrightarrow{\Delta r_i} \right\}$$



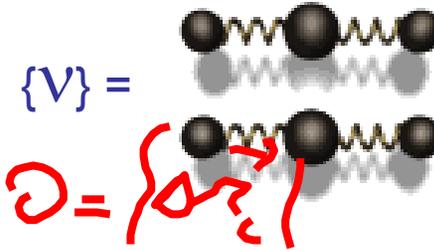
Vibrational state

# Coarse-graining by reduction of degrees of freedom

$$\{\sigma\} = \{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N\}$$



Configurational arrangement



$$\{V\} =$$

Vibrational state

$$\rightarrow Q = \sum_{\{\sigma\}} \sum_v \exp(-\beta E(\{\sigma\}, v(\{\sigma\})))$$

$$Q = \sum_{\{\sigma\}} \exp(-\beta F(\{\sigma\}))$$

Partition Function of an Ising-like Model

Two approximations for F

$$F(\{\sigma\}) = -kT \ln \left[ \sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

F is Effective Hamiltonian for  $\{\sigma\}$  degree of freedom

## Approximations to $F(\{\sigma\})$ determine which excitations (entropies) are included in the total free energy

1. Approximate  $F(\{\sigma\})$  by  $E(\{\sigma\})$

$$F(\{\sigma\}) = -kT \ln \left[ \sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

when doing Monte Carlo and free energy integration, only get configurational entropy

2. Approximate  $F(\{\sigma\})$  by  $E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\})$

when doing Monte Carlo and free energy integration, get configurational entropy and electronic

3.  $F(\{\sigma\}) = E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\}) - TS_{\text{vib}}(\{\sigma\})$

when doing Monte Carlo and free energy integration, get configurational entropy + electronic + vibrational

## Summary so far

The model on the time scale of the substitutional excitations is an Ising-like model (i.e. excitations are changes of occupation variables)

The Hamiltonian of the Ising-like model is the free energy of the faster excitations (e.g. vibrations, electronic excitations).

Only approximation is separation of time scales



**But need a practical form for the Ising-like Hamiltonian**