Thermodynamics and Phase Diagrams from Cluster Expansions

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SUMMER SCHOOL ON COMPUTATIONAL MATERIALS SCIENCE

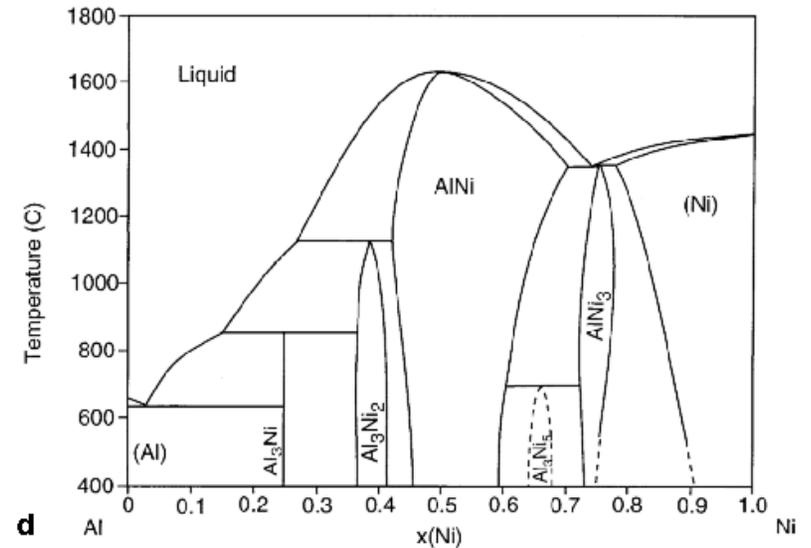Hands-on introduction to Electronic Structure and Thermodynamics Calculations of Real Materials

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The Cluster Expansion and Phase Diagrams

Cluster Expansion

α = cluster functions
σ = atomic configuration on a lattice

H. Okamoto, *J. Phase Equilibria,* '93

How do we get the phase diagram from the cluster expansion Hamiltonian?

Outline

- Phase Diagram Basics
- Stable Phases from Cluster Expansion - the Ground State Problem
  - Analytical methods
  - Optimization (Monte Carlo, genetic algorithm)
  - Exhaustive search
- Phase Diagrams from Cluster Expansion: Semi-Analytical Approximations
  - Low-T expansion
  - High-T expansion
  - Cluster variation method
- Phase Diagrams from Cluster Expansion: Simulation with Monte Carlo
  - Monte Carlo method basics
  - Covergence issues
  - Determining phase diagrams without free energies.
  - Determining phase diagrams with free energies.

Phase Diagram Basics

What is A Phase Diagram?

- **Phase:** A chemically and structurally homogeneous portion of material, generally described by a distinct value of some parameters ('order parameters'). E.g., ordered $L1_0$ phase and disordered solid solution of Cu-Au

- Gibb's phase rule for fixed pressure:
  - F(degrees of freedom) = C(# components) - P(# phases) + 1
  - Can have 1 or more phases stable at different compositions for different temperatures
  - For a binary alloy (C=2) can have 3 phases with no degrees of freedom (fixed composition and temperature), and 2 phases with 1 degree of freedom (range of temperatures).

- The stable phases at each temperature and composition are summarized in a phase diagram made up of boundaries between single and multiple phase regions. Multi-phase regions imply separation to the boundaries in proportions consistent with conserving overall composition.
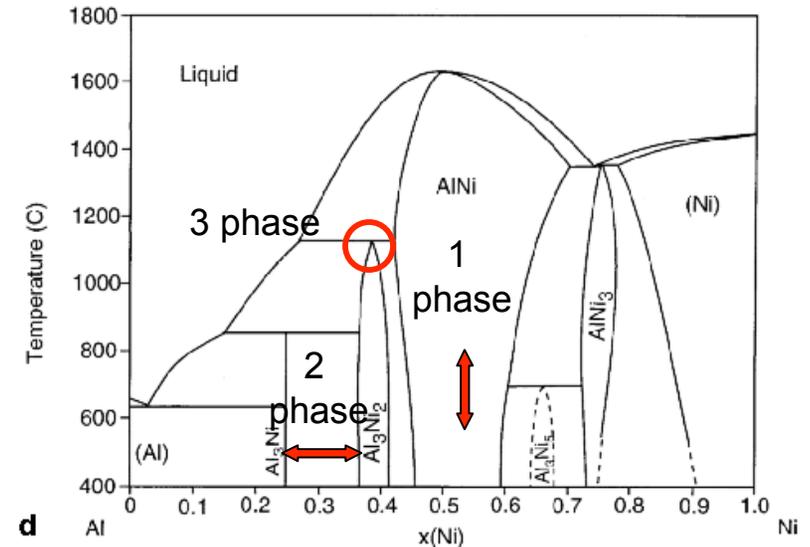
H. Okamoto, *J. Phase Equilibria,* '93

The stable phases can be derived from optimization of an appropriate thermodynamic potential.

Thermodynamics of Phase Stability

- ## The stable phases minimize the total thermodynamic potential of the system

  - The thermodynamic potential for a phase α of an alloy under atmospheric pressure:

 - The total thermodynamic potential is

  - The challenges:
    - **What phases δ might be present?**
    - **How do we get the F^δ from the cluster expansion?**
    - **How use F^δ to get the phase diagram?**
  - Note: Focus on binary systems (can be generalized but details get complex), focus on single parent lattice (multiple lattices can be treated each separately)

Stable Phases from Cluster Expansion – the Ground State Problem

Determining Possible Phases

- Assume that the phases that might appear in phase diagram are ground states (stable phases at T=0). This could miss some phases that are stabilized by entropy at T>0.

- T=0 simplifies the problem since T=0 $\Rightarrow$ F is given by the cluster expansion directly. Phases δ are now simply distinguished by different fixed orderings σ^δ.
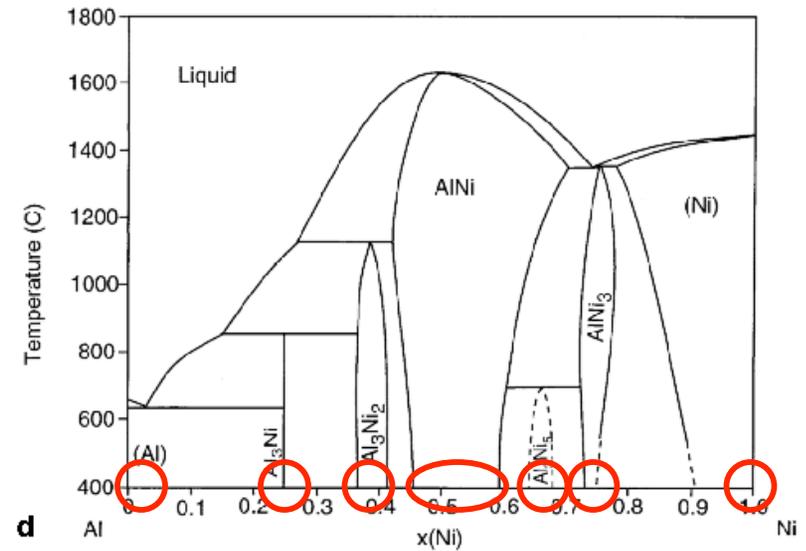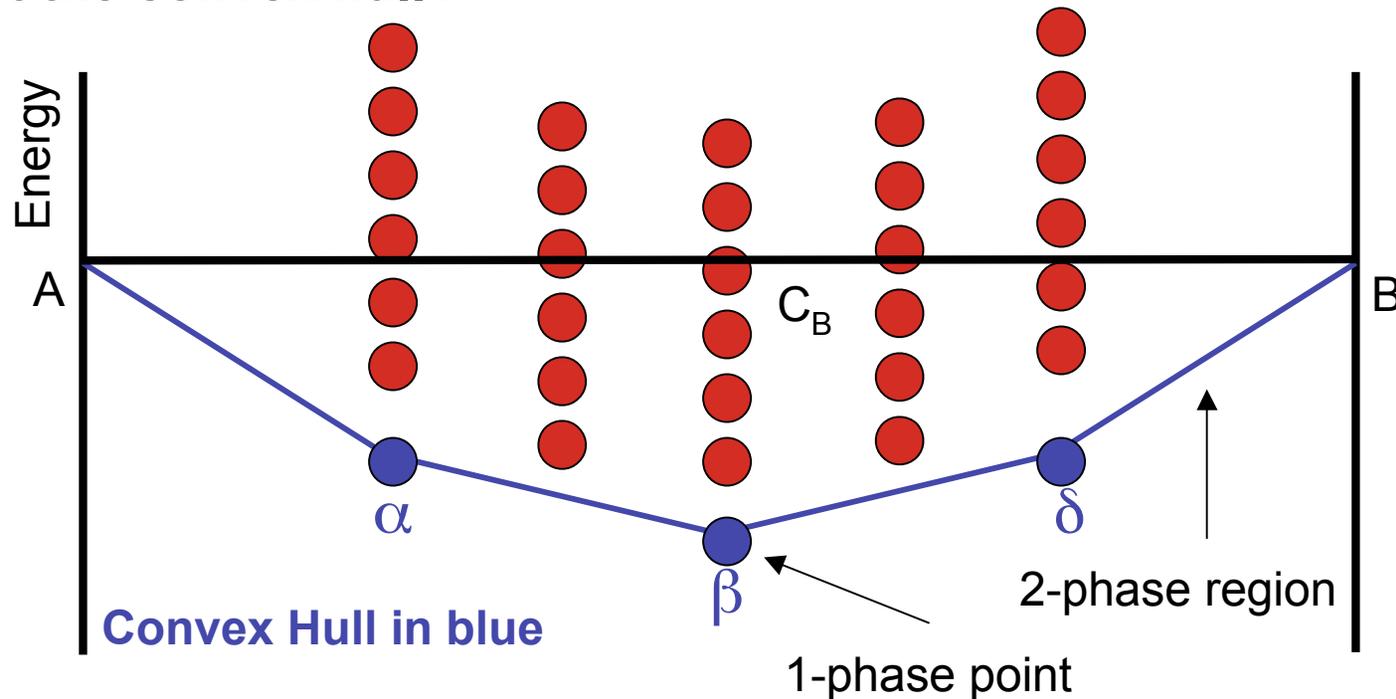
- So we need only find the σ that give the T=0 stable states. These are the states on the convex hull.

H. Okamoto, *J. Phase Equilibria,* '93

The Convex Hull

- None of the red points give the lowest $F=\Sigma F^\delta$. Blue points/lines give the lowest energy phases/phase mixtures.

- Constructing the convex hull given a moderate set of points is straightforward (Skiena '97)

- **But the number of points (structures) is infinite! So how do we get the convex hull?**

Getting the Convex Hull of a Cluster Expansion Hamiltonian

- **Linear programming methods**
  - Elegantly reduce infinite discrete problem to finite linear continuous problem.
  - Give sets of Lattice Averaged (LA) cluster functions $\{LA(\phi)\}$ of all possible ground states through robust numerical methods.
  - But can also generate many "inconstructable" sets of $\{LA(\phi)\}$ and avoiding those grows exponentially difficult.

- **Optimized searching**
  - Search configuration space in a biased manner to minimize the energy (Monte Carlo, genetic algorithms).
  - Can find larger unit cell structures that brute force searching
  - Not exhaustive – can be difficult to find optimum and can miss hard to find structures, even with small unit cells.

- **Brute force searching**
  - Enumerate all structures with unit cells < N_{max} atoms and build convex hull from that list.
  - Likely to capture most reasonably small unit cells (and these account for most of what are seen in nature).
  - Not exhaustive – can miss larger unit cell structures.

(Blum and Zunger, *Phys. Rev. B*, '04)

(Zunger, *et al.*, http://www.sst.nrel.gov/topics/new_mat.html)

Phase Diagrams from Cluster Expansion: Semi-Analytical Approximations

Semi-Analytic Expressions for *F* (Φ)

From basic thermodynamics we can write *F* in terms of the cluster expansion Hamiltonian

Cluster expansion

For a binary alloy on a fixed lattice the number of particles is conserved since $N_A+N_B=N=$# sites, thus we can write the **semi-grand canonical potential** Φ in terms of one chemical potential and N_B (Grand canonical = particle numbers can change, Semi-Grand canonical = particle types can change but overall number is fixed)

But this is an infinite summation – how can we evaluate Φ?

- High-temperature expansion
- Low-temperature expansion
- Mean-field theory

High-Temperature Expansion

Assume x=$\beta(E-\mu n)$ is a small number (high temperature) and expand the ln(exp(-x))

Could go out to many higher orders …

High-Temperature Expansion Example
(NN Cluster Expansion)

z = # NN per atom
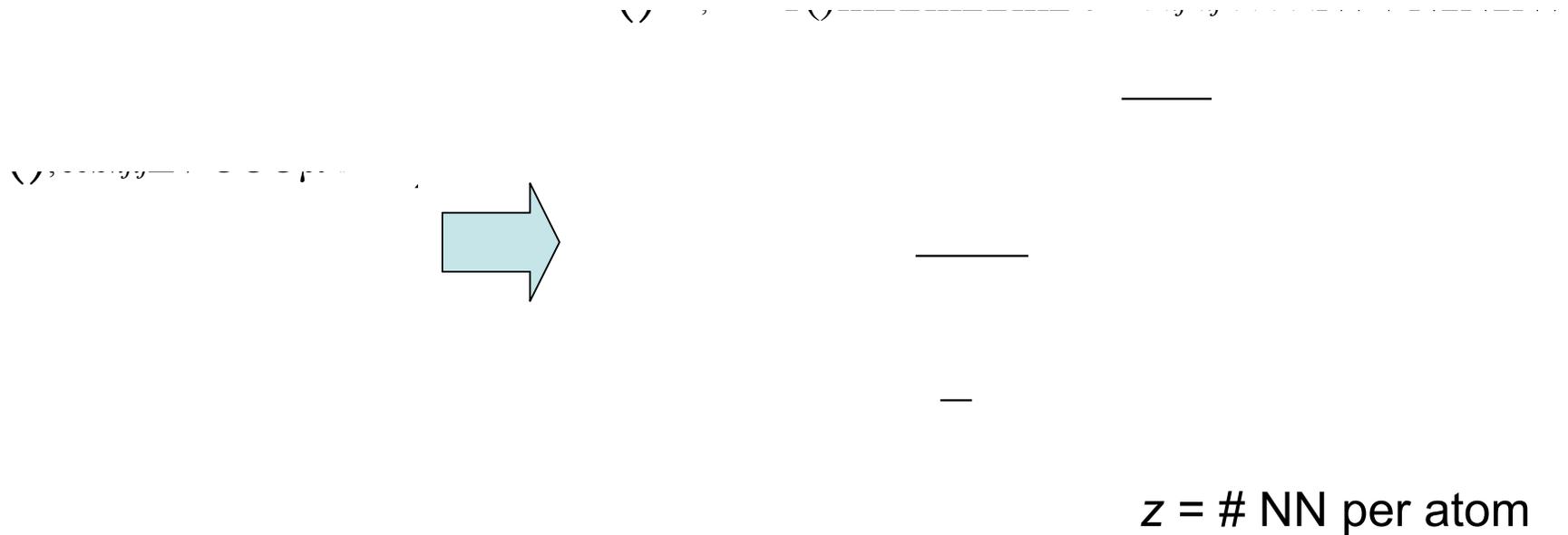
So first correction is second order in βV_{NN} and reduces the free energy

Low-Temperature Expansion

Start in a known ground state α, with chemical potentials that stabilize α, and assume only lowest excitations contribute to F

This term
assumed small

Expand ln in
small term

Keep contribution from single spin flip at a site s

Low-Temperature Expansion Example
(NN Cluster Expansion)

Assume an unfrustrated ordered phase at c=1/2
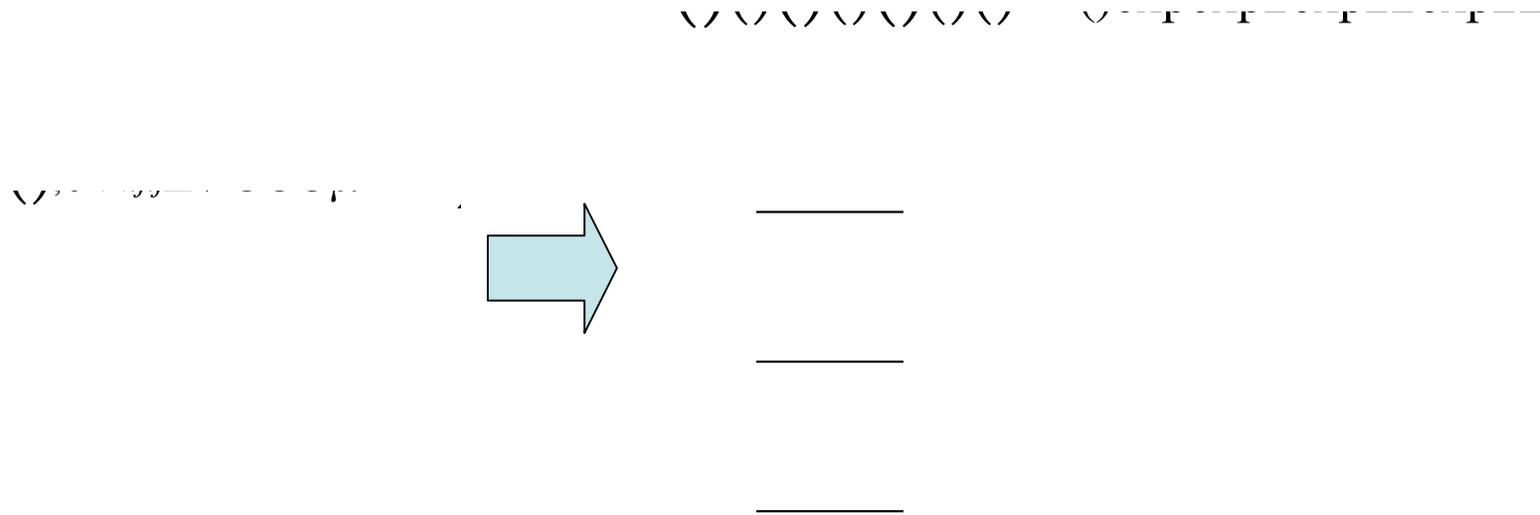
So first correction goes as exp(-2zβV_{NN}) and reduces the free energy

Transition Temperature from LT and HT Expansion

NN cluster expansion on a simple cubic lattice (z=6)

$V_{NN} > 0 \Rightarrow$ antiferromagnetic ordering

$k_B T_c/|zV| = 0.721$ (0th), 0.688 (1st), 0.7522 (best known)
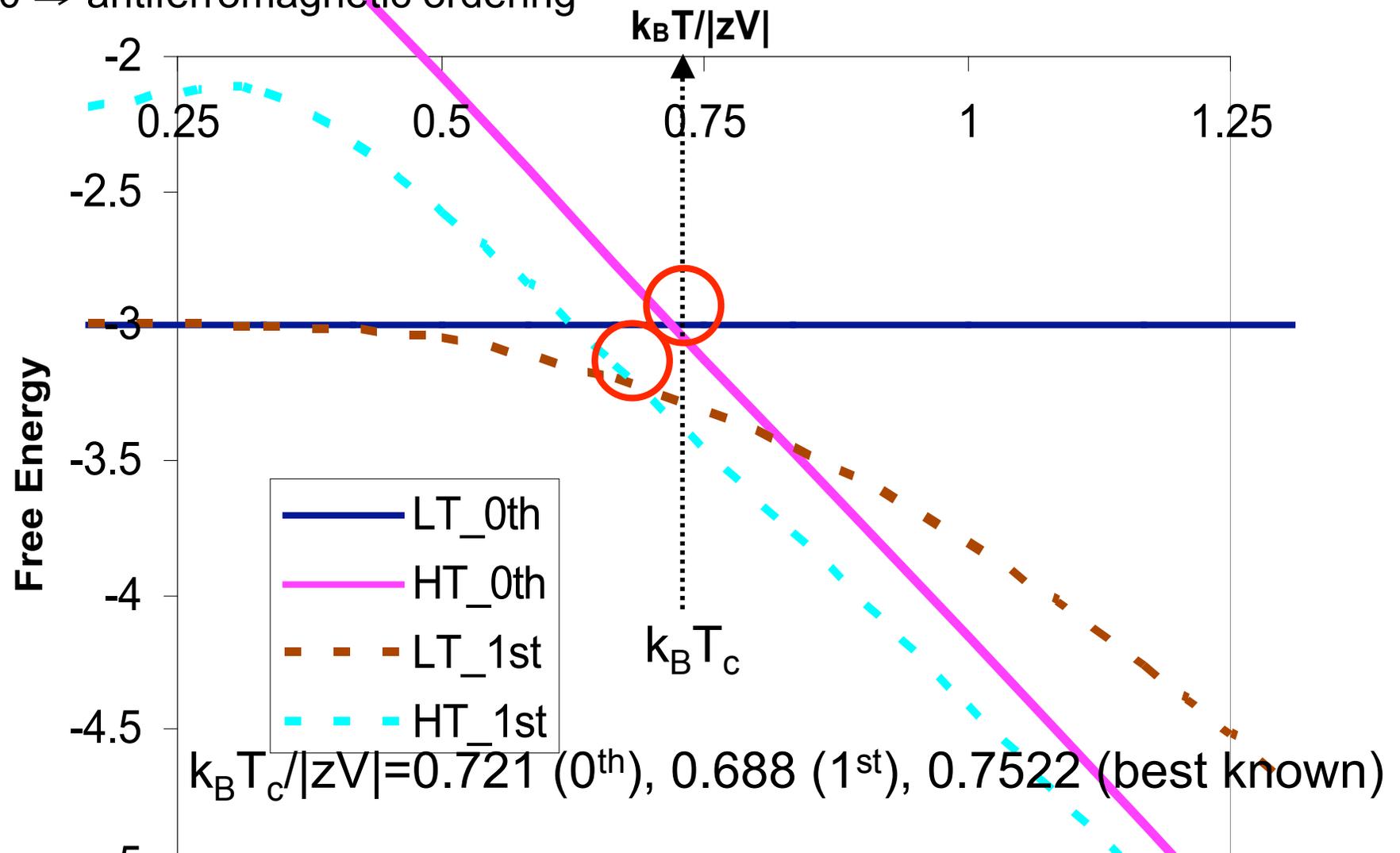
Mean-Field Theory – The Idea

The general idea: Break up the system into small clusters in an average "bath" that is not treated explicitly

For a small finite lattice with N-sites finding ϕ is not hard – just sum 2^N terms

For an infinite lattice just treat subclusters explicitly with mean field as boundary condition

Treated fully
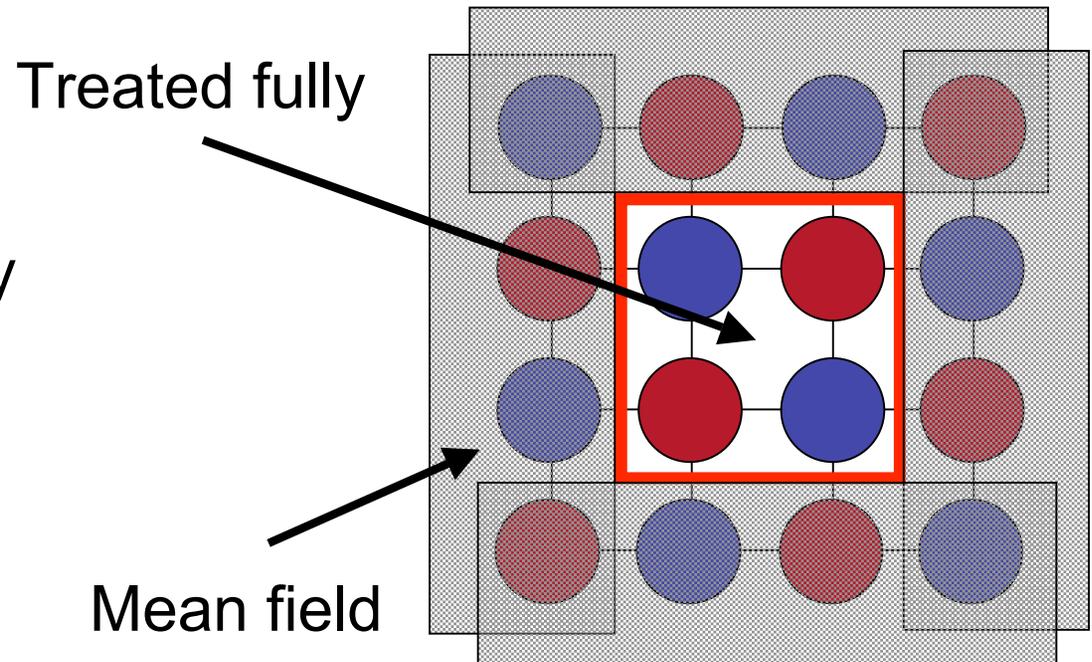
Mean field

Implementing Mean-Field Theory
The Cluster Variation Method

- Write thermodynamic potential Φ in terms of probabilities of each configuration $\rho(\sigma)$, $\Phi[\{\rho(\sigma)\}]$.

- The true probabilities and equilibrium Φ are given by minimizing $\Phi[\{\rho(\sigma)\}]$ with respect to $\{\rho(\sigma)\}$, ie, $\delta\Phi[\{\rho(\sigma)\}]/\delta\{\rho(\sigma)\}=0$.

- Simplify $\rho(\sigma)$ using mean-field ideas to depend on only a few variables to make solving $\delta\Phi[\{\rho(\sigma)\}]/\delta\{\rho(\sigma)\}=0$ tractable.
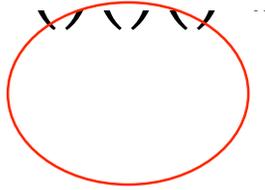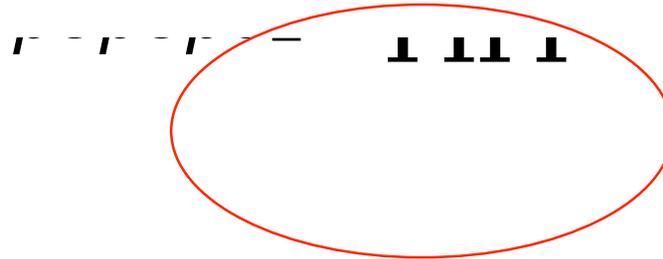
Writing $\phi[\{\rho(\sigma)\}]$.
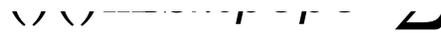
Where
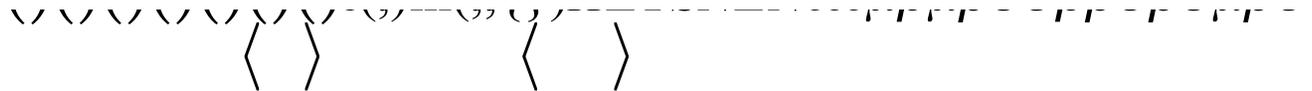
Factoring the Probability to Simplify $\rho(\sigma)$

Has 2^N values

Has $2^{N_\eta M}$ values – much smaller

Cluster of lattice points.

Maximal size cluster of lattice points to treat explicitly.

Irreducible probabilities. Depend on only spin values in cluster of points η. Have value 1 if the sites in η are uncorrelated (even if subclusters are correlated)

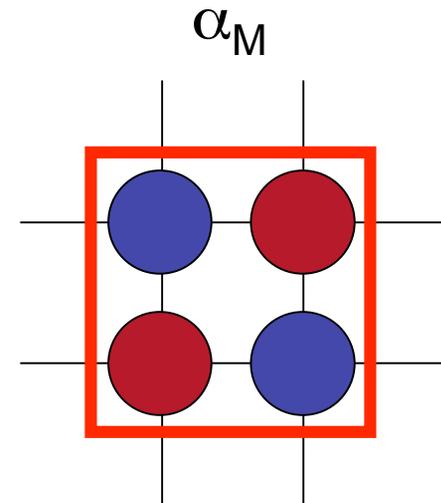Probability of finding spins σ_η on cluster of sites η.

Kikuchi-Barker coefficients

Truncating the Probability Factorization = Mean Field
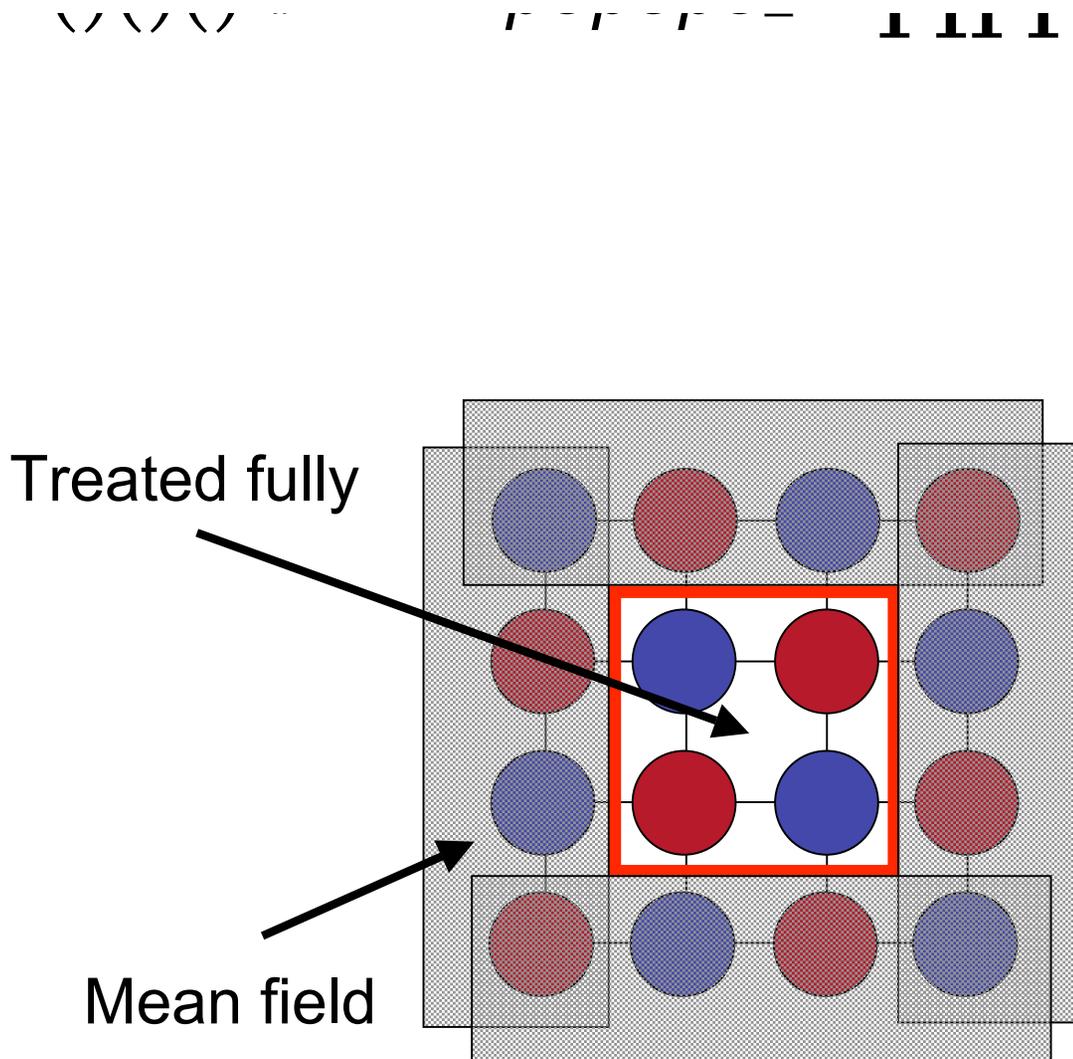
Setting

treats each cluster α_M explicitly and embeds it in the appropriate average environment

Treated fully

Mean field

α_M

The Mean-Field Potential

Φ now depends on only

and can be minimized to
get approximate
probabilities and potential

The Modern Formalism

- Using probabilities as variables is hard because you must
  - Maintain normalization (sums = 1)
  - Maintain positive values
  - Include symmetry

- A useful change of variables is to write probabilities in terms of correlation functions – this is just a cluster expansion of the probabilities

The CVM Potential

For a multicomponent alloy

δ The phase

α,β Clusters of sites

τ Cluster functions for each cluster – associated with multiple species

m Number of species

$\{\alpha_M\}$ Set of possible maximal clusters

D Degeneracies (multiplicities)

a Kikuchi-Barker coefficients

O_δ Orbit of clusters under symmetry operations of phase δ

V V matrix that maps correlation functions to probabilities

ξ Correlation function (thermally averaged cluster functions)

α_M=Single point on lattice

For a disorderd phase on a lattice with one type of site

$\langle \; \rangle$

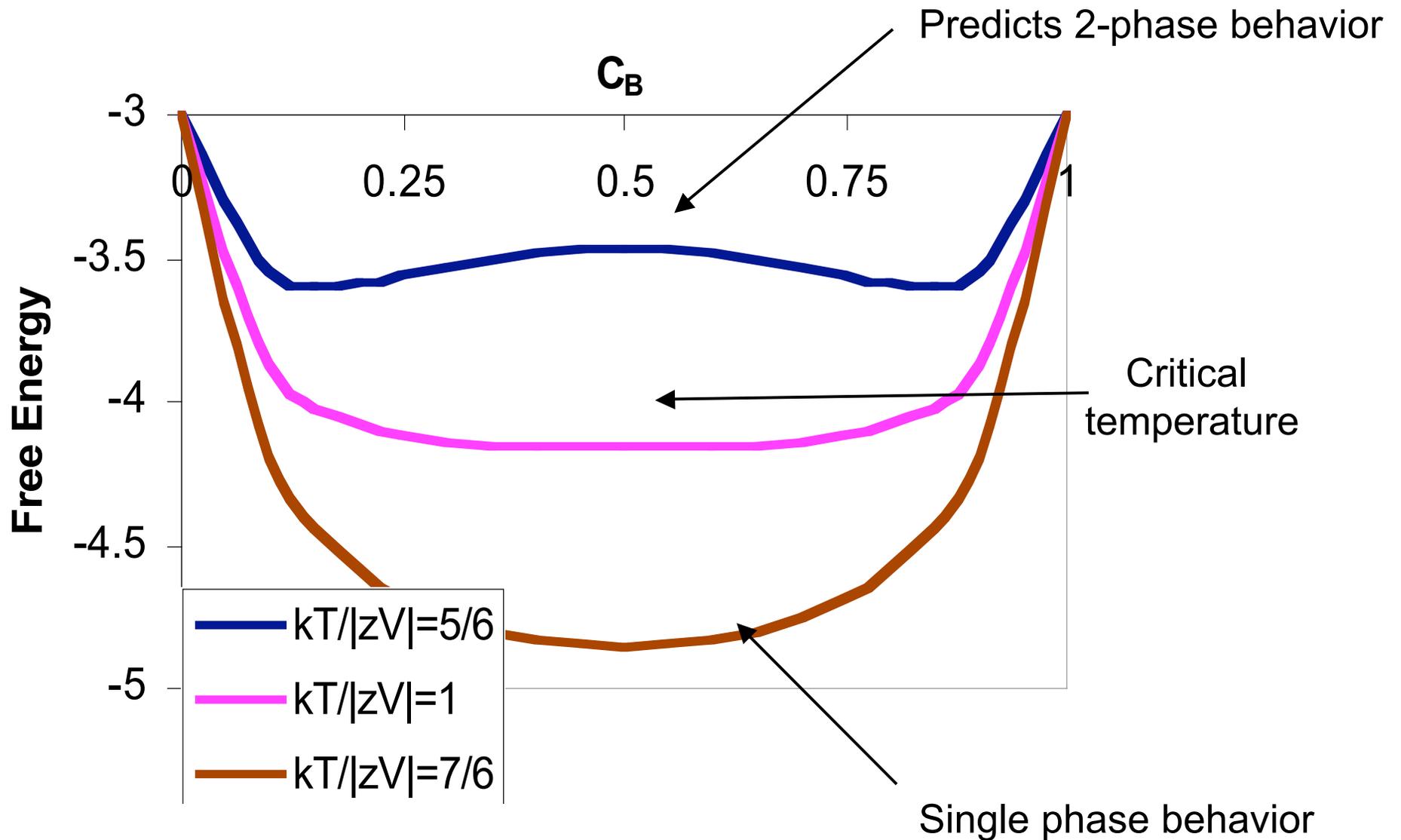$\langle \; \rangle$ $\langle \; \rangle$

$\langle \; \rangle$
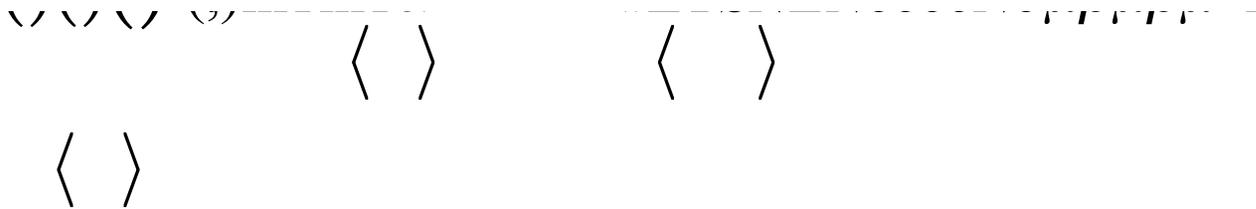
CVM Point Approximation - Bragg-Williams (NN Cluster Expansion)
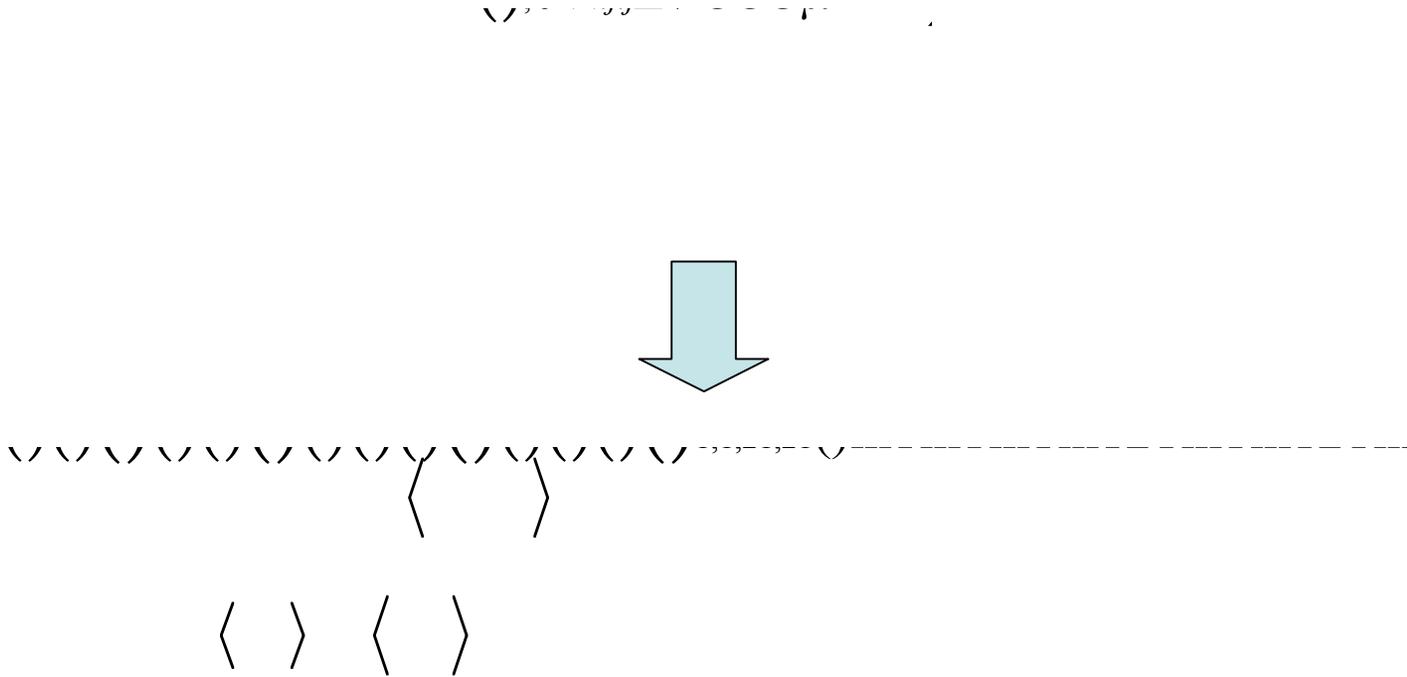
Disordered phase – more complex for ordered phases

Bragg-Williams Approximation
(NN Cluster Expansion)

Comparison of Bragg-Williams and High-Temperature Expansion

Assume

High-temperature

Bragg-Williams

Optimize F over c_B to get lowest value $\Rightarrow$ $c_B=1/2$ $\Rightarrow$

Bragg-Williams has first term of the high-temperature expansion, but not second. Second term is due to correlations between sites, which is excluded in BW (point CVM)

Critical Temperatures

A. General results[a]

Transition point in units of $k_B T/\lvert z^{(1)} V_1 \rvert$ with $V_j = 0$ ($j \geq 2$)	Phase separation (Ising ferromagnet)					Ordering	
	2-D Square lattice	2-D Triangular lattice	3-D Simple cubic	BCC Also L2$_0$ ordering	Phase separation	FCC L1$_0$	L1$_2$
Coordination $z^{(1)}$	4	6	6	8	12	12	12
Point approximation (Reg. sol., B–W)	1.0	1.0	1.0	1.0	1.0	0.3333	0.2734[b]
CV pair (Bethe approximation)	0.7212	0.8222	0.8222	0.8690	0.9142	0	0
CV square or triangle	0.6057	0.6525	0.7683	0.8454	—	—	—
CV cube or tetrahedron	—	—	0.7628	0.8113	0.8354	0.1577[b]	0.1604[b]
Exact (or best known)	0.567	0.6062	0.7522	0.7944	0.8163	NA[c]	NA[c]

[a] R. Kikuchi, *Phys. Rev.* **81**, 988 (1951); D.M. Burley *in* "Phase Transitions and Critical Phenomena" (C. Domb and M.S. Green, eds.), Vol. 2, p. 329. Academic Press, New York, 1972.
[b] First-order transitions; all others second-order.
[c] NA: not available.

HT/LT approx: $k_B T_c/\lvert zV \rvert = 0.721$ (0th), 0.688 (1st)

B. More recent results for Ising ferromagnet[d]

Approximation	$k_B T_c / 12 V_1$
Tetrahedron	0.83544
Double tetrahedron	0.84045
Octahedron–tetrahedron	0.83394
Double tetrahedron–octahedron	0.82981
High T expansion	0.81627

[d] J.M. Sanchez and D. de Fontaine, *Phys. Rev. B* **17**, 2926 (1978).

de Fontaine, *Solid State Physics* '79

Limitations of the CVM (Mean-Field), High- and Low-Temperature Expansions

- **CVM**
  - Inexact at critical temperature, but can be quite accurate.
  - Number of variable to optimize over (independent probabilities within the maximal cluster) grows exponentially with maximal cluster size.
  - Errors occur when Hamiltonian is longer range than CVM approximation – want large interactions within the maximal cluster.
  - Modern cluster expansions use many neighbors and multisite clusters that can be quite long range.
  - CVM not applicable for most modern long-range cluster expansions. Must use more flexible approach **– MonteCarlo!**
- **High- and Low-Temperature Expansions**
  - Computationally quite complex with many terms
  - Many term expansions exist but only for simple Hamiltonians
  - Again, complex long-range Hamiltonians and computational complexity requires other methods **– Monte Carlo!**
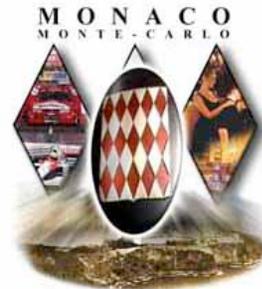
Phase Diagrams from Cluster Expansion: Simulation with Monte Carlo

What Is MC and What is it for?

- MC explores the states of a system **stochastically** with probabilities that match those expected physically

- **Stochastic** means involving or containing a random variable or variables, which is practice means that the method does things based on values of random numbers

- MC is used to get **thermodynamic averages, thermodynamic potentials (from the averages),** and study **phase transitions**

- MC has many other applications outside materials science, where is covers a large range of methods using random numbers

- Invented to study the neutron diffusion in bomb research at end of WWII

- Called Monte Carlo since that is where gambling happens – lots of chance!

http://www.monte-carlo.mc/principalitymonaco/entertainment/casino.html   http://www.monte-carlo.mc/principalitymonaco/index.html

MC Sampling

$\langle \rangle$

$\rho(\sigma)$ is the probability of a having configuration σ
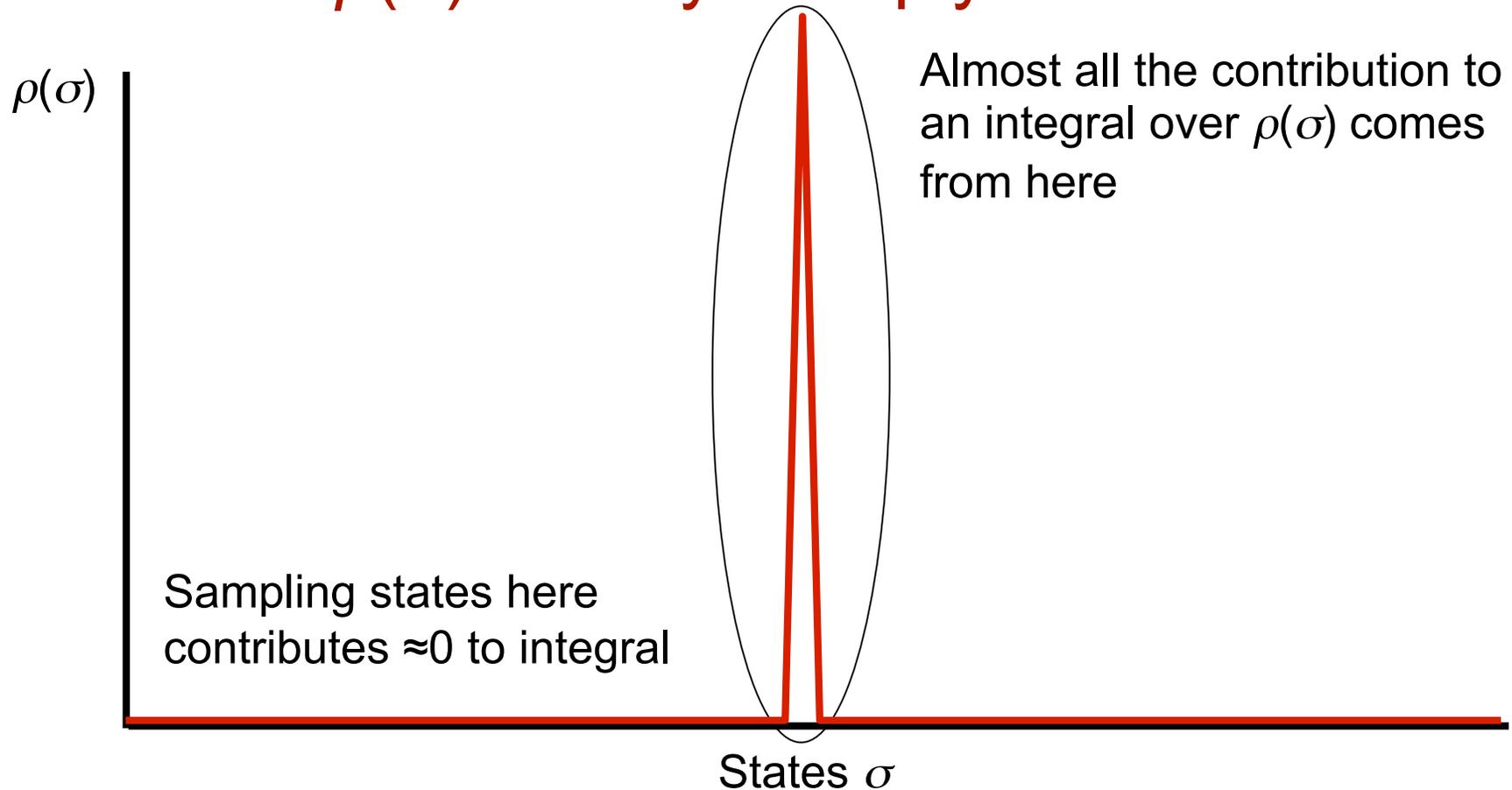
- **Can we perform this summation numerically?**
- **Simple Monte Carlo Sampling**: Choose states s at random and perform the above summation. Need to get Z, but can also do this by sampling at random
- This is impractically slow because you sample too many terms that are near zero

Problem with Simple MC Sampling
$\rho(\sigma)$ is Very Sharply Peaked

$\rho(\sigma)$

Almost all the contribution to an integral over $\rho(\sigma)$ comes from here

Sampling states here contributes ≈0 to integral

States σ

E.g., Consider a non-interacting cluster expansion spin model with H=-μN_B. For β=μ=1 c_B=1/(1+e)=0.27. For N=1000 sites the probability of a configuration with c_B=0.5 compared to cB=0.27 is

$$P(c_B=0.5)/P(C_B=0.27)=\exp(-N\Delta c_B)=10^{-100}$$

Better MC Sampling

- We need an algorithm that naturally samples states for which $\rho(\sigma)$ is large. Ideally, we will choose states with exactly probability $\rho(\sigma)$ because

  - When $\rho(\sigma)$ is small (large), those σ will not (will) be sampled

  - In fact, if we choose states with probability $\rho(\sigma)$, then we can write the thermodynamic average as

$$\langle \quad \rangle = \underline{\qquad}$$

  - $\rho(\sigma)$ is the true equilibrium thermodynamic distribution, so our sampling will generate states that match those seen in an equilibrium system, which make them easy to interpret

- The way to sample with the correct $\rho(\sigma)$ is called the **Metropolis algorithm**

Detailed Balance and The Metropolis Algorithm

- We wants states to occur with probability $\rho(\sigma)$ in the equilibrated simulation and we want to enforce that by how we choose new states at each step (how we transition).

- Impose detailed balance condition (at equilibrium the flux between two states is equal) so that equilibrium probabilities will be stable

$$\rho(o)\pi(o\_n)=\rho(n)\pi(n\_o)$$

- **Transition** matrix $\pi(o\_n) = \alpha(o\_n) \times acc(o\_n)$, where α is the **attempt** matrix and acc is the **acceptance** matrix.

- Choose $\alpha(o\_n)$ symmetric (just pick states uniformly): $\alpha(o\_n)=\alpha(n\_o)$

- Then
$$\rho(o)\pi(o\_n)=\rho(n)\pi(n\_o) \Rightarrow \rho(o)xacc(o\_n)=\rho(n)xacc(n\_o)$$
$$\Rightarrow acc(o\_n)/acc(n\_o) = \rho(n)/\rho(o) = \exp(-\beta\Phi(n))/\exp(-\beta\Phi(o))$$

- So choose
$$acc(o\_n) = \rho(n)/\rho(o) \text{ if } \rho(n)<\rho(o)$$
$$1 \qquad \text{if } \rho(n)>=\rho(o)$$

This keeps detailed balance (stabilizes the probabilities $\rho(\sigma)$) and equilibrates the system if it is out of equilibrium – this is the **Metropolis Algorithm**
There are other solutions but this is the most commonly used

The Metropolis Algorithm (General)

- An algorithm to pick a series of configurations so that they asymptotically appear with probability $\rho(\sigma)=\exp(-\beta E(\sigma))$

  1. Assume we are in state σ_i

  2. Choose a new state σ^*, and define $\Delta E=E(\sigma^*)-E(\sigma)$

  3. If $\Delta E<0$ then accept σ^*

  4. If $\Delta E>0$ then accept σ^* with probability $\exp(-\beta\Delta E)$

  5. If we accept σ^* then increment i, set $\sigma_i=\sigma^*$ and return to 1. in a new state

  6. If we reject σ^* then return to 1. in the same state state σ_i

- This is a Markov process, which means that the next state depends only on the previous one and none before.

Metropolis Algorithm for Cluster Expansion Model (Real Space)

- We only need to consider spin states

    1. Assume the spins have value $(\sigma_1, \dots \sigma_j, \dots, \sigma_N)$

    2. Choose a new set of spins by flipping, $\sigma_j^* = -\sigma_j$, where i is chosen at random

    3. Find $\Delta\Phi = E(\sigma_1, \dots -\sigma_j, \dots, \sigma_N) - E(\sigma_1, \dots \sigma_j, \dots, \sigma_N) - \mu\sigma_j$ (note that this can be done quickly be only recalculating the energy contribution of spin i and its neighbors)

    4. If $\Delta\Phi < 0$ then accept spin flip

    5. **If $\Delta\Phi > 0$ then accept spin flip with probability exp(-$\beta\Delta\Phi$)**

    6. If we reject spin flip then change nothing and return to 1

- The probability of seeing any set of spins σ will tend asymptotically to

Obtaining Thermal Averages From MC

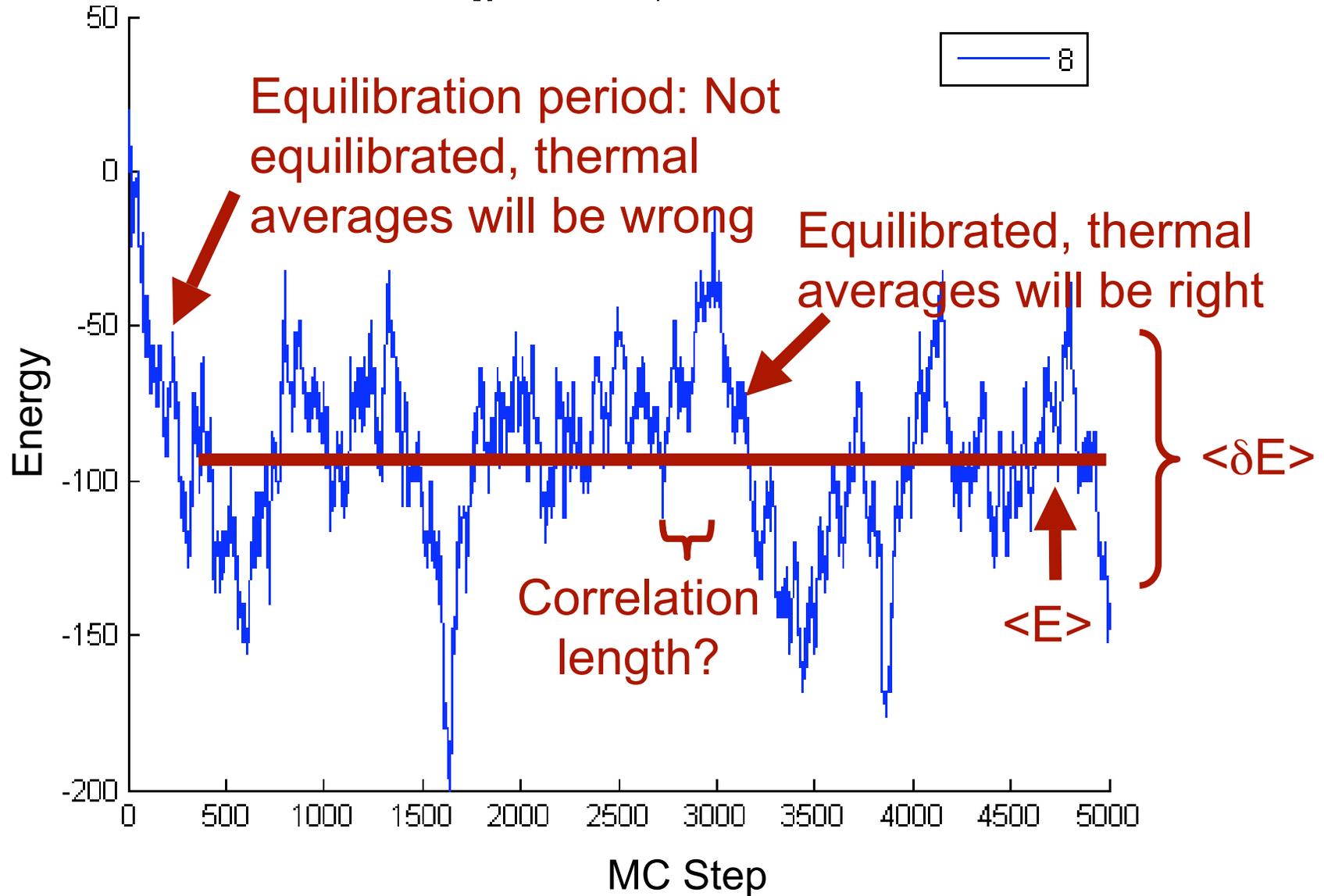- The MC algorithm will converge to sample states with probability $\rho(\sigma)$. So a thermal average is given by

$$\langle \quad \rangle$$

- Note that N_{mcs} should be taken after the system equilibrates

- Fluctuations are also just thermal averages and calculated the same way

$$\langle \quad \langle \quad \rangle \quad \rangle \quad \langle \quad \rangle$$

Energy Vs. MC Step

Energy vs. MC Step - Real time

Equilibration period: Not equilibrated, thermal averages will be wrong

Equilibrated, thermal averages will be right

$\langle \delta E \rangle$

Correlation length?

$\langle E \rangle$

Energy

MC Step

Measuring Accuracy of Averages

$$\langle \ \rangle \quad - \quad$$

What is the statistical error in *<A>*?

For uncorrelated data

$$\sqrt{} \qquad \sqrt{}$$

But MC steps are correlated, so we need more thorough statistics

$$\langle \ \rangle \quad - \qquad | \ | \qquad \overline{} \qquad \langle \ \rangle$$

V$_l$ is the covariance and gives the autocorrelation of *A*
with itself *l* steps later
Longer correlation length $\Rightarrow$ less independent data $\Rightarrow$
Less accurate *<A>*

Example of Autocorrelation Function

Energy Autocorr vs. Delta MC Step
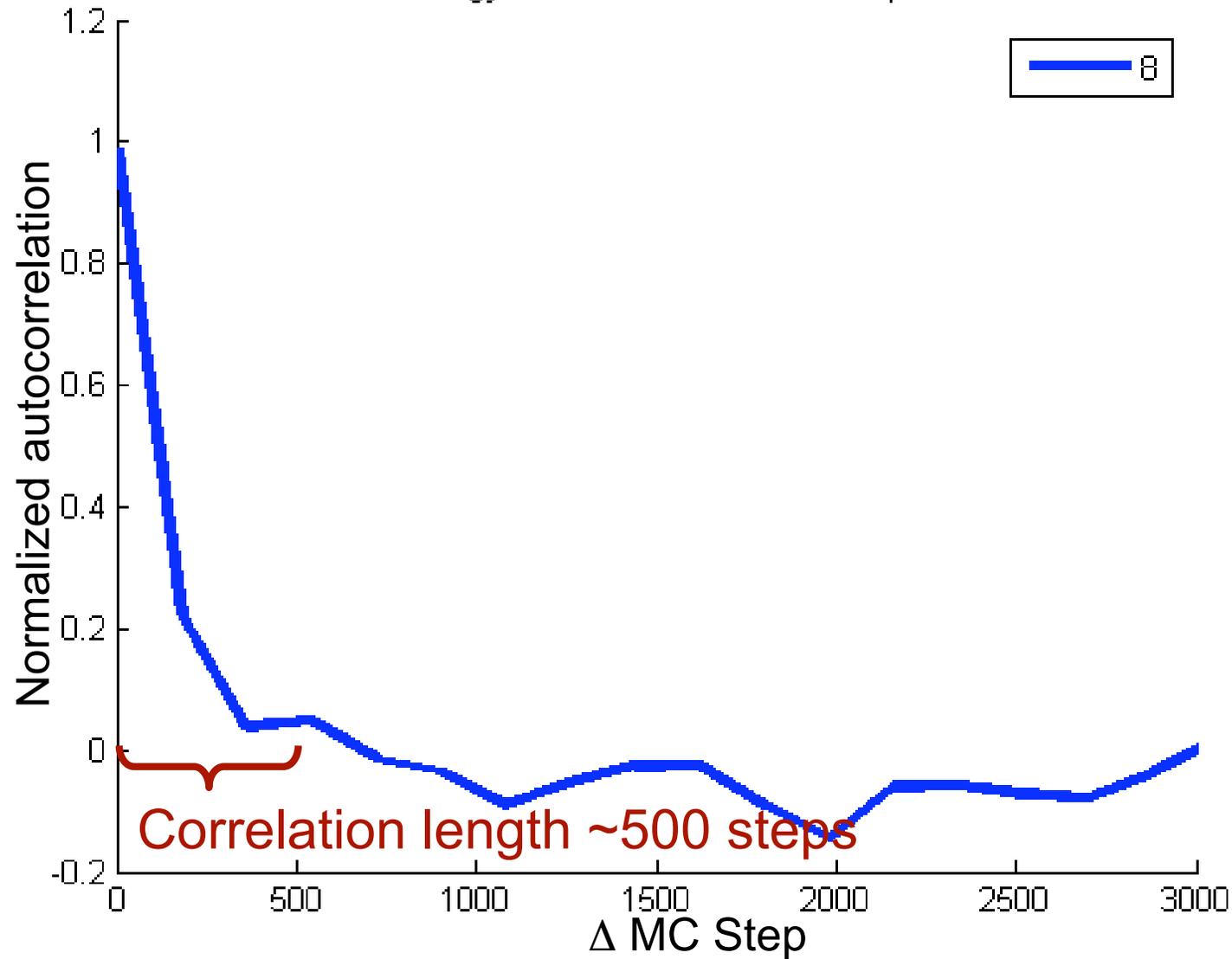
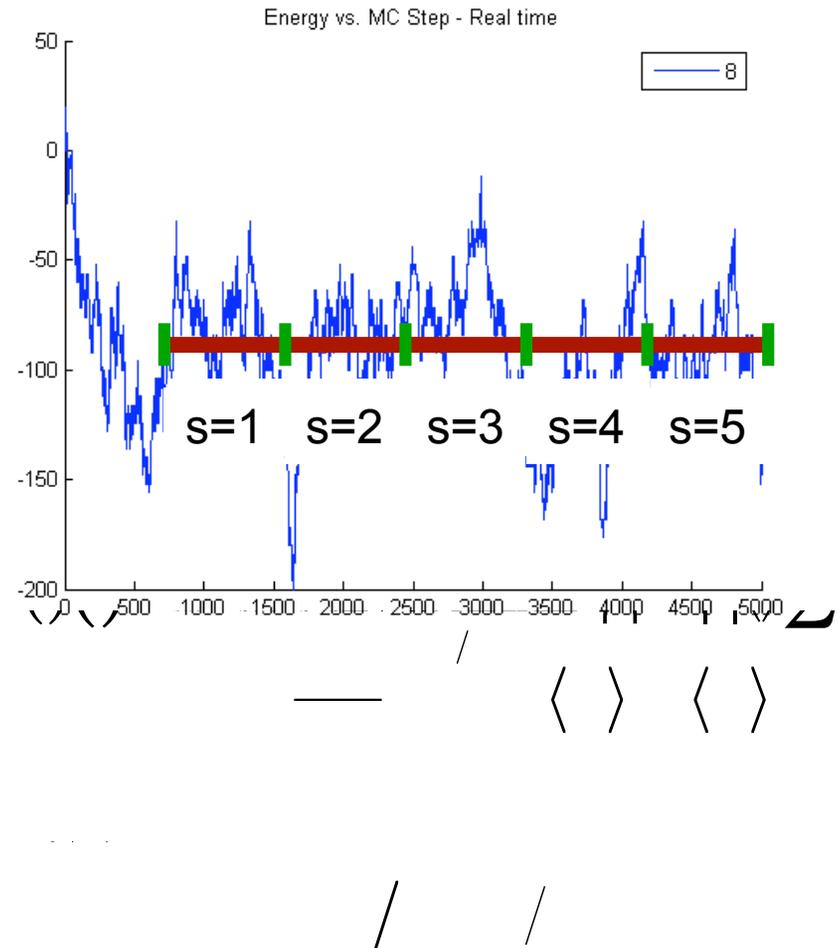# Semiquantitative Understanding of Role of Correlation in Averaging Errors

If we assume V_I decays to ~zero in $L_c \ll L$ steps, then

$$\langle \quad \rangle \qquad \overline{\quad} \qquad | \quad | \quad \overline{\quad} \qquad || \qquad \overline{\quad\quad}$$

$$\sqrt{\quad\quad\quad} \qquad \sqrt{\overline{\quad\quad}}$$
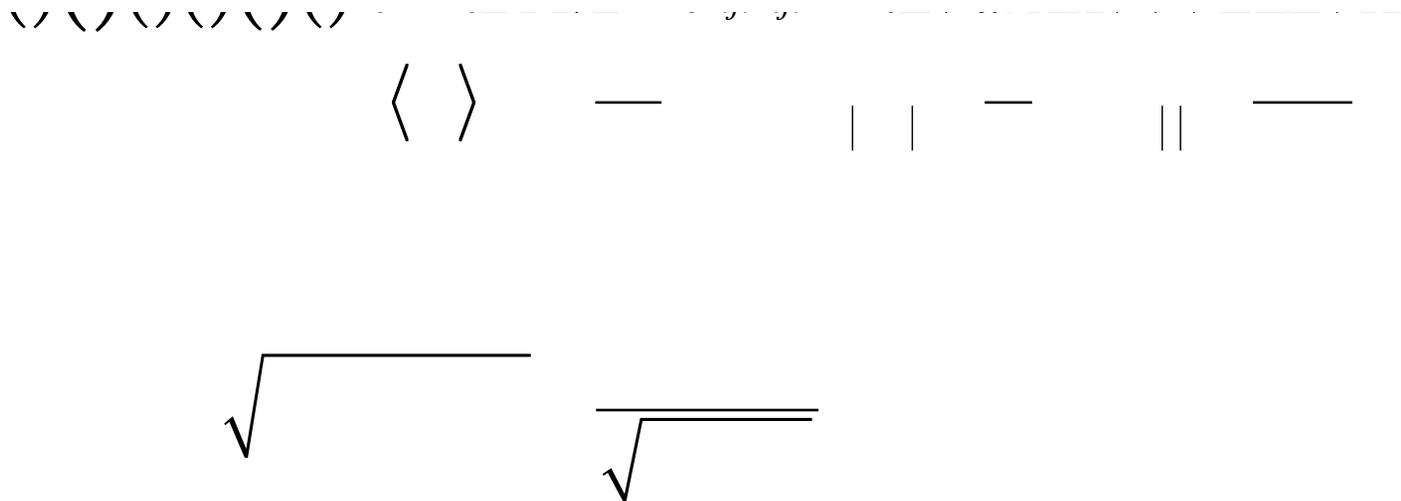
This makes sense! Error decreases with sqrt of the number of uncorrelated samples, which only occur every $\sim L/L_c$ steps. As L_c_1 this becomes result for uncorrelated data.

Methods to Test Convergence Efficiently

- Set a bound on $VAR(A_L)$ and then keep simulating until you meet it.
- Different properties can converge at different rates – must test each you care about
- Calculating $VAR(A_L)$ exactly is very slow – $O(L^2)$
- One quick estimate is to break up the data into subsets s of length L_{sub}, average each, and take the VAR of the averages. Can depend on set lengths
- Another estimate is to assume a single correlation length which implies

Find where $V_0/V_I = e$ to estimate L_c and VAR in $O(N\ln N)$ calcs (ATAT)

Energy vs. MC Step - Real time

s=1   s=2   s=3   s=4   s=5

van de Walle and Asta, *MSMSE* '02

Finding Phases With MC

- MC automatically converges to correct thermodynamic state – Can we just scan space of (c,T) to get phase diagram?

- **Issue 1 - Identification**: How do we recognize what phase we are in?

  - Comparison to ground state search results to give guidance

  - Order parameters: concentration, site occupancies of lattice

  - Visualize structure (challenging due to thermal disorder)

  - Transition signified by changes in values of derivatives of free energy (E, C_v, …)
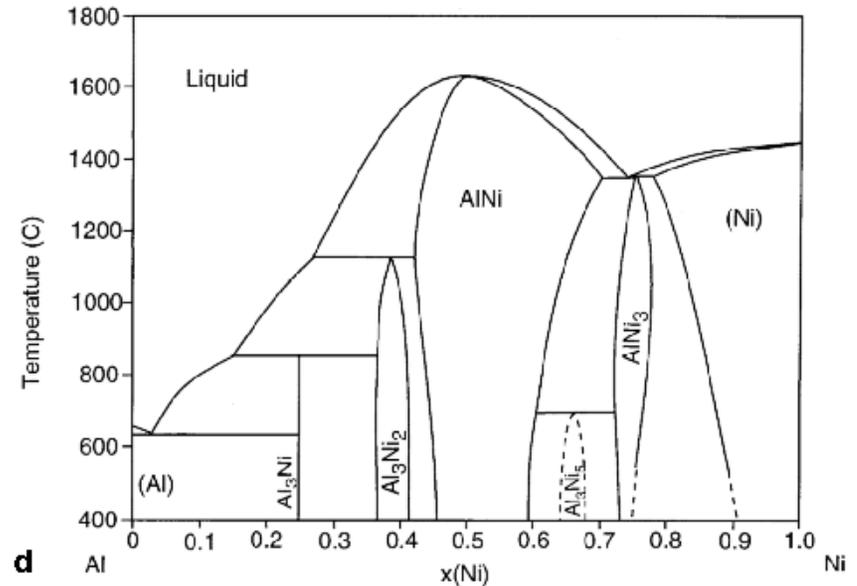

H. Okamoto, *J. Phase Equilibria,* '93

Finding Phases with MC
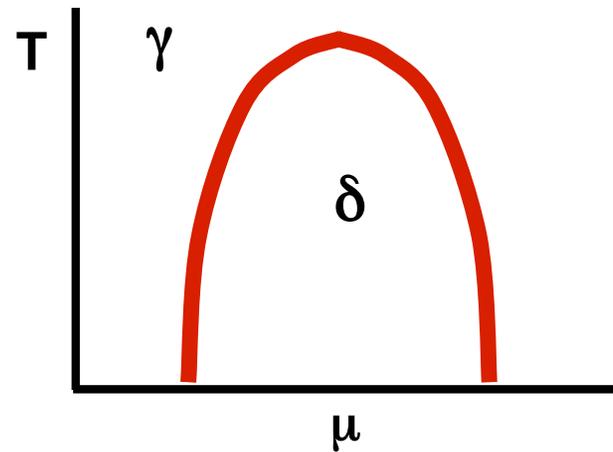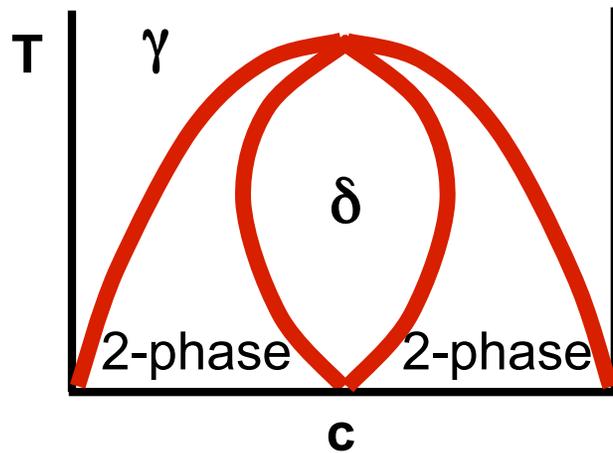
- **Issue 2 – 2-phase regions:** What happens in 2-phase regions?
  - System will try to separate – hard to interpret.
  - So scan in (μ,T) space (materials are stable single phase for any given value of (μ,T))

Finding Phases with MC

- **Issue 3 – Hysteresis**: Even in (T,μ) space the MC may not converge to correct phase
  - Multiple phases can only be stable at the phase boundary values of (μ,T), but phases are always somewhat metastable near boundary regions
  - Therefore, the starting point will determine which phase you end up in near the phase boundary
  - **To get precise phase boundaries without hysteresis you must equate thermodynamic potentials. How do we get thermodynamic potentials out of MC?**

Metastable boundaries

$\Phi^\gamma < \Phi^\delta \qquad \Phi^\gamma = \Phi^\delta \qquad \Phi^\gamma > \Phi^\delta$

γ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ δ

T

μ
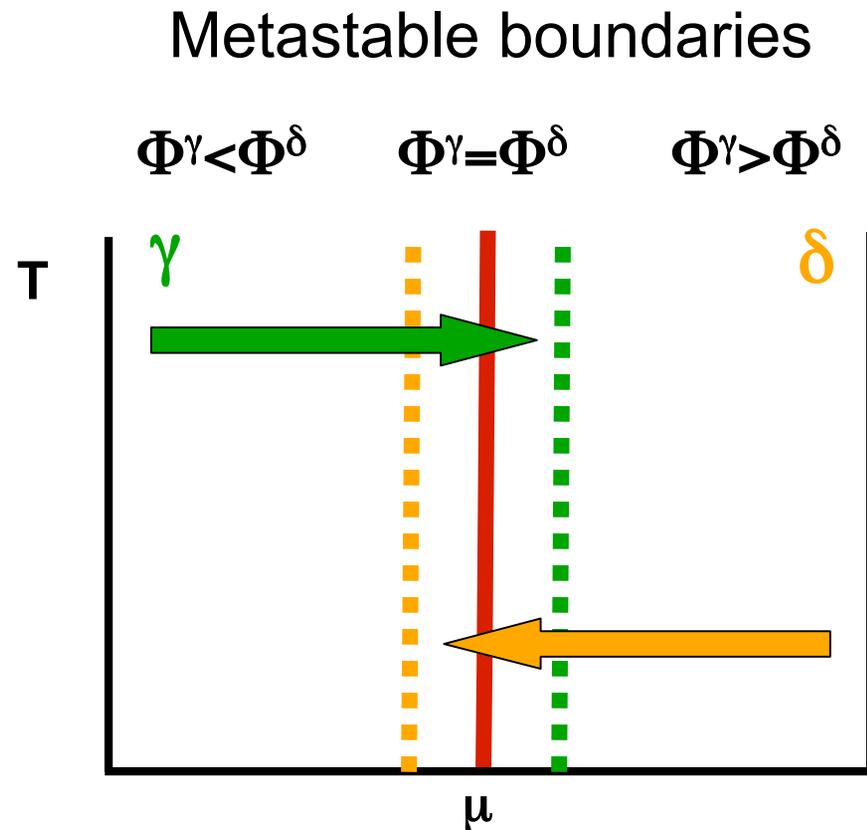
Thermodynamic Potentials in MC

- All phase boundaries are defined by the set of points where $\Phi^\delta(\mu,\beta)=\Phi^\gamma(\mu,\beta)$ for all possible phases a, g. If we know Φ we can find these points of intersection numerically. Then we can get (c,T) phase diagram from c(μ), which comes naturally from the MC, or the relation c=-dΦ/dμ. But how do we get $\Phi^\delta(\mu,\beta)$ for each phase?

$$\langle\ \rangle \qquad \langle\ \ \rangle$$

- Thermodynamic potentials cannot be calculated by simple direct MC thermal averaging – why? Because S is not the thermodynamic average of anything!! We always measure + calculate derivatives of potentials

- **But changes in thermodynamic potentials are given by thermodynamic averages!!**

- So we can find a potential by finding a state where the potential is know and integrating the changes (given by MC thermal averages) from the known state to the desired state. **This is Thermodynamic Integration!**

- There are other ways to get thermodynamic potentials with MC (e.g., umbrella sampling) but these will not be discussed here and are not used much for cluster expansion Hamiltonians.

Thermodynamic Integration

vandeWalle and Asta, *MSMSE* '02

The total differential of the semi-grand canonical potential is

This can be integrated to give

This allows one to calculate any $\Phi(\mu_1,\beta_1)$ given
- A starting value $\Phi(\mu_0,\beta_0)$ – obtain from high and low T expansions
- MC simulations of the expectation values – use methods just discussed
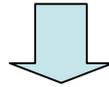- Must be done for each phase – can be efficient in only calculating values near boundaries

Efficiently implemented in ATAT! http://cms.northwestern.edu/atat/

Example of Thermodynamic Integration

Get phase boundary points

$\Phi^{\gamma}(\mu^*,T^*)=\Phi^{\delta}(\mu^*,T^*)$

$c_{\gamma}^* = c_{\gamma}(\mu^*,T^*)$

$c_{\delta}^* = c_{\delta}(\mu^*,T^*)$
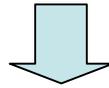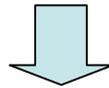
Thermodynamic integration paths
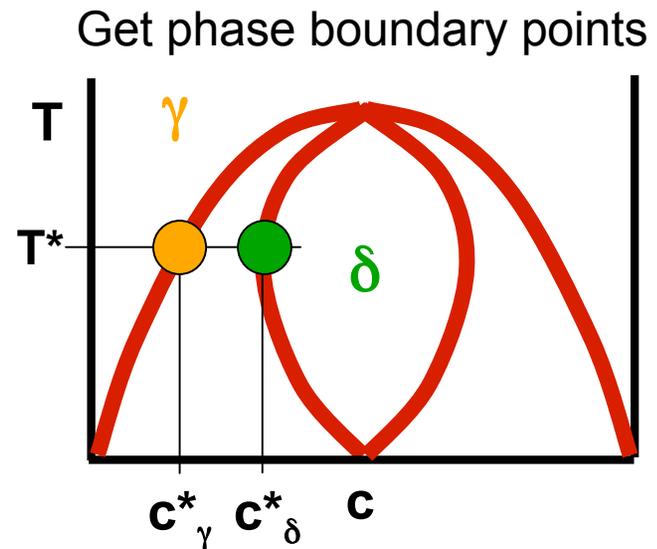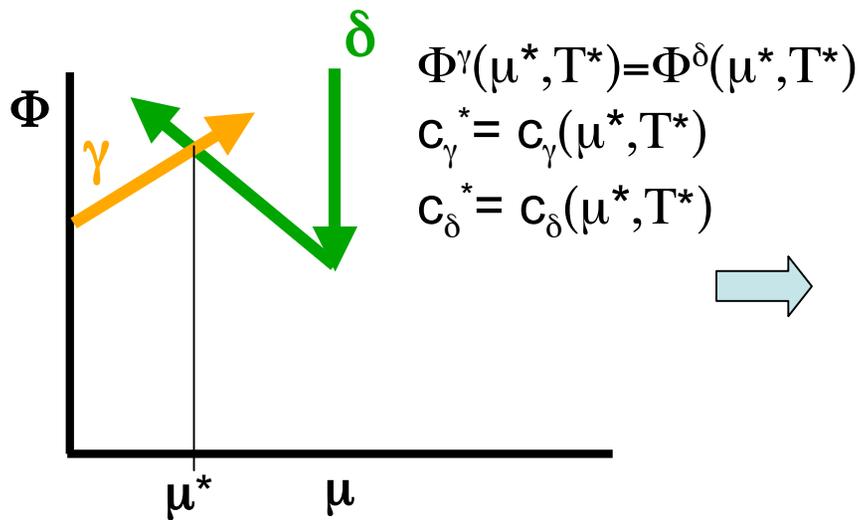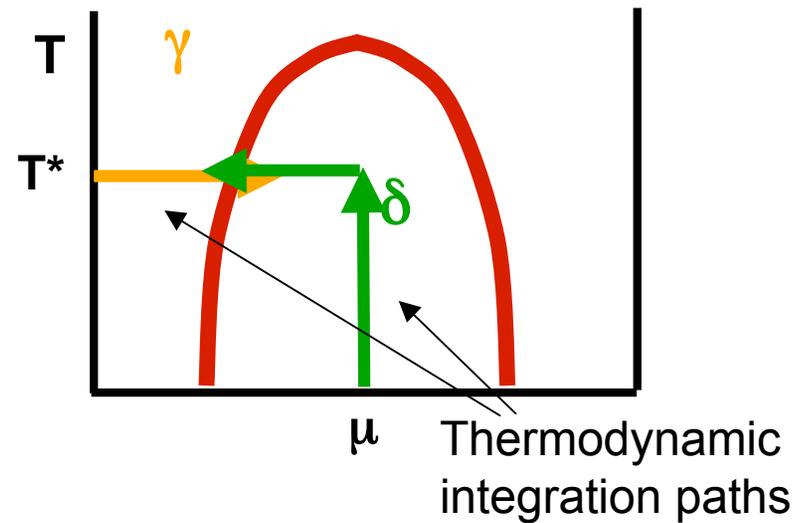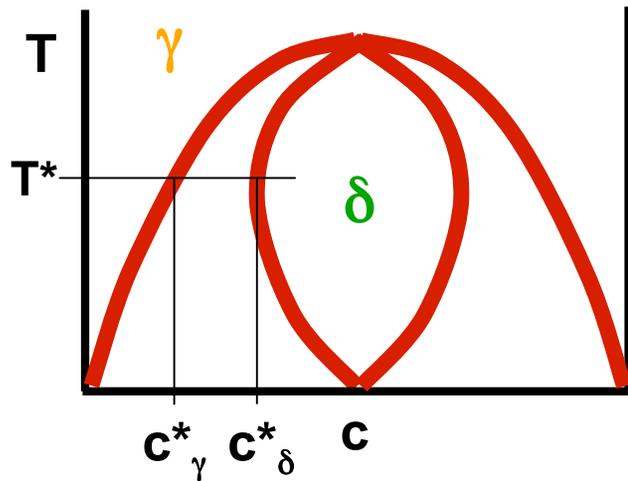
Summary

Cluster Expansion

⬇

Identify possible phases: Ground states

⬇

MC/semi-analytic functions to identify qualitative phase diagram

⬇

MC + Thermodynamic integration to get quantitative phase diagram
Use semi-analytic functions for integration starting points