Mean-field Methods

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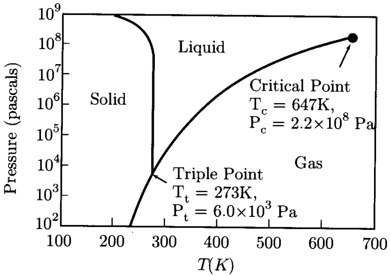
Outline

Phase transitions

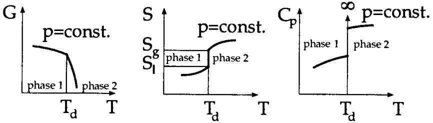
Changes in control parameters can lead to phase transitions

- **Phase transition:** transition between two equilibrium phases characterised by singularity or discontinuity in some observable property
- **Order parameter:** quantity distinguishing an ordered from a disordered phase
  - Reflects symmetry of the Hamiltonian
  - Equally zero in the disordered phase
  - Microscopic variable or thermodynamic parameter

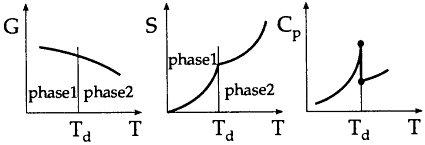


Phase transitions

- **First order phase transition:**
  - Discontinous first derivatives of free energy (S,$\overline{V}$).
  - Latent heat $T\Delta S$
  - Reasonable well described by mean-field models
  - Nucleation and growth



- **Second order phase transition:**
  - Continuous first derivatives of free energy. Order parameter disappears continuously
  - Strong fluctuations in order parameter
  - Molecular details irrelevant
  - Mean-field models: qualitatively wrong



Outline

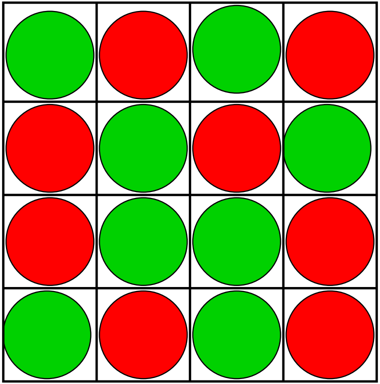
Lattice gas model

Ideal to study second order PT:
No molecular details

- **System:** regular array of space filling cells (M lattice sites)
- **Degrees of freedom:** occupation numbers:

$$n_i = \begin{cases} 0 & molecule \;\; A \\ 1 & molecule \;\; B \end{cases}$$

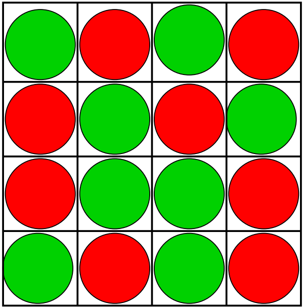
- **Incompressible binary mixture:**
  - Two molecular types A and B
  - Number of molecules $N = N_A + N_B = M_{sites} \rightarrow 2^{M_{sites}}$ cofigurations



Lattice gas model

- **Nearest-neighbour interactions:**

$$\epsilon = \begin{cases} -\epsilon_{AA} \\ -\epsilon_{AB} \\ -\epsilon_{BB} \end{cases}$$



- **Hamiltonian:**

$$\begin{aligned} \mathcal{H}(\{n_i\}) &= -\sum_{(i,j)} \epsilon_{AA}(1-n_i)(1-n_j) + \\ &\quad \epsilon_{AB}(1-n_i)n_j + \epsilon_{AB}n_i(1-n_j) \\ &\quad \epsilon_{BB}n_in_j \end{aligned}$$

that can be rewritten as:

$$\mathcal{H}(\{n_i\}) = \epsilon \sum_{(i,j)} n_i(1-n_j) - 2B\sum_i n_i + C$$

where $(i,j) \rightarrow$ sum over all zN/2 pairs of cells

Lattice gas model

- Where $\epsilon = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$, $B = -z(\epsilon_{AA} - \epsilon_{BB})/4$ and $C = -Nz\epsilon_{AA}/2$
  - $\epsilon_{AA} + \epsilon_{BB} < 2\epsilon_{AB}$ ($\epsilon < 0$) favors **mixing**
  - $\epsilon_{AA} + \epsilon_{BB} > 2\epsilon_{AB}$ ($\epsilon > 0$) favors **segregation**
- **Order parameter:** concentration, ϕ, of B molecules

$$\phi = \frac{N_B}{N} = \frac{1}{N} \left\langle \sum_i^N n_i \right\rangle \tag{1}$$

- **Ensemble:** Semi-grand canonical $\rightarrow$ one chemical potential $\mu = \mu_A - \mu_B$ conjugate to $N_B \in [0 - N]$

$$\Xi(\mu, N, T) = \prod_{i=1}^{N} \sum_{n_i=0,1} \exp\left(-\beta\left[\mathcal{H}(\{n_i\}) - \mu \sum_j n_j\right]\right) \tag{2}$$

and

$$\Omega(\mu, N, T) = -k_B T \ln(\Xi) \tag{3}$$

Bragg-William theory

- **Helmholtz free energy:**

$$f(\phi, T) = \frac{1}{N}F(\phi, N, T) = \frac{1}{N}\Omega(\mu, N, T) + \mu\phi$$
$$\frac{1}{N}(U - TS) = u - Ts$$

- **Aim:** Calculate $f(\phi, T)$ by evaluating u and s
- **Method:** Mean field approach → neglect correlations between occupation numbers n_i :

$$\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle \quad \forall \quad (i, j)$$

Bragg-William theory

- **Entropy:**
  - For uncorrelated particles $S = S_{mix}^{ideal} = k_B \ln(\Omega_c)$
  - Calculating $\Omega_c = \frac{N!}{N_B!(N-N_B)!}$ and using Stirling's formula:

$$S = -Nk_B \left[\phi \ln(\phi) + (1-\phi)\ln(1-\phi)\right]$$

- **Internal energy:**
  - Statistical average of $\mathcal{H}(\{n_i\})$
  - Focus on symmetric case: $\epsilon_{AA} = \epsilon_{BB} \rightarrow B = 0$

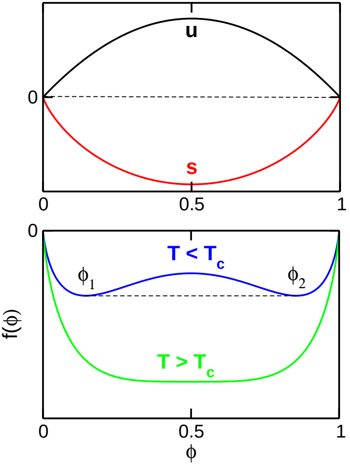
$$U = \epsilon \sum_{(i,j)} \langle n_i(1-n_j)\rangle \approx \epsilon \sum_{(i,j)} \langle n_i\rangle \langle (1-n_j)\rangle = \frac{Nz\epsilon}{2}\phi(1-\phi)$$

- **Free energy:**

$$\boxed{f = \frac{z\epsilon}{2}\phi(1-\phi) + k_B\left[\phi\ln(\phi) + (1-\phi)\ln(1-\phi)\right]}$$

Bragg-William theory

- $\epsilon < 0$: the two contributions to f are negative
  - For all T, f is a convex function of ϕ
  - Single maximum at $\phi = 0.5$. **Complete miscibility**
- $\epsilon > 0$: u and s compete
  - For $T < T_c$: two minima $\rightarrow \phi_1$ and ϕ_2 separated by a concave region with a maximum at $\phi = 0.5$
  - Concavity $\rightarrow$ **Phase separation for $\phi_1 < \phi < \phi_2$**
  - For $T > T_c$: **Complete miscibility**



Bragg-William theory

Phase diagram: $\mu(\phi, T) = \left(\frac{\partial f}{\partial \phi}\right)_T$

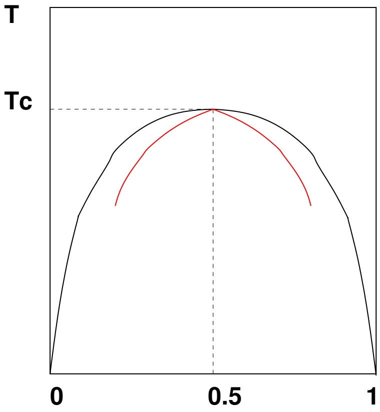
Result:

$$\phi = \frac{1}{2}\left[1 + \tanh\left(\frac{\beta}{2}\left(\mu + \epsilon z(\phi - \frac{1}{2})\right)\right)\right]$$

which must solved numerically or graphically

Coexistence curve:

- At coexistence $\mu = \mu_A - \mu_B = 0$ by symmetry
- Coexistence composition determined by double-tangent construction: $\rightarrow \mu(\phi_1) = \mu(\phi_2)$
- Setting $\mu = 0$:



$$(\phi - 0.5) = \frac{1}{2}\tanh\left(\frac{\beta\epsilon z}{2}(\phi - 0.5)\right) \rightarrow \textit{Nonzero solution if } T < T_c = \epsilon z/4k_B$$

Bragg-William theory

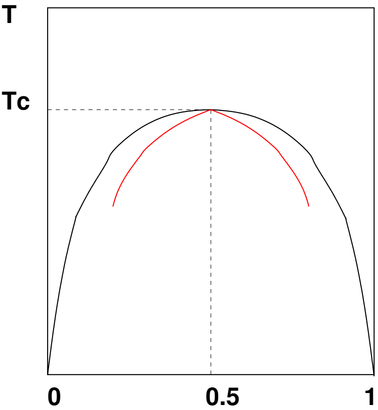
Stability and spinodal line: Consider the equation:

$$\phi = -\frac{1}{N}\left(\frac{\partial\Omega}{\partial\mu}\right)_{N,T}$$

since $\Omega = -kBT \ln(\Xi)$ it is simple to show:

$$k_B T\left(\frac{\partial\phi}{\partial\mu}\right)_{N,T} = -\frac{k_B T}{N}\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{N,T} = \frac{1}{N}\left(\left\langle N_B^2\right\rangle - \langle N_B\rangle^2\right) > 0$$

and using $\mu = \left(\frac{\partial f}{\partial\phi}\right)_T$



$$\left(\frac{\partial^2 f}{\partial\phi^2}\right)_{N,T} > 0$$ **Spinodal line : Locus of points where** $\left(\frac{\partial^2 f}{\partial\phi^2}\right)_{N,T} = 0$

Outline

The Bogoliubov variational theorem

In many cases the exact configurational energy of a system can be written as:

$$\mathcal{H} \quad = \quad \mathcal{H}_i + \mathcal{H}_{i,j} = \textbf{Single particle term} \quad + \quad \textbf{Pairwise potential}$$

Propose *family* of Hamiltonians of the form:

$$\begin{aligned}\mathcal{H}(\lambda) &= \mathcal{H}_0 + \lambda \mathcal{H}_I \quad \textit{with} \quad 0 \leq \lambda \leq 1 \\ &= \textbf{Reference (non - interacting)} + \textbf{Correction term}\end{aligned}$$

Bogoliubov theorem:

In terms of Helmholtz free energy,

$$F \leq F_0 + \langle \mathcal{H}_I \rangle_0 \quad \textbf{Upper bound to F}$$

The Bogoliubov variational theorem

In the previous expression:

- $F_0 \rightarrow$ Free energy of reference system
- $\langle \mathcal{H}_I \rangle_0 \rightarrow$ Ground state expectation value of the correction term $\mathcal{H}_I$

$$\langle \mathcal{H}_I \rangle_0 = \frac{\int d\mathbf{\Gamma} \mathcal{H}_I(\mathbf{\Gamma}) \exp\left(-\beta \mathcal{H}_0(\mathbf{\Gamma})\right)}{\int d\mathbf{\Gamma} \exp\left(-\beta \mathcal{H}\right)(\mathbf{\Gamma})}$$

Aim: Obtain the best estimate of the exact free energy F for a given choice of reference system

Strategy:

- Choose a trial Hamiltonian, $\mathcal{H}_0$, which is soluble
- Minimize $F_0 + \langle \mathcal{H}_I \rangle_0$ with respect to λ

Proof of the Bogoliubov inequality

In the canonical ensemble, the exact free energy is:

$$-\beta F(\lambda) = \ln\left(\int d\mathbf{\Gamma}\, \exp\left(-\beta\mathcal{H}(\mathbf{\Gamma};\lambda)\right)\right)$$

Differentiate both sides w.r.t. λ and cancel factors of β,

$$\left(\frac{\partial F}{\partial\lambda}\right) = \frac{\int d\mathbf{\Gamma}\mathcal{H}_I \exp\left(-\beta(\mathcal{H}_0+\lambda\mathcal{H}_I)\right)}{\int d\mathbf{\Gamma}\exp\left(-\beta(\mathcal{H}_0+\lambda\mathcal{H}_I)\right)} = \langle\mathcal{H}_I\rangle$$

Differentiate again w.r.t. λ to obtain:

$$\frac{\partial^2 F}{\partial\lambda^2} = -\beta\left(\left\langle\mathcal{H}_I^2\right\rangle - \langle\mathcal{H}_I\rangle^2\right) = -\beta\left\langle(\mathcal{H}_I - \langle\mathcal{H}_I\rangle)^2\right\rangle \leq 0$$

F is a concave function of λ

Proof of the Bogoliubov inequality

The previous inequality implies that $F(\lambda)$ lies below its tangent at $\lambda = 0$, or:

$$F(\lambda) \leq F(\lambda = 0) + \lambda \left(\frac{\partial F}{\partial \lambda} \right)_{\lambda=0} + \cdots$$

Using,

$$\left(\frac{\partial F}{\partial \lambda} \right)_{\lambda=0} = \langle \mathcal{H}_I \rangle_0$$

The proof is completed as:

$$F(\lambda) \leq F_0 + \lambda \langle \mathcal{H}_I \rangle_0$$

and setting $\lambda = 1$

$$\boxed{F \leq F_0 + \langle \mathcal{H}_I \rangle_0}$$

Outline

Application to the Ising model

Consider the Ising model in an external field B:

$$\mathcal{H} = -\sum_{i,j} J_{i,j} S_i S_j - B \sum_i S_i$$

- $J_{i,j} = J$ if i, j are nearest neighbors
- $J_{i,j} = 0$ otherwise

Mean field approach: choose the reference system as:

$$\mathcal{H}_0 = -\sum_i B' S_i - B \sum_i S_i$$

where B' is the **molecular field** felt by spin i and due to all the other spins.

The **partition function of the reference system** is:

$$Q_0 = \sum_{S_i=\pm 1} \cdots \sum_{S_N=\pm 1} \exp -\beta(\mathcal{H}_0) = [\exp(\beta B_e) + \exp(-\beta B_e)]^N$$

with $B_e = B' + B$

Application to the Ising model

$$Q_0 = [2\cosh(-\beta B_e)]^N \rightarrow F_0 = -\frac{N}{\beta}\ln[2\cosh(-\beta B_e)]$$

Expressing the correction term as the difference between the exact and the reference system, Bogoliubov inequality reads:

$$\boxed{F \leq F_0 + \langle \mathcal{H}_I \rangle_0 = F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0}$$

Substituting the Ising Hamiltonian:

$$F \leq F_0 - \sum_{i,j} J_{i,j} \langle S_i S_j \rangle - B' \sum_j \langle S_j \rangle_0$$

Need to calculate averages over reference (non-interacting) system:

- $\sum_j \langle S_j \rangle_0 = N \langle S \rangle_0$
- $\sum_{i,j} J_{i,j} \langle S_i S_j \rangle = \sum_{i,j} J_{i,j} \langle S_i \rangle_0 \langle S_j \rangle_0 = \frac{JNz}{2} \langle S \rangle_0^2$

Application to the Ising model

Substituting the previous results into the expression for F and using $B_e = B' + B$,

$$F \leq F_0 - \frac{JNz}{2} \langle S \rangle_0^2 + (B_e - B) N \langle S \rangle_0$$

and $\langle S \rangle_0$ can be obtained as $-\frac{1}{N}\left(\frac{\partial F}{\partial B_e}\right)$ to give:

$$\langle S \rangle_0 = \tanh\left(\beta B_e\right)$$

Next step: use variational method to obtain the effective field, B_e, that minimises F

Ising model: the variational method

Using B_e as the control parameter, the condition for and extremum is:

$$\left(\frac{\partial F}{\partial B_e}\right) = 0$$

and since: $F = F_0 - \frac{JNz}{2}\langle S\rangle_0^2 + (B_e - B)N\langle S\rangle_0$

$$\left(\frac{\partial F}{\partial B_e}\right) = (B_e - B)N\left(\frac{\partial\langle S\rangle_0}{\partial B_e}\right) - NzJ\langle S\rangle_0\left(\frac{\partial\langle S\rangle_0}{\partial B_e}\right) = 0$$

which leads to:

$$\boxed{B_e = B + zJ\langle S\rangle_0 \qquad \textit{condition for minimum free energy}}$$

and the reference system magnetisation is:

$$\langle S\rangle_0 = \tanh\left(\beta B + zJ\beta\langle S\rangle_0\right)$$

What about the total system ?

Ising model: optimal free energy

Using previous expression for F_0 and B_e:

$$F = -\frac{N}{\beta}\ln\left[2\cosh\left(\beta B_e\right)\right] + \frac{N}{2zJ}\left(B_e - B\right)^2$$

with $B_e = B + zJ\left\langle S\right\rangle_0$, and since $\left\langle S\right\rangle = -\frac{1}{N}\left(\frac{\partial F}{\partial B_e}\right)$

$$\left\langle S\right\rangle = \frac{1}{zJ}\left(B_e - B\right) = \left\langle S\right\rangle_0$$

and

$$\left\langle S\right\rangle = \tanh\left(\beta B + zJ\beta\left\langle S\right\rangle\right)$$

Phase transition identified by setting $B = 0$, so

$$\left\langle S\right\rangle = \tanh\left(zJ\beta\left\langle S\right\rangle\right)$$

admits solutions with $\left\langle S\right\rangle \neq 0$ only if $zJ/k_BT > 1 \rightarrow T_c = zJ/k_B$

Bibliography

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