PHASE TRANSITIONS

Up to now, we have considered systems with no interactions (ideal gases), or homogeneous systems (liquids) that can be described using the radial distribution function formalism. Nothing up to now has indicated that it is possible to have phase transitions, in other words coexistence between phases of different densities and compositions. From an engineering standpoint, phase equilibria are extremely important since they form the basis for most separations. In the following, we will attempt to clarify the microscopic basis for phase transitions. We will do this by introducing a very simple model for interactions between parts of a system, the Ising model.

Ising model

The Ising model was initially proposed in order to describe ferromagnetism, the presence of spontaneous magnetization in metals such as Fe or Ni, below a critical temperature (the Curie point). In the terminology of magnetism, the Ising model is described as follows: Consider a lattice of magnetic dipoles (cubic in three dimensions), as illustrated in the figure below.

Each dipole has magnitude $m$, and can point up or down. In the presence of an external magnetic field of magnitude $H$, the energy of a microstate $\nu$ is given by

$$U_\nu = - \sum_{i=1}^{N} H m s_i - J \sum_{i=1}^{N-1} \left( \sum_{j > i, j \text{ n. n. of } i}^{N} s_i s_j \right)$$

(1)

where the first term represents the interaction between the spins and the external field, with $s_i = \pm 1$, corresponding to the spin pointing up or down. The second term represents the interactions among spins. $J$ is a positive constant, so that configurations with neighboring spins aligned are favored. Only interactions between immediate (nearest) neighbors are present. The partition function for this model can be immediately obtained as.

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1 Material in this section is partly based on Chapter 5 of Chandler
\[ Q(\beta, N, H) = \sum_v \exp(-\beta U_v) = \sum_{s_1} \sum_{s_2} \ldots \sum_{s_N = \pm 1} \exp \left( \beta mH \sum_{i=1}^{N} s_i + \beta J \sum_{i=1}^{N-1} \sum_{j \neq i, j \text{n.n. of } i}^{N} s_i s_j \right) \]  

(2)

By a change of names the Ising model can be made to simulate systems other than a ferromagnet. Of particular interest is the so-called "lattice gas" system. A lattice gas is a collection of atoms whose positions can take only discrete values. Each lattice site can be occupied by at most one atom. For example, the lattice gas configuration corresponding to the schematic of the magnetic Ising model on the previous page is:

The circles correspond to atoms, and blank spaces in the lattice to absence of atoms. The potential of the system is an attractive short-range interaction between nearest neighbors (strength is proportional to \( J \) of equation 1). What is the analog of the external field \( H \)? It turns out that \( H \) plays the role of the chemical potential of the gas. The canonical partition function for the ferromagnetic model (equation 2) is then the \textit{grand} canonical partition function for the lattice gas model. The two-dimensional lattice gas model is physically relevant for the description of adsorption.

Physically, we expect that a model such as the Ising model might show "spontaneous magnetization" in the absence of an external field at sufficiently low temperatures, since alignment of nearest spins is energetically favored. Since, in the absence of an external field, the up and down directions are equivalent, the spontaneous magnetization will be doubly degenerate, with an "up" phase and a "down" phase. In the terminology of the lattice gas, there should be a dense (liquid) phase and a dilute (gas) phase.

In the following, we will examine the behavior of the Ising model with respect to phase transitions, in one- two- or three- dimensions. As we will show, dimensionality plays an extremely important role in phase transitions.

One-dimensional Ising model

The partition function \( Q \) of the one-dimensional Ising model can be evaluated with relative ease. Consider a one-dimensional system as follows

\[
\begin{array}{cccccccccccc}
\uparrow & \uparrow & \downarrow & \downarrow & \uparrow & \uparrow & \downarrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow \\
1 & 2 & 3 & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & N-1 & N
\end{array}
\]
The line connecting cell 1 and N-1 implies that the system is under “periodic” boundary conditions so that there are no boundaries to the system, even though it is finite. The partition function is

\[
Q(\beta, N, H) = \sum_{s_1} \sum_{s_2} \ldots \sum_{s_{N\pm 1}} \exp \left( \sum_{i=1}^{N} \frac{\beta m H}{2} (s_i + s_{i+1}) + \beta J s_i s_{i+1} \right)
\]

(3)

where it is implied that \( N+1 \equiv 1 \) to satisfy the periodic boundary conditions. Now consider the matrix

\[
q = \begin{bmatrix} 
\exp(-\beta m H + \beta J) & \exp(-\beta J) \\
\exp(-\beta J) & \exp(+\beta m H + \beta J)
\end{bmatrix}
\]

and the vectors \( s_i = [1 \ 0] \) if \( s_i = -1 \)

\( s_i = [0 \ 1] \) if \( s_i = +1 \)

Then each term in the partition function can be expressed as

\[
\exp \left( \frac{\beta m H}{2} (s_i + s_{i+1}) + \beta J s_i s_{i+1} \right) = s_i \cdot q \cdot s_{i+1}^T
\]

(4)

Then,

\[
Q(\beta, N, H) = \sum_{s_1} \sum_{s_2} \ldots \sum_{s_{N\pm 1}} \exp \left( \sum_{i=1}^{N} \frac{\beta m H}{2} (s_i + s_{i+1}) + \beta J s_i s_{i+1} \right) = \\
= \sum_{s_1} \sum_{s_2} \ldots \sum_{s_{N\pm 1}} \prod_{i=1}^{N} \exp \left( \frac{\beta m H}{2} (s_i + s_{i+1}) + \beta J s_i s_{i+1} \right) = \sum_{s_1} \sum_{s_2} \ldots \sum_{s_{N\pm 1}} \prod_{i=1}^{N} s_i \cdot q \cdot s_{i+1}^T = \sum_{s_i \pm 1} s_1 \cdot q^N \cdot s_1^T
\]

where we have used that \( s_i \cdot q \cdot s_{i+1}^T s_{i+1} \cdot q \cdot s_{i+2}^T = s_i \cdot q \cdot q \cdot s_{i+2}^T \). The final result can be expressed as the trace (sum of diagonal elements) of the \( N \)-th power of the matrix \( q \), which is best found by diagonalizing the matrix:

\[
Q(\beta, N, H) = \text{Tr}(q^N) = \text{Tr} \left[ \lambda_+^N \begin{bmatrix} 0 & 0 \\ 0 & \lambda_-^N \end{bmatrix} \right] = \text{Tr} \left[ \lambda_+^N \begin{bmatrix} 0 & 0 \\ 0 & \lambda_-^N \end{bmatrix} \right] = \lambda_+^N + \lambda_-^N
\]

Eigenvalues of the 2x2 matrix, \( q \), are easily found:

\[
\det(q - \lambda I) = 0 \Rightarrow (\exp(-\beta m H + \beta J) - \lambda)(\exp(+\beta m H + \beta J) - \lambda) - \exp(-2\beta J) = 0 \Rightarrow \\
\Rightarrow \lambda^2 - \lambda \exp(\beta J)(\exp(-\beta m H) + \exp(+\beta m H)) + \exp(2\beta J) - \exp(-2\beta J) \Rightarrow \\
\Rightarrow \lambda_+ = \exp(\beta J) \cosh(\beta m H) \pm \sqrt{\exp(2\beta J) \cosh^2(\beta m H) - \left(\exp(2\beta J) - \exp(-2\beta J)\right)} \Rightarrow \\
\Rightarrow \lambda_- = \exp(\beta J) \left( \cosh(\beta m H) \pm \sqrt{\sinh^2(\beta m H) + \exp(-4\beta J)} \right)
\]

Since \( \lambda_+ > \lambda_- \), at the limit of large \( N \), only the largest eigenvalue contributes to the partition function:
\[ \ln Q = N \ln \lambda_+ \]  \hspace{1cm} (5)

For \( H = 0 \), we obtain from (5),
\[ Q = (\lambda_+)^N = \left( \exp(\beta J)\left[ (1 + \exp(-2\beta J)) \right] \right)^N = (2 \cosh(\beta J))^N \]

The average magnetization per spin is given by
\[
<s_1> = \frac{1}{N} \sum_{\text{all states}} s_i \exp(-\beta U_v) = \frac{1}{N} \frac{\partial \ln Q}{\partial (\beta mH)} = \frac{1}{\lambda_+} \left( \frac{\sinh(\beta mH) + \frac{\sinh(\beta mH) \cosh(\beta mH)}{\sqrt{\sinh^2(\beta mH) - \exp(-4\beta J)}}}{\sqrt{\sinh^2(\beta mH) - \exp(-4\beta J)}} \right)
\]

Since \( \sinh(0) = 0 \), \( <s_1> = 0 \) when \( H = 0 \), so that there is no spontaneous magnetization and no phase transition.

**Two-dimensional Ising model**

The exact solution, by Lars Onsager in the 1940's, of the two-dimensional Ising model is one of the greatest achievements of statistical mechanics. This is the only non-trivial model with a phase transition that can be solved exactly. The partition function (at zero field) is (“short-cut” proof takes about 20 typeset pages)

\[ Q(\beta, N, H = 0) = \left( 2 \cosh(\beta J) \exp(I) \right)^N, \]  \hspace{1cm} (6)

where
\[ I = \frac{1}{2\pi} \int_0^\pi \ln \left( \frac{1}{2} \left[ 1 + (1 - \kappa^2 \sin^2 \phi)^{1/2} \right] \right) d\phi \quad \text{where} \quad \kappa = \frac{2\sinh(2\beta J)}{\cosh^2(2\beta J)} \]

At all temperatures below \( T_c(2-D) = 2.269 J/k_B \) there are two symmetric non-zero solutions for the average magnetization \( <s_1> \) at zero field, \( H = 0 \). The critical temperature \( T_c \) is the solution to the equation \( \sinh(2J/k_BT_c) = 1 \). This can be shown by a differentiation of the full partition function in a manner similar to the one we used for the one-dimensional system, but this is too tedious to perform here. This simple system shows spontaneous symmetry breaking and a phase transition.

An important characteristic of the partition function for the two-dimensional Ising model is that the associated free energy is nonanalytic, that is, cannot be locally approximated by any polynomial of integer exponents. It turns out that this has profound implications about the behavior of the system at the vicinity of critical points that are universal in character. No approximate equation (e.g. van der Waals equation of state, or any other conceivable equation that is analytic) can reproduce this non-analytic behavior.

What is the reason that a model that undergoes a phase transition in two dimensions no longer does so in one dimension? The reasons are related to the energy cost of creating an interface in the system. For the one-dimensional Ising model, one of the two states of lowest energy is
and has an energy of $-NJ$ and a net magnetization per particle of $m$. This is also the most ordered state. The disordered state

\[
\uparrow \uparrow \uparrow \uparrow \ldots \uparrow \uparrow \uparrow \ldots \ \downarrow \downarrow \downarrow \ldots
\]

with magnetization zero has energy $(-N+2)J$, since we have introduced 2 unfavorable interactions. This small increase in energy, of the order of 1 part in $N$, is insufficient to stabilize the ordered state at any finite temperature. Therefore, at all temperatures, the spontaneous magnetization is zero. Actually, this conclusion is very general. It can be shown that no one-dimensional thermodynamic system with finite-range potentials can have a phase transition at a finite temperature.

In a two dimensional system, however, the excitation energy to a disordered state is much greater. For example, the energy for the configuration

\[
\ldots \uparrow \uparrow \uparrow \uparrow \ldots \uparrow \uparrow \uparrow \ldots
\]

\[
\ldots \downarrow \downarrow \downarrow \ldots \downarrow \downarrow \downarrow \ldots
\]

is $N^{1/2}$ parts out of $N$ higher than the energy of the perfectly ordered state. This difference turns out to be sufficient to stabilize the ordered state at sufficiently low temperatures.

**Three-dimensional Ising model**

The three dimensional Ising model has not been solved exactly to date. Simulations have established that the critical temperature in the three-dimensional Ising model is approximately

\[ T_c (3-D) \approx 4.4J/k_B \]

The range of the two-phase coexistence region increases relative to the two-dimensional case because the relative cost of creating an interface in the system is now still greater.

**Broken symmetry**

One feature of the phase transition of the Ising model should cause concern to all but the most casual observer. In the absence of a magnetic field, the model is symmetric with regard to the up and down directions of the spin. Indeed, the ground state with all spins aligned is two-fold degenerate since the total alignment can be either up or down. Therefore, in the absence of an external field, we should expect the overall magnetization

\[ < M > = Q^{-1} \sum_{\nu} \left( \sum_{i=1}^{N} m \nu_i \right) \exp(-\beta U_\nu) \] (7)
to be always zero, since symmetric configurations with cancelling up and down spins should be weighted equally in the ensemble average. However, this is not the case below the critical temperature. The transition from above the critical point (where the average magnetization is zero) to below the critical point (where the overall magnetization is not zero, even though there is no preferred spatial direction is called "broken symmetry"). The system "freezes" in one of the two possible states. To explain this, let us consider the figure on the following page. We plot the free energy, $A_M$, of a system at a given magnetization, obtained by Boltzmann-averaging over all states that have a given magnetization. Above the critical temperature, $A_M$ will be symmetric and the minimum occurs at $M = 0$. At the critical temperature, the minimum is very flat. Below the critical temperature, there will be two minima for $A_M$, at the values of the spontaneous magnetization. There is a large free-energy barrier that has to be overcome to convert the system from one state to the one with opposite magnetization. Which state a real macroscopic system will select is decided by random fluctuations as the system passes through the critical point.

**Mean field theory for the Ising model**

In general, the theoretical treatment of systems undergoing phase transitions requires the use of approximations. A simple approximation that has been widely used in statistical mechanics and thermodynamics is the so-called “mean field theory”. In mean field theory, we focus on a given particle (in the case of the Ising model a spin), and assume that the role of the neighboring particles is to form an average (magnetic) field which acts on the particle in the center. Although this might not be obvious, similar mean-field ideas are behind the large class of engineering equations for the properties of fluids that originated with the van der Waals equation of state. Let us write the energy per particle, $U_{\nu}$, by decomposing the total energy:

$$U_{\nu} = -\sum_{i=1}^{N} H m s_i - J \sum_{i=1, j>i}^{N-1} \sum_{\text{n.n. of } i}^{N} s_i s_j$$

The field felt by a particle because of the presence of the neighboring spins is

$$-\left(\frac{\partial U_{\nu}}{\partial s_i}\right) \equiv m H_i = m H + \sum_{j \text{ n.n. of } i} J s_j$$

The average field acting on a particle is $<m H_i> = m H + Jz <s_i>$ where $z$ is the number of nearest neighbors (coordination number) in the lattice. We now **assume** (and this is the basic assumption in mean field theory) that we can write the thermodynamics of the system by using the average field $<m H_i>$ instead of the actual field $m H_i$. In other words, we neglect the effects of
correlations of the spin in question with nearby spins, as well as the effect of fluctuations in the local field experienced by a spin. The canonical partition function for the system, as well as any average quantities can then be calculated analytically. For example, the average magnetization per spin is:

\[
<s_i> = \frac{\sum_i P_v s_i}{\sum_i P_v} = \frac{\exp(\beta <mH_i>)}{\exp(\beta <mH_i>)+\exp(-\beta <mH_i>)} = \tanh(\beta <mH_i>) \Rightarrow
\]

\[
<s_i> = \tanh(\beta mH + \beta Jz <s_i>)
\]

We thus have an explicit equation in \( <s_i> \). For \( H=0 \), we have a non-trivial solution to equation (8), provided that \( \beta Jz > 1 \Rightarrow kBT < J_z \). This can be seen in the figure to the left, in which \( \tanh(\beta Jz <s_i>) \) and \( <s_i> \) are plotted for \( \beta Jz > 1 \) and \( <1 \).

The critical temperature predicted by mean field theory is then

\[
k_B T_c/J = T_c^* = \frac{z}{2D}
\]

where \( D \) is the dimensionality (e.g. there are 4 nearest neighbors for the two-dimensional Ising model.) We can compare the results of the mean-field theory for the critical behavior of the Ising model with the exact results in the table below. As can be seen from the table, the relative error of the mean field theory decreases with the dimensionality. This is not accidental, since the main approximation in mean field theory is the neglect of fluctuations. As we have seen, it is fluctuations that destroy the long-range order in one dimension, but the energy cost of fluctuations becomes relatively higher in higher dimensions, and thus fluctuations play a less important role as the dimensionality is increased. It turns out that fluctuations play a negligible role for \( D=4 \) and above.

<table>
<thead>
<tr>
<th>Dimensionality</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_B T_c/J ) (Mean Field)</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>( k_B T_c/J ) (Exact)</td>
<td>No ( T_c )</td>
<td>2.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>