

What are the properties of the Phase Transition?

I- Power-Law: Denote the critical temperature by T_c and introduce the quantity $t = (T - T_c)/T_c$ and as $T \rightarrow T_c$ and $B = 0$ one finds:

$$\text{Heat Capacity: } C \sim |t|^{-\alpha},$$

$$\text{Magnetisation: } m \sim |t|^\beta,$$

$$\text{Susceptibility: } \chi \sim |t|^{-\gamma},$$

$$\text{Correlation Length: } \xi \sim |t|^{-\nu},$$

In the table values of the critical exponents in some systems are listed. The dimension of the order parameter n is the number of its independent components.

Table. Examples of critical exponents. d and n are dimensions of space and order parameter, respectively.

System	d	n	α, α'	β	γ, γ'	δ	ν
Landau theory ‡			0^*	$\frac{1}{2}$	1	3	$\frac{1}{2}$
Ising model $d = 2$ ‡	2	1	0^\dagger	$\frac{1}{8}$	$\frac{7}{4}$	15	1
Ising model $d = 3$	3	1	0.11	0.325	1.24	4.82	0.63
Heisenberg model	3	3	0	0.339	1.322		0.667
Real ferromagnet	3	3	0	0.34	1.32	4.2	0.6
Liquid-gas	3	1	0.11	0.32	1.24	4.82	0.62
Λ transition of ^4He	3	2	-0.016				0.67

‡ exact; * discontinuity; † logarithmic singularity

II- Order Parameter:

III- Symmetry breaking:

IV- Scale Invariance:

V- Universality:

VI- Critical Dimension:

Comment about the difference between the first and second order phase transition:

☞ The second kind of PT is continuous in the sense that the state of the body changes continuously. Although the symmetry changes discontinuously at the transition point, at each instant the body belongs to one of the two phases. In another words, the states of the two phases are the same.

☞ The first kind of PT, the bodies in two different states are in equilibrium.

What is the meaning of the cooperative phenomena?

☞ The term **cooperative phenomenon** is adopted because of the fact that these phenomena are caused by interaction of a great number of elementary particles such as electron, atoms, etc. These interactions extend over distances which are enormously greater than the usual action radii of the elementary particles.

☞ **Certain subsystems, like spins or atoms, cooperate due to exchange interactions to form units below a certain critical point.**

COOPERATIVE PHENOMENA: ISING MODEL*

In this Section, we are discussing various approaches to obtain a mean-field solution to the Ising model. In fact, several of the approaches will yield exactly identical results. The reason they are presented is that they highlight different ways of carrying out the approximation(s) that are commonly referred to as “mean-field approximations”. Essentially, they differ by whether:

- 1- neglects spin fluctuations around the mean or
- 2- Considers spins to behave statistically independently and by which part of the system one treats exactly (Bethe-Peierls mean-field theory).

1- Phase transition of the second kind

Consider ferromagnetic substances, like iron and nickel. Some of the spins of the atoms become spontaneously (without any external field) polarized in the same direction, below the Curie temperature T_c (the critical temperature). This creates a macroscopic magnetic field. As temperature is raised, the thermal energy makes it possible for some of the aligned spins to flip over. This tends to destroy the initial ordered state. For $T > T_c$, the spins get oriented at random and the spontaneous magnetization vanishes. As T_c is approached, from both sides, the heat capacity of the metal approaches ∞ . The transition from the non-ferromagnetic state to the ferromagnetic state is called a *phase transition of the second kind*. It is associated with some kind of change in symmetry of the lattice. For example, in ferromagnetism the symmetry of spins is involved. The energy levels of the system are given by

$$E\{\sigma_i\} = -\sum_{i,j}^N J_{ij}\sigma_i\sigma_j - h\sum_i^N \sigma_i \quad \begin{array}{cccccccc} \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet \\ \dots & i-1 & i & i+1 & \dots & & & \end{array} \quad (1)$$

where, on each lattice site i ,

- i- the spin quantum number σ_i is +1 or -1,
- ii- J_{ij} is the interaction energy (the spin-spin couplings),
- iii- $h = \mu_B H$ is the interaction energy associated with the external magnetic field H , and
- iv- μ_B is the magnetic moment associated with the spin. For spontaneous configuration, $h = 0$.

The change of symmetry can also occur due to the change in the ordering of the crystal. For example, in an alloy AB the atoms may be substituted for one another on a set of given lattice sites. Then we can say that a $\sigma_i = +1$ for an atom A on the site i , and $\sigma_i = -1$ for an atom B on that site. At low temperatures the alloy AB is ordered. Above a transition temperature it becomes disordered.

The difference between the non-ferromagnetic-ferromagnetic transition and the order-disorder transition is that in the former case ‘up’ and ‘down’ spins can be transformed freely into one another, while in the latter case the total number of A type and B type atoms is fixed. However similar theoretical results hold in both the cases.

***The one-dimensional Ising model:** is a chain of N spins, each spin interaction with its neighbor and with external magnetic field \bar{B} .

2- ISING MODEL

The theory of cooperative phenomena is very complicated; especially when all interactions are included and three-dimensional systems are considered.

We assume that in (1) the ε_{ij} acts only between nearest neighbors in the lattice. This is the basic assumption of the *Ising model*. Then (1) is written as

$$E\{\sigma_i\} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \quad (2)$$

where $\langle i, j \rangle$ means that the sum is over pairs of nearest neighbors, and the interactions are **isotropic**, that is, all J_{ij} have the same value J . For $J > 0$, the neighboring spins tend to be parallel and ferromagnetism is possible. The spontaneous configuration of least energy is the **completely polarized (ordered)** configuration in which all the Ising spins are oriented in the same direction. This configuration is attained at $T = 0$. For $J < 0$, the neighboring spins tend to be antiparallel and **antiferromagnetism** results. We will assume $J > 0$.

In (2) no distinction is made between $\langle i, j \rangle$ and $\langle j, i \rangle$. The sum over $\langle i, j \rangle$ has $nN/2$ terms, where

- i- n is the number of nearest neighbors of a site (**coordination number of the lattice**) and
- ii- N the number of spins, for example:

$$n = \begin{cases} 2 & \text{in one dimension;} \\ 4 & \text{in two dimensions (square lattice);} \\ 6 & \text{in three dimensions (simple cubic lattice);} \\ 8 & \text{in three dimensions (body-centered cubic lattice);} \\ 12 & \text{in three dimensions (face-centered cubic lattice).} \end{cases}$$

On a hypercubic lattice in d dimensions has $n = 2d$ nearest neighbors

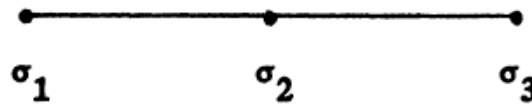
The thermodynamic quantities require the evaluation of the partition function

$$Z(N, h, T) = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} e^{-\beta E\{\sigma_i\}} = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} e^{\beta \left[J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \right]} \quad (3)$$

where $\beta = 1/k_B T$ and the sum is taken over all the 2^N possible combinations of the N spins.

It is extremely difficult to calculate (3). Several approximate methods have been developed for this. The Weiss theory and Bragg-Williams (BW) approximation are the simplest. More approximations are elaborate, such as: Fowler-Guggenheim approximation and Kirkwood method.

Example: Calculate the partition function Z for the following configuration:



with the Hamiltonian:

$$H = J(\sigma_1\sigma_2 + \sigma_2\sigma_3) + h(\sigma_1 + \sigma_2 + \sigma_3),$$

Answer: To simplify our problem, let us take $h=0$. Try to do the following tree-diagram.

$E = \sigma_1\sigma_2 + \sigma_2\sigma_3$

Configuration $\{\sigma_1, \sigma_2, \sigma_3\}$	Energy E
$\{1, 1, 1\}$	2
$\{1, 1, -1\}$	0
$\{1, -1, 1\}$	-2
$\{1, -1, -1\}$	0
$\{-1, 1, 1\}$	0
$\{-1, 1, -1\}$	-2
$\{-1, -1, 1\}$	0
$\{-1, -1, -1\}$	2

$$Z_3 = 4e^0 + 2e^{-2\beta E} + 2e^{2\beta E}$$

$$= 2^3 \cosh^2 k, \quad k = \beta E$$

The partition function

$$Z = \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} e^{-\beta H(\sigma_i)} = \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} e^{-\beta [J(\sigma_1\sigma_2 + \sigma_2\sigma_3)]} = \sum e^{-K(\sigma_1, \sigma_2, \sigma_3)}, \quad K = \beta J$$

$$= e^{-K(1,1,1)} + e^{-K(1,1,-1)} + e^{-K(1,-1,1)} + e^{-K(-1,1,1)} + e^{-K(1,-1,-1)} + e^{-K(-1,1,-1)} + e^{-K(-1,-1,1)} + e^{-K(-1,-1,-1)}$$

$$= e^{-K(1+1)} + e^{-K(1-1)} + e^{-K(-1-1)} + e^{-K(-1+1)} + e^{-K(-1+1)} + e^{-K(-1-1)} + e^{-K(1-1)} + e^{-K(1+1)}$$

$$= e^{-2K} + 1 + e^{2K} + 1 + 1 + e^{2K} + 1 + e^{-2K}$$

$$= 4 + 2e^{-2K} + 2e^{2K}$$

This could be simplified to:

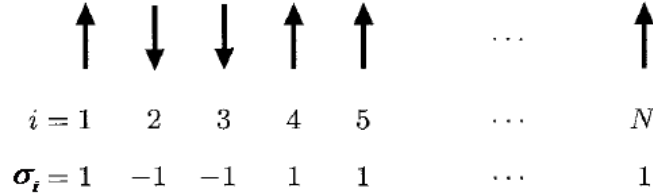
$$Z = 2^3 \cosh^2(K)$$

Check

$$\text{In[4]:= } y = 2^3 \left(\frac{e^K + e^{-K}}{2} \right)^2 \quad // \text{ ExpandAll}$$

$$\text{Out[4]= } 4 + 2 e^{-2K} + 2 e^{2K}$$

3- **Exact one-dimensional Ising (open ended chain):** The one-dimensional Ising model consists of a chain of N spins, each spin interacting only with its two nearest neighbors.



A one-dimensional Ising model with N elementary dipoles.

The Hamiltonian takes the form:

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} = -J [\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \dots + \sigma_{N-1} \sigma_N] \quad J > 0$$

The partition function is given by

$$Z_N = \sum_{\{\sigma_i = \pm 1\}} e^{\beta J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}} = \sum_{\sigma_1 = \pm 1} \sum_{\sigma_2 = \pm 1} \dots \sum_{\sigma_N = \pm 1} e^{K \sigma_1 \sigma_2} e^{K \sigma_2 \sigma_3} \dots e^{K \sigma_{N-1} \sigma_N}, \quad (1)$$

Where $K = \beta J$. Notice that the final sum, over, gives:

$$\sum_{\sigma_N = \pm 1} e^{K \sigma_{N-1} \sigma_N} = 2 \cosh(\sigma_{N-1} K) \quad (2)$$

Regardless of whether σ_{N-1} is $+1$ or -1 . With this sum done, the sum over σ_{N-1} can now be evaluated in the same way, then the sum over σ_{N-2} , and so on down to σ_2 , yielding $N - 1$ factors of $2 \cosh K$. The remaining sum over $\sum_{\sigma_1 = \pm 1} [2^{N-1} \cosh(K)^{N-1}] = 2 [2^{N-1} \cosh(K)^{N-1}]$, gives another factor

of 2. Hence, the partition function becomes

$$Z_N = 2^N (\cosh K)^{N-1} \approx (2 \cosh K)^N \quad (3)$$

where the last approximation is valid when N is large.

The internal energy and the specific heat:

The free energy per spin is given by:

$$F = -k_B T \ln Z_N = -N k_B T \ln \{2 \cosh(K)\},$$

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -NJ \tanh(K) = \begin{cases} 0 & K \rightarrow 0, T \rightarrow \infty \\ -NJ & K \rightarrow \infty, T \rightarrow 0 \end{cases} \quad (4)$$

which goes to $-NJ$ as $T \rightarrow 0$ and to 0 as $T \rightarrow \infty$. Therefore the dipoles must be randomly aligned at high temperature (so that half the neighboring pairs are parallel and half are antiparallel), but lined **up** parallel to each other at $T = 0$ (achieving the minimum possible energy).

The heat capacity C_V is

$$C_V = \frac{\partial U}{\partial T} = k_B K^2 \cosh^2(K) \quad (5)$$

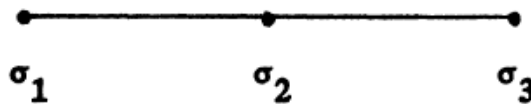
The energy and heat capacity are smoothly varying, always finite functions of temperature, exhibiting no phase transition.

Notice that,

- both Z and U for this system are exactly the same as for a two-state paramagnet, if you replace the magnetic interaction energy μH with the neighbor-neighbor interaction energy J . Here, however, the dipoles like to line up with each other, instead of with an external field.
- while this system *does* become more ordered (less random) as its temperature decreases, the order sets in gradually. The behavior of U as a function of T is perfectly smooth, with no abrupt transition at a nonzero critical temperature. Apparently, the one-dimensional Ising model does *not* behave like a real three-dimensional ferromagnet in this crucial respect. Its tendency to magnetize is not great enough, because each dipole has only two nearest neighbors.

So our next step should be to consider Ising models in higher dimensions. Unfortunately, though, such models are *much* harder to solve. The two-dimensional Ising model on a square lattice was first solved in the 1940s by Lars Onsager. Onsager evaluated the exact partition function as $N \rightarrow \infty$ in closed form, and found that this model *does* have a critical temperature, just like a real ferromagnet. Because Onsager's solution is extremely difficult mathematically, we will not attempt to present it in this lecture. In any case, nobody has ever found an exact solution to the three-dimensional Ising model. The most fruitful approach from here, therefore, is to give up on exact solutions and rely instead on approximations.

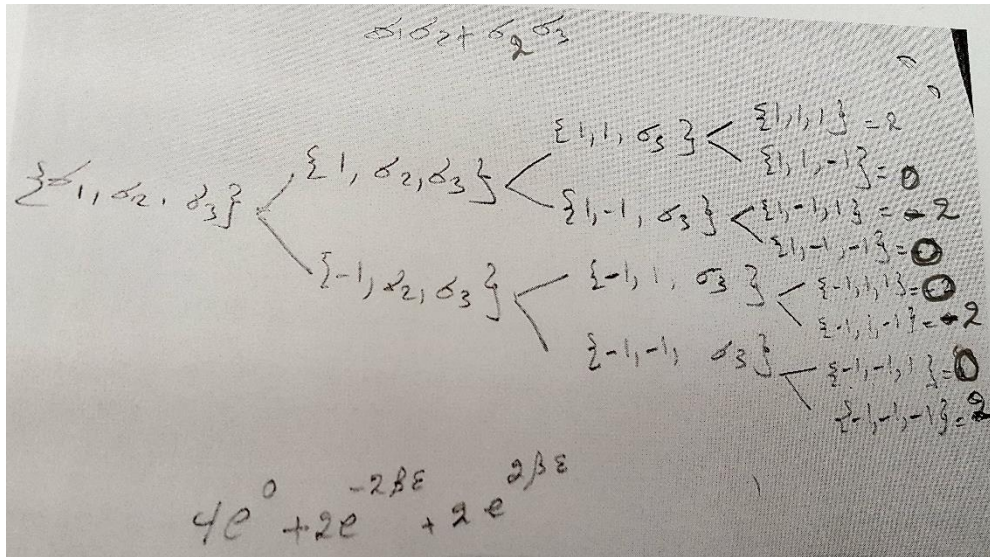
Example: Calculate the partition function Z for the following configuration:



with the Hamiltonian:

$$H = J(\sigma_1\sigma_2 + \sigma_2\sigma_3) + h(\sigma_1 + \sigma_2 + \sigma_3),$$

Answer: To simplify our problem, let us take $h = 0$. Try to do the following tree-diagram.



The partition function

$$\begin{aligned}
 Z &= \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} e^{-\beta H(\sigma_i)} = \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} e^{-\beta [J(\sigma_1 \sigma_2 + \sigma_2 \sigma_3)]} = \sum e^{-K(\sigma_1, \sigma_2, \sigma_3)}, \quad K = \beta J \\
 &= e^{-K(1,1,1)} + e^{-K(1,1,-1)} + e^{-K(1,-1,1)} + e^{-K(-1,1,1)} + e^{-K(1,-1,-1)} + e^{-K(-1,1,-1)} + e^{-K(-1,-1,1)} + e^{-K(-1,-1,-1)} \\
 &= e^{-K(1+1)} + e^{-K(1-1)} + e^{-K(-1-1)} + e^{-K(-1+1)} + e^{-K(-1+1)} + e^{-K(-1-1)} + e^{-K(1-1)} + e^{-K(1+1)} \\
 &= e^{-2K} + 1 + e^{2K} + 1 + 1 + e^{2K} + 1 + e^{-2K} \\
 &= 4 + 2e^{-2K} + 2e^{2K}
 \end{aligned}$$

This could be simplified to:

$$Z = 2^3 \cosh^2(K)$$

Check

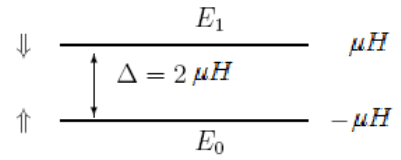
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In[4]:= y = 2^3 ((e^K + e^-K) / 2)^2 // ExpandAll
Out[4]= 4 + 2 e^-2 K + 2 e^2 K
    
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Appendix

A spin 1/2 atoms in a uniform magnetic field

Assume N -monatomic Boltzmann ideal gas of spin 1/2 atoms in a uniform magnetic field, in addition to its usual kinetic energy, a magnetic energy of $\varepsilon_1 = -\varepsilon$ and $\varepsilon_2 = \varepsilon$ per atom, $\varepsilon = \mu H$, where μ is the magnetic moment. (It is assumed that the gas is so dilute that the interaction of magnetic moments may be neglected.)



a- Discuss qualitatively the energy of such an atom?

Answer: There are two possible states, and they are:

state	condition	Magnetic energy	probability
(+)	$\mu \uparrow H \uparrow$	$\varepsilon_+ = -\mu H$	$P_+ = C e^{\beta \mu H}$
(-)	$\mu \downarrow H \uparrow$	$\varepsilon_- = \mu H$	$P_- = C e^{-\beta \mu H}$

ε_+ is lower energy \Rightarrow atom is more likely to be found
 ε_- is higher energy \Rightarrow atom is less likely to be found

b- Calculate the partition function of the system.

$$z = e^{-\beta \varepsilon_1} + e^{\beta \varepsilon_2} = e^{-\eta} + e^{\eta} = 2 \cosh(\eta), \quad \eta = \beta \varepsilon$$

$$\bar{E} = \frac{1}{z} \left(\varepsilon_1 e^{-\beta \varepsilon_1} + \varepsilon_2 e^{\beta \varepsilon_2} \right) = \frac{\varepsilon e^{-\eta} - \varepsilon e^{\eta}}{2 \cosh(\eta)} = -\varepsilon \tanh(\eta)$$

and the total energy $U = N \bar{E} = -N \varepsilon \tanh(\eta)$.

In summary:

Quantity	Formula
Partition function	$z = 2 \cosh(\eta) \Rightarrow Z = z^N = 2^N \cosh^N(\eta)$
Helmholtz free energy	$F = -k_B T \ln(Z) = -N k_B T \ln \{ 2 \cosh(\eta) \}$
Entropy	$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = N k_B \ln [2 \cosh(\eta) - \eta \tanh(\eta)]$
Internal energy	$U = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V, N} = -N \mu H \tanh(\eta)$