Understanding phase transition in statistical mechanics

Link: https://www.youtube.com/watch?v=xzR7J0uqStM

AMA4004: Statistical mechanics

Core Question: The nature of Phase Transitions.

Phase transitions in statistical mechanics and the thermodynamic limit

In order to figure out the nature of phase transitions, we need the 2-D Ising Model.

(Partition function for this model is very complicated)

In this case, we are going to focus on the 1D Ising Model.

Phase transitions in classical thermodynamics a reminder

1st order phase transition if this is discontinuous

$$F(s+\delta s) = F(s) + \frac{\mathrm{d}F}{\mathrm{d}s}\delta s + \frac{1}{2!}\frac{\mathrm{d}^2 F}{\mathrm{d}s^2}(\delta s)^2 + \dots$$

Infinite at phase boundary. Hence, series does not converge

When a system undergoes a phase transition, some thermodynamic variable generally changes discontinuously. Furthermore, we also noted from classical thermodynamics that the thermodynamic variables are always related to the derivatives of some thermodynamic potential and that as such the thermodynamic potential must change non-analytically as one crosses the phase boundary. In other words, if moving from s to s+δs, the system crosses a phase boundary, the thermodynamic potential cannot be calculated using Taylor series shown here. As the derivatives and hence the coefficients in this series are equal to infinity.

What is important to understand is that the existence of phase transition implies that the thermodynamic potential cannot be expressed as an analytic function of the underlying thermodynamic variables.

Phase transitions in classical thermodynamics a reminder

1st order phase transition if this is discontinuous

continuous phase transition if this or higher terms are discontinuous

$$F(s+\delta s) = F(s) + \frac{\mathrm{d}F}{\mathrm{d}s}\delta s + \frac{1}{2!}\frac{\mathrm{d}^2 F}{\mathrm{d}s^2}(\delta s)^2 + \dots$$

A problem for statistical mechanics

=> Big Challenge for Early-day Thermodynamics

On the other hand,

Thermodynamic potential is everywhere analytic. There are no discontinuities and as such no phase transitions

Thermodynamic potentials

$$F = -k_B T \ln Z$$

free energy

Z: canonical partition function

Analytic on its domain

Finite sum of analytic functions is analytic

$$Z = e^{\Psi} = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}$$

A function that is analytic for all values of beta

We should remember that the thermodynamic potential is related to the logarithm of the partition function.

So here we got our big problems! In the previous 2 slides, we said that thermodynamic potential cannot be expressed as an analytic function of the underlying thermodynamic variables. However, on the other hand, we concluded from this slide (Reason is shown in the bottom part of the slide) that thermodynamic potential should be analytic everywhere.

Actually, there is **NO way** of getting around this logic whenever we have a system containing a **Finite number of atoms**. The number of micro-states will be finite. And as such the thermodynamic potential will be an analytic function of the thermodynamic variables. Finite size systems do NOT undergo phase transitions. The solution to this dilemma comes when you recognizes that the real systems that we want to study contain a lot of atoms that we can essentially assume that there are an **Infinite number of atoms**. The fact that there are infinite number of atoms ensures that the finite sum over micro-states in the partition function **becomes an infinite sum over micro-states**. If we take a sum of an infinite number of analytic functions, the function that emerges from the summation **can change Non-analytically**.

The thermodynamic limit

Classical thermodynamics Only emerges from statistical mechanics when we consider systems with an infinite number of atoms.

All systems with fewer numbers of atoms exhibit fluctuations in the values of the quantities that are calculated by performing ensemble averages.

This limit, as we make the number of atoms in the system **infinite**, is known as the *thermodynamic limit*.

In this limit, all the fluctuations in the thermodynamic quantities disappear.

Question will also ask: How to calculate the value of some extensive thermodynamic quantity in the thermodynamic limit.

1st, it is not asking us to calculate the total value of the extensive quantity for a system containing n particles. Such a request makes no sense as the value of an extensive thermodynamic variable will in general depend on the number of particles in the system. Hence in a system containing an infinite number of particles, the value of any extensive variable will be infinite. When you are thus asked to calculate the value of the energy in the thermodynamic limit, **what we are being asked to calculate is the average energy per site in the limit as *n* tends to infinity**. In other words, what we are being asked to calculate is the value of the limit of $\langle E\rangle(n) / n$ as n tends to infinity. See the slide below.

The thermodynamic limit continued

Ensemble average for system containing n sites/atoms/molecules

$$\langle E\rangle_{TL} = \lim_{n\to\infty} \frac{\langle E\rangle(n)}{n} = -\lim_{n\to\infty} \frac{1}{n}\left(\frac{\partial[\ln Z(n)]}{\partial\beta}\right)$$

Average energy (per site/atom/molecule) in thermodynamic limit

Remember, we can get the energy as a function of *n* by taking minus of the first derivative of the partition function with respect to β.

A first (easy) example

A system composed of non-interacting spins sitting on a lattice and interacting with a magnetic field

$$Z = 2^N \cosh^N(\beta\mu H)$$

$$\langle E \rangle = -N\mu H \tanh(\beta\mu H)$$

$$\langle E \rangle_{TL} = -\lim_{N\to\infty} \frac{1}{N} N\mu H \tanh(\beta\mu H) = -\mu H \tanh(\beta\mu H)$$

The average energy per spin.

This is the energy per spin

As for our original question about the nature of phase transitions, in this expression (in the bottom of the left picture), *<E> is an analytic function of β so we have admitted no discontinuities*, and as would be expected, this model system thus undergoes NO phase transitions at any temperature.

To have phase transitions, we must have interactions between particles. In this case, it's reasonable to look at the system of interacting particles we have examined before --- Ising model.

See below.

A second (more complicated) example - The Ising Model

tends to be 0.

$$Z_c = \lambda_1^N + \lambda_2^N = \lambda_1^N \left[1 + \cancel{\left(\frac{\lambda_2}{\lambda_1} \right)}^N \right]$$

Eigenvalues of transfer matrix : A

Theorem (Perron-Frobeius theorem)

Any square matrix with all positive real elements:

- *is diagonalizable :* $\mathbf{A} = \mathbf{V}\Lambda\mathbf{V}^{-1}$
- *has a unique largest eigenvalue* $\lambda_1 > \lambda_2 > \lambda_3 > \cdots > \lambda_n$

From the previous videos, they show that the partition function for the Ising model could be written as the **sum of powers of the eigenvalues** of the so-called **Transfer Matrix**.

Thermodynamic limit for Ising model

$$F(N) = -k_B T \log Z(N)$$ **In general**

For 1D, closed Ising model $Z(N) = \lambda_1^N \left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right]$

$$\lim_{N\to\infty} \frac{F(N)}{N} = -\lim_{N\to\infty} \frac{k_B T}{\cancel{N}} \left\{\cancel{N} \log \lambda_1 + \cancel{\log\left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right]}\right\}$$

0

0

$$\lim_{N\to\infty} \frac{F(N)}{N} = -k_B T \log \lambda_1$$

Free energy per site in the thermodynamic limit

Inserting our solution

The largest one?

The principle eigenvalue of transfer matrix A is λ_1.

$$\lim_{N\to\infty} \frac{F(N)}{N} = -k_B T \log \lambda_1$$

$$\lambda_1 = e^{\beta J} \cosh(\beta H) + \sqrt{e^{2\beta J} \sinh^2(\beta H) + e^{-2\beta J}}$$

Inserting our solution

$$\lim_{N\to\infty} \frac{F(N)}{N} = -k_B T \log \lambda_1$$

$$\lambda_1 = e^{\beta J} \left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}} \right]$$

Inserting our solution

$$\lim_{N\to\infty} \frac{F(N)}{N} = -k_B T \log \lambda_1$$

$$\lambda_1 = e^{\beta J} \left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}} \right]$$

$$\lim_{N\to\infty} \frac{F(N)}{N} = -J - k_B T \ln \left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}} \right]$$

$$\langle M \rangle = \overset{k_B T}{\cancel{\frac{1}{\beta}}} \left(\frac{\partial \ln Z}{\partial H} \right)_T \qquad \left(\frac{\partial \ln Z}{\partial H} \right)_T = \frac{\partial \ln Z}{\partial(\beta H)} \overset{\beta}{\cancel{\frac{\partial(\beta H)}{\partial H}}}$$

Inserting our solution

$$\lim_{N\to\infty} \frac{F(N)}{N} = -k_B T \log \lambda_1$$

$$\lambda_1 = e^{\beta J}\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right]$$

$$\lim_{N\to\infty} \frac{F(N)}{N} = -J - k_B T \ln\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right]$$

Magnetization (average)

$$\langle M \rangle = -\left(\frac{\partial F}{\partial H}\right)_T \qquad \left(\frac{\partial \ln Z}{\partial H}\right)_T = \frac{\partial \ln Z}{\partial(\beta H)} \frac{\partial(\beta \cancel{H})}{\partial H}$$

β

Average magnetization

$$= \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial H}\right)_T \overset{\beta = \frac{1}{k_B T}}{=\!=} k_B T \left(\frac{\partial \ln Z}{\partial H}\right)_T$$

since β is NOT dependent on H.

Now we come back to phase transitions. Remember, **when a system crosses a phase boundary**, the **thermodynamic potential changes Non-analytically**. Then as such, **one of the thermodynamic potential must diverge and become infinity (or minus infinity)**. We thus must demonstrate that, the one of the derivatives of the thermodynamic potential we have calculated is **infinite** at some particular value of β.

Showing that this is the case would prove that the system undergoes a phase transition.

(By the way, **taking suitable derivatives of the logarithm of partition function is equivalent to the process of taking derivatives of the thermodynamic potential**).

Inserting our solution

$$\lim_{N\to\infty} \frac{F(N)}{N} = -k_B T \log \lambda_1$$

$$\lambda_1 = e^{\beta J}\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right]$$

$$\lim_{N\to\infty} \frac{F(N)}{N} = -J - k_B T \ln\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right]$$

$$\langle M \rangle = -\left(\frac{\partial F}{\partial H}\right)_T \qquad \left(\frac{\partial \ln Z}{\partial H}\right)_T = \frac{\partial \ln Z}{\partial(\beta H)} \frac{\partial(\beta \cancel{H})}{\partial H}$$

β

$$\langle M \rangle = \frac{\sinh(\beta H)\left[1 + \frac{\cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}}\right]}{\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}}$$

Inserting our solution

$$\lim_{N\to\infty}\frac{F(N)}{N} = -k_B T \log \lambda_1$$

$$\lambda_1 = e^{\beta J}\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right]$$

$$\lim_{N\to\infty}\frac{F(N)}{N} = -J - k_B T \ln\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right]$$

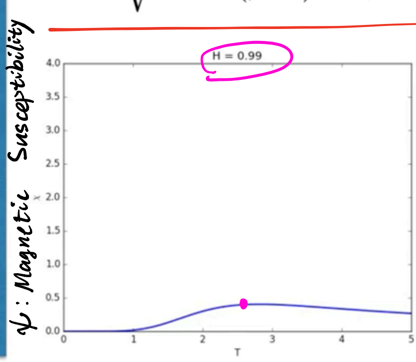
$$\langle M\rangle = -\left(\frac{\partial F}{\partial H}\right)_T \qquad \left(\frac{\partial \ln Z}{\partial H}\right)_T = \frac{\partial \ln Z}{\partial(\beta H)}\cancelto{\beta}{\frac{\partial(\beta H)}{\partial H}}$$

$$\langle M\rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}}$$

The susceptibility

$$\langle M\rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} \qquad \chi = \left(\frac{\partial\langle M\rangle}{\partial H}\right)_T$$

$$\chi = \frac{\beta\cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} - \frac{\beta\cosh(\beta H)\sinh^2(\beta H)}{(\sinh^2(\beta H) + e^{-4\beta J})^{\frac{3}{2}}}$$

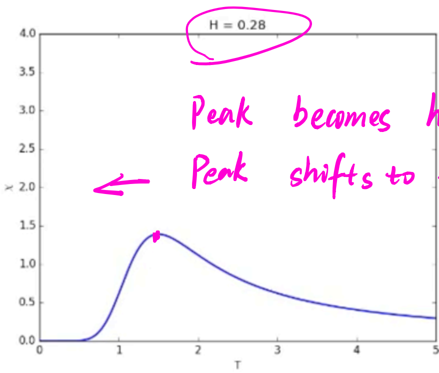


We can continue on this expression of <M> and arrive at an expression for the magnetic susceptibility in the thermodynamic limit by taking the derivative of it with respect to H one more time.

The susceptibility

$$\langle M \rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} \qquad \chi = \left(\frac{\partial \langle M \rangle}{\partial H}\right)_T$$

$$\chi = \frac{\beta \cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} - \frac{\beta \cosh(\beta H) \sinh^2(\beta H)}{(\sinh^2(\beta H) + e^{-4\beta J})^{\frac{3}{2}}}$$

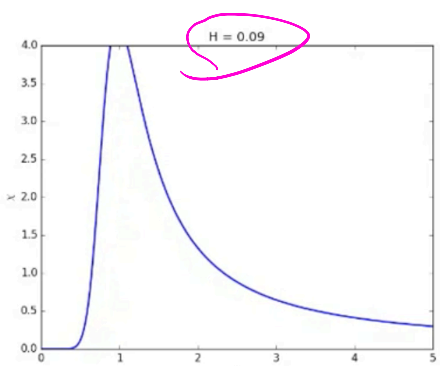


Peak becomes higher
Peak shifts to the left } for H = 0.28 from H=0.99

The susceptibility

$$\langle M \rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} \qquad \chi = \left(\frac{\partial \langle M \rangle}{\partial H}\right)_T$$

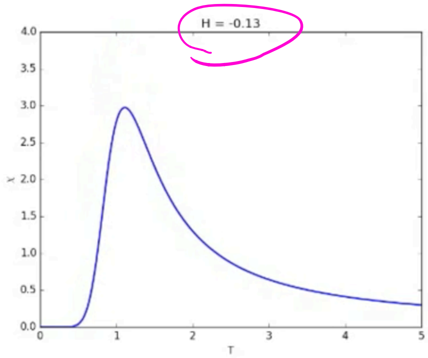
$$\chi = \frac{\beta \cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} - \frac{\beta \cosh(\beta H) \sinh^2(\beta H)}{(\sinh^2(\beta H) + e^{-4\beta J})^{\frac{3}{2}}}$$



The susceptibility

$$\langle M\rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} \qquad \chi = \left(\frac{\partial\langle M\rangle}{\partial H}\right)_T$$

$$\chi = \frac{\beta\cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} - \frac{\beta\cosh(\beta H)\sinh^2(\beta H)}{(\sinh^2(\beta H) + e^{-4\beta J})^{\frac{3}{2}}}$$

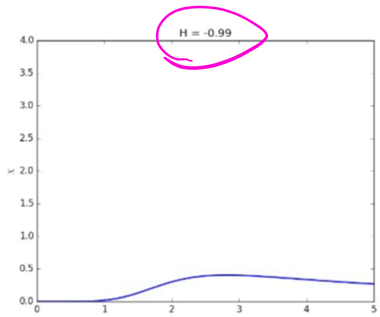


The susceptibility

$$\langle M\rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} \qquad \chi = \left(\frac{\partial\langle M\rangle}{\partial H}\right)_T$$

$$H = 0$$

$$\chi = \frac{\beta\cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} - \frac{\beta\cosh(\beta H)\cancelto{0}{\sinh^2(\beta H)}}{(\sinh^2(\beta H) + e^{-4\beta J})^{\frac{3}{2}}}$$



The larger the |H| value, the peak becomes lower and shifts to the right. The lower the |H| value, the peak becomes higher and shifts to the left.

In fact, it looks as if the magnetic susceptibility diverges when H=0. And there, thus, must be something resembling a phase transition when H=0 and T=0.

Let's confirm this to ourselves by setting H=0 in our expression here. In this case, the expression simplifies considerably.

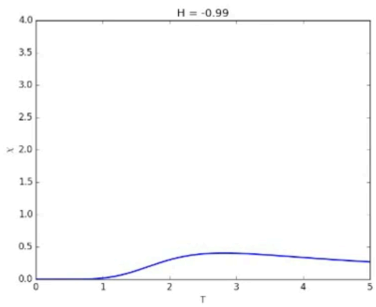
See next picture.

The susceptibility

$$\langle M \rangle = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} \qquad \chi = \left(\frac{\partial \langle M \rangle}{\partial H} \right)_T$$

$$H = 0$$

$$\chi = \frac{\overset{\to 1}{\beta \cosh(\beta H)}}{\sqrt{\overset{\to 0}{\sinh^2(\beta H)} + e^{-4\beta J}}} - \overset{\to 0}{\cancel{\frac{\beta \cosh(\beta H) \sinh^2(\beta H)}{(\sinh^2(\beta H) + e^{-4\beta J})^{\frac{3}{2}}}}}$$



$$\overset{\to \infty}{\chi} = \beta e^{2\beta J}$$

As $T \to 0 \quad \beta \to \infty$

$\chi \to \infty$

In this case, the magnetic susceptibility simplifies to the expression in the bottom of the left figure.

This expression shows that the **magnetic susceptibility does indeed diverge as T tends to 0**.

The key points

Phase transitions occur at points where a thermodynamic potential changes non-analytically.

logarithm of partition function

There are no phase transitions in finite sized systems

Thermodynamic limit: $$F_{TL} = -k_B T \lim_{N \to \infty} \frac{\ln Z(N)}{N}$$

Free energy per site/atom/molecule

Derivatives of F_{TL} can diverge. **Phase transitions can therefore occur in systems with infinite size.**