Phase transitions

Lee-Yang theory

A phase transition happens at an exactly determined temperature which depends on the density, pressure and other intensive properties of the system. Since the state variables behave differently on each side of the transition point the partition sum must be non analytic at the transition point. The energy spectrum $\{E_n\}$ of finite number particles in a finite volume is discrete so the state sum

$$Z_N = \sum_n e^{-\beta E_n}$$

is a positive and, on the positive real axis $\beta > 0$ and in the neighbourhood of it, an analytic function of its argument β. In this kind of a system there can be no sharp phase transition point. Phase transition can thus occur only in the *thernodynamic limit* where

$$V \to \infty \text{ and } N \to \infty \text{ but } \frac{N}{V} \to \rho = \text{constant}.$$

The model by Lee and Yang explains how the analytic state sum develops toward non-analytic form when we approach the thermodynamic limit. We consider a system of hard spheres confined in the volume V. Let V_0 be the volume of one sphere. Then

$$N_m \approx \frac{V}{V_0}$$

is the maximum number of spheres. The state sum

$$Z_G(T,V,\mu) = \sum_{N=0}^{N_m} z^N Z(T,V,N)$$

is a polynomial of degree N_m of the fugacity

$$z = e^{\beta\mu}.$$

We use the shorthand notation

$$Z(z) = Z_G(T,V,\mu).$$

Let $\xi_1, \xi_2, \ldots, \xi_{N_m}$ be the zeros of the polynomial $Z(z)$. Since $Z(0) = 1$, we have, according to the fundamental theorem of algebra,

$$Z(z) = \prod_{n=1}^{N_m} \left(1 - \frac{z}{\xi_n}\right).$$

Because $Z(z)$ is real when z is real the zeros must occur as conjugate pairs, i.e. for every root ξ_n there must be the root ξ_n^*.

When we approach the thermodynamic limit the number of zeros of the partition function $Z(z)$ tends to infinity. One can assume that the real axis remains clean of the zeros excluding, maybe, some separate points. In the vicinity of those points the density of zeros is very high and the function $Z(z)$ non-analytic.

Let's suppose that the zeroes of the partition function $Z(z)$ close to the real axis condense on the curve C. The function $Z(z)$ is analytic on both sides of the curve but its analytic properties are different on different sides. When the zeros lying on the curve C condense to continuum we can write

$$\begin{aligned} \ln Z(z) &= \sum_n \ln\left(1 - \frac{z}{\xi_n}\right) \\ &\to \int_C d\xi\, w(\xi) \ln\left(1 - \frac{z}{\xi}\right). \end{aligned}$$

Here

$$dn = d\xi\, w(\xi)$$

is the number of zeroes on the arc $d\xi$ of the curve. The density $w(\xi)$ is $\propto N_m \propto V$ and so an extensive quantity. From this expression for the partition function one can clearly see that $Z(z)$ is not analytic if z happens to lie on the curve formed by the zeroes.

As an example we consider the state sum which in the vicinity of z_0 behaves like

$$Z(z) \approx e^{\Phi(z)} \cosh\left[\frac{\pi}{b}(z - z_0)\right],$$

where $\Phi(z)$ is analytic. The zeroes of the state sum are then at the points

$$\xi_n = z_0 + ib\left(n + \frac{1}{2}\right),\ n = 0, \pm 1, \pm 2, \ldots.$$

Since

$$\ln Z(z) = \Phi(z) + \ln\cosh\left[\frac{\pi}{b}(z - z_0)\right]$$

is extensive the argument $\pi/b(z - z_0)$ must be extensive. The only possibility is that $1/b \propto V$. We denote

$$b = \frac{v_0}{V},$$

so in the thermodynamic limit

$$V \to \infty \text{ or } b \to 0 \text{ but } v_0 = \text{constant}$$

we get

$$\begin{aligned} \frac{1}{V}\ln Z &= \frac{1}{V}\Phi(z) + \frac{1}{V}\ln\cosh\left[\frac{\pi V}{v_0}(z - z_0)\right] \\ &\to \begin{cases} \frac{1}{V}\Phi(z) + \frac{1}{V}\ln\frac{1}{2} + \frac{\pi}{v_0}(z_0 - z), & z < z_0 \\ \frac{1}{V}\Phi(z) + \frac{1}{V}\ln\frac{1}{2} + \frac{\pi}{v_0}(z - z_0), & z > z_0. \end{cases} \end{aligned}$$

Because in the grand canonical ensemble we have

$$\begin{aligned} pV &= k_B T \ln Z \\ N &= z\frac{\partial \ln Z}{\partial z}, \end{aligned}$$

we see that now

$$\begin{aligned} pV &= k_B T\Phi(z) + \frac{\pi}{v_0} k_B T V|z - z_0| \underset{z\to z_0}{\to} k_B T\Phi(z_0) \\ N &= z\frac{\partial\Phi(z)}{\partial z} + \pi\frac{V}{v_0} z\,\mathrm{sgn}(z - z_0). \end{aligned}$$

We are thus dealing with a typical first order phase transition where the density jump is

$$\Delta\rho = \frac{2\pi z_0}{v_0}.$$

Isings model

Practically the only exactly solvable models are the one and two dimensional models by Ising.
We consider one dimensional chain of spins

$$\begin{array}{c}\uparrow\uparrow\downarrow\uparrow \quad \downarrow \\ 1234\cdots N,\end{array}$$

where we apply periodic boundary conditions, i.e. we set

$$\sigma_{N+1} = \sigma_1.$$

The Hamiltonian operator of the system is then

$$\begin{aligned} H &= -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - h\sum_{i=1}^{N}\sigma_i \\ &= -J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1} - J\sigma_N\sigma_1 - h\sum_{i=1}^{N}\sigma_i, \end{aligned}$$

where each spin variable can attain the values

$$\sigma_i = \pm 1.$$

The state sum is

$$\begin{aligned} Z &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} e^{\beta J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + \beta h\sum_{i=1}^{N}\sigma_i} \\ &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N}\prod_{i=1}^{N} e^{\beta J\sigma_i\sigma_{i+1} + \frac{1}{2}\beta h(\sigma_i+\sigma_{i+1})}. \end{aligned}$$

We define the 2×2 *transition matrix* T so that

$$T_{\sigma\sigma'} = e^{\beta J\sigma\sigma' + \frac{1}{2}\beta h(\sigma+\sigma')},$$

where $\sigma, \sigma' = \pm 1$. The state sum can now be written as

$$\begin{aligned} Z &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} T_{\sigma_1\sigma_2}T_{\sigma_2\sigma_3}\cdots T_{\sigma_N\sigma_1} \\ &= \sum_{\sigma_1}\left(T^N\right)_{\sigma_1\sigma_1} = \operatorname{Tr} T^N. \end{aligned}$$

Looking at the matrix

$$T = \begin{pmatrix} e^{\beta J+\beta h} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J-\beta h} \end{pmatrix}$$

we see that the transition matrix is symmetric. Thus its eigenvalues

$$\lambda^{\pm} = e^{\beta J}\left[\cosh(\beta J) \pm \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}\right],$$

are real. Let S be a orthoganal matrix diagonalizing T (composed of the eigenvectors of T), i.e.

$$T = S^{-1}\begin{pmatrix} \lambda^+ & 0 \\ 0 & \lambda^- \end{pmatrix}S.$$

Now

$$T^N = S^{-1}\begin{pmatrix} \left(\lambda^+\right)^N & 0 \\ 0 & \left(\lambda^-\right)^N \end{pmatrix}S$$

and, due to the cyclic property of the trace,

$$\begin{aligned} Z &= \operatorname{Tr} T^N = \operatorname{Tr} SS^{-1}\begin{pmatrix} \left(\lambda^+\right)^N & 0 \\ 0 & \left(\lambda^-\right)^N \end{pmatrix} \\ &= \left(\lambda^+\right)^N + \left(\lambda^-\right)^N. \end{aligned}$$

The logarithm of the state sum is

$$\begin{aligned} \ln Z &= \ln\left[\left(\lambda^+\right)^N + \left(\lambda^-\right)^N\right] \\ &= N\ln\lambda^+ + \ln\left[1 + \left(\frac{\lambda^-}{\lambda^+}\right)^N\right]. \end{aligned}$$

Since in the thermodynamic limit, $N\to\infty$,

$$\left(\frac{\lambda^-}{\lambda^+}\right)^N \to 0,$$

holds we get

$$\lim_{N\to\infty}\ln Z \to N\left[\ln\lambda^+ + \frac{1}{N}\left(\frac{\lambda^-}{\lambda^+}\right)^N\right] \underset{N\to\infty}{\to} N\ln\lambda^+.$$

Just like in the free spin system the free energy is interpreted as the magnetic Gibbs function. Its value per spin is

$$\begin{aligned} \frac{G}{N} &= -\frac{k_BT}{N}\ln Z \\ &= -J \\ &\quad -k_BT\ln\left[\cosh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{-4\beta J}}\right]. \end{aligned}$$

The equilibrium values of other thermodynamic variables can be calculated from the Gibbs function. In particular, the average of the spin variable is

$$\begin{aligned} \sigma &\equiv \langle\sigma_i\rangle = \frac{1}{N\beta}\frac{\partial\ln Z}{\partial h} = -\frac{\partial G/N}{\partial h} \\ &= \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}. \end{aligned}$$

The expectation value σ is an *order parameter* of the system: $\sigma = 0$ corresponds to completely stochastically oriented spins whereas $|\sigma| = 1$ corresponds to the case where all spins are ordered themselves parallely.
The order parameter σ is analogous to the magnetization M of the free spin system when h corresponds to the magnetic field H. The susceptivity is analogically

$$\chi = \frac{\partial M}{\partial H} \Leftrightarrow \frac{\partial\sigma}{\partial h}.$$

In the weak field limit $h\to 0$ we get then

$$\chi = \left.\frac{\partial\sigma}{\partial h}\right|_{h=0} = \frac{1}{k_BT}e^{\frac{2J}{k_BT}}.$$

When the coupling is ferromagnetic ($J > 0$) the system magnetizes strongly at low temperatures. When the external field is removed the system returns to the

disordered state $\sigma = 0$: there is no *spontaneous symmetry break*.
If the coupling is antiferromagnetic ($J < 0$) the polarization is damped exponentially.
The one dimensional Ising chain is thus a paramagnetic system without any phase transitions. However, since it does not obey Curie's law it is not a Curie paramagnet.
Two dimensional Ising model can be solved exactly generalizing the transition matrix method (Onsager, 1944). It turns out that in this case there is a phase transition at the temperature

$$T_c = \frac{2J}{\ln(1+\sqrt{2})} \approx 2.269\, J.$$

The specific heat diverges logarithmically at the critical point $T = T_c$ and the phase transition is continuous.

Monte Carlo methods
Because, in general, interacting systems can not be solved analytically numerical methods are of great value. An important class of numerical methods, *Monte Carlo methods*, handles interacting systems using stochastic simulations. Suitable simulations for continuum systems, like ^{3}He- ^{4}He-liquids and electron gas, are mostly based on *Green's function Monte Carlo*.
In discretized systems one can often apply *Metropolis' Monte Carlo method*:

- Let the possible configurations of the system be

  $$j \in J = \{1, 2, \ldots, K\}$$

  and $E(j)$ the corresponding energies.
- Form a chain $j_1, j_2, \ldots, j_n$ of configurations.
- Choose the next configuration, $(n+1)$'th, in the chain drawing randomly from the set J of the possible configurations. The drawed configuration, j', will be
  - accepted if $\Delta E = E(j') - E(j_n) < 0$.
  - accepted with the probability $\propto e^{-\beta\,\Delta E}$ if $\Delta E > 0$.
- When the length N of the chain $\{j_n\}$ increases $(N \to \infty)$ the probability for each configuration j approaches

  $$P(j) \propto e^{-\beta E(j)}.$$
- The chain is thus a canonical ensemble which can be used to evaluate expectation values.

Note The method assumes that the energy eigenstates of the system are known. So it can be applied for handling of e.g. Isings models and all classical systems.
If the energy states are unknown the quantization must be included in the simulation.