Singularities in Free Energy: Lee-Yang Theory

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Abstract

Phase Transition is associated with drastic change in some observable (ordered parameter) of the system when the controlled parameter is tuned smoothly. Lee-Yang theory of phase transition is discussed which is related to accumulation of singularities of free energy, equivalently complex roots of Grand Partition function (Partition function) at points on positive real axis in complex fugacity plane; and more general \((p + 1)\) phase system is discussed, and also the case when \((w + 2)\) phases coexist together. Comparison to Mayer’s theory is also presented.

Studying the Analytic behavior of Grand Partition Function can reveal lot about Phase Transition and Condensation phenomena. The fugacity\(^1\) is promoted to Complex values. Only real values of the fugacity is directly of physical interest, but the analytic behavior of the Thermodynamic Functions can only be revealed by going to Complex fugacity plane.

1 A Simple Model

The purpose of this section is to study a simple model \([1]\), so that when the abstract general theory is presented, it does not looks alien. Consider a system with \(N\) spin in thermal contact with the heat reservoir, with quantized energy levels \(E = n\epsilon\) with \(n = 0, 1, 2, ..., N\) and \(g(n)\) is the number of microstates in the \(n\)th energy level\(^2\).

The Canonical Partition function becomes \(Z_N = \sum_{n=0}^{N} g(n) \exp(-\beta n\epsilon)\). Define \(z = \exp(-\beta \epsilon)\), then \(Z_N = \sum_{n=0}^{N} g(n) z^n\) becomes a polynomial of degree \(N\) in \(z\). Let \(z_n\) be the zeros of this complex polynomial, then we can write the Complex Partition function as

\[
Z_N = \kappa \prod_{n=1}^{N} \left(1 - \frac{z}{z_n}\right)
\]

where \(\kappa\) is some constant which appears for normalization of the expression and can be ignored for most of the purpose. Now we define the Complex Free Energy\(^3\) \(h_N(z) \equiv \ln \frac{Z_N(z)}{N}\) on \(\mathbb{C}\{z_1, z_2, ..., z_N\}\).

Using eqn.(1) we can write

\[
h_N(z) = \frac{1}{N} \sum_{n=1}^{N} \ln \left(1 - \frac{z}{z_n}\right)
\]

The Taylor series expansion of \(h_N(z)\) around \(z \neq z_n\) has radius of convergence \(r(z) = \min_{z_n} |z - z_n|\). Phase transitions are identified with the discontinuities in the derivative of free energy; so if the phase transition occurs at \(z_0 \in \mathbb{R} \subset \mathbb{C}\), then we must have one zero of the partition function in an arbitrary small region around \(z_0\). For finite \(N\) this is not possible for any point on real line. But if \(N \to \infty\) then we can have a possibility of complex roots accumulating near some positive real \(z_0\), and thus phase transition is possible for this infinite system. The existence of the thermodynamic limit \(h(z) = \lim_{N \to \infty} \left(\ln \frac{Z_N(z)}{N}\right)\) is the consequence of Lee-Yang theorem (sec.2)\(^2\). We can write it as

\[
h(z) = \int dz' \rho(z') \ln \left(1 - \frac{z}{z'}\right)
\]

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\(^1\)A thermodynamic property of a real gas which if substituted for the temperature or pressure or partial pressure in the equations for an ideal gas gives equations applicable to the real gas, etc.

\(^2\)\(E = N\epsilon\) correspond to the energy level when all the spin are in excited state

\(^3\)Defined upto the factors of \(-1/\beta\), this factor will not play any role in deciding properties of singularity, so we can safely ignore this for simplicity.
where \( \rho(z) \) is the Local density of roots of the partition function in the thermodynamic limit \( N \to \infty \). Define the real part of \( h(z) \) to be the potential\(^4\)

\[
\phi(z) \equiv \text{Re}\{h(z)\} = \int dz' \rho(z') \ln \left| 1 - \frac{z}{z'} \right| \quad \text{and} \quad \psi(z) \equiv \text{Im}\{h(z)\} \tag{4}
\]

Note that \( \ln |z| \) is green function for laplacian in 2d, so it follows \( \nabla^2 \ln |1 - \frac{z}{z'}| = 2\pi \delta(z - z') \); which then implies \( \rho(z) = \frac{1}{2\pi} \nabla^2 \phi(z) \) (which is analogous to electrostatic poisson equation). Now we consider two points in the complex plane \( z_1 \neq z_2 \), then \( D(z_1, r(z_1)) \cap D(z_2, r(z_2)) \) is not empty as evident from properties of circle and triangle inequality. So if we consider the local analytic expression of the potential around those points \( \phi_1(z) \) and \( \phi_2(z) \), then \( \phi_1(z) \neq \phi_2(z) \). In order to ensure continuity of free energy, the potential must be continuous at all points in the complex plane; so there must exist a phase boundary \( C = \{ z \in C : \phi_1(z) = \phi_2(z) \} \). The derivatives of the potential will not be generically continuous and this is the reminiscent of Phase Transition. Since only the real positive value of \( z \) are of physical interest directly, so the phase transition occurs at the point where the curve \( C \) intersects the positive real axis, say at some point \( z_0 \). As we have already established, phase transition occurs at \( z_0 \) in the thermodynamic limit if the complex roots of the partition function accumulate near \( z_0 \). So we are interested in density of roots along the curve \( C \). Let \( s \) denote the arc length along the curve \( C \), with \( s = 0 \) at \( z_0 \). We want to obtain an expression for line density of roots per unit length of the curve \( C \mu(s) \). Integrating \( \rho(z) \) over the infinitesimal area \( A \) as shown in the figure gives

\[
\int_A dz \rho(z) = \frac{1}{2\pi} \int_A dz \nabla \cdot [\nabla \phi(z)] = -\frac{\delta s}{2\pi} \nabla \cdot [\nabla \phi_1(z) - \nabla \phi_1(z)] \cdot \hat{n} \tag{5}
\]

In terms of the normal \( \hat{n} \) and tangent \( \hat{t} \) to the curve \( C \), the Cauchy Riemann equation can be written as \( \nabla \phi(z) \cdot \hat{n} = \nabla \psi(z) \cdot \hat{t} \). Along with the definition \( \int_A dz \rho(z) = \mu(s) ds \) and with the fact \( \hat{t} \cdot \nabla = d/ds \) it follows

\[
\mu(s) = \frac{1}{2\pi} \frac{d}{ds} [\psi_2(z) - \psi_1(z)] \tag{6}
\]

The leading behavior of free energy on either side of the transition point \( z_0 \) in terms of \( \tilde{z} = z - z_0 \) is \( f_{1,2} = h(z_0) + b_{1,2} \tilde{z} + c_{1,2} \tilde{z}^2 + \ldots \) with \( f_1(\tilde{z}) \) valid for \( \text{Re}\{\tilde{z}\} < 0 \) and \( f_2(\tilde{z}) \) valid for \( \text{Re}\{\tilde{z}\} > 0 \). From the continuity of \( \text{Re}\{h(z)\} \) across phase boundary, it follows that the boundary \( C \) lies along the curve \( y^2 = x^2 + \frac{b_{1,2}}{c_{1,2}} x \). The coefficients \( b \) and \( c \) must also be real, because \( f \in \mathbb{R}_{>0} \) on \( z \in \mathbb{R}_{>0} \).

1. **First-order Transition** \( b_1 \neq b_2 \), \( C \) is hyperbola passing through \( z_0 \), and the density of root at \( z_0 \) is \( \mu(0) = \frac{b_{1,2} - b_{1,2}}{2\pi} \) is non zero, which implies first derivative of free energy is discontinuous and hence First-order Transition.

2. **Second-order Transition** \( b_1 = b_2, c_1 \neq c_2 \), the curve \( C \) obeys \( y = \pm x \). So the zeros approach \( z_0 \) along straight line that meet at right angles. Considering say \( x = y = s/\sqrt{2} \) we find \( \mu(s) = \frac{\sqrt{2}}{\pi} \). This manifests Second-order transition because the density of zeros linearly decrease to zero at \( z_0 \), so the first derivative of free energy is continuous but not the higher derivatives.

3. **Higher-order Transition** With the leading behavior \( f_2(u) - f_1(u) \sim u^\alpha \). Then the condition \( \text{Re}\{f_2(u) - f_1(u)\} = 0 \) implies that the zeroes approach the real axis at angle \( \pi/2\alpha \). \( \text{Im}\{f_2(u) - f_1(u)\} \sim |u|^\alpha \) which implies that density of zeroes behaves as \( s^{\alpha-1} \) for small arc-length \( s \). So \( \mu(0) \) is finite if \( \alpha \geq 1 \).

Although we had discussed the theory of partition function for specific model, the idea holds true more generally. We are not restricted to the Canonical ensemble; actually in the original work of Lee and Yang, they had worked with Grand Canonical ensemble, and then promoted fugacity to Complex plane which we study in the next section.

\(^4\)the name potential is justified because we will see that it satisfies the 2d analogue of Electrostatics Poisson equation.

\(^5\)\( D(z, r) = \{ z' \in C : |z' - z| < r \} \) denotes open disk of radius \( r \) with center \( z \) in the complex plane.
2 Statistical Theory of Equation of State and Phase Transition: Lee-Yang Theory

Understanding the occurrence of discontinuities with phase transitions in the thermodynamic functions and seeking for a workable theory of properties of matter led to the study of complex zeros of the thermodynamic functions and understanding their singularities. We consider a monoatomic gas with the interaction $U = \sum u(r_{ij})$, where $r_{ij}$ is the distance between the atoms. The atoms are taken to have finite impenetrable core with diameter $a$ ($u(r) = +\infty$ for $r \leq a$), with finite range $b$ interaction ($u(r) = 0$ for $r \geq b$), and $u(r)$ is nowhere minus infinity. Consider a box of volume $V$ in a thermal bath of temperature $T$, which is allowed to exchange atoms at a given chemical potential $\mu$ per atom. Because of the nature of interaction, only finite amount of atoms can reside inside the box. The relative probability of having $N$ atoms in the box is $Q_N z^N/N!$ where the configurational part of the partition function for $N$ atoms is $Q_N = \int \cdots \int d\tau_1 \cdots d\tau_N \exp(-U/k_BT)$ and $z = (2\pi nk_BT/h^2)^{3/2} \exp(\mu/k_BT)$ with the quantities having there usual meaning. The Grand Partition function of the gas $Q_V$ in the volume $V$ is $Q_V = \sum_{N=0}^{M} Q_N^\gamma z^N$, where $M$ is the maximum numbers of atoms that can be put inside the box ($M$ is roughly $\sim 6V/(\pi a^3)$). $Q_V$ can be read as a polynomial in $z$ with finite degree, so we factorise it as $Q_V = \prod_{n=1}^{M} (1 - \frac{z}{z_n})$ where $z_n$ are roots of $Q_V$. Similar to what we saw in sec.1, none of the roots will be real and positive because all the coefficients in the polynomial $Q_V$ are positive. Phase transition is not possible for finite system because roots will not be able to accumulate near some $z_0$ positive and real; so we go to thermodynamic limit $M \to \infty$ which is effectively $V \to \infty$ which follows from our rough estimate of $M$.

In the thermodynamic limit the pressure $p$ and the density $\rho$ is given by

$$\frac{p}{k_BT} = \lim_{V \to \infty} \frac{1}{V} \ln Q_V \quad \text{and} \quad \rho = \lim_{V \to \infty} \frac{\partial}{\partial \ln z} \left( \frac{1}{V} \ln Q_V \right)$$

(7)

The existence of this thermodynamic limit is quite unclear at phase transition. The following theorem by Lee-Yang [2] resolves the doubt, and thus eqn.(7) gives complete description of the equation of state for both the phase across the transition point.

**Theorem 1** \( \forall z \in \mathbb{R}_{>0}, \ V^{-1} \ln Q_V \) approaches to a continuous, monotonically increasing function of $z$ as $V \to \infty$. And the limit is independent of the shape of $V$. Assumption: The shape of $V$ is not so queer that its surface area increases faster than $V^{2\pi}$.

**Theorem 2** Let $R$ be a region in the complex $z$ plane containing a segment of positive real axis which is always free of roots, then in the thermodynamic limit $V \to \infty$ the quantities $(\frac{\partial}{\partial \ln z})^{(n)} (\frac{1}{V} \ln Q_V) \forall n \in \mathbb{N}$ approaches to analytic function of $z$. And the operations $\frac{\partial}{\partial \ln z}$ and $\lim_{V \to \infty}$ commute.

From theorem 1 and 2 it follows that the equation of state becomes $\rho = (\frac{\partial}{\partial \ln z})(p/k_BT)$. Note that the quantity $(\frac{\partial}{\partial \ln z}) V^{-1} \ln Q_V$ does not always approach the limit $\rho$; it depends on the nature of region $R$ mentioned in Theorem 2. It can be shown that $\rho$ is an increasing function of $z$ [1]. $p$ is already increasing function of $z$ due to Theorem 1.

**PHASE TRANSITION**

(1) \( \exists \) region $R \supset \mathbb{R}_{>0}$ which is free of roots of $Q_V(z) = 0$. So, its a **Single Phase system**.

Roots of $Q_V(z) = 0$ close into the real axis as $V \to \infty$ at the points in the ascending order:

(2) $y_0$, and the regions $R_1, R_2$ are free of roots: **Double Phase System**.

(3) $y_1, y_2$, and the regions $R_1, R_2, R_3$ are free of roots: **Triple Phase System**.

(4) $y_1, y_2, \ldots, y_p$, and the regions $R_1, R_2, \ldots, R_p, R_{p+1}$ are free of roots: **$(p+1)$ Phase System**.

Within each region $R_j$, the system is in single phase because $p$ and $\rho$ are analytic and increasing function of $z$ defined by eqn.(7); and on the isotherm $p$ increases analytically as the specific volume $v$ decreases. At the transition point $y_j$, $p$ is discontinuous but increases across the discontinuity. As the temperature is varied the points $y_j$ will in general move along the real $z$ axis.
If at a certain temperature $T_c^{(j)}$ the roots ceases to close onto say $y_j$ then $T_c^{(j)}$ is actually the critical temperature for the transition

$$\text{phase}(j) \xleftarrow{T_c^{(j)}} \text{phase}(j + 1).$$

If at some temperature $T_0^{(j)}$ the roots $y_j, y_{j+1}$ merge, we would have triple point at $T_0^{(j)}$ where the three phases $\text{phase}(j), (j + 1), (j + 2)$ coexist. More generally, if at some temperature $T_0^{[j,j+w]}$ the roots $y_j, y_{j+1}, \ldots, y_{j+w}$ merge, we have $(w + 2) - \text{point}$ where $(w + 2)$ phases $\text{phase}(j), (j + 1), \ldots, (j + w + 2)$ coexist. The nature of collapse of zeros at $y_j$ determines the order of phase transition. The density $\rho$ can be continuous in some cases at the transition point (not its derivatives in general), and this is reminiscent of higher order phase transition. The theory can be generalized to many body forces and forces with weak long tail decay; and actually the generalization will not lead to any change in the conclusion described above.

**Comparison with MAYER’S THEORY**

Expanding $\ln \mathcal{Q}_V$ in powers of $z$ gives $\sum_{l=1}^\infty b_l(V) z^l$ where $b_l(V) = \frac{(-1)^l}{l!} \sum_{j=1}^M (z_j)^{-l}$. From the definition of $z$ it follows then that $\frac{\mathcal{Q}_V}{N!}$ is the coefficient of $y^N$ in $\mathcal{Q}_V = \exp \left( V \sum_{l=1}^\infty b_l(V) z^l \right)$. Comparison with
Mayer’s theory shows that \( b_l \)’s are actually Reducible Cluster integral defined by Mayer [3],

\[
b_l = \frac{1}{l!V} \int \cdots \int \sum_{l \geq 1, i > j \geq 1} \prod_{l \geq 1, i > j \geq 1} f_{ij} \, d\tau_1 \cdots d\tau_l
\]

but here we see that it is also related to moments of the roots \( z_n \) of \( Q_V = 0 \). Mayer considered the series \( \chi(z) = \sum_{l=1}^{\infty} b_l(\infty) z^l \) and its analytic continuation along \( \mathbb{R}_{>0} \). Let \( y_1 \in \mathbb{R}_{>0} \) be the first singularity of \( \chi(z) \): then for densities \( \rho < \rho_1 = \lim_{z \to y_1} -z \chi'(z) \) the system exists in a single phase; and for \( \rho \geq \rho_1 \), the pressure \( p \) at a given temperature becomes independent of the density. We identify \( \rho_1 \) as the density of gas at condensation. The problem with Mayer’s theory is that it does not allow existence of liquid phase with finite density; because isotherm becomes horizontal for all specific volume less than \( \rho_1^{-1} \).

Conclusion

Here we saw how the singularity behavior of free energy, which is essentially read as zeros of Grand Partition function (Partition function) can reveal phase transition. Although free energy and the fugacity are real numbers, but we promote it to complex values and we find that the accumulation of complex singularities of free energy (equivalently accumulation of zeros of Partition function) at a point lying on real positive fugacity axis embedded in the complex plane leads to phase transition. We also studied the more general \((p+1)\) phase system, and more general case of \((w+2)\) phases coexisting together. We also see why there is no liquid phase in Mayer’s theory, and how does the Lee-Yang theory resolves the remedy.

Acknowledgement

I would like to thank Prof. Anirban Sain who guide me to work and understand Lee-Yang theory; and also Prof. G.K.Srinivasan who always supported me and revealed the gift of mathematics and its beauty to me.

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