6.3: Lee-Yang Theory

Analytic Properties of the Partition Function

How can statistical mechanics describe phase transitions? This question was addressed in some beautiful mathematical analysis by Lee and Yang[7]. Consider the grand partition function Ξ,

$$\Xi(T,V,z)=\sum_{N=0}^{\infty} z^N\,Q_N(T,V)\,\lambda_T^{-dN}\ , \tag{6.3.1}$$

where

$$Q_N(T,V)=\frac{1}{N!}\int\!d^d x_1\cdots\int\!d^d x_N\ e^{-U(\mathbf{x}_1\,,\,\ldots\,,\,\mathbf{x}_N)/k_BT} \tag{6.3.2}$$

is the contribution to the N-particle partition function from the potential energy U (assuming no momentum-dependent potentials). For two-body central potentials, we have

$$U(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\sum_{i<j} v\big(|\mathbf{x}_i-\mathbf{x}_j|\big). \tag{6.3.3}$$

Suppose further that these classical particles have hard cores. Then for any *finite* volume, there must be some maximum number N_V such that $Q_N(T,V)$ vanishes for $N>N_V$. This is because if $N>N_V$ at least two spheres must overlap, in which case the potential energy is infinite. The theoretical maximum packing density for hard spheres is achieved for a hexagonal close packed (HCP) lattice[8], for which $f_{HCP}=\frac{\pi}{3\sqrt{2}}=0.74048$. If the spheres have radius r_0, then $N_V=V/4\sqrt{2}r_0^3$ is the maximum particle number.

Thus, if V itself is finite, then $\Xi(T,V,z)$ is a *finite* degree polynomial in z, and may be factorized as

$$\Xi(T,V,z)=\sum_{N=0}^{N_V} z^N\,Q_N(T,V)\,\lambda_T^{-dN}=\prod_{k=1}^{N_V}\bigg(1-\frac{z}{z_k}\bigg)\ , \tag{6.3.4}$$

where $z_k(T,V)$ is one of the N_V zeros of the grand partition function. Note that the $\mathcal{O}(z^0)$ term is fixed to be unity. Note also that since the configuration integrals $Q_N(T,V)$ are all positive, $\Xi(z)$ is an increasing function along the positive real z axis. In addition, since the coefficients of z^N in the polynomial $\Xi(z)$ are all real, then $\Xi(z)=0$ implies $\overline{\Xi(z)}=\Xi(\bar{z})=0$, so the zeros of $\Xi(z)$ are either real and negative or else come in complex conjugate pairs.

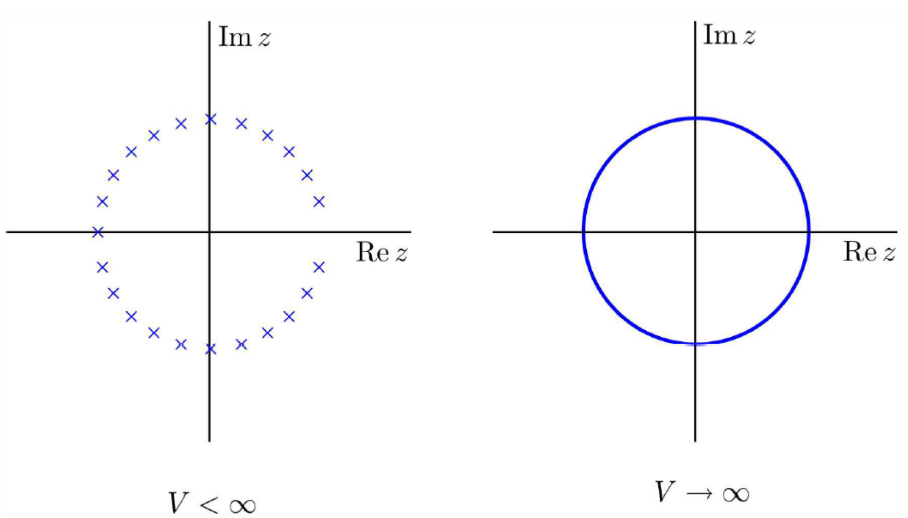

Figure 6.3.1: In the thermodynamic limit, the grand partition function can develop a singularity at positive real fugacity z. The set of discrete zeros fuses into a branch cut.

For finite N_V, the situation is roughly as depicted in the left panel of Figure 6.3.1, with a set of N_V zeros arranged in complex conjugate pairs (or negative real values). The zeros aren't necessarily distributed along a circle as shown in the figure, though.

They could be anywhere, so long as they are symmetrically distributed about the $Re(z)$ axis, and no zeros occur for z real and nonnegative.

Lee and Yang proved the existence of the limits

$$\begin{aligned}\frac{p}{k_B T} &= \lim_{V\to\infty} \frac{1}{V} \ln \Xi(T,V,z) \\ n &= \lim_{V\to\infty} z \frac{\partial}{\partial z}\left[\frac{1}{V} \ln \Xi(T,V,z)\right] ,\end{aligned}$$

and notably the result

$$n = z \frac{\partial}{\partial z}\left(\frac{p}{k_B T}\right) , \tag{6.3.5}$$

which amounts to the commutativity of the thermodynamic limit $V \to \infty$ with the differential operator $z \frac{\partial}{\partial z}$. In particular, $p(T,z)$ is a smooth function of z in regions free of roots. If the roots do coalesce and pinch the positive real axis, then then density n can be discontinuous, as in a first order phase transition, or a higher derivative $\partial^j p / \partial n^j$ can be discontinuous or divergent, as in a second order phase transition.

Electrostatic Analogy

There is a beautiful analogy to the theory of two-dimensional electrostatics. We write

$$\begin{aligned}\frac{p}{k_B T} &= \frac{1}{V} \sum_{k=1}^{N_V} \ln\left(1 - \frac{z}{z_k}\right) \\ &= -\sum_{k=1}^{N_V}\left[\phi(z - z_k) - \phi(0 - z_k)\right] ,\end{aligned}$$

where

$$\phi(z) = -\frac{1}{V} \ln(z) \tag{6.3.6}$$

is the complex potential due to a line charge of linear density $\lambda = V^{-1}$ located at origin. The number density is then

$$n = z \frac{\partial}{\partial z}\left(\frac{p}{k_B T}\right) = -z \frac{\partial}{\partial z} \sum_{k=1}^{N_V} \phi(z - z_k) , \tag{6.3.7}$$

to be evaluated for physical values of z, $z \in \mathbb{R}^+$. Since $\phi(z)$ is analytic,

$$\frac{\partial\phi}{\partial\bar{z}} = \frac{1}{2} \frac{\partial\phi}{\partial x} + \frac{i}{2} \frac{\partial\phi}{\partial y} = 0 . \tag{6.3.8}$$

If we decompose the complex potential $\phi = \phi_1 + i\phi_2$ into real and imaginary parts, the condition of analyticity is recast as the Cauchy-Riemann equations,

$$\frac{\partial\phi_1}{\partial x} = \frac{\partial\phi_2}{\partial y} \qquad , \qquad \frac{\partial\phi_1}{\partial y} = -\frac{\partial\phi_2}{\partial x} . \tag{6.3.9}$$

Thus,

$$\begin{aligned}-\frac{\partial\phi}{\partial z} &= -\frac{1}{2} \frac{\partial\phi}{\partial x} + \frac{i}{2} \frac{\partial\phi}{\partial y} \\ &= -\frac{1}{2}\left(\frac{\partial\phi_1}{\partial x} + \frac{\partial\phi_2}{\partial y}\right) + \frac{i}{2}\left(\frac{\partial\phi_1}{\partial y} - \frac{\partial\phi_2}{\partial x}\right) \\ &= -\frac{\partial\phi_1}{\partial x} + i \frac{\partial\phi_1}{\partial y} = E_x - iE_y ,\end{aligned}$$

where $\mathbf{E} = -\boldsymbol{\nabla}\phi_1$ is the electric field. Suppose, then, that as $V \to \infty$ a continuous charge distribution develops, which crosses the positive real z axis at a point $x \in \mathbb{R}^+$. Then

$$\frac{n_+ - n_-}{x} = E_x(x^+) - E_x(x^-) = 4\pi\sigma(x)\ , \tag{6.3.10}$$

where σ is the linear charge density (assuming logarithmic two-dimensional potentials), or the two-dimensional charge density (if we extend the distribution along a third axis).

Example

As an example, consider the function

$$\begin{aligned}\Xi(z) &= \frac{(1+z)^M\,(1-z^M)}{1-z}\\ &= (1+z)^M\,\big(1+z+z^2+\ldots+z^{M-1}\big)\ .\end{aligned}$$

The $(2M-1)$ degree polynomial has an M^{th} order zero at $z=-1$ and $(M-1)$ simple zeros at $z = e^{2\pi i k/M}$, where $k \in \{1,\ldots,M{-}1\}$. Since M serves as the maximum particle number N_V, we may assume that $V = Mv_0$, and the $V \to \infty$ limit may be taken as $M \to \infty$. We then have

$$\begin{aligned}\frac{p}{k_BT} &= \lim_{V\to\infty}\frac{1}{V}\,\ln\Xi(z)\\ &= \frac{1}{v_0}\lim_{M\to\infty}\frac{1}{M}\ln\Xi(z)\\ &= \frac{1}{v_0}\lim_{M\to\infty}\frac{1}{M}\Big[M\ln(1+z) + \ln\big(1-z^M\big) - \ln(1-z)\Big]\ .\end{aligned}$$

The limit depends on whether $|z|>1$ or $|z|<1$, and we obtain

$$\frac{p\,v_0}{k_BT} = \begin{cases} \ln(1+z) & \text{if } |z|<1\\[2ex] \Big[\ln(1+z) + \ln z\Big] & \text{if } |z|>1\ .\end{cases} \tag{6.3.11}$$

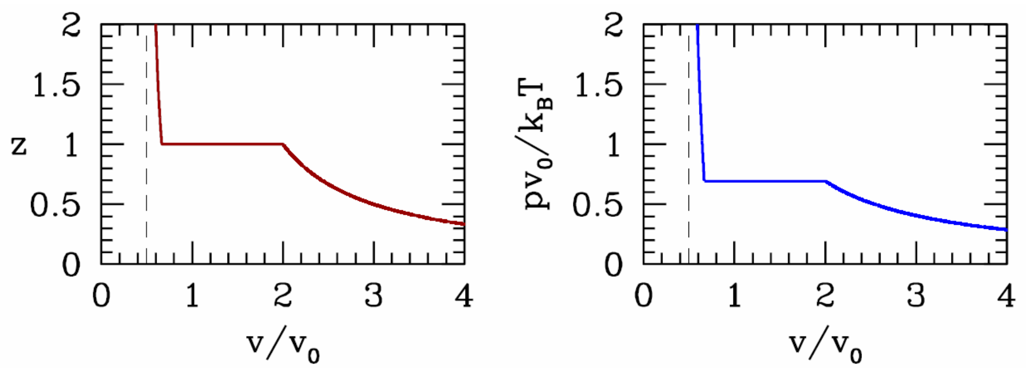

Figure 6.3.2: Fugacity z and pv_0/k_BT *versus* dimensionless specific volume v/v_0 for the example problem discussed in the text.

Thus,

$$n = z\frac{\partial}{\partial z}\bigg(\frac{p}{k_BT}\bigg) = \begin{cases} \frac{1}{v_0}\cdot\frac{z}{1+z} & \text{if } |z|<1\\[2ex] \frac{1}{v_0}\cdot\Big[\frac{z}{1+z}+1\Big] & \text{if } |z|>1\ .\end{cases} \tag{6.3.12}$$

If we solve for $z(v)$, where $v = n^{-1}$, we find

$$z = \begin{cases} \frac{v_0}{v - v_0} & \text{if } v > 2v_0 \\ \\ \frac{v_0 - v}{2v - v_0} & \text{if } \frac{1}{2}v_0 < v < \frac{2}{3}v_0 \ . \end{cases} \tag{6.3.13}$$

We then obtain the equation of state,

$$\frac{p\,v_0}{k_B T} = \begin{cases} \ln\Big(\frac{v}{v - v_0}\Big) & \text{if } v > 2v_0 \\ \\ \ln 2 & \text{if } \frac{2}{3}v_0 < v < 2v_0 \\ \\ \ln\Big(\frac{v(v_0 - v)}{(2v - v_0)^2}\Big) & \text{if } \frac{1}{2}v_0 < v < \frac{2}{3}v_0 \ . \end{cases} \tag{6.3.14}$$