S7.C. The Yang-Lee Theory of Phase Transition

Consider a system of particles interacting via a short-ranged attractive hard core potential

$$\mathcal{V}(q_{ij}) = \begin{cases} \infty & \text{for} \quad q_{ij} < a \\ -\varepsilon & \text{for} \quad a \le q_{ij} \le b \\ 0 & \text{for} \quad b < q_{ij} \end{cases} \tag{7.255}$$

where ε, a & b are positive constants,

$$q_{ij} = |\, \mathbf{q}_{ij} \,| \qquad\qquad \mathbf{q}_{ij} = \mathbf{q}_j - \mathbf{q}_i$$

and $\mathbf{q}_i$ is the position of the i^{th} particle. Owing to the hard core, there is a maximum number M of particles that can fit in a box of volume V. The grand partition function is therefore

$$Z_\mu(T,V) = \sum_{N=0}^{M} \frac{e^{\beta\mu' N}}{N!\, h^{3N}} \int d^{3N}p \int d^{3N}q \exp\left\{-\beta\left[\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j=1}^{N(N-1)/2} \mathcal{V}(q_{ij})\right]\right\} \tag{7.256a}$$

Using

$$\int \frac{d^3 p_i}{h^3} \exp\left(-\beta \frac{p_i^2}{2m}\right) = \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} = \frac{1}{\lambda_T^3} \qquad [\ (7.135)\text{ used.}\ ]$$

(7.256a) becomes

$$Z_\mu(T,V) = \sum_{N=0}^{M} \frac{e^{\beta\mu' N}}{N!\, \lambda_T^{3N}} Q_N(T,V) \tag{7.256}$$

where

$$Q_N(T,V) = \int d^{3N}q \exp\left[-\beta \sum_{i<j=1}^{N(N-1)/2} \mathcal{V}(q_{ij})\right] \tag{7.257}$$

is known as the configuration integral. It contains all informations about the deviations from the ideal gas behavior. Note that the constraint $N \le M$ is equivalent to

$$Q_N(T,V) = 0 \qquad\qquad \forall\ N > M \tag{7.257a}$$

Let

$$y = \frac{e^{\beta\mu'}}{\lambda_T^3} \tag{7.258a}$$

then (7.256) becomes

$$Z_\mu(T,V) = \sum_{N=0}^{M} \frac{y^N}{N!} Q_N(T,V) \tag{7.258}$$

which is a polynomial of order M in y with positive real coefficients.

Since the constant term in (7.258) is

$$\left. \frac{y^N}{N!} Q_N(T,V) \right|_{N=0} = Q_0(T,V) = 1$$

(7.258) can be written as

$$Z_\mu(T,V) = \sum_{i=1}^{M} \left(1 - \frac{y}{y_i}\right) \tag{7.259}$$

where y_i is the i^{th} root of $Z_\mu(T,V)$. Since the coefficients of the polynomial are all real, complex y_i must appear in conjugate pairs.

Since Z_μ appears in the denominator of the statistical average,

$$\langle X \rangle = \frac{1}{Z_\mu} \text{Tr}\left[\hat{X}\, e^{-\beta(\hat{H} - \mu' \hat{N})}\right]$$

we must have

$$Z_\mu(T, V) \neq 0 \qquad \forall\ y \qquad (7.259a)$$

if the thermodynamic functions are to be well behaved. (7.259) then requires

$$y \neq y_i \qquad \forall\ i$$

$$\to \quad y_i \notin (0, \infty)$$

i.e., none of the roots of Z_μ can be real and positive. In other words, there is a region in the complex y plane around the positive real y axis that does not contain any roots of Z_μ [see Fig.7.27a].

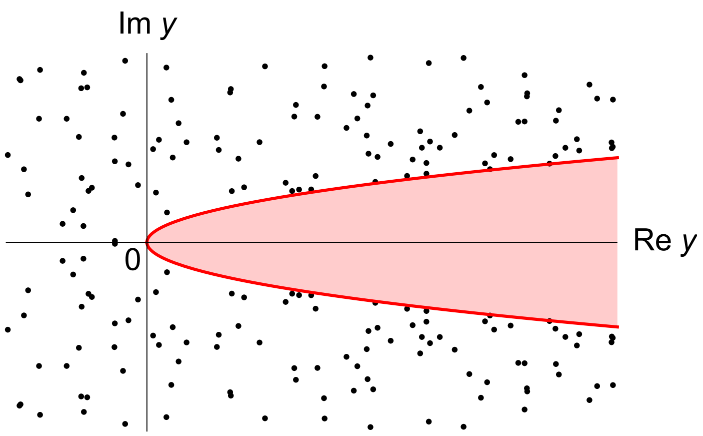

Fig.7.27a. Schematic plot of the distribution of roots (black dots) of Z_μ in the complex y-plane. Root-free region is in red.

One exception to the condition (7.259a) happens when the system is at the transition point, where many of the thermodynamic functions are singular. The root-free region in the complex y plane is therefore “pinched” to expose this root on the positive real axis [see Fig.7.27b].

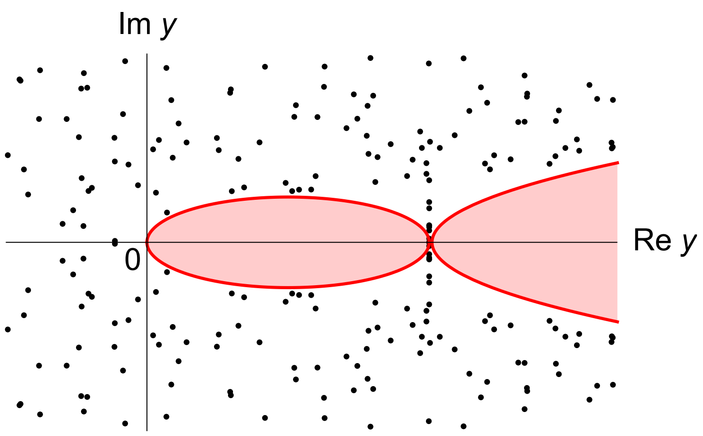

Fig.7.27b. Pinching of the root-free region (in red) at the critical point on the real y axis.

Now, not all thermodynamic functions are singular at the transition point. Two examples are the pressure

$$P = -\frac{\Omega}{V} = \frac{k_B T}{V} \ln Z_\mu \qquad (7.260a)$$

and the particle volume v given by

$$\frac{1}{v} \equiv \frac{\langle N \rangle}{V} = \frac{1}{V Z_\mu} \sum_{N=0}^{M} N \frac{y^N}{N!} Q_N(T, V) = \frac{1}{V Z_\mu} y \frac{\partial}{\partial y} \sum_{N=0}^{M} \frac{y^N}{N!} Q_N(T, V) = \frac{1}{V Z_\mu} y \frac{\partial Z_\mu}{\partial y}$$

$$= \frac{1}{V} y \frac{\partial}{\partial y} \ln Z_\mu$$

$$= y \frac{\partial}{\partial y}\left(\frac{1}{V} \ln Z_\mu\right) \qquad [\, V \;\&\; y \text{ are independent variables.} \,] \qquad (7.261a)$$

The simplest way to keep P & v finite as $Z_\mu \to 0$ is to invoke the thermodynamic limit. For the purpose, Yang & Lee derived the following two theorems.

Theorem I.

$$\lim_{V\to\infty} \frac{1}{V} \ln Z_\mu = f(y)$$

where f is a continuous and monotonically increasing function of y.

Theorem II.

Let R be a region in the complex y plane that contains a segment of the positive real axis.
If R is always free of roots of Z_μ, then

$$\lim_{V\to\infty} \frac{1}{V} \ln Z_\mu = f(y)$$

$$\& \quad \lim_{V\to\infty} \left(y \frac{\partial}{\partial y}\right)^n \frac{1}{V} \ln Z_\mu = g(y) \qquad n = 1, 2, 3, \ldots \qquad (7.261b)$$

where f & g are analytic functions of y. Furthermore

$$\lim_{V\to\infty} y \frac{\partial}{\partial y}\left(\frac{1}{V} \ln Z_\mu\right) = y \frac{\partial}{\partial y}\left(\lim_{V\to\infty} \frac{1}{V} \ln Z_\mu\right) \qquad (7.261c)$$

Note: In general, $\frac{\partial}{\partial y}$ & V commute since y & V are independent variables.

However, since Z_μ is a function of V, it is possible that $\frac{\partial}{\partial y}$ & $\lim_{V\to\infty}$ in (7.261c) do not commute.

In the thermodynamic limits, (7.260a) & (7.261a) becomes

$$P = \lim_{V\to\infty} \frac{k_B T}{V} \ln Z_\mu \qquad (7.260)$$

$$\frac{1}{v} = \lim_{V\to\infty} \frac{1}{V} y \frac{\partial}{\partial y} \ln Z_\mu \qquad (7.261)$$

$$= y \frac{\partial}{\partial y} \lim_{V\to\infty} \frac{1}{V} \ln Z_\mu \qquad [\, (7.261c) \text{ used.} \,]$$

$$= y \frac{\partial}{\partial y} \frac{P}{k_B T} \qquad [\, (7.260) \text{ used.} \,] \qquad (7.262)$$

Since v is always finite, so must be $\frac{\partial}{\partial y} \frac{P}{k_B T}$ for all y. Hence, $\frac{P}{k_B T}$ must be at least continuous function of y. In a single phase region (or region R of theorem II), v is also continuous; so must be $\frac{\partial}{\partial y} \frac{P}{k_B T}$. At a 1st order transition point, v is discontinuous, as is $\frac{\partial}{\partial y} \frac{P}{k_B T}$.

From (7.261a), we have

$$y \frac{\partial}{\partial y} \frac{1}{v} = \left(y \frac{\partial}{\partial y}\right)^2 \left(\frac{1}{V} \ln Z_\mu\right) = \frac{1}{V}\left(y \frac{\partial}{\partial y}\right)^2 \ln Z_\mu$$

$$= \frac{1}{V}\left(y \frac{\partial}{\partial y}\right)^2 \ln\left[\sum_{N=0}^{M} \frac{y^N}{N!} Q_N(T, V)\right]$$

$$= \frac{1}{V}\left(y \frac{\partial}{\partial y}\right)\left[\frac{1}{Z_\mu} \sum_{N=0}^{M} N \frac{y^N}{N!} Q_N(T, V)\right] = \frac{1}{V} y \frac{\partial \langle N \rangle}{\partial y}$$

$$= \frac{1}{V}\left[-\frac{1}{Z_\mu^2} y \frac{\partial Z_\mu}{\partial y} \sum_{N=0}^{M} N \frac{y^N}{N!} Q_N(T, V) + \frac{1}{Z_\mu} \sum_{N=0}^{M} N^2 \frac{y^N}{N!} Q_N(T, V)\right]$$

$$= \frac{1}{V}\left[-\langle N\rangle^2 + \langle N^2\rangle\right] = \frac{1}{V}\operatorname{var}(N)$$
$$= \frac{1}{V}\left\langle \left(N - \langle N\rangle\right)^2 \right\rangle$$
$$\geq 0$$

$$\to \quad -\frac{y}{v^2}\frac{\partial v}{\partial y} \geq 0$$

$$\therefore \quad \frac{\partial v}{\partial y} \leq 0 \qquad [\text{ Since } y,\ v \geq 0 \text{ always.}]$$

Thus, in case of a discontinuity, v will jump down in the direction of increasing y.

Yang & Lee applied the theory to the 2-D Ising model and found that the roots of Z_μ all lie on the unit circle around the origin of the complex y-plane, i.e.,

$$y_k = e^{2\pi i k/(M+1)} \qquad k = 1, \ldots, M \qquad (7.263a)$$

Thus, for finite M, none of y_k is on the positive real axis, with y_1 & y_M being the closest [see Fig.7.28].

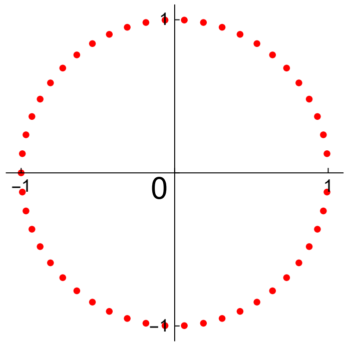

Fig.7.28. Roots of Z_μ for $M = 50$.

Returning to the PVT system considered earlier. (7.263a) inspired a grand partition function that exhibits a 1st order transition:

$$Z_\mu = (1+y)^V \frac{1 - y^V}{1 - y} \qquad (7.263)$$

Since the denominator $1 - y$ removes the positive real root $y = 1$ from $1 - y^V$, the roots of Z_μ are

$$y = -1 \quad (\,V\text{-folded}\,)$$
$$\& \quad y_k = e^{2\pi i k/V} \qquad k = 1, 2, \ldots, V-1 \qquad (7.263b)$$

Thus, Z_μ has no positive real roots if V is finite. However, there is a positive real root at $y = 1$ if $V = \infty$.

Note that the root $y = -1$ is included (not included) in $y_k = e^{2\pi i k/V}$ if V is even (odd). The factor $(1+y)^V$ therefore does not alter the positions of the roots given by $\frac{1 - y^V}{1 - y}$ as $V \to \infty$. It is added to modify the magnitude of Z_μ for real y.

Using (7.260), we have

$$\frac{P}{k_B T} = \lim_{V\to\infty} \frac{1}{V} \ln\left[(1+y)^V \frac{1 - y^V}{1 - y}\right]$$
$$= \ln(1+y) + \lim_{V\to\infty} \frac{1}{V} \ln\left(1 - y^V\right)$$

$$= \begin{cases} \ln(1+y) + \lim\limits_{V\to\infty} \dfrac{1}{V}(-y^V + \ldots) & \text{if } \; y<1 \\ \ln(1+y) + \lim\limits_{V\to\infty} \dfrac{1}{V}\left[i\,\pi + \ln y^V + \ln\left(1 - y^{-V}\right) \right] & \text{if } \; y>1 \end{cases}$$

$$= \begin{cases} \ln(1+y) & \text{if } \; y<1 \\ \ln(1+y) + \ln y & \text{if } \; y>1 \end{cases} \qquad (7.264)$$

Note that $\dfrac{P}{k_B T}$ remains continuous at the transition point $y=1$, as it must be for all y. Also, the term $\ln(1+y)$ can be traced back to the factor $(1+y)^V$ in Z_μ [see (7.263)].

(7.262) then gives

$$\frac{1}{v} = \begin{cases} \dfrac{y}{1+y} & \text{if } \; y<1 \\ \dfrac{y}{1+y} + 1 & \text{if } \; y>1 \end{cases} \qquad (7.265)$$

$$\to \quad \frac{1}{v} = \begin{cases} \dfrac{1}{2} & \text{if } \; y = 1_- \\ \dfrac{3}{2} & \text{if } \; y = 1_+ \end{cases} \qquad [\; 1_\pm \equiv 1 \pm \delta \;\; \text{with} \;\; \delta \to 0_+ \;] \qquad (7.265a)$$

so that there is a discontinuity at the transition point $y=1$. The transition is therefore 1st order.

(7.265) can be inverted as

$$y = \begin{cases} \dfrac{1}{v-1} & \text{if } \; y<1 \\ \dfrac{1-v}{2v-1} & \text{if } \; y>1 \end{cases} = \begin{cases} \dfrac{1}{v-1} & \text{if } \; v>2 \\ \dfrac{1-v}{2v-1} & \text{if } \; \dfrac{2}{3} > v > \dfrac{1}{2} \end{cases} \qquad (7.265b)$$

where the lower bound $\frac{1}{2}$ for v was added to ensure $y>0$. Meanwhile, (7.265a) gives

$$y = 1 \qquad \text{for} \quad 2 > v > \frac{2}{3} \qquad (7.265c)$$

(7.264) can therefore be converted to

$$\frac{P}{k_B T} = \begin{cases} \ln\left(1 + \dfrac{1}{v-1}\right) & \text{if } \; v>2 \\ \ln 2 & \text{if } \; 2 > v > \dfrac{2}{3} \\ \ln\left(1 + \dfrac{1-v}{2v-1}\right) + \ln\left(\dfrac{1-v}{2v-1}\right) & \text{if } \; \dfrac{2}{3} > v > \dfrac{1}{2} \end{cases}$$

$$= \begin{cases} \ln\left(\dfrac{v}{v-1}\right) & \text{if } \; v>2 \\ \ln 2 & \text{if } \; 2 > v > \dfrac{2}{3} \\ \ln\left[\dfrac{v(1-v)}{(2v-1)^2}\right] & \text{if } \; \dfrac{2}{3} > v > \dfrac{1}{2} \end{cases} \qquad (7.266)$$

For a fixed T (P), (7.266) gives an isotherm (isobar) in the P-v ($\frac{1}{T}$-v) plane [see Fig.7.29], with $2 > v > \frac{2}{3}$ being the coexistence region.

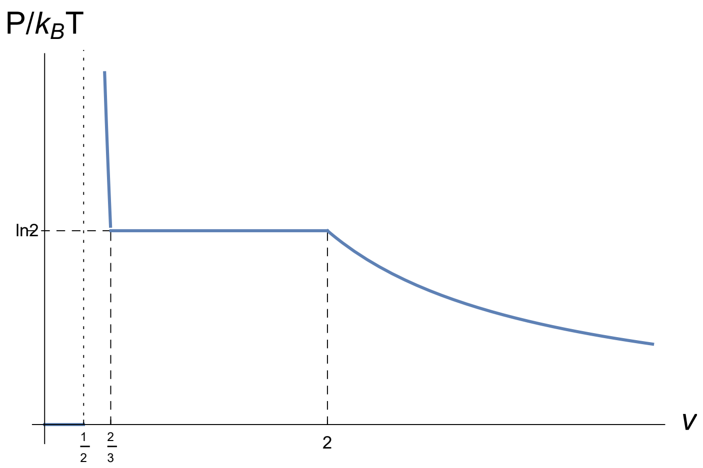

Fig.7.29. Plot of $P/k_B T$ vs v. The region $v < \frac{1}{2}$ is physically inaccessible.

Code

```
In[•]:= ranP[xRange_, yRange_] := Module[{p},
            p = { RandomReal[xRange], RandomReal[yRange]};
            If[ p⟦1⟧ > 0 && Abs[p⟦2⟧] < √p⟦1⟧ , p⟦2⟧ = RandomReal[{1, 2}] √p⟦1⟧ ];
            p
   ]

In[•]:= xRange = {-1.5, 5}; yRange = 5 {-1, 1};
        ranP[xRange, yRange]

Out[•]= {3.53249, 2.77452}

In[•]:= nR = 100;
        roots = Table[p = ranP[xRange, yRange];
            {p, {p⟦1⟧, -p⟦2⟧}}, {n, nR}] // Flatten[#, 1] &;

In[•]:= (* Fig.7.27a *)
        Plot[{√x , -√x }, {x, 0, 5},
            AxesLabel → { "Re y", "Im y"},
            PlotRange → 5 {{-.3, 1}, {-1, 1}},
            PlotStyle → Red,
            Filling → Axis, Ticks → None,
            Prolog → {Text["0", .3 {-.5, -1.5}],
                    Point[roots]}
        ]
```

In[ ]:=
```
(* Fig.7.27b *)
a = 1.5;
xroots = Table[p = {2 a , b RandomReal[{0, 1}]};
    {p, {p[[1]], -p[[2]]}}, {b, -2, 2, .5}] // Flatten[#, 1] &;
Plot[{.8 {Sqrt[a^2 - (x - a)^2], -Sqrt[a^2 - (x - a)^2]}, 1.5 {Sqrt[x - 2.02 a], -Sqrt[x - 2.02 a]}}, {x, 0, 5},
    AxesLabel → {"Re y", "Im y"},
    PlotRange → 5 {{-.3, 1}, {-1, 1}},
    PlotStyle → Red,
    Filling → Axis, Ticks → None,
    Prolog → {Text["0", .3 {-.5, -1.5}],
        Point[roots], Point[xroots]}
]
```

In[ ]:=
```
(* Fig.7.28 *)
m = 50;
rL = Table[θ = 2 π k / m; {Cos[θ], Sin[θ]}, {k, 1, m - 1}];
ListPlot[rL,
    AxesLabel → {"Re y", "Im y"},
    PlotRange → 1.1 {{-1, 1}, {-1, 1}},
    Ticks → {{-1, 0, 1}, {-1, 0, 1}},
    PlotStyle → {PointSize[.02], Red}, AspectRatio → Automatic,
    Prolog → {Text["0", -.1 {1, 1}]
        }
]
```

In[ ]:=
$$P[v\_] := \begin{cases} \text{Log}\left[\frac{v}{v-1}\right] & v > 2 \\ \text{Log}[2] & 2 \geq v \geq \frac{2}{3} \\ \text{Log}\left[\frac{v\,(1-v)}{(2v-1)^2}\right] & \frac{2}{3} > v > \frac{1}{2} \end{cases}$$

In[ ]:=
```
(* Fig.7.29 *)
Plot[P[v], {v, .26, 4},
    AxesLabel → {"v", "P/k_B T"},
    Ticks → {{1/2, 2/3, 2}, {{Log[2], "ln2"}}},
    Prolog → {Dashed, Line[{{2/3, 0}, {2/3, Log[2]}}],
        Line[{{2, 0}, {2, Log[2]}}],
        Line[{{0, Log[2]}, {2/3, Log[2]}}],
        Dotted, Line[{{1/2, 0}, {1/2, 2 Log[2]}}]
    }
]
```