8.333 Fall 2025 Recitations 8: Interactions recap

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These notes are largely a conglomeration of the previous years' recitation notes by Julien Tailleur, Arkya Chatterjee, and Sara Dal Cengio.

For a more comprehensive resource, see Ch. 5 of Mehran Kardar's *Statistical Physics of Particles,* along with Ch. 7 of his *Statistical Physics of Fields* for section 2. For even more information about the statistical mechanics of gases and liquids, you can check out Hansen & McDonald's *Theory of Simple Liquids.*

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1 Interacting gases

Consider a classical gas of N particles interacting via the spherically-symmetric potential $U(r)$, with the Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} U(r_{ij}) \tag{1}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and for any vector $\mathbf{v}$, $v = |\mathbf{v}|$.

In the previous chapter, we learned many ways to relate thermodynamic variables to their conjugates (e.g. $P = T\frac{\partial S}{\partial V}\big|_{E,N}$ and $\frac{1}{T} = \frac{\partial S}{\partial E}\big|_{E,N}$). We also learned a few equations of state, relating thermodynamic variables to other thermodynamic variables which are *not* their conjugates (e.g. $PV = Nk_BT$ for the ideal gas; $E = N\epsilon/(1+e^{\beta\epsilon})$ for the 2-level system). The thermodynamic relationships remain true in any extensive system, including our interacting gas (1). This section will be dedicated to finding its equations of state.

1.1 Introducing the virial expansion

We have already studied extremely dilute (ideal) gases. What about the leading-order correction due to interactions? We will calculate the pressure as an expansion in the density $n = N/V$ as follows:

$$\beta P = n\left[1 + B_2(T)n + B_3(T)n^2 + \dots\right] . \tag{2}$$

This is called the **virial expansion**. Recall the thermodynamic relation

$$PV = -G(\mu, T, V) , \tag{3}$$

where $G(\mu, T, V)$ is the grand potential

$$G(\mu, T, V) = -k_B T \ln Q(\mu, T, V) \, , \qquad Q(\mu, T, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, T, V) \, . \tag{4}$$

Thus we will first calculate the canonical partition function $Z(N, T, V)$, to get the grand partition function $Q(\mu, T, V)$, then the grand potential $G(\mu, T, V)$, then the pressure P. This roundabout method just turns out to be the most convenient in practice.

1.2 The canonical partition function

To do so, we first calculate the canonical partition function. Let's calculate this, and integrate out the momentum variables:

$$Z(T, V, N) = \frac{1}{N!} \int \prod_{i=1}^{N} \left(\frac{d^3\mathbf{r}_i d^3\mathbf{p}_i}{h^3} \right) \exp\left[-\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i<j} U(r_{ij}) \right] = \frac{1}{N!} \left(\frac{1}{\Lambda^3} \right)^N \int \prod_{i=1}^{N} d^3\mathbf{r}_i \exp\left[-\beta \sum_{i<j} U(r_{ij}) \right] \tag{5}$$

$$\equiv \frac{1}{N!} \left(\frac{1}{\Lambda^3} \right)^N \left\langle \exp\left[-\sum_{i<j} v_{ij} \right] \right\rangle^0 \tag{6}$$

where we have defined $v(r) \equiv \beta U(r)$; $v_{ij} \equiv v(r_{ij})$; and the spatial integration operation:

$$\langle \mathcal{O}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \rangle^0 \equiv \int \prod_{i=1}^{N} d^3\mathbf{r}_i \mathcal{O}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \, . \tag{7}$$

We can re-write this as

$$Z(T, V, N) = \frac{1}{N!} \left(\frac{1}{\Lambda^3} \right)^N \left\langle \prod_{i<j} e^{-\beta v_{ij}} \right\rangle^0 \, . \tag{8}$$

This integral is, in general, very hard to do. We must resort to perturbative methods to perform it. There are two possible approaches:

1. Taylor expand in v_{ij}; i.e. for high temperatures relative to interaction forces
2. Define the "Mayers function" $f(r_{ij}) \equiv e^{-\beta v(r_{ij})} - 1$, visualized in Fig. 1, and Taylor expand in $f(r_{ij})$.

Because we are interested in forces with short-ranged repulsion, i.e. with $v(r) \to \infty$ as $r \to 0$, approach 1 is not very well-defined. Noting that

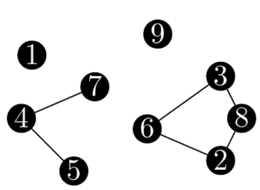
$$f_{ij} \equiv f(r_{ij}) \longrightarrow \begin{cases} 0 \, , & r_{ij} \to \infty \\ -1 \, , & r_{ij} \to 0 \end{cases} \, , \tag{9}$$

an expansion in this quantity is more well-defined. Thus, we will take approach 2.

We can re-write the partition function (8) in terms of the Mayers functions as

$$Z(N, V, T) N! \Lambda^{3N} = \left\langle \prod_{i<j} (f_{ij} + 1) \right\rangle^0 = 1 + \sum_{i<j} \langle f_{ij} \rangle^0 + \sum_{i<j} \sum_{k<\ell} \langle f_{ij} f_{k\ell} \rangle^0 + \ldots \, . \tag{10}$$

There's a useful diagrammatic representation for this sum. Each term is an integral over all coordinates, containing some factors of f_{ij}, $f_{k\ell}$, etc. Represent each particle by a point, and a factor of f_{ij} as an edge connecting points i and j. Then, Eq. (10) is simply the sum over all graphs with N distinguishable nodes. For example, if $N = 9$, then in the 6th term of Eq. (10) there appears the following term:



$$= \int \left(\prod_{i=1}^{9} d^3\mathbf{r}_i \right) f_{47} f_{45} f_{26} f_{28} f_{38} f_{36}$$

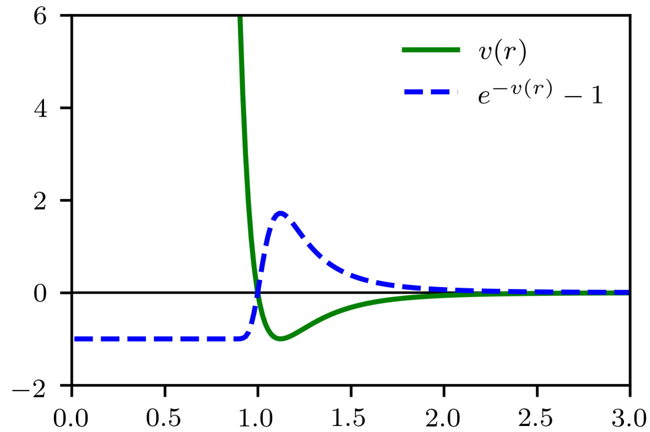
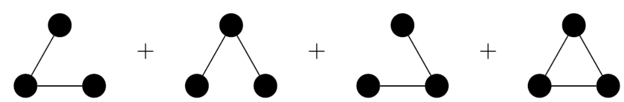


Figure 1:A typical scaled interaction potential $v(r) = \beta U(r)$, and the corresponding Mayers function $f(r) = e^{-v(r)} - 1$.

Let us now rearrange the summation based on possible groupings of points. For a set of integers $\{n_\ell\}$ such that $\sum_\ell \ell n_\ell = N$, there are $W[\{n_\ell\}]$ ways of grouping the points into ℓ group of n_ℓ ordered points, with

$$W[\{n_\ell\}] = \frac{N!}{\prod_\ell (\ell!)^{n_\ell} n_\ell!} \, . \tag{11}$$

For a group of ℓ labeled points, let's define the sum of all its possible connected graphs as b_ℓ. (Since all particles are identical, the choice of points doesn't matter.) For example,

$b_3 =$ 

Then, we can re-write Eq. (10) as

$$Z(N,V,T) = \frac{1}{N!\Lambda^{3N}} \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} \frac{N!}{\prod_\ell (\ell!)^{n_\ell} n_\ell!} \prod_\ell b_\ell^{n_\ell} \, . \tag{12}$$

To simplify this, we move to the grand canonical ensemble.

1.3 The grand partition function

Let's now calculate the grand partition function $Q(\mu, V, T)$:

$$Q(\mu,V,T) = \sum_{N=0}^{\infty} Z(N,V,T) e^{\beta\mu N} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda^3}\right)^N \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} \frac{N!}{\prod_\ell (\ell!)^{n_\ell} n_\ell!} \prod_\ell b_\ell^{n_\ell} \, . \tag{13}$$

Note that

$$\sum_{N=0}^{\infty} \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} f(N, \{n_\ell\}) = \sum_{\{n_\ell\}} f\Big(\sum_\ell \ell n_\ell, \{n_\ell\}\Big). \tag{14}$$

Define also the fugacity $z \equiv e^{\beta\mu}/\Lambda^3$. Thus, we can write Eq. (13) as

$$Q(\mu,V,T) = \sum_{\{n_\ell\}} z^{\sum_\ell \ell n_\ell} \prod_\ell \frac{b_\ell^{n_\ell}}{\prod_\ell (\ell!)^{n_\ell} n_\ell!} = \sum_{\{n_\ell\}} \prod_\ell \frac{1}{n_\ell!} \left(\frac{b_\ell z^\ell}{\ell!}\right)^{n_\ell} \tag{15}$$

$$= \prod_\ell \sum_{n_\ell=0}^{\infty} \frac{1}{n_\ell!} \left(\frac{b_\ell z^\ell}{\ell!}\right)^{n_\ell} = \prod_\ell \exp\left[z^\ell \frac{b_\ell}{\ell!}\right] = \exp\left[\sum_{\ell=1}^{\infty} z^\ell \frac{b_\ell}{\ell!}\right] . \tag{16}$$

Thus the grand potential is

$$G(\mu, V, T) = -k_B T \ln Q(\mu, V, T) = -k_B T \sum_{\ell=1}^{\infty} z^\ell \frac{b_\ell}{\ell!} \tag{17}$$

and finally

$$P = \frac{k_B T}{V} \sum_{\ell=1}^{\infty} z^\ell \frac{b_\ell}{\ell!} \ . \tag{18}$$

Now we can see why we moved to the grand canonical ensemble.

Finally, note that each term in each b_ℓ contains an integral over the center of mass of all particles, which contributes a factor of V, making them extensive. We thus define new intensive quantities

$$c_\ell \equiv \frac{b_\ell}{V} \tag{19}$$

to re-write

$$G(\mu, V, T) = -k_B T V \sum_{\ell=1}^{\infty} z^\ell \frac{c_\ell}{\ell!} \tag{20}$$

$$\beta P = \sum_{\ell=1}^{\infty} z^\ell \frac{c_\ell}{\ell!} \ . \tag{21}$$

1.4 The virial expansion

Let's now turn Eq. (21) into a virial expansion (2). Now, N is a fluctuating quantity, but in a large system is well-approximated by its average

$$N = -\frac{\partial G}{\partial \mu} = V \sum_{\ell=1}^{\infty} \frac{z^\ell c_\ell}{(\ell-1)!} \qquad \Longrightarrow \qquad n = \sum_{\ell=1}^{\infty} \frac{z^\ell c_\ell}{(\ell-1)!} \ . \tag{22}$$

We would like to eliminate z in favor of n. We can do this perturbatively in n:

$$z = n - c_2 n^2 + \left(2c_2^2 - \frac{c_3}{2}\right) n^3 + \mathcal{O}(n^4) \tag{23}$$

so that

$$\beta P = \left[n - c_2 n^2 + \left(2c_2^2 - \frac{c_3}{2}\right) n^3\right] c_1 + \left(n - c_2 n^2\right)^2 \frac{c_2}{2!} + n^3 \frac{c_3}{3!} + \mathcal{O}(n^4) \tag{24}$$

$$= n c_1 + n^2 \left(\frac{c_2}{2} - c_1 c_2\right) + n^3 \left[c_1 \left(2c_2^2 - \frac{c_3}{2}\right) - c_2^2 + \frac{c_3}{3!}\right] + \mathcal{O}(n^4) \ . \tag{25}$$

Using $c_1 = 1$, we find

$$\beta P = n - \frac{c_2}{2} n^2 + \left(c_2^2 - \frac{c_3}{3}\right) n^3 + \mathcal{O}(n^4) \equiv n + \sum_{\ell=2}^{\infty} B_\ell(T) n^\ell \ . \tag{26}$$

Let's calculate the first few contributions:

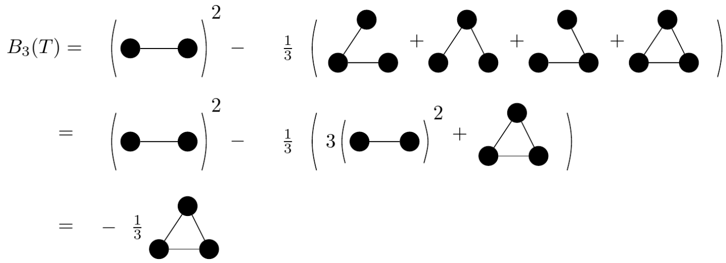
$$B_2(T) = -\frac{c_2}{2} = -\frac{1}{2V} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 f(r_{12}) = -\frac{1}{2} \int d^3\mathbf{r} \left(e^{-v(r)} - 1\right) \tag{27}$$

$$B_3(T) = c_2^2 - \frac{c_3}{3} = \left(\int d^3\mathbf{r} f(r)\right)^2 - \frac{1}{3V} \left[\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 f(r_{12}) f(r_{23}) + \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 f(r_{12}) f(r_{23}) f(r_{31})\right] \tag{28}$$

$$= \left(\int d^3\mathbf{r} f(r)\right)^2 - \frac{1}{3} \left[3 \int d^3\mathbf{r}_1 f(r_1) \int d^3\mathbf{r}_2 f(r_2) + \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 f(r_{12}) f(|\mathbf{r}_{21} - \mathbf{r}_{31}|) f(r_{31})\right] \tag{29}$$

$$= -\frac{1}{3} \int d^3\mathbf{r}_{12} d^3\mathbf{r}_{13} f(r_{12}) f(|\mathbf{r}_{12} - \mathbf{r}_{13}|) f(r_{13}) \ . \tag{30}$$

In calculating $B_3(T)$, we have found that only the **1-particle irreducible** diagram remains; that is, diagrams that can't be made disconnected by severing a single link:



This turns out to be true at all orders:

$$B_\ell(T) = -\frac{(\ell-1)}{\ell!} c_\ell \Big|_{1\text{PI}} \, . \tag{31}$$

I won't prove it, but it's useful to keep in mind.

Thus we can write our equation of state to 3rd order as

$$\beta P = n - \frac{n^2}{2} \int d^3\mathbf{r} \left(e^{-v(r)} - 1\right) - \frac{n^3}{3} \int d^3\mathbf{r}_{12} d^3\mathbf{r}_{13} \left(e^{-v(r_{12})} - 1\right)\left(e^{-v(r_{13})} - 1\right)\left(e^{-v(\mathbf{r}_{12} - \mathbf{r}_{13})} - 1\right) + \mathcal{O}(n^4) \, . \tag{32}$$

1.5 Stability considerations

Recall our in-class discussion of mechanical balance in a canonical ensemble (N, V, T). If the system is split by a movable wall into two chambers of volumes V_1 and $V_2 = V - V_1$, then the wall will relax to a position such that the total free energy

$$F_1(N_1, V_1, T) + F_2(N_2, V - V_1, T) \equiv F_1(V_1) + F_2(V - V_1) \tag{33}$$

is minimized. This requires the following two conditions:

$$\frac{\partial F_1(V_1)}{\partial V_1}\bigg|_{V_1^*} - \frac{\partial F_2(V_2)}{\partial V_2}\bigg|_{V - V_1^*} = 0 \tag{34}$$

$$\frac{\partial^2 F_1(V_1)}{\partial V_1^*}\bigg|_{V_1^*} + \frac{\partial^2 F_2(V_2)}{\partial V_2^2}\bigg|_{V = V_1^*} > 0 \, . \tag{35}$$

The second condition is a stability condition. In terms of the pressure, this is

$$P_1 = P_2 \tag{36}$$

$$\frac{\partial P_1}{\partial V_1} + \frac{\partial P_2}{\partial V_2} < 0 \, . \tag{37}$$

In the limit of very large V_2 such that P_2 is fixed, we find

$$\frac{\partial P}{\partial V} < 0 \, . \tag{38}$$

This makes intuitive sense: if decreasing the volume also decreased the pressure, the system would be unstable to collapse.

2 The Ising model

In this section, we will show that the high-temperature limit of the Ising model has quite a similar treatment to a dilute gas. We will work without an external field h, and in the 2d lattice. Recall the Hamiltonian, for spins $s_i \in \{-1, +1\}$:

$$\beta H[\vec{s}] = -\beta J \sum_{\langle i,j \rangle} s_i s_j \equiv -K \sum_{\langle i,j \rangle} s_i s_j \tag{39}$$

where the summation is over all pairs i, j, and we have defined $K = \beta J$.

2.1 Introducing the high-temperature expansion

We are interested in the possibility of a phase transition in the Ising model, and maybe we aren't sure about the mean-field approximation. Note that, using the fact that $(s_i s_j)^2 = 1$, we can exactly re-write $e^{K s_i s_j}$ as

$$e^{K s_i s_j} = 1 + K s_i s_j + \frac{K^2 (s_i s_j)^2}{2} + \frac{K^3 (s_i s_j)^3}{3!} + \frac{K^4 (s_i s_j)^4}{4!} + \ldots = 1 + K s_i s_j + \frac{K^2}{2} + \frac{K^3 s_i s_j}{3!} + \frac{K^4 s_i s_j}{4!} + \ldots \tag{40}$$

$$= \frac{e^K + e^{-K}}{2} + \frac{e^K - e^{-K}}{2} s_i s_j = (1 + s_i s_j \tanh K) \cosh K \equiv (1 + t s_i s_j) \cosh K \ . \tag{41}$$

Note that a high-temperature expansion is a low-β expansion and thus a low-K expansion, and this is equivalent to a low-$t = \tanh K$ expansion.

Suppose the system has N_b edges, or bonds. We can thus write the partition function as

$$Z = (\cosh K)^{N_b} \sum_{\vec{s}} \prod_{\langle i,j \rangle} (1 + t s_i s_j) \equiv (\cosh K)^{N_b} \left\langle \prod_{\langle i,j \rangle} (1 + t s_i s_j) \right\rangle^0 . \tag{42}$$

We have introduced the averaging operation

$$\langle \mathcal{O}[\vec{s}] \rangle^0 = \sum_{\vec{s}} \mathcal{O}[\vec{s}]. \tag{43}$$

Note the similarity between Eq. (10) and Eq. (42). We can likewise write it as a series

$$\frac{Z}{(\cosh K)^{N_b}} = 1 + t \sum_{\langle i,j \rangle} \langle s_i s_j \rangle^0 + t^2 \sum_{\langle i,j \rangle} \sum_{\langle k,\ell \rangle \neq \langle i,j \rangle} \langle s_i s_j s_k s_\ell \rangle^0 + \ldots \ . \tag{44}$$

The sum is over bonds $\langle i, j \rangle$, thus $\langle k, \ell \rangle \neq \langle i, j \rangle$ implies that both indices are not equal. Thus, this sum is over all *graphs* with nodes given by lattice sites, and edges given by the bonds.

Note that if a site i appears only once in a term, e.g. $\langle s_i s_j s_k s_\ell \rangle^0$ with $j, k, \ell \neq i$, it can be rearranged as

$$\langle s_i s_j s_k s_\ell \rangle^0 = \sum_{s_j, s_k, s_\ell} s_j s_k s_\ell \underbrace{\sum_{s_i} s_i}_{=0} = 0 \ . \tag{45}$$

The same is true if it appears 3 times, or any odd number of times. Thus only the terms where each spin appears an even number of times remain. This corresponds to only closed loops, so the sum is over closed loops. We find the first few terms in the partition function of the 2d lattice

$$\frac{Z}{(\cosh K)^{2N}} = 2^N \left[1 + N (\tanh K)^4 + 2N (\tanh K)^6 + \mathcal{O}((\tanh K)^8) \right] . \tag{46}$$

Completing this sum to arbitrary order is nontrivial, since it requires knowledge about the number of closed, non-self-overlapping loops in the 2d lattice (see 7.6-7.7 of Kardar's *Statistical Physics of Fields*). However, there are some uncontrolled approximations that we can make, with the knowledge in hindsight that they give the right answer.

Let's first restrict ourselves to sums over *connected* closed loops; i.e. loops with only one component. Let's also, for now, allow self-intersection and self-overlapping. A closed loop of length L must have even L, so $L = 2n$. It must consist of k steps to the right, k steps to the left, $n - k$ steps up, and $n - k$ steps down. These can occur in any order, and it can start and end at any of the N lattice points. Because the loop could start at any of the L points, we correct this overcounting by dividing by L. Thus, the total number W_L of such loops is

$$W_{2n} = \frac{N}{2n} \sum_{k=0}^{n} \frac{(2n)!}{k! k! (n-k)! (n-k)!} = \frac{N}{2n} \frac{(2n)!}{n! n!} \sum_{k=0}^{n} \binom{2n}{k}^2 = \frac{N}{2n} \binom{2n}{n}^2 . \tag{47}$$

We have used a combinatorial identity. This, however, only keeps track of one-component loops. The partition function (42) is a sum over all closed loops, with any number of components. To calculate this, we can note that

$$\exp\left(\sum_{n=0}^{\infty} W_{2n} t^{2n} \right) = 1 + \sum_{n=0}^{\infty} W_{2n} t^{2n} + \frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} W_{2n} W_{2m} t^{2n+2m} + \frac{1}{3!} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{\ell=0}^{\infty} W_{2n} W_{2m} W_{2\ell} t^{2n+2m+2\ell} + \ldots \tag{48}$$

is *almost* equal to the sum over all closed loops, including the disconnected ones. It overcounts a bit, because it's possible that a loop represented by W_{2n} and a loop represented by W_{2m} share some bonds. However, let's ignore this for now and proceed.

We immediately find that

$$\ln Z \approx \ln\left[2^N (\cosh K)^{2N} \exp\left(\sum_{n=0}^{\infty} W_{2n} t^{2n}\right)\right] = N \ln[2\cosh^2 K] + \sum_{n=0}^{\infty} W_{2n} t^{2n} = N \ln[2\cosh^2 K] + \sum_{n=0}^{\infty} \frac{N}{2n} \binom{2n}{n}^2 t^{2n} \tag{49}$$

$$\implies \frac{\ln Z}{N} = \ln[2\cosh^2 K] + \sum_{n=0}^{\infty} \frac{(\tanh K)^{2n}}{2n} \binom{2n}{n}^2 . \tag{50}$$

Does the series converge for every K? Use the ratio test:

$$a_n \equiv \frac{(\tanh K)^{2n}}{2n} \binom{2n}{n}^2 \tag{51}$$

$$\implies \lim_{n\to\infty} \left|\frac{a_{n+1}}{a_n}\right| = \lim_{n\to\infty} \frac{[2(n+1)]![2(n+1)]!n!n!}{[(2n)!]^4[(n+1)!]^4} \frac{n}{n+1} \tanh^2 K = \lim_{n\to\infty} \frac{(2n+2)^2(2n+1)^2}{(n+1)^4} \frac{n}{n+1} \tanh^2 K \tag{52}$$

$$= \lim_{n\to\infty} \frac{4n(2n+1)^2}{(n+1)^3} \tanh^2 K = 16 \tanh^2 K . \tag{53}$$

This in fact converges only when

$$\tanh^2 K < 1/16 \qquad \implies \qquad \tanh K < 1/4 . \tag{54}$$

Around $\tanh K \sim 1/4$, there is a singularity, which is the signal for a phase transition. This can be proven in a more careful exact calculation.