AEP 4230: Interacting classical systems and phase transitions

Contents

In this section, we introduce some basic concepts in applying statistical mechanics to systems with interactions. In the previous section, we dealt with systems where the Hamiltonian was a sum of one-particle terms and the associated partition function could be expressed as a product of the individual one-particle partition functions. This non-interacting structure renders these problems exactly and simply solvable. But arguably the most striking and fascinating phenomena in equilibrium statistical mechanics, such as phase transitions like the melting of ice or the evaporation of water, are a byproduct of interactions. The topic of interactions in statistical mechanics is a complex and fascinating one and an entire course could be devoted to this topic alone. Instead, this short unit is devoted to just scratching the surface, developing a few important ideas, among them: the van der Waals equation of state, mean-field theory, critical points, and fluctuations near phase transitions.

I. VAN DER WAALS EQUATION OF STATE

A. Cluster expansion

Recall in the previous unit that in order to compute the equation of state of an ideal gas ($P(T, V) = ...$), we can evaluate the partition function in the canonical ensemble and then take a derivative of the associated free energy. We can also compute the grand partition function in the grand canonical ensemble, compute the grand potential and use $\mathcal{G} = -PV$. It turns out that the analysis is somewhat simpler in the grand canonical ensemble and so we undertake the analysis there. In any event, the grand canonical partition function is related to the partition function of an N particle system by $Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N$, where Z_N is the canonical partition function. The canonical partition function is given as usual as

$$Z_N = \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3q_i d^3p_i}{h^3} \, \exp\left[-\beta \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{q}_1 \cdots \mathbf{q}_n) \right) \right], \tag{1}$$

where $U(\mathbf{q}_1 \cdots \mathbf{q_n})$ is the potential energy associated with any given configuration of the gas. Before describing the typical form of this potential, we note that if $U = 0$, this reduces to the ideal gas partition function $Z_{\text{ideal}} = \frac{1}{N!}(V/\lambda^3)^N \equiv \tilde{V}^N/N!$. We already see that the momentum degrees of freedom can be integrated, and we may write

$$Z_N = \frac{\tilde{V}^N}{N!} \frac{1}{V^N} \int \prod_{i=1}^{N} d^3q_i \, e^{-\beta U(\mathbf{q}_1 \cdots \mathbf{q}_n)} = \frac{\tilde{V}^N}{N!} \langle e^{-\beta U} \rangle^0. \tag{2}$$

The last equation we will not use much but conceptually it is important to see that the partition function in the interacting case is a product of the ideal gas partition function and an average Boltzmann factor associated with the interaction, averaged against the ideal gas position probability distribution (which is just the uniform distribution with probability density V^{-N}). The averaging against the ideal gas probability distribution is denoted by the superscript 0.

One approach to attacking this problem is to expand the exponential in the previous equation and evaluate averages order-by-order, treating βU as a perturbation parameter. This approach is called the *cumulant expansion* and can be made to work, but it is complicated by the fact that the potential U diverges when two particles approach each other. A canonical potential energy function for an interacting gas is a two-body potential of the form

$$U = \sum_{i>j=1}^{N} V(r_{ij}), \tag{3}$$

where $r_{ij} = |\mathbf{q}_i - \mathbf{q}_j|$.

The potential function V has different short-range and long-range behaviors. To capture the physics, we can take a simplified model for the potential where, when the particles are greater than distance r_0 apart, their interactions are governed by the usual van der Waals potential (whose origin we will get to at the end of this class):

$$V(r) = -u_0(r_0/r)^6, \ r > r_0, \tag{4}$$

where u_0 is a constant representing the van der Waals interaction energy at $r = r_0$. When the particles get closer than r_0 from each other, we treat the potential as infinitely repulsive

$$V(r) = +\infty, \ r \leq r_0. \tag{5}$$

In other words, we treat the gas as a collection of hard spheres that attract each other. The true potential (often taken as a Lennard-Jones potential) is softer than an abrupt jump to infinity, but still goes to infinity as $r \to 0$ and does so very rapidly (in the Lennard-Jones description, as r^{-12}). Therefore the true potential essentially also has an infinity that undermines a naive Taylor expansion.

It turns out that a much better expansion parameter is $e^{-\beta U} - 1$: when $U \to \infty$, this quantity approaches -1 instead of $-\infty$. When there are no interactions, this quantity vanishes, and in general this quantity is small if the average interparticle separation of $d \sim n^{-1/3}$ is large. Therefore, we express the partition function as

$$Z_N = \frac{\tilde{V}^N}{N!}\frac{1}{V^N}\int \prod_{i=1}^{N} d^3q_i e^{-\beta \sum\limits_{i>j} V(r_{ij})} = \frac{\tilde{V}^N}{N!}\frac{1}{V^N}\int \prod_{i=1}^{N} d^3q_i \prod_{\alpha>\beta=1}^{N} (1 + f_{\alpha\beta}), \tag{6}$$

where $f_{\alpha\beta} = e^{-\beta V(r_{\alpha\beta})} - 1$.

The basic idea is to now recognize that for a given product of fs, they will only be non-vanishing if the two particles indexed are close to each other. For example, the quantity $f_{12}(r)$ only becomes significant as the distance between particles 1 and 2 approaches r_0. Similarly, the quantity $f_{12}f_{34}$ only is significant is 1 and 2 are close *and* 3 and 4 are close (with no restriction imposed between for example 1 and 3 or 1 and 4 etc.). Now consider a quantity like $f_{12}f_{34}f_{15}$. This requires 1 to be close to 2 and 5 simultaneously, representing a three-body collision. We will make the approximation that configurations of particles involving three-body collisions never need to be taken into account, and that we only worry about configurations of two-body collisions, even if there are many such two-body collisions in a given configuration. Therefore, we shall include all terms where we have products of fs where all indices are different.

In other words, we wish to evaluate

$$Z_N = \frac{\tilde{V}^N}{N!}\frac{1}{V^N}\sum_{k=0}^{\infty} S_k, \tag{7}$$

where

$$S_k = \int \prod_{i=1}^{N} d^3q_i \times (\text{sum of all terms with } k \text{ instances of } f \text{ where no index is shared})\,. \tag{8}$$

You can convince yourself that all such terms in S_k are equal and so $S_k = \mathcal{N}_k I_k$ where $\mathcal{N}_k$ is the number of such terms and

$$I_k = \int d^3q_1 \cdots d^3q_{2k} f_{12} f_{34} \cdots f_{2k-1,2k} \int d^3q_{2k+1} \cdots d^3q_N = V^{N-2k} \times \left(\int d^3q_1 d^3q_2 f_{12} \right)^k, \tag{9}$$

which under a change in variables can be written as

$$I_k = V^{N-2k} \times \left(V \int d^3r (e^{-\beta V(r)} - 1) \right)^k = V^{N-k} \times \left(\int dr\, 4\pi r^2 (e^{-\beta V(r)} - 1) \right)^k \equiv V^{N-k} b^k. \tag{10}$$

Therefore, what we must now evaluate is $\mathcal{N}_k$. This is simply a product of two factors: for the kth term, we need to pick $2k$ particles out of N (this guarantees that all the indices are different). The number of choices is simply $\binom{N}{2k}$. Then we have to ask how many ways we can take those 2k indices and group them into pairs. This number is $(2k-1)!! = \frac{(2k)!}{2^k k!}$. Therefore:

$$Z_N = \frac{\tilde{V}^N}{N!} \sum_{k=0}^{N/2} \frac{N!}{(N-2k)!k!} \left(\frac{b}{2V} \right)^k. \tag{11}$$

From this, we may compute the grand partition function as

$$\mathcal{Q} = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{\tilde{V}^N}{N!} \sum_{k=0}^{N/2} \frac{N!}{(N-2k)!k!} \left(\frac{b}{2V} \right)^k = \sum_{k=0}^{\infty} \sum_{N=2k}^{\infty} e^{\beta\mu N} \frac{\tilde{V}^N}{(N-2k)!k!} \left(\frac{b}{2V} \right)^k. \tag{12}$$

where I have used the fact that the sums can be reversed. Taking $N \to N + 2k$ yields

$$\mathcal{Q} = \sum_{k=0}^{\infty} \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{\tilde{V}^N}{N!k!} \left(e^{2\beta\mu} \frac{bV}{2\lambda^6} \right)^k = \exp\left[e^{\beta\mu} \frac{V}{\lambda^3} \right] \exp\left[e^{2\beta\mu} \frac{bV}{2\lambda^6} \right] = \exp\left[e^{\beta\mu} \frac{V}{\lambda^3} \left(1 + e^{\beta\mu} \frac{b}{2\lambda^3} \right) \right]. \tag{13}$$

The pressure is then found as (from $\mathcal{G} = -k_BT \ln \mathcal{Q} = -PV$)

$$\frac{P}{k_BT} = \frac{e^{\beta\mu}}{\lambda^3} \left(1 + e^{\beta\mu} \frac{b}{2\lambda^3} \right), \tag{14}$$

which in the limit of no interactions, reduces to the form expected for the ideal gas. We now wish to find an "updated" equation of state in the presence of these interactions, computed up to "second-order" in the cluster expansion (considering only 2-particle clusters).

1. Van der Waals approximate equation of state from cluster expansion

We can use the second-order cluster expansion of the partition function to approximately reproduce the van der Waals equation of state in the high temperature (and low density) limit. At higher density, higher-order terms in the cluster expansion become important. To do this, we need to express P as a function of the number density in the gas n. The number density is given by

$$n = \frac{1}{V}\frac{\partial \ln Q}{\partial(\beta\mu)} = .\frac{1}{\lambda^3}\left(e^{\beta\mu} + e^{2\beta\mu}\frac{b}{\lambda^3}\right). \tag{15}$$

To proceed, it will be useful to define $z = e^{\beta\mu}$ and $p = P/k_BT$ so that we may write $p = \frac{z}{\lambda^3} + \frac{bz^2}{2\lambda^6}$ and $n = \frac{z}{\lambda^3} + \frac{bz^2}{\lambda^6}$. We can solve for n as $z = \frac{\lambda^3}{2b}(-1 + \sqrt{1 + 4nb}) \approx \frac{\lambda^3}{2b}(2nb - 2(nb)^2) = n\lambda^3(1 - nb)$. Plugging this in to the expression for the pressure and retaining terms only up to second order in the density, we arrive at

$$\frac{P}{k_BT} = n + B_2 n^2, \tag{16}$$

where $B_2 = -b/2$ is called the *second virial coefficient.*

To proceed, we should evaluate b for the van der Waals gas. We take the simplified form of the potential described earlier. Performing the integration at high temperature, so that we may Taylor expand the exponential to first order in βV, we find:

$$B_2 = \frac{\Omega}{2}\left(1 - \frac{u_0}{k_BT}\right), \tag{17}$$

where $\Omega \equiv \frac{4}{3}\pi r_0^3$ is eight times the atomic volume (or simply the "excluded volume" of a collision). Plugging this into the equation of state, we find

$$\left(P + a\left(\frac{N}{V}\right)^2\right) = \frac{Nk_BT}{V}\left(1 + b\frac{N}{V}\right) \approx \frac{Nk_BT}{V - Nb}, \tag{18}$$

where we have defined $a = \frac{1}{2}\Omega u_0$ and $b = \frac{1}{2}\Omega$. This is the celebrated van der Waals equation of state. The equation has a greater range of validity than the approximation suggests (for example the equality of $1 + x$ and $(1 - x)^{-1}$ is only approximate for small x while it turns out that the $(1 - x)^{-1}$ form holds out to even higher density). We will get at this result from mean-field theory soon. But we see now that by approximating the partition function in the interacting case using $e^{-\beta V} - 1$ as an expansion parameter, it is possible to find experimentally accurate corrections to the ideal gas law!

The interpretation of the terms in the van der Waals equation is as follows: there is an *excluded volume* which tends to enhance the pressure because of the hard-core repulsion between atoms. There is a reduction in pressure due to the van der Waals attraction because the molecules, as they approach the walls of their container, lose energy as they exit the potential made by all of the other atoms.

B. Van der Waals equation from mean-field theory

There is a powerful set of techniques under the guise of *mean-field theory* that allows us to make simplifications of these complex interacting problems. The core idea of mean-field theory is that we can think of each particle as being feeling an average one-body potential due to all other particles. In the case of a uniform density gas, this is a uniform attractive potential felt by each particle that depends on the overall density. To see how this arises, let us write

$$Z_N = \frac{\tilde{V}^N}{N!}\frac{1}{V^N}\int \prod_{i=1}^{N} d^3q_i\, e^{-\beta U(\mathbf{q}_1\cdots\mathbf{q}_n)}. \tag{19}$$

We split the potential into the repulsive part at $r < r_0$ and the attractive part at $r > r_0$:

$$U \equiv U_{\text{rep}} + U_{\text{att}} \equiv \sum_{i>j=1}^{N} V_{\text{rep}}(r_{ij}) + V_{\text{att}}(r_{ij}), \tag{20}$$

where $V_{\text{rep}}(r_{ij}) = (\infty)\theta(r_0 - r_{ij})$ and $V_{\text{att}}(r_{ij}) = -u_0(r_0/r)^6\theta(r_{ij} - r_0)$. We may then re-express the partition function as

$$Z_N = \frac{\tilde{V}^N}{N!}\frac{1}{V^N}\int \prod_{i=1}^{N} d^3q_i\, e^{-\beta U_{\text{att}}(\mathbf{q}_1\cdots\mathbf{q}_n)}\eta(\mathbf{q}_1\cdots\mathbf{q}_N), \tag{21}$$

where $\eta(\mathbf{q}_1\cdots\mathbf{q}_N) = 0$ for any configuration where at least two particles are less than a distance of r_0 apart. The remaining attractive potential, we may re-write as follows:

$$U_{\text{att}} = \frac{1}{2}\int d^3r d^3r' V(\mathbf{r}-\mathbf{r}')n(\mathbf{r})n(\mathbf{r}'), \tag{22}$$

where $n(\mathbf{r}) = \sum\limits_{ij} \delta(\mathbf{r}-\mathbf{r}_{ij})$. This is exactly equivalent to $\sum\limits_{i>j} V_{\text{att}}(r_{ij})$ provided we define $V_{\text{att}}(0) = 0$.

The mean-field approximation amounts to expressing

$$n(\mathbf{r}) = \langle n(\mathbf{r})\rangle + \delta n(\mathbf{r}), \tag{23}$$

where $\delta n(\mathbf{r}) = n(\mathbf{r}) - \langle n(\mathbf{r})\rangle$. For a gas, the average density is constant over the volume (ignoring boundary effects), and so we can write (defining $\langle n(\mathbf{r})\rangle = n$):

$$U_{\text{att}} = \frac{-Vn^2u}{2} + O(\delta n), \tag{24}$$

where $-u \equiv \int dr\ 4\pi r^2 V_{\text{att}}(r)$. We argue that the fluctuations around the average density are negligible, as, in the thermodynamic limit, we know that the particle number fluctuations in any given volume go like $\sqrt{\langle N\rangle} \ll \langle N\rangle$. This logic can only be applied when the repulsive part of the potential is removed, otherwise, small fluctuations in the density get weighted by an infinity in the potential. Therefore, one can only make this approximation after separating out the hard core of the potential. Making this approximation, we have

$$Z_N = \frac{\tilde{V}^N}{N!}\frac{1}{V^N}e^{\frac{u}{2}\beta n^2 V}\left(\int d^3q_1\cdots d^3q_N\eta(\mathbf{q}_1\cdots\mathbf{q}_N)\right) \approx \frac{\tilde{V}^N}{N!}\frac{1}{V^N}e^{\frac{u}{2}\beta n^2 V}V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega), \tag{25}$$

where the term $V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)$ is the approximate joint excluded volume (this neglects edge cases where 3 or more particles are near each other, but these corrections are suppressed by a factor of Ω/V, where $\Omega = 8\times\frac{4}{3}\pi r_0^3$. Using the approximation

$$V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega) \approx \left(V - \frac{N\Omega}{2}\right)^N = (V-Nb)^N, \tag{26}$$

we have

$$Z_N = \frac{1}{N!}\left(\frac{V-Nb}{\lambda^3}\right)^N e^{\frac{u}{2}\beta n^2 V}, \tag{27}$$

and the pressure is given by

$$P = -\frac{\partial F}{\partial V}\bigg|_{T,N} = \frac{Nk_BT}{V-Nb} - a\left(\frac{N}{V}\right)^2, \tag{28}$$

reproducing the van der Waals equation of state when we assign $a = \frac{u}{2}$.

II. VALIDITY OF THE VAN DER WAALS EQUATION

The van der Waals equation is not universally valid for all pressures and volumes: in other words, the stability criteria discussed in the unit on Thermodynamics are violated. One consequence of the stability criteria is that the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,N} > 0. \tag{29}$$

To see this, remember that for fixed temperature and particle number, the stability criterion implies that $\delta P \delta V < 0$ which implies from the definition of the isothermal compressibility that $-\kappa_T V(\delta P)^2 < 0 \implies \kappa_T > 0$. We can plot the isotherms $P = Nk_BT(V-Nb)^{-1} - uN^2(2V^2)^{-1}$ and we will find regions where $\frac{\partial P}{\partial V} > 0 \implies \kappa_T < 0$. This means that the system is able to spontaneously lower its energy by adjusting for example its volume (or equivalently, density).

Another perspective on the positivity of the isothermal compressibility comes from considering the system in the grand canonical ensemble. Recall that in the grand canonical ensemble, we showed that the probability of the system having a certain particle number $p(N)$ is a tight Gaussian with the mean and variance set by

$$\langle N\rangle = V\frac{\partial P}{\partial \mu}, \sigma_N^2 = \langle N\rangle \times nk_BT\kappa_T. \tag{30}$$

This was found by taking the particle number probability distribution $p(N) = e^{\beta\mu N}Z(V,T,N)/Q$ and finding the extremum, as well as the second-derivative of the distribution at the extremum. If κ_T is positive, then the extremum is a maximum, and we have found the most likely state of the system. If κ_T is negative, then the extremum is a *minimum*, meaning that the system is *least* likely to be in that state. When $\frac{\partial P}{\partial V}$ goes from positive to negative, crossing through zero, it means that the compressibility diverges, suggesting infinite fluctuations in the particle number or density, and suggesting that the system is able to reach very high densities. Those added particles come from the outside of some control volume of gas, and suggest that the system starts to *condense*.

From mean-field theory, we can actually show that at the temperature where the isothermal compressibility diverges, called the *critical isotherm*, corresponds to a case where there is more than one probability extremum, one representing the gaseous phase, and the other representing the liquid phase!

To see this, let us construct the probability distribution for particle number based on mean-field theory. We know that the grand partition function is given by:

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} \times \frac{1}{N!}\left(\frac{(V-Nb)}{\lambda^3}\right)^N e^{\frac{\beta u}{2}n^2 V}, \tag{31}$$

which can be written as

$$Q = \sum_{N=0}^{\infty} \exp\left[\beta\mu N + N\ln(V-Nb) - N\ln\lambda^3 - N\ln N + N + \frac{\beta u N^2}{2V}\right]. \tag{32}$$

This can be approximated in the thermodynamic limit by the largest value in the sum. To make notation convenient, define:

$$\Psi(n) \equiv V\left((\beta\mu + 1 - \ln\lambda^3)n + n\ln(n^{-1} - b) + \frac{1}{2}\beta u n^2\right). \tag{33}$$

Using this notation, we may now approximate:

$$Q \approx \exp[\Psi(n_*)], \tag{34}$$

where $\Psi(n_*)$ is the value of Ψ at the density n_* that maximizes Ψ. The pressure is given by

$$P = \frac{k_B T}{V}\Psi(n_*). \tag{35}$$

The possible values of the density satisfy $\Psi' = 0$ or

$$\left(\beta\mu + 1 - \ln\lambda^3\right) + \ln(n_*^{-1} - b) - \frac{n_*^{-1}}{n_*^{-1} - b} + \beta u n = 0, \tag{36}$$

which can be re-written as

$$\left(\beta\mu + 1 - \ln\lambda^3\right) + \ln(n_*^{-1} - b) = \frac{n_*^{-1}}{n_*^{-1} - b} - \beta u n_*. \tag{37}$$

The corresponding pressure is

$$P = \frac{k_B T}{V}\Psi(n_*) = k_B T\left(\frac{1}{n_*^{-1} - b} - \frac{1}{2}\beta u n_*^2\right) = \frac{N_* k_B T}{V - N_* b} - \frac{1}{2}u\left(\frac{N_*}{V}\right)^2. \tag{38}$$

In other words, the pressure is what you expected from the van der Waals equation of state, for the maximum density. It is possible that the equation $\Psi'(n_*) = 0$ has multiple solutions: in that case, the pressure is the one associated with the n_* that maximizes Ψ. However, as is seen from the previous equation, $P \sim \Psi$ and so the pressure is the one corresponding to the density that leads to the largest pressure.

This competition between different densities (phases) can be used to understand the mechanism of a phase transition. The phase transition associated with going from vapor to liquid, *condensation* is what is called an emphfirst-order phase transition: in other words, as some control parameter is varied, such as temperature (think about going below the boiling point of water), the properties of the system change *abruptly*, or *discontinuously* with temperature. For example, infinitesimally away from the boiling point of water on both sides of the phase transition, the densities are different. The discontinuity manifests in the relevant thermodynamic potential itself (for example, the grand potential changes discontinuously). The discontinuous nature of these phase transitions is to be contrasted with so-called *second-order* phase transitions, where the free energy does not abruptly change, although the derivative changes abruptly, causing response functions (related to second-derivatives) to diverge. Second-order phase transitions describe things such as magnets undergoing a transition from paramagnetism to ferromagnetism.

Take the expression

$$Q = \sum_{N=0}^{\infty} e^{\Psi(N)}, \tag{39}$$

assume that we have two maxima: N_l and N_g (e.g., for liquid and gas). Then by means of approximating by the largest terms in the sum, we could write

$$Q = e^{\Psi(N_g)} + e^{\Psi(N_l)} = e^{\beta V P(n_g)} + e^{\beta V P(n_l)}. \tag{40}$$

Of course, whichever of these is larger dominates the sum, reproducing the manipulations that led to $P = P(n_*)$. The point is this: suppose at high temperature that $P(n_g) > P(n_l)$ so that the system has the density associated with the gas phase. As we lower temperature, what happens is that $P(n_l) = P(n_g)$ at some *critical temperature* T_c. Below this critical temperature, $P(n_l) > P(n_g)$, In the thermodynamic limit, as $V \to \infty$, the larger of the two terms is always infinitely larger than the other. That is because $r^\infty = \infty$ if $r > 1$ where r is the ratio of the two contributions to the grand partition function. And so, when T passes through T_c there is an abrupt jump from one density to the other, and an associated discontinuity in the grand potential $\ln \mathbf{Q}$ whose derivatives generate all thermodynamic observables. It is important to understand that n_l and n_g themselves vary continuously with T: it is the process of constructing two pressures, summing them, and exponentiating them by an infinite power that creates the discontinuity.

When V is *finite*, there is a smooth crossover from one term to the other. Therefore, the phase transitions "no longer exists" in the sense that the variation is not truly discontinuous. However, for finite systems common to our experience, this transition is extremely sharp, approximating very well the infinite limit.

III. MEAN-FIELD THEORY OF FERROMAGNETISM

In what follows, we will consider one more example of mean-field theory in describing the magnetic ordering of a collection of spins. A rudimentary model of a magnetic material like iron is a lattice of spin 1/2 particles. In the absence of an applied magnetic field, we know that iron is magnetic: that is, iron is in a *ferromagnetic* phase. In the ferromagnetic phase, the spins are aligned in a common direction. In contrast, if we heat up a ferromagnet, it will undergo a phase transition into being a paramagnet and the spins on average will be equally likely to point up or down on each site of the lattice. Let us now use statistical mechanics to describe the phase transition.

We will simplify the problem severely by considering a d-dimensional chain of spin 1/2 atoms on a lattice (the dimensionality does not show up in what follows), but the same idea can be applied in higher dimensions. The Hamiltonian, in the presence of an applied magnetic field B_{ext} in the z-direction, which is taken to be the quantization axis of the spins, is given by

$$H = -\sum_i \gamma B_{\text{ext}} \sigma_i - \sum_{ij} J_{ij} \sigma_i \sigma_j, \tag{41}$$

where $\sigma = \pm 1$ represents the state of the spins with $+1$ representing spin along the external magnetic field (spin up) while -1 represents spin down. The second term is an interaction between spins that favors the alignment of spins i and j if $J_{ij} > 0$.

While this problem turns out to have an exact solution in one dimension and two dimensions, we will explore a simpler solution based on mean-field theory which applies in any dimension. The "guess" we will take for our mean-field theory is that we think of each spin as existing in an average magnetic field created by all other spins. Assuming that J_{ij} is a function of the distance between particles $J_{ij} = J(r_{ij})$, and that the lattice is ordered, we have

$$H = -\gamma \sum_i (B_{\text{ext}} + B_{\text{eff},i})\sigma_i, \tag{42}$$

where we have defined an effective magnetic field B_{eff} as

$$\gamma B_{\text{eff},i} = \sum_j J_{ij}\sigma_j. \tag{43}$$

So far, we have not made any approximation. Now, we make the mean-field approximation which is to say that in defining this effective magnetic field, we can replace it by its average, which in an ordered lattice, does not vary

$$\gamma B_{\text{eff},i} \to \gamma\langle B_{\text{eff},i}\rangle = \sum_j J_{ij}\langle\sigma_j\rangle = \left(\sum_j J_{0j}\right)\langle\sigma\rangle \equiv \gamma A\langle\sigma\rangle, \tag{44}$$

where I have defined a constant A such that $\langle B_{\text{eff}}\rangle = A\langle\sigma\rangle$. Therefore, we can write

$$H_{\text{eff}} = -\gamma B \sum_i \sigma_i, \tag{45}$$

where $B = B_{\text{ext}} + \langle B_{\text{eff}}\rangle$. We have in the mean-field approximation a sum of non-interacting Hamiltonians of individual spins in a magnetic field. Suppose we wanted to find the average value of σ for such a system. This is straightforwardly done in the canonical ensemble as

$$\langle\sigma\rangle = (+1)p(\sigma = 1) + (-1)p(\sigma = -1) = \frac{e^{\beta\gamma B} - e^{-\beta\gamma B}}{e^{\beta\gamma B} + e^{-\beta\gamma B}} = \tanh\beta\gamma B. \tag{46}$$

If B were an externally chosen field, we would say that given B, there is a definite expectation value for σ: at high magnetic field, tanh goes to 1 and the spin is aligned with the field, representing the lowest energy state. If $B = 0$, then $\langle\sigma\rangle = 0$ and the spins are as likely to be up as they are down at any temperature.

Because of interactions, the magnetic field here depends on $\langle\sigma\rangle$ and so instead we have

$$\langle\sigma\rangle = \tanh\beta\gamma\left(B_{\text{ext}} + A\langle\sigma\rangle\right). \tag{47}$$

This equation has a finite solution for $\langle\sigma\rangle$ (the mean *magnetization*) even in the absence of the applied magnetic field. We need to solve the transcendental equation

$$\langle\sigma\rangle = \tanh \beta\gamma A\langle\sigma\rangle. \tag{48}$$

When $\beta\gamma A < 1$, or equivalently, when $T > T_c \equiv \gamma A/k_B$, the only solution to this equation is zero, as can be seen by sketching tanh and noting that $\tanh \alpha x \approx \alpha x$ for small x and that the slope only gets smaller as x increases. For $T < T_c$, we consider two limits. First: $T \to 0 \implies \beta\gamma A \to \infty$. The solution here is $\langle\sigma\rangle = \pm 1$: all the spins are either aligned up or aligned down (without a magnetic field externally applied, both options seem equally viable for the ferromagnet from an energetic perspective).

Next, let us consider what happens when $T \approx T_c$ (but $T < T_c$ still). In this case, we approximate $\tanh \alpha x \approx \alpha x\left(1 - \frac{(\alpha x)^2}{3}\right)$ (because $\langle\sigma\rangle$ is expected to be nearly zero). Solving for $\langle\sigma\rangle$ yields

$$\langle\sigma\rangle = \frac{3}{\alpha}\sqrt{1 - \frac{1}{\alpha}} = \frac{\sqrt{3}k_B T}{\gamma A}\sqrt{1 - \frac{k_B T}{\gamma A}}. \tag{49}$$

Expressed in terms of the critical temperature, and keeping in mind that $T \approx T_c$, we can write this as:

$$\langle\sigma\rangle = \sqrt{3}\sqrt{1 - \frac{T}{T_c}}. \tag{50}$$

The magnetization continuously drops to zero as we approach the critical temperature. This is the hallmark sign of an *second-order phase transition*, unlike the first-order condensation transition where the density abruptly changes.

Additionally, we can compute the magnetic susceptibility of this system

$$\chi = \frac{\partial M}{\partial B_{\text{ext}}}\Big|_{B_{\text{ext}}=0} = N\mu_B \frac{\partial\langle\sigma\rangle}{\partial B_{\text{ext}}}|_{B_{\text{ext}}=0}. \tag{51}$$

We will instead focus on the quantity $\tilde{\chi} = \frac{\partial\langle\sigma\rangle}{\partial B_{\text{ext}}}|_{B_{\text{ext}}=0}$, which is given as

$$\tilde{\chi} = \frac{\beta\gamma + \beta\gamma A\tilde{\chi}}{\cosh^2 \beta\gamma A\langle\sigma\rangle}, \tag{52}$$

which may be re-written as

$$\tilde{\chi} = \frac{\beta\gamma}{\cosh^2 \beta\gamma A\langle\sigma\rangle - \beta\gamma A}. \tag{53}$$

In the paramagnetic phase $\sigma \to 0$ so:

$$\tilde{\chi} = \frac{\gamma}{k_B(T - T_c)}. \tag{54}$$

This is the well-known *Curie-Weiss law* and diverges as $T \to T_c$, a common phenomenon in second-order phase transitions.

In the ferromagnetic phase, just below the critical temperature, we use the expression $\cosh^2 x \approx 1 + x^2$ and so we have $\cosh k_B T_c \langle \sigma \rangle \approx 1 + 3(1 - T/T_c)$. Therefore:

$$\tilde{\chi} = \frac{\gamma}{2(T_c - T)}. \tag{55}$$

This also diverges as $T \to T_c$ (from below) but with a different constant of proportionality!

Finally, we note that at high-temperatures, the T^{-1} dependence of the susceptibility in the paramagnetic phase holds up well against experiments. The specific form of the susceptibility divergence is not completely accurate in mean-field theory but gets the idea right. Mean-field theory gets more and more accurate in higher dimensions.