

Recapitulation and today's lecture

Last time, we discussed the stability of *phase transitions* with two physical examples: liquid/gas, and a ferro/paramagnetic transition that can be analyzed in terms of simple order parameters. We also discussed the microscopic origin of the transition and order of the transition. Today, we will continue with the topic of phase transitions and its relation with the partition function.

We will introduce the Ising model, which can be used to describe ferromagnetism (and many other simple systems), which arises when the spins of many atoms cooperatively align so that their associated magnetic moments all point in the same direction (spin is a vector) and yields a net *macroscopic* magnetic moment. We will also introduce a powerful method to study phase transitions: the *Monte Carlo Simulation*. The Monte Carlo simulation uses randomly generated thermal perturbations—in the case of the Ising model, the spins are randomly flipped and exhibits a temperature—applied-field dependent phase transition.

Transitions and the Partition Function

In general, the choice of the variables with which we want to study a system (in particular during a phase transition) imposes the choice of the thermodynamic potential. The appropriate thermodynamic potential is the one that is minimized for particular constraints on the system—and thus, the choice of potential in modeling a phase transitions depends on the experiment that is being modeled. Hence, when we work with the variables P and T , the free energy $G = U - TS + PV$ which is the appropriate potential. In the case where we want to study a system as a function of its fixed T and V , it is the free energy $F = U - TS$ which is the pertinent potential. We have the following relation:

$$\begin{aligned} dU &= TdS - PdV, & dF &= -SdT - PdV, \\ dH &= TdS + VdP, & dG &= SdT + VdP \end{aligned} \quad (1)$$

We can think of the PV term as a *place-holder* for how reversible work is being stored. Consider a system that *only* stores work by responding to applied magnetic field \vec{H} . Thus, the case of a magnetic system in presence of a magnetic induction \vec{B} and \vec{H} being the applied magnetic field, we could have the potentials:

$$F = U - TS \quad \text{and} \quad G = U - TS - \vec{H} \cdot \vec{B} \quad (2)$$

Below, we will drop the vector notation and consider it understood that a dot product like $\vec{F} \cdot d\vec{x}$ or $\vec{H} \cdot d\vec{B}$. From these relations, we can deduce the following examples for a fluid system:

$$\begin{aligned} C_v &= -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V \quad \text{and} \\ k_T &= -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2} \right)_T \end{aligned} \quad (3)$$

and for a magnetic system:

$$\begin{aligned} C_B &= -T \left(\frac{\partial^2 F}{\partial T^2} \right)_B \quad \text{and} \\ k_T &= \frac{1}{B} \left(\frac{\partial^2 G}{\partial H^2} \right)_T \end{aligned} \quad (4)$$

Thus, in the case of a magnetic system, we have analogous expression: the magnetic susceptibility being the analogous of the compressibility for a fluid.

To model a particular material's equilibrium and phase transition properties, one needs the potential (which is generic for the particular experiment) and the relations between the derivatives of the potential (which are material properties). For example, we need $G(H, T)$ and, for example, $\partial B(H, T)/\partial T$. To proceed, We must choose a model which is a simplified representation of the physical reality, *and* which is simple enough to calculate the thermodynamic potential as a function of the useful variables of states.

For example, we can take a case of a liquid or solid binary solution with two constituents, A and B with compositions respectively equal to x_A and x_B .

We can take the free energy of the solution $G(x_A, x_B)$ to be given by the *Regular Solution model*: (Here we work on a per mole basis, so that all free energies below are *molar free energies*.)

$$G(x_A, x_B) = x_A G_A^0 + x_B G_B^0 + u x_A x_B + RT(x_A \ln x_A + x_B \ln x_B) \quad (5)$$

where the G_A^0 and G_B^0 are the free energy of pure A and pure B and R is the ideal gas constant.

In this expression, we assume that the interaction energy between constituents A and B of the mixing is proportional to the product of their concentrations (it is the term $u x_A x_B$).

This expression (5) can be derived from the following assumptions:

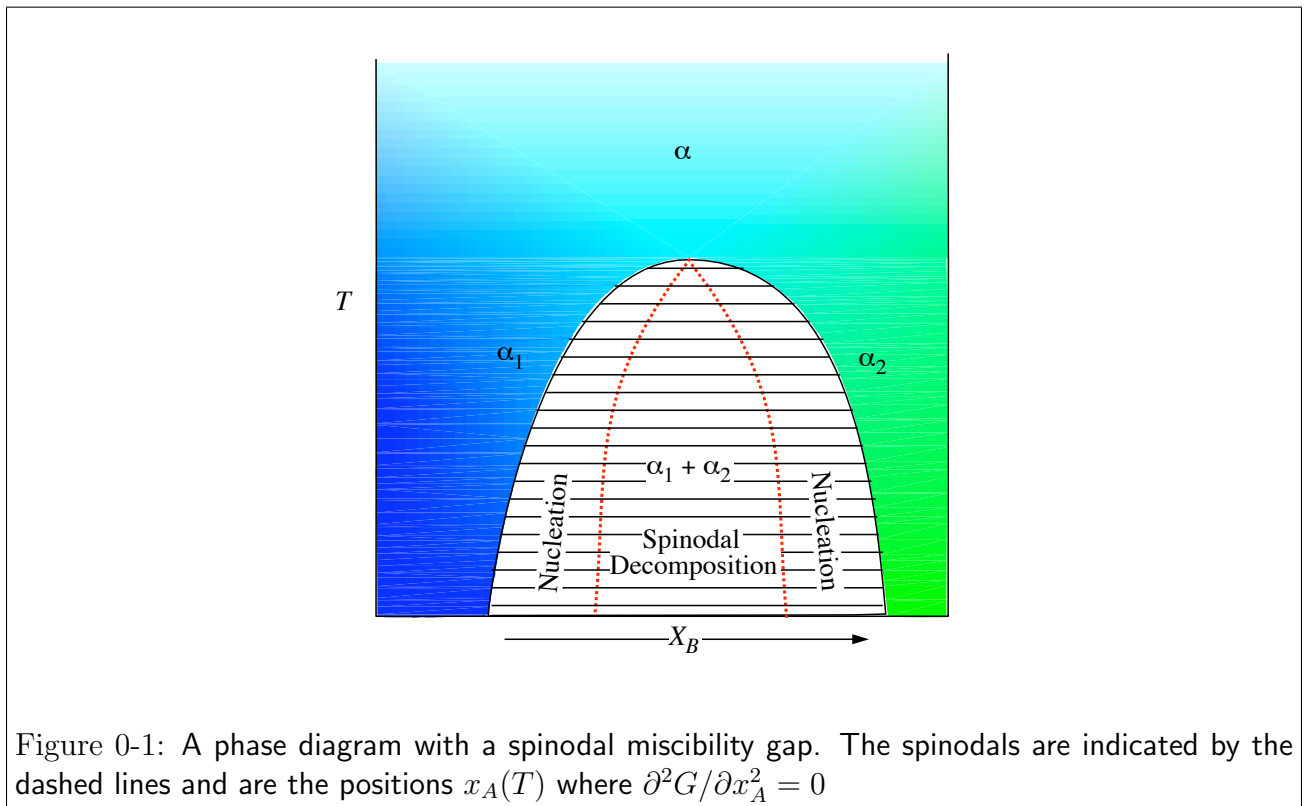
- The particles have the same number of nearest neighbors.
- The mixing is perfectly random.
- We have short range interactions between particles and we can take into account only the nearest neighbors— this is the origin of the u factor.

The $Rx \log x$ terms in equation (5) collectively define the ideal mixing entropy, $-\Delta S^{\text{id. mix}}$ and contribute to the free energy via $\Delta G = \Delta H - T\Delta S$. The regular-solution enthalpy of mixing, ΔH can be identified directly.

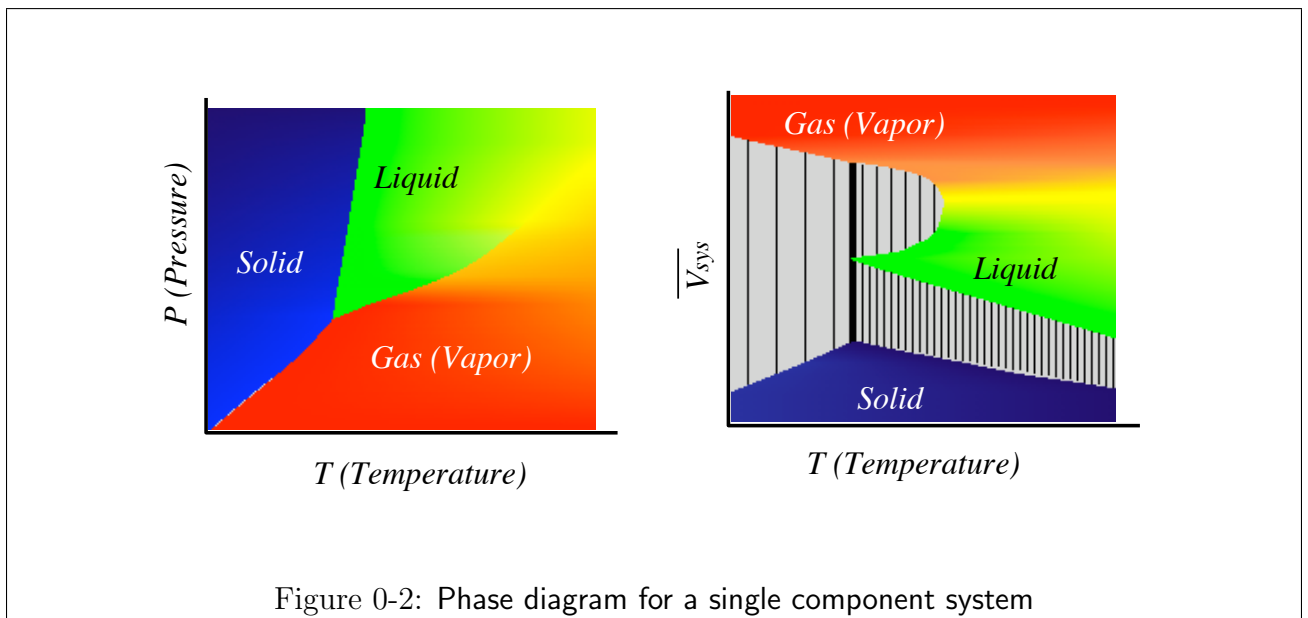
A solution where the energy is given by the equation of G is called a *regular solution*. This expression for G fully determines the phase transitions (with respect to composition changes) of the regular-solution model. In particular, we can find the limit of meta-stability which is given by the condition of

$$\frac{\partial^2 \bar{G}}{\partial x_A^2} = 0 \quad (6)$$

where $x_A + x_B = 1$



This figure can be compared to the pair of diagrams for a single component system where molar volume is the order parameter:



Setting $x = x_A$ and $x_A + x_B = 1$, we have $x_B = 1 - x$. We can rewrite equation (5) as

$$G = xG_A^0 + (1-x)G_B^0 + ux(1-x) + RT[x \ln x + (1-x) \ln(1-x)] \quad (7)$$

$\delta^2 G$ becomes $-2ux(1-x) + RT = 0$.

This is the equation of a curve which gives the shape of the spinodal. There is a critical point at coordinates $x = 1/2$ and $T_c = u/2R$. Above T_c , the constituents A and B form an homogeneous solution over the entire composition range—below that temperature, there is a range of composition where the system is composed of two phases that differ in the compositions at the end of the tie-lines.

The critical point, which is the top of both the spinodal and the coexistence curve, is a point of the second-order transition as defined by Ehrenfest.

The coexistence curve is calculated from the condition that chemical potential of μ_A is the same in each phase (that $\mu_B^\alpha = \mu_B^\beta$ is satisfied when $\mu_A^\alpha = \mu_A^\beta$ follows from the fact that there is only one free composition variable—this gives rise to the famous *common tangent construction*. In the case of a regular solution, we easily find that the equation of the curve of coexistence is given by:

$$\frac{1-x}{x} = \exp\left(\frac{(1-2x)u}{RT}\right) \quad (8)$$

(Students should see if they can derive this expression)

This model describing the regular solution is very general.

In a general manner, we use the correspondence between the thermodynamic quantities and the statistical physics. Thus, the internal energy which is the mean energy of the system can be written as

$$U = \frac{\sum_i E_i \exp(-\beta E_i)}{Z} \quad (9)$$

The above equation has a physical interpretation that illuminates the meaning of the partition function Z and its relation to the average energy U . The terms inside the sum are factors, E_i , of the energy of each state; and the number of states $\propto \exp(-\beta E_i)$ that have that energy. (i.e., the average age of people in the room is the sum of factors: Age_i and the number of people of that age N_i divided by a *normalization factor* N_{total}). The partition function plays the role of normalization.

We have a sum which runs over all the microscopic states of the system of energy E_i , where Z being the partition function:

$$Z = \sum_i \exp(-\beta E_i) \quad (10)$$

where $\beta = 1/(k_B T)$ is the inverse the Boltzmann temperature. So, we can have

$$\begin{aligned} G &= -\frac{1}{\beta} \frac{\partial(V \ln Z)}{\partial V}, \\ U &= -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V, \\ F &= -k_B T \ln Z, \\ P &= -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V}\right)_T, \\ C_v &= \left(\frac{\partial U}{\partial T}\right)_V = k_B \beta^2 \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_V \end{aligned} \quad (11)$$

The calculation of the thermodynamic quantities is then always a function of the partition function Z . If the Z can be computed from a microscopic model of the system—then the macroscopic physics can be computed from the statistics of the microscopic physics. To model the microscopic physics, one usually tries to find a model for a function of many variables that describes the energy: e.g., the Hamiltonian \mathcal{H} . The choice of \mathcal{H} , depends on what kind of interactions occur within the material that we are modeling: a liquid, a gas, an alloy, a ferromagnetic material,

From previous lectures, we have a phenomenological representation of what is a phase transition. Nevertheless, certain questions remain unanswered. How to explain the occurrence of a singularity within the macroscopic quantity from a microscopic description? Which physical mechanisms are hidden behind these transitions? How are ordered or not the microscopic entities at the critical point? What is the role of the fluctuation?

Ising Model

Consider a solid consisting of N identical atoms arranged in a regular lattice. Each atom has a net electronic spin S and associated magnetic moment μ . (Here we model the spin of having only two states, *up* and *down*, and neglect the vector nature of spin; “up” means aligned with the applied magnetic field.) The magnetic moment of an atom is related to its spin by $\mu = g\mu_0 S$ where μ_0 is the Bohr magneton and the g factor is of order of unity. In presence of an externally applied magnetic field H_0 along the z direction, the Hamiltonian \mathcal{H}_0 representing the interactions of atoms with this field is

$$\mathcal{H}_0 = -g\mu_0 \sum_{j=1}^N S_j \cdot H_0 = -g\mu_0 H_0 \sum_{j=1}^N S_{ij} \quad (12)$$

In addition, each atom interacts with neighboring atoms. To produce a ferromagnetic transition, this interaction must be more than the magnetic dipole-dipole interaction due to the magnetic field produced by one atom at the position of another one. Another much stronger interaction is responsible for the interaction energy and this is known as “exchange” interaction. The exchange interaction is a consequence of the Pauli exclusion principle: two electrons cannot occupy the same state (spin and positions), electrons with parallel spins on neighboring atoms repel each other. On the other hand, no such restriction applies if the electrons have anti-parallel spins. That is, they are already in different states, and there is no exclusion-principle restriction and there is no repelling force. Since different spatial separations of the electron give rise to different electrostatic interactions between them. This qualitative discussion shows that the electrostatic interaction between two neighboring atoms does also depend on the relative orientations of their electrons’ spins. This is the origin of the exchange interactions, which for two atoms j and k , it can be written as:

$$\mathcal{H}_{jk} = -2JS_{jz}S_{kz} \quad (13)$$

J is a parameter which describes the strength of the exchange interaction. If $J > 0$, the interaction energy \mathcal{H}_{jk} is lower when the spins are parallel than they are anti-parallel. The state of lowest energy will then be one which leads to produce ferromagnetism.

The Hamiltonian \mathcal{H}' representing the interaction energy between their atoms can then be written as:

$$\mathcal{H}' = \frac{1}{2}(-2J \sum_{j=1}^N \sum_{k=1}^N S_{jz} S_{kz}) \quad (14)$$

J is the exchange constant for neighboring atoms and the index that refers to atoms in the nearest neighbor shell surrounding the atom j . The factor $1/2$ is introduced because the interaction between the same atoms is counted twice while summing up the energy.

The total Hamiltonian of the N atoms is then

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad (15)$$

The goal is to calculate the thermodynamic function of this system, e.g., its mean magnetic moment $\langle M \rangle$, as a function of the temperature T and the applied magnetic field H_0 . The presence of interaction is what makes this problem interesting. The problem is fairly straightforward in one dimensions. It is quite complicated to do, but the problem has been solved exactly for a two-dimensional array of spin for the special case $H_0 = 0$. No one has solved the 3D problem.

We can however attack the problem by another way—by simulation. We can compute very interesting properties for very complicated systems—barriers such as not having a solution in 3D need not stop progress.

Monte Carlo Method

The Monte Carlo Method has been introduced in 1953 at the beginning of the computer science. It generates a large set of states i, j, k, \dots by stochastic (i.e., random with transition rules built-in) process. As we will see, the probability to obtain one instance of a collection of states depends on the temperature, and the characteristic energy differences from its prior state. From this, statistical distributions of physical macroscopic properties can be derived. One goal of the statistical physics is to calculate the mean value $\langle X \rangle$ of thermodynamic quantities characteristic of the system (energy, pressure, magnetization, etc ...). $\langle X \rangle$ can be written in the space phase as:

$$\langle X \rangle = \frac{\sum_i X_i \exp(-\beta \mathcal{H}_i)}{\sum_i \exp(-\beta \mathcal{H}_i)} \quad (16)$$

where \mathcal{H} is the Hamiltonian of the system in the configuration i . For example, consider a magnetic material represented by an Ising model (two values for the spins) comprising a lattice with N states: its Hamiltonian can be calculated by brute force. We can perform by repeated computation by generating random numbers and sum on $\langle X \rangle$ which run over 2^N states. This number of states, or configurations, is an increased function of, N , the number of atoms in the lattice. For $N = 3 \times 3 \times 3$, we have $2^9 = 512$ possible states and for $N = 100$, the number of possible configurations is $2^{100} \approx 10^{30}$. Numerical calculation of this mean value then becomes impossible—however, we can compute the nature of convergence as the number of states sampled increases.

Furthermore, we can improve our convergence if we take into account the fact that in statistical physics, we know that the system will spend the major part of its time in states for which we

can associate thermodynamic quantities closed to those at equilibrium. We can imagine a strategy of calculation limits the number of states that we take to realize the average-calculation. This is accomplished with a famous algorithm, the *Metropolis Algorithm*, for the calculation of Monte Carlo simulations. The principle of this calculation can be described with the Ising model. If we take for example the spin model, the following steps will be:

1. We start from an initial state with N spins representing a certain state (i) (the state is the set of all spins).
2. Perform one or more than one random exchange, $\uparrow \rightarrow \downarrow$, we will obtain a possible new state called a trial state. Taking E_i and E_f , which are respectively the current and trial energy of the system, we will have $\Delta E = E_i - E_f$, which is the energy change associated to the reversal of spin.
3. If $\Delta E < 0$, we accept the trial state and continue; otherwise:

(Boltzmann) We calculate a Boltzmann factor, depending on the difference in energy and the system temperature, T

$$w = \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (17)$$

(Random) Chose a random number r for a uniform distribution, $0 < r < 1$,

(Comparison) Compare r and w .

(Reject) If $w < r$, we reject the trial state and leave the system in its current configuration and continue. (No change.)

(Accept) If $w > r$, we accept the trial state. (Incremental change).

In such an algorithm, the thermodynamic quantities associated with the progression of states f is obtained. It has the property that at low temperatures, the system evolves towards the lower energy configuration—but it can become stuck if the “energy landscape” is too rough. At high temperatures, the system samples many more configurations of higher energy—its entropy is increased.

This method is a stochastic method; it generates states following a Markov chain (i.e., each state depends only on its proceeding state and no other). Thus a Markov process is a random chain of event which occurs randomly, the system maintains no long-term history, and most importantly, doesn't depend on the starting state.

The Monte Carlo method and the Metropolis Algorithm allows us to simulate behavior of system using the Gibbs distribution function. The probability of transition from a state to another one must satisfy the principle of microscopic reversibility, this is also known as the condition of *detailed balance*.

If $P(i \rightarrow f)$ is the probability of transition from a state to another one, w_i , and w_f , are the probability to find the system in states (i) and (f) , we should have:

$$w_i P(i \rightarrow f) = w_f P(f \rightarrow i) \quad (18)$$

In other words, many states may exchange, but if the probability of transition is unaffected by the local changes, then the system is in equilibrium.