

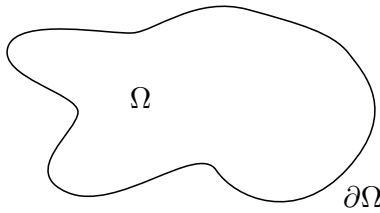
# Chapter 1

## Statistical mechanics and phase transitions

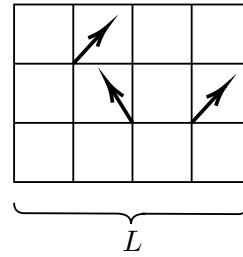
### 1.1 Statistical mechanics of phase transitions

From the microscopic degrees of freedom one compute the partition function in the appropriate ensemble, then the corresponding thermodynamic potential and from it all the thermodynamic properties of the system as *equilibrium phases* and, if present *phase transitions*. Actually, until the '30 there were strong concerns about the possibility that statistical mechanics could describe phase transitions.

**Lecture 5.**  
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(a) Description



(b) Description

**Figure 1.1:** Description

Let us consider a system with a region  $\Omega$  of volume  $V(\Omega)$  and boundary  $\partial\Omega$  of area  $S(\Omega)$ . Denoting by  $L$  a characteristic length of the system

$$V(\Omega) \propto L^d, \quad S(\partial\Omega) \propto L^{d-1} \quad (1.1)$$

where  $d$  is the spatial dimension.

*Remark.* Space  $\Omega$  can be either *discrete* or *continuous*.

Suppose the system is *finite*. Formally we can write

$$\mathcal{H}_\Omega = - \sum_n k_n \Theta_n \quad (1.2)$$

where

- $k_n$ : are the coupling constants. In general, but not always, they are *intensive thermodynamic variables*.
- $\Theta_n$ : is a linear of higher order combination of the dynamical microscopic degrees of freedom (local operators in quantum statistical mechanics).

- $k_n \Theta_n$ : must obey the symmetry of the system. It is important that in principle the term satisfies the symmetry of the system. This is a master rule!

To fix the idea let us consider two classical examples: the magnetic system and the fluid system.

### 1.1.1 Magnetic system

The degrees of freedom are the *spins* lying on a Bravais lattice  $\vec{\mathbf{S}}_i$  with  $1 \leq i \leq N(\Omega)$ , where the  $N(\Omega)$  are the number of lattice sites (Figure 1.1b). A configuration is the orientation of the spin in each site  $\mathcal{C} = \{\vec{\mathbf{S}}_1, \dots, \vec{\mathbf{S}}_N\}$ . We have:

$$\Theta_1 = \sum_i \vec{\mathbf{S}}_i \quad (1.3a)$$

$$\Theta_2 = \sum_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j \quad (1.3b)$$

We consider the trace operation that is the sum over all possible values that each degree of freedom can assume:

$$\text{Tr} \equiv \sum_{\{\mathcal{C}\}} \equiv \sum_{\vec{\mathbf{S}}_1} \sum_{\vec{\mathbf{S}}_2} \cdots \sum_{\vec{\mathbf{S}}_N} \quad (1.4)$$

where  $\sum$  can also indicate an integration if values are continuous. The canonic partition function is

$$Q_\Omega(T, \{k_n\}) = \text{Tr} \left( e^{-\beta \mathcal{H}_\Omega} \right) \quad \text{with} \quad \beta \equiv \frac{1}{k_B T} \quad (1.5)$$

### 1.1.2 Fluid system (gran canonical)

Consider  $N$  particles in a volume  $V$ , with number density  $\rho = N/V$ . The  $2dN$  degrees of freedom are

$$\{\mathcal{C}\} = \{(\vec{\mathbf{x}}_i, \vec{\mathbf{p}}_i)_{i=1, \dots, N}\} \quad (1.6)$$

and

$$\Theta_1 = \sum_i \left[ \frac{\vec{\mathbf{p}}_i^2}{2m_i} + U_1(\vec{\mathbf{x}}_i) \right] \quad (1.7a)$$

$$\Theta_2 = \frac{1}{2} \sum_{i>j} U(|\vec{\mathbf{x}}_i - \vec{\mathbf{x}}_j|) \quad (1.7b)$$

The trace operation is

$$\text{Tr} \equiv \sum_{\{\mathcal{C}\}} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{(d\vec{\mathbf{p}}_i)(d\vec{\mathbf{x}}_i)}{h^{dN}} \quad (1.8)$$

$$\mathcal{F}_\Omega = \text{Tr} \left( e^{-\beta(\mathcal{H}_\Omega - \mu N)} \right) \quad (1.9)$$

For a generic partition function  $Q_\Omega(T, \{k_n\})$  we can define the finite system *free energy* as

$$F_\Omega[T, \{k_n\}] = -k_B T \ln Q_\Omega(T, \{k_n\}) \quad (1.10)$$

The relation with thermodynamic is through the *thermodynamic limit*. Since the free energy is an extensive function

$$F_\Omega \propto V(\Omega \sim L^d) \quad (1.11)$$

In general, one can write

$$F_\Omega[T, \{k_n\}] = V(\Omega)f_b[T, \{k_n\}] + S(\Omega)f_s[T, \{k_n\}] + O(L^{d-2}) \quad (1.12)$$

where  $f_b[T, \{k_n\}]$  is the bulk free energy density.

**Definition 1.** We define

$$f_b[T, \{k_n\}] \equiv \lim_{V(\Omega) \rightarrow \infty} \frac{F_\Omega[T, \{k_n\}]}{V(\Omega)} \quad (1.13)$$

If the limit exists (to prove for each system) and does not depend on  $\Omega$ .

For a system defined on a lattice we have

$$L(\Omega) \propto N(\Omega)^{1/d}, \quad V(\Omega) \propto N(\Omega) \quad (1.14)$$

$$f_b[T, \{k_n\}] = \lim_{N(\Omega) \rightarrow \infty} \frac{1}{N(\Omega)} F_N[T, \{k_n\}] \quad (1.15)$$

To get information on surface property of the system

$$f_s[T, \{k_n\}] \equiv \lim_{S(\Omega) \rightarrow \infty} \frac{F_\Omega[T, \{k_n\}] - V(\Omega)f_b}{S(\Omega)} \quad (1.16)$$

## 1.2 Thermodynamic limit with additional constraints

For a fluid we cannot simply take the limit  $V(\Omega) \rightarrow \infty$  by keeping  $N$  fixed, otherwise we will always get a infinite system with *zero density*. One has to take also the limit  $N(\Omega) \rightarrow \infty$  such that:

$$\frac{N(\Omega)}{V(\Omega)} \equiv \rho = \text{const} \quad (1.17)$$

In general is not so easy to prove the existence of the limit and it depends on the range of the particle-particle interactions.

### 1.2.1 Statistical mechanics and phase transitions

Since all the thermodynamic information of a system can be obtained by the partition function, in principle also the ones concerning the existence and nature of the phase transition must be contained in  $Z$  (or  $Q$ ). On the other hand we know from thermodynamic that phase transitions are characterized by singularities in the derivation of  $F$ . Also  $Z$  must display these singularities. On the other hand  $Z$  is a sum of exponentials

$$Z_\Omega = \text{Tr} \left( e^{-\beta \mathcal{H}_\Omega} \right) \quad (1.18)$$

These are analytic functions everywhere (it converges), therefore  $Z_\Omega$  is analytic for  $\Omega$  finite! The question is: where the singularities came from? It is only in the thermodynamic limit that singularities in  $F$  and hence points describing phase transitions can arise!

For summarizing, there is no way in you can produce singularities out of this. The singularities will develop in the thermodynamic limits. For reach singularities we have to reach so precision in thermodynamic that we are not able to go exactly into the critical point. How can we relate singularities in the behaviour of the system geometrically?

### 1.3 Critical point and correlations of fluctuations

From thermodynamics we know that, at the critical point, some response functions may diverge. We now show that this is a consequence of the onset of microscopic fluctuations that are spatially correlated over long distances. To see this let us compute the response of a ferromagnetic in presence of an external magnetic field  $H$ . The Gibbs partition function of a generic magnetic system is

$$Z_{\text{Gibbs}}[T, \{k_n\}] = \text{Tr} \left( e^{-\beta(\mathcal{H}(\mathcal{C}) - HM(\mathcal{C}))} \right) = \sum_{M, E} e^{-\beta E + \beta HM} \Omega(E, M) \quad (1.19)$$

*Remark.* The term  $-HM$  is the work done by the system against the external field  $H$  to maintain a given magnetization  $M$ .

$$\langle M \rangle = \left. \frac{\partial \ln Z_G}{\partial(\beta H)} \right|_T = \frac{1}{Z_G} \text{Tr} \left[ M(\mathcal{C}) e^{-\beta(\mathcal{H}(\mathcal{C}) - HM(\mathcal{C}))} \right] \quad (1.20)$$

$$\chi_T = \frac{\partial \langle M \rangle}{\partial H} = \left\{ \frac{\beta}{Z_G} \text{Tr} \left[ M^2(\mathcal{C}) e^{-\beta\mathcal{H} + \beta HM} \right] - \frac{\beta}{Z_G^2} \left[ \text{Tr} \left[ M(\mathcal{C}) e^{-\beta\mathcal{H} + \beta HM} \right] \right]^2 \right\} \quad (1.21)$$

$$\chi_T = \frac{1}{k_B T} \left( \langle M^2 \rangle - \langle M \rangle^2 \right) \quad (1.22)$$

The thermodynamic response function  $\chi_T$  in statistical mechanics is related to the variance of the magnetization. We can relate the above expression with the correlation of the microscopic by performing a coarse-graining of the system where the magnetization  $M(\mathcal{C})$  can be computed an integral

$$M(\mathcal{C}) = \int d^3\vec{r} m(\vec{r}) \quad (1.23)$$

Hence

$$k_B T \chi_T = \int d\vec{r} d\vec{r}' \left[ \langle m(\vec{r}) m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle \right] \quad (1.24)$$

Let us assume the *translational symmetry*:

$$\begin{cases} \langle m(\vec{r}) \rangle = m & \text{homogeneous} \\ \langle m(\vec{r}) m(\vec{r}') \rangle \equiv G(\vec{r} - \vec{r}') & \text{two-point correlation function} \end{cases} \quad (1.25)$$

Let us consider instead the *connected correlation function* i.e. the correlation function of the fluctuations  $\delta m = m - \langle m \rangle$ :

$$\langle m(\vec{r}) m(\vec{r}') \rangle_C \equiv \langle (m(\vec{r}) - \langle m(\vec{r}) \rangle) (m(\vec{r}') - \langle m(\vec{r}') \rangle) \rangle = G(\vec{r} - \vec{r}') - m^2 \quad (1.26)$$

Given the translational invariance one can centre the system such that its centre of mass coincides with the origin

$$\vec{r}_{CM} \Rightarrow \vec{r}_0 \equiv \vec{0} \quad (1.27)$$

$$\Rightarrow \int d\vec{r} \int d\vec{r}' [G(\vec{r} - \vec{r}_0) - m^2] \quad (1.28)$$

The integration over  $\vec{r}'$  gives the volume  $V(\Omega)$  of the system

$$\underbrace{k_B T \chi_T}_{\text{response function}} = V(\Omega) \int d\vec{r} \underbrace{\langle m(\vec{r}) m(\vec{r}_0) \rangle_C}_{\substack{\text{correlation function} \\ \text{of the fluctuations} \\ \text{of the local magnetization}}} \quad (1.29)$$

The Equation (1.29) is called the **fluctuation-dissipation relation**.

How  $G_c(\vec{r})$  behaves? In general one has

$$G_c(\vec{r}) \sim e^{-|\vec{r}|/\xi} \quad (1.30)$$

Meaning that for  $|\vec{r}| > \xi$  the fluctuations are uncorrelated. We define the  $\xi$  as the *correlation length*. It is related to the correlation function. In general is finite but if you approach  $T_c$  diverges. In fact, at the critical point this correlation will expand in the whole space and reaches the size of all the system, it goes to infinity. When  $\xi$  will diverge, there is not anymore the exponential and the integrall cannote be kepted finite.

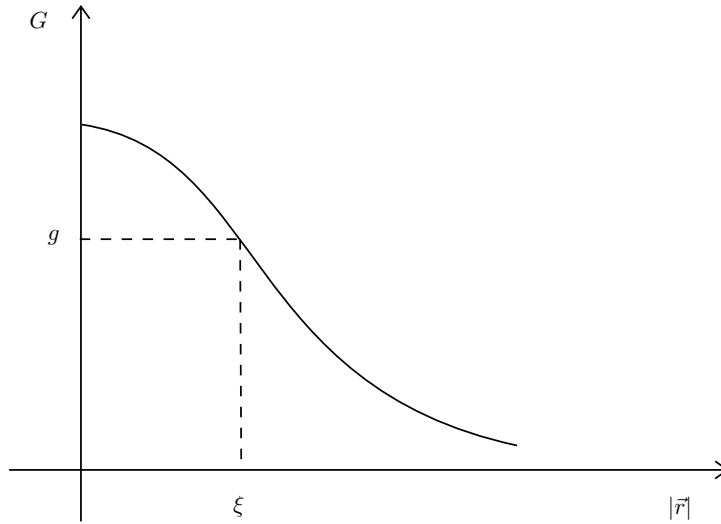
Let  $g$  be the value of  $G_c$  for  $|\vec{r}| < \xi$ :

$$k_B T \chi_T \leq V g \xi^3 \quad (1.31)$$

where there is an inequality because we are underestimating the integral (see Figure 1.2):

$$\frac{k_B T \chi_T}{V} < g \xi^3 \quad (1.32)$$

Hence if  $\chi_T$  diverges at the critical point it implies  $\xi \rightarrow \infty$ . In particular one can see



**Figure 1.2:** Description.

that for  $H = 0$  and  $T \rightarrow T_C^\pm$ :

$$\xi_\pm(T, H = 0) \sim |t|^{-\nu_\pm} \quad (1.33)$$

where  $\nu_+ = \nu_- = \nu$  is the correlation length critical exponent.

*Remark.* It does not derive from thermodynamic considerations.

Scaling (1.33) is often used as the most general definition of a critical point. One can also show that at  $T = T_c$  (i.e.  $t = 0$ )

$$G_c(r) \sim \frac{1}{r^{d-2+\mu}} \quad (1.34)$$

where  $\mu$  is the correlation critical exponent. The formula is a power law decays instead than exponential.

## 1.4 Finite size effects and phase transitions

Actually the thermodynamic limit is a mathematical trick and in real systems it is never reached. Is it then physically relevant?

If we had instruments with *infinite* precision each change of the physical properties of a system would occur within a finite range, therefore we would observe a smooth crossover instead than a singularity. In this respect the notion of correlation length  $\xi$  is extremely important. To illustrate this point let us consider the gas-liquid system in proximity of its critical point ( $T \sim T_c$ ). If we approach  $T_c$  from the gas phase there will be fluctuations of  $\rho$  with respect to  $\rho_G$ ,  $\Delta\rho = \rho - \rho_G$ , due to the presence of denser droplets (liquid) in the continuum gas phase. These droplets will have different diameters, but the average size would be  $\xi$ , where it is the typical size of the liquid droplets. Clearly  $\xi = \xi[T]$  and, in proximity of the critical point  $\xi \stackrel{t \rightarrow 0}{\sim} |t|^{-\nu}$ .

On the other hand, in a finite system,  $\xi$  cannot diverge since it is bounded above,  $\xi \leq L$ , where  $L$  is the linear system size.

As  $T \rightarrow T_c$ , where  $\xi$  should be larger than the system size, the behaviour of the system should deviate from the one expected by the theory that is obtained in the limit  $L \rightarrow \infty$ . How far the real system would be from the critical point  $t = 0$  where singularities develop? Let us try to give an estimate of this deviation.

Let us consider a system of size  $L = 1 \text{ cm}$  and  $t \equiv (T - T_c)/T_c$  and  $\xi \sim \xi_0 t^{-\nu}$ . Let us assume  $\xi_0 = 10 \text{ \AA}$ , the lattice distance:

$$t \sim \left( \frac{\xi}{\xi_0} \right)^{-1/\nu} \sim \left( \frac{L}{10 \text{ \AA}} \right)^{-1/\nu} \sim (10^{10})^{-1/\nu} \quad (1.35)$$

we will see that  $\nu < 1$  and close to  $1/2$ :

$$t \sim (10^{10})^{-2} = 10^{-20} \quad (1.36)$$

Therefore we have  $t \approx 10^{-20}$  as distance from  $T_c$ .

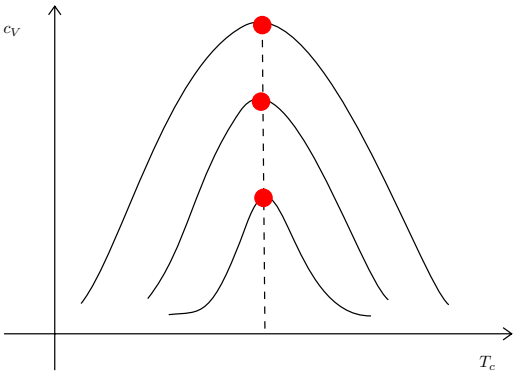
This estimate suggests that the experimental instrument that measures temperature must have a precision of  $10^{-20}$  to see deviations from the results obtained in the thermodynamic limit.

## 1.5 Numerical simulations and phase transitions

In this case the size  $L$  of the simulated system is few multiples of  $\xi_0$  and the finite-size effects of the simulated data can strongly affect the location and the scaling laws of the phase transition under numerical investigation.

Finite size scaling analysis of the numerical data is needed.

We can find the critical point by doing Montecarlo simulation. Supposing a Montecarlo simulation of a Ising model, for which there is no an analytic solution and compute the energy. Try to extrapolate for example the position of the peak as  $N$  increases. If we start to see this behaviour it shown that something is happening. Nevertheless, there are two approaches: studying the system by looking for all the details. An example could be a protein, that interact with other proteins; we can look at all the electrons (or atoms). Even if we think at the simple protein that exist there are a lot of degree of freedom. For doing a simulation, if we are interested in long time behaviour and in large scale behaviour, details are not important. What it is important are symmetries, ranges of interaction. Therefore, we can forget about all the details. We can introduce the effective potentials as wander-walls or Lenard Jones potential and studying collective effects. This is the second approach.



**Figure 1.3:** Description.