Fluctuation

Let ε_r be the energy of the microstate labeled by i , and let us suppose that the system is in thermal equilibrium with a heat-bath at temperature T. Then:

The probability p_r of the system being found in the microstate r is proportional to $e^{-\beta \varepsilon_r}$

$$i.e.\ \ p_r \propto e^{-\beta \varepsilon_r}\ .$$

It is usually written $\beta = 1/k_B T$ where k_B is **Boltzmann's constant**, = 1.38 x 10^{-23} J K^{-1}. The quantity

$e^{-\beta \varepsilon_r}$ is known as the **Boltzmann factor**. This fundamental result of statistical mechanics will be the starting point of our analysis. From it will follow all the time-independent properties of a system in thermal equilibrium.

Since the system must always be in *some* state, the total of the p_r should be one, and the normalized probability p_r is therefore

$$p_r = \frac{e^{-\beta \varepsilon_r}}{Z} \qquad\qquad (1)$$

where the normalizing factor Z is

$$Z = \sum_i e^{-\beta \varepsilon_r} \qquad\qquad (2)$$

Equation (1) is the **Gibbs probability distribution**. From it we can calculate the thermal average $\langle X \rangle$ of any property X of the system, provided that:

1.   We know the microstates a of the system;
2.   We know the energy ε_r of each microstate;
3.   We know the value X_r taken by X in each microstate *r*;
4.   We can perform the sum

$$\langle X \rangle = \sum_r p_r X_r = \frac{1}{Z} \sum_r X_r e^{-\beta \varepsilon_r} \qquad (3)$$

The fourth of these in particular can be very hard if not impossible to do exactly, but this is a problem of technique and not of principle. The Gibbs distribution provides a remarkably simple and universal connection between the microscopic laws governing a system and its behavior when in thermal equilibrium.

The quantity Z defined in (2) is called the partition function; and is a function of temperature. Less obviously, it is also a function of the parameters which determine the energy ε_r of each microstate. We shall refer to these parameters as **constraints**. For example, if our system consists of molecules of gas inside a rigid container, this can be represented by a potential $U(x)$ which is zero inside the container but infinite outside it. In this case the 'constraint' $U(x)$ does literally constrain the system. Or if a system of spins s_i is put in an external magnetic field **B** there will be an addition to the energy $-\sum_i s_i \cdot B$, reflecting this. In this case the external field **B** is the constraint. We shall denote the set of constraints applied to a general system by {V}. It is by varying the constraints that mechanical work is done on the system. Far from Z being just a normalizing constant, we shall see that all the properties of the system can be obtained from the functional dependence of Z on the temperature and the constraints.

There remains the question of what the averages we calculate with the Gibbs distribution mean. There are two possibilities:
1- We can imagine a very large number of copies of a system, and ask what the distribution of the microstates of these copies is at one particular time. Or

2- we can imagine carrying out a series of measurements on one particular system at different times, and asking how these measurements are distributed.

Usually it is correct to assume these two distributions to be equal to each other and to the Gibbs distribution, but problems can arise if it takes a long time for the system to travel between different parts of the space of microstates available to it. It may be that the microstates of a single system follow the Gibbs distribution over a sufficiently long time, but over the time of observation they do not.

Fluctuations

Statistical mechanics can also be used to study quantities about which classical thermodynamics has nothing to say. For example, consider the fluctuations that occur in the energy of a system at given values of temperature and constraints. The energy will not always have its equilibrium value, and it would be interesting to know over what sort of range the energy fluctuates. The thermal average of $(E - \langle E \rangle)^2$ tells us this. Consider a small system with fixed volume and number of particles in thermal contact with a heat path at temperature T.

The mean energy of a system in thermal equilibrium is,

$$U = \langle E \rangle = \sum_r p_r \varepsilon_r = \frac{1}{Z} \sum_r \varepsilon_r e^{-\beta \varepsilon_r}, \qquad Z = \sum_i e^{-\beta \varepsilon_r}$$

This is the sum of the energy of each microstate over all microstates r, weighted by the probability that the system will be in that microstate. From the definition (2) of the partition function Z it follows that

$$U = \frac{1}{Z} \sum_r \varepsilon_r e^{-\beta \varepsilon_r} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{\{V\}} = -\left(\frac{\partial (\log Z)}{\partial \beta}\right)_{\{V\}} \tag{A}$$

and

$$\langle E^2 \rangle = \sum_r p_r \varepsilon_r^2 = \frac{1}{Z} \sum_r \varepsilon_r^2 e^{-\beta \varepsilon_r} = \frac{1}{Z}\sum_r \left(-\frac{\partial}{\partial \beta}\right)\left(-\frac{\partial}{\partial \beta}\right)e^{-\beta \varepsilon_r} = \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \beta^2}\right)_{\{V\}} \tag{B}$$

then.

$$\left(\delta U\right)^2 = \langle (\Delta E)^2 \rangle = \langle \left(E - \langle E \rangle\right)^2 \rangle$$

$$= \langle E^2 - 2E\langle E \rangle + \langle E^2 \rangle \rangle = \langle \langle E^2 \rangle - \langle E \rangle^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(-\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{\{V\}}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\frac{\partial}{\partial \beta}(\log Z)$$

$$\Rightarrow \qquad \left(\delta U\right)^2 = \left(\frac{\partial^2 (\log Z)}{\partial \beta^2}\right)_{\{V\}} \tag{C}$$

Using (A), one gets:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial \beta}\right)_{V,N}\left(\frac{\partial \beta}{\partial T}\right)^* = \left(\frac{\partial U}{\partial \beta}\right)_{V,N}(-k_B\beta^2) = -\left(\frac{\partial^2 \log Z}{\partial \beta^2}\right)_{V,N}(-k_B\beta^2)$$

$$= k_B\beta^2\left(\frac{\partial^2 \log Z}{\partial \beta^2}\right)_{V,N} \tag{D}$$

Equating (C) and (D), we have:

$$C_V = k_B \beta^2 \left(\delta U\right)^2$$

δU is the RMS fluctuation in the energy of the system

$$\delta U = T\sqrt{k_B C_V} \tag{E}$$

We used the identities: $^*\beta = \dfrac{1}{kT} \Rightarrow \dfrac{\partial \beta}{\partial T} = -1/kT^2,\ \dfrac{\partial}{\partial \beta} = \dfrac{\partial T}{\partial \beta}\dfrac{\partial}{\partial T} = -kT^2\dfrac{\partial}{\partial T}$

Equation (E) is a completely general result, and does not depend on any particular properties of the system being considered. For 1 kg of water at room temperature δU is about 4.2×10^{-8} J, which is small—the amount of energy needed to change the water's temperature by 1 K is 10^{11} times this. Note that since the heat capacity C_V grows linearly with the size of the system, the fractional energy fluctuations $\dfrac{\delta U}{U} \propto \dfrac{1}{\sqrt{V}}$ fall as the square root of the system size. They therefore become negligible in the limit that the size goes to infinity. Because of this, this limit is called the **thermodynamic limit**. The exception to this is when the heat capacity of the system diverges, as it does at a critical point. Then the fluctuations do not go away as the system becomes larger, but are present on **all scales**.

It was surprisingly easy to find something as interesting as the fluctuations in the energy. The technique of differentiating the partition function to find thermal averages is a very powerful one. If the partition function is known as a function of the appropriate constraints, the thermal average of any quantity can be found. If the required constraint term is not already present in the Hamiltonian, it can be added in.
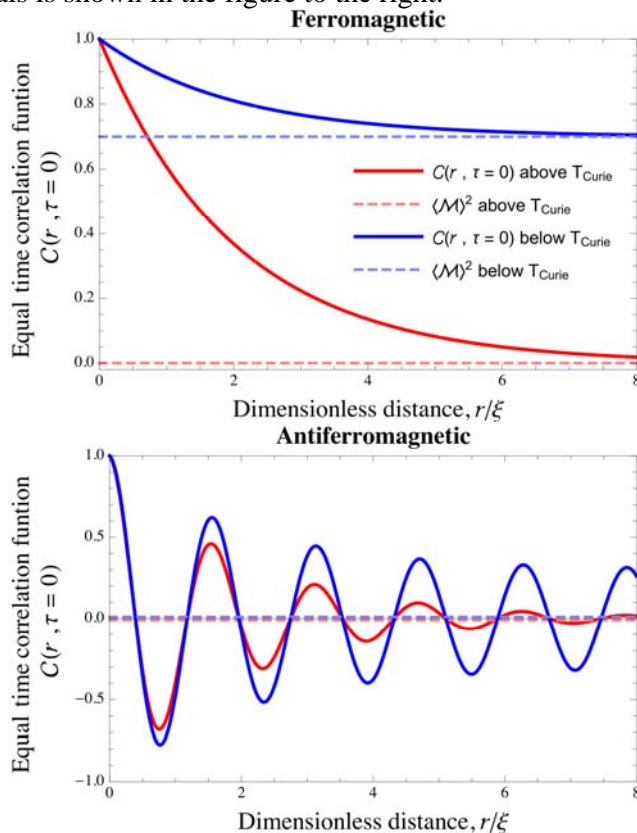
Correlation Function (CF)

A **correlation function** is a statistical correlation between random variables at two different points in space or time, usually as a function of the spatial or temporal distance between the points. If one considers the correlation function between random variables representing the same quantity measured at two different points then this is often referred to as an autocorrelation function being made up of autocorrelations. Correlation functions of different random variables are sometimes called **cross correlation functions** to emphasise that different variables are being considered and because they are made up of cross correlations.
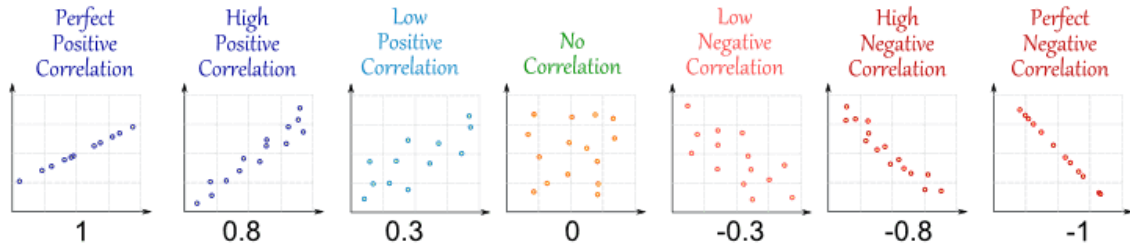
Correlation functions are a useful indicator of dependencies as a function of distance in time or space, and they can be used to assess the distance required between sample points for the values to be effectively uncorrelated. In addition, they can form the basis of rules for interpolating values at points for which there are no observations.

Correlation functions used in astronomy, financial analysis, and statistical mechanics differ only in the particular stochastic processes they are applied to. In quantum field theory there are correlation functions over quantum distributions.

In statistical mechanics, the **correlation function** is a measure of the order in a system, as characterized by a mathematical correlation function. Correlation functions describe how microscopic variables, such as spin and density, at different positions are related. More specifically, the correlation function quantifies how microscopic variables co-vary with one another on average across space and time. A classic example of such spatial correlations is in ferro- and antiferromagnetic materials, where the spins prefer to align parallel and antiparallel with their nearest neighbors, respectively. The spatial correlation between spins in such materials is shown in the figure to the right.

Like this:

Perfect Positive Correlation	High Positive Correlation	Low Positive Correlation	No Correlation	Low Negative Correlation	High Negative Correlation	Perfect Negative Correlation
1	0.8	0.3	0	-0.3	-0.8	-1

Correlation can have a value:

       1 is a perfect positive correlation

       0 is no correlation (the values don't seem linked at all)

       -1 is a perfect negative correlation

Time correlation function

Time-correlation functions are an effective and intuitive way of representing the dynamics of a system, and are one of the most common tools of time-dependent quantum mechanics. They provide a statistical description of the time-evolution of a variable for an ensemble at thermal equilibrium. They are generally applicable to any time-dependent process for an ensemble, but are commonly used to describe random (or stochastic) and irreversible processes in condensed phases. We will use them in a description of spectroscopy and relaxation phenomena.

      If we consider a series of measurements with the value of the measurement $A(t)$ changing randomly but continuously. Then at times t and t' that are close together the values $A(t)$ and $A(t')$ are *correlated* if they have similar values. Whereas for the measurements at times t and t' that are far apart we could consider no relationship between the values $A(t)$ and $A(t')$, so they are *uncorrelated*. The *correlation* plotted against time would then start at some value and decay with time.
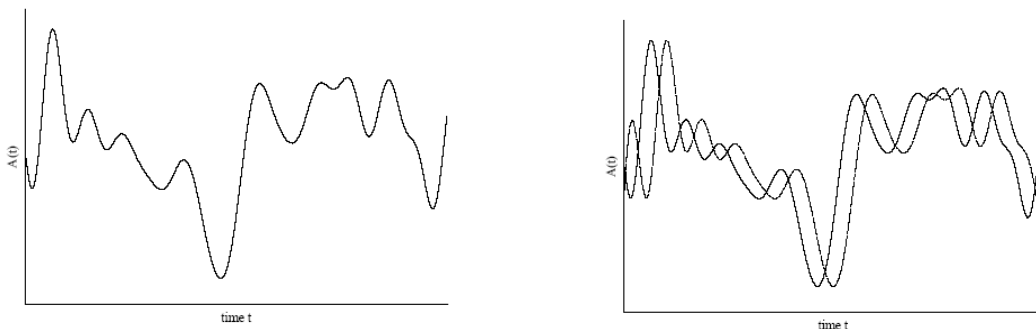
If we shift the data by a time τ and multiply the values of the new plot to the original one we get a big value if the curves have both high and low values at the same place.

The operation of multiplying two curves together and integrate them over the x-axis is called an *overlap integra*. The overlap integral is also called the *Correlation function*

$$G^{(2)}(\tau) = \langle A(t)A(t+\tau)\rangle \quad (A.1)$$

The correlation is not a function of time, it is a function of the shift in time or the *correlation time* τ.

The correlation function of the one-dimensional Ising model

We proceed to calculate the correlation function of two spins S_i and S_j it is defined as the average value $G^{(2)}(i,j) = \langle S_i S_j \rangle$ of the product $S_i S_j^*$. The correlation function is a measure of the influence exerted by a given spin, say S_i, whose direction is fixed; it is easy to show that the conditional probability for having $S_j = +1$, given that $S_i = +1$, is $\frac{1}{2}\left(1 + \langle S_i S_j \rangle\right)$. Since the interaction favors the alignment of spins, a nearby spin S_j will tend to assume the same orientation as S_i however, thermal agitation counteracts this tendency and exerts a de-correlating effect. Qualitatively speaking one expects some correlation that weakens as the distance between S_i and S_j increases; at a fixed distance apart the correlation will be stronger when the temperature is lower.

Exampe 1: For the Hamiltonian of the one-dimensional Ising model in the form:

$$H = H_o = -J \sum_{i=1}^{N-1} S_i S_{i+1} \quad J > 0$$

the value of $\langle S_i S_j \rangle$ is calculated as a standard statistical average:

$$\langle S_i S_j \rangle = \frac{1}{Z} \sum_{\{S_l\}} S_i S_j e^{-H/kT} = \frac{1}{Z} (\cosh K)^{N-1} \sum_{\{S_l\}} S_i S_j \prod_{l=1}^{N-1} (1 + S_l S_{l+1} \tanh K).$$

(A)

with $K = \beta J$ and the factors S_i and S_j outside the product. The end-result for $\langle S_i S_j \rangle$ reads

$$\left.\begin{array}{l} \langle S_i S_j \rangle = \dfrac{1}{Z} (\cosh K)^{N-1} 2^N (\tanh K)^{|i-j|} = (\tanh K)^{|i-j|}, \\[2mm] \langle S_i S_j \rangle = e^{-|i-j|\,|\ln \tanh K|} = e^{-|i-j|\,|\ln \tanh (J/kT)|}. \end{array}\right\}$$

(B)

Note that: More frequently we will use the relation: $X^A = e^{A \ln X}$
H.W. Prove equation (B).

The correlation function decreases exponentially with the distance $|i-j|$ (see Figure). With "a" the lattice spacing, the distance between spins S_i and S_j in cm is $a|i-j| = r_{ij}$ the *correlation length* ξ is defined by

$\langle S_i S_j \rangle$ as a function of $(i-j)$

$$\left\langle S_i S_j \right\rangle = e^{r_{ij}/\xi},$$

(C)

and for the one-dimensional Ising model equation (B) yields

$$\xi = \frac{a}{\left|\ln\left[\tanh\left(J/kT\right)\right]\right|} = \begin{cases} \infty & T = 0 \\ 0 & T = \infty \end{cases}$$

(D)

This expression shows that the correlation length decreases with rising temperature; it tends to zero as $T \to \infty$, and to infinity as $T \to 0$, thus confirming the intuitive argument given earlier. Note also that equation (B) confirms the absence of spontaneous magnetization:

$$\lim_{|i-j| \to \infty} \left\langle S_i S_j \right\rangle = \left\langle S_i \right\rangle \left\langle S_j \right\rangle = \left\langle S \right\rangle^2 = 0 \qquad \text{(Uncorrelated)}$$

Thermodynamic variables like the magnetization or the entropy are macroscopic properties. But, it became apparent that a much fuller understanding of phase transitions could be obtained by considering what was happening on a microscopic level. To be able to do this in a more quantitative way we introduce the connected correlation functions. For example the spin-spin connected correlation function, defined to measure the correlation between the spins on sites i and j, is

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Fluctuation_correlation
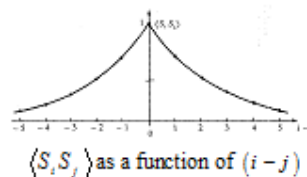
$$G_c^{(2)}(i,j) = G(\vec{r}_i,\vec{r}_j) = \left\langle \left(S_i - \langle S_i \rangle\right)\left(S_j - \langle S_j \rangle\right)\right\rangle \tag{1}$$

where $\vec{r}_i$ is the position vector of site i and $\langle \cdots \rangle$ denotes a thermal average. If the system is translationally invariant $\langle S_i \rangle = \langle S_j \rangle = \langle S \rangle$ and G depends only on $(\vec{r}_i - \vec{r}_j)$

$$G_c^{(2)}(i,j) = G(\vec{r}_i,\vec{r}_j) = \left\langle S_i S_j \right\rangle - \langle S \rangle^2 \tag{2}$$

Away from the critical point, as $r \to \infty$, the spins become uncorrelated; and hence the correlation function decays to zero. Note that this is true not only above but also below the critical temperature, although here the mean value of the spin $\langle S \rangle \neq 0$, because, as is evident from eqn (1), the correlations are measured between the fluctuations of the spins away from their mean values. The correlations decay to zero exponentially with the distance between the spins

$$G(\vec{r}) \sim r^{-\tau} e^{-r/\xi} \tag{3}$$

where τ is some number.

Equation (3) provides a definition of the correlation length, ξ, which was used as an estimate of the size of the largest ordered clusters in the Monte Carlo generated snapshots of an Ising model. We have assumed that ξ is independent of the direction of $\vec{r}$. This is usually the case for large r near criticality.

If we assume that G_{ij} falls exponentially $(G_{ij} \sim \exp(-r_{ij}/\xi))$, then we find the behaviour shown qualitatively in Fig. 1.12 for the two cases $T > T_c$ and $T < T_c$
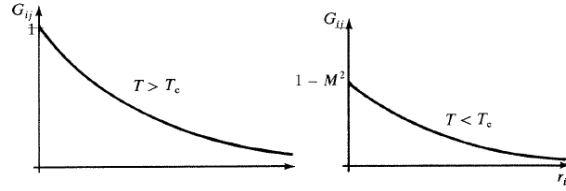

Fig. 1.12

At the critical point itself long-range order develops in the system. The correlation length becomes infinite and eqn (3) breaks down. Evidence from experiments and exactly soluble models shows that here the correlation function decays as a power law

$$G(\vec{r}) \sim r^{-(d-2+\eta)} \tag{4}$$

where η, is the a critical exponent and d is the dimension of the space..

It is possible to relate the spin-spin correlation function to the fluctuations in the magnetization and hence to the susceptibility.

Definition and generating function

The correlation function for two spins, $G^{(2)}(i,j) = \left\langle S_i S_j \right\rangle$, has been introduced already. Since this construct will play a crucial role through all that follows, we proceed to list several definitions and useful properties. The present section uses an elementary example to introduce some techniques that will be developed more systematically in our course.

We defined the correlation function $G^{(2)}(i,j) = \left\langle S_i S_j \right\rangle$ of two spins as the expectation value. This definition is satisfactory when $\langle S_i \rangle = 0$, or in other words when $T > T_c$ and $B = 0$. When $\langle S_i \rangle \neq 0$, the assertion that two spins are uncorrelated means that $\left\langle S_i S_j \right\rangle = \langle S_i \rangle \langle S_j \rangle = M^2$.

Thus it is logical to formulate the definition of $G^{(2)}(i,j)$ in the general case as (connected correlation function):

$$G_{ij} = G_c^{(2)}(i,j) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$$

It proves useful to relate G_{ij} to a second derivative of the partition function $Z[B_i]$ in a site-dependent, non-uniform field B_i:

$$Z[B_i] = \sum_{\{S_K\}} e^{-\beta\left(H_o - \sum_K B_K S_K\right)} \tag{1.4.2}$$

Where $\beta = 1/k_B T$ and $H = H_o = -J \sum_{i=1}^{N-1} S_i S_{i+1}$ $J > 0$. The expectation value $\langle S_i \rangle$ is given by:

$$\langle S_i \rangle = \frac{1}{Z} \sum_{\{S_K\}} S_i \, e^{-\left(\beta H_o - \sum_K B_K S_K\right)}$$

Define $K_i = \beta B_i$, whence

$$\langle S_i \rangle = \frac{1}{Z} \frac{\partial Z}{\partial K_i} = \frac{\partial(\ln Z)}{\partial K_i} \tag{1.4.3}$$

Continue by differentiating once more, with respect to K_i

$$\langle S_i S_j \rangle = \frac{1}{Z} \sum_{\{S_K\}} S_i S_j \, e^{-\left(\beta H_o - \sum_K B_K S_K\right)}$$

whence

$$\langle S_i S_j \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial K_i \partial K_j}$$

This entails

$$G_c^{(2)}(i,j) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial K_i \partial K_j} - \left(\frac{1}{Z} \frac{\partial Z}{\partial K_i}\right)\left(\frac{1}{Z} \frac{\partial Z}{\partial K_j}\right) = \frac{\partial^2(\ln Z)}{\partial K_i \partial K_j}$$

whence

$$G_c^{(2)}(i,j) = \frac{\partial^2(\ln Z)}{\partial K_i \partial K_j} \tag{1.4.4}$$

The mean value $\langle S_i \rangle$ and the correlation $G^{(2)}(i,j)$ are found by differentiating the partition function; the process could be extended to correlation functions for several spins. Because of this, $Z[B_i]$ is called the **generating function** (or **generator**) of the *correlation functions*. Note further that differentiation of $Z[B_i]$ yields $\langle S_i S_j \rangle$, while differentiation of $\ln Z[B_i]$ yields directly; the latter is called the **connected correlation function**, More generally the logarithm $\ln Z[B_i]$ of $Z[B_i]$ is the *generator* of the *connected correlation functions*. Moreover, even if there is no physical applied *B*-field it can prove useful to introduce a fictitious one in order to calculate the correlation functions from (1.4.4); we merely set $B = 0$ in the end-result:

$$G_c^{(2)}(i,j)\Big|_{K=0} = \frac{\partial^2(\ln Z)}{\partial K_i \partial K_j}\Bigg|_{K=0}$$

One very important property of the correlation function is that (up to a factor $\beta\mu$) it represents *the response of the spin S_i to a variation of the B-field at the site j*. In order to show this, we need merely evaluate $\dfrac{\partial \langle S_i \rangle}{\partial B_j}$ from (1.4.3):

$$\frac{\partial \langle S_i \rangle}{\partial K_j} = \frac{\partial^2 \ln Z}{\partial K_i \partial K_j} = (\beta) G_c^{(2)}(i,j) \tag{1.4.5}$$

Notice that it is indeed the connected correlation function that is featured in (1.4.5). This leads us to make an important observation on the state at $T < T_c$. On physical grounds, we expect that the response of a spin S_i to the variation of the B-field at site j should vanish at large values of $\left\| \vec{r}_i - \vec{r}_j \right\|$; this will indeed be the case if the *connected* correlation function G_{ij} tends to zero when $\left\| \vec{r}_i - \vec{r}_j \right\| \to \infty$. One then says that the corresponding state obeys the clustering property. We have obtained the state at $T < T_c$ in the thermodynamic limit, in the presence of an infinitesimal, spatially homogeneous, magnetic field the magnetization takes then one of two possible values $+M_0$ or $-M_0$ (for simplicity we restrict our discussion to an order parameter with dimension $n = 1$). Such states are called pure states.

With other external conditions, we could obtain a state whose magnetization would not be equal to $+M_0$ or $-M_0$ for example, in zero external fields the magnetization would be zero, from symmetry arguments. Such states are called mixed states. There is a rigorous theorem which states that pure states are in one-to-one correspondence with clustering states; thus, in a pure state, the connected correlation function vanishes at large distances, while this is not the case for mixed states. One can also obtain a pure state by taking a very large lattice and assigning a well-defined orientation to the spins on the boundary. If for example all spins on the boundary are directed upward, one can show that the magnetization M_0 is obtained in the limit of an infinite lattice.

Simple calculation: calculate $\langle S_n S_{n+r} \rangle$. Note that $Z_N \approx 2^N \left\{ \cosh(K) \right\}^{N-1} = 2^N \prod_{i=1}^{N-1} \cosh(K_i)$

Define:

$$G_n(r) = \langle S_n S_{n+r} \rangle.$$

r is distance between sites, measured in units of lattice constant a.

$$G_n(r) = \mathcal{Z}_N^{-1} \sum_{\{s\}} S_n S_{n+r} e^{\sum_{i=1}^{N-1} K_i S_i S_{i+1}}; \quad K_i \equiv \frac{J_i}{kT}.$$

Re-write

$$\mathcal{Z}_N G_n(r) = \sum_{\{s\}} S_n S_{n+r} e^{\sum K_i S_i S_{i+1}}.$$

Consider nearest neighbour case: $r = 1$.

$$
\begin{aligned}
\mathcal{Z}_N G_n(1) &= \sum_{\{s\}} S_n S_{n+1} \, e^{\sum K_i S_i S_{i+1}} = \frac{\partial}{\partial K_n} \sum_{\{s\}} e^{\sum K_i S_i S_{i+1}} \\
&= \frac{\partial}{\partial K_N} \mathcal{Z}_N
\end{aligned}
$$

and inductively

$$Z_N G_n(r) = \frac{\partial}{\partial K_n} \frac{\partial}{\partial K_{n+1}} \cdots \frac{\partial}{\partial K_{n+r-1}} \mathcal{Z}_N.$$

Hence:

$$2^N \Pi_{i=1}^{N-1} \cosh K_i G_n(1) = 2^N \Pi_{i=1}^{N-2} \cosh K_i \times \sinh K_n,$$

therefore

$$G_n(1) = \tanh K_n,$$

$$G_n(r) = \Pi_{i=1}^{r} \tanh K_{n+i-1}.$$

Uniform interaction $\Rightarrow G_n(r) = \tanh^r K$.

Consider limit $r \to \infty$. $T > 0$, $\tanh K < 1$ and $G_n \to 0$ as $r \to \infty$. Hence for $T = 0$, $K \to \infty$ and $G_n \to 1$.