
LECTURE NOTES
OF
STATISTICAL MECHANICS

COLLECTION OF THE LECTURES NOTES OF PROFESSOR ORLANDINI.

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Abstract

In this document I have tried to reorder the notes of the statistical mechanics course held by Professor Enzo Orlandini at the Department of Physics of the University of Padua during the first semester of the 2019-20 academic year of the master's degree.

The notes are **fully** integrated with the material provided by the professor in the Moodle platform. In addition, I will integrate them, as best as possible, with the books recommended by the professor.

There may be formatting errors, wrong marks, missing exponents etc. If you find errors, let me know (alice.pagano@studenti.unipd.it) and I will correct them, so that this document can be a good study support.

Padova, Friday 31st January, 2020

Alice Pagano

Contents

Introduction	ix
1 Recall of Thermodynamics	1
1.1 A short recap of thermodynamics definitions	1
1.2 Equilibrium states	1
1.3 Equations of states	3
1.4 Legendre transform and thermodynamic potentials	5
1.5 Maxwell relations	8
1.6 Response functions	10
1.6.1 Response functions and thermodynamic stability	12
2 Equilibrium phases and thermodynamics of phase transitions	15
2.1 Equilibrium phases as minima of Gibbs free energy	15
2.2 First order phase transition and phase coexistence	15
2.2.1 Critical points	19
2.2.2 Ferromagnetic system	19
2.3 Second order phase transition	21
2.3.1 Helmholtz free-energy	22
2.4 Thermodynamic of phase coexistence	22
2.4.1 Lever Rule	22
2.4.2 Phase coexistence (one component system)	23
2.4.3 Clausius-Clapeyron equation	24
2.4.4 Application of C-C equation to the liquid-gas coexistence line	25
2.5 Order parameter of a phase transition	27
2.6 Classification of the phase transitions	28
2.6.1 Thermodynamic classification	28
2.6.2 Eherenfest classification	28
2.6.3 Modern classification	29
2.7 Critical exponents	29
2.7.1 Divergence of the response functions at the critical point	30
2.7.2 Critical exponents definition	30
2.7.3 Law of the corresponding states	32
2.7.4 Thermodynamic inequalities between critical exponents	32
3 Recall of statistical mechanics and theory of ensembles	35
3.1 Statistical ensembles	35
3.2 The canonical ensemble	36
3.2.1 Energy fluctuations in the canonical ensemble	39
3.3 Isothermal and isobaric ensemble	40
3.3.1 Saddle point approximation	42
3.4 Gran canonical ensemble	42
4 Statistical mechanics and phase transitions	43

4.1	Statistical mechanics of phase transitions	43
4.1.1	Magnetic system (canonical)	44
4.1.2	Fluid system (gran canonical)	44
4.1.3	Thermodynamic limit with additional constraints	45
4.1.4	Statistical mechanics and phase transitions	45
4.2	Critical point and correlations of fluctuations	46
4.3	Finite size effects and phase transitions	48
4.4	Numerical simulations and phase transitions	49
5	Role of the models in statistical mechanics	51
5.1	Role of the models	51
5.2	The Ising model	51
5.2.1	d -dimensional Ising model	52
5.2.2	Mathematical properties of the Ising model with nearest neighbours interactions	53
5.2.3	Ising model and \mathbb{Z}^2 symmetry.	56
5.3	Lattice gas model	57
5.4	Fluid system in a region Ω	58
5.4.1	From the continuous to the lattice gas model	59
6	Some exactly solvable models of phase transitions	61
6.1	1-dim Ising model	61
6.1.1	Recursive method	61
6.1.2	Transfer Matrix method	64
6.2	General transfer matrix method	66
6.2.1	The free energy	67
6.2.2	The correlation function	68
6.2.3	Results for the 1-dim Ising model	71
6.3	Classical Heisenberg model for $d=1$	74
6.4	Zipper model	76
6.4.1	Transfer matrix method for the Zipper model	80
6.5	Transfer matrix for $2 - \text{dim}$ Ising	81
7	The role of dimension, symmetry and range of interactions in phase transitions	85
7.1	Energy-entropy argument	85
7.1.1	1-dim Ising	85
7.1.2	$d\text{-dim}$ Ising	87
7.2	Role of the symmetry	90
7.3	Continuous symmetries and phase transitions	91
7.4	Role of the interaction range	94
7.4.1	Ising model with infinite range	94
8	Mean field theories of phase transitions and variational mean field	97
8.1	Mean field theories	97
8.1.1	Mean field for the Ising model (Weiss mean field)	97
8.1.2	Free-energy expansion for $m \simeq 0$	100
8.1.3	Mean field critical exponents	101
8.2	Mean field variational method	104
8.2.1	Mean field approximation for the variational approach	105
8.2.2	First approach: Bragg-Williams approximation	106
8.2.3	Second approach: Blume-Emery-Griffith model	111
8.2.4	Mean field again	116

9 Non ideal fluids: Mean field theory, Van der Waals, Virial expansion and Cluster expansion	121
9.1 Mean field theory for fluids	121
9.2 Van der Waals equation	122
9.2.1 Critical point of Van der Waals equation of state	123
9.2.2 Law of corresponding states	125
9.2.3 Region of coexistence and Maxwell's equal area rule	125
9.2.4 Critical exponents of Van der Waals equation	127
9.3 Theories of weakly interacting fluids	129
9.3.1 Van der Waals and virial expansion	130
9.3.2 Cluster expansion technique for weakly interacting gases	131
9.3.3 Computation of virial coefficients for some interaction potentials Φ	134
9.3.4 Higher order terms in the cluster expansion	137
10 Landau theory of phase transition for homogeneous systems	143
10.1 Introduction to Landau theory	143
10.2 Landau theory for the Ising model	144
10.2.1 Construction of \mathcal{L}	144
10.2.2 Equilibrium phases	145
10.3 Critical exponents in Landau's theory	146
10.4 First-order phase transitions in Landau theory	148
10.4.1 Phase stability and behaviour of χT	152
10.4.2 Computation of T^{**}	153
10.4.3 Computation of T^*	153
10.5 Multicritical points in Landau theory	153
10.6 Liquid crystals	157
10.6.1 What are liquid crystals?	157
10.6.2 Definition of an order parameter for nematic liquid crystals . .	158
10.6.3 Landau-de Gennes theory for nematic liquid crystals	160
11 Role of fluctuations in critical phenomena: Ginzburg criterium, Coarse-graining and Ginzburg-Landau theory of phase transitions	163
11.1 Importance of fluctuations: the Ginzburg criterium	163
11.1.1 Fluctuation-dissipation relation	165
11.1.2 Computation of E_{TOT}	166
11.1.3 Estimation of E_{TOT} as $t \rightarrow 0^-$	166
11.2 Functional partition function and coarse graining	167
11.3 Coarse graining procedure for the Ising model	168
11.3.1 Computation of $\mathcal{H}_{eff}[m(\vec{r})]$	169
11.3.2 Magnetic non-homogeneous field	172
11.3.3 Functional derivatives	172
11.4 Saddle point approximation: Landau theory for non-homogeneous systems	173
11.5 Correlation function in the saddle point approximation for non-homogeneous systems	175
11.5.1 Solution of (11.42) by Fourier transform	177
11.6 Including fluctuations at the Gaussian level (non interacting fields) . .	179
11.6.1 Gaussian approximation for the Ising model in Ginzburg-Landau theory	180
12 Widom's scaling theory. Block-spin Kadanoff's transformation	187
12.1 Introduction	187

12.2	Widom's static scaling theory	188
12.2.1	Homogeneous functions of one or more variables	189
12.2.2	Widom's scaling hypothesis	191
12.3	Relations between critical exponents	191
12.3.1	Exponent β (scaling of the magnetization)	191
12.3.2	Exponent δ	192
12.3.3	Exponent γ	192
12.3.4	Exponent α (scaling of the specific heat)	193
12.3.5	Griffiths and Rushbrooke's equalities	194
12.3.6	An alternative expression for the scaling hypothesis	194
12.3.7	Scaling of the equation of state	194
12.4	Kadanoff's block spin and scaling of the correlation function	195
12.4.1	Kadanoff's argument for the Ising model	195
12.4.2	Kadanoff's argument for two-point correlation functions	198
13	Renormalization group theory. Universality	201
13.1	Renormalization group (RG)	201
13.1.1	Main goals of RG	201
13.1.2	Singular behaviour in RG	203
13.1.3	Zoology of the fixed points	203
13.1.4	Linearization of RG close to the fixed points and critical exponents	204
13.2	RG and scaling	206
13.3	Real space renormalization group on 1D Ising model ($H = 0$)	208
13.3.1	Decimation procedure for $D = 1$	208
13.3.2	Decimation procedure for $D > 1$ (proliferation of interactions)	210
14	Spontaneous symmetry breaking	211
14.1	Spontaneous symmetry breaking	211
14.2	Spontaneous breaking of continuous symmetries and the anset of Goldstone particles	213
14.2.1	Quantum relativistic case (field theory)	213
14.3	Interpretation in relativistic quantum mechanics	215
14.4	Spontaneous symmetry breaking in Gauge symmetries	217
14.5	Fiedl theory analog	217
14.5.1	Non abelian gauge theories	220
14.6	Extension of Higgs mechanism to non abelian theories	220
14.6.1	GWS model	220
14.6.2	Higgs mechanism	221
	Conclusions	223
	Bibliography	225

Introduction

The goal of statistical mechanics [1] is to predict the macroscopic properties of bodies, most especially their thermodynamic properties, on the basis of their microscopic structure.

The macroscopic properties of greatest interest to statistical mechanics are those relating to thermodynamic equilibrium. As a consequence, the concept of thermodynamic equilibrium occupies a central position in the field.

The microscopic structure of systems examined by statistical mechanics can be described by means of mechanical models: for example, gases can be represented as systems of particles that interact by means of a phenomenologically determined potential. Other examples of mechanical models are those that represent polymers as a chain of interconnected particles, or the classical model of crystalline systems, in which particles are arranged in space according to a regular pattern, and oscillate around the minimum of the potential energy due to their mutual interaction. The models to be examined can be, and recently increasingly are, more abstract, however, and exhibit only a faint resemblance to the basic mechanical description (more specifically, to the quantum nature of matter). The explanation of the success of such abstract models is itself the topic of one of the more interesting chapters of statistical mechanics: the theory of universality and its foundation in the renormalization group.

The models of systems dealt with by statistical mechanics have some common characteristics. We are in any case dealing with systems with a large number of degrees of freedom: the reason lies in the corpuscular (atomic) nature of matter. The degrees of freedom that one considers should have more or less comparable effects on the global behavior of the system. This state of affairs excludes the application of the methods of statistical mechanics to cases in which a restricted number of degrees of freedom “dominates” the others—for example, in celestial mechanics, although the number of degrees of freedom of the planetary system is immense, an approximation in which each planet is considered as a particle is a good start. In this case, we can state that the translational degrees of freedom (three per planet)—possibly with the addition of the rotational degrees of freedom, also a finite number—dominate all others. These considerations also make attempts to apply statistical concepts to the human sciences problematic because, for instance, it is clear that, even if the behavior of a nation’s political system includes a very high number of degrees of freedom, it is possible to identify some degrees of freedom that are disproportionately important compared to the rest. On the other hand, statistical methods can also be applied to systems that are not strictly speaking mechanical—for example, neural networks (understood as models of the brain’s components), urban thoroughfares (traffic models), or problems of a geometric nature (percolation).

The simplest statistical mechanical model is that of a large number of identical particles, free of mutual interaction, inside a container with impenetrable and perfectly elastic walls. This is the model of the ideal gas, which describes the behavior of real gases quite well at low densities, and more specifically allows one to derive the well-known equation of state.

The introduction of pair interactions between the particles of the ideal gas allows us to obtain the standard model for simple fluids. Generally speaking, this model cannot be resolved exactly and is studied by means of perturbation or numerical techniques. It allows one to describe the behavior of real gases (especially noble gases), and the liquid–vapor transition (boiling and condensation).

The preceding models are of a classical (nonquantum) nature and can be applied only when the temperatures are not too low. The quantum effects that follow from the inability to distinguish particles are very important for phenomenology, and they can be dealt with at the introductory level if one omits interactions between particles.

In many of the statistical models we will describe, however, the system’s fundamental elements will not be “particles,” and the fundamental degrees of freedom will not be mechanical (position and velocity or impulse). If we want to understand the origin of ferromagnetism, for example, we should isolate only those degrees of freedom that are relevant to the phenomenon being examined (the orientation of the electrons’ magnetic moment) from all those that are otherwise pertinent to the material in question.

The simplest case is that in which there are only two values—in this fashion, we obtain a simple model of ferromagnetism, known as the Ising model, which is by far the most studied model in statistical mechanics. The ferromagnetic solid is therefore represented as a regular lattice in space, each point of which is associated with a degree of freedom, called spin, which can assume the values $+1$ and -1 . This model allows one to describe the paramagnet-ferromagnet transition, as well as other similar transitions.

In this course, classical statistical mechanics of system at equilibrium is treated. The exam is divided into two parts: first, common oral exam (same exercise and question for everyone, it is a written part), second part, oral.

Outline of the course

1. Brief recap of thermodynamics.
2. Equilibrium phases and thermodynamics of the phase transitions.
3. Statistical mechanics and theory of ensembles.
4. Thermodynamic limit and phase transitions in statistical mechanics.
5. Order parameter and critical point.
6. The role of modelling in the physics of phase transitions.
7. The Ising model.
8. Exact solutions of the Ising model.
9. Transfer matrix method.
10. Role of dimension and range of interactions in critical phenomena (lower critical dimension).
11. Approximations: *Meanfield theory Weiss* and *variational mean field*.
12. Landau theory of phase transitions: the role of symmetries.
13. Relevance of fluctuations: the *Ginzburg criterium* and the notion of the *upper critical dimension*.
14. The Ginzburg-Landau model.
15. Landau theory for non-homogeneous system. The ν exponent.
16. Gaussian fluctuations in the G-L theory.
17. Widom's scaling theory.
18. Kadanoff's theory of scaling.
19. The theory of renormalisations group and the origin of *universality* in critical phenomena.
20. Spontaneous symmetry breaking.

Chapter 1

Recall of Thermodynamics

1.1 A short recap of thermodynamics definitions

The systems we are considering are

1. In equilibrium with an external bath at fixed temperature T .
2. Made by a (large) number N of degrees of freedom. For instance, we remind that $1 \text{ mol} \approx N_A \sim 10^{23}$ elementary units.

Thermodynamic is a macroscopic theory of matter at equilibrium. It starts either from experimental observations or from *axiomatic assumptions* and establishes rigorous relations between macroscopic variables (**observables**) to describe systems at equilibrium. One of the first important concept is the one of **extensive variables**. For instance, the *extensive variables* that characterize the system at equilibrium are the internal energy U , volume V , number of particles N and magnetization \vec{M} that "scale with the system". In general, the extensive variable are *additive*.

In thermodynamic, it is important the concept of **walls and thermodynamic constraints** that are necessary for a complete definition of a thermodynamic system. With their presence or absence it is possible to control and redistribute the thermodynamic variables for changing the system. The typical walls are:

- *Adiabatic walls*: no heat flux. If it is removed we obtain a *diathermic walls*.
- *Rigid walls*: no mechanical work. If it is removed we obtain a *flexible or mobile walls*.
- *Impermeable walls*: no flux of particles (the number of particles remain constraints). If it is removed we obtain a *permeable walls*.

1.2 Equilibrium states

Consider a system in an equilibrium state, if the system changes our aim is to study the next equilibrium state of the system. Therefore, we move from a system in equilibrium to another. The fundamental problem of thermodynamics is how to characterize the new system.

Now, we define the concept of **equilibrium states**. Consider macroscopic states that are fully described by extensive variables such as the internal energy U , the volume V , the number of particles N , the magnetization \vec{M} , etc If these variables are time independent, the system is in a *steady state*. Moreover, if there are no macroscopic currents, the system is at *equilibrium*. Therefore, we describe a system by characterizing all the extensive variables at equilibrium.

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Suppose that the system changes slow in time, it goes from an equilibrium state to another one and the transformation is so slow that in each Δt the system is at equilibrium. Hence, considering a sequence of equilibrium states, the **quasi-static transformation** are described by the *1st Law of Thermodynamic*:

$$dU = \delta Q - \delta W \quad (1.1)$$

The variation of the internal energy of the systems depends by two factors, δw that is the work done by the system during a *quasi-static process* (infinitive slow), and δQ that is the heat absorbed by the system during the process. Remember that we write dU because it is a differential quantity, while the other quantities with the δ are only small quantities. Therefore, dU is a function of state, the other are not.

Remark. The convention is $\delta Q > 0$ if the heat is absorbed by the system, and $\delta W > 0$ if the work is done by the system.

For example, considering a simple fluid with a given pressure, if we change the volume, the work done by the systems is $\delta W = P dV$. For a magnetized system, we have $\delta W = -\vec{H} \cdot d\vec{M}$.

In conclusion, starting from an equilibrium state and removing some constraints (i.e. wall properties), we want to find the new equilibrium state compatible with the new constraints.

Suppose a system with adiabatic rigid impermeable constraints. The system on the left is characterized by V_1, N_1, U_1 , the one on the right by V_2, N_2, U_2 . There are many ways for solving this problem. We use the most general way, that is by using the *maximum entropy principle*. If exists a function S of the extensive variables of the system that is defined for all equilibrium states, we call it **entropy** and the *1st fundamental relation* is

$$S = S(U, V, N) \quad (1.2)$$

The new values taken by the extensive parameters when a constraint has been removed are the ones that *maximize* S . It means $dS = 0$ and $d^2S < 0$, given the remaining constraint.

The properties of S are:

1. S is an *additive function* with respect to the subsystems in which the system is partitioned:

$$S = \sum_{\alpha} S^{(\alpha)} \quad (1.3)$$

2. S is *differentiable* and *monotonically increasing* with respect to the internal energy U . It means that $\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$.

3. For each subsystem (α) we have:

$$S^{(\alpha)} = S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N^{(\alpha)}) \quad (1.4)$$

This fundamental relation holds for each subsystem.

4. S is an *homogeneous function* of *1st order* with respect to the extensive parameters, namely:

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N), \quad \forall \lambda > 0 \quad (1.5)$$

It means that S is an extensive quantity.

Remark. Since S is monotonically increasing in U , the following inequality holds:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$$

Therefore, we have $\left(\frac{\partial S}{\partial U}\right)_{V,N} \neq 0$ and it can be inverted locally.

Afterwards, $S = S(U, V, N)$ inverted in U gives the 2st *fundamental relation*

$$U = U(S, V, N) \quad (1.6)$$

It means that, we can look at S or U and, when these quantities are known, all the informations about the system can be obtained.

By taking the differential of the fundamental relation

$$U = U(S, V, N_1, \dots, N_r)$$

one gets

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N_j}}_{\substack{T \\ \text{absolute} \\ \text{temperature}}} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N_j}}_{\substack{-P \\ \text{pressure}}} dV + \sum_{j=1}^r \underbrace{\left(\frac{\partial U}{\partial N_j}\right)_{S,V}}_{\substack{\mu_j \\ \text{electrochemical} \\ \text{potential}}} dN_j \quad (1.7)$$

1.3 Equations of states

Now, we define another set of variables that are called **intensive variables**. The term *intensive* means that it is independent of the size of the system, namely that the value of the variable relative to a subsystem is equal to that of the whole system. The intensive variables are themselves functions of S, V, N , and examples of intensive variables are the pressure, P , and the temperature of the system, T .

The **state equations** are defined as:

$$T = T(S, V, N_1, \dots, N_r) \quad (1.8a)$$

$$P = P(S, V, N_1, \dots, N_r) \quad (1.8b)$$

$$\mu_j = \mu_j(S, V, N_1, \dots, N_r) \quad (1.8c)$$

Remark. If all the state equations are known, the fundamental relation is determined apart from a constant. It means that the coefficients of the differential (1.7) are known.

Example 1

Let us see some examples of equations of state:

- For an *ideal gas*:

$$PV = Nk_bT \quad (1.9)$$

- *Van-Der Waals* equation of the state:

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - Nb) = Nk_bT \quad (1.10)$$

- For magnetic systems, another equation of state is the *Curie Law*:

$$M = \frac{CH}{T} \quad (1.11)$$

Remark. We compute $\left(\frac{\partial U}{\partial M}\right)_{S,N} = H$.

The equations of state are homogeneous functions of *zero* degree. For example, considering the temperature T :

$$T(\lambda S, \lambda V, \lambda N) \stackrel{0}{=} T(S, V, N)$$

It means that at equilibrium the temperature of a subsystem is equal to the one of the whole system. Similarly,

$$P(\lambda S, \lambda V, \lambda N) = P(S, V, N)$$

Now, we keep the S parameter separates from the other that are substituted by *generalized displacements*, as $(V, N_1, \dots, N_r) \rightarrow X_j$. The fundamental relation becomes

$$U = U(S, X_1, \dots, X_{r+1}) \quad (1.12)$$

and we define:

$$\left(\frac{\partial U}{\partial S}\right) \equiv T \quad (1.13a)$$

$$\left(\frac{\partial U}{\partial X_j}\right) \equiv P_j \quad (1.13b)$$

The differential is written as the following:

$$dU = T dS + \sum_{j=1}^{r+1} P_j dX_j \quad (1.14)$$

where $X_1 = V$ is the volume and $P_1 = -P$ is the pressure.

From the equilibrium condition,

$$dU = 0$$

one can get a relation between intensive variables in differential form as the **Gibbs-Duhem relation**:

$$S dT + \sum_{j=1}^{r+1} X_j dP_j = 0 \quad (1.15)$$

For a one-component simple fluid system, the equation (1.15) simplifies into

$$S dT - V dP + N d\mu = 0$$

and dividing by the number of moles N

$$d\mu = -s dT + v dP \quad (1.16)$$

that is the Gibbs-Duhem relation in a *molar form*.

For a magnetic system, we have

$$dU = T dS + \vec{\mathbf{H}} \cdot d\vec{\mathbf{M}} + \mu dN \quad (1.17)$$

Remark. Note that $\mu = \mu(T, P)$ is a relation between intensive variables.

To summarize, the fundamental relations are $S = S(U, V, N_1, \dots, N_r)$ or $S = S(U, \vec{\mathbf{M}}, N_1, \dots, N_r)$ for magnetic systems. In the energy representation we have $U = U(S, V, N_1, \dots, N_r)$ or $U = U(S, \vec{\mathbf{M}}, N_1, \dots, N_r)$.

1.4 Legendre transform and thermodynamic potentials

In many situations, it is convenient to change some extensive variables with their conjugate intensive ones that became independent and free to vary. We have new thermodynamic potentials. It works as following; suppose we have a function as

$$Y = Y(X_0, X_1, \dots, X_k, \dots, X_{r+1}) \quad (1.18)$$

such that Y is *strictly convex* in say, X_k ($\frac{\partial^2 Y}{\partial X_k^2} > 0$) and smooth¹. The idea is to find a transformation such that

$$Y = Y(X_0, X_1, \dots, P_k, \dots, X_{r+1}) \quad (1.19)$$

where

$$X_k \rightarrow P_k \equiv \frac{\partial Y}{\partial X_k} \quad (1.20)$$

i.e. P_k substitutes X_k as a new independent variable. In mathematics this is called *Legendre transform*.

The **thermodynamic potentials** are extremely useful tools, whose name derives from an analogy with mechanical potential energy: as we will later see, in certain circumstances the work obtainable from a macroscopic system is related to the change of an appropriately defined function, the thermodynamic potential. They are useful because they allow one to define quantities which are experimentally more easy to control and to rewrite the fundamental thermodynamic relations in terms of them.

Mathematically, *all the thermodynamic potentials are the result of a Legendre transformation of the internal energy*, namely they are a rewriting of the internal energy so that a variable has been substituted with another.

Example 2: How to calculate thermodynamic potentials

Suppose we want to replace the entropy S with its conjugate derivative

$$T = \frac{\partial U}{\partial S}$$

One starts from the fundamental relation

$$U = U(S, V, N_1, \dots)$$

and transforms U such that S is replaced by T as a new independent variable. Let us consider the transformation

$$A \equiv U - S \frac{\partial U}{\partial S} = U - TS$$

By differentiating A we get

$$dA = dU - T dS - S dT$$

On the other hand

$$dU = T dS + \sum_j P_j dX_j$$

It implies that

$$dA = -S dT + \sum_j P_j dX_j$$

For such a system we have $A = A(T, V, N_1, \dots, N_r)$. It is a function of T instead of S , as wanted. Similarly for a magnetic system $A = A(T, \vec{M}, N_1, \dots, N_r)$.

¹A smooth function is a function that has continuous derivatives up to some desired order over some domain.

Helmholtz free energy

The **Helmholtz free energy** is defined as:

$$A \equiv U - TS \quad (1.21)$$

In terms of heat and mechanical work, since $dU = \delta Q - \delta W$:

$$dA = dU - d(TS) = \delta Q - T dS - S dT - \delta W$$

Hence,

$$\delta W = (\delta Q - T dS) - S dT - dA \quad (1.22)$$

On the other hand, for a *reversible transformation* we have

$$\delta Q = T dS$$

which implies

$$\delta W = -S dT - dA \quad (1.23)$$

If the reversible transformation is also *isothermal*, $dT = 0$ and we obtain $dA = dW$. It is reminiscent of a potential energy.

Remark. For an isothermal but *not reversible* (spontaneous) process we know the *2nd Law of Thermodynamics*

$$\delta Q \leq T dS$$

which implies

$$(\delta W)_{irr} = \delta Q - T dS - dA \leq -dA. \quad (1.24)$$

Hence, if $\delta W = 0$ and $dT = 0$, we have $dA \leq 0$. Therefore, in a spontaneous (irreversible) process, the thermodynamic system, as a function of T, V, N etc, evolves towards a *minimum* of the Helmholtz free energy $A = A(T, V, N_1, \dots, N_r)$.

In the case of a system with (P, V, T) , we have:

$$dA = -S dT - P dV + \sum_j \mu_j dN_j \quad (1.25)$$

where

$$-S = \left(\frac{\partial A}{\partial T} \right)_{V, N_j} \quad (1.26a)$$

$$-P = \left(\frac{\partial A}{\partial V} \right)_{T, N_j} \quad (1.26b)$$

$$\mu_j = \left(\frac{\partial A}{\partial N_j} \right)_{T, V} \quad (1.26c)$$

For a magnetic system (\vec{H}, \vec{M}, T) :

$$dA = -S dT + \vec{H} \cdot d\vec{M} + \sum_j \mu_j dN_j \quad (1.27)$$

with

$$H_\alpha = \left(\frac{\partial A}{\partial M_\alpha} \right)_{T, \{N_j\}} \quad (1.28)$$

Hentalpy

The **Hentalpy** is the partial Legendre transform of U that replaces the volume V with the pressure P as independent variable.

Consider $U = U(S, V, N_1, \dots, N_r)$ and $-P = \frac{\partial U}{\partial V}$, we define the hentalpy as

$$H = U + PV \quad (1.29)$$

Remark. Note that the plus sign in the definition of the hentalpy is just because the minus of the P .

We have:

$$\begin{aligned} dH &= dU + P dV + V dP \\ &= T dS - P dV + \sum_j \mu_j dN_j + P dV + V dP \\ &= T dS + V dP + \sum_j \mu_j dN_j \end{aligned} \quad (1.30)$$

Finally, we obtain the relation $H = H(S, P, N_1, \dots, N_r)$.

Gibbs potential

The **Gibbs potential** is obtained by performing the Legendre transform of U to replace S and V with T and P .

Consider again $U = U(S, V, N_1, \dots, N_r)$ and $T = \frac{\partial U}{\partial S}$, $-P = \frac{\partial U}{\partial V}$, then we have:

$$G = U - TS + PV = A + PV \quad (1.31)$$

For a simple fluid system

$$\begin{aligned} dG &= dU - T dS - S dT + P dV + V dP \\ &= T dS - P dV + \sum_j \mu_j dN_j - T dS - S dT + P dV + V dP \\ &= -S dT + V dP + \sum_j \mu_j dN_j \end{aligned} \quad (1.32)$$

Hence, $G = G(T, P, N_1, \dots, N_r)$.

For a magnetic system, the Gibbs potential is defined as

$$G = A - \vec{\mathbf{M}} \cdot \vec{\mathbf{H}} \quad (1.33)$$

and

$$\begin{aligned} dG &= dA - d\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} = d(U - TS) - d(-\vec{\mathbf{M}} \cdot \vec{\mathbf{H}}) \\ &= dU - T dS - S dT - d\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot d\vec{\mathbf{H}} \\ &= T dS + \vec{\mathbf{H}} \cdot d\vec{\mathbf{M}} - T dS - S dT - d\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot d\vec{\mathbf{H}} \\ &= -S dT - \vec{\mathbf{M}} \cdot d\vec{\mathbf{H}} \end{aligned} \quad (1.34)$$

and finally $G = G(T, \vec{\mathbf{H}})$ and also

$$S = -\left(\frac{\partial G}{\partial T}\right)_{\vec{\mathbf{H}}} \quad (1.35a)$$

$$\vec{\mathbf{M}} = -\left(\frac{\partial G}{\partial \vec{\mathbf{H}}}\right)_T \quad (1.35b)$$

Lecture 2.Friday 11th

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31st January, 2020.**Grand canonical potential**

The **grand canonical potential** is obtained by performing the Legendre transform of U to replace S and N with T and μ . The corresponding Legendre transform is

$$\Omega = U - TS - \sum_{i=1}^r \mu_i N_i = A - \sum_{i=1}^r \mu_i N_i \quad (1.36)$$

Differentiating this relation we obtain:

$$\begin{aligned} d\Omega &= dU - S dT - T dS - \sum_{ij} d\mu_j N_j - \sum_{i=1}^r \mu_i dN_i \\ &= (\delta Q - T dS) - \delta W - S dT - \sum_{j=1}^r d\mu_j N_j - \sum_{j=1}^r \mu_j dN_j \end{aligned} \quad (1.37)$$

Hence, $\Omega = \Omega(T, P, \{\mu_j\})$.

1.5 Maxwell relations

Internal energy U and entropy S are homogeneous function of the first order. A consequence of this fact is the relation called **Euler equation**:

$$U = TS - PV + \sum_j \mu_j N_j \quad (1.38)$$

Example 3: How to derive the Euler equation

Using the additive property of the internal energy U , we can derive a useful thermodynamic relation, the Euler equation.

$$U(\lambda S, \lambda V, \lambda N_1, \dots, \lambda N_m) = \lambda U(S, V, N_1, \dots, N_m)$$

Let us differentiate this “extensivity condition” with respect to λ :

$$\frac{\partial U(\lambda S, \dots)}{\partial(\lambda S)} S + \frac{\partial U(\lambda S, \dots)}{\partial(\lambda V)} V + \sum_{i=1}^m \frac{\partial U(\lambda S, \dots)}{\partial(\lambda N_i)} N_i = U(S, V, N_1, \dots, N_m)$$

Setting $\lambda = 1$ in the above equation, we obtain:

$$\frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \frac{\partial U}{\partial N_1} N_1 + \dots + \frac{\partial U}{\partial N_m} N_m = U$$

Using the definition of the intensive parameters, we arrive at the Euler equation:

$$U = TS - PV + \sum_{i=1}^m \mu_i N_i$$

Instead, the **Maxwell relations** are relations between the mixed derivatives of the thermodynamic potentials. They can be obtained from the expressions of dU, dH, dA, dG and $d\Omega$ and from the Schwarz theorem on mixed partial derivatives.

Due to Schwarz theorem, if a thermodynamic potential depends on $t+1$ variables there will be $\frac{t(t+1)}{2}$ independent mixed derivatives.

Example 4: Internal energy $U = U(S, V, N)$

$$dU = T dS - P dV + \mu dN \quad (1.39)$$

where

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \quad -P = \left(\frac{\partial U}{\partial V} \right)_{S,N}$$

It implies that

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V} \right)_{S,N} \underset{\text{from Schwarz inequality}}{=} \frac{\partial^2 U}{\partial S \partial V} = - \left(\frac{\partial P}{\partial S} \right)_{V,N}$$

therefore, we have the 1° *Maxwell relation* :

$$\left(\frac{\partial T}{\partial V} \right)_{S,N} = - \left(\frac{\partial P}{\partial S} \right)_{V,N}$$

All the 3 *Maxwell relations* obtained by the differential (1.39) with $t = 2$, for which we have $t + 1 = 3$ and $\frac{t(t+1)}{2} = 3$ ($[S, V, N]$), are

$$(S, V) : \quad \left(\frac{\partial T}{\partial V} \right)_{S,N} = - \left(\frac{\partial P}{\partial S} \right)_{V,N} \quad (1.40a)$$

$$(S, N) : \quad \left(\frac{\partial T}{\partial N} \right)_{V,S} = \left(\frac{\partial \mu}{\partial S} \right)_{V,N} \quad (1.40b)$$

$$(V, N) : \quad - \left(\frac{\partial P}{\partial N} \right)_{S,V} = \left(\frac{\partial \mu}{\partial V} \right)_{S,N} \quad (1.40c)$$

Example 5: Helmholtz $A = A(T, V, N)$

$$dA = -S dT - P dV + \mu dN \quad (1.41)$$

In this case the 3 *Maxwell relations* ($[T, V, N]$) are

$$(T, V) : \quad \left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N} \quad (1.42a)$$

$$(T, N) : \quad - \left(\frac{\partial S}{\partial N} \right)_{T,V} = \left(\frac{\partial \mu}{\partial T} \right)_{V,N} \quad (1.42b)$$

$$(V, N) : \quad - \left(\frac{\partial P}{\partial N} \right)_{V,T} = \left(\frac{\partial \mu}{\partial V} \right)_{T,N} \quad (1.42c)$$

Example 6: Gibbs $G = G(T, P, N)$

$$dG = -S dT + V dP + \mu dN \quad (1.43)$$

In this case the 3 *Maxwell relations* $([T, P, N])$ are

$$(T, P) : \quad -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad (1.44a)$$

$$(T, N) : \quad -\left(\frac{\partial S}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,N} \quad (1.44b)$$

$$(P, N) : \quad \left(\frac{\partial V}{\partial N}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \quad (1.44c)$$

1.6 Response functions

Response functions are quantities that express how a system reacts when some external parameters are changed.

In fact, aim of most experiments is to measure the response of a thermodynamic system write respect to controlled variations of thermodynamic variables. Any observation is just the perturbation of a system and looking for the response. A list of the commonly used response functions is the following:

- *Thermal expansion coefficient at constant pressure.*

$$\alpha_P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad (1.45)$$

- *Adiabatic compressibility.*

$$k_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{S,N} \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \quad -\frac{1}{V} \left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \quad (1.46)$$

- *Isothermal compressibility.*

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,N} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \quad -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \quad (1.47)$$

Remark. Remember that k_T it is the second derivative of the Gibbs potential write respect to pressure.

- *Molar heat capacity at constant pressure.*

$$c_P = \left(\frac{\delta Q}{dT}\right)_{P,N} = T \left(\frac{\partial S}{\partial T}\right)_{P,N} \quad S = \left(\frac{\partial G}{\partial T}\right)_{P,N} \quad -T \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \quad (1.48)$$

- *Specific heat at constant volume.* Consider a quasi static transformation.

$$c_V = \left(\frac{\delta Q}{dT}\right)_{V,N} = T \left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial(-\partial A/\partial T)_{V,N}}{\partial T}\right)_{V,N} = -T \left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} \quad (1.49)$$

- *Magnetic susceptibility* ($d=1$) for a magnetic system (\vec{M}, \vec{H}, T) .

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \quad M = -\left.\frac{\partial G}{\partial H}\right|_T \quad -\left(\frac{\partial^2 G}{\partial H^2}\right)_T \quad (1.50)$$

More generally, $\vec{\mathbf{M}}, \vec{\mathbf{H}}$ we have

$$\chi_{\alpha\beta} = \left(\frac{\partial M_\alpha}{\partial H_\beta} \right)_T, \quad M_\alpha = - \left. \frac{\partial G}{\partial H_\alpha} \right|_T \Rightarrow \chi_{\alpha\beta} = \left. \frac{\partial^2 G}{\partial H_\beta \partial H_\alpha} \right|_T \quad (1.51)$$

Remark. Note that the response functions, when used with the Maxwell relations, allow to express observables usually inaccessible to experiments with measurable quantities.

Let us illustrate a lemma useful for calculation:

Lemma 1

Let x, y, z be quantities that satisfy the relation $f(x, y, z) = 0$. If w is a function of two any variables chosen between x, y, z , then:

1. $\left(\frac{\partial x}{\partial y} \right)_w \left(\frac{\partial y}{\partial z} \right)_w = \left(\frac{\partial x}{\partial z} \right)_w$
2. $\left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z}$
3. $\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$ (concatenation relation or triple product rule).

Example 7

The Maxwell relation

$$\left(\frac{\partial S}{\partial P} \right)_{T,N} = - \left(\frac{\partial V}{\partial T} \right)_{P,N}$$

obtained from

$$dG = -S dT + V dP$$

((T, P) equation) used with the response function α_P , permits to write

$$\underbrace{\left(\frac{\partial S}{\partial P} \right)_{T,N}}_{\substack{\text{inaccessible} \\ \text{to experiments}}} = \underbrace{-V \alpha_P}_{\text{measurable}} \quad (1.52)$$

Example 8

Let us start with the Maxwell relation

$$\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N}$$

obtained from ((T, V) equation)

$$dA = -S dT - P dV$$

From some property of multi-variable differential calculus one has the *triple product rule*:

$$\left(\frac{\partial P}{\partial T} \right)_{V,N} \left(\frac{\partial V}{\partial P} \right)_{T,N} \left(\frac{\partial T}{\partial V} \right)_{P,N} = -1$$

Hence

$$\begin{aligned} \left(\frac{\partial P}{\partial T} \right)_{V,N} &= \frac{-1}{\left(\frac{\partial V}{\partial P} \right)_{T,N} \left(\frac{\partial T}{\partial V} \right)_{P,N}} = - \frac{\left(\frac{\partial V}{\partial T} \right)_{P,N}}{\left(\frac{\partial V}{\partial P} \right)_{T,N}} \\ &= \frac{-V \alpha_P}{-V k_T} = \frac{\alpha_P}{k_T} \end{aligned} \quad (1.53)$$

1.6.1 Response functions and thermodynamic stability

Now, we analyze the concept of *thermal stability*. If one injects heat in a system either at constant volume or at constant pressure, its temperature will inevitably increase

$$\begin{cases} c_V \equiv \left(\frac{\delta Q}{dT} \right)_V \geq 0 \\ c_P \equiv \left(\frac{\delta Q}{dT} \right)_P \geq 0 \end{cases} \quad (1.54)$$

Remark. The thermal capacities are *non-negative functions*!

It is useful also the concept of *mechanical stability*. If one compress a system by keeping T constant, we would expect that it shrinks

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \geq 0 \quad (1.55)$$

Similar considerations for a magnetic system, gives

$$c_H \geq 0, \quad c_M \geq 0, \quad \chi_T \geq 0 \quad (1.56)$$

Remark. In diamagnetic systems χ_M can also be negative.

Exercise 1

By using Maxwell relations show that

$$c_P - c_V = \frac{TV\alpha_P^2}{k_T} = \frac{1}{Vk_T} T \left(\frac{\partial V}{\partial T} \right)_P^2 \quad (1.57a)$$

$$c_H - c_M = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)_H^2 \quad (1.57b)$$

Solution. Let us start considering a system with a fixed number of particles (namely $dN = 0$) and such that S is explicitly expressed in terms of T and V . Then:

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

Dividing by dT both sides keeping the pressure constant, and then multiplying by T :

$$T \left(\frac{\partial S}{\partial T} \right)_P - T \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

it implies

$$c_P - c_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

Now, using the Maxwell relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$ and using the triple product rule we obtain

$$\left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

we get:

$$c_P - c_V = -T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P^2 = -T \alpha_P^2 V^2 \left(\frac{\partial P}{\partial V} \right)_T = \frac{TV}{k_T} \alpha_P^2$$

It can be shown similarly for magnetic systems.

A consequence is that, since the right hand terms are non negative, it follows that

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \quad (1.58)$$

For resuming, we have seen the thermodynamic of a phase, where the equilibrium state can be described by the maximum of the entropy. If we have a given phase, we can look for the Gibbs function. If we have more phases, we want to change between these phases.

Chapter 2

Equilibrium phases and thermodynamics of phase transitions

2.1 Equilibrium phases as minima of Gibbs free energy

Experimentally, any element or compound can be found, depending on the thermodynamic conditions in which it is, in different phases. When we say that a system is in a particular phase we mean that its physical properties (like density or magnetization) are uniform.

Equilibrium states are given by *maxima* of the entropy and *minima* of internal energy, or by *minima* of thermodynamics potentials such as A and G . Let us consider for example the Gibbs potential per particle of a fluid system

$$\frac{G}{N} \equiv g = g(T, P) \quad (2.1)$$

that depends on two intensive variables T and P and is not anymore a function of N because we have divided for N . Let us define α as the phase of a one-component system (say $\alpha = \text{gas or liquid}$). Therefore, the thermodynamic properties are described by surfaces of function $g_\alpha(T, P)$ and for all equilibrium phase we have a surface on the space (T, P, g) . For each value of T and P the thermodynamically stable phase is the one for which $g_\alpha(T, P)$ is minimum.

2.2 First order phase transition and phase coexistence

Let us suppose for example that the system can be found in two phases α and β (for example liquid and solid). Consider the surface g_α and g_β , we are looking for the lower one.

For given values of T and P the stable phase will be that with the lowest value of g : for example, if we have $g_\alpha(T, P) < g_\beta(T, P)$ then the system will be in phase α . Therefore there will be regions in (T, P) space where the most stable phase will be α and others in which it will be β . If we now plot the values of g as a function of T and P in (g, P, T) space for every phase of the system, we can determine the regions where the two phases will be the stable ones, namely we can determine the phase diagram of the system, as illustrated in Figure 2.1.

The very interesting region of this space (and the one on which we will focus our attention in this section) is the line where the surfaces of the two phases intersect: along this the two phases coexist, and when the system crosses it we say that it undergoes a *phase transition*. The coexistence line is the projection on the (T, P)

plane of the intersection between different surfaces, so the *coexistence condition* is:

$$g_\alpha(T, P) = g_\beta(T, P) \quad (2.2)$$

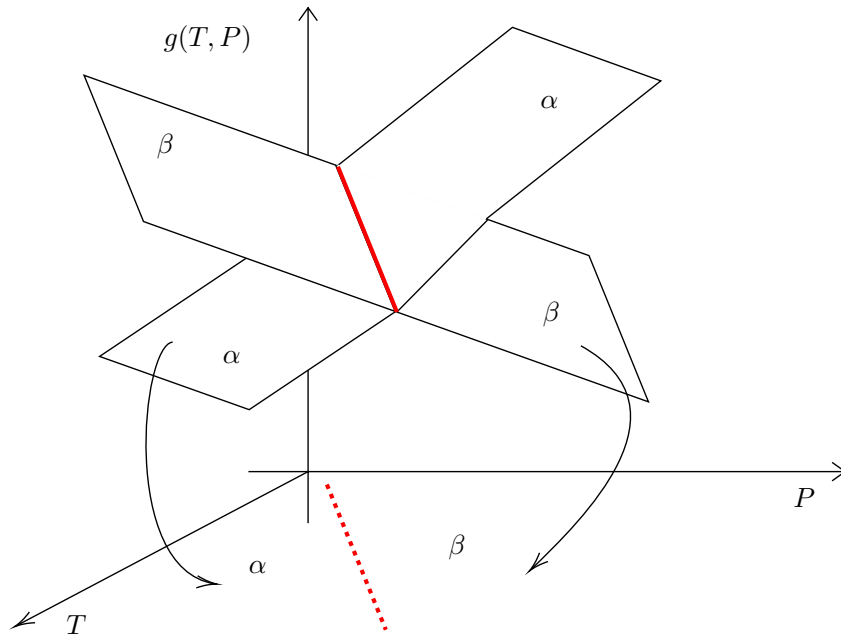


Figure 2.1: Phase diagram: stability of phases.

To fix the ideas, let us choose a given value of pressure $P = P^*$ and study the behavior of $g(T, P^*)$ as a function of T when we go from solid to gas, as illustrated in Figure 2.2.

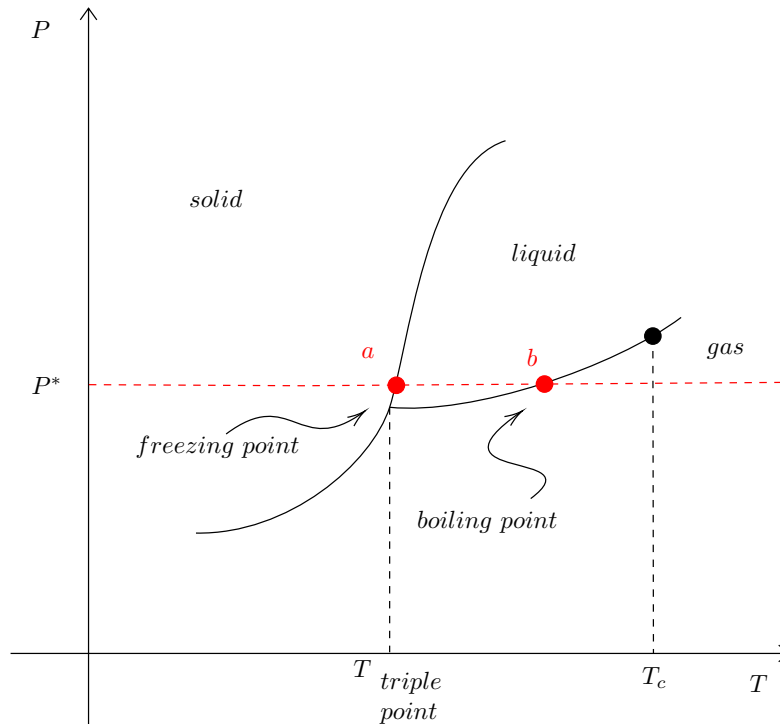


Figure 2.2: (T, P) projection.

The existence of a critical point has a very intriguing consequence: since the liquid-gas coexistence line ends in a point, this means that a liquid can continuously

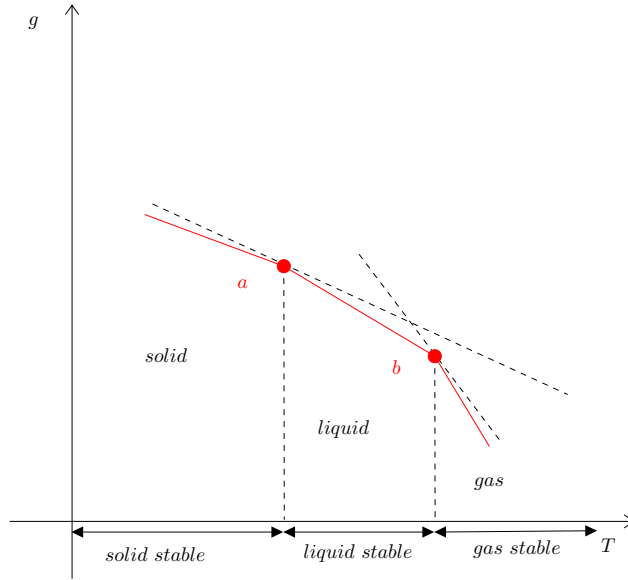


Figure 2.3: (g, T) projection at a fixed pressure $P = P^*$. The red line is the coexistence line of the two phases α and β .

be transformed in a gas (or viceversa), and in such a way that the coexistence of liquid and gaseous phases is never encountered.

At the coexistence line, $g_{\text{solid}}(T_a, P^*) = g_{\text{liq}}(T_a, P^*)$ and $g_{\text{liq}}(T_b, P^*) = g_{\text{gas}}(T_b, P^*)$, as shown in Figure 2.3.

Note also that:

- At the coexistence points a and b of the two phases, one has $g_\alpha(T) = g_\beta(T)$.
- $g(T)$ is a continuous function of T .
- Note that, $S = -\left(\frac{\partial G}{\partial T}\right)_V$ and $c_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P > 0$. This implies that $g(T)$ is concave in T at fixed P .

How about its derivatives? Since P is fixed we can vary T and look for $s = -\left(\frac{\partial g}{\partial T}\right)_P$. As we cross different phases we have discontinuities, where $\Delta s T$ is called the *latent heat*. It is illustrated in Figure 2.4.

If there is a finite discontinuity in one, or more, of the *first* derivatives of the appropriate thermodynamic potential, the transition is called *first order transition*. In general, *a phase transition is signaled by a singularity in a thermodynamic potential*.

We can also fix the temperature $T = T^*$ and look at the variation of P , as shown in Figure 2.5.

Note that, we have $v = \left(\frac{\partial g}{\partial P}\right)_T > 0$:

$$\left(\frac{\partial^2 g}{\partial P^2}\right) = \left(\frac{\partial v}{\partial P}\right)_T = -vk_T < 0 \quad (2.3)$$

so, also in this case we had a jump of the first order derivative of the thermodynamic potential g . It is illustrated in Figure 2.6.

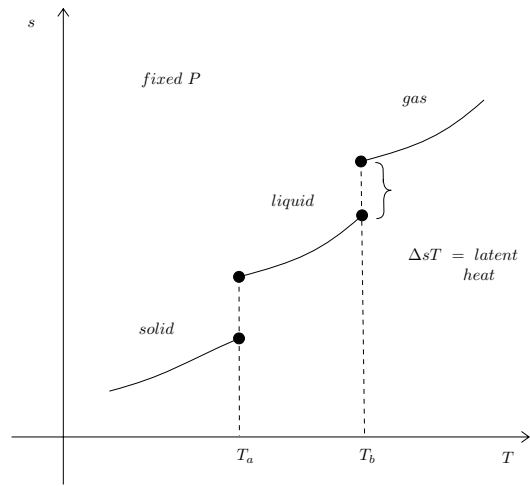


Figure 2.4: (s, T) projection.

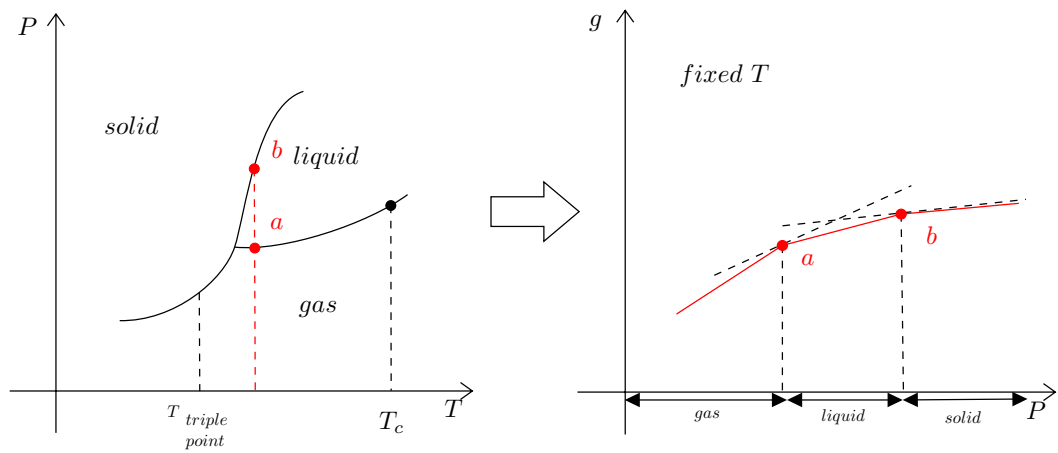


Figure 2.5: Left: (T, P) projection. Right: (g, P) projection at a fixed temperature $T = T^*$.

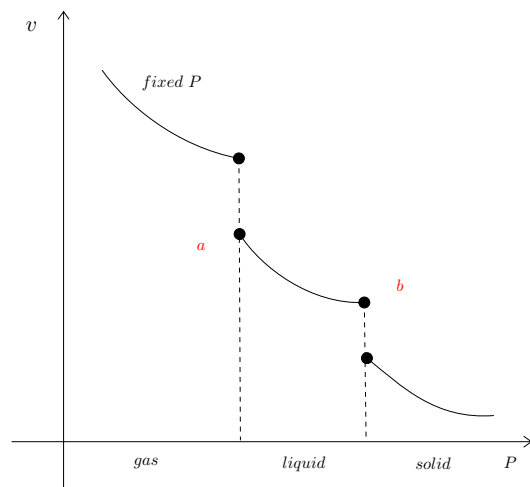


Figure 2.6: (v, P) projection.

2.2.1 Critical points

At the critical point (P_c, T_c) the system can pass from the liquid to the gas phase (and vice versa) in a continuous way

$$\Delta s = \Delta v = 0$$

Usually, critical points are end point of first order transition phases. Why there is no critical point between solid and liquid? The crossover between phases having the same symmetry define the Landau point. There is a break of symmetry, for instance we can think about the structure of the bravais lattice. Instead, from gas to liquid symmetries are not broken.

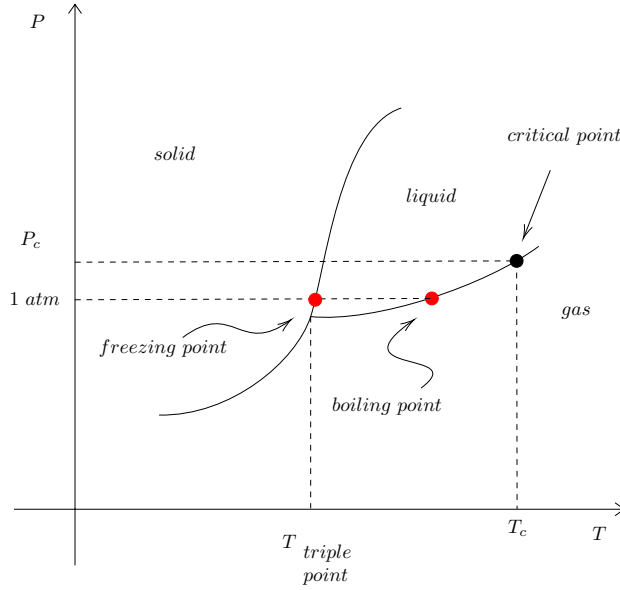


Figure 2.7: Phase diagram of a fluid. All the phase transition are first-order except at the critical point C . Beyond C it is possible to move continuously from liquid to a gas. The boundary between the solid and liquid phases is thought to be always first-order and not to terminate in a critical point.

2.2.2 Ferromagnetic system

A similar behaviour can be encountered in magnetic systems. We can have a magnetization different from 0 even when there is no magnetic field. Supposing $P \leftrightarrow H, V \leftrightarrow M$, we have $(P, T) \leftrightarrow (H, T)$.

The magnetization M has a jump at $H = 0$ for temperatures lower than the critical one; in this case since $M = -\frac{\partial F}{\partial H}$ we see that the first derivative of the free energy F with respect to H has a jump discontinuity. For instance, consider Figure 2.9. At the critical point the magnetization would pass through zero.

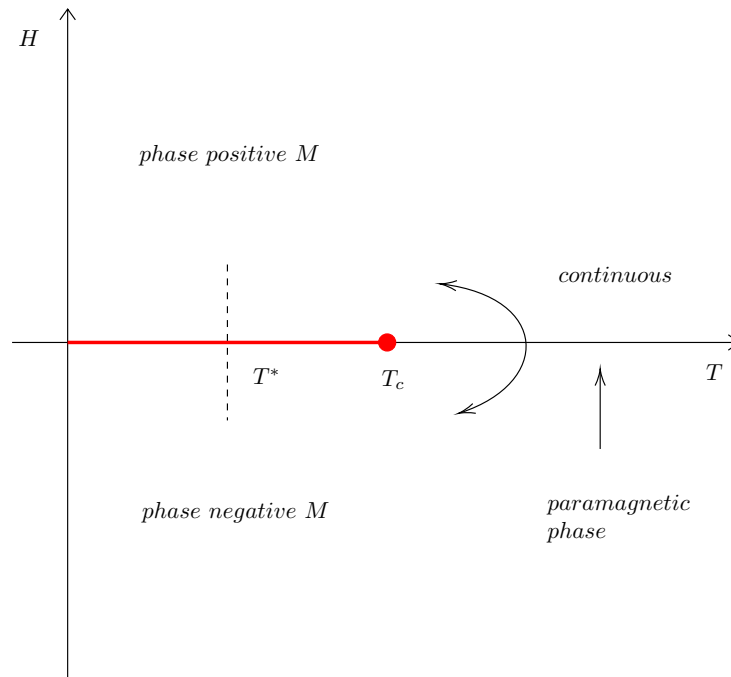


Figure 2.8: Phase diagram for a magnetic system in (T, H) space. A line of first-order transitions at zero field ends in a critical point at a temperature T_c .

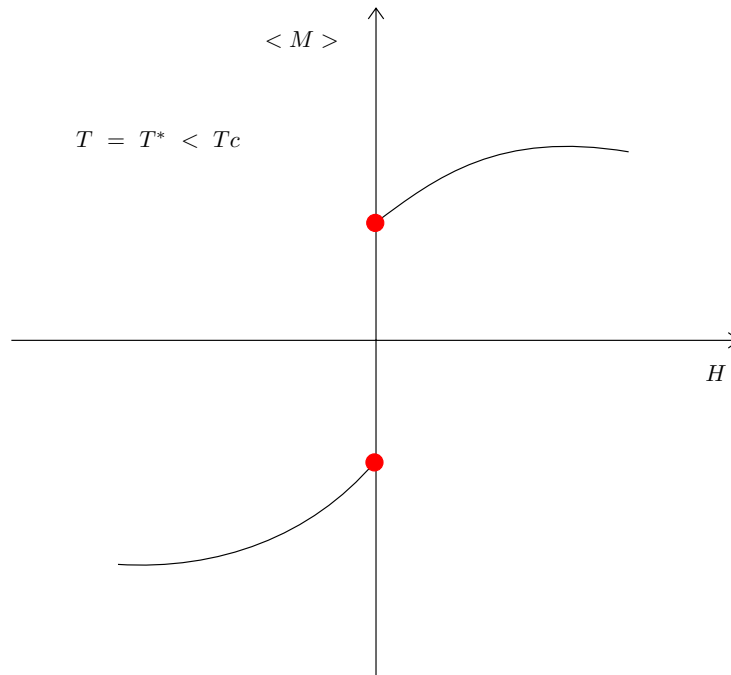


Figure 2.9: Plot of the Magnetization for $T = T^* < T_c$.

2.3 Second order phase transition

The transitions are classified in the first order transition and continuous transition. If the first derivatives are continuous, but second derivatives are discontinuous, or infinite, the transition will be described as higher order, *continuous* or critical. This is different from the previous situation, in which we had a jump for the first order derivative of a thermodynamic potential. Some examples are illustrated in Figure 2.10.

Let us suppose that

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \quad (2.4a)$$

$$\left(\frac{\partial g}{\partial P}\right)_T = v \quad (2.4b)$$

are continuous. We suppose also that

$$\left(\frac{\partial^2 g}{\partial T \partial P}\right) = \left(\frac{\partial v}{\partial T}\right)_P = v\alpha_p \quad (2.5)$$

is discontinuous. An example is *superconductivity*.

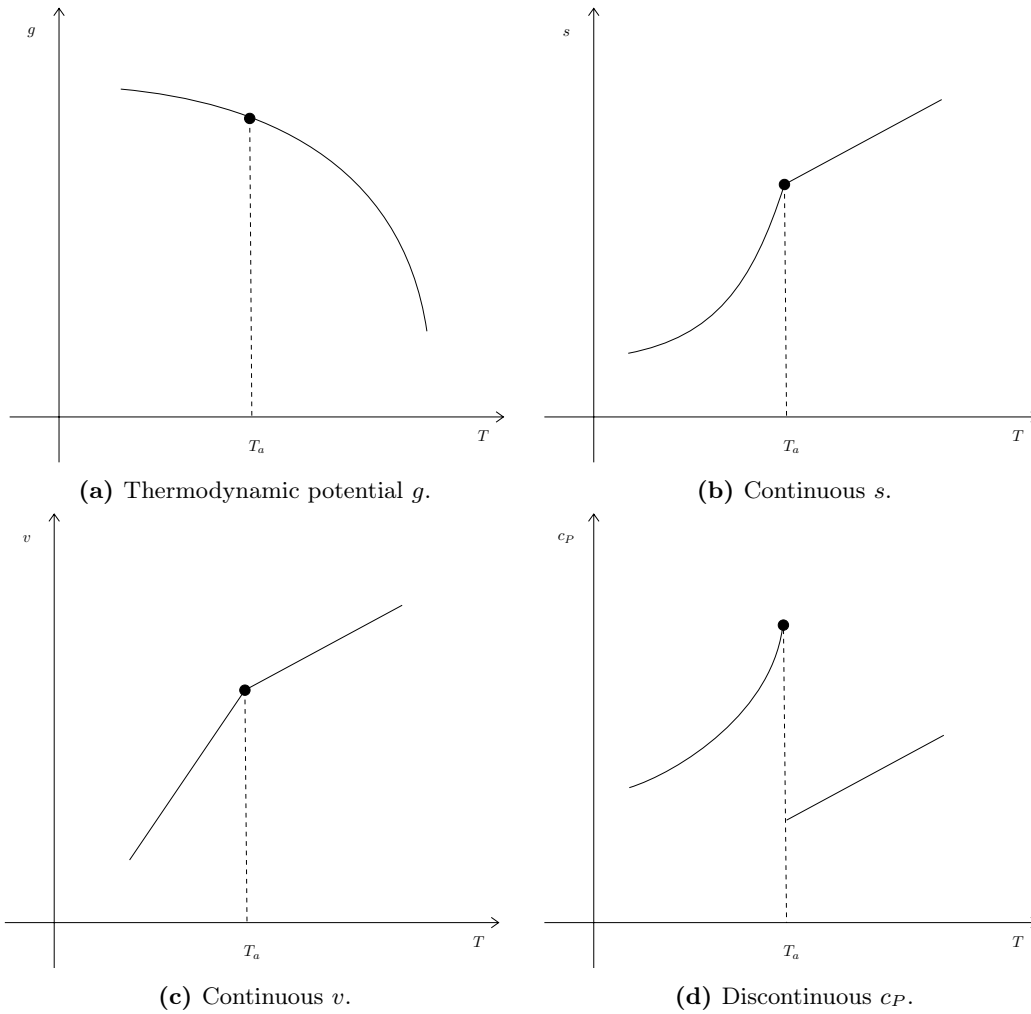


Figure 2.10: Example of a second order phase transition.

If we look for example at the specific heat c_P in Figure 2.10d, it represents the transition from superconducting.

The critical point is special because there is not a jump, so we can go continuously from gas to liquid. The response function when we plot this point shows that the specific heat diverges.

The *superfluid transition* is a transition where the second derivative of the thermodynamic potential diverges. There are many phase transitions that can be classified in different ways.

Remark. Note that at the coexistence line we increase V , but the pressure remains constant. At the coexistence line we see bubbles. It is the density that is changing locally, the bubbles becomes bigger and bigger and at the V_G , becomes a liquid.

2.3.1 Helmholtz free-energy

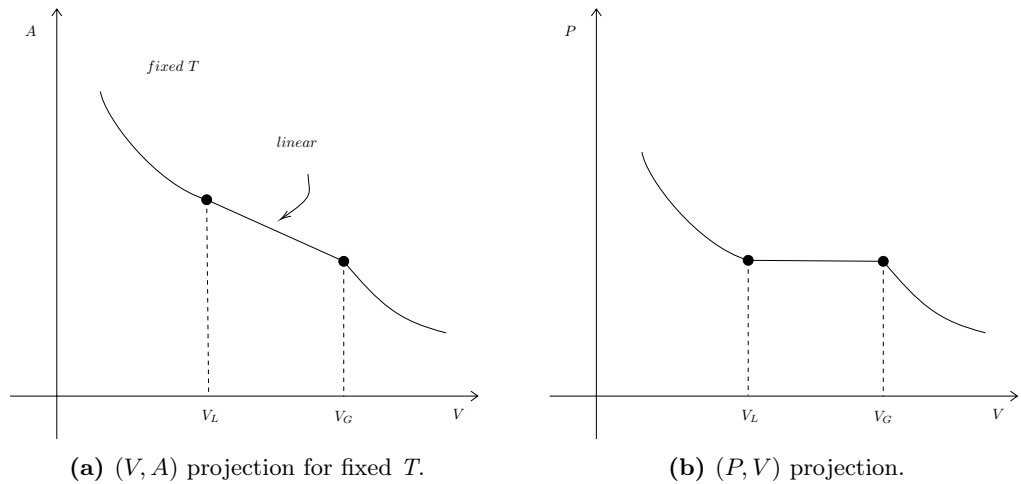


Figure 2.11: Helmholtz free-energy and phase transition.

Consider $A = A(T, V, N)$, here P is replaced by V which has the derivative discontinuous at the first order transition. Moreover, $P > 0$ implies $\partial A / \partial V < 0$ and

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_T = \frac{1}{V} \left(\frac{\partial^2 A}{\partial V^2} \right)_T > 0 \quad (2.6)$$

so, A is an overall convex function of V . The behaviour of A when there is a first order phase transition is as in Figure 2.11a. The linear sector becomes an horizontal one in the $P = -(\partial A / \partial V)_T = P(V)$ curve (Figure 2.11b).

2.4 Thermodynamic of phase coexistence

2.4.1 Lever Rule

The lever rule [2] is a rule used to determine the mole fraction of each phase of a binary equilibrium phase diagram. For instance, it can be used to determine the fraction of liquid and solid phases for a given binary composition and temperature that is between the liquid and solid line.

In an alloy or a mixture with two phases, α and β , which themselves contain two elements, A and B , the lever rule states that the mass fraction of the α phase is

$$w^\alpha = \frac{w_B - w_B^\beta}{w_B^\alpha - w_B^\beta} \quad (2.7)$$

where

Lecture 3.
 Wednesday 16th
 October, 2019.
 Compiled: Friday
 31st January, 2020.

- w_B^α : is the mass fraction of element B in the α phase.
- w_B^β : is the mass fraction of element B in the β phase.
- w_B : is the mass fraction of element B in the entire alloy or mixture.

Example 9

Consider Figure 2.12; at all points between A and B the system is a mixture of gas and liquid. Points D has global density $\rho_D = \rho_A + \rho_B$ and therefore $v_D = \frac{1}{\rho_D}, v_A = \frac{1}{\rho_A}, v_B = \frac{1}{\rho_B}$ which implies:

$$v_D = \frac{N_A}{N}v_A + \frac{N_B}{N}v_B = x_A v_A + x_B v_B$$

Since $x_A + x_B = 1$ we have $(x_A + x_B)v_D = x_A v_A + x_B v_B$ and finally by rearranging, one finds the *Lever Rule*. It shows that the relative concentration of the liquid-gas mixture changes with V :

$$\frac{x_A}{x_B} = \frac{v_B - v_D}{v_D - v_A}$$

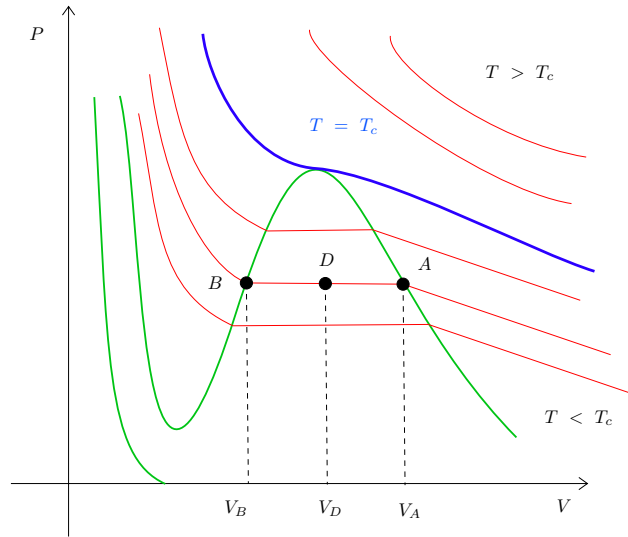


Figure 2.12: (V, P) projection. In the region between A and B the gas and the liquid phase coexist by keeping the pressure constant.

2.4.2 Phase coexistence (one component system)

Consider a (P, V, T) system as a mixture of two species $(1, 2)$ at temperature T_1, T_2 , pressure P_1, P_2 and chemical potentials μ_1, μ_2 . The equilibrium condition is given by the maximum of the total entropy $S = S_1 + S_2$ and gives the conditions

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2 \quad (2.8)$$

this is the *coexistence condition* of the two phases.

In terms of the Gibbs potential $G = U - TS + PV$, where U is given by the Euler equation $U = TS - PV + \mu_1 N_1 + \mu_2 N_2$, the Gibbs per mole is

$$g_1(T, P) \equiv \frac{G_1}{N_1} = \mu_1 \quad (2.9a)$$

$$g_2(T, P) \equiv \frac{G_2}{N_2} = \mu_2 \quad (2.9b)$$

Therefore, on the coexistence line it should hold the relation

$$g_1(T, P) = g_2(T, P) \quad (2.10)$$

2.4.3 Clausius-Clapeyron equation

The coexistence curves [3], as the one illustrated in Figure 2.13, are less arbitrary than is immediately evident; the slope dP/dT of a coexistence curve is fully determined by the properties of the two coexisting phases.

The slope of a coexistence curve is of direct physical interest. Consider cubes of ice at equilibrium in a glass of water. Given the ambient pressure, the temperature of the mixed system is determined by the liquid-solid coexistence curve of water; if the temperature were not on the coexistence curve some ice would melt, or some liquid would freeze, until the temperature would again lie on the coexistence curve (or one phases would become depleted). If the ambient pressure were to decrease perhaps, by virtue of a change in altitude, then the temperature of the glass of water would appropriately adjust to a new point on the coexistence curve. If ΔP were the change in pressure, then the change in temperature would be $\Delta T = \Delta P / (dP/dT)_{coex}$, where the derivative in the denominator is the slope of the coexistence curve.

Remark. Ice skating presents another interesting example. The pressure applied to the ice directly beneath the blade of the skate shifts the ice across the solid-liquid coexistence curve, providing a lubricating film of liquid on which the skate slides. The possibility of ice skating depends on the negative slope of the liquid-solid coexistence curve of water.

Now, suppose to know the position on the coexistence line (for example the melt temperature T_m at the atmospheric pressure P_0). Is it possible to find other points on the curve? For example T_m at lower or higher pressure?

The answer is yes for small deviations of T and P from a . The idea is to compute the slope of the tangent of the coexistence curve, i.e. (dP/dT) . This is given by the Clausius-Clapeyron equation. Both at a and b the two phases 1 and 2 coexist. This means that at the coexistence line

$$\begin{cases} g_1^{(a)} = g_2^{(a)} \\ g_1^{(b)} = g_2^{(b)} \end{cases} \quad (2.11)$$

Hence, if a and b are very close:

$$\begin{cases} dg_1 = g_1^{(b)} - g_1^{(a)} \\ dg_2 = g_2^{(b)} - g_2^{(a)} \end{cases} \quad (2.12)$$

Therefore, the *starting point* for *Clausius-Clapeyron* is

$$\Rightarrow dg_1 = dg_2 \quad (2.13)$$

From the molar version of the Gibbs-Duhem relation, we have

$$\begin{cases} dg_1 = -s_1 dT + v_1 dP = d\mu_1 \\ dg_2 = -s_2 dT + v_2 dP = d\mu_2 \end{cases} \quad (2.14)$$

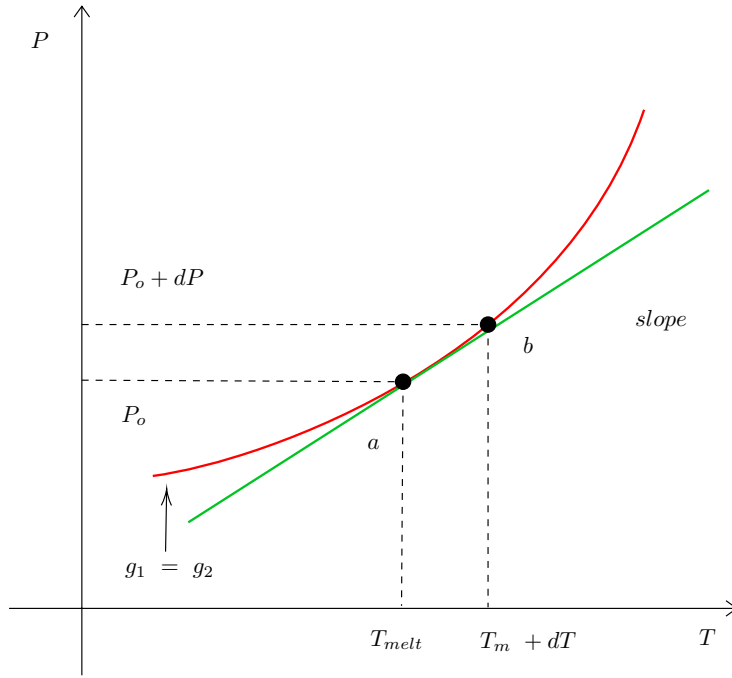


Figure 2.13: (T, P) projection. The coexistence line is represented in red, while in green the slope between the two points a and b .

taking the difference, one obtains

$$-(s_2 - s_1) dT + (v_2 - v_1) dP = 0$$

The slope is called **Clausius-Clapeyron equation**:

$$\left(\frac{dP}{dT} \right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{\Delta s}{\Delta v} \quad (2.15)$$

Remark. Since $(dP/dT)_{coex}$ is finite, the equation explains why a first order transition is characterised by discontinuous changes in entropy and volume (or density). ΔS gives the latent heat L_{12} ¹:

$$L_{12} = T \Delta s \quad (2.16)$$

whence, the Clapeyron equation is

$$\frac{dP}{dT} = \frac{L_{12}}{T \Delta v} \quad (2.17)$$

2.4.4 Application of C-C equation to the liquid-gas coexistence line

Now, we go from gas (region 2) to liquid (region 1), we have:

$$\left(\frac{dP}{dT} \right)_{coex} = \frac{s_2 - s_1}{v_2 - v_1}$$

The Clapeyron equation embodies the *Le Chatelier principle*². Consider a liquid-gas transition (the coexistence curves are shown in Figure 2.14):

$$\left(\frac{dP}{dT} \right)_{coex} > 0 \Rightarrow \frac{s_2 - s_1}{v_2 - v_1} > 0$$

¹The latent heat of fusion is the quantity of heat required to melt one mole of solid.

²"When a settled system is disturbed, it will adjust to diminish the change that has been made to it".

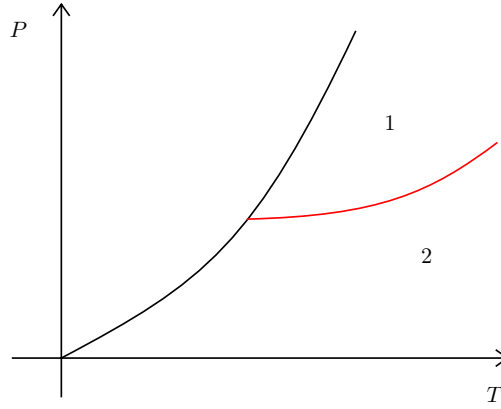


Figure 2.14: (T, P) projection. Region 1: liquid. Region 2: gas. The lines represent the combinations of pressures and temperatures at which two phases can exist in equilibrium.

and since $v_2 > v_1$, we have $s_2 > s_1$. The gas has more entropy as it should be. The slope of the phase curve is positive, then an increase in pressure at constant temperature tends to drive the system to the more dense (solid) phase, and an increase in temperature tends to drive the system to the more entropic (liquid) phase.

When going from a low-temperature phase to a high-temperature phase entropy always increases $\Delta S > 0$, because $c_P \equiv T(\partial S / \partial T)_P > 0$.

The sign of ΔV is more uncertain though. To see this point, let us consider the C-C equation at the solid-liquid (now solid is region 1 and liquid region 2) coexistence curve. At the melt temperature:

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\delta Q_{melt}}{T_{melt} \Delta v_{melt}}, \quad \delta Q_{melt} = Q_{liq} - Q_{solid} > 0$$

In general, $\Delta v_m = v_{liq} - v_{solid} > 0$ which implies $(dP/dT)_{coex} > 0$. There are cases, however, where $\Delta v_m = v_{liq} - v_{solid} < 0$ because $\rho_{liq} > \rho_{solid}$ (for instance the H_2O , or also Silicon and Germanium). The paradigmatic example is the freezing of water where $v_{ice} > v_{liq}$ since ice is less dense than liquid water at the coexistence ($0 < T < 4$). This implies that $dP/dT < 0$.

Example 10: Melting point on Everest

Consider $T = 237K$ and $P = P_0$. If we suppose that

$$\delta Q_m = 6.01 kJ/mol, \quad \Delta v = -1.7 cm^3/mol$$

we have

$$\begin{aligned} \frac{dP}{dT} &= \frac{\delta Q_m}{T \Delta v} = \frac{6.0110^3 J/mol}{273 \cdot (-1.7 cm^3/mol)} = -1.29 \cdot 10^4 J/m^3 = -1.29 bar/K \\ \Rightarrow \Delta T &= \frac{\Delta P}{(-1.29 Pa/K)} = \frac{(P_0 - P_{Everest})}{(-1.29 Pa/K)} = \frac{(1 - 0.36) atm}{(-1.29 Pa/K)} = -0.5^\circ C \\ &\Rightarrow T_m(Everest) = T_m(P_0) + 0.5^\circ C \end{aligned}$$

Example 11: Boiling point on Everest

Let us consider

$$P_{Everest} = 0.36 atm, \quad \rho(T = 100^\circ C) = 0.598 kg/m^3, \quad L_{gl} = 2.257 \cdot 10^3 J/g$$

The density of the vapour (gas) is about 1000 less than water (liquid), it implies

that:

$$\Delta V = V_g - V_l \approx V_g = \frac{1}{\rho_g}$$

We have:

$$\frac{dP}{dT} = \frac{L_{ge}}{T\Delta V} = \frac{L_{ge}\rho_g}{T} = \frac{2.25 \cdot 10^3 J/g \cdot 0.593 kg/m^3}{373 K} = \frac{3.6 \cdot 10^3 J}{K} \frac{kg}{g} \frac{1}{m^3} = 3.6 \cdot 10^3 \frac{Pa}{K}$$

$$\Rightarrow \Delta T \approx \Delta P / (3.6 \cdot 10^3 Pa/K) = 18^\circ C$$

$$\Rightarrow T_0 - T_{Everest} = 18^\circ C \quad \Rightarrow T_{Everest} \approx 80^\circ C$$

2.5 Order parameter of a phase transition

An order parameter is a measure of the degree of order across the boundaries in a phase transition system. In particular, *order parameters* are macroscopic observable that are equal to zero above the critical temperature, and different from zero below:

$$O_p = \begin{cases} \neq 0 & T < T_c \\ = 0 & T \rightarrow T_c^- \end{cases} \quad (2.18)$$

When a phase transition implies a breaking of a phase symmetry, the order parameter is related to this symmetry. Therefore, the order parameter reflects the symmetry of the system. Recall that, at T_c the system has a symmetry broken.

For instance, consider the densities of liquid and gas and the related order parameter of the gas-liquid transition $\Delta\rho = \rho_l - \rho_g$, that is $\neq 0$ for $T \neq T_c$ but $\rightarrow 0$ when $T \rightarrow T_c$ (see Figure 2.15).

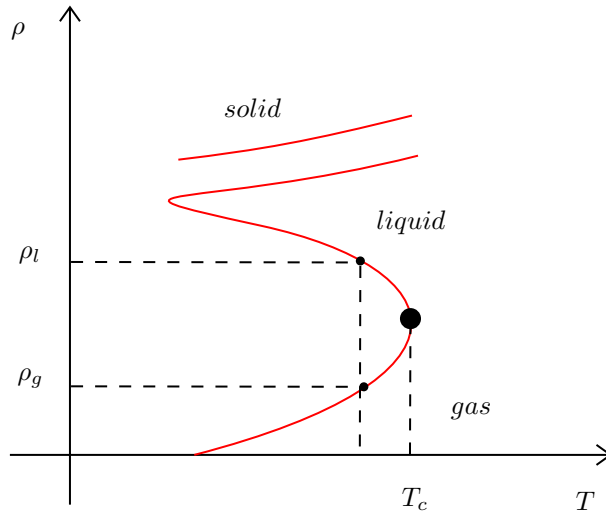


Figure 2.15: (T, ρ) projection of the (P, V, T) system, where $\rho = N/V$.

Remark. Note that $\rho = \frac{N}{V} = \frac{1}{v}$ hence either N or V varies.

In Figure 2.16 is shown the behaviour for a ferromagnetic system. We have

$$H = 0 \Rightarrow \begin{cases} M \neq 0 & T < T_c \\ M \rightarrow 0 & T \rightarrow T_c^- \end{cases}$$

Clearly $M \neq 0$ if $H \neq 0$. Recall that M is the order parameter of the paramagnetic-ferromagnetic phase transition.

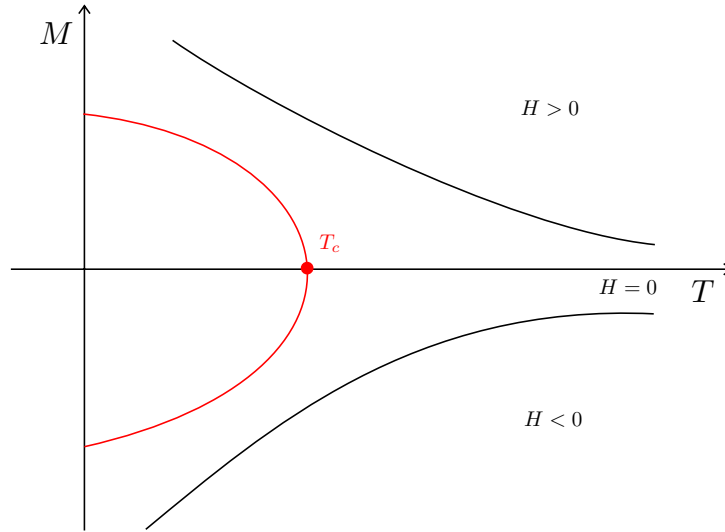


Figure 2.16: Magnetization of a ferromagnet. In red: zero-field magnetization. Below the critical temperature there is a spontaneous magnetization.

Variable conjugate to O_P

- *Ferromagnetic system:* $\vec{M} \rightarrow \vec{H}$ (magnetic field).
- *Ferroelectric:* $\vec{P} \rightarrow \vec{E}$ (electric field).
- *Liquid crystals:* $Q_{\alpha\beta} \rightarrow \vec{E}, \vec{H}$.
- *Fluid:* $V \rightarrow P$ (pressure), or $\rho \rightarrow \mu$.

2.6 Classification of the phase transitions

2.6.1 Thermodynamic classification

Thermodynamically, one can distinguish two kinds of phase transitions:

1. Ones who develop latent heat.
2. Ones who do not develop latent heat. The entropy changes continuously at the transition.

2.6.2 Eherenfest classification

The *Eherenfest classification* is based on the behaviour of the derivatives of the thermodynamic potentials.

A phase transition is of order n if all the $(n - 1)$ derivatives are continuous and the n^{th} derivative displays a finite discontinuity.

Example 12

For instance, a first order transition in which $S = -(\partial G / \partial T)_P$ has finite discontinuity.

Remark. There are first order transitions where S is continuous (no latent heat), but ρ is discontinuous ($v = (\partial G / \partial P)_T$).

Example 13

Second order transition. The specific heat displays a finite jump, see Figure 2.17c in the conductor-superconductor transition.

Another example is a second order transition but with divergence. Consider the fluid-superfluid transition (or λ transition) of the He_4 (Figure 2.17d).

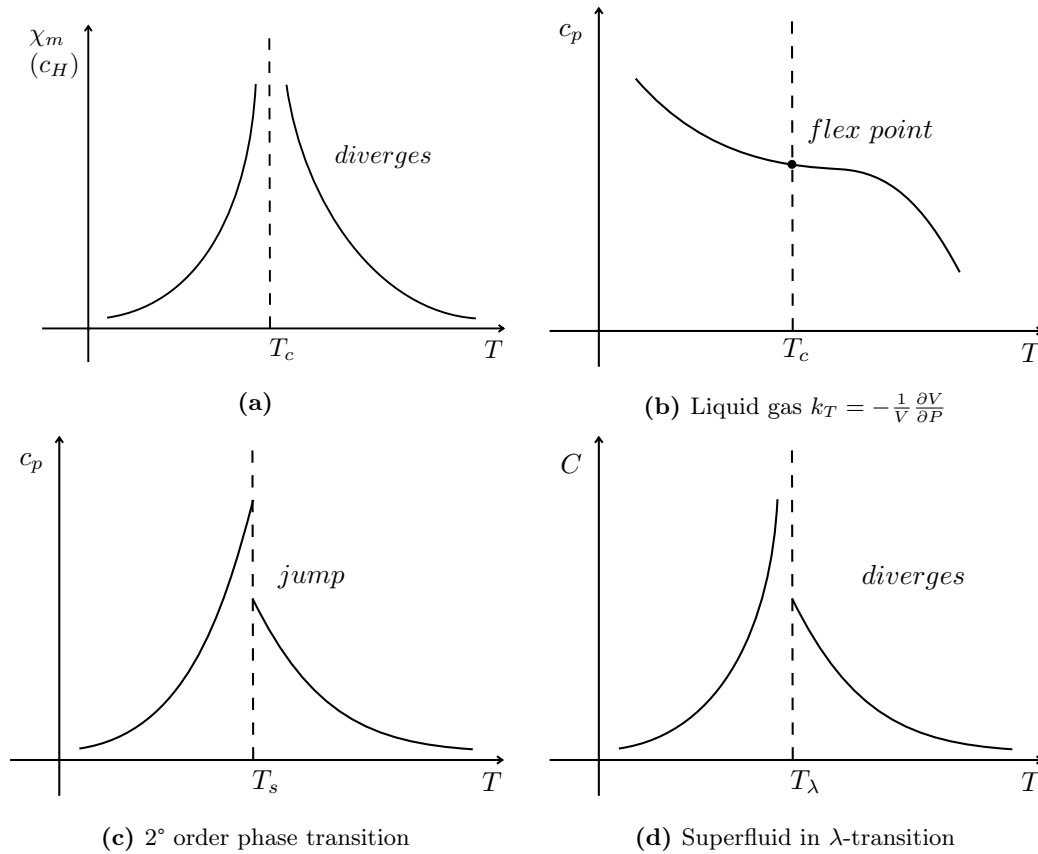


Figure 2.17: Plots of response functions.

Remark. λ transition: a second-order or higher-order transition, in which the heat capacity shows either a discontinuity (second-order) or a vertex (higher-order) at the transition temperature. It is so named because the shape of the specific heat versus temperature curve resembles the Greek letter λ .

2.6.3 Modern classification

A phase transition is of the first order if exists a finite discontinuity in either one or more partial derivatives of the thermodynamic potentials. Instead, if the first derivatives are all continuous, but the second are either discontinuous, or infinite, one talks of continuous transitions. A critical point is a continuous transition.

2.7 Critical exponents

At the critical point response functions may diverge. How are these divergence? In general, when you are close to T_c , there are singularities. Now, we can ask, how the curve diverges? What is the behaviour close to the critical point? Power law, so which are the values of these critical exponents?

2.7.1 Divergence of the response functions at the critical point

While at the critical point the order parameter goes to zero continuously as $T \rightarrow T_c^-$, the response function may develop divergences.

Example 14

In a fluid system since at $T = T_c$ the curve $P = P(V)$ develops an horizontal flex (Figure 2.18), we have $k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \rightarrow \infty$. Similarly, in a magnetic since the curve is like Figure 2.16, we have $\chi_T = \left(\frac{\partial M}{\partial H} \right)_T \xrightarrow{T \rightarrow T_c} \infty$.

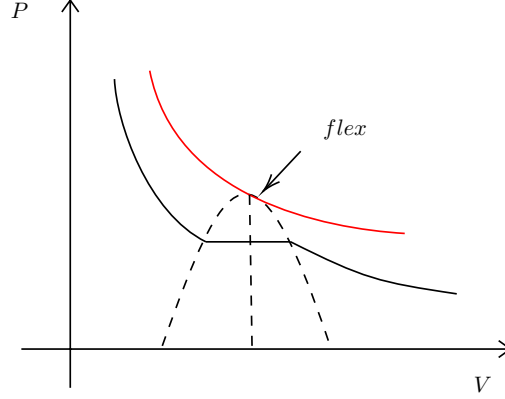


Figure 2.18: (V, T) projection.

2.7.2 Critical exponents definition

The notion of *critical exponent* describes the behaviour of the order parameter and the response functions in proximity of the critical point. In order to answer to these questions, let us define:

Definition 1: Critical Exponent, or Scale Exponent

Let us define the adimensional parameter measuring the distance from the critical point $t \equiv \frac{T - T_c}{T_c}$, the *critical exponent* λ associated to the function $F(t)$ is defined as:

$$\lambda_{\pm} = \lim_{t \rightarrow 0^{\pm}} \frac{\ln |F(t)|}{\ln |t|} \quad (2.19)$$

We note that it behaves like a power law. One can also write the *power law*:

$$F(t) \stackrel{t \rightarrow 0^{\pm}}{\sim} |t|^{\lambda_{\pm}} \quad (2.20)$$

More generally, for $t \ll 1$:

$$F(t) = A|t|^{\lambda_{\pm}}(1 + bt^{\lambda_1} + \dots), \quad \lambda_1 > 0 \quad (2.21)$$

where all other terms are less important.

Definition 2: Thermodynamic Critical Exponents

- **Exponent β :** tells how the order parameter goes to zero. Consider Figure 2.19a, we have $M \stackrel{t \rightarrow 0^-}{\sim} (-t)^{\beta}$. No sense in going from above ($t \rightarrow 0^+$) where it stays 0.

- **Exponent γ_{\pm}** (susceptibility): related to the response function. Consider Figure 2.19b, we have $\chi_T \stackrel{t \rightarrow 0^{\pm}}{\sim} |t|^{-\gamma_{\pm}}$. In principle, the value of γ can depend on the sign of t i.e. $\gamma^+ \neq \gamma^-$, but they are the same in reality and we have $\gamma^+ = \gamma^- = \gamma$.
- **Exponent α_{\pm}** : how specific heat diverges (second order derivative in respect of T). For instance see Figure 2.19c, we have $c_H \sim |t|^{-\alpha_{\pm}}$.
- **Exponent δ** : in this case one consider the isotherm $T = T_c$ and look for the behaviour of M at the critical point at small H (or viceversa). The result is $M \sim H^{1/\delta}$. In Figure 2.19d, $H \sim |M|^{\delta} \text{sign}(M)$.

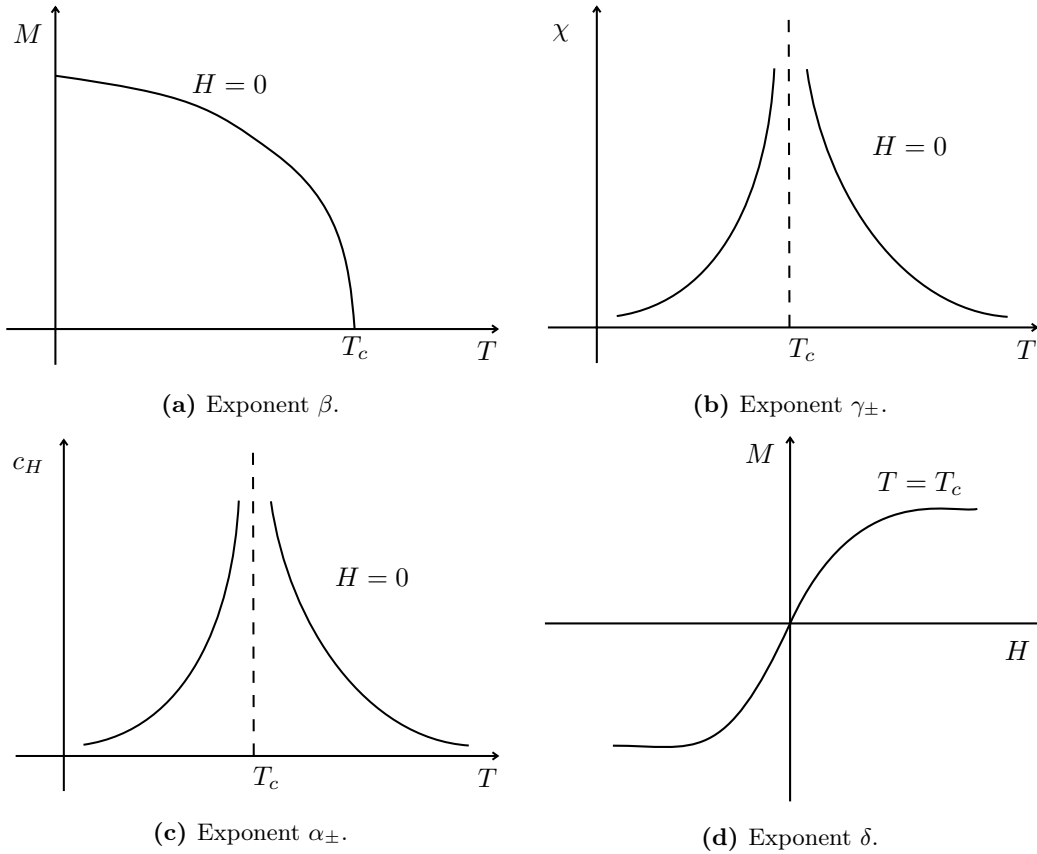


Figure 2.19

Zero-field specific heat	$C_H \sim t ^{-\alpha}$
Zero-field magnetization	$M \sim (-t)^{\beta}$
Zero-field isothermal susceptibility	$\chi_T \sim t ^{-\gamma}$
Critical isotherm ($t = 0$)	$H \sim M ^{\delta} \text{sign}(M)$
Correlation length	$\xi \sim t ^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim \frac{1}{r^{d-2+\eta}}$

Table 2.1: Definitions of the most commonly used critical exponents for a magnetic system [4].

Remark. In compiling Table 2.1 and 2.2 we have made the as yet totally unjustified

Specific heat at constant volume V_c	$C_V \sim t ^{-\alpha}$
Liquid-gas density difference	$(\rho_l - \rho_g) \sim (-t)^\beta$
Isothermal compressibility	$k_T \sim t ^{-\gamma}$
Critical isotherm ($t = 0$)	$P - P_c \sim \rho_l - \rho_g ^\delta \text{sign}(\rho_l - \rho_g)$
Correlation length	$\xi \sim t ^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim \frac{1}{r^{d-2+\eta}}$

Table 2.2: Definitions of the most commonly used critical exponents for a fluid system [4].

assumption that the critical exponent associated with a given thermodynamic variable is the same as $T \rightarrow T_c$ from above or below.

2.7.3 Law of the corresponding states

The system displays correlation at very long distance, these goes to the size of the system when $T \rightarrow T_c$. We are talking about long range correlation. The *correlation function* is $\xi \sim t^{-\nu}$. For instance, consider a polymer as in Figure 2.20a.

Having defined the critical exponents, we need to justify why they are interesting and why they are more interesting than the critical temperature T_c itself. It turns out that, whereas T_c depends sensitively on the details of the interatomic interactions, the critical exponents are to a large degree *universal* depending only on a few fundamental parameters.

To summarize, the critical exponents are more interesting than T_c since their values do not depend on microscopic details, but only on few parameters such as the space dimension d and the symmetry of the system.

One of the first experimental evidence of this universality was given by the work of Guggenheim on the coexistence curves of g different fluids: A, Kn, χ_e , Ne, N_2 , CO_2 and O_2 . By plotting T/T_c versus ρ/ρ_c (Figure 2.20b) he found that all the data collapse on the same curve, i.e. different sets of data fit the same function. Moreover for $t \rightarrow 0$:

$$(\rho_l - \rho_c) \sim (-t)^\beta$$

and $\beta \sim 1/3 \approx 0.335$. Therefore, close to the critical point all the data lie on the same curve and hence can be described by the same exponent β . A further test of universality is to compare this value to that obtained for a phase transition in a completely different system with a scalar order parameter. For instance, if we do the same for a string ferromagnetic the result is $\beta = 1/3$ too.

Remark. The law of corresponding states gives a universal liquid-gas coexistence curve.

2.7.4 Thermodynamic inequalities between critical exponents

It is possible to obtain several rigorous inequalities between the critical exponents. The easiest to prove is due to Rushbrooke.

Rushbrocke inequality

It follows from the well known thermodynamic relation between the specific heats at constant field and constant magnetization. Remember the relation between response functions:

$$k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2}\left(\frac{\partial v}{\partial T}\right)_P^2 = T\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P^2$$

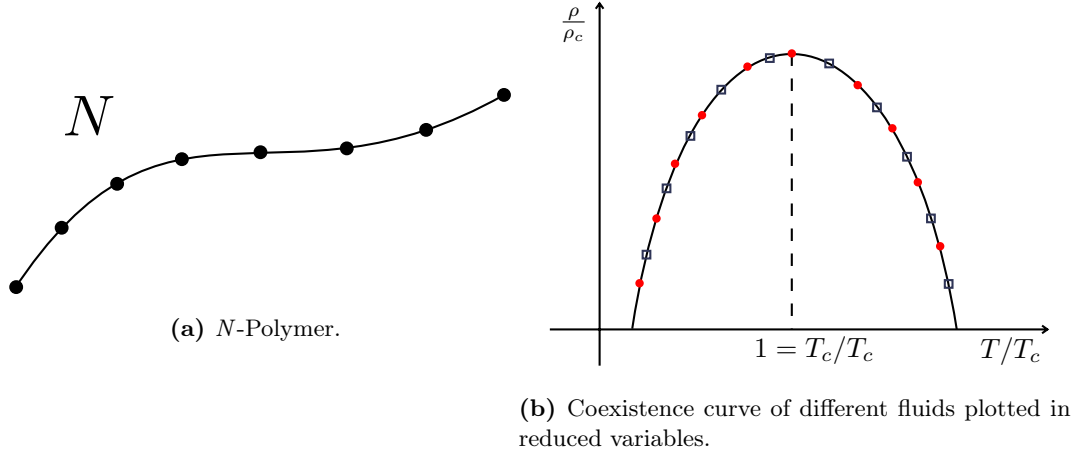


Figure 2.20

For magnetic systems one has

$$\chi_T(c_H - c_M) = T \underbrace{\left(\frac{\partial M}{\partial T} \right)_H^2}_{\geq 0}$$

From thermodynamic stability we have $c_M \geq 0, c_H \geq 0, \chi_T \geq 0$. Hence, from the previous relation we have

$$c_H = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)_H^2 + \underbrace{c_M}_{\geq 0}$$

which implies

$$c_H \geq \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)_H^2 \quad (2.22)$$

On the other hand, for $T \rightarrow T_c^-$ ($t \rightarrow 0^-$) and $H = 0$ (zero field) we have

$$\begin{cases} c_H \sim (-t)^{-\alpha} \\ \chi_T \sim (-t)^{-\gamma} \\ M \sim (-t)^\beta \end{cases}$$

that implies

$$\left(\frac{\partial M}{\partial T} \right)_{H=0} \sim (-t)^{\beta-1}$$

Since the inequality (2.22) is valid for all temperature T , it follows that can only be obeyed if

$$B(T_c - T)^{-\alpha} \geq B'T \frac{[(T_c - T)^{\beta-1}]^2}{(T_c - T)^{-\gamma}}$$

with $B, B' > 0$. Take the limit $T \rightarrow T_c^-$, we have:

$$\lim_{T \rightarrow T_c^-} (T_c - T)^{2-\alpha-2\beta-\gamma} \geq \frac{B'T}{B} > 0$$

Since the left hand side must be strictly greater than zero, we have the *RushBrook inequality*:

$$\alpha + 2\beta + \gamma \geq 2 \quad (2.23)$$

Griffith inequality

The *Griffith inequality* is obtained from the convexity property (in T and V) of the Helmholtz free energy and from $A \sim t^{2-\alpha}$:

$$\Rightarrow \alpha + \beta(1 + \delta) \geq 2 \quad (2.24)$$

We have introduced two very new ideas, universality and inequalities between the critical exponents, which appear to hold as equalities (see Sec.12.3.5).

In the intervening chapters, we look at models of systems which undergo phase transitions and how to calculate their critical exponents and other properties.

Chapter 3

Recall of statistical mechanics and theory of ensembles

3.1 Statistical ensembles

Statistical mechanics roughly speaking was born as a sort of theory from microscopic and try to compute the macroscopic length using thermodynamics. The problem is going from the countinuous problems to the macroscopic problems. In origin was statistical mechanics of equilibrium system. Each microstate with a given energy fixed, will have the same probability, this is the equal probability statement.

In general, if we consider a system with N, V (number of particles and volume) fixed and also the total energy E fixed, we call $\Omega(E, V, N)$ the number of microstate with total energy E , volume V and number of particles N .

If the system is *isolated* and in *equilibrium* the rule of **equal probability** of the microstates holds:

If the system is isolated and in equilibrium with energy E it visits each microstate consistent with energy E with equal probability.

Another way to say is: the system spends the same amount of time in each of the $\Omega(E, V, N)$ microstates.

Therefore, we call a single configuration of a given microstate \mathcal{C} . A configuration is just when you have the spatial part, because momentum can be obtained by integrating. Let us suppose to compute the probability of a given configuration \mathcal{C} , $P_{\mathcal{C}}$; because of equal probability we have:

$$P_{\mathcal{C}} = \frac{1}{\Omega(E, V, N)} \quad (3.1)$$

Now, let us now consider two subsystem 1 and 2 that can exchange energy, volume and/or particles. The number of microstates, of the combined system, of total energy $E_T = E_1 + E_2$, total volume $V_T = V_1 + V_2$ and $N_T = N_1 + N_2$ is given by:

$$\Omega(E_T, V_T, N_T) = \sum_{E_1, V_1, N_1} \Omega_1(E_1, V_1, N_1) \Omega_2(E_T - E_1, V_T - V_1, N_T - N_1) \quad (3.2)$$

One can show that, in the thermodynamic limit, $\Omega(E_T, V_T, N_T)$ is strongly peaked around a given point (E_1^*, V_1^*, N_1^*) and the fluctuations around this value are rare and small. Writing $\Omega(E_T, V_T, N_T)$ as

$$\Omega(E_T, V_T, N_T) \propto e^{\frac{S(E_T, V_T, N_T)}{k_B}} = \sum_{E_1, V_1, N_1} \exp \left[\frac{1}{k_B} (S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)) \right] \quad (3.3)$$

Lecture 4.
Friday 18th
October, 2019.
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(the proportionality becomes from the Boltzmann definition of entropy).

The values (E_1^*, V_1^*, N_1^*) are obtained by the max entropy condition that can be written as

$$\frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2} \Rightarrow T_1 = T_2 \quad (3.4a)$$

$$\frac{d \ln \Omega_1}{dV_1} = \frac{d \ln \Omega_2}{dV_2} \Rightarrow P_1 = P_2 \quad (3.4b)$$

$$\frac{d \ln \Omega_1}{dN_1} = \frac{d \ln \Omega_2}{dN_2} \Rightarrow \mu_1 = \mu_2 \quad (3.4c)$$

We next consider these properties to the case in which 1 is the system we want to study and 2 is a much larger system than 1 (a bath). This setup will bring us to the *canonical ensemble*.

3.2 The canonical ensemble

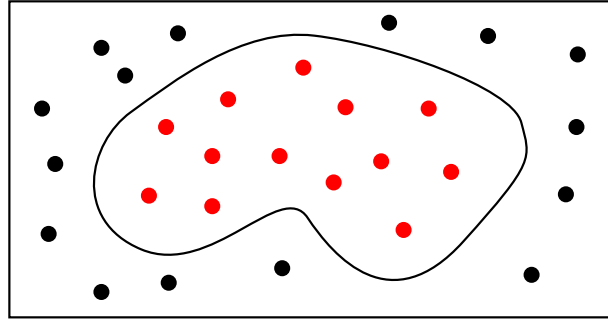


Figure 3.1: Isolated system. There are two subsystems, S constituted by red points and B constituted by the black one.

Let us consider an isolated system made by two subsystems, one S and one much larger, B , that we call *thermal bath* (Figure 3.1). The total number of particles is given by $N_T = N_B + N_S$ with $N_B \gg N_S \gg 1$ (they are both large but B is much larger than S), where N_B are the particles in the thermal bath and N_S the particle of the system.

Let E_T be the energy of the composite system. The two subsystems can exchange energy but the whole system has constant energy E_T . Therefore, let the energy to be free to fluctuate in time at fixed temperature T_B (isothermal ensembles). Note that V_S, N_S, V_B, N_B are fixed (no exchange of volume and particles).

For resuming, other quantities fixed are the temperature of the bath T_B , the number of the total particles of the system N_T , and also the total volume V_T . We have also $V_T = V_B + V_S$, with $V_B \gg V_S$.

The key to the canonical formalism is the determination of the probability distribution of the system among its microstates. And this problem is solved by the realization that the system plus the bath constitute a closed system, with fixed temperature, to which the principle of equal probability of microstates applies.

If one assumes that the system and the bath are *weakly coupled* (neglect interaction energy):

$$E_T = E_S + E_B = \text{const} \quad E_B \gg E_S$$

Let \mathcal{C} be the microstate of the system S , and \mathcal{G} the microstate of the heat bath B . A given microstate of the isolated composite system B - S is given from a pair $(\mathcal{C}, \mathcal{G})$

of microstate $\mathcal{C} \in S$ and $\mathcal{G} \in B$. The number of microstates of the isolated system with total energy E_T and system energy E_S is given by:

$$\Omega_T(E_T, E_S) = \Omega(E_S)\Omega_B(E_T - E_S)$$

Remark. In this analysis V and N are fixed. Since E_T is fixed

$$\Omega_T(E_T) = \sum_{E_S} \Omega(E_S)\Omega_B(E_T - E_S) \quad (3.5)$$

From the principle of equal probability for microstates at equilibrium, the probability of a composed microstate ($\mathcal{C} \circ \mathcal{G}$) is given by:

$$P_{\mathcal{C} \circ \mathcal{G}} = \begin{cases} \frac{1}{\Omega_T(E_T)} & E_{\mathcal{C}} + E_{\mathcal{G}} = E_T \\ 0 & \text{otherwise} \end{cases} \quad (3.6)$$

Since we are not interested to the microstates of the heat bath

$$P_{\mathcal{C}} = \sum_{\substack{\text{all } \mathcal{G} \\ \text{such that} \\ g(E_T - E_{\mathcal{C}} - E_{\mathcal{G}})}} P_{\mathcal{C} \circ \mathcal{G}} = \sum_{\substack{\text{all } \mathcal{G} \\ \text{such that} \\ g(E_T - E_{\mathcal{C}} - E_{\mathcal{G}})}} \frac{1}{\Omega_T(E_T)} = \frac{1}{\Omega_T} \sum_{\mathcal{G}} 1 \quad (3.7)$$

The number of microstates \mathcal{G} with energy $E_{\mathcal{G}} = E_T - E_{\mathcal{C}}$ is given by:

$$\Omega_B(E_{\mathcal{G}}) = \Omega_B(E_T - E_{\mathcal{C}})$$

This implies that the probability of a given configuration is related to the number of microstate of the bath:

$$\Rightarrow P_{\mathcal{C}} = \frac{\Omega_B(E_T - E_{\mathcal{C}})}{\Omega_T(E_T)} \propto \Omega_B(E_T - E_{\mathcal{C}}) \quad (3.8)$$

It is more convenient to deal with the logarithmic of $P_{\mathcal{C}}$ that is smoother

$$\Rightarrow k_B \ln \Omega_B(E_T - E_{\mathcal{C}}) = S_B \quad (3.9)$$

This is the entropy of B and is a function of N_B . Since $E_{\mathcal{C}} \ll E_B \simeq E_T$ we can expand $S_B(E_T - E_{\mathcal{C}})$ around $x_0 = E_T$ by the small amount

$$\Delta \equiv x - x_0 = (E_B) - (E_T) = -E_{\mathcal{C}}$$

$$f(E_B) = f(E_T) + \left. \frac{df}{dE_B} \right|_{E_B=E_T} (E_B - E_T) + \dots$$

Therefore:

$$k_B \ln \Omega_B(E_B) = S_B(E_B) = S_B(E_T) - E_{\mathcal{C}} \left(\frac{\partial S_B}{\partial E_B} \right)_{E_B=E_T} + \frac{E_{\mathcal{C}}^2}{2} \left(\frac{\partial^2 S_B}{\partial E_B^2} \right)_{E_B=E_T} + \dots \quad (3.10)$$

To make explicit the N_B dependence, let us consider the molar version

$$S_B \rightarrow N_B s_B \quad E_B \rightarrow N_B e_B$$

$$S_B = N_B s_B = N_B s_B(E_T) - E_{\mathcal{C}} \left(\frac{\partial s_B}{\partial e_B} \right)_{e_B=e_T} + \frac{E_{\mathcal{C}}^2}{2N_B} \left(\frac{\partial^2 s_B}{\partial e_B^2} \right)$$

Let us consider the limit in which the system size is fixed, while the one of the heat bath is going to ∞ :

$$\lim_{N_B \rightarrow \infty} \frac{E_T}{N_B} = \frac{E_S + \overbrace{N_B e_B}^{E_B}}{N_B} \rightarrow e_B \quad (3.11a)$$

$$\lim_{N_B \rightarrow \infty} k_B \ln \Omega_B(E_T - E_c) \rightarrow N_B s_B - E_c \frac{ds_B}{de_B} \quad (3.11b)$$

On the other hand,

$$\frac{ds_B}{de_B} \equiv \frac{1}{T_B} = \frac{1}{T}$$

which implies

$$P_c \propto \Omega_B(E_T - E_c) = \exp\left(\frac{S_B}{k_B}\right) = \exp\left(\frac{N_B s_B}{k_B} - \frac{E_c}{k_B T}\right)$$

Since the first term does not depend on \mathcal{C} , it can be absorbed in the constant and what we get by expanding considering the huge number of particles

$$P_c \propto \exp(-E_c/k_B T) \quad (3.12)$$

Remark. Since the energy of the system fluctuates, its microstates are not anywhere equiprobable, but are visited with probability given by (3.12).

Remark. Since the bath is very large, T is the only property of the bath that affects the system. The *Boltzmann factor* is defined as:

$$\beta \equiv \frac{1}{k_B T} \quad (3.13)$$

The normalization consists in dividing by the normalization factor, that is the sum of all microstates

$$P_c = \frac{e^{-\beta E_c}}{\sum_c e^{-\beta E_c}} \quad (3.14)$$

Finally, the **canonical partition function** is defined as

$$Q(T, V, N) \equiv \sum_{\substack{\text{all } \mathcal{C} \\ \text{with } V, N \\ \text{fixed}}} \exp(-\beta E_c) \quad (3.15)$$

Given $Q(T, V, N)$, one gets the *Helmholtz free energy*:

$$A(T, V, N) = -k_B T \ln Q(T, V, N) \quad (3.16)$$

that is the free energy describing the isothermal (or canonical) ensemble at fixed T , volume V and number of particles N .

Remark.

$$Q(T, V, N) = \sum_{\substack{\mathcal{C} \\ V, N \text{ fixed}}} e^{-\beta E(\mathcal{C})} = \sum_E e^{-\beta E} \Omega(E, V, N)$$

What we have done is a *foliation* in energy of the space, that is a sum over the energy (keeping $\{V, N\}$ fixed):

$$Q(T, V, N) = \sum_E e^{-\beta E} \Omega(E, V, N) = \sum_E e^{-\beta E} e^{S/k_B} = \sum_E e^{-\beta(E - TS)}$$

Hence,

$$Q(T, V, N) = e^{-\beta A} \Rightarrow A = -k_B T \ln Q(T, V, N)$$

We have formulated a complete algorithm for the calculation of a fundamental relation in the canonical formalism. Given a list of states of the system, and their energies E_c , we calculate the partition function (3.15). The partition function is thus obtained as a function of temperature and of the parameters that determine the energy levels. The fundamental relation is (3.16) that determines the Helmholtz potential.

The probability of a configuration can be written as (3.14), that is a very useful form. Indeed, the average energy is expected to be

$$U = \sum_c E_c P_c = \frac{\sum_c E_c e^{-\beta E_c}}{\sum_c e^{-\beta E_c}} \quad (3.17)$$

or

$$U = -\frac{\partial}{\partial \beta} \ln Q \quad (3.18)$$

3.2.1 Energy fluctuations in the canonical ensemble

Despite energy in the canonical ensemble fluctuates, while in the microcanonical one is constant, this does not contradict the equivalence principle of the ensemble (in the thermodynamic limit). The reason is that the relative size of the energy fluctuation decreases in the large system limit. To see it, let us compute the average square fluctuations of E .

$$\langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \quad (3.19)$$

Remark. Remember that thermodynamic assume that the number of number of freedom is related to the number of Avogadro.

On the other hand,

$$\begin{aligned} \langle E \rangle &= \sum_c P_c E_c = \sum_c E_c \frac{e^{-\beta E_c}}{\sum_c e^{-\beta E_c}} = - \left(\frac{\frac{\partial Q(T,V,N)}{\partial \beta}}{Q} \right) = - \left(\frac{\partial}{\partial \beta} \ln Q \right)_{N,V} \\ \langle E^2 \rangle &= \sum_c P_c E_c^2 = \frac{\left(\frac{\partial^2 Q}{\partial \beta^2} \right)}{Q} \end{aligned}$$

Therefore,

$$\begin{aligned} \langle (\delta E)^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle = \frac{1}{Q} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{N,V} - \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V}^2 \\ &= \left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{N,V} = - \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N,V} \end{aligned}$$

Since

$$c_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \quad (3.20)$$

we have

$$\langle (\delta E)^2 \rangle = k_B T^2 c_V \quad (3.21)$$

Both c_V and $\langle E \rangle$ are extensive

$$\frac{\sqrt{\langle (\delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{k_B T^2 c_V}}{\langle E \rangle} \sim O\left(\frac{1}{\sqrt{N}}\right) \Rightarrow 0$$

because $N \sim 10^{23}$.

3.3 Isothermal and isobaric ensemble

Now, the system is coupled both to a thermal and a volumic bath at temperature T_B and pressure P_B . The idea is: consider the same system with the bath; the difference is that in this case the system can exchange energy but also volume (we continue to keep the temperature of the bath fixed). At this point the ensemble is *isothermal* and *isobaric*. All the assumptions done before are valid, in particular, assuming as before *weak coupling* between the degrees of freedom of the bath and those of the system

$$\begin{aligned} E_T &= E + E_B \\ V_T &= V + V_B \end{aligned}$$

We look for the partition function that describes this isothermal and isobaric ensemble. Similarly to the previous case, one can write

$$P_{\mathcal{C}} \propto \Omega_B(E_B, V_B) \propto \Omega_B(E_T - E_{\mathcal{C}}, V_T - V_{\mathcal{C}}) \propto \exp[S_B(E_T - E_{\mathcal{C}}, V_T - V_{\mathcal{C}})/k_B] \quad (3.23)$$

Remark. Now, \mathcal{C} is specified both by its volume V and energy E . As before, one can expand $\log \Omega_B$ both in E_B and in V_B (around E_T and V_T) and take the limit $N_B \rightarrow \infty$.

$$P_{\mathcal{C}} \propto \exp \left[\frac{S_B(E_T, V_T)}{k_B} - \frac{E_{\mathcal{C}}}{k_B} \frac{\partial S_B}{\partial E_B} \Big|_{E_T, V_T} - \frac{V_{\mathcal{C}}}{k_B} \frac{\partial S_B}{\partial V_B} \Big|_{V_T, E_T} + \left(\text{term} \simeq \frac{1}{N_B} \right) \right] \quad (3.24)$$

Recalling that

$$\frac{dS}{dV} \Big|_E = \frac{P}{T} \quad \text{with} \quad \begin{cases} P_B \rightarrow P \\ T_B \rightarrow T \end{cases} \quad (3.25)$$

$$\Rightarrow P_{\mathcal{C}} \propto \exp \left[-\frac{E_{\mathcal{C}}}{k_B T} - \frac{P V_{\mathcal{C}}}{k_B T} \right] \quad (3.26)$$

If we normalize:

$$P_{\mathcal{C}} = \frac{e^{-\beta(E_{\mathcal{C}} + P V_{\mathcal{C}})}}{\Delta(T, P, N)} \quad (3.27)$$

where

$$\Delta(T, P, N) = \sum_{\mathcal{C}} e^{-\beta(E(\mathcal{C}) + P V(\mathcal{C}))} \quad (3.28)$$

is called the **Gibbs partition function**.

Remark. Note that

$$\begin{aligned} \Delta(T, P, N) &= \sum_V e^{-\beta P V} \left(\sum_{\substack{\mathcal{C} \\ V, N \text{ fixed}}} e^{-\beta E_{\mathcal{C}}} \right) = \sum_V e^{-\beta P V} Q(T, V, N) \\ &= \underbrace{\sum_V \sum_E}_{\text{fluctuating variables}} e^{-\beta(E + P V)} \Omega(E, V, N) \end{aligned}$$

By summing over all the microstates compatible with E and V :

$$P(E, V) = \frac{\Omega(E, V, N)}{\Delta(T, P, N)} e^{-\beta(E + P V)} \quad (3.29)$$

Remark.

$$\Delta(T, P, N) = \underbrace{\sum_E \sum_V e^{-\beta E - \beta PV}}_{\text{Laplace transform}} \Omega(E, V, N) = \sum_{E, V} e^{-\beta E - \beta PV + S(E, V, N)/k_B} \quad (3.30)$$

Classical systems (fluids)

$$\Delta(T, P, N) = \int_0^\infty dV e^{-\beta PV} \left[\frac{1}{h^{3N} N!} \int d\vec{p}_1 \dots d\vec{p}_N e^{-\beta \mathcal{H}(p^N, r^N)} \right] \quad (3.31)$$

which implies

$$\Delta(T, P, N) = \int_0^\infty dV e^{-\beta PV} Q(T, V, N) \quad (3.32)$$

that is the Laplace transform of the canonical partition function Q .

We also define

$$\beta P \equiv \frac{P}{T} = \frac{\partial S}{\partial V} \quad (3.33)$$

Remark. Let us remind that

Definition 3: Laplace transform

The Laplace transform of a function $f(t)$, defined for all real numbers $t \geq 0$, is the function $F(s)$, which is a unilateral transform defined by

$$F(s) = \int_0^\infty f(t) e^{-st} dt$$

where s is a complex number frequency parameter with real numbers σ and ω :

$$s = \sigma + i\omega$$

Magnetic system

Ensemble in which both E and M can fluctuate. In particular, we have $\Omega(E, M)$ (with T_B and H_B fixed).

$$P_{\mathcal{C}} \propto e^{\frac{S_B(E_T, M_T)}{k_B} - \frac{E_{\mathcal{C}}}{k_B} \frac{dS_B}{dE_B} - \frac{M_{\mathcal{C}}}{k_B} \frac{dS_B}{dM_B}} \quad (3.34)$$

Since $\frac{dS_B}{dM_B} = -\frac{H_B}{T_B}$ and $\frac{dS_B}{dE_B} = \frac{1}{T_B}$:

$$\Rightarrow P_{\mathcal{C}} \propto \exp[-\beta(E_{\mathcal{C}} - HM_{\mathcal{C}})], \quad T_B \rightarrow T, H_B \rightarrow H \quad (3.35)$$

The normalization function is:

$$\Delta(T, H, N) = \sum_{\mathcal{C}} e^{-\beta(E_{\mathcal{C}} - HM_{\mathcal{C}})} = \sum_{E, M} e^{-\beta E + \beta M H} \Omega(E, M) \quad (3.36)$$

that is the *Gibbs partition function* for magnetic systems.

3.3.1 Saddle point approximation

The sum (3.30) can be approximated by the maximum of the integrand (this is fair for highly peaked functions):

$$\sum_{E,V} \exp[-\beta E - \beta PV + S(E, V, N)/k_B] \approx e^{-\beta E^* - \beta PV^* + S(E^*, V^*, N)/k_B}$$

where

$$\left(\frac{dS(E^*, V^*, N)}{dE} \right)_{V,N} = \frac{1}{T}, \quad \left(\frac{dS(E^*, V^*, N)}{dV} \right)_{E,N} = \frac{P}{T}$$

this implies

$$-k_B T \ln \Delta(T, P, N) \simeq E^* + PV^* - TS$$

Hence, we define the **Gibbs free energy** as:

$$G(T, P, N) = -k_B T \ln \Delta(T, P, N) \quad (3.37)$$

3.4 Gran canonical ensemble

In this case N varies instead than V . Thus we have

$$\begin{aligned} P_{\mathcal{C}} &= \exp \left[\frac{S_B(E_T - E_{\mathcal{C}}, N_T - N_{\mathcal{C}})}{k_B} \right] \\ &\sim \exp \left[\frac{S_B(E_T, N_T)}{k_B} - \frac{E_{\mathcal{C}}}{k_B} \frac{dS_B}{dE_B} - \frac{N_{\mathcal{C}}}{k_B} \frac{dS_B}{dN_B} + \left(\text{terms of order } \leq \frac{1}{V_B} \right) \right] \\ &= \frac{\exp[-\beta E_{\mathcal{C}} + \beta \mu N_{\mathcal{C}}]}{\Theta(T, V, \mu)} \end{aligned} \quad (3.38)$$

where

$$\Theta(T, V, \mu) = \sum_N \sum_{\substack{\mathcal{C} \\ V, N \text{ fixed}}} e^{-\beta(E_{\mathcal{C}} - \mu N)} \quad (3.39)$$

is the **grancanonical partition function**.

Remark. Remember that

$$\frac{dS}{dE} = \frac{1}{T}, \quad \frac{dS}{dN} = \frac{\mu}{T} \quad (3.40)$$

The *fugacity* is defined as:

$$z \equiv e^{\beta \mu} \quad (3.41)$$

and we rewrite

$$\Theta(T, V, \mu) = \sum_{N=0}^{\infty} z^N \left(\sum_{\substack{\mathcal{C} \\ V, N \text{ fixed}}} e^{-\beta E_{\mathcal{C}}} \right) \quad (3.42)$$

In principle, if one is able to compute the partition function is able to compute the thermodynamic quantities.

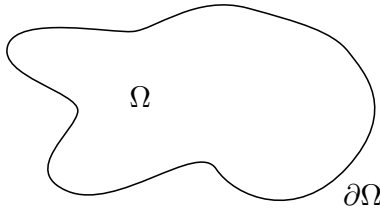
Chapter 4

Statistical mechanics and phase transitions

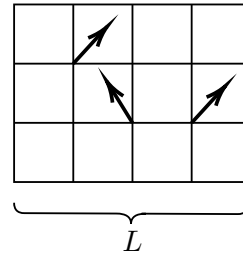
4.1 Statistical mechanics of phase transitions

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) Region Ω with boundary $\partial\Omega$.



(b) Magnetic system with characteristic length L .

Figure 4.1

Let us consider a system with a region Ω of volume $V(\Omega)$ and boundary $\partial\Omega$ of area $S(\Omega)$ (Figure 4.1a). Denoting by L a characteristic length of the system

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

where d is the spatial dimension.

Remark. Space Ω can be either *discrete* or *continuous*.

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

$$\mathcal{H}_\Omega = - \sum_n k_n \Theta_n \quad (4.1)$$

where

- k_n : are the coupling constants. In general, but not always, they are *intensive thermodynamic variables*.
- Θ_n : is a linear, or 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.

4.1.1 Magnetic system (canonical)

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 4.1b). A configuration is the orientation of the spin in each site $\mathcal{C} = \{\vec{\mathbf{S}}_1, \dots, \vec{\mathbf{S}}_N\}$. We have:

$$\Theta_1 = \sum_i \vec{\mathbf{S}}_i \quad (4.2a)$$

$$\Theta_2 = \sum_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j \quad (4.2b)$$

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

$$\text{Tr} \equiv \sum_{\{\mathcal{C}\}} \equiv \sum_{\vec{\mathbf{S}}_1} \sum_{\vec{\mathbf{S}}_2} \cdots \sum_{\vec{\mathbf{S}}_N} \quad (4.3)$$

where \sum can also indicate an integration if values are continuous.

The *canonic partition function* is

$$Q_\Omega(T, \{k_n\}) = \text{Tr} \left(e^{-\beta \mathcal{H}_\Omega} \right) \quad (4.4)$$

with $\beta \equiv \frac{1}{k_B T}$.

4.1.2 Fluid system (gran canonical)

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

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

and

$$\Theta_1 = \sum_i \left[\frac{\vec{\mathbf{p}}_i^2}{2m_i} + U_1(\vec{\mathbf{x}}_i) \right] \quad (4.5a)$$

$$\Theta_2 = \frac{1}{2} \sum_{i>j} U(|\vec{\mathbf{x}}_i - \vec{\mathbf{x}}_j|) \quad (4.5b)$$

The trace operation is

$$\text{Tr} \equiv \sum_{\{\mathcal{C}\}} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{(d\vec{\mathbf{p}}_i)(d\vec{\mathbf{x}}_i)}{h^{dN}} \quad (4.6)$$

The *gran canonical partition function* is:

$$\mathcal{F}_\Omega = \text{Tr} \left(e^{-\beta(\mathcal{H}_\Omega - \mu N)} \right) \quad (4.7)$$

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

$$F_\Omega[T, \{k_n\}] = -k_B T \ln Q_\Omega(T, \{k_n\}) \quad (4.8)$$

The relation with thermodynamic is through the *thermodynamic limit*.

Since the free energy is an extensive function,

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

In general, one can write

$$F_\Omega[T, \{k_n\}] = V(\Omega)f_b[T, \{k_n\}] + S(\Omega)f_s[T, \{k_n\}] + O(L^{d-2}) \quad (4.9)$$

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

Definition 4: Bulk free energy density

We define the *bulk free energy density* as

$$f_b[T, \{k_n\}] \equiv \lim_{V(\Omega) \rightarrow \infty} \frac{F_\Omega[T, \{k_n\}]}{V(\Omega)} \quad (4.10)$$

if the limit exists (to prove for each system) and does not depend on Ω .

For a system defined on a lattice we have

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

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

To get information on surface property of the system, let us calculate

$$f_s[T, \{k_n\}] \equiv \lim_{S(\Omega) \rightarrow \infty} \frac{F_\Omega[T, \{k_n\}] - V(\Omega)f_b[T, \{k_n\}]}{S(\Omega)} \quad (4.11)$$

4.1.3 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:

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

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

4.1.4 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

$$Z_\Omega = \text{Tr} \left(e^{-\beta \mathcal{H}_\Omega} \right) \quad (4.12)$$

the exponentials are analytic functions everywhere (they converge), hence Z_Ω is analytic for Ω finite!

The question is: where do singularities come 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 out of this for producing singularities. The singularities will develop in the thermodynamic limits. For reaching 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, geometrically, in the behaviour of the system?

4.2 Critical point and correlations of fluctuations

From thermodynamics, we know that, at the critical point, some response functions may diverge (see Section 2.7.1). Now, we 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 as equation (3.36):

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

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

$$\langle M \rangle = \left. \frac{\partial \ln Z_G}{\partial(\beta H)} \right|_T = \frac{1}{Z_G} \text{Tr} \left[M(\mathcal{C}) e^{-\beta(\mathcal{H}(\mathcal{C}) - HM(\mathcal{C}))} \right] \quad (4.13)$$

$$\chi_T = \frac{\partial \langle M \rangle}{\partial H} = \left\{ \frac{\beta}{Z_G} \text{Tr} \left[M^2(\mathcal{C}) e^{-\beta\mathcal{H} + \beta HM} \right] - \frac{\beta}{Z_G^2} \left[\text{Tr} \left[M(\mathcal{C}) e^{-\beta\mathcal{H} + \beta HM} \right] \right]^2 \right\} \quad (4.14)$$

Hence,

$$\chi_T = \frac{1}{k_B T} \left(\langle M^2 \rangle - \langle M \rangle^2 \right) \quad (4.15)$$

The thermodynamic response function χ_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 as an integral

$$M(\mathcal{C}) = \int d^3\vec{r} m(\vec{r}) \quad (4.16)$$

Hence,

$$k_B T \chi_T = \int d\vec{r} d\vec{r}' \left[\langle m(\vec{r}) m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle \right] \quad (4.17)$$

Let us assume the *translational symmetry*:

$$\begin{cases} \langle m(\vec{r}) \rangle = m & \text{homogeneous} \\ \langle m(\vec{r}) m(\vec{r}') \rangle \equiv G(\vec{r} - \vec{r}') & \text{two-point correlation function} \end{cases} \quad (4.18)$$

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

$$\langle m(\vec{r}) m(\vec{r}') \rangle_c \equiv \langle (m(\vec{r}) - \langle m(\vec{r}) \rangle) (m(\vec{r}') - \langle m(\vec{r}') \rangle) \rangle = G(\vec{r} - \vec{r}') - m^2 \quad (4.19)$$

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

$$\begin{aligned}\vec{r}_{CM} &\Rightarrow \vec{r}_0 \equiv \vec{0} \\ &\Rightarrow \int d\vec{r} \int d\vec{r}' [G(\vec{r} - \vec{r}_0) - m^2]\end{aligned}$$

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

$$\underbrace{k_B T \chi_T}_{\text{response function}} = V(\Omega) \int d\vec{r} \underbrace{\langle m(\vec{r}) m(\vec{r}_0) \rangle_c}_{\text{correlation function of the fluctuations of the local magnetization}} \quad (4.20)$$

The equation (4.20) is called the **fluctuation-dissipation relation**.

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

$$G_c(\vec{r}) \sim e^{-|\vec{r}|/\xi} \quad (4.21)$$

meaning that for $|\vec{r}| > \xi$ the fluctuations are uncorrelated, where ξ is the *correlation length*. The correlation length is related to the correlation function. In general, it is finite but, if you approach T_c , it diverges. In fact, at the critical point this correlation will expand in the whole space and reaches the size of all the system, in other words, it goes to infinity ($\xi \rightarrow \infty$). When ξ will diverge, there will not be anymore the exponential and the integral cannot be kepted finite.

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

$$k_B T \chi_T \leq V g \xi^3$$

where there is an inequality because we are underestimating the integral (Figure 4.2).

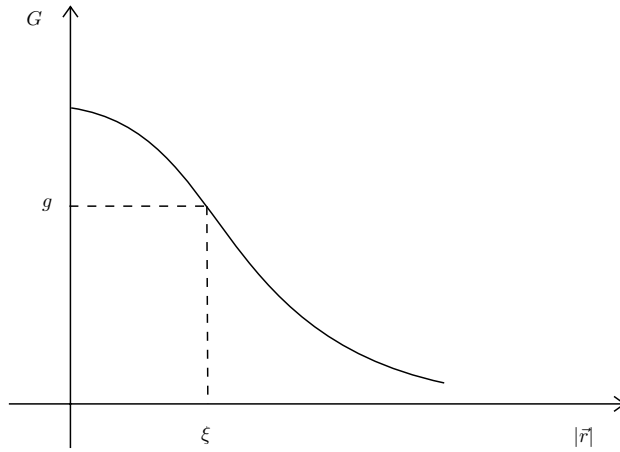


Figure 4.2: Plot of the two-point correlation function, G .

Rearranging the terms, we obtain

$$\frac{k_B T \chi_T}{V} \leq g \xi^3 \quad (4.22)$$

Hence, if χ_T diverges at the critical point it implies $\xi \rightarrow \infty$.

In particular, one can see that for $H = 0$ and $T \rightarrow T_c^\pm$:

$$\xi_\pm(T, H = 0) \sim |t|^{-\nu_\pm} \quad (4.23)$$

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

Remark. It does not derive from thermodynamic considerations.

Scaling (4.23) is often used as the most general definition of a critical point.

One can also show that at $T = T_c$ (i.e. $t = 0$)

$$G_c(r) \sim \frac{1}{r^{d-2+\eta}} \quad (4.24)$$

where η is the correlation critical exponent.

Remark. The formula is a power law decay instead than exponential.

4.3 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 ξ 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 ρ with respect to ρ_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 ξ , where it is the typical size of the liquid droplets. Clearly $\xi = \xi[T]$ and, in proximity of the critical point $\xi \xrightarrow{t \rightarrow 0} |t|^{-\nu}$.

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

As $T \rightarrow T_c$, where ξ 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 $L = 1$ cm and

$$t \equiv (T - T_c)/T_c, \quad \xi \sim \xi_0 t^{-\nu}$$

Let us assume that the lattice distance is $\xi_0 = 10 \text{ \AA}$. Hence,

$$t \sim \left(\frac{\xi}{\xi_0} \right)^{-1/\nu} \sim \left(\frac{L}{10 \text{ \AA}} \right)^{-1/\nu} \sim (10^{10})^{-1/\nu} \quad (4.25)$$

In the next chapters, we will see that $\nu < 1$ and close to $1/2$, hence:

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

Therefore we have $t \approx 10^{-20}$ as a 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.

4.4 Numerical simulations and phase transitions

In this case, the size L of the simulated system is few multiples of ξ_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.

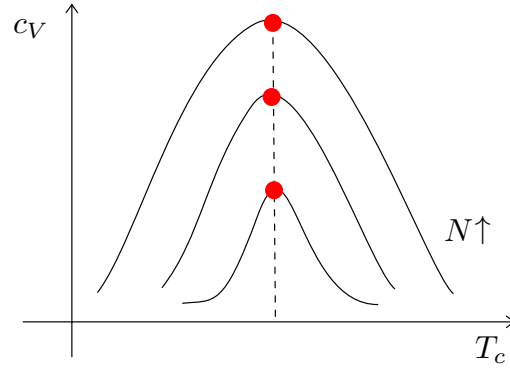


Figure 4.3: (T_c, C_V) plot at different N .

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 the behaviour as in Figure 4.3, something is happening. There are two approaches we can use.

The first approach is studying the system by looking for all the details. An example could be a protein, that interact with other proteins; in this case we can look at all the electrons (or atoms). Nevertheless, even if we thought at the simple protein that exists, there would be a lot of degrees 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 Van der Waals or Lenard Jones potential and studying collective effects. This is the second approach.

Chapter 5

Role of the models in statistical mechanics

5.1 Role of the models

Which is the role of models in statistical mechanics? There are two possible approaches:

1. The model must describe the real system in a very detailed way. The maximum number of details and parameters to be tuned are included. The *pro* is the closer to the real specific system (faithfull description). The *drawback* is that the model is so complicated that no analytical solution is possible. Moreover, even numerically, these models can be studied for very short times and small sizes. An example is the simulation of the folding dynamics that can be performed for few nanoseconds. On the other hand, the introduction of many details are often not crucial if one is interested in large scale properties.
2. Try to introduce (coarse-graining approach) the most simple model that satisfies few essential properties of the real system such as its symmetries, dimensionality, range of interactions etc. Since most of the microscopic details are integrated, these models cannot describe the full physics of a specific system but they can reproduce its main features. Moreover, these models can be studied numerically and, to some extent, also analytically (exact solution).

It is the latter approach that we shall take here. Let us start by introducing what is, perhaps, the most paradigmatic model in the statistical mechanics of phase transition, the *Ising model*.

5.2 The Ising model

Suggested by Lenz to Ising for his PHD thesis (1925), it is supposed to describe a magnetic system that undergoes a transition between a paramagnetic and a ferromagnetic phase. In $d = 1$ the model was solved exactly by Ising. Unfortunately, he found that for $T > 0$ the model does not display a phase transition.

The wrong conclusion was that this model was not able to describe a phase transition. In fact, it turns out that, for $d > 1$, the model does display a paramagnetic-ferromagnetic phase transition.

Let us first discuss some general feature of the model for any dimension d .

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5.2.1 d -dimensional Ising model

For hypercubic lattice with given $N(\Omega)$ sites $\{i\}_{i=1,\dots,N(\Omega)}$ and linear size $L(\Omega)$, we have

$$N(\Omega) = L^d$$

The microscopic degrees of freedom are the spins S_i , defined at each i -esim lattice site. Each spin can assume the values $S_i = \pm 1$, that means that at each site the possible values are the spin up or down. For a lattice with $N(\Omega)$ spins, there are $2^{N(\Omega)}$ possible configurations.

Remark. Since we do not consider the spin as a vector, this is a model for a strongly anisotropic ferromagnet (along a given direction).

The minimal model that can try to capture the interaction between the spin is the following. Suppose to have also an external magnetic field H_i (it values depends on the site i). One can consider interactions between spins whose strength are described by functions J_{ij}, k_{ijk}, \dots . For instance, there is a coupling that derives from electrons coupling

$$J_{ij} = f(|\vec{r}_i - \vec{r}_j|)$$

The physical origin is the overlap between the electronic orbitals of the neighbouring atoms forming the Bravais lattice. Remember that a term as $\sum_i S_i$ is not correlated, while we need an interaction for describing the model.

A general Hamiltonian of the model can be written as:

$$\mathcal{H}_\Omega(\{S_i\}) = \sum_{ij} J_{ij} S_i S_j - \sum_i H_i S_i - \sum_{ijk} S_i S_j S_k + \dots$$

Standard Ising model one keeps only the two-body interactions:

$$\mathcal{H}_\Omega(\{S_i\}) = -\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j - \sum_{i=1}^N H_i S_i \quad (5.1)$$

where the first term represents a two body interaction that is a quadratic term, while the second term is a one body interaction. We have put the minus because we want to minimize the energy, but it depends on the sign of J .

For this model, the sum over all configurations on trace is given by

$$\text{Tr} \equiv \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \equiv \sum_{\{S\}}$$

Our problem is to find the partition function with N sites, which depends on T and in principle depends on the configuration given (it is fixed both for H and J !). Hence, the *canonical partition function* is given by

$$Z_\Omega(T, \{H_i\}, \{J_{ij}\}) = \text{Tr} e^{-\beta \mathcal{H}_\Omega(\{S\})} \quad (5.2)$$

and the corresponding *free-energy*,

$$F_\Omega(T, \{H_i\}, \{J_{ij}\}) = -k_B T \ln Z_\Omega \quad (5.3)$$

The *bulk limiting free energy* is:

$$f_b(T, \{H_i\}, \{J_{ij}\}) = \lim_{N \rightarrow \infty} \frac{1}{N} F_\Omega \quad (5.4)$$

How do we know that the above limit does exist? It must be proven. The surface is not important in the bulk limit. Note that we are assuming that the *interaction between the spin is a short range force*, it is not as the size of the system.

For this model it is possible to show that the limit exists if

$$\sum_{j \neq i} |J_{ij}| < \infty \quad (5.5)$$

Remark. In general what determines the existence of the limit of these spin models are the *dimension* d and the *range* of the spins *interactions*.

For example it is possible to show that, if

$$J_{ij} = A|\vec{r}_i - \vec{r}_j|^{-\sigma} \quad (5.6)$$

so it is a long range interaction, the limit exists when

$$\sigma > d$$

Remark. If the interaction is *dipolar*, since it decays as $1/r^3$, for the case $d = 3$ the limit does not exist. However, it is still possible to prove the existence of the limit for this case if one assumes that not all dipoles are fully aligned.

Assuming that the thermodynamic limit exists, we now look at some additional rigorous results on the limiting free energy and its derivatives.

5.2.2 Mathematical properties of the Ising model with nearest neighbours interactions

For simplicity, let us consider the case in which the external magnetic field is homogeneous, i.e. $H_i \equiv H$, and the spin-spin interaction is only between spins that are nearest-neighbours (n.n.) on the lattice:

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are n.n.} \\ 0 & \text{otherwise} \end{cases} \quad (5.7)$$

Now, the model is very simple:

$$-\mathcal{H}_\Omega(\{S\}) = J \sum_{\langle ij \rangle}^{N(\Omega)} S_i S_j + H \sum_i^{N(\Omega)} S_i \quad (5.8)$$

where the notation $\langle ij \rangle$ means a double sum over i and j , with the constraint that i and j are nearest-neighbours.

Since H is uniform, the average magnetization per spin is

$$\langle m \rangle = \frac{1}{N(\Omega)} \sum_{i=1}^{N(\Omega)} \langle S_i \rangle \quad (5.9)$$

where $\langle \dots \rangle$ means average over the chosen ensemble.

Remark. For $J = 0$, (5.8) is the Hamiltonian of a paramagnet. The only influence ordering the spins is the field H . They do not interact, there are no cooperative effects and hence no phase transition.

Since

$$\sum_{i=1}^N \langle S_i \rangle = \frac{1}{Z} \text{Tr} \left[\sum_i S_i e^{-\beta \mathcal{H}_\Omega(\{S_i\})} \right] = \frac{1}{Z} \text{Tr} \left[\sum_i S_i \exp \left(\beta J \sum_{\langle ij \rangle}^{N(\Omega)} S_i S_j + \beta H \sum_i^{N(\Omega)} S_i \right) \right]$$

it is easy to show that:

$$\langle m \rangle = -\frac{1}{N} \frac{\partial F_\Omega}{\partial H} \quad (5.10)$$

where

$$F_\Omega(T, J, H) = -k_B T \ln Z_\Omega(T, J, H) \quad (5.11)$$

Now, let us consider the properties of the limiting free-energy

$$f_b = \lim_{N \rightarrow \infty} \frac{1}{N} F_\Omega = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T \ln Z_N) \quad (5.12)$$

It is possible to prove the following properties:

1. $f_b < 0$.
2. $f_b(T, J, H)$ is a *continuous* function of T, J and H .
3. The right and left derivatives of $f_b(T, J, H)$ exist and are equal almost everywhere.
4. The molar entropy $s = -\frac{\partial f_b}{\partial T} \geq 0$ almost everywhere.
5. $\frac{\partial f_b}{\partial T}$ is a *monotonic non increasing* function of T . That is $\frac{\partial^2 f_b}{\partial T^2} \leq 0$. This implies that:

$$c_H = T \left(\frac{\partial S}{\partial T} \right)_H = -T \left(\frac{\partial^2 f_b}{\partial T^2} \right)_H \geq 0$$

6. $\frac{\partial f_b}{\partial H}$ is a *monotonic non increasing* function of H . That is

$$\frac{\partial^2 f_b}{\partial H^2} \leq 0$$

This implies that

$$\chi_T = \left(\frac{\partial M}{\partial H} \right)_T = - \left(\frac{\partial^2 f_b}{\partial H^2} \right)_T \geq 0$$

Remark. The above properties have been postulated in thermodynamics, but here they have been rigorously proved for the Ising model using statistical mechanics.

Proof of property (4). Almost everywhere, we have to prove that

$$s \equiv -\frac{\partial f_b}{\partial T} \geq 0$$

Let us consider a finite system

$$\begin{aligned} -\frac{\partial F_\Omega}{\partial T} &= k_B \ln (\text{Tr } e^{-\beta \mathcal{H}_\Omega}) + k_B T \frac{1}{k_B T^2} \frac{\text{Tr}(\mathcal{H}_\Omega e^{-\beta \mathcal{H}_\Omega})}{\text{Tr}(e^{-\beta \mathcal{H}_\Omega})} \\ &= k_B \left[\ln Z_\Omega + \frac{\text{Tr}(\beta \mathcal{H}_\Omega e^{-\beta \mathcal{H}_\Omega})}{Z_\Omega} \right] \stackrel{\text{to do}}{=} -k_B T \text{Tr}(\rho_\Omega \ln \rho_\Omega) \end{aligned}$$

where

$$\rho_\Omega = \frac{e^{-\beta \mathcal{H}_\Omega}}{Z_\Omega}$$

is the probability distribution.

Since $\rho_\Omega \leq 1$ it implies $\ln \rho_\Omega \leq 0$ and so $-\text{Tr}(\rho_\Omega \ln \rho_\Omega)$ is positive. Then, let us divide by $N(\Omega)$ and take the thermodynamic limit:

$$\lim_{N \rightarrow \infty} -\frac{1}{N} \frac{\partial F_\Omega}{\partial T} = -k_B T \lim_{N \rightarrow \infty} \frac{1}{N} \underbrace{\text{Tr}(\rho_\Omega \ln \rho_\Omega)}_{S_\Omega} = Ts \geq 0 \quad \Rightarrow \quad s \geq 0$$

■

All the other properties listed before (except (1)) are consequences of the *convexity* property of f_b .

Theorem 1

$f_b(T, J, H)$ is an upper convex (i.e. concave) function of H .

Proof. The proof is based on the Hölder inequality for two sequences $\{g_k\}, \{h_k\}$:

Definition 5: Hölder inequality

Given $\{g_k\}, \{h_k\}$ with $g_k, h_k \geq 0, \forall k$ and two non negative real numbers α_1, α_2 such that $\alpha_1 + \alpha_2 = 1$, the following inequality holds

$$\sum_k (g_k)^{\alpha_1} (h_k)^{\alpha_2} \leq \left(\sum_k g_k \right)^{\alpha_1} \left(\sum_k h_k \right)^{\alpha_2} \quad (5.13)$$

Now, consider the partition function:

$$Z_\Omega(H) = \text{Tr} \left[\exp \left(\beta H \sum_i S_i \right) \underbrace{\exp \left(\beta J \sum_{\langle ij \rangle} S_i S_j \right)}_{G(S)} \right] = \text{Tr} \left[\exp \left(\beta H \sum_i S_i \right) G(S) \right]$$

It implies that

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) = \text{Tr} \left(\exp \left\{ \beta \alpha_1 H_1 \sum_i S_i + \beta \alpha_2 H_2 \sum_i S_i \right\} G(S) \right)$$

On the other hand, since $\alpha_1 + \alpha_2 = 1$:

$$G(S) = G(S)^{\alpha_1} G(S)^{\alpha_2}$$

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) = \text{Tr} \left[(e^{\beta H_1 \sum_i S_i} G(S))^{\alpha_1} (e^{\beta H_2 \sum_i S_i} G(S))^{\alpha_2} \right]$$

If we now apply the Hölder inequality we get

$$\begin{aligned} Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) &\leq \left(\text{Tr} \left(e^{\beta H_1 \sum_i S_i} G(S) \right)^{\alpha_1} \right) \left(\text{Tr} \left(e^{\beta H_2 \sum_i S_i} G(S) \right)^{\alpha_2} \right) \\ &= Z_\Omega(H_1)^{\alpha_1} Z_\Omega(H_2)^{\alpha_2} \end{aligned}$$

If we now take the logs and multiply by $-k_B T$ both sides, we have

$$\lim_{N \rightarrow \infty} -\frac{1}{N} k_B T \ln Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) \geq -\lim_{N \rightarrow \infty} \frac{\alpha_1}{N} k_B T \ln Z_\Omega(H_1) - \lim_{N \rightarrow \infty} \frac{\alpha_2}{N} k_B T \ln Z_\Omega(H_2)$$

It implies

$$f_b(H_1 \alpha_1 + H_2 \alpha_2) \geq \alpha_1 f_b(H_1) + \alpha_2 f_b(H_2)$$

That is a concave function of H ¹.

■

¹A real-valued function f on an interval is said to be concave if, for any x and y in the interval and for any $\alpha \in [0, 1]$, $f((1 - \alpha)x + \alpha y) \geq (1 - \alpha)f(x) + \alpha f(y)$.

5.2.3 Ising model and \mathbb{Z}^2 symmetry.

The symmetry of the system in sense of the Hamiltonian is: we can invert the value of the S and the Hamiltonian does not change. It is valid when $H = 0$, otherwise it is not true. Let us see the \mathbb{Z}^2 symmetry and the following interesting relation:

Lemma 2

\forall function Φ of the configuration $\{S_i\}$, the following relation holds:

$$\sum_{\{S_i=\pm 1\}} \Phi(\{S_i\}) = \sum_{\{S_i=\pm 1\}} \Phi(\{-S_i\}) \quad (5.14)$$

this is true for all function of the spin.

Now, we consider the Hamiltonian of the Ising model:

$$-\mathcal{H}_\Omega = J \sum_{\langle ij \rangle}^{N(\Omega)} S_i S_j + H \sum_i^{N(\Omega)} S_i$$

Clearly,

$$\mathcal{H}(H, J, \{S_i\}) = \mathcal{H}_\Omega(-H, J, \{-S_i\}) \quad (5.15)$$

This is a spontaneous broken symmetry.

Hence,

$$\begin{aligned} Z_\Omega(-H, J, T) &= \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{S_i\})] \stackrel{(5.14)}{=} \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{-S_i\})] \\ &\stackrel{(5.15)}{=} \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(H, J, \{S_i\})] = Z_\Omega(H, J, T) \end{aligned} \quad (5.16)$$

Taking $-k_B T \ln$, we got:

$$F_\Omega(T, J, H) = F_\Omega(T, J, -H) \quad (5.17)$$

If we take the thermodynamic limit $\lim_{N \rightarrow \infty} \frac{1}{N}$, we have

$$\Rightarrow f_b(T, J, H) = f_b(T, J, -H) \quad (5.18)$$

and it means that the *free energy density is an even function of H* !

Remark. From the finite-size relation (5.17), one can show that a *finite-size* Ising model does not display a transition to a ferromagnetic phase (for all dimension d). Indeed,

$$N(\Omega)M(H) = -\frac{\partial F(H)}{\partial H} \stackrel{(5.17)}{=} -\frac{\partial F(-H)}{\partial(H)} = \frac{\partial F(-H)}{\partial(-H)} = -N(\Omega)M(-H) \quad (5.19)$$

Therefore:

$$M(H) = -M(-H), \quad \forall H \quad (5.20)$$

If $H = 0$, we have $M(0) = -M(0)$, that is valid if and only if $M(0) = 0$!

The magnetization of a finite system is, at $H = 0$, always zero. This is simply consequence of the symmetry argument shown above. We have not a phase transition.

Hence, it is only in the thermodynamic limit, where the symmetry is spontaneously broken, that the model displays a transition.

For resuming, although the Hamiltonian is invariant with respect to the transformation $H \rightarrow -H, \{S_i\} \rightarrow \{-S_i\}$, the thermodynamic state is not. This situation is called *spontaneous symmetry breaking*.

5.3 Lattice gas model

Even if we had not seen any transition, the Ising model is interesting because we can use this model to solve other problems that seems different but are not. In fact, the importance of the Ising model relies also on the fact that it can be mapped into other discrete systems. Despite its simplicity, the Ising model is widely applicable because it describes any interacting two-state system. One of these applications is the *lattice gas model*, where a gas is put in a lattice.

What is a lattice gas model in more details? The archetypal lattice gas is a model where each lattice site can either be occupied by an atom or vacant. Let us consider a d -dimensional lattice with coordination number z and lattice spacing a , divided into cells, as in Figure 5.1. Let us suppose that each cell is either empty or occupied by a single particle (this is more true if $a \sim \text{\AA}$).

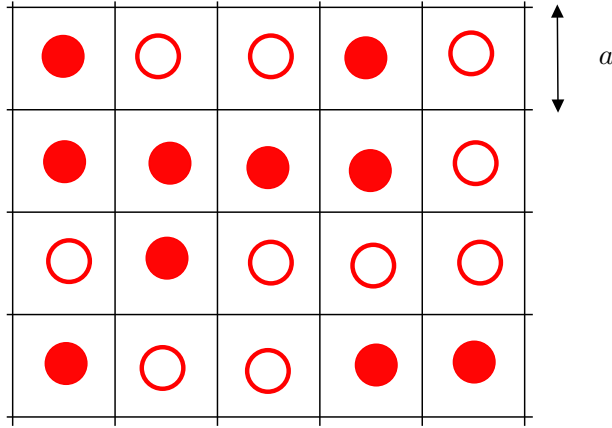


Figure 5.1: d -dimensional lattice with lattice spacing a .

The n_i is the occupation of the i -esim cell and it is:

$$n_i = \begin{cases} 0 & \text{if empty} \\ 1 & \text{if occupied} \end{cases}$$

We have:

$$N_\Omega = \sum_{i=1}^{N_c} n_i \quad (5.21)$$

where N_c is the number of the lattice cells. In particular, $N_c > N_\Omega$.

The Hamiltonian of the model is

$$\mathcal{H}_\Omega = \sum_{i=1}^{N_c} U_1(i)n_i + \frac{1}{2} \sum_{ij}^{N_c} U_2(i,j)n_i n_j + O(n_i n_j n_k) \quad (5.22)$$

where U_1 is for instance an external field, while U_2 is a many body interaction.

Since we want to work in the gran-canonical ensemble,

$$\mathcal{H}_\Omega - \mu N_\Omega = \sum_{i=1}^{N_c} (\cancel{U_1(i)} - \mu)n_i + \frac{1}{2} \sum_{ij} U_2(i,j)n_i n_j + \dots$$

and we will put $U_1 = 0$ for convenience.

A formal relation with the Ising model can be obtained by choosing

$$n_i = \frac{1}{2}(1 + S_i), \quad \text{with } S_i = \pm 1 \quad (5.23)$$

The one body term becomes:

$$\sum_i (U_1(i) - \mu) \frac{1}{2} (1 + S_i) = \frac{1}{2} \sum_i (U_1(i) - \mu) + \frac{1}{2} \sum_i S_i (U_1(i) - \mu) \quad (5.24)$$

while the two bodies term is equal to:

$$\frac{1}{2} \sum_{ij} U_2(i, j) \left[\frac{1}{4} (1 + S_i)(1 + S_j) \right] = \frac{1}{8} 2 \sum_{ij}^{N_c} U_2(i, j) S_i + \frac{1}{8} \sum_{ij}^{N_c} U_2(i, j) S_i S_j + \frac{1}{8} \sum_{ij}^{N_c} U_2(i, j)$$

Let us consider only short-range interactions, i.e.

$$U_2(i, j) = \begin{cases} U_2 & i, j \text{ are n.n.} \\ 0 & \text{otherwise} \end{cases}$$

It implies

$$\frac{1}{2} \sum_{ij} U_2(i, j) \left[\frac{1}{4} (1 + S_i)(1 + S_j) \right] = \frac{1}{4} z U_2 \sum_i S_i + \frac{U_2}{4} \sum_{\langle ij \rangle} S_i S_j + \frac{1}{8} U_2 z N_c \quad (5.25)$$

Remark. Note that the \sum_{ij} becomes $z \sum_i$, where z is the coordination number of neighbours.

Remember that, for simplicity, we put $U_1 = 0$. We can rewrite:

$$\mathcal{H}_\Omega - \mu N_\Omega = E_0 - H \sum_{i=1}^{N_c} S_i - J \sum_{\langle ij \rangle} S_i S_j \quad (5.26)$$

where

$$E_0 = -\frac{1}{2} \mu N_c + \frac{z}{8} U_2 N_c \quad (5.27a)$$

$$-H = -\frac{1}{2} \mu + \frac{z}{4} U_2 \quad (5.27b)$$

$$-J = \frac{U_2}{4} \quad (5.27c)$$

and remember that z is the coordination number of neighbours. J is a nearest neighbour interaction which favours neighbouring sites being occupied.

The last equation implies that, in the gran canonical ensemble, we have:

$$Z_{LG} = \text{Tr}_{\{n\}} (e^{-\beta(\mathcal{H}_\Omega - \mu N_\Omega)}) = e^{-\beta E_0} Z_{\text{Ising}}(H, J, N_c) \quad (5.28)$$

We have seen that the Ising model is something more general than the magnetization transition. In the next section, we show how to pass from the partition Z of a fluid, in the continuum, to the Z_{LG} of the lattice gas model.

5.4 Fluid system in a region Ω

We can consider the system with periodic boundary condition, or within a box, or confined by an external one-body potential.

The Hamiltonian for N particles in d -dimension is

$$\mathcal{H}_\Omega = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U_1(\vec{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_i, \vec{r}_j) + \frac{1}{3!} \sum_{i \neq j \neq k} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) \quad (5.29)$$

In the gran-canonical ensemble, we have:

$$Z_\Omega = \text{Tr} \left(e^{-\beta(\mathcal{H}_\Omega - \mu N)} \right) = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{d^d \vec{\mathbf{p}}_i d^d \vec{\mathbf{r}}_i}{h^{dN}} \left(e^{-\beta(\mathcal{H}_\Omega - \mu N)} \right) \quad (5.30)$$

and the gran-canonical potential is

$$\omega_\Omega(T, \mu, U_1, U_2, \dots) = -k_B T \ln Z_\Omega \quad (5.31)$$

Remark. Even if $\omega_\Omega(\dots)$ contains an infinite sum, it is not singular if Ω is finite!

Indeed, if U_2 is an hard-core repulsion, each particle has a finite volume and, within a finite Ω , only N_{max} particles can fit in

$$\Rightarrow \sum_{N=0}^{\infty} \sim \sum_{N=0}^{N_{max}}$$

In the thermodynamic limit, it corresponds to

$$\omega_b(T, \mu, U_1, U_2, \dots) = \lim_{V(\Omega) \rightarrow \infty} \frac{\omega_\Omega}{V(\Omega)}$$

with the constraint

$$\rho = \lim_{V, N \rightarrow \infty} \frac{\langle N \rangle}{V(\Omega)} = \text{const}$$

Remember also that

$$d\omega_b(T, \mu) = -\sigma dT - \rho d\mu = -P \quad (5.32)$$

Now:

$$Z_N = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\prod_{i=1}^N \left\{ \int_{-\infty}^{+\infty} d^d \vec{\mathbf{p}} \frac{1}{h^{dN}} e^{-\beta \vec{\mathbf{p}}_i^2 / 2m} \right\} Q_N(T) e^{\beta \mu N} \right] \quad (5.33)$$

where

$$Q_N(T) = \int \prod_{i=1}^N d\vec{\mathbf{r}}_i e^{-\beta(U(\vec{\mathbf{r}}))} \quad (5.34)$$

On the other hand, since $\int dx e^{-\alpha x^2} = \sqrt{2\pi/\alpha}$,

$$\int_{-\infty}^{+\infty} d^d \vec{\mathbf{p}} \frac{1}{h^d} e^{-\beta \vec{\mathbf{p}}_i^2 / 2m} = \frac{1}{\Lambda(T)^d}$$

where

$$\Lambda(T) = \frac{h}{2\sqrt{\pi m k_B T}} \quad (5.35)$$

Hence,

$$Z_\Omega = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta \mu}}{\Lambda^d(T)} \right)^N Q_N \quad (5.36)$$

5.4.1 From the continuous to the lattice gas model

Let us divide Ω in discrete cells of size a . If a is approximate a repulsive range between particles, we have that the probability that there is more than one particle sits in a cell is $\ll 1$. The potentials of the continuous model depend on $\{\vec{\mathbf{r}}_i\}$.

Consider the occupation numbers $n_\alpha = n_\alpha(\vec{\mathbf{r}}_i)$. We have:

$$\sum_{\alpha} n_\alpha = N = \int_{\Omega} d^d \vec{\mathbf{r}} \sum_{i=1}^N \delta(\vec{\mathbf{r}}_i - \vec{\mathbf{r}}) = \int_{\Omega} d^d \vec{\mathbf{r}} \rho(\vec{\mathbf{r}}) \quad (5.37)$$

where

$$\rho(\vec{r}) = \sum_{i=1}^N \delta(\vec{r}_i - \vec{r}) \quad (5.38)$$

Moreover,

$$\sum_i U_1(\vec{r}_i) = \sum_i \int_{\Omega} d^d \vec{r} U_1(\vec{r}) \delta(\vec{r}_i - \vec{r}) = \int_{\Omega} d^d \vec{r} U_1(\vec{r}) \rho(\vec{r}) \quad (5.39)$$

We have $U(\{\vec{r}_i\}) \rightarrow U(\{n_{\alpha}\})$:

$$Q_N \propto \int \prod_{i=1}^N d^d \vec{r}_i \rightarrow \sum_{\{n_{\alpha}\}}$$

Indeed, for each configuration specified by the set $\{n_{\alpha}\}$ there are $N!$ possible configurations of $\{\vec{r}_i\}$. This is because the particles can exchange position between occupied cells. Hence, more precisely,

$$Q_N \propto \int \prod_{i=1}^N d^d \vec{r}_i \simeq N!(a^d)^N \sum'_{\{n_{\alpha}=0,1\}} \dots$$

Remark. The symbol \sum' means that the sum has the constraint that the total number of particles is fixed to N , that is $\sum_{\alpha} n_{\alpha} = N$.

Therefore,

$$Q_N \propto N!(a^d)^N \sum'_{\{n_{\alpha}\}} e^{-\beta U(\{n_{\alpha}\})} \quad (5.40)$$

and we can rewrite the equation (5.36) as

$$Z_{\Omega} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda^{d(T)}} \right)^N Q_N = \sum_{N=0}^{\infty} \left[e^{\beta\mu} \left(\frac{a}{\Lambda(T)} \right)^d \right]^N \sum'_{\{n_{\alpha}\}} e^{-\beta U(\{n_{\alpha}\})} \quad (5.41)$$

where $\sum' = \sum_{\{n_{\alpha}\}}$ with the constraint $\sum_{\alpha} n_{\alpha} = N$.

Remark. In general it is difficult to perform sum with constraints. Fortunately, we are considering the gran-canonical ensemble. Indeed, we can write

$$\sum_{N=0}^{\infty} \sum'_{\{n_{\alpha}\}} f(n_{\alpha}) = \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=0}} f(n_{\alpha}) + \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=1}} f(n_{\alpha}) \dots + \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=\infty}} f(n_{\alpha}) = \sum_{\{n_{\alpha}\}} f(n_{\alpha})$$

with no restriction.

Remark. In the final sum all the 2^N possible microscopic states are included (considering $U_1 = 0$)

Eventually, we have²

$$Z_{\Omega}^{GC} \propto \sum_{\{n_{\alpha}\}} \exp \left[-\beta \left(-\mu - \frac{d}{\beta} \log \frac{a}{\Lambda} \right) \sum_{\alpha=0}^{N_c} n_{\alpha} + \beta U_2 \sum_{\langle \alpha \beta \rangle} n_{\alpha} n_{\beta} + \dots \right] \quad (5.42)$$

$$\Rightarrow Z_{\Omega} = \text{Tr} e^{-\beta(\mathcal{H}_{\Omega} - \tilde{\mu}N)} = Z_{LG}(\tilde{\mu}) \quad (5.43)$$

where

$$\tilde{\mu} = \mu_{LG} = \mu_{phys} + dk_B T \log \frac{a}{\Lambda} \quad (5.44)$$

² $b^a = e^{a \ln b} \Rightarrow e^{\beta\mu} \left(\frac{a}{\Lambda} \right)^d = e^{\beta\mu} \exp(d \ln(\frac{a}{\Lambda}))$

Chapter 6

Some exactly solvable models of phase transitions

6.1 1-dim Ising model

In this section, we arrive at the exact solution of the one dimensional Ising model. There are two techniques for solving the model:

1. the *recursive method*;
2. the *transfer matrix method*.

6.1.1 Recursive method

Case with $H = 0$ and free boundary conditions

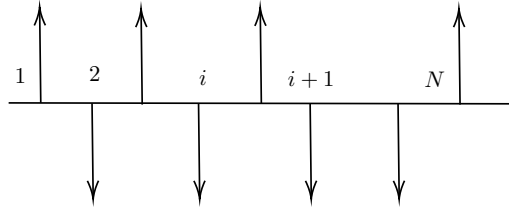


Figure 6.1: One dimensional Bravais Lattice.

Let us consider a Bravais lattice in the one dimensional case, that is just a one dimensional lattice, as in Figure 6.1.

The canonical partition function of such a system is:

$$Z_N(T) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \exp \left[\overbrace{\beta J}^K \sum_{i=1}^{N-1} S_i S_{i+1} \right] \quad (6.1)$$

The two body interaction is the sum in all the neighbours that in that case are $(i-1)$ and $(i+1)$, but we have only to consider the one after, because the one behind is yet taken by the behind site.

We want to solve this partition function. If we consider *free boundary* condition, the N does not have a $N+1$, almost for the moment. Let us define

$$K \equiv \beta J, \quad h \equiv \beta H \quad (6.2)$$

Making explicit the sum in the exponential:

$$Z_N(K) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} e^{K(S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N)}$$

What does happen if we just add another spin at the end S_{N+1} ? Which is the partition function with that new spin? We obtain:

$$Z_{N+1}(K) = \sum_{S_{N+1}=\pm 1} \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \dots \sum_{S_N=\pm 1} e^{K(S_1 S_2 + S_2 S_3 + \dots + S_{N-1} S_N)} e^{K S_N S_{N+1}}$$

On the other hand, this sum is just involving this term:

$$\sum_{S_{N+1}=\pm 1} e^{K S_N S_{N+1}} = e^{K S_N} + e^{-K S_N} = 2 \cosh(K S_N) = 2 \cosh(K)$$

where the last equivalence derive from the fact that \cosh is an even function and it does not depend on ± 1 . Therefore,

$$Z_{N+1}(K) = (2 \cosh(K)) Z_N(K) \quad \text{and} \quad Z_N(K) = (2 \cosh(K)) Z_{N-1}(K)$$

By performing a backward iteration,

$$Z_N(K) = Z_1 (2 \cosh(K))^{N-1}$$

Since $Z_1 = \sum_{S_1=\pm 1} 1 = 2$, we have

$$Z_N(T) = 2(2 \cosh(K))^{N-1} \quad (6.3)$$

The free energy is

$$F_N(K) = -k_B T \ln Z_N(K) = -k_B T \ln 2 - k_B T (N-1) \ln (2 \cosh(K)) \quad (6.4)$$

and taking the thermodynamic limit it becomes

$$f_b(T) \equiv \lim_{N \rightarrow \infty} \frac{1}{N} F_N(K) = -k_B T \ln \left(2 \cosh \left(\frac{J}{k_B T} \right) \right) \quad (6.5)$$

As one can see (Figure 6.2) $f_b(T)$ is an analytic function of T , so we have no phase transition at $T \neq 0$.

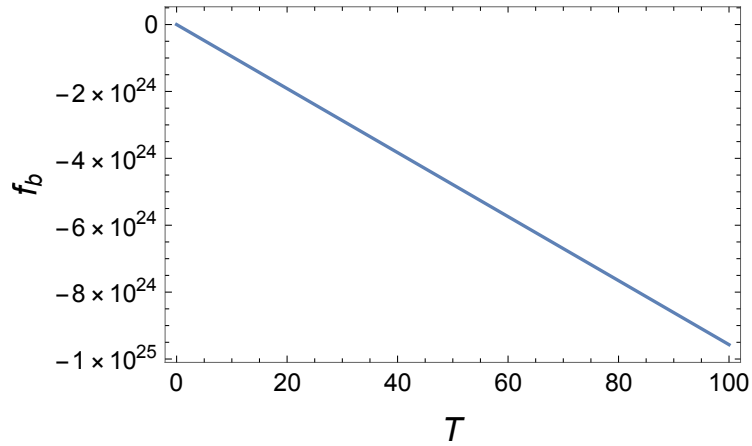


Figure 6.2: Free energy function in thermodynamic limit for the one dimensional Ising model, for $k_B = 1.38 \times 10^{23}$, $J = 1$.

Now, let us compute the magnetization (the average over the spin $\langle S_j \rangle$) for a generic site j (assume again that $S_i = \pm 1$). This can be done in many ways. Here, we choose one that consider another way to compute Z for the 1 - dim Ising model. This method can be useful for other calculations. It is based on the following identity:

$$\exp[K S_i S_{i+1}] \underset{(proof)}{=} \cosh(K) + S_i S_{i+1} \sinh(K) = \cosh(K) [1 + S_i S_{i+1} \tanh(K)] \quad (6.6)$$

Proof of identity (6.6). Remind that

$$\cosh x = \frac{e^x + e^{-x}}{2}, \quad \sinh x = \frac{e^x - e^{-x}}{2}$$

Hence,

$$e^x = \cosh x + \sinh x$$

In our case,

$$e^{KS_i S_{i+1}} = \cosh(KS_i S_{i+1}) + \sinh(KS_i S_{i+1}) = \cosh K + S_i S_{i+1} \sinh K$$

where the last step was obtained considering that \cosh is an even function, while \sinh is an odd one. ■

Using identity (6.6), we obtain

$$Z_N(K) = \sum_{\{S\}} \exp \left[K \sum_{i=1}^{N-1} S_i S_{i+1} \right] = \sum_{\{S\}} \prod_{i=1}^{N-1} [\cosh(K)(1 + S_i S_{i+1} \tanh(K))]$$

by rearranging,

$$Z_N(K) = (\cosh K)^{N-1} \sum_{\{S\}} \prod_{i=1}^{N-1} (1 + S_i S_{i+1} \tanh K) \quad (6.7)$$

If we now expand the products, we get terms of the following form:

$$\sum_{\substack{S_{i_e} = \pm 1 \\ e=1, \dots, M}} (\tanh K)^M S_{i_1} S_{i_1+1} S_{i_2} S_{i_2+1} \dots S_{i_M} S_{i_M+1} = 0 \quad (6.8)$$

where $i_1 \dots i_M$ is a set of M sites of the lattice.

Remark. The terms above, when summed over $\{S\}$ are zero, except the term with $M = 0$ that is equal to 1 and, when summed over $\{S\}$, gives 2^N .

Therefore:

$$Z_N(K) = 2^N (\cosh K)^{N-1}$$

that coincides with the result obtained before.

If we now compute the average $\langle S_j \rangle$, the procedure is similar but now there will be terms as (6.8) with the addition of an S_j :

$$(\tanh K)^M S_{i_1} S_{i_1+1} S_{i_2} S_{i_2+1} \dots S_{i_M} S_{i_M+1} S_j \quad (6.9)$$

that, when one sums over $\{S\}$ are all zero, included the term with $M = 0$ that now is equal to S_j and $\sum_{S_j = \pm 1} = 0$. Hence, we have the result

$$\langle S_j \rangle = 0 \quad \forall j \quad (6.10)$$

The magnetization is always zero $\forall j \neq \infty$!

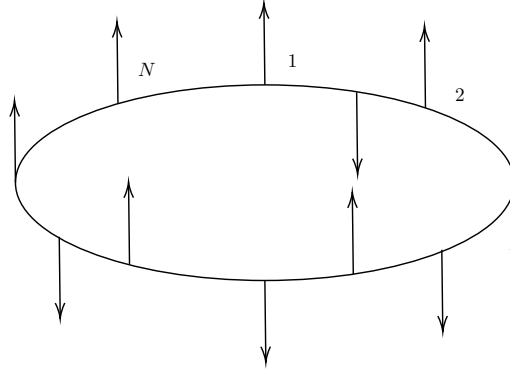


Figure 6.3: One dimensional lattice ring: Ising model with periodic boundary conditions.

Case with $H \neq 0$ and periodic boundary conditions

Consider the spins sitting on a 1D lattice ring as in Figure 6.3. The periodic boundary conditions are:

$$S_{N+1} = S_1$$

We have:

$$-\beta \mathcal{H}_\Omega(\{S\}) = K \sum_{i=1}^N S_i S_{i+1} + h \sum_{i=1}^N S_i \quad (6.11)$$

where

$$K \equiv \beta J, \quad h \equiv \beta H$$

The 1 – *dim* Ising model with this setup can be solved in several ways. Here we will use the method of the transfer matrix. This is a quite general technique that we will discuss within the Ising model.

Lecture 7.

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6.1.2 Transfer Matrix method

Given the Hamiltonian (6.11)¹ we can write the corresponding partition function in the following symmetric form:

$$Z_N(k, h) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \left[e^{K S_1 S_2 + \frac{h}{2}(S_1 + S_2)} \right] \left[e^{K S_2 S_3 + \frac{h}{2}(S_2 + S_3)} \right] \cdots \left[e^{K S_N S_1 + \frac{h}{2}(S_N + S_1)} \right]$$

We want to write the partition function in a form similarly to $\sum_j M_{ij} P_{jk}$. Note that, in the previous form Z_N can be written as a product of matrices

$$\begin{aligned} Z_N(h, k) &= \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \prod_{i=1}^N \exp \left[K S_i S_{i+1} + \frac{h}{2}(S_i + S_{i+1}) \right] \\ &= \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \langle S_1 | \mathbb{T} | S_2 \rangle \langle S_2 | \mathbb{T} | S_3 \rangle \cdots \langle S_N | \mathbb{T} | S_1 \rangle \end{aligned} \quad (6.12)$$

where \mathbb{T} is a 2×2 matrix defined as

$$\langle S | \mathbb{T} | S' \rangle = \exp \left[K S S' + \frac{h}{2}(S + S') \right] \quad (6.13)$$

Remark. Note that the labels of the matrix corresponds to the values of S_i . Hence, its dimension depends on the number of possible values a spin S_i can assume. It can also depends on how many spins are involved in the interacting terms that are present in the Hamiltonian ($k_{LL} \sum S_i S_{i+1} S_{i+2} S_{i+3}$).

¹The choice of boundary conditions becomes irrelevant in the thermodynamic limit, $N \rightarrow \infty$.

For the Ising model, we have $S_i = \pm 1$ and nearest neighbour interaction implies that we have two values and that \mathbb{T} is a 2×2 matrix whose components are

$$\langle +1 | \mathbb{T} | +1 \rangle = \exp[K + h] \quad (6.14a)$$

$$\langle +1 | \mathbb{T} | -1 \rangle = \langle -1 | \mathbb{T} | +1 \rangle = \exp[-K] \quad (6.14b)$$

$$\langle -1 | \mathbb{T} | -1 \rangle = \exp[K - h] \quad (6.14c)$$

The explicit representation is

$$\mathbb{T} = \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix} \quad (6.15)$$

Let us introduce some useful notations and relations using the bra-ket formalism:

$$|S_i^{(+)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_i \quad |S_i^{(-)}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_i \quad (6.16a)$$

$$\langle S_i^{(+)}| = (1^*, 0)_i \quad \langle S_i^{(-)}| = (0, 1^*)_i \quad (6.16b)$$

The identity relation is:

$$\sum_{S_i=\pm 1} |S_i\rangle \langle S_i| = |S_i^{(+)}\rangle \langle S_i^{(+)}| + |S_i^{(-)}\rangle \langle S_i^{(-)}| = \mathbb{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (6.17)$$

By using the identity property, we can rewrite the partition function as

$$\begin{aligned} Z_N(K, h) &= \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \langle S_1 | \mathbb{T} | S_2 \rangle \langle S_2 | \mathbb{T} | S_3 \rangle \cdots \langle S_i | \mathbb{T} | S_{i+1} \rangle \cdots \\ &= \sum_{S_1=\pm 1} \langle S_1 | \mathbb{T}^N | S_1 \rangle = \text{Tr}[\mathbb{T}^N] \end{aligned} \quad (6.18)$$

this is exactly the trace of the matrix, which is most usefully expressed in terms of the eigenvalues. Being \mathbb{T} symmetric, we can diagonalize it by an unitary transformation as

$$\mathbb{T}_D = \mathbb{P}^{-1} \mathbb{T} \mathbb{P} \quad (6.19)$$

with $\mathbb{P} \mathbb{P}^{-1} = \mathbb{1}$. Hence,

$$\begin{aligned} \text{Tr}[\mathbb{T}^N] &= \text{Tr} \left[\underbrace{\mathbb{T} \mathbb{T} \mathbb{T} \cdots \mathbb{T}}_N \right] = \text{Tr}[\mathbb{P} \mathbb{P}^{-1} \mathbb{T} \mathbb{P} \mathbb{P}^{-1} \mathbb{T} \mathbb{P} \cdots \mathbb{P}^{-1} \mathbb{T} \mathbb{P} \mathbb{P}^{-1}] \\ &= \text{Tr}[\mathbb{P} \mathbb{T}_D^N \mathbb{P}^{-1}] \underset{\substack{\text{cyclic property} \\ \text{of the trace}}}{=} \text{Tr}[\mathbb{T}_D^N \mathbb{P}^{-1} \mathbb{P}] \\ &= \text{Tr}[\mathbb{T}_D^N] \end{aligned}$$

where

$$\mathbb{T}_D = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \Rightarrow \mathbb{T}_D^N = \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix} \quad (6.20)$$

with λ_{\pm} are the eigenvalues with $\lambda_+ > \lambda_-$.

Remark. \mathbb{P} is the similitude matrix whose columns are given by the eigenvectors of λ_{\pm} .

We finally have:

$$Z_N(K, h) = \text{Tr}[\mathbb{T}_D^N] = \lambda_+^N + \lambda_-^N \quad (6.21)$$

Remark. As mentioned previously the dimension of the transfer matrix \mathbb{T} and hence the number of eigenvalues $\{\lambda\}$ depend both on the possible values of S_i and on the number of sites involved in terms of the Hamiltonian (range of interaction).

Example 15

For example, consider the Ising ($S_i = \pm 1$) with n. n. and next n. n. interactions. The Hamiltonian is:

$$\mathcal{H} = k_1 \sum_i S_i S_{i+1} + k_2 \sum_i S_i S_{i+1} S_{i+2} S_{i+3}$$

Because of the second term, now there are $2^4 = 16$ possible configurations that can be described by using a 4×4 transfer matrix that we can write formally as

$$\langle S_i S_{i+1} | \mathbb{T} | S_{i+2} S_{i+3} \rangle$$

Example 16

For example, suppose $S_i = +1, 0, -1$, therefore the spin can assume three different values. This is a *diluted* Ising model.

Now, let us consider the transfer matrix formalism in a more general setting.

6.2 General transfer matrix method

The aim of this section is to describe how transfer matrices can be used to solve classical spin models. The idea is to write down the partition function in terms of a matrix, the transfer matrix. The thermodynamic properties of the model are then wholly described by the eigenspectrum of the matrix. In particular, the free energy per spin in the thermodynamic limit depends only on the largest eigenvalue and the correlation length only on the two largest eigenvalues through simple formulae.

Let \mathbb{T} be a square matrix $(n+2) \times (n+2)$ that, for example, it is built if the spin variables may assume $(n+2)$ possible values. The k -esim value can be defined by the bra-ket notation where the two vectors are given by a sequence of "0" and a single "1" at the k -esim position.

Example 17

If $k = 3$ and there are $(n+2)$ possible values:

$$\langle S_i^{(3)} | = (0, 0, 1^*, 0, \dots, 0) \quad | S_i^{(3)} \rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix}$$

these are the bra-ket at the k -esim position.

Similarly to the 2×2 Ising case, it is easy to show the identity property

$$\sum_{S_i} |S_i\rangle \langle S_i| = \mathbb{1}, \quad \mathbb{1} \in (n+2) \times (n+2) \quad (6.22)$$

where now the sum is over $(n+2)$ values.

Let us consider the *diagonal matrix* \mathbb{S}_i , where the elements along the diagonal are all the $(n+2)$ possible values of the i -esim spin (or of some of their combination if longer interaction terms are considered)

$$\mathbb{S}_i \equiv \sum_{S_i} |S_i\rangle S_i \langle S_i| \quad (6.23)$$

Example 18

Ising model $n + 2 = 2$

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} S^{(1)}(1^*, 0) + \begin{pmatrix} 0 \\ 1 \end{pmatrix} S^{(2)}(0, 1^*) = \begin{pmatrix} S^{(1)} & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & S^{(2)} \end{pmatrix} = \begin{pmatrix} S^{(1)} & 0 \\ 0 & S^{(2)} \end{pmatrix}$$

Ising: $S^{(1)} = +1, S^{(2)} = -1$.

Remark. Note that in this case the matrix \mathbb{S}_i is equal to the Pauli matrix σ_z .

Remark. By construction $\langle S_i |$ and $| S_i \rangle$ are the eigenvectors related to the eigenvalues $S_i = S^{(1)}, S^{(2)}, \dots, S^{(n+2)}$.

Similarly, let $\langle t_i |$ and $| t_i \rangle$ be the eigenvectors related to the $(n + 2)$ eigenvalues of the transfer matrix \mathbb{T} : $\{\lambda_+, \lambda_-, \lambda_1, \dots, \lambda_n\}$, with $\lambda_+ > \lambda_- \geq \lambda_1 \geq \dots \geq \lambda_n$.

Clearly,

$$\mathbb{T} = \mathbb{P} \mathbb{T}_D \mathbb{P}^{-1} = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i \langle t_i| \quad (6.24)$$

Indeed

$$\mathbb{T} |t_j\rangle = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i \langle t_i | t_j \rangle = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i \delta_{ij} = \lambda_j |t_j\rangle \quad (6.25)$$

Given the set of λ described above, the N particle partition function is given by

$$Z_N = \lambda_+^N + \lambda_-^N + \sum_{i=1}^n \lambda_i^N \quad (6.26)$$

6.2.1 The free energy

Now, let us consider the free energy

$$F_N = -k_B T \log Z_N$$

In particular, we are interested in the limit of the bulk free energy. Looking at the thermodynamic limit $N \rightarrow \infty$ we have

$$f_b = \lim_{N \rightarrow \infty} \frac{1}{N} F_N = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T) \log \left[\lambda_+^N + \lambda_-^N + \sum_{i=1}^n \lambda_i^N \right]$$

by factorizing λ_+ , we obtain

$$f_b = \lim_{N \rightarrow \infty} \frac{-k_B T}{N} \log \left[\lambda_+^N \left(1 + \frac{\lambda_-^N}{\lambda_+^N} + \sum_{i=1}^n \left(\frac{\lambda_i}{\lambda_+} \right)^N \right) \right]$$

Since $\lambda_+ > \lambda_- > \lambda_1 > \dots > \lambda_n$,

$$\left(\frac{\lambda_-}{\lambda_+} \right)^N \xrightarrow{N \rightarrow \infty} 0, \quad \left(\frac{\lambda_i}{\lambda_+} \right)^N \xrightarrow{N \rightarrow \infty} 0 \quad \forall i$$

The result is

$$f_b = -k_B T \log \lambda_+ \quad (6.27)$$

The *limiting bulk free-energy depends only on the largest eigenvalue of the transfer matrix \mathbb{T}* ! This is important since sometimes it is much simpler to compute only the largest eigenvalue than the whole spectrum of \mathbb{T} . Also an important theorem about λ_+ exists.

Theorem 2: Perron-Frobenius

Let \mathbb{A} be a $n \times n$ matrix. If \mathbb{A} is finite ($n < \infty$) and $\mathbb{A}_{ij} > 0, \forall i, j$, ($\mathbb{A}_{ij} = \mathbb{A}_{ij}(\vec{x})$), therefore its largest eigenvalue λ_+ has the following properties:

1. $\lambda_+ \in \mathbb{R}^+$
2. $\lambda_+ \neq$ from $\{\lambda_i\}_{i=1, \dots, n-1}$. It means there is no degeneracy.
3. λ_+ is a analytic function of the parameters of \mathbb{A} .

Remark. Since in our case $\mathbb{A} \leftrightarrow \mathbb{T}$, λ_+ is related to f_b from the theorem. This means that f_b is an analytic function!

If the conditions of the Perron-Frobenius theorem are satisfied by \mathbb{T} , the model described by \mathbb{T} cannot display a phase transition!

Remark. This is true for $T > 0$ since for $T = 0$ some \mathbb{T}_{ij} can be either 0 or ∞ violating the hypothesis of the theorem.

Remark. If \mathbb{T} has infinite dimension (see $d > 1$) the hypothesis of the theorem are not valid anymore and f_b can be non-analytic.

6.2.2 The correlation function

A second important quantity which is simply related to the eigenvalues of the transfer matrix is the correlation length. To calculate this, we need the spin-spin correlation function which serves as an example of how to obtain averages of products of spins using transfer matrices.

Let us consider the two point correlation between two spins at distance R to another. The fluctuation with respect to the average is:

$$\Gamma_R \equiv \langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle \quad (6.28)$$

Since

$$\Gamma_R \underset{R \rightarrow \infty}{\sim} \exp[-R/\xi]$$

we can define the correlation length ξ as

$$\xi^{-1} \equiv \lim_{R \rightarrow \infty} \left[-\frac{1}{R} \log |\langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle| \right] \quad (6.29)$$

Now, let us compute the terms $\langle S_1 S_R \rangle_N$ and $\langle S_1 \rangle_N \langle S_R \rangle_N$.

Term $\langle S_1 S_R \rangle_N$

From the definition of average we obtain

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{\{S\}} S_1 S_R \exp[-\beta \mathcal{H}_N] \quad (6.30)$$

Remark. The subscript N denotes that we are again considering a ring of N spins. Z_N is known from equation (6.26).

Writing this expression by using the transfer matrix formalism, one obtains

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{\{S\}} S_1 \langle S_1 | \mathbb{T} | S_2 \rangle \dots \langle S_{R-1} | \mathbb{T} | S_R \rangle S_R \langle S_R | \mathbb{T} | S_{R+1} \rangle \dots \langle S_N | \mathbb{T} | S_1 \rangle$$

Summing over the free spins,

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{S_1, S_R} S_1 \langle S_1 | \mathbb{T}^{R-1} | S_R \rangle S_R \langle S_R | \mathbb{T}^{N-R+1} | S_1 \rangle \quad (6.31)$$

On the other hand, since

$$\mathbb{T} = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i \langle t_i|$$

we have

$$\mathbb{T}^{R-1} = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i^{R-1} \langle t_i| \quad (6.32a)$$

$$\mathbb{T}^{N-R+1} = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i^{N-R+1} \langle t_i| \quad (6.32b)$$

Hence,

$$\langle S_1 | \mathbb{T}^{R-1} | S_R \rangle = \sum_{i=1}^{n+2} \langle S_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | S_R \rangle \quad (6.33a)$$

$$\langle S_R | \mathbb{T}^{N-R+1} | S_1 \rangle = \sum_{j=1}^{n+2} \langle S_R | t_j \rangle \lambda_j^{N-R+1} \langle t_j | S_1 \rangle \quad (6.33b)$$

and plugging these expressions in (6.31) one gets

$$\sum_{\{S\}} S_1 S_R e^{-\beta \mathcal{H}_N} = \sum_{S_1 S_R} S_1 \sum_{i=1}^{n+2} \langle S_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | S_R \rangle S_R \sum_{j=1}^{n+2} \langle S_R | t_j \rangle \lambda_j^{N-R+1} \langle t_j | S_1 \rangle$$

Since the term $\langle t_j | S_1 \rangle$ is a scalar, it can be moved at the beginning of the product. Remembering the notations

$$\mathbb{S}_1 = \sum_{S_1} |S_1\rangle S_1 \langle S_1| \quad (6.34a)$$

$$\mathbb{S}_R = \sum_{S_R} |S_R\rangle S_R \langle S_R| \quad (6.34b)$$

one gets

$$\sum_{\{S\}} S_1 S_R e^{-\beta \mathcal{H}_N} = \sum_{ij} \langle t_j | \mathbb{S}_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | \mathbb{S}_R | t_j \rangle \lambda_j^{N-R+1} \quad (6.35)$$

Since $\sum_k \lambda_k^N = Z_N$ for $k = +, -, 1, \dots, n$, we have

$$\langle S_1 S_R \rangle_N = \frac{\sum_{ij} \langle t_j | \mathbb{S}_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | \mathbb{S}_R | t_j \rangle \lambda_j^{N-R+1}}{\sum_{k=1}^n \lambda_k^N}$$

If we now multiply and divide by λ_+^N , we get

$$\langle S_1 S_R \rangle_N = \frac{\sum_{ij} \langle t_j | \mathbb{S}_1 | t_i \rangle (\lambda_i / \lambda_+)^{R-1} \langle t_i | \mathbb{S}_R | t_j \rangle (\lambda_j / \lambda_+)^{N-R+1}}{\sum_{k=1}^n (\lambda_k / \lambda_+)^N}$$

Remark. In the thermodynamic limit $N \rightarrow \infty$, only the terms with $j = +$ and $k = +$ will survive in the sum. Remind that R is fixed.

Lecture 8.
Wednesday 6th
November, 2019.
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$$\langle S_1 S_R \rangle = \lim_{N \rightarrow \infty} \langle S_1 S_R \rangle_N = \sum_{i=\pm, 1, \dots, n} \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle$$

Remember that $\lambda_+ > \lambda_- \geq \lambda_1 \geq \dots \geq \lambda_n$:

$$\langle S_1 S_R \rangle = \langle t_+ | \mathbb{S}_1 | t_+ \rangle \langle t_+ | \mathbb{S}_R | t_+ \rangle + \sum_{i \neq +}^n \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle$$

Since one can prove

$$\lim_{N \rightarrow \infty} \langle S_R \rangle_1 = \langle t_+ | \mathbb{S}_1 | t_+ \rangle, \quad \lim_{N \rightarrow \infty} \langle S_R \rangle_N = \langle t_+ | \mathbb{S}_R | t_+ \rangle \quad (6.36)$$

we obtain

$$\langle S_1 S_R \rangle = \langle S_1 \rangle \langle S_R \rangle + \sum_{i \neq +}^n \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle \quad (6.37)$$

Example 19: Show relation (6.36)

Let us prove (6.36) by a method analogous to that followed above.

$$\begin{aligned} \langle S_1 \rangle_N &= \frac{1}{Z} \sum_{\{S\}} S_1 e^{-\beta \mathcal{H}_N} = \frac{1}{Z} \sum_{S_1} S_1 \langle S_1 | \mathbb{T}^N | S_1 \rangle = \frac{1}{Z} \sum_{S_1} S_1 \sum_i \langle S_1 | t_i \rangle \lambda_i^N \langle t_i | S_1 \rangle \\ &= \frac{1}{Z} \sum_i \lambda_i^N \langle t_i | \mathbb{S}_1 | t_i \rangle = \frac{\sum_i (\lambda_i / \lambda_+)^N \langle t_i | \mathbb{S}_1 | t_i \rangle}{\sum_{k=1}^n (\lambda_k / \lambda_+)^N} \end{aligned}$$

Taking the limit $N \rightarrow \infty$:

$$\langle S_1 \rangle = \lim_{N \rightarrow \infty} \langle S_1 \rangle_N = \langle t_+ | \mathbb{S}_1 | t_+ \rangle$$

The correlation function follows immediately from (6.37),

$$\Gamma_R = \langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle = \sum_{i \neq +}^n \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle \quad (6.38)$$

Remark. Γ_R depends only on the eigenvalues and eigenvectors of the transfer matrix \mathbb{T} and by the values of the spins S_1 and S_R .

A much simpler formula is obtained for the correlation length (6.29). Taking the limit $R \rightarrow \infty$ the ratio (λ_- / λ_+) dominates the sum and hence

$$\begin{aligned} \xi^{-1} &= \lim_{R \rightarrow \infty} \left\{ -\frac{1}{R-1} \log |\langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle| \right\} \\ &= \lim_{R \rightarrow \infty} \left\{ -\frac{1}{R-1} \log \left[\left(\frac{\lambda_-}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_- \rangle \langle t_- | \mathbb{S}_R | t_+ \rangle \right] \right\} \\ &= -\log \left[\left(\frac{\lambda_-}{\lambda_+} \right) \right] - \lim_{R \rightarrow \infty} \frac{1}{R-1} \log \langle t_+ | \mathbb{S}_1 | t_- \rangle \langle t_- | \mathbb{S}_R | t_+ \rangle \\ &= -\log \left(\frac{\lambda_-}{\lambda_+} \right) \end{aligned}$$

The important result is

$$\xi^{-1} = -\log \left(\frac{\lambda_-}{\lambda_+} \right) \quad (6.39)$$

It means that the correlation length does depend only on the ratio between the two largest eigenvalues of the transfer matrix \mathbb{T} .

6.2.3 Results for the 1-dim Ising model

Let us now return to the example of the nearest neighbour Ising model in a magnetic field, to obtain explicit results for the bulk free energy f_b , the correlation function Γ and the correlation length ξ .

Recall that the transfer matrix of such a system is given by

$$\mathbb{T} = \begin{pmatrix} \exp(K+h) & \exp(-K) \\ \exp(-K) & \exp(K-h) \end{pmatrix}$$

Now, let us calculate the eigenvalues:

$$|\mathbb{T} - \lambda \mathbb{1}| = (e^{K+h} - \lambda)(e^{K-h} - \lambda) - e^{-2K} = 0$$

The two solutions are

$$\lambda_{\pm} = e^K \cosh(h) \pm \sqrt{e^{2K} \sinh^2(h) + e^{-2K}} \quad (6.40)$$

The free energy

The free energy is

$$\begin{aligned} f_b &\equiv \lim_{N \rightarrow \infty} \frac{-k_B T}{N} \log Z_N(K, h) \\ &= -k_B T \lim_{N \rightarrow \infty} \frac{1}{N} \log \left[\lambda_+^N \left(1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right) \right] \\ &= -k_B T \log \lambda_+ \end{aligned}$$

and inserting the explicit expression of λ_+ for the Ising model, we get

$$\begin{aligned} f_b &= -k_B T \log \left(e^K \cosh h + \sqrt{e^{2K} \sinh^2(h) + e^{-2K}} \right) \\ &= -K k_B T - k_B T \log \left(\cosh(h) + \sqrt{\sinh^2(h) + e^{-4K}} \right) \end{aligned} \quad (6.41)$$

Remark. Remember that $K \equiv \beta J, h \equiv \beta H$.

Exercise 2

Check that if $h = 0$ we get back the expression found previously with the iterative method. What is the importance of boundary conditions?

Solution. If $h = 0$, we obtain

$$\begin{aligned} f_b &= -K k_B T - k_B T \log \left(1 + \frac{1}{e^{2K}} \right) = -k_B T (\log e^K + \log(1 + e^{-2K})) \\ &= -k_B T \log(e^K + e^{-K}) = -k_B T \log \left(2 \frac{e^K + e^{-K}}{2} \right) \\ &= -k_B T \log(2 \cosh K) = -k_B T \log \left(2 \cosh \left(\frac{J}{k_B T} \right) \right) \end{aligned}$$

The choice of boundary conditions becomes irrelevant in the thermodynamic limit, $N \rightarrow \infty$.

Let us now consider the limits $T \rightarrow 0$ and $T \rightarrow \infty$ by keeping H fixed and J fixed.

- Case: $T \rightarrow 0 \Rightarrow K \rightarrow \infty, h \rightarrow \infty$.

$$e^{-4K} \xrightarrow{K \rightarrow \infty} 0$$

$$\sqrt{\sinh^2 h} \xrightarrow{h \rightarrow \infty} \sinh(h)$$

We have

$$\cosh h + \sinh h \sim \frac{2e^h}{2} \simeq e^h$$

and

$$f \xrightarrow{K \rightarrow \infty} -Kk_B T - k_B T \log e^h \sim -J - H \quad \text{const} \quad (6.43)$$

Therefore, as $T \rightarrow 0^+$, f goes to a constant that depends on J and H .

- Case: $T \rightarrow \infty \Rightarrow K \rightarrow 0, h \rightarrow 0$. In this case we suppose also that H and J (fixed) are also finite.

$$e^{-4K} \simeq 1$$

$$\sqrt{\sinh^2 h + e^{-4K}} \sim \sqrt{1}$$

Since $\cosh h \xrightarrow{h \rightarrow 0} 1$:

$$f_B \sim -Kk_B T - k_B T \log(1 + 1) \sim -J - k_B T \ln 2 \quad (6.45)$$

Therefore, as $T \rightarrow \infty$, the free energy goes linearly to zero, as in Figure 6.4.

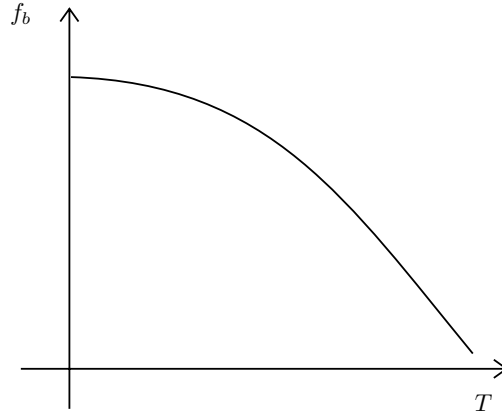


Figure 6.4: Plot of the free energy f_b in function of the temperature T . For $T \rightarrow 0$, the free energy becomes constant, while for $T \rightarrow \infty$ it goes linearly to zero.

The magnetization

This can be obtained by differentiating the negative of the free energy with respect to the magnetic field H (or by using equation (6.36)):

$$m = -\frac{\partial f_b}{\partial H} = -\frac{1}{k_B T} \frac{\partial f_b}{\partial h} = \frac{\partial}{\partial h} \left[\log \left(\cosh(h) + \sqrt{\sinh^2(h) + e^{-4K}} \right) \right]$$

The result is

$$m = \frac{\sinh h + \frac{\sinh h \cosh h}{\sqrt{\sinh^2 h + e^{-4K}}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4K}}} = \frac{\sinh h}{\sqrt{\sinh^2 h + e^{-4K}}} \quad (6.46)$$

- Case: $T > 0$ fixed, $H \rightarrow 0 \Rightarrow h \rightarrow 0$.

$$\begin{aligned}\sinh h &\sim h \sim 0, \\ \cosh h &\sim 1\end{aligned}$$

In zero field $h \rightarrow 0$, we have $m \rightarrow 0$ for all $T > 0$. It means that there is no spontaneous magnetization!

The magnetic susceptibility

$$\chi_T \equiv \frac{\partial m}{\partial H} = \frac{1}{k_B T} \frac{\partial m}{\partial h} \quad (6.48)$$

If we consider the case $h \ll 1$, it is convenient first expand the (6.46) for $h \rightarrow 0$ and take the derivative to get χ_T .

Since $\sinh(h) \sim h + h^3$ and $\cosh(h) \sim 1 + h^2$, we have

$$m \underset{h \ll 1}{\sim} \frac{h(1 + e^{2K})}{1 + e^{-2K}}$$

If we now derive with respect to h

$$\chi_T = \frac{1}{k_B T} \frac{\partial m}{\partial h} \underset{h \ll 1}{\approx} \frac{1}{k_B T} \frac{(1 + e^{2K})}{(1 + e^{-2K})}$$

- Case: $T \rightarrow \infty \Rightarrow K \rightarrow 0$.

$$e^{2K} \simeq e^{-2K} \simeq 1$$

The *Curie's Law* for paramagnetic systems is:

$$\chi_T \sim \frac{1}{k_B T} \quad (6.49)$$

- Case: $T \rightarrow 0 \Rightarrow K \rightarrow \infty$.

$$e^{-2K} \simeq 0$$

The *Curie's Law* for paramagnetic systems is:

$$\chi_T \sim \frac{1}{k_B T} e^{2K} \sim \frac{1}{k_B T} e^{2J/k_B T} \quad (6.50)$$

The correlation length

$$\xi^{-1} = -\log \left(\frac{\lambda_-}{\lambda_+} \right) = -\log \left[\frac{\cosh h - \sqrt{\sinh^2 h + e^{-4K}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4K}}} \right] \quad (6.51)$$

For $h = 0$, we have $\cosh h \rightarrow 1$, $\sinh h \rightarrow 0$:

$$\xi^{-1} = -\log \left[\frac{1 - e^{-2K}}{1 + e^{-2K}} \right] = -\log \left[\frac{1}{\coth K} \right]$$

Therefore:

$$\xi = \frac{1}{\log(\coth K)}, \quad \text{for } h = 0 \quad (6.52)$$

- Case: $T \rightarrow 0 \Rightarrow K \rightarrow \infty$.

$$\coth K = \frac{e^K + e^{-K}}{e^K - e^{-K}} \stackrel{K \rightarrow \infty}{\simeq} 1 + 2e^{-2K} + \dots \stackrel{K \rightarrow \infty}{\longrightarrow} 1$$

It implies

$$\xi \stackrel{K \gg 1}{\sim} \frac{1}{\ln(1 + 2e^{-2K})} \sim \frac{e^{2K}}{2}$$

Hence,

$$\xi \stackrel{T \rightarrow 0}{\sim} \frac{1}{2} e^{J/k_B T} \quad (6.53)$$

It diverges exponentially $\xi \rightarrow \infty$ as $T \rightarrow 0$.

- Case: $T \rightarrow \infty \Rightarrow K \rightarrow 0$.

$$\coth K = \frac{e^K + e^{-K}}{e^K - e^{-K}} \stackrel{K \rightarrow 0}{\simeq} \frac{1 + K + \frac{K^2}{2} + 1 - K + \frac{K^2}{2}}{1 + K + \frac{K^2}{2} - 1 + K - \frac{K^2}{2}} \sim \frac{2 + 2\frac{K^2}{2}}{2K} \sim \frac{1 + K^2}{K}$$

$$\xi^{-1} = \log(\coth K) \stackrel{K \rightarrow 0}{\simeq} \ln \frac{1}{K} + \ln(1 + K^2) \sim +\infty$$

Therefore

$$\xi \stackrel{K \rightarrow 0}{\longrightarrow} 0$$

More precisely,

$$\xi \stackrel{K \rightarrow 0}{\sim} \frac{1}{\ln(1/K) + \ln(1 + K^2)} \stackrel{K \rightarrow 0}{\sim} -\frac{1}{\ln K} \quad (6.54)$$

6.3 Classical Heisenberg model for $d=1$

Now, let us suppose to study something different from the Ising model. Indeed, from a physicist's point of view the Ising model is highly simplified, the obvious objection being that the magnetic moment of a molecule is a vector pointing in any direction, not just up or down. One can build this property, obtaining the classical Heisenberg model. We do not anymore assume spin that can assume values as -1 or +1, but spin that can assume a continuous value. Unfortunately, this model has not been solved in even two dimensions [8].

Let us take a $d = 1$ dimensional lattice. In the classical Heisenberg model, the spins are unit length vectors $\vec{\mathbf{S}}_i$, i.e. $\vec{\mathbf{S}}_i \in \mathbb{R}^3$, $|\vec{\mathbf{S}}_i|^2 = 1$ (continuous values on the unit sphere). We have

$$\vec{\mathbf{S}}_i = (S_i^x, S_i^y, S_i^z)$$

with periodic boundary condition

$$\vec{\mathbf{S}}_{N+1} = \vec{\mathbf{S}}_1$$

Assuming $H = 0$, the model is defined through the following Hamiltonian:

$$-\beta \mathcal{H}(\{\vec{\mathbf{S}}\}) = K \sum_{i=1}^N \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1} \quad (+ \sum_i \vec{\mathbf{h}} \cdot \vec{\mathbf{S}}_i) \quad (6.55)$$

This model satisfies $O(3)$ symmetry. In the transfer matrix formalism:

$$Z_N(K) = \sum_{\{\vec{\mathbf{S}}\}} e^{-\beta \mathcal{H}} = \sum_{\{\vec{\mathbf{S}}\}} e^{K \sum_{i=1}^N \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1}} = \text{Tr}(\mathbb{T}^N) \quad (6.56)$$

where

$$\langle \vec{\mathbf{S}}_i | \mathbb{T} | \vec{\mathbf{S}}_{i+1} \rangle = e^{K \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1}}$$

Similarly to the Ising case,

$$\mathbb{T} = \sum_i |t_i\rangle \lambda_i \langle t_i|$$

and

$$\mathbb{T}_D = \mathbb{P}^{-1} \mathbb{T} \mathbb{P}$$

The problem is computing the eigenvalues λ_i of \mathbb{T} .

Formally, we should find

$$\exp[K \vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2] = \langle \vec{\mathbf{S}}_1 | \mathbb{T} | \vec{\mathbf{S}}_2 \rangle = \sum_{i \in \text{eigenvalues}} \lambda_i \langle \vec{\mathbf{S}}_1 | t_i \rangle \langle t_i | \vec{\mathbf{S}}_2 \rangle = \sum_i \lambda_i f_i(\vec{\mathbf{S}}_1) f^*(\vec{\mathbf{S}}_2)$$

Remark. We start by noticing that the term $e^{K \vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2}$ is similar to the plane wave $e^{i \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}}$, that in scattering problems is usually expanded in spherical coordinates. Plane wave can be expanded as a sum of spherical harmonics as

$$e^{i \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l (i)^l j_l(qr) Y_{lm}^*(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{r}})$$

where

$$j_l(qr) = -\frac{(i)^l}{2} \int_0^\pi \sin(\theta) e^{iqr \cos(\theta)} P_l(\cos(\theta)) d\theta$$

are the *spherical Bessel functions*, while the $P_l(\cos(\theta))$ are the *Legendre polynomial* of order l .

From a formal comparison we have

$$\vec{\mathbf{S}}_1 \leftrightarrow \hat{\mathbf{S}}_1, \quad \begin{cases} i \vec{\mathbf{q}} \cdot \vec{\mathbf{r}} = iqr \\ K \vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2 = K |\vec{\mathbf{S}}_1| |\vec{\mathbf{S}}_2| = K \end{cases} \quad (6.57)$$

multiplying by $(-i)$ we can write

$$qr = -iK |\vec{\mathbf{S}}_1| |\vec{\mathbf{S}}_2| = -iK \quad (6.58)$$

In our case, we have $\hat{\mathbf{q}} = \vec{\mathbf{S}}_1, \hat{\mathbf{r}} = \vec{\mathbf{S}}_2$. Hence,

$$e^{K \vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l (i)^l j_l(-iK) Y_{lm}^*(\vec{\mathbf{S}}_1) Y_{lm}(\vec{\mathbf{S}}_2) = \sum_i \lambda_i f_i(\vec{\mathbf{S}}_1) f^*(\vec{\mathbf{S}}_2) \quad (6.59)$$

where

$$\lambda_i = \lambda_{lm}(K) = 4\pi (i)^l j_l(-iK) \quad (6.60)$$

Remark. Note that λ_i does not depend on m !

If $l = 0$, the largest eigenvalue is:

$$\lambda_+ = \lambda_0(K) = 4\pi j_0(-iK) = 4\pi \frac{\sin K}{K}$$

and

$$\lambda_- = \lambda_1(K) = 4\pi i j_1(-iK) = 4\pi \left[\frac{\cosh K}{K} - \frac{\sinh K}{K^2} \right]$$

Exercise 3

Given the largest eigenvalue λ_+ ,

$$\lambda_+ = 4\pi \frac{\sin K}{K}$$

find the bulk free energy density of the model and discuss its behaviour in the limits of low ($T \rightarrow 0$) and high ($T \rightarrow \infty$) temperatures.

Solution. The bulk free energy is

$$f_b = -k_B T \log \lambda_+ = -k_B T \log \left(4\pi \frac{\sin K}{K} \right)$$

Remind that $K \equiv \beta J$ and consider the limits

- Case: $T \rightarrow 0 \Rightarrow K \rightarrow \infty$.

$$f_b = -\frac{J}{K} \log \left(4\pi \frac{\sin K}{K} \right) \stackrel{K \rightarrow \infty}{\sim} -\frac{J}{K} \log \left(\frac{1}{K} \right) = \frac{J}{K} \log(K)$$

Hence,

$$f_b \stackrel{K \rightarrow \infty}{\sim} 0$$

- Case: $T \rightarrow \infty \Rightarrow K \rightarrow 0$.

$$\begin{aligned} \sin K &\stackrel{K \rightarrow 0}{\sim} K \\ \Rightarrow f_b &= -k_B T \log \left(4\pi \frac{K}{K} \right) = -k_B T \log(4\pi) \end{aligned}$$

In this case the free energy f_b goes linearly with respect to the temperature.

How can we violate the hypothesis of the Perron-Frobenius theorem hoping to find a phase transition also in a $d = 1$ model? One of the hypothesis of the Perron-Frobenius theorem is the one in which $A_{ij} > 0$ for all i, j . Hence, one possibility is to build a model in which its transfer matrix has same A_{ij} that are equal to zero also for $T \neq 0$.

6.4 Zipper model

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The Zipper model is an unusually simple and interesting member of the class of one dimensional systems which exhibit a phase transition. It is a model introduced by Kittel [9] to describe oligomers undergoing *denaturation transition*. Simplest model of DNA thermal denaturation transition (no bubbles). Better model for the denaturation of short oligomers.

The hypothesis are: the binding energy between two bases located at the end of the molecule is smaller than the one for pairs away from the ends. The unbinding starts and develops from the ends as a *zipper*.

In this denaturation transition we do not allow bubbles. Let us consider first the single-ended zipper, i.e. a molecular zipper of N parallel links that can be opened only from one end as in Figure 6.6. The single-ended zipper is simpler than any related problem which has been treated, and it offers a good way to introduce a biophysics example into a course of statistical mechanics.

If the first k bonds (or links) are open (unbounded pairs) the energy to open the $k+1$ is ε_0 . Note that if at least one of the previous k bond is closed the energy needed to open the $k+1$ band is infinite! We specify further that the last link, $k = N$, cannot be opened; this minor features serves only to distinguish one end from the other, and

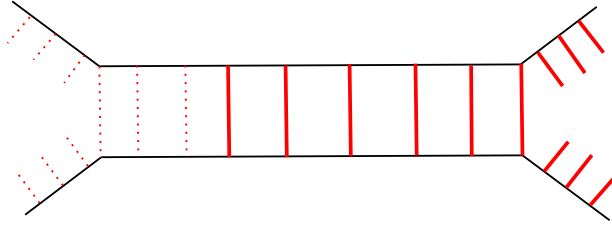


Figure 6.5: Sequential unzipping from the ends.

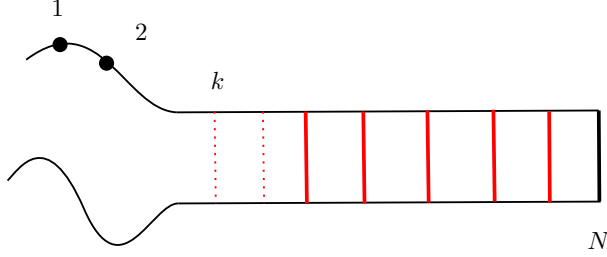


Figure 6.6: Open and closed links in a single-ended zipper.

we shall say that the zipper is open when $N - 1$ links are open.

We suppose that there are G orientations which each open link can assume: that is, the open state of a link is G -fold degenerate, corresponding to the rotational freedom of a link. Hence, once a bond is open it can orient itself in G different ways. In other words, there is an entropy

$$S_0 = k_B \log G \quad (6.61)$$

associated to each open band. In the problem of DNA the empirical value of G may be of the order of 10^4 .

Partition function

Let us suppose that the energy required to open the first k links is ε_0 . If k links are open, the degeneracy is G^k , and the contribution of this configuration to the partition function is

$$G^k e^{-k\varepsilon_0/k_B T}$$

By summing over the possible values of k , the partition function is

$$Z_N(T, G, \varepsilon_0) = \sum_{k=0}^{N-1} G^k e^{-k\varepsilon_0/k_B T} = \sum_{k=0}^{N-1} e^{k(S_0 T - \varepsilon_0)/k_B T} \quad (6.62)$$

Let us call

$$\chi \equiv G e^{-\varepsilon_0/k_B T} \quad (6.63)$$

and simplify the previous expression

$$Z_N = \sum_{k=0}^{N-1} \chi^k = \frac{1 - \chi^N}{1 - \chi} \quad (6.64)$$

We see immediately there is a single pole singularity.

The free energy is

$$F_N = -k_B T \ln Z_N = -k_B T \ln \left[\frac{1 - \chi^N}{1 - \chi} \right] \quad (6.65)$$

We can now compute some observables of interest. The correct procedure is to evaluate thermodynamic quantities for finite N and then to examine the limit $N \rightarrow \infty$.

Calculate average number of open links

The thermodynamic average number of open links is

$$\langle k \rangle_N \equiv \frac{\sum_{k=0}^{N-1} k \chi^k}{\sum_{k=0}^{N-1} \chi^k} = \chi \frac{d}{d\chi} \ln Z_N = \frac{N \chi^N}{\chi^N - 1} - \frac{\chi}{\chi - 1} \quad (6.66)$$

The function is plotted in Figure 6.7. We examine the behaviour of $\langle k \rangle_N$ in the vicinity of the point $\chi_c = 1$ for which the denominators are equal to zero (pole).

Remark. In this model, we consider the average number of open links instead of the magnetization.

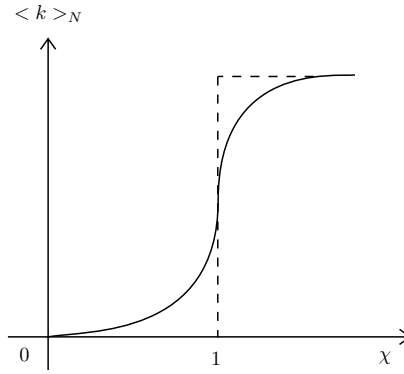


Figure 6.7: Thermodynamic average number of open links in a single-ended zipper of N links.

In order to analyze what happens near 1, we expand $\chi \equiv 1 + \varepsilon$:

$$\begin{aligned} \log Z_N(\chi) &= \log \left[\frac{1 - (1 + \varepsilon)^N}{1 - (1 + \varepsilon)} \right] \\ &= \log \left[\frac{1 - (1 + \varepsilon N + \frac{N(N-1)}{2!} \varepsilon^2 + \frac{N(N-1)(N-2)}{3!} \varepsilon^3 + O(\varepsilon^4))}{\varepsilon} \right] \\ &= \log \left[N + \frac{N(N-1)}{2} \varepsilon + \frac{N(N-1)(N-2)}{6} \varepsilon^2 + \dots \right] \\ &= \log N + \log \left[1 + \frac{N-1}{2} \varepsilon + \frac{(N-1)(N-2)}{6} \varepsilon^2 \right] \\ &= \log N + \log \left[1 + \frac{N\varepsilon}{2} + \frac{N^2 \varepsilon^2}{6} + \dots \right] \\ &= \log N + \left(\frac{N\varepsilon}{2} + \frac{N^2 \varepsilon^2}{6} + \dots \right) + \frac{1}{2} \left(\frac{N\varepsilon}{2} + \frac{N^2 \varepsilon^2}{6} + \dots \right)^2 + \dots \\ &= \log N + \frac{N\varepsilon}{2} + \frac{N^2 \varepsilon^2}{24} + \dots \end{aligned} \quad (6.67)$$

By doing the same for $\langle k \rangle_N = \frac{N\chi^N}{\chi^N - 1} - \frac{\chi}{\chi - 1}$, one gets

$$\langle k \rangle_N = \frac{N}{2} \left(1 + \frac{N\varepsilon}{6} - \frac{N^3\varepsilon^3}{360} + \dots \right) \quad (6.68)$$

this is true for $N \gg 1, \varepsilon \ll 1$.

At the transition point $\chi_c = 1$, where $\varepsilon = 0$:

$$\langle k \rangle_N \simeq \frac{N}{2}$$

We can define the variation (slope per site) as a response function (the derivative with respect to the parameter):

$$\frac{1}{N} \frac{d\langle k \rangle}{d\varepsilon} \simeq \frac{N}{12} - \frac{N^3\varepsilon^3}{240} + \dots \quad (6.69)$$

is a maximum at $\varepsilon = 0$, and the slope at the transition point becomes infinite as $N \rightarrow \infty$ (linearly). The response function diverges linearly to N , this is a good signal that we have a transition.

Transition temperature

The temperature T_c corresponding to the pole $\chi_c = 1$ is given by

$$Ge^{-\varepsilon_0/k_B T_c} = 1$$

Hence,

$$T_c = \frac{\varepsilon_0}{k_B \log G} \quad (6.70)$$

Note that as $G \rightarrow 1$, $T_c \rightarrow 0$. For $G = 1$ there is no solution at a finite temperature and hence the model does not display a phase transition for any finite T ! This is telling you that if $G = 1$ what is important it is the energy, you have no entropy as disorder. At that point everything can happen.

There is a finite transition temperature if $G > 1$. One might perhaps argue that the model is now not strictly one-dimensional, for the degeneracy G arises from the rotational freedom of an open link.

Remark. Despite the model is 1-dim, for $G > 1$ there is a phase transition. This is due to two contributions:

1. Existence of forbidden configuration (infinite energy). It is a necessary condition, but not sufficient, for a phase transition in $d = 1$ with finite range interactions.
2. A further requirement may be that the degeneracy of the excited state (G) of a structural unit must be higher than the degeneracy of the ground state².

Unwinding from both ends

When the zipper is allowed to unwind from both ends, there are $k+1$ ways in which a total of k links may be opened, so that the partition function for a double-ended zipper of N links is

$$Z_N(T, G, \varepsilon_0) = \sum_{k=0}^{N-1} (k+1) G^k e^{-k\varepsilon_0/k_B T} \quad (6.71)$$

and to this should be added a term for the state of N open links. This terminal term for a simple zipper is $G^N \exp(-N\varepsilon_0/k_B T)$.

²In the mean-field approximation no transition can occur if the degeneracy of the ground state is higher than that of the excited state.

6.4.1 Transfer matrix method for the Zipper model

The idea is: we want to map the Zipper model to an Ising model. The spin like model consists on associating to each bond a spin such that $S_i = 0$ if the i -esim bond is *closed*, while $S_i = 1, \dots, G$ if the i -esim bond is *open* with G possible orientations. Therefore,

- Case: $S_i \neq 0$ open. We have two subcases:
 - S_{i-1} open: $S_{i-1} \neq 0 \Rightarrow E(S_i \neq 0 | S_{i-1} \neq 0) = \varepsilon_0$.
 - S_{i-1} closed: $S_{i-1} = 0 \Rightarrow E(S_i \neq 0 | S_{i-1} = 0) = \varepsilon_0 + V_0$
- Case: $S_i = 0$ closed. We have $E(S_i = 0) = 0$ irrespective of S_{i-1} .

Hence, considering all these cases, the energy results

$$E(S_i, S_{i-1}) = (\varepsilon_0 + V_0 \delta_{S_{i-1}, 0})(1 - \delta_{S_i, 0}) \quad (6.72)$$

The boundary condition is $S_N = 0$ (always closed). The full Hamiltonian of the model can be written as (it could be also a function of delta, but it is not a problem):

$$\mathcal{H}_N = \varepsilon_0(1 - \delta_{S_1, 0}) + \sum_{i=2}^{N-1} (\varepsilon_0 + V_0 \delta_{S_{i-1}, 0})(1 - \delta_{S_i, 0}) \quad (6.73)$$

The Kittel's version is obtained by assuming $V_0 = \infty$.

The partition function is

$$Z_N = \sum_{\{S\}} \exp(-\beta \mathcal{H}_N)$$

In order to implement the transfer matrix formalism we rewrite Z_N as follows

$$Z_N = \sum_{\{S\}} e^{-\beta \varepsilon_0(1 - \delta_{S_1, 0})} \prod_{i=1}^{N-2} e^{-\beta \varepsilon_0(1 - \delta_{S_{i+1}, 0})} \left[1 + (e^{-\beta V_0} - 1) \delta_{S_i, 0}(1 - \delta_{S_{i+1}, 0}) \right] \quad (6.74)$$

Let us consider the Kittel model, the condition $V_0 = \infty$ implies $\exp(-\beta V_0) = 0$. Hence, we can define the transfer matrix as

$$\mathbb{T} = \{ \langle S | \mathbb{T} | S' \rangle \equiv t_{S, S'} \} \quad (6.75)$$

where

$$t_{S, S'} = e^{-\beta \varepsilon_0(1 - \delta_{S', 0})} [1 - \delta_{S, 0}(1 - \delta_{S', 0})] \quad (6.76)$$

or in matrix form

$$\mathbb{T} = \begin{bmatrix} 1 & 0 & \dots & 0 \\ 1 & a & \dots & a \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ 1 & a & \dots & a \end{bmatrix}, \quad \text{with } a \equiv e^{-\beta \varepsilon_0}$$

The first think to notice is that the constraint that the bond S_{i+1} cannot be open if bond S_i is closed ($S_i = 0$) yields the null entries in the first row of \mathbb{T} . This violates the hypothesis of the Perron-Frobenius theorem!

The matrix \mathbb{T} has three different eigenvalues

$$\lambda_1 = Ga, \quad \lambda_2 = 1, \quad \lambda_3 = 0 \quad (6.77)$$

The partition function can be written as

$$Z_N = (1, a, \dots, a) \mathbb{T}^{N-2} \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} \quad (6.78)$$

Moreover, we have

$$\lambda_1 \rightarrow \vec{v}_1 = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \quad \lambda_2 \rightarrow \vec{v}_2 = \begin{pmatrix} 1 - Ga \\ 1 \\ \vdots \\ 1 \end{pmatrix}$$

and we can then write

$$\begin{pmatrix} 1 \\ a \\ \vdots \\ a \end{pmatrix} = \frac{a(1 - Ga) - 1}{1 - Ga} \vec{v}_1 + \frac{1}{1 - Ga} \vec{v}_2$$

$$\begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} = \frac{-Ga}{1 - Ga} \vec{v}_1 + \frac{1}{1 - Ga} \vec{v}_2$$

Therefore,

$$Z_N = \frac{1 - (Ga)^N}{1 - Ga} = \frac{1 - (Ge^{-\beta\epsilon_0})^N}{1 - Ge^{-\beta\epsilon_0}} = \frac{1}{1 - Ge^{-\beta\epsilon_0}} (-\lambda_1^N + \lambda_2^N) \quad (6.80)$$

Since in the thermodynamic limit only the contribution of the largest eigenvalue matters for f_b we have

$$f_b = -k_B T \ln \max(\lambda_1, \lambda_2)$$

Remark. Given that the λ_1 and λ_2 are positive, analytic function of T ($\lambda_1 = Ga, \lambda_2 = 1$). In order to have a phase transition (i.e. non analyticity of f_b) the two eigenvalues must cross for a given value of T . It is true if and only if:

$$Ga_c = 1 \Leftrightarrow Ge^{-\beta_c \epsilon_0} = 1 \Leftrightarrow T_c = \frac{\epsilon_0}{k_B \ln G} \quad (6.81)$$

that agree with previous calculation (see Eq.(6.70)).

6.5 Transfer matrix for **2 – dim** Ising

The two-dimensional Ising model for a system of interacting spins on a square lattice is one of the very few nontrivial many-body problems that is exactly soluble and shows a phase transition [6]. The exact solution in the absence of an external magnetic field ($H = 0$) was first given almost eighty years ago in a famous paper by Onsager [5], using the theory of Lie algebras. In particular, from Onsager's solution we can see that already in two dimensions an Ising model can exhibit phase transitions, showing a non null spontaneous magnetization for temperatures low enough.

Let us therefore consider a two-dimensional Ising model, defined on a lattice made of N rows and M columns, as in Figure 6.8. We apply periodic boundary conditions to the system in both directions (geometrically, this can be thought of as defining the

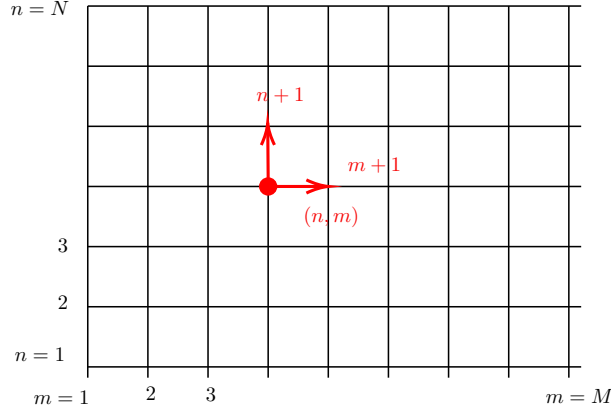


Figure 6.8: 2-dimensional Ising lattice of N rows and M columns.

model on a torus), and we consider only nearest neighbour interactions. The spin in a site is identified by $S_{\text{site}} = S_{m,n}$.

We consider a set of spin arranged on a square lattice, interacting only with nearest neighbors and with a magnetic field $H \neq 0$. The reduced Hamiltonian of the system will be:

$$\begin{aligned} -\beta\mathcal{H}_{\Omega}(\{S\}) &= K \sum_{\langle ij \rangle} S_i S_j + h \sum_i S_i \\ &= K \sum_{n=1}^N \sum_{m=1}^M (S_{m,n} S_{m+1,n} + S_{m,n} S_{m,n+1}) + h \sum_{n=1}^N \sum_{m=1}^M S_{m,n} \end{aligned}$$

This can be rewritten as follows:

$$-\beta\mathcal{H}_{\Omega}(\{S\}) = \sum_{m=1}^M [E[\mu_m, \mu_{m+1}] + E[\mu_m]] \quad (6.82)$$

where

$$E[\mu_m, h] = K \sum_{n=1}^N S_{m,n} S_{m,n+1} + h \sum_{n=1}^N S_{m,n} \quad (6.83a)$$

$$E[\mu_m, \mu_{m+1}, h] = K \sum_{n=1}^N S_{m,n} S_{m+1,n} \quad (6.83b)$$

the first equation is the one body interaction, while the second equation represents the interaction between nearest neighbours columns (two body interaction).

Moreover, μ is a m dimensional vector; in particular, each μ_m represents the set of N spins along column m :

$$\mu_m = \{S_{m,1}, S_{m,2}, \dots, S_{m,N}\} \quad (6.84)$$

We can write a transfer matrix between columns, permitting to transfer along the m . To make it simpler, suppose $h = 0$ (so the energy does not depend on h):

$$\langle \mu_m | \mathbb{T} | \mu_{m+1} \rangle = \exp[k(E[\mu_m, \mu_{m+1}] + E[\mu_m])] \quad (6.85)$$

Now, we have to diagonalize.

Remark. In the 2x2 transfer matrix in the 2-dim we have two possible values. Now, we have to do the same in principle, but we have to do for all of the (6.84).

Remark. \mathbb{T} is a matrix of dimension $2^N \times 2^N$, hence, in the thermodynamic limit is an infinite matrix (violation of Perron-Frobenius).

According to the formalism

$$Z_N(K, h) = \text{Tr}(\mathbb{T}^N)$$

To find the eigenvalues of \mathbb{T} given by (6.85) is highly non trivial. The big problem it is that in the thermodynamic limit is that the dimension of the transfer matrix goes to infinity, then it is difficult to be diagonalized. This was first achieved by Onsanger in 1944, as said, for the case $H = 0$ and in the $N \rightarrow \infty$ limit. Onsanger has shown that the free energy of the system is given by

$$f_b(T) = -k_B T \log(2 \cosh(2\beta J)) - \frac{k_B T}{2\pi} \int_0^{2\pi} \log \left[\frac{1}{2} \left(1 + \sqrt{1 - g^2 \sin^2(\Phi)} \right) \right] d\Phi \quad (6.86)$$

where

$$g = \frac{2}{\cosh(2\beta J) \coth(2\beta J)}$$

and also that the magnetization is:

$$m = \begin{cases} [1 - \sinh^{-4}(2\beta J)]^{1/8} & T < T_c \\ 0 & T > T_c \end{cases} \quad (6.87)$$

where T_c is the temperature given by the condition

$$2 \tanh^2 \left(\frac{2J}{k_B T_c} \right) = 1$$

which yields the numeric result:

$$\Rightarrow T_c \simeq 2,264J/k_B \neq 0$$

hence, we have a phase transition at a critical temperature T_c different from 0!

Onsager also showed that the critical exponents of this model are:

$$\alpha = 0, \quad \beta = \frac{1}{8}, \quad \gamma = \frac{7}{4}$$

where $\alpha = 0$ because the specific heat diverges logarithmically for $T \sim T_c$:

$$c \propto A \left[-\ln \left(1 - \frac{T}{T_c} \right) + B \right]$$

It means that the specific heat displays at the transition a logarithmic divergence (no power law!).

Chapter 7

The role of dimension, symmetry and range of interactions in phase transitions

Which is the role of the dimension in phase transition? Consider d , the dimension of the system. For the Ising model, we have seen that in $d = 1$ there is no phase transition, while the Onsager solution tell us that for $d = 2$ there is a paramagnetic-ferromagnetic transition for $T_c > 0$. Therefore, the dimension seems a crucial parameter! Since in general analytic solutions are not available, is there a simple argument to establish the existence of a phase transition? In the case of a para-ferro transition, may we establish whether a phase with long range order exists and is stable within a range of $T > 0$?

Lecture 10.
Wednesday 13th
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7.1 Energy-entropy argument

We need an argument that can tell us which kind of system has a phase transition. The idea is to use the entropy energy argument. Indeed, our systems are ruled by a free energy and the previous states are found by making derivative. We have energy and entropy: low energy state can be stable with respect to thermal fluctuations, but the fluctuations will destroy the long range order. This idea can be generalized.

Let us consider:

$$dF = \underbrace{dU}_{\text{energy}} - T \underbrace{dS}_{\text{entropy}} \quad (7.1)$$

We expect that:

- $T \gg 1$: entropy should dominates.
- $T \ll 1$: energy should dominates.

Question: there is a temperature different to zero in which this is compatible?

7.1.1 1-dim Ising

Let us study the stability of the states with minimum energy to fluctuations for $T \neq 0$, for a system of size N .

We already know that, for $T = 0$, two ground states exist, either all spins up or all spins down. For instance, suppose that we have the ground state with all the spin up; the energy of the state is

$$E_G = -JN \quad (7.2)$$

and it is the same for the other configuration.

Now, let us consider $T \neq 0$, there could be a given number of elementary excitations of the kind spin up/down. What happens if we swap one or more spins? These are defects with respect to the ground state and they are also called *domain walls*. This is in the one dimensional case, but is valid also in many dimensional. Therefore, which is the variation in energy ΔE with respect to the ground state? For each excitation there is an energy penalty $\Delta E = 2J$, indeed, if we suppose that we have only one swap, we have

$$E_G = -JN, \quad E^* = -J(N-1) + J \quad \Rightarrow \Delta E = 2J$$

For a finite concentration x of domain walls, we can write $M = Nx$, giving

$$\Delta E_M = 2MJ \quad (7.3)$$

Now, let us compute the change in entropy. The entropy of the ground state can be computed immediately: this is zero because it is the logarithm of the number of configurations, but in this case we have only one configuration, namely $S_G = \ln 1 = 0$. Hence, the difference between the entropy of the ground state and the entropy of the new state is just the entropy of the new state. Therefore, we want to estimate the entropy of the states with M domain walls. The number of possible ways to insert M domains in N positions, namely the number of configurations, is

$$\# = \binom{N}{M} = \binom{N}{xN} \quad (7.4)$$

We have:

$$S_M = k_B \log \binom{N}{M} \quad (7.5)$$

the difference is

$$\Delta S = S_M - S_G = S_M = k_B \ln \binom{N}{xN}$$

Let us calculate

$$\begin{aligned} \Delta F &= F_M - F_G = \Delta E - T \Delta S \\ &= 2MJ - k_B T \ln \binom{N}{M} \\ &= 2xNJ - k_B T \ln \binom{N}{xN} \\ &= N \{ 2xJ + k_B T [x \ln x + (1-x) \ln (1-x)] \} \end{aligned}$$

where we have used the Stirling approximation

$$\ln N! = N \ln N - N$$

Since the equilibrium states are obtained by the minimum of F , we can minimize with respect to x . We are interested in the free energy in the bulk, hence, firstly we normalize and then we derive for finding the minimum

$$\Delta f_{b_N} = \frac{\Delta F_N}{N}, \quad \frac{\partial \Delta f_b}{\partial x} = 0 \quad (7.6)$$

this gives

$$\begin{aligned} \frac{\partial}{\partial x} \{ 2xJ + k_B T [x \ln x + (1-x) \ln (1-x)] \} &= 2J + k_B T [\ln x + 1 - \ln (1-x) - 1] \\ &= 2J + k_B T [\ln x - \ln (1-x)] = 0 \end{aligned}$$

hence,

$$\ln \frac{x}{1-x} = -\frac{2J}{k_B T} \Rightarrow \frac{x}{1-x} = e^{-2J/k_B T}$$

and finally the results is

$$x = \frac{1}{1 + e^{2J/k_B T}} \quad (7.7)$$

It means that $\forall T \neq 0$ exist a finite concentration x of domain walls. The ground state is unstable $\forall T > 0$. Indeed, if you have a finite density of x , no long range order exist for $T > 0$. From (7.7), we can see that as $T \rightarrow 0$, we have $x \rightarrow 0$ as expected. Now, let us try to do the same for d dimensions.

7.1.2 d -dim Ising

What is a *domain wall* in d dimensions? The domain walls is an hypersurface of size L^{d-1}

$$\Delta E \propto 2JL^{d-1} \quad (7.8)$$

Computing the entropy it is a very difficult problem. Indeed, the entropy of a fluctuating hypersurface is difficult to estimate. For a single domain wall, we can say

$$S \geq k_B \ln L \quad (7.9)$$

where L is the number of ways to place a straight wall within a system of linear size L . The ΔS is just S because the entropy of the ground state is again zero.

Remark. If we underestimate S , we obtain

$$\Delta F = 2JL^{d-1} - k_B T \ln L \quad (7.10)$$

it means that now energy can win if the temperature is different from zero. Therefore, for $d = 2$, or greater ($d > 1$), that long range order can survive thermal fluctuations and the system could present an ordered phase!

Peierls argument

The Peierls argument [10] is a mathematically rigorous and intuitive method to show the presence of a non-vanishing spontaneous magnetization in some lattice models. This argument is typically explained for the $d = 2$ Ising model in a way which cannot be easily generalized to higher dimension. The idea is trying to perturb the system using an external magnetic field as perturbation (it is very small h). In that way, we are breaking explicitly the symmetry, but then, taking the limit $h \rightarrow 0$ and switching off the magnetic field, we see the stability.

We know that for finite systems, from the \mathbb{Z}^2 symmetry, it follows

$$\langle m \rangle_N = 0$$

This is true for finite systems, however, in the thermodynamical limit $N \rightarrow \infty$, if $d \geq 2$ the magnetization $\langle m \rangle_\infty$ vanishes only in the high temperature paramagnetic phase. In the low temperature ferromagnetic phase, the value of $\langle m \rangle_\infty$ is not well defined and depends on how the thermodynamical limit is performed. In this case the \mathbb{Z}^2 symmetry is said to be spontaneously broken.

The breaking of a symmetry can be thought as a form of thermodynamical instability: the particular value acquired by $\langle m \rangle_\infty$ in the ferromagnetic phase is determined by small perturbations.

A conventional way to uniquely define $\langle m \rangle_\infty$ in the broken phase (where it is called spontaneous magnetization) is to use an infinitesimal magnetic field:

$$\langle m \rangle_\infty = \lim_{h \rightarrow 0^+} \lim_{N \rightarrow \infty} \langle m \rangle_N^{(h)} \quad (7.11)$$

where it is crucial to perform the thermodynamical limit before switching off the magnetic field $h \rightarrow 0^+$. The instability manifests itself in that using $h \rightarrow 0^-$ would change the sign of $\langle m \rangle_\infty$.

A different approach to expose the instability is the use of appropriate boundary conditions: we can for example, if we want $\langle m \rangle_\infty > 0$, impose in all the sites i on the lattice boundary ($i \in \partial\Omega$) the condition $S_i = +1$, as in Figure 7.1.

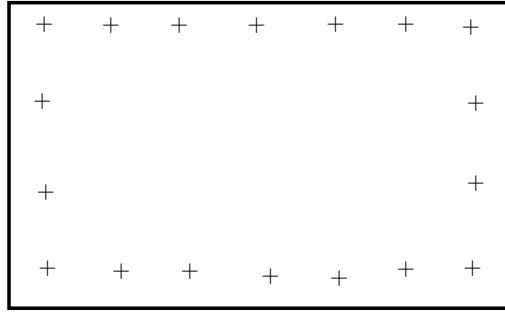


Figure 7.1: System with boundary condition with all the spins in the surface up.

In the paramagnetic phase the effect of boundary conditions does not survive the thermodynamical limit, while in the ferromagnetic phase their effect is analogous to that of the infinitesimal magnetic field.

This is the boundary condition chosen by Pierls to establish the existence of a $T_c \neq 0$ for the $d = 2$ Ising model. Let us give just a qualitative presentation of the (rigorous) result.

Let N_+, N_- be the number of spin up and down respectively. Clearly,

$$N = N_+ + N_-$$

On a finite lattice the mean value of the magnetization can be written in the form

$$\langle m \rangle_N = \frac{\langle N_+ \rangle - \langle N_- \rangle}{N} = 1 - 2 \frac{\langle N_- \rangle}{N}$$

In order to show that $\langle m \rangle_\infty > 0$ (remember that we are considering boundary conditions with spin up at $\partial\Omega$), it is sufficient to show that for every N we have

$$\frac{\langle N_- \rangle}{N} < \frac{1}{2} - \varepsilon \quad (7.12)$$

with $\varepsilon > 0$ and N -independent. Indeed, if (7.12) holds

$$\langle m \rangle_N \geq 2\varepsilon \quad \forall N \quad (7.13)$$

The Peierls argument is a simple geometrical construction that can be used to prove this bound. The outcome of the Peierls argument for the model in d dimensions is an estimate of the form

$$\frac{\langle N_- \rangle}{N} \leq f_D(x) \quad (7.14)$$

where x is defined by

$$x = 9e^{-4J\beta} \quad (7.15)$$

and f_D is a continuous function of x (independent on N) and such that

$$\lim_{x \rightarrow 0} f_D(x) = 0$$

In particular, for small enough T we have the bound

$$\frac{\langle N_- \rangle}{N} < \frac{1}{2} - \varepsilon$$

which ensures that $\langle m \rangle_\infty \geq 2\varepsilon$ and the \mathbb{Z}^2 symmetry is spontaneously broken. More precisely, for $d = 2$, one has

$$\frac{\langle N_- \rangle}{N} \leq \frac{x^2}{36} \frac{2-x}{(1-x)^2} \quad (7.16)$$

where $x = 9e^{-4J\beta} < 1$.

Remark. Note that above bound gives also a lower bound on the critical temperature

$$\frac{\langle N_- \rangle}{N} \leq \frac{x^2}{36} \frac{2-x}{(1-x)^2} < \frac{1}{2} - \varepsilon$$

As long as $\frac{\langle N_- \rangle}{N} < \frac{1}{2} - \varepsilon$, the system is in the ferromagnetic phase. The critical value $x_c \equiv x(\beta_c)$ must be outside the interval $[0, x_{1/2}]$ where $x_{1/2}$ is the smallest positive solution of the equation

$$\frac{x^2}{36} \frac{2-x}{(1-x)^2} = \frac{1}{2}$$

From the solution $x_{1/2}$ and the condition $x_c > x_{1/2}$, one has

$$J\beta_c \leq J\beta_{1/2}$$

where $J\beta_{1/2} = \frac{1}{4} \log 9/x_{1/2}$. Hence, $T_c > T_{1/2}$.

Exercise 4

The following equation gives $x_{1/2}$:

$$x^3 + 16x^2 - 36x + 18 = 0$$

Find $T_{1/2}$.

Solution. This equation has three real solutions:

$$x_1 = -18.05, \quad x_2 = 0.79, \quad x_3 = 1.26$$

The smallest positive solutions is $x_{1/2} \equiv x_2$, hence

$$\frac{J}{k_B T_{1/2}} = \frac{1}{4} \log 9/x_{1/2} \quad \Rightarrow \quad T_{1/2} = \frac{4J}{k_B \log 9/x_{1/2}}$$

7.2 Role of the symmetry

Interacting systems can be classified with respect to their *global symmetry group*. Let us illustrate some examples.

Example 20: Ising model

$$\mathcal{H}_{\text{Ising}} = - \sum_{i < j} J_{ij} \sigma_i \sigma_j \quad (7.17)$$

where $\sigma_i \in \{-1, 1\}$. The symmetry group of this Hamiltonian is \mathbb{Z}^2 , which has two elements $\{1, \eta\}$. We have

$$1 : \text{identity}, \quad \eta \sigma_i = -\sigma_i, \quad \eta^2 = 1$$

Example 21: Potts model

The Potts model, a generalization of the Ising model, is a model of interacting spins on a crystalline lattice. The Hamiltonian is

$$\mathcal{H}_{q\text{-Potts}} = - \sum_{i < j} J_{ij} \delta_{\sigma_i, \sigma_j} \quad (7.18)$$

where $\sigma_i \in \{1, 2, 3, \dots, q\}$. $\mathcal{H}_{q\text{-Potts}}$ is invariant under the permutation group of the sequence $\{1, 2, 3, \dots, q\}$. There are $q!$ elements, for example $\{2, 1, 3, \dots, q\}$. The symmetry group is denoted by S_q .

Remark. The difference between a \mathbb{Z}_q and S_q symmetry is that an Hamiltonian has symmetry \mathbb{Z}_q if it is invariant with respect to *cyclic permutations*¹

$$\eta = \begin{pmatrix} 1 & 2 & \dots & q-1 & q \\ 2 & 3 & \dots & q & 1 \end{pmatrix} \quad (7.19)$$

and its powers η^l with $l = 0, \dots, q-1$. Both models satisfy a *discrete global symmetry*.

Now, we jump into the case in which we consider *continuous* symmetries.

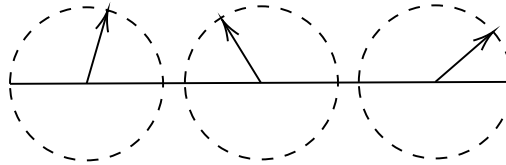


Figure 7.2: Spin can assume all values around the circles.

Example 22: XY model

This is a spin model that is invariant with respect to the continuous global symmetry $\theta_i \rightarrow \theta_i + \alpha$. Indeed, the Hamiltonian of this model is

$$\mathcal{H}_{XY} = - \sum_{i < j} J_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j \quad (7.20)$$

¹In mathematics, and in particular in group theory, a cyclic permutation (or cycle) is a permutation of the elements of some set X which maps the elements of some subset S of X to each other in a cyclic fashion, while fixing (that is, mapping to themselves) all other elements of X . If S has k elements, the cycle is called a k -cycle. Cycles are often denoted by the list of their elements enclosed with parentheses, in the order to which they are permuted.

where \vec{S}_i is a $2D$ spin vector

$$\vec{S}_i = (S_{x_i}, S_{y_i})$$

that can assume values on the unit circle ($|\vec{S}_i| = 1$). Suppose that spins are sitting in hyper dimensional and can rotate along circles. They can assume all the value as in Figure 7.2.

The simplest way to parametrize the Hamiltonian is by the angle. Denoting by θ_i the direction angle of spins \vec{S}_i , the Hamiltonian can be rewritten as

$$\mathcal{H}_{XY} = - \sum_{i < j} J_{ij} \cos(\theta_i - \theta_j) \quad (7.21)$$

with $\theta_i \in [0, 2\pi]$.

Remark. The interaction term $\cos(\theta_i - \theta_j)$ can be written also as

$$\frac{1}{2} (Z_i^* Z_j + Z_i Z_j^*)$$

where $Z_j = \exp(i\theta_j)$.

The model is invariant under the global transformation

$$Z_i \rightarrow e^{i\alpha} Z_i \quad (7.22)$$

The phase $\exp(i\alpha)$ form a group under multiplication known as $U(1)$ that is equivalent to $O(2)$. Indeed, the interaction term can be written also as

$$\hat{\Omega}_i \cdot \hat{\Omega}_j$$

where $\hat{\Omega}_i = (\cos \theta_i, \sin \theta_i)$.

Remark. In n -dimensions $\hat{\Omega}$ has n components $\hat{\Omega} = \{\Omega^1, \Omega^2, \dots, \Omega^n\}$ and the corresponding Hamiltonian is

$$\mathcal{H} = - \sum_{i < j} J_{ij} \hat{\Omega}_i \cdot \hat{\Omega}_j \quad (7.23)$$

It is symmetric with respect to the global symmetry group $O(n)$.

Which are the domain walls for continuous symmetries? Which are the implications for the stability of the ordered phase?

7.3 Continuous symmetries and phase transitions

When the symmetry is continuous the domain walls interpolate smoothly between two ordered regions (see Figure 7.3). The energy term that in Ising is proportional to $2JL^{d-1}$, how does it change here?

Let us consider the XY model and suppose that the variation of the direction between two nearest neighbours sites is very small, i.e. $(\theta_i - \theta_j) \ll 1$ for i, j nearest neighbours. Now, we can dilute the energy, in other words we weak the energy term.

Let us do a Taylor expansion of the interaction term

$$\cos(\theta_i - \theta_j) \simeq 1 - \frac{1}{2}(\theta_i - \theta_j)^2 \Rightarrow \sum_{\langle ij \rangle} \left(1 - \frac{1}{2}(\theta_i - \theta_j)^2 \right) \quad (7.24)$$

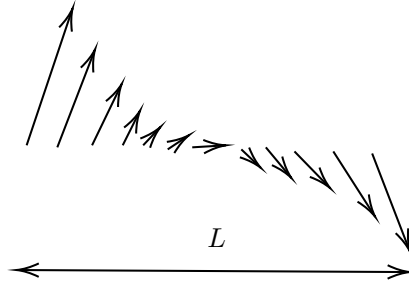


Figure 7.3: For continuous symmetry the domain walls interpolate smoothly between two ordered regions.

The Hamiltonian can be written as

$$\mathcal{H} \simeq -J \sum_{\langle ij \rangle} \left(1 - \frac{1}{2}(\theta_i - \theta_j)^2 \right) \quad (7.25)$$

The (7.24) corresponds to the discrete differential operator where $\theta_i - \theta_j = \partial_x \theta$, hence

$$\mathcal{H} = E_0 + \underbrace{\frac{J}{2} \int d\vec{r} (\nabla \theta)^2}_{E \equiv \text{Stiffness energy}} \quad (7.26)$$

where $E_0 = 2JN$ is the energy corresponding to the case in which all the spins are oriented along a given direction.

Definition 6: Stiffness energy

The Stiffness energy is defined as

$$E = \frac{J}{2} \int d\vec{r} (\nabla \theta)^2 \quad (7.27)$$

where $\theta(\vec{r})$ is the angle of a local rotation around an axis and J is the *spin rigidity*. For an ordered phase $\theta(\vec{r}) = \theta_0$.

Let us now imagine a domain wall where $\theta(\vec{r})$ rotates by 2π (or $2\pi m$) by using the entire length of the system (see again Figure 7.3):

$$\theta(\vec{r}) = \frac{2\pi n x}{L}$$

where n is the total number of 2π turn of θ in L .

Remark. Note that there is no variation along the other $d - 1$ dimensions, therefore we just doing over one dimension.

We consider only the term E (Stiffness energy) of the Hamiltonian

$$E = \frac{J}{2} L^{d-1} \int_0^L dx \left(\frac{d}{dx} \left(\frac{2\pi n x}{L} \right) \right)^2 = \frac{J}{2} L^{d-1} \int_0^L dx \left(\frac{2\pi n}{L} \right)^2 \approx 2\pi^2 n^2 J L^{d-2} \quad (7.28)$$

Remark. Unlike the Ising model where $E \sim L^{d-1}$, here $E \sim L^{d-2}$! Hence, if $S \geq k_B \ln L$ for a single domain wall, S should dominate if $d \leq 2$, the ordered phase is always unstable and no phase transition is expected for $T \neq 0$!

Definition 7: Lower critical dimension

The Lower Critical dimension d_c is the dimension at which (and below which) the system does not display a ordered phase (there is no long range order). In other words if $d \leq d_c$, we have $T_c = 0$.

From what we have found before we can say that

- For discrete global symmetries: $d_c = 1$.
- For continuous global symmetries: $d_c = 2$ (Mermin-Wagner theorem)².

Example 23: XY model transition

The XY model in $d = 2$ is rather special. While the Mermin-Wagner theorem prevents any spontaneous symmetry breaking on a global scale, ordering transitions of Kosterlitz-Thouless-type may be allowed. This is the case for the XY model where the continuous (internal) $O(2)$ symmetry on a spatial lattice of dimension $d \leq 2$, remains zero for any finite temperature $T \neq 0$ (it do not display an ordered phase).

Remark. This transition does not imply the spontaneous breaking of the $O(2)$ symmetry!

However, the theorem does not prevent the existence of a phase transition in the sense of a diverging correlation length ξ . To this end, the model has two phases:

- a conventional disordered phase at high temperature with dominating exponential decay of the correlation function $G(r) \sim \exp(-r/\xi)$ for $r/\xi \gg 1$;
- a low-temperature phase with quasi-long-range order where $G(r)$ decays according to some power law, which depends on the temperature, for "sufficiently large", but finite distance r ($a \ll r \ll \xi$ with a the lattice spacing).

The transition from the high-temperature disordered phase with the exponential correlation to this low-temperature quasi-ordered phase is a Kosterlitz-Thouless transition. It is a phase transition of infinite order.

In the $d = 2$ XY model, vortices are topologically stable configurations. It is found that the high-temperature disordered phase with exponential correlation decay is a result of the formation of vortices. Vortex generation becomes thermodynamically favorable at the critical temperature T_{KT} of the KT transition. At temperatures below this, vortex generation has a power law correlation (hence, there is no long range order for $T < T_{KT}$).

Many systems with KT transitions involve the dissociation of bound anti-parallel vortex pairs, called vortex-antivortex pairs, into unbound vortices rather than vortex generation. In these systems, thermal generation of vortices produces an even number of vortices of opposite sign. Bound vortex-antivortex pairs have lower energies than free vortices, but have lower entropy as well.

In order to minimize free energy, $F = E - TS$, the system undergoes a transition at a critical temperature, T_{KT} . Below T_{KT} there are only bound vortex-antivortex pairs. Above T_{KT} , there are free vortices.

²In statistical mechanics, the Mermin-Wagner theorem states that continuous symmetries cannot be spontaneously broken at finite temperature in systems with sufficiently short-range interactions in dimensions $d \leq 2$. Intuitively, this means that long-range fluctuations can be created with little energy cost and since they increase the entropy they are favored.

7.4 Role of the interaction range

So far we have considered models where the interactions were short range. How things change if long range are considered instead? How does the symmetry broken depends on the range of interactions?

One can show, for example, that if

$$J_{ij} = \frac{J}{|\vec{r}_i - \vec{r}_j|^\alpha}, \quad 1 \leq \alpha \leq 2 \quad (7.29)$$

phase with long range order is stable for $0 < T < T_c$ also for $d = 1$!

Remark. If $\alpha > 2 + \varepsilon$ we get back the physics found for short range interactions. If $\alpha < 1$ the thermodynamic limit does not exist.

A limiting case of long range interaction is the *infinite range* case where all the spins interact one to another with the same intensity independently on their distance. No metric is involved (instead of previously where the definition of J of before is a metric.). It can be solve exactly and later we will see why.

7.4.1 Ising model with infinite range

Let us consider the Hamiltonian

$$-\mathcal{H}_N(\{S\}) = \frac{J_0}{2} \sum_{i,j}^N S_i S_j + H \sum_i S_i \quad (7.30)$$

with $S_i \in [-1, +1]$.

Remark. The sum over i, j is an unrestricted double sum.

The problem with the double sum is that

$$\sum_{i,j} S_i S_j \propto O(N^2)$$

and the thermodynamic limit is ill-defined. To circumvent this problem Mark Kac suggested to consider a strength

$$J_0 = \frac{J}{N} \quad (7.31)$$

this is called the *kac approximation*. Hence,

$$-\mathcal{H}_N(\{S\}) = \frac{J}{2N} \sum_{i,j}^N S_i S_j + H \sum_i S_i \quad (7.32)$$

with this choice we recover $E \sim O(N)$.

The partition function is

$$Z_N(T, J, H) = \sum_{\{S\}} \exp \left[\frac{\beta J}{2N} \sum_{i,j} S_i S_j + \beta H \sum_i S_i \right] \quad (7.33)$$

Since there are no restrictions on the double sum, we can write

$$\sum_{i,j} S_i S_j = \left(\sum_i S_i \right) \left(\sum_j S_j \right) = \left(\sum_i S_i \right)^2$$

Rewriting the partition function, we have:

$$Z_N(T, J, H) = \sum_{\{S\}} \exp \left[\frac{K}{2N} \left(\sum_i S_i \right)^2 + h \sum_i S_i \right] \quad (7.34)$$

Lecture 11.
Wednesday 20th
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Remark. Recall that we have defined $K = \beta J$ and $h = \beta H$.

In order to transform the quadratic term into a linear one we make use of the integral identity known as the *Hubbard–Stratonovich transformation* (we can do it in any dimension). Let

$$x \equiv \sum_i S_i$$

The key identity in the Hubbard–Stratonovich method is simply an observation of the result of a Gaussian integral. In the present case it takes the form

$$e^{\frac{Kx^2}{2N}} = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} e^{-\frac{NK}{2}y^2 + Kxy} dy, \quad \text{Re } K > 0 \quad (7.35)$$

where y is a random field that follows a random distribution.

Proof of Hubbard–Stratonovich identity. To show the identity (7.35) it is sufficient to complete the square

$$-\frac{NK}{2}y^2 + Kxy = -\frac{NK}{2}\left(y - \frac{x}{N}\right)^2 + \frac{Kx^2}{2N}$$

and then shifting the integral to one over $z \equiv \left(y - \frac{x}{N}\right)$.

Hence,

$$e^{\frac{Kx^2}{2N}} \int_{-\infty}^{+\infty} e^{-\frac{NK}{2}\left(y - \frac{x}{N}\right)^2} dy \stackrel{(a)}{=} e^{\frac{Kx^2}{2N}} \sqrt{\frac{2\pi}{NK}}$$

where in (a) we have considered $z \equiv \left(y - \frac{x}{N}\right)$, $dz = dy$ and the integral

$$\int_{-\infty}^{+\infty} e^{-\alpha z^2} dz = \sqrt{\frac{\pi}{\alpha}}$$

with $\alpha \equiv \frac{NK}{2}$. ■

By using (7.35) in the partition function, we have

$$Z_N(K, h) = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} dy e^{-\frac{NK}{2}y^2} \underbrace{\left[\sum_{\{S\}} e^{(h+Ky)\sum_i S_i} \right]}_{Q_y} \quad (7.36)$$

where

$$Q_y = \sum_{\{S\}} e^{(h+Ky)\sum_{i=1}^N S_i} = \prod_{i=1}^N \left(\sum_{S_i=\pm 1} \exp[(h+Ky)S_i] \right) = (2 \cosh(h+Ky))^N \quad (7.37)$$

Remark. y is called *auxiliary field* and is a fluctuating external field with Gaussian distribution.

The partition function becomes

$$Z_N(K, h) = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} dy e^{-\frac{NK}{2}y^2} (2 \cosh(h+Ky))^N = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} dy e^{N\mathcal{L}(K, h, y)} \quad (7.38)$$

where

$$\mathcal{L}(K, h, y) = \ln [2 \cosh(h+Ky)] - \frac{K}{2}y^2 \quad (7.39)$$

Remark. In the limit $N \rightarrow \infty$ the integral can be computed exactly by the *saddle point method*. We can replace the medium of the integral with the maximum of the integrand, we say that all the information is coming only from a bit of information. Replacing the all integral with the integrand computed where it is maximum is an approximation and we are loosing information. It also depends on the form of the function. For example, for a delta function it works better. In general:

$$\int_{-\infty}^{+\infty} f(x) dy \rightarrow f(\bar{x})$$

where $\bar{x} = \max_x f(x)$.

Indeed as $N \rightarrow \infty$, since the integrand is $\exp(N\mathcal{L}(K, h, y))$, the integral is dominated by the global maximum in y of the function $\mathcal{L}(K, h, y)$:

$$Z_N(K, h) \stackrel{N \gg 1}{\approx} \sqrt{\frac{NK}{2\pi}} \max_y \left[e^{N\mathcal{L}(K, h, y)} \right]$$

Let y_s be the value of y at which

$$\mathcal{L}(K, h, y_s) = \max_y \mathcal{L}(K, h, y)$$

hence,

$$Z_N(K, h) \stackrel{N \gg 1}{\approx} \sqrt{\frac{NK}{2\pi}} e^{N\mathcal{L}(K, h, y_s)} \quad (7.40)$$

When we are able to compute the y_s we can do this approximation and we can compute the bound free energy as

$$f_b(K, h) = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T \log Z_N) = -k_B T \mathcal{L}(K, h, y_s) \quad (7.41)$$

Example 24: How to compute y_s

Looking for y_s , we consider the condition of maximum $\frac{\partial \mathcal{L}}{\partial y} = 0$:

$$\frac{\partial \mathcal{L}}{\partial y} = \frac{\sinh(h + Ky)K}{\cosh(h + Ky)} - Ky = 0 \Rightarrow y_s = \tanh(h + Ky_s) \quad (7.42)$$

The last one is an implicit equation that can be solved graphically as a function of K and h .

The magnetization in the $N \rightarrow \infty$ limit is given by

$$\begin{aligned} m &= - \left(\frac{\partial f}{\partial H} \right)_T = \lim_{N \rightarrow \infty} \frac{1}{\beta N} \frac{\partial \ln Z_N(K, h)}{\partial H} \\ &= \frac{\partial \mathcal{L}(K, h, y_s)}{\partial h} + \frac{O(\log N)}{N} = \frac{2 \sinh(Ky_s + h)}{2 \cosh(Ky_s + h)} \\ &= \tanh(Ky_s + h) \end{aligned}$$

Hence, showing that y_s is determined by Eq.(7.42) plays the role of an effective field acting on each spin. Comparing Eq.(7.42) with the last result, gives us the self consistency condition for m

$$m \equiv y_s \Rightarrow m = \tanh(h + Km) \quad (7.43)$$

Remark. We have solved analitically this problem. This is the usual “mean field” result.

Remark. The a Hubbard-Stratonovich transformation is generally useful for transforming an interacting problem to a sum or integration over non-interacting problems.

Chapter 8

Mean field theories of phase transitions and variational mean field

8.1 Mean field theories

Increasing the dimension of the systems, the effort to solve analytically the problems increase; indeed, we have seen that

- In $d = 1$: many (simple) models can be solved exactly using techniques such as the transfer matrix method.
- In $d = 2$: few models can still be solved exactly (often with a lot of effort).
- In $d = 3$: almost no model can be exactly solved.

Hence, approximations are needed. The most important and most used one is the *mean field approximation*. It has different names depending on the system considered:

- Magnetic systems: Weiss theory.
- Fluids systems: Van der Waals.
- Polymers: Flory's theory.

The idea is trying to simplify the problem by neglecting the correlation between the fluctuations of the order parameter. It is equivalent to a statistical independence of the microscopic degrees of freedom.

8.1.1 Mean field for the Ising model (Weiss mean field)

Let us start from the generic Ising model

$$\mathcal{H}[\{S\}] = -\frac{1}{2} \sum_{ij} J_{ij} S_i S_j - H \sum_i S_i \quad (8.1)$$

where the double sum over i and j have no restrictions, while H is homogeneous.

The partition function is

$$Z_N(T, H, \{J_{ij}\}) = \sum_{\{S\}} e^{-\beta \mathcal{H}[\{S\}]} = \exp(-\beta F_N(T, H, \{J_{ij}\})) \quad (8.2)$$

Since H is uniform, the magnetization per spin is

$$\langle S_i \rangle = \langle S \rangle \equiv m$$

Let us now consider the identity

$$\begin{aligned} S_i S_j &= (S_i - m + m)(S_j - m + m) \\ &= (S_i - m)(S_j - m) + m^2 + m(S_j - m) + m(S_i - m) \end{aligned}$$

Remark. The mean field approximation consists in neglecting the term

$$(S_i - m)(S_j - m) = (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle)$$

that measures correlation between fluctuations.

Hence, using the mean field approximation, the above identity becomes

$$S_i S_j \approx m^2 + m(S_i - m) + m(S_j - m)$$

and

$$\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j \stackrel{MF}{\approx} \frac{1}{2} \sum_{i,j} J_{ij} [-m^2 + m(S_i + S_j)]$$

Let us focus on the term

$$\frac{1}{2} \sum_{i,j} J_{ij} m(S_i + S_j) = 2 \frac{1}{2} m \sum_{i,j} J_{ij} S_i \quad (8.3)$$

If we do not make any assumption on J_{ij} , the mean field Hamiltonian is

$$\mathcal{H}_{MF}[\{S\}] = \frac{1}{2} m^2 \sum_{ij} J_{ij} - m \sum_{ij} J_{ij} S_i - H \sum_i S_i \quad (8.4)$$

and by calling

$$\bar{J}_i \equiv \sum_j J_{ij}$$

we get

$$\mathcal{H}_{MF}[\{S\}] = \frac{1}{2} m^2 \sum_i \bar{J}_i - \frac{m}{2} \sum_i \bar{J}_i S_i - H \sum_i S_i$$

Remark. Note the coefficient emphasized in green (1/2) is needed to avoid the double counting of bonds.

Moreover, if we suppose that

$$\bar{J}_i \rightarrow \bar{J}$$

we have

$$\mathcal{H}_{MF}[\{S\}] = \frac{1}{2} m^2 N \bar{J} - \left(\frac{m}{2} \bar{J} + H \right) \sum_i S_i \quad (8.5)$$

Remark. In the standard Ising model, where

$$\frac{1}{2} \sum_{ij} J_{ij} S_i S_j \rightarrow \sum_{\langle ij \rangle} J_{ij} S_i S_j$$

the term $2m \sum_{\langle ij \rangle} J_{ij} S_i$ of Eq.(8.3) can be written as follows. Let

$$\sum_{j \in \text{n.n. of } i} J_{ij} = z \hat{J}_i$$

where z is the coordination number of the underlying lattice (for the hypercubic lattice $z = 2d$). By assuming $\hat{J}_i = \hat{J}$ and inserting the 1/2 to avoid double counting, we have that equation (8.3) becomes

$$2m \sum_{\langle ij \rangle} J_{ij} S_i = 2m \frac{1}{2} z \hat{J} \sum_{i=1}^N S_i \quad (8.6)$$

Hence, in this case the Hamiltonian is

$$\mathcal{H}_{MF}[\{S\}] = \frac{1}{2}m^2Nz\hat{J} - (mz\hat{J} + H)\sum_{i=1}^N S_i \quad (8.7)$$

The partition function becomes

$$\begin{aligned} Z_N(T, H, \hat{J}) &= e^{-N\beta\hat{J}\frac{z}{2}m^2} \sum_{\{S\}} e^{\beta(\hat{J}zm + H)\sum_{i=1}^N S_i} \\ &= e^{-N\beta\hat{J}\frac{z}{2}m^2} \sum_{\{S\}} \prod_{i=1}^N \exp\left(\beta(\hat{J}zm + H)S_i\right) \\ &= e^{-N\beta\hat{J}\frac{z}{2}m^2} \left(\sum_{S=\pm 1} \exp\left(\beta(\hat{J}zm + H)S\right) \right)^N \\ &= e^{-N\beta\hat{J}\frac{z}{2}m^2} \left(2 \cosh\left[\beta(\hat{J}zm + H)\right] \right)^N \end{aligned} \quad (8.8)$$

Remark. We are replacing the interaction of the J with a field close to the S_i . We called $\hat{J}zm = H_{eff}$, the mean field!

The free energy per spin is

$$\begin{aligned} \frac{F_N(T, H, \hat{J})}{N} &= \frac{1}{N} \left(-k_B T \ln Z_N(T, H, \hat{J}) \right) \\ &= \frac{1}{2}\hat{J}zm^2 - k_B T \ln \left[\cosh\left(\beta(\hat{J}zm + H)\right) \right] - k_B T \ln 2 \end{aligned} \quad (8.9)$$

Sometimes it is useful to use the *dimensionless variables* defined as

$$\bar{f} \equiv \frac{F_N}{Nz\hat{J}}, \quad \theta \equiv \frac{k_B T}{z\hat{J}}, \quad \bar{H} \equiv \frac{H}{z\hat{J}} \quad (8.10)$$

Hence,

$$\bar{f}(m, \bar{H}, \theta) = \frac{1}{2}m^2 - \theta \ln \left(2 \cosh(\theta^{-1}(m + \bar{H})) \right) \quad (8.11)$$

In order to be a self-consistent, the last equation has to satisfy the thermodynamic relation:

$$m = - \left(\frac{\partial f}{\partial H} \right)_T \Rightarrow m = \tanh\left(\beta(\hat{J}zm + H)\right)$$

Remark. The results of m is similar to the Ising with infinite range ($\hat{J}z \leftrightarrow J$).

Now, let us consider the $H = 0$ case, we have

$$m = \tanh\left(\beta(\hat{J}zm)\right) \quad (8.12)$$

and the graphical solution is shown in Figure 8.1 (hyperbolic function). We can distinguish three cases:

- Case $\beta\hat{J}z > 1$: there are three solutions, one at $m = 0$ and two symmetric at $m = \pm m_0$. Magnetization is $\neq 0$ ($= |m_0|$) for $H = 0$ (*ordered phase*). The two solution are symmetric because they are related by the \mathbb{Z}^2 symmetry.
- Case $\beta\hat{J}z < 1$: single solution at $m = 0$ (*disordered or paramagnetic phase*).
- Case $\beta\hat{J}z = 1$: the three solutions coincide at $m = 0$ (*critical point*). The critical temperature T_c is given by

$$\beta_c \hat{J}z = 1 \Rightarrow \frac{z\hat{J}}{k_B T_c} = 1 \Rightarrow T_c = \frac{z\hat{J}}{k_B} \neq 0!$$

Remark. T_c depends on z and hence on d !

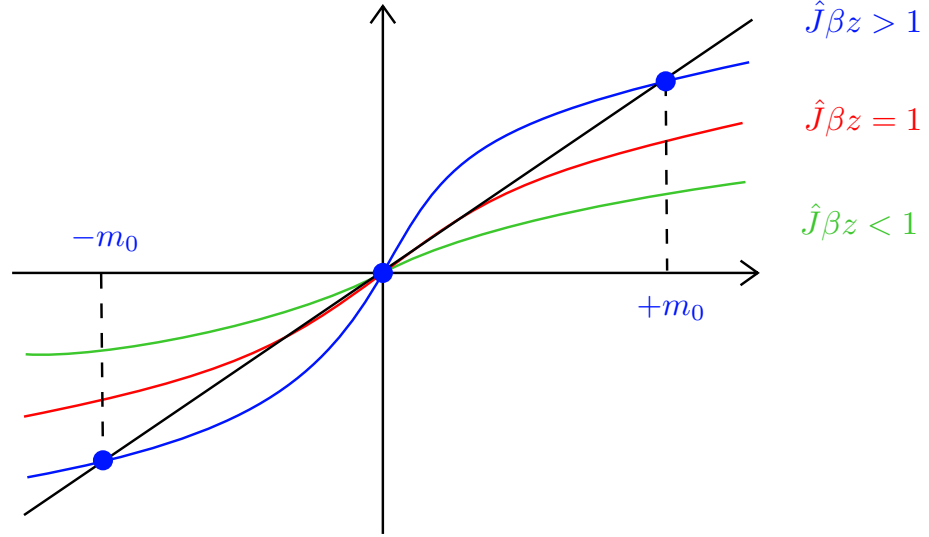


Figure 8.1: Graphical solution of equation $m = \tanh(\beta(\hat{J}zm))$ (case $H = 0$).

8.1.2 Free-energy expansion for $m \simeq 0$

The critical point is characterized by the order parameter that is zero. Now, we want to expand the free energy around the critical point. Let us put $H = 0$:

$$f(m, 0, T, \hat{J}) = \frac{1}{2} \hat{J} z m^2 - k_B T \ln [\cosh(\beta(\hat{J} z m))] \quad (8.13)$$

Define $x \equiv \beta \hat{J} z m \simeq 0$ and by expanding in Taylor series

$$\cosh(x) \simeq 1 + \underbrace{\frac{x^2}{2} + \frac{x^4}{4!}}_{t \simeq 0} + \dots$$

$$\log(1+t) \simeq t - \frac{1}{2} t^2$$

Hence,

$$\log(\cosh x) \simeq \frac{x^2}{2} + \frac{x^4}{4!} - \frac{1}{2} \frac{x^4}{4} + O(x^6) = \frac{x^2}{2} - \frac{x^4}{12} + O(x^6)$$

This gives the result

$$f(m, 0, T, \hat{J}) \simeq \text{const} + \frac{A}{2} m^2 + \frac{B}{4} m^4 + O(m^6) \quad (8.14)$$

with

$$A \equiv \hat{J} z (1 - \beta \hat{J} z) \quad (8.15a)$$

$$B \equiv \beta^2 \frac{(\hat{J} z)^4}{3} > 0 \quad (8.15b)$$

We have three cases:

- Case $\beta \hat{J} z > 1 \Rightarrow A < 0$: two stable symmetric minima at $m = \pm m_0$ (Figure 8.2). Coexistence between the two ordered phases.
- Case $\beta \hat{J} z < 1 \Rightarrow A > 0$: one minimum at $m = 0$ (Figure 8.3).

- Case $\beta\hat{J}z = 1 \Rightarrow A = 0$: 3 minima coincide at $m = 0$ (Figure 8.4).

Remark. Note that in the computations we have just made we have never imposed a particular value for the dimensionality of the system. This means that the results of this approximation should be valid also for $d = 1$, but we know that in one dimension the Ising model does not exhibit a phase transition. This is an expression of the fact that in the one-dimensional case mean field theory is not a good approximation (again, the dimensionality of the system is still too low).

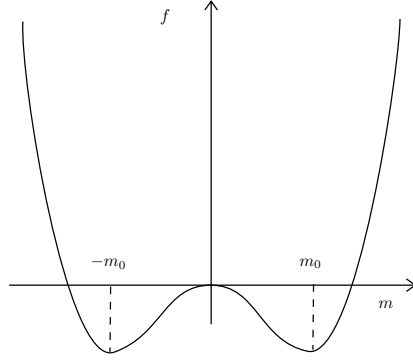


Figure 8.2: Plot of the free energy: case $\beta\hat{J}z > 1 \Rightarrow A < 0$.

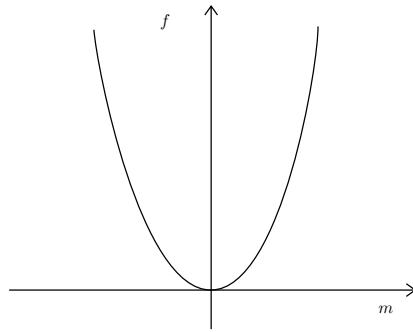


Figure 8.3: Plot of the free energy: case $\beta\hat{J}z < 1 \Rightarrow A > 0$.

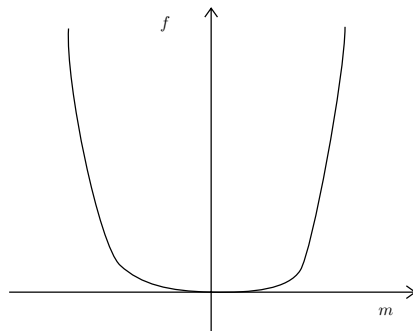


Figure 8.4: Plot of the free energy: case $\beta\hat{J}z = 1 \Rightarrow A = 0$.

8.1.3 Mean field critical exponents

Let us consider the equation

$$f(m, T, 0) \approx \text{const} + \frac{A}{2}m^2 + \frac{B}{4}m^4 + O(m^6)$$

Lecture 12.
 Friday 22nd
 November, 2019.
 Compiled: Friday
 31st January, 2020.

with $B > 0$, so we do not need more term to find the minima of the solution. This is called stabilization. What is most important is the coefficient $A = \hat{J}z(1 - \beta\hat{J}z)$, that means that A can change sign.

β exponent

The β exponential observe the order parameter. Consider $H = 0$, $t \equiv \frac{T-T_c}{T_c}$ and $m \stackrel{t \rightarrow 0^-}{\sim} -t^\beta$. The condition of equilibrium is

$$\frac{\partial f}{\partial m} = 0$$

which implies

$$\left. \frac{\partial f}{\partial m} \right|_{m=m_0} = Am_0 + Bm_0^3 = [\hat{J}z(1 - \beta\hat{J}z) + Bm_0^2]m_0 = 0$$

Since at the critical point we have $T_c = \frac{\hat{J}z}{k_B}$:

$$0 = \frac{k_B T_c}{T}(T - T_c)m_0 + Bm_0^3$$

The solution are $m_0 = 0$ and

$$m_0 \simeq (T_c - T)^{1/2} \quad (8.16)$$

Hence, the mean field value is $\beta = 1/2$.

δ exponent

Now, let us concentrate in the δ exponent. We are in the only case in which we are in $T = T_c$ and we want to see how the magnetization decrease: $H \sim m^\delta$.

Starting from the self-consistent equation, we have

$$m = \tanh(\beta(\hat{J}zm + H)) \quad (8.17)$$

Inverting it

$$\beta(\hat{J}zm + H) = \tanh^{-1} m$$

On the other hand, for $m \sim 0$

$$\tanh^{-1} m \simeq m + \frac{m^3}{3} + \frac{m^5}{5} + \dots$$

Therefore, by substituting

$$\begin{aligned} H &= k_B T \left(m + \frac{m^3}{3} + \dots \right) - \hat{J}zm = (k_B T - \hat{J}z)m + k_B T \frac{m^3}{3} + \dots \\ &\simeq k_B (T - T_c)m + \frac{k_B T}{3} m^3 \end{aligned}$$

At $T = T_c = \frac{\hat{J}z}{k_B}$, we have

$$H \sim k_B T_c \frac{m^3}{3} \quad (8.18)$$

The mean field value is $\delta = 3$.

α exponent

Consider the α exponent, for $H = 0$, $c_H \sim t^{-\alpha}$ and $t = (T - T_c)/T_c$. Compute the specific heat at $H = 0$. Consider first $T > T_c$, where $m_0 = 0$,

$$f(m, H) = \frac{\hat{J}zm^2}{2} - \frac{1}{\beta} \ln \left(2 \cosh \left(\beta(\hat{J}zm + H) \right) \right) - k_B T \ln 2$$

If $m = 0$, $\cosh 0 = 1$ and

$$f = -k_B T \ln 2$$

it is called paramagnetic phase. Indeed,

$$c_H = -T \left(\frac{\partial^2 f}{\partial T^2} \right) = 0 \quad (8.19)$$

The mean field value is $\alpha = 0$.

Remark. For $T < T_c$, $m = m_0 \neq 0$. This implies that $c_H \neq 0$, but still $f = -k_B T \ln A$ with $A = \text{const}$. We obtain $\alpha = 0$ also in this case.

$$m_0 = \pm \sqrt{-\frac{\hat{J}z}{2T_c}(T - T_c)}$$

 γ exponent

Now we consider the γ exponent, for $H = 0$, $\chi \sim t^{-\gamma}$. Starting again from equation (8.17):

$$m = \tanh \left(\beta(\hat{J}zm + H) \right)$$

and developing it around $m \simeq 0$, as shown before we get

$$H = mk_B(T - T_c) + \frac{k_B T}{3} m^3$$

$$\Rightarrow \chi_T = \frac{\partial m}{\partial H} = \frac{1}{\frac{\partial H}{\partial m}}$$

Since $\frac{\partial H}{\partial m} \simeq k_B(T - T_c) + K_B T m^2$, as $m \rightarrow 0$

$$\chi \sim (T - T_c)^{-1} \quad (8.20)$$

The mean field value is $\gamma = 1$.

Summary

The mean field critical exponents are

$$\beta = \frac{1}{2}, \quad \gamma = 1, \quad \delta = 3, \quad \alpha = 0 \quad (8.21)$$

We can immediately note that these exponents are different from those found by Onsager for the Ising model in two dimensions, so the mean field theory is giving us wrong predictions. This is because mean field theories are good approximations only if the system has a high enough dimensionality (and $d = 2$ is still too low for the Ising model, see Coarse graining procedure for the Ising model).

Remark. In the mean field critical exponents the dimension d does not appear. T_c instead depends on the number of z of nearest neighbours and hence on the embedding lattice (on the dimension)!

Remark. (lesson) The ν exponent define the divergence of the correlation lengths. In order to do that, in principle we should compute the correlation function, but which are the correlation we are talking about? The correlation or the fluctuation with respect to the average? In the ferromagnetic we have infinite correlation lengths, but it is not true, because instead of that we consider the variation correlated! Which is the problem here? In mean field we were neglecting correlation between fluctuation. We thought: let us compute neglecting correlation. How we can compute the correlation function within the mean field theory with thermal fluctuations? We look at the response of the system. Experimentally what can we do? It is a magnetic field, but we cannot use homogeneous magnetic field. Another way to compute the correlation function without looking at thermal fluctuation it is by considering a non homogeneous magnetic field. If we make a variation in H_i in the system, what happened in the H_j ? This is an important point.

8.2 Mean field variational method

The mean field variational method is a general approach to derive a mean field theory. The method is valid for all T and is sufficiently flexible to deal with complex systems. The method is similar to the one used in quantum mechanics, namely it is based on the following inequality

$$E_\alpha = \langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle \geq E_0 \quad (8.22)$$

valid for all trial function ψ_α .

Remark. E_0 is the ground state energy.

Example 25

In many body problem we have Hartree and Hartree-Fock variational methods.

The closest bound to E_0 is the one that is obtained by minimizing E_α , i.e. $\langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle$ over $|\psi_\alpha\rangle$, where the $|\psi_\alpha\rangle$ are functions to be parametrized in some convenient way.

The method is based on the following inequalities

1. Let Φ be a random variable (either discrete or continuous) and let $f(\Phi)$ be a function of it.

For all function f of Φ , the mean value with respect to a distribution function $p(\Phi)$ is given by

$$\langle f(\Phi) \rangle_p \equiv \text{Tr}(p(\Phi)f(\Phi)) \quad (8.23)$$

If we consider the function

$$f(\Phi) = \exp[-\lambda\Phi] \quad (8.24)$$

it is possible to show the inequality

$$\langle e^{-\lambda\Phi} \rangle_p \geq e^{-\lambda\langle\Phi\rangle_p}, \quad \forall p \quad (8.25)$$

Proof of inequality (8.25). $\forall \Phi \in \mathbb{R}$, $e^\Phi \geq 1 + \Phi$. Hence,

$$e^{-\lambda\Phi} = e^{-\lambda\langle\Phi\rangle} e^{-\lambda[\Phi - \langle\Phi\rangle]} \geq e^{-\lambda\langle\Phi\rangle} (1 - \lambda(\Phi - \langle\Phi\rangle))$$

Taking the average of both sides, we get

$$\rightarrow \langle e^{-\lambda\Phi} \rangle_p \geq \langle (1 - \lambda(\Phi - \langle\Phi\rangle)) e^{-\lambda\langle\Phi\rangle} \rangle_p = e^{-\lambda\langle\Phi\rangle_p}$$

■

2. The second inequality refers to the free energy. Let $\rho(\Phi)$ be a probability distribution, i.e. such that

$$\text{Tr}(\rho(\Phi)) = 1, \quad \rho(\Phi) \geq 0 \quad \forall \Phi \quad (8.26)$$

Hence,

$$e^{-\beta F_N} = Z_N = \text{Tr}_{\{\Phi\}} e^{-\beta \mathcal{H}[\{\Phi\}]} = \text{Tr}_{\{\Phi\}} \rho e^{-\beta \mathcal{H} - \ln \rho} = \left\langle e^{-\beta \mathcal{H} - \ln \rho} \right\rangle_{\rho}$$

From the inequality (8.25),

$$e^{-\beta F_N} = \left\langle e^{-\beta \mathcal{H} - \ln \rho} \right\rangle_{\rho} \geq e^{-\beta \langle \mathcal{H} \rangle_{\rho} - \langle \ln \rho \rangle_{\rho}}$$

Taking the logs one has

$$F \leq \langle \mathcal{H} \rangle_{\rho} + k_B T \langle \ln \rho \rangle_{\rho} = \text{Tr}(\rho \mathcal{H}) + k_B T \text{Tr}(\rho \ln \rho) \equiv F_{\rho} \quad (8.27)$$

Whenever we are able to write the last equation by using a ρ , then we will minimize it. This is the variational approach of statistical mechanics. The question is: which is the ρ that minimizes?

The functional F_{ρ} will reach its minimum value with respect to the variation of ρ with the constraint $\text{Tr}(\rho) = 1$, when

$$\bar{\rho} = \rho_{eq} = \frac{1}{Z} e^{-\beta \mathcal{H}} \quad (8.28)$$

So far so good but not very useful, since we are back to the known result that the distribution that best approximates the free energy of the canonical ensemble is given by the Gibbs-Boltzmann distribution. To compute ρ_{eq} , we need some approximation!

8.2.1 Mean field approximation for the variational approach

Let us now try to compute the Z by starting from the inequality (8.27). Up to now everything is exact. The idea is to choose a functional form of ρ and then minimize F_{ρ} with respect to ρ . Note that ρ is the N -point probability density function (it is a function of all the degrees of freedom):

$$\rho = \rho(\Phi_1, \dots, \Phi_N)$$

it is a N -body problem, where Φ_{α} is the random variables associated to the α -sim degree of freedom. This is in general a very difficult distribution to deal with. This is equivalent exactly at

$$\psi_{\alpha}(\vec{\mathbf{r}}_1, \vec{\mathbf{P}}_1, \dots, \vec{\mathbf{r}}_N, \vec{\mathbf{P}}_N)$$

The mean-field approximation consists in factorising ρ into a product of 1-point distribution function:

$$\rho(\Phi_1, \dots, \Phi_N) \stackrel{MF}{\simeq} \prod_{\alpha=1}^N \rho^{(1)}(\Phi_{\alpha}) \equiv \prod_{\alpha=1}^N \rho_{\alpha} \quad (8.29)$$

where we have used the short-hand notation $\rho^{(1)}(\Phi_{\alpha}) \rightarrow \rho_{\alpha}$.

Remark. Approximation (8.29) is equivalent to assume statistical independence between particles (or more generally between different degrees of freedom). The independence of the degree of freedom is a very strong assumption!

Example 26

Let us consider the spin model on a lattice; what is the Φ_α ? We have:

$$\Phi_\alpha \rightarrow S_i$$

Hence, $\rho = \rho(S_1, S_2, \dots, S_N)$ and (8.29) becomes

$$\rho \stackrel{MF}{\simeq} \prod_{i=1}^N \rho^{(1)}(S_i) \equiv \prod_{i=1}^N \rho_i$$

With Eq.(8.29) and the condition $\text{Tr}(\rho_\alpha) = 1$, we compute the two averages in the Eq.(8.27) given the field. We have:

$$\text{Tr}_{\{\Phi\}}(\rho \ln \rho) = \text{Tr} \left(\prod_{\alpha} \rho_{\alpha} \left(\sum_{\alpha} \ln \rho_{\alpha} \right) \right) \stackrel{\text{to do}}{=} \sum_{\alpha} \text{Tr}^{(\alpha)}(\rho_{\alpha} \ln \rho_{\alpha}) \quad (8.30)$$

where $\text{Tr}^{(\alpha)}$ means sum over all possible values of the random variable Φ_α (with α fixed and $\text{Tr}^{(\alpha)} \rho_{\alpha} = 1$).

We end up that

$$F_{\rho_{MF}} = \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \sum_{\alpha} \text{Tr}^{(\alpha)}(\rho_{\alpha} \ln \rho_{\alpha}) \quad (8.31)$$

Remark. $F_{\rho_{MF}} = F(\{\rho_{\alpha}\})$ and we have to minimize it with respect to ρ_{α} .

How can we parametrize ρ_{α} ? There are two approaches that are mostly used:

1. Parametrize $\rho_{\alpha} \equiv \rho^{(1)}(\Phi_{\alpha})$ by the average of Φ_{α} with respect to ρ_{α} , $\langle \Phi_{\alpha} \rangle_{\rho_{\alpha}}$ (in general is the local order parameter):

$$\rho_{\alpha} = \rho^{(1)}(\Phi_{\alpha}) \rightarrow \langle \Phi_{\alpha} \rangle_{\rho_{\alpha}}$$

This means that there are two constraints in the minimization procedure:

$$\text{Tr}^{(\alpha)} \rho_{\alpha} = 1, \quad \text{Tr}^{(\alpha)}(\rho_{\alpha} \Phi_{\alpha}) = \langle \Phi_{\alpha} \rangle$$

where the second is the self-consistent equation.

Remark. In this case the variational parameter coincides with the order parameter.

2. In the second approach is ρ_{α} itself the variational parameter. $F_{\rho_{MF}}$ is minimized by varying ρ_{α} . It is a more general approach, that involves functional minimization.

8.2.2 First approach: Bragg-Williams approximation

We apply this approach to the Ising model with non uniform magnetic field. The Hamiltonian of such a system is

$$\mathcal{H}[\{S\}] = -J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i \quad (8.32)$$

It means that

$$\Phi_{\alpha} \rightarrow S_i = \pm 1$$

and that the variational parameter becomes the order parameter

$$\langle \Phi_{\alpha} \rangle \rightarrow \langle S_i \rangle \equiv m_i$$

Remark. Note that this time $H \rightarrow H_i$ (non-uniform), hence m_i depends on the site i .

We have to define a 1-particle probability density distribution $\rho_i \equiv \rho^{(1)}(S_i)$ such that

$$\rho_i \equiv \rho^{(1)}(S_i) \rightarrow \begin{cases} \text{Tr } \rho_i = 1 \\ \text{Tr } \rho_i S_i = m_i \end{cases} \quad (8.33)$$

Since we have to satisfy these two constraints, we need two free parameters. A linear functional form is sufficient. Denoting by:

- a : statistical weight associated to the value $S_i = -1$.
- b : statistical weight associated to all the remaining possible values of S_i (for an Ising only one value remains, i.e. $S_i = +1$).

The simplest function form with two parameters is the linear function, namely

$$\rho_i \equiv \rho^{(1)}(S_i) = a(1 - \delta_{S_i,1}) + b\delta_{S_i,1} \quad (8.34)$$

Using the constraints

$$\begin{cases} \text{Tr}^{(i)}(\rho_i) = 1 & \rightarrow a + b = 1 \\ \text{Tr}^{(i)}(\rho_i S_i) = m_i & \rightarrow a - b = m_i \end{cases}$$

where a, b are the functions of the order parameter. In that case we have not to write the functions for all the i . For $S_i = 1$ we have one value, for all the other values another one. The results of the previous equation are:

$$\begin{cases} a = \frac{1-m_i}{2} \\ b = \frac{1+m_i}{2} \end{cases}$$

Hence,

$$\rho_i = \frac{1-m_i}{2}(1 - \delta_{S_i,1}) + \frac{1+m_i}{2}\delta_{S_i,1} \quad (8.35)$$

that in matrix form can be expressed as

$$\rho_i = \begin{pmatrix} \frac{(m_i+1)}{2} & 0 \\ 0 & \frac{(1-m_i)}{2} \end{pmatrix} \quad (8.36)$$

Mean field energy term

Let us consider the average of the Hamiltonian

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = \left\langle -J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i \right\rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_{\rho_{MF}} - \sum_i H_i \langle S_i \rangle_{\rho_{MF}} \quad (8.37)$$

Since we have

$$\rho_{MF} = \prod_{i=1}^N \rho_i$$

the term $\langle S_i S_j \rangle_{\rho_{MF}}$ will transform into

$$\langle S_i S_j \rangle_{\rho_{MF}} = \langle S_i \rangle_{\rho_{MF}} \langle S_j \rangle_{\rho_{MF}}$$

Lecture 13.
Wednesday 27th
November, 2019.
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Moreover, for all function g of S_i we can write

$$\begin{aligned}\langle g(S_i) \rangle_{\rho_{MF}} &= \text{Tr}^{(i)}(g(S_i)\rho_i) = \sum_{S_i=\pm 1} g(S_i)\rho_i \\ &= \sum_{S_i=\pm 1} g(S_i) \left[\frac{1+m_i}{2} \delta_{S_i,1} + \frac{1-m_i}{2} (1 - \delta_{S_i,1}) \right] \\ &= \frac{1+m_i}{2} g(1) + \frac{1-m_i}{2} g(-1)\end{aligned}$$

Note that, if $g(S_i) = S_i$, we have $g(1) = +1$ and $g(-1) = -1$, hence

$$\langle S_i \rangle_{\rho_{MF}} = m_i$$

as expected. Taken this into account, the Hamiltonian can be rewritten as

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} m_i m_j - \sum_i H_i m_i \quad (8.38)$$

Remark. This has the form of the original Hamiltonian where S_i had been replaced by their statistical averages.

The entropy term is:

$$\begin{aligned}\langle \ln \rho \rangle_{\rho_{MF}} &= \text{Tr}(\rho \ln \rho) \stackrel{MF}{=} \sum_i \text{Tr}^{(i)}(\rho_i \ln \rho_i) \\ &= \sum_i \left[\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right]\end{aligned} \quad (8.39)$$

The total free energy in Eq.(8.27) becomes:

$$\begin{aligned}F_{\rho_{MF}} &= \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \langle \ln \rho \rangle_{\rho_{MF}} \\ &= -J \sum_{\langle ij \rangle} m_i m_j - \sum_i H_i m_i + k_B T \sum_i \left[\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right]\end{aligned} \quad (8.40)$$

We now look for the values $m_i = \bar{m}_i$, that minimizes $F_{\rho_{MF}}$ (equilibrium phases):

$$\left. \frac{\partial F_{\rho_{MF}}}{\partial m_i} \right|_{m_i=\bar{m}_i} = 0$$

This gives:

$$0 = -J \sum_{j \in n.n. \text{ of } i} \bar{m}_j - H_i + \frac{k_B T}{2} \ln \left[\frac{1+\bar{m}_i}{1-\bar{m}_i} \right]$$

To solve it, remember that

$$\tanh^{-1}(x) = \frac{1}{2} \ln \frac{1+x}{1-x} \quad |x| < 1$$

Hence,

$$k_B T \tanh^{-1}(\bar{m}_i) = J \sum_{j \in n.n. \text{ of } i} \bar{m}_j + H_i$$

which implies

$$\bar{m}_i = \tanh \left[(k_B T)^{-1} \left(J \sum_{j \in n.n. \text{ of } i} \bar{m}_j + H_i \right) \right]$$

We have again found the self-consistency equation for the magnetization that we have already encountered in the Weiss mean field theory for the Ising model! This is again a confirmation that all mean field theories are equivalent. Defining

$$zm_i \equiv \sum_{j \in \text{n.n. of } i} m_j$$

we get

$$m_i = \tanh [\beta(Jzm_i + H_i)] \quad (8.41)$$

this is the Bragg-William approximation.

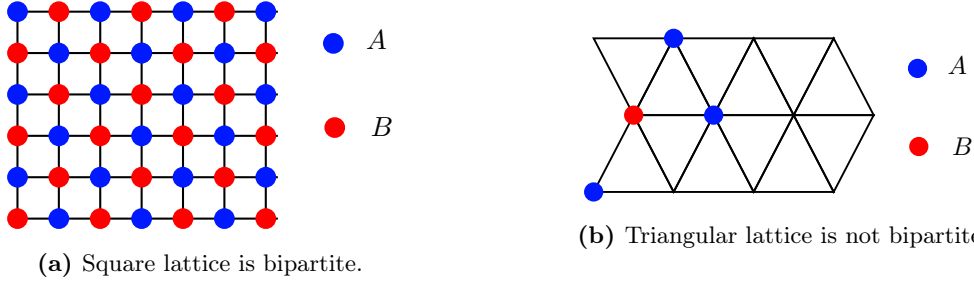


Figure 8.5: Ising anti-ferromagnet in an external field.

Example 27: Ising anti-ferromagnet in an external field

Let us consider the model

$$\mathcal{H} = +J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i, \quad (8.42)$$

Note the + sign before J , this means that the interactions are anti-ferromagnetic. Let us consider two cases:

- If $H = 0$ ferromagnetic and anti-ferromagnetic behave similarly when the interactions are between nearest neighbours on a *bipartite lattice*, i.e. a lattice that can be divided into two sublattices, say A and B , such that a A site has only B neighbours and a B site only A ones.

Remark. FCC is not bipartite, while BCC it is. See Figure 8.5.

If the lattice is bipartite and J_{ij} is non zero only when i and j belong to different sublattices (they do not have to be only n.n.), one can redefine the spins such that

$$S'_j = \begin{cases} +S_j & j \in A \\ -S_j & j \in B \end{cases}$$

Clearly, $S'_i S'_j = -S_i S_j$. It is like if the J_{ij} have changed sign and we are formally back to ferromagnetic model for the two sublattices:

$$\mathcal{H}^* = -J \sum_{\langle ij \rangle} S'_i S'_j \quad (8.43)$$

i.e. a ferromagnetic Ising.

- In presence of a magnetic field H , we need to reverse its sign when applied to sites B .

The thermodynamic of a ferromagnetic Ising model on a bipartite lattice in a uniform magnetic field H is identical to the one of the Ising antiferromagnetic model in presence of the so called *staggered field*, i.e. $H_A = H$ and $H_B = -H$. The Hamiltonian is

$$\mathcal{H}^*[S] = -J \sum_{\langle r_A r_B \rangle} S(r_A)S(r_B) - H \sum_{r_A} S(r_A) + H \sum_{r_B} S(r_B), \quad J > 0, H > 0 \quad (8.44)$$

The average magnetization per spin is

$$m \equiv \frac{1}{2}(m_A + m_B)$$

while

$$m_S = \frac{1}{2}(m_A - m_B)$$

is the *staggered magnetization*.

In order to use the variational density matrix method for this problem we consider two independent variational parameters m_A and m_B for sublattice A and B respectively. On each sublattice, the model is like the standard Ising

$$\begin{cases} \rho_A^{(1)}(S) = \frac{1+m_A}{2}\delta_{S,1} + \frac{1-m_A}{2}\delta_{S,-1} \\ \rho_B^{(1)}(S) = \frac{1+m_B}{2}\delta_{S,1} + \frac{1-m_B}{2}\delta_{S,-1} \end{cases}$$

Remark. Note that, being H uniform, $\langle S_i \rangle = m$, i.e. does not depend on i . Same for the 1-particle distribution functions $\rho_A^{(1)}(S)$ and $\rho_B^{(1)}(S)$.

By performing the calculation for the terms

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_{\rho_{MF}} - H \sum_i \langle S_i \rangle_{\rho_{MF}}$$

$$\langle \ln \rho \rangle_{\rho_{MF}} = \sum_i \text{Tr}^{(i)}(\rho_i \ln \rho_i)$$

as before, but remembering to partition the procedure into the two sublattices A and B , one can show that the variational free energy is given by

$$\frac{F(m_A, m_B)}{N} = \frac{z\hat{J}}{2}m_A m_B - \frac{1}{2}H(m_A + m_B) - \frac{1}{2}k_B T s(m_A) - \frac{1}{2}k_B T s(m_B) \quad (8.45)$$

where the entropy term is

$$s(m) = \left[\frac{1+m}{2} \ln \left(\frac{1+m}{2} \right) + \frac{1-m}{2} \ln \left(\frac{1-m}{2} \right) \right]$$

By differentiating $\frac{F}{N}$ with respect to m_A and m_B , one gets

$$\begin{aligned} \frac{\partial(F/N)}{\partial m_A} = 0 & \Rightarrow m_B = \frac{H}{z\hat{J}} - \frac{k_B T}{z\hat{J}} \ln \left(\frac{1+m_A}{1-m_A} \right) \\ \frac{\partial(F/N)}{\partial m_B} = 0 & \Rightarrow m_A = \frac{H}{z\hat{J}} - \frac{k_B T}{z\hat{J}} \ln \left(\frac{1+m_B}{1-m_B} \right) \end{aligned}$$

As before, since

$$\tanh^{-1}(x) = \frac{1}{2} \ln \frac{1+x}{1-x}$$

these self-consistent equations can be written as

$$\begin{cases} m_A = \tanh\left(\beta\left(H - z\hat{J}m_B\right)\right) \\ m_B = \tanh\left(\beta\left(H - z\hat{J}m_A\right)\right) \end{cases} \quad (8.47)$$

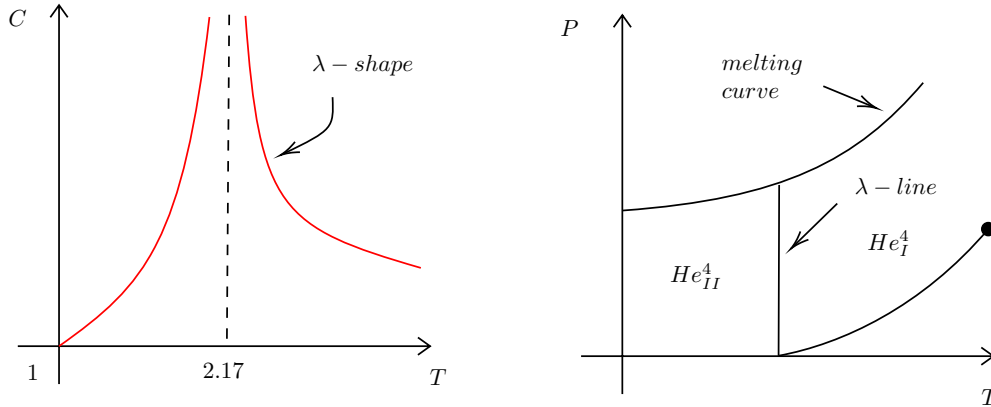
The sites $\in A$ experience an internal field $H_{A,MF} = -z\hat{J}m_B$ from the B neighbours and vice versa for the sites $\in B$.

8.2.3 Second approach: Blume-Emery-Griffith model

We apply this approach to the so called *Blume-Emery-Griffith model*. This is a spin model with vacancies that describes the phase diagram and the critical properties of an interacting system displaying a *tricritical point*. Perhaps the most famous of these systems is the $\text{He}^3 - \text{He}^4$ mixture undergoing a fluid-superfluid transition.

Remark. He^4 is a non radiative isotope with two protons and two neutrons. Roughly 1/4 of the universe matter is He^4 ! From a quantum statistical point of view He^4 is a *boson*.

A gas of He^4 undergoes a fluid-superfluid transition at $T_\lambda = 2.17\text{K}$ and $P = P_0$. It is known as λ -transition since at $T \sim T_\lambda$ the specific heat $c(T)$ behaves as in Figure 8.6a: the plot of the specific heat as a function of the temperature has a shape that resembles a λ . The λ -transition is a genuine critical point (second order). For $T < T_\lambda$, He^4 is in the superfluid phase and it can be described by a two-fluids model in which one component has zero viscosity and zero entropy.



(a) Plot of the specific heat $c(T)$. It has the shape of a λ .

(b) (P, T) phase diagram.

Figure 8.6

The BEG model is used to describe what happens when we add some He^3 to the system constituted by He^4 ; it does not consider quantum effects, but only the "messing up" due to the He^3 impurities.

Remark. He^3 is a non-radioactive isotope with 2 protons and 1 neutron. From a quantum statistical point of view is a *fermion*.

Experimentally when He^3 is added to He^4 the temperature of the fluid-superfluid transition decreases. More specifically, if inserted in a system of He^4 it will "dilute"

its bosonic property. Then, one expects that T_λ decreases, as observed. Denoting by x the concentration of He^3 , one observes

$$T_\lambda = T_\lambda(x)$$

with $T_\lambda(x)$ that decreases as x increases.

For small concentration of He^3 the mixture remains homogeneous, and the only effect is the change of T_λ . However, when the concentration x of He^3 reaches the critical value x_t

$$x > x_t = \frac{n_3}{n_3 + n_4} \sim 0.67$$

He^3 and He^4 separate into two phases (just like oil separates from water, the mixture undergoes a separation between a phase rich and a phase poor of He^3) and the λ transition becomes first-order (namely, discontinuous). The transition point (x_t, T_t) where the system shifts from a continuous λ -transition to a discontinuous one is that where the phase separation starts and is called tricritical point (i.e. it is a critical point that separates a line of second order transition from a line of first order transition). The BEG model was introduced to describe such a situation.

BEG Model

As we have anticipated, the BEG Model is a lattice gas model and so it is based on an Ising-like Hamiltonian. In particular, it is the model of a diluted ferromagnetic system. On the sites of this lattice we define a variable S_i which can assume the values $-1, 0$ and $+1$: we decide that when an He^4 atom is present in a lattice site then $S_i = \pm 1$, while when $S_i = 0$ it means that the site is occupied by an He^3 atom. We then define our order parameter to be

$$\langle S_i \rangle = m_i$$

In the Ising model $\langle S_i^2 \rangle$ can only be equal to 1, while in this case it can be either 0 or 1: we can thus interpret $\langle S_i^2 \rangle$ as the concentration of He^4 atoms, and

$$x \equiv 1 - \langle S_i^2 \rangle$$

as the fraction of He^3 . We also define

$$\Delta \propto \mu_{\text{He}^3} - \mu_{\text{He}^4}$$

to be the difference of the chemical potentials of He^3 and He^4 ; since this parameter is related to the number of He^3 and He^4 atoms, we expect that when

- $x \rightarrow 0$ (namely, there is only He^4), we have $\Delta \rightarrow -\infty$.
- $x \rightarrow 1$ (namely, there is only He^3), we have $\Delta \rightarrow +\infty$.

and the order parameter for the λ -transition becomes

$$\langle S_i \rangle = \begin{cases} 0 & T > T_\lambda \\ m & T < T_\lambda \end{cases}$$

We consider the following Hamiltonian for the system:

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j + \Delta \sum_{i=1}^N S_i^2 - \Delta N \quad (8.48)$$

Remark. N is the total number of lattice sites. The ΔN term is a typical term for a gas in grand canonical ensemble.

Variational mean field approach to BEG

Since we want to apply the second variational method that we have seen, we write the mean field probability density as:

$$\rho_{MF} = \prod_i \rho_i = \prod_i \rho(S_i)$$

and the free energy:

$$G(T, J, \Delta) = \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \sum_i \text{Tr}(\rho_i \ln \rho_i) \quad (8.49)$$

The mean value of the Hamiltonian is:

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle + \Delta \sum_i \langle S_i^2 \rangle - N\Delta$$

and since $\langle S_i S_j \rangle = \langle S_i \rangle \langle S_j \rangle$ (it's the fundamental hypothesis of mean field theories) we get

$$\langle \mathcal{H} \rangle_{\rho_{MF}} \stackrel{MF}{\simeq} -J \sum_{\langle ij \rangle} \langle S_i \rangle \langle S_j \rangle + \Delta \sum_i \langle S_i^2 \rangle - N\Delta$$

We have also

$$\langle S_i \rangle = \langle S_j \rangle \equiv m$$

Therefore, the free energy of the system is:

$$G(T, J, \Delta)_{MF} = -\frac{1}{2} N J z (\text{Tr}_{S_i}(\rho_i S_i))^2 + N \Delta \text{Tr}_{S_i}(\rho_i S_i^2) - N \Delta + N k_B T \text{Tr}_{S_i}(\rho_i \ln \rho_i) \quad (8.50)$$

where z is the coordination number of the lattice.

We now must minimize this expression with respect to ρ_i , with the constraint $\text{Tr}_{S_i}(\rho_i) = 1$:

$$\frac{dG}{d\rho_i} = 0$$

Let us consider each term

$$\begin{aligned} \frac{d}{d\rho_i} (\text{Tr}(\rho_i S_i))^2 &= 2(\text{Tr}(\rho_i S_i)) S_i = 2 \langle S_i \rangle S_i = 2m S_i \\ \frac{d}{d\rho_i} (\text{Tr}(\rho_i S_i^2)) &= S_i^2 \\ \frac{d}{d\rho_i} (\text{Tr}(\rho_i \ln \rho_i)) &= \ln \rho_i + 1 \end{aligned}$$

then,

$$\frac{dG}{d\rho_i} = -J N z m S_i + N \Delta S_i^2 + N k_B T \ln \rho_i + N k_B T = 0$$

Dividing by $N k_B T$,

$$\ln \rho_i \equiv \ln \rho^{(1)}(S_i) = \beta J z m S_i - \beta \Delta S_i^2 - 1$$

which leads to

$$\rho^{(1)}(S_i) = \frac{1}{A} e^{\beta(z J m S_i - \Delta S_i^2)} \quad (8.52)$$

where we have reabsorbed e^{-1} into the normalization constant A . The constant A can be found by imposing the constraint $\text{Tr}_{S_i} \rho^{(1)}(S_i) = 1$, we find

$$A = 1 + 2e^{-\beta \Delta} \cosh(\beta z J m) \quad (8.53)$$

Example 28: How to compute A

By imposing the constraint $\text{Tr}_{S_i} \rho^{(1)}(S_i) = 1$ (recall that $S_i = \pm 1, 0$), we get

$$1 = \frac{1}{A} \left(e^{\beta(zJm(+1) - \Delta(+1)^2)} + e^{\beta(zJm(-1) - \Delta(-1)^2)} + e^{\beta(zJm(0) - \Delta(0)^2)} \right)$$

Hence, by rearranging

$$1 = \frac{1}{A} \left(2e^{-\beta\Delta} \cosh(\beta zJm) + 1 \right) \Rightarrow A = 1 + 2e^{-\beta\Delta} \cosh(\beta zJm)$$

Given $\rho^{(1)}(S_i)$ it is possible to show

$$\langle S_i^2 \rangle = \text{Tr}_{S_i}(\rho_i S_i^2) = \frac{1}{A} 2e^{-\beta\Delta} \cosh(\beta zJm)$$

and

$$x = 1 - \langle S_i^2 \rangle = \frac{A - 2e^{-\beta\Delta} \cosh(\beta zJm)}{A} \Rightarrow x = \frac{1}{A}$$

Hence, substituting this expression of ρ_i into G , after some mathematical rearrangement we get:

$$\frac{G(T, \Delta, m, J)}{N} = \frac{z}{2} Jm^2 - \Delta - k_B T \ln A \quad (8.54)$$

In order to find the equilibrium state for any T and Δ , we must minimize this expression of $G(T, \Delta, m, J)$ with respect to m . If we expand G for small values of m , keeping in mind the Taylor expansions

$$\cosh(t) = 1 + \frac{t^2}{2} + \frac{t^4}{24}, \quad \ln(1+t) = t - \frac{t^2}{2}$$

we get

$$G(T, \Delta, J, m) = a_0(T, \Delta) + a(T, \Delta)m^2 + b(T, \Delta)m^4 + \frac{c(T, \Delta)}{6}m^6 \quad (8.55)$$

where

$$\begin{cases} a_0(T, \Delta) = -k_B T \ln(1 + 2e^{-\beta\Delta}) - \Delta \\ a(T, \Delta) = \frac{zJ}{2} \left(1 - \frac{zJ}{\delta k_B T} \right) \\ b(T, \Delta) = \frac{zJ}{8\delta^2} (\beta zJ)^3 \left(1 - \frac{\delta}{3} \right) \\ c(T, \Delta) > 0 \end{cases} \quad (8.56)$$

and the parameter δ is

$$\delta \equiv 1 + \frac{e^{\beta\Delta}}{2} = \delta(T, \Delta) \quad (8.57)$$

Note that unlike the Ising model in the Weiss approximation in this case both the quadratic and the quartic terms, a and b , can change sign when the parameters assume particular values. Let us also note that the order parameter of the system, namely the concentration of He^3 , is:

$$x(T, \Delta, J) = 1 - \langle S_i^2 \rangle = \frac{1}{A} = \frac{1}{1 + 2e^{-\beta\Delta} \cosh(\beta zJm)}$$

Therefore, in the disordered phase (both He^3 and He^4 are present) we have $m = 0$ and the concentration of He^3 becomes:

$$x(T, \Delta, J) = \frac{1}{1 + 2e^{-\beta\Delta}} = 1 - \frac{1}{\delta} \quad (8.58)$$

This way we can determine how the temperature of the λ -transition depends on x ; in fact, the critical temperature will be the one that makes a change sign, so we can determine it from the condition $a = 0$:

$$a(T_c(\Delta)) = \frac{zJ}{2} \left(1 - \frac{zJ}{\delta k_B T_c} \right) = 0 \quad \Rightarrow \quad T_c = \frac{zJ}{k_B \delta}$$

Since as we have just seen $1/\delta = 1 - x$, we have

$$T_c(x) = T_c(0)(1 - x) \quad (8.59)$$

where $T_c(0) = zJ/k_B$. The other transition (from the continuous λ to the discontinuous one) will occur when the quartic term b changes sign, and so we can determine the critical value of x_c at which it occurs from the condition $b = 0$. Hence, the tricritical point is the one that satisfies the conditions

$$\begin{cases} a(T_t, \Delta_t) = 0 \\ b(T_t, \Delta_t) = 0 \end{cases} \quad \Rightarrow \quad \begin{cases} \delta_t = \frac{zJ}{k_B T_t} \\ \delta_t = 3 \end{cases}$$

and the value of the concentration of He^3 results

$$x(T_t, \Delta_t) = 1 - \frac{1}{\delta_t} = \frac{2}{3} \quad (8.60)$$

which is in astonishingly good agreement with the experimental result of $x_t \sim 0.67$.

Exercise 5: Expansion of G for small values of m

Expand the free-energy per site

$$\frac{G}{N} = \frac{z}{2} J m^2 - \Delta - k_B T \ln A$$

where $A = 1 + 2e^{-\beta\Delta} \cosh(\beta z J m)$ for small values of m .

Solution. Let us define

$$x \equiv \beta z J m, \quad B \equiv 2e^{-\beta\Delta}$$

Since $\cosh x \simeq 1 + \frac{x^2}{2} + \frac{x^4}{24}$, we can expand A as

$$A = 1 + B \cosh x \simeq 1 + B \left(1 + \frac{x^2}{2} + \frac{x^4}{24} \right)$$

Hence,

$$\begin{aligned} \ln A &= \ln \left(1 + B + \frac{Bx^2}{2} + \frac{Bx^4}{24} \right) \\ &\simeq \ln \left[(1 + B) \left(1 + \frac{B}{2(1+B)} x^2 + \frac{B}{24(1+B)} x^4 \right) \right] \\ &= \ln(1 + B) + \ln(1 + t) \end{aligned}$$

where

$$t \equiv \frac{B}{2(1+B)} x^2 + \frac{B}{24(1+B)} x^4$$

Let us first consider the term

$$\frac{B}{1+B} = \frac{2e^{-\beta\Delta}}{1 + 2e^{-\beta\Delta}} = \frac{2}{2 + e^{\beta\Delta}} = \frac{1}{\delta}$$

Since $\ln(1+t) = t - \frac{t^2}{2}$, we have

$$\Rightarrow \ln A = \ln(1+B) + \frac{x^2}{2\delta} + \left(\frac{1}{24\delta} - \frac{1}{4\delta^2}\right)x^4 - \frac{1}{24\delta^2}x^6$$

If we remember that $x \equiv \beta z J m$, we obtain

$$\begin{aligned} -\frac{\ln A}{\beta} + \frac{z}{2} J m^2 - \Delta &\simeq a_0(T, \Delta) + \left(\frac{z}{2} J - \frac{\beta z^2 J^2}{2\delta}\right) m^2 \\ &+ \left(\frac{1}{8\delta} - \frac{1}{24\delta}\right) \beta^3 z^4 J^4 m^4 + \frac{1}{24\delta^2} \beta^5 z^6 J^6 m^6 \end{aligned}$$

Hence, the free energy G for small values of m is

$$G(T, \Delta, J, m) = a_0(T, \Delta) + a(T, \Delta) m^2 + b(T, \Delta) m^4 + c(T, \Delta) m^6$$

where

$$\begin{aligned} a(T, \Delta) &= \frac{zJ}{2} \left(1 - \frac{\beta z J}{\delta}\right) \\ b(T, \Delta) &= \frac{\beta^3 z^4 J^4}{8\delta} \left(\frac{1}{\delta} - \frac{1}{3}\right) = \frac{\beta^3 z^4 J^4}{8\delta^2} \left(1 - \frac{\delta}{3}\right) \\ c(T, \Delta) &= \frac{\beta^5 z^6 J^6}{24\delta^2} > 0 \end{aligned}$$

8.2.4 Mean field again

Another way to introduce the variational approach and the mean field approximation often discussed starts from the general expression of the variational free energy

$$F_{var} = \langle \mathcal{H} \rangle_{\rho_{TR}} + k_B T \langle \ln \rho_{TR} \rangle_{\rho_{TR}} \quad (8.62)$$

We have to choose a family of distribution. If one assumes that the family of trial distribution is of the Gibbs-Boltzmann form

$$\rho_{TR} = \frac{e^{-\beta \mathcal{H}_{TR}}}{Z_{TR}} \quad (8.63)$$

with

$$Z_{TR} = e^{-\beta F_{TR}} = \sum_{\{\Phi_i\}} e^{-\beta \mathcal{H}_{TR}(\{\Phi_i\})} \quad (8.64)$$

then, since

$$\ln \rho_{TR} = -\beta \mathcal{H}_{TR} - \ln Z_{TR}$$

we have

$$k_B T \langle \ln \rho_{TR} \rangle_{\rho_{TR}} = k_B T \left\langle \frac{-\mathcal{H}_{TR}}{k_B T} \right\rangle + k_B T \underbrace{\langle -\ln Z_{TR} \rangle}_{\beta F_{TR}}$$

By rearranging,

$$k_B T \langle \ln \rho_{TR} \rangle_{\rho_{TR}} = \langle -\mathcal{H}_{TR} \rangle + F_{TR}$$

Hence, the variational free energy becomes

$$F_{var} = \langle \mathcal{H} \rangle_{\rho_{TR}} - \langle \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} = \langle \mathcal{H} - \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} \quad (8.65)$$

Clearly, $F \leq F_{var}$ and one has to look for the minima of F_{var} by varying ρ_{TR} . Within this approach, the mean field approximation is still given by

$$\rho_{TR}^{MF}(\Phi_1, \dots, \Phi_N) = \prod_{i=1}^N \rho_{TR}^{(1)}(\Phi_i)$$

that in this case becomes

$$\prod_{i=1}^N \rho_{TR}^{(1)}(\Phi_i) = \frac{1}{Z_{TR}^{MF}} e^{-\beta \sum_i b_i \Phi_i} \quad (8.66)$$

and

$$Z_{TR} = \sum_{\{\Phi\}} e^{-\beta \sum_i b_i \Phi_i} \quad (8.67)$$

where b_i are the variational parameters. The Hamiltonian is

$$\mathcal{H}_{TR} = - \sum_i b_i \Phi_i \quad (8.68)$$

If we consider again the Ising model (remind that it means $\Phi_i \rightarrow S_i = \pm 1$), the Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

Hence, Eq.(8.65) becomes

$$\begin{aligned} F_{var} &= \langle \mathcal{H} - \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} \\ &= F_{TR} + \left\langle \left(-J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i \right) - \left(- \sum_i b_i S_i \right) \right\rangle_{\rho_{TR}} \\ &= F_{TR} + \left\langle -J \sum_{\langle ij \rangle} S_i S_j + \sum_i (b_i - H) S_i \right\rangle_{\rho_{TR}} \\ &= F_{TR} - J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_{\rho_{TR}} + \sum_i (b_i - H) \langle S_i \rangle_{\rho_{TR}} \end{aligned}$$

Since $\rho_{TR} = \prod_{i=1}^N \rho_i$, we have

$$\langle S_i S_j \rangle_{\rho_{TR}} = \langle S_i \rangle_{\rho_{TR}} \langle S_j \rangle_{\rho_{TR}}$$

Therefore,

$$F_{var} = F_{TR} - J \sum_{\langle ij \rangle} \langle S_i \rangle_{\rho_{TR}} \langle S_j \rangle_{\rho_{TR}} + \sum_i (b_i - H) \langle S_i \rangle_{\rho_{TR}}$$

Let us minimize the last equation, we consider the condition:

$$\frac{\partial F_{var}}{\partial b_i} = 0, \quad \forall i$$

which gives

$$0 = \frac{\partial F_{var}}{\partial b_i} = \left[-J \sum_{j \in n.n. i} \langle S_i \rangle_{\rho_{TR}} + b_i - H \right] \frac{\partial \langle S_i \rangle}{\partial b_i}$$

The variational parameters are equal to

$$b_i = J \sum_{j \in n.n. i} \langle S_j \rangle_{\rho_{TR}} + H$$

Let us calculate the average of the spin $\langle S_i \rangle_{\rho_{TR}}$:

$$\begin{aligned} \langle S_i \rangle_{\rho_{TR}} &= \frac{1}{Z_{TR}} \sum_{\{S\}} S_i e^{\beta \sum_k S_k b_k} = \frac{\prod_k \sum_{S_k} S_i e^{\beta S_k b_k}}{\prod_k \sum_{S_k} e^{\beta S_k b_k}} \\ &= \frac{\sum_{S_i=\pm 1} S_i e^{\beta S_i b_i}}{\sum_{S_i=\pm 1} e^{\beta S_i b_i}} = \frac{\sinh(\beta b_i)}{\cosh(\beta b_i)} = \tanh(\beta b_i) \end{aligned}$$

Finally, the variational parameters are

$$b_i = J \sum_{j \in n.n. i} \tanh(\beta b_j) + H \quad (8.69)$$

Remark. The main step to understand is how to derive F_{var} from a ρ_{TR} . This is nice to see a variation with respect to the real hamiltonian. Consider a bunch of data, for instance a million of configuration, which is the distribution of the configuration? Usually, we build up a model with a distribution that depends on parameters and what we want to do is statistical inference. Starting from the model and the data we have to obtain the real distribution.

Exercise 6

Consider again the antiferromagnetic Ising model

$$\mathcal{H}[\{S\}] = -J \sum_{\langle \vec{r}_A \vec{r}_B \rangle} S(\vec{r}_A) S(\vec{r}_B) - H \sum_{\vec{r}_A} S(\vec{r}_A) + H \sum_{\vec{r}_B} S(\vec{r}_B)$$

with $J > 0$ and $H > 0$. Remember that

- \vec{r}_A denotes the site on the A sublattice.
- \vec{r}_B denotes the site on the B sublattice.

Let us find again the mean-field solution, but now using the variational ansatz

$$F \leq F_{var} = \langle \mathcal{H} \rangle_{\rho_{TR}} - \langle \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} = \langle \mathcal{H} - \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR}$$

Remark. Since the problem can be splitted in two sublattices, it is convenient to use

$$\mathcal{H}_{TR} = -H_A \sum_{r_A} S(r_A) - H_B \sum_{r_B} S(r_B)$$

In particular:

- show that F_{var} has the following expression:

$$\begin{aligned} F_{var} &= F_{TR}(\beta H_A, \beta H_B) - 4NJ \langle S_A \rangle_{\rho_{TR}} \langle S_B \rangle_{\rho_{TR}} \\ &\quad - \frac{1}{2}NH \left(\langle S_A \rangle_{\rho_{TR}} - \langle S_B \rangle_{\rho_{TR}} \right) + \frac{1}{2}N \left(H_A \langle S_A \rangle_{\rho_{TR}} + H_B \langle S_B \rangle_{\rho_{TR}} \right) \end{aligned}$$

where

$$\begin{aligned} \langle S_A \rangle_{\rho_{TR}} &\equiv m_A + n \\ \langle S_B \rangle_{\rho_{TR}} &\equiv m_B - n \end{aligned}$$

with $m = m_A + m_B$, and

$$m_A = \tanh(\beta H - 4\beta J m_B)$$

$$m_B = \tanh(\beta H - 4\beta J m_A)$$

- Expand the free energy F_{var} in powers of m of the form

$$F_{var} = A + Bm^2 + Cm^4 + O(m^6)$$

and find the explicit expression of A, B and C as a function of T, H and n .

Chapter 9

Non ideal fluids: Mean field theory, Van der Waals, Virial expansion and Cluster expansion

9.1 Mean field theory for fluids

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Ideal gases are exceedingly idealised systems and are not suited to describe the behaviour of real systems: they always obey the same state equation and never undergo phase transitions (for example they never condense). We must therefore step a little further: using the "philosophy" of mean field theories we can make the description of fluids a little bit more realistic. As we will see this will also lead to the derivation of the Van der Waals equation, which better describes the behaviour of real fluids (even if, as we will shortly see, it still has some problems).

In general, in a real gas all the atoms or molecules interact through a certain potential $\Phi(\{\vec{r}_i\})$ that will depend on the positions of all the particles. For a fluid system of N particles with position vectors $\{\vec{r}_i\}_{i=1,\dots,N}$, the configurational contribution to the (grandcanonical) partition function will therefore be:

$$Q_N(T) = \int_V \prod_{i=1}^N d\vec{r}_i e^{-\beta(\Phi(\{\vec{r}_i\}) + \sum_{i=1}^N \psi_{ext}(\vec{r}_i))} \quad (9.1)$$

where ψ_{ext} is a one body external potential, but we do not consider it because it is not the aim of our problem. In general,

$$\Phi(\{\vec{r}_i\}) = \sum_{i \neq j} U_2(\vec{r}_i, \vec{r}_j) + \sum_{i \neq j \neq \mu} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_\mu) + \dots$$

(where U_n can be a generic n -body interaction potential). For simplicity, we do not consider U_3 , that is the three body interaction. Let us suppose

$$U_2(\vec{r}_i, \vec{r}_j) \rightarrow U_2(|\vec{r}_i - \vec{r}_j|)$$

Therefore,

$$Q_N(T) = \int_V \prod_{i=1}^N d\vec{r}_i e^{-\beta \sum_{i \neq j} U_2(|\vec{r}_i - \vec{r}_j|)}$$

Now, we replace all this story with just a field, it is a sort of average of the interactions. Doing the mean field assumption for U_2 , we obtain

$$\sum_{i,j>1} U_2(|\vec{r}_i - \vec{r}_j|) \rightarrow \sum_i \Phi_{MF}(\vec{r}_i)$$

Generally ψ_{ext} does not pose great problems while it is Φ that makes Q_N impossible to compute exactly, forcing us to resort to approximations. In the framework of mean field theories, we substitute the interaction potential Φ with an effective single-particle potential that acts on every particle in the same way. Hence, the *mean field approximation* consists in substituting the multi-body interaction potential $\Phi(\{\vec{r}_i\})$ with an effective one body potential $\Phi(\vec{r})$ with which all the particles move:

$$\Phi(\{\vec{r}_i\}) = \sum_i \Phi_{MF}(\vec{r}_i) \quad (9.2)$$

As said, for simplicity consider $\psi_{ext} = 0$, hence mean field theories allow us to compute Q_N as

$$Q_N^{MF}(T) \simeq \left[\int_V d^D \vec{r} e^{-\beta \Phi_{MF}(\vec{r})} \right]^N \quad (9.3)$$

Remark. The integral depends on the form of $\Phi_{MF}(\vec{r})$. Of course, every particular mean field theory will provide a different form of $\Phi_{MF}(\vec{r})$ which will lead to different results.

If one assumes *spatial isotropy*, what it is important is not anymore the vector but only the distance; hence, it is important just the integral over the modulus:

$$\Phi_{MF}(\vec{r}) = \Phi_{MF}(|\vec{r}|) = \Phi_{MF}(r)$$

9.2 Van der Waals equation

The Van der Waals equation can be obtained considering the atoms of a gas as hard spheres. In this case, in fact, the mean field has the form:

$$\Phi_{MF}(r) = \begin{cases} \infty & r < r_0 \quad \text{repulsion} \\ u < 0 & r > r_0 \quad \text{attraction} \end{cases} \quad (9.4)$$

as plotted in Figure 9.1.

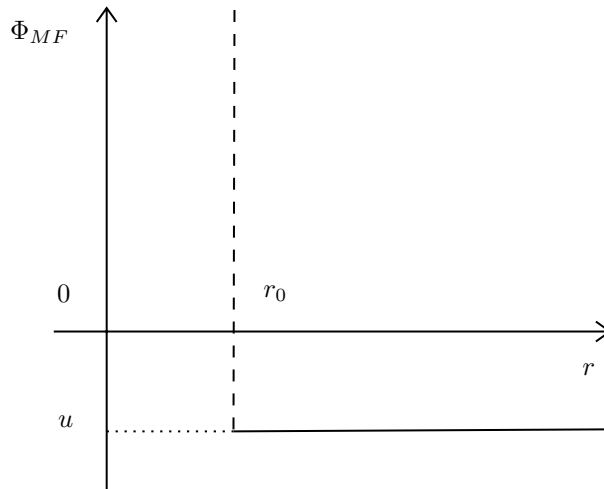


Figure 9.1: Plot of the potential $\Phi_{MF}(r)$.

The partition function becomes

$$Q_N^{MF}(T) = \left[V_{ex} e^{-\infty} + (V - V_{ex}) e^{-\beta u} \right]^N$$

where $V_{ex} \simeq r_0^3$ is the volume not accessible by the particle. Finally, the result is

$$Q_N^{MF}(T) = \left[(V - V_{ex}) e^{-\beta u} \right]^N \quad (9.5)$$

The free energy is $F_N = -k_B T \ln Q_N$, hence

$$F_N^{MF}(T) = -Nk_B T [\ln(V - V_{ex}) - \beta u] \quad (9.6)$$

Let us calculate the pressure

$$P_N^{MF} = - \left. \frac{\partial F_N^{MF}}{\partial V} \right|_T = \frac{Nk_B T}{V - V_{ex}} - N \left(\frac{\partial u}{\partial V} \right)_T \quad (9.7)$$

Remark. In general, the deep u can go up and down depending on the V : $u = u(V)$. This is because u is the attractive well of the mean field potential and, for $r \geq r_0$ must be proportional to the fluid density

$$u \sim -N/V$$

where the minus sign means attraction. On the other hand, also V_{ex} , the volume not accessible, must be proportional to N .

Hence, we have

$$u = -a \frac{N}{V}, \quad V_{ex} = bN$$

where b is the volume of a single particle. Inserting the last term in (9.7), we obtain the *Van der Waals equation of state*:

$$P_N^{MF}(V, T) = \frac{Nk_B T}{V - bN} - a \left(\frac{N}{V} \right)^2 \quad (9.8)$$

9.2.1 Critical point of Van der Waals equation of state

Let us define the specific volume as

$$v \equiv \frac{1}{\rho} = \frac{V}{N}$$

Hence, the equation of state becomes

$$P = \frac{K_B T}{v - b} - \frac{a}{v^2} \quad (9.9)$$

The behaviour of the Van der Waals isotherms is shown in Figure 9.2a. As we can see this changes with the temperature and resembles that of real isotherms; however, Van der Waals isotherms are always analytic and have a non physical behaviour in certain regions of (v, P) plane, called spinodal curves, if $T < T_c$: for some values of v we have $\partial P / \partial v > 0$ which is physically impossible. This is a consequence of the roughness of the approximation we have made, since it can be shown that it doesn't ensure that the equilibrium state of the system globally minimizes the Gibbs free energy. As we will shortly see, however, this problem can be solved "by hand" with Maxwell's equal area rule, or Maxwell's Construction. Overall, we have this effect because it is a mean field, so the curve in Figure 9.2a it is replaced by the curve in Figure 9.2b. Moreover, for $T < T_c$ the equation $P(v) = \text{const}$ has 3 distinct solutions. For $T > T_c$ only one solution $\in \mathbb{R}$.

Let us now see how to determine the critical point of a system obeying Van der Waals equation.

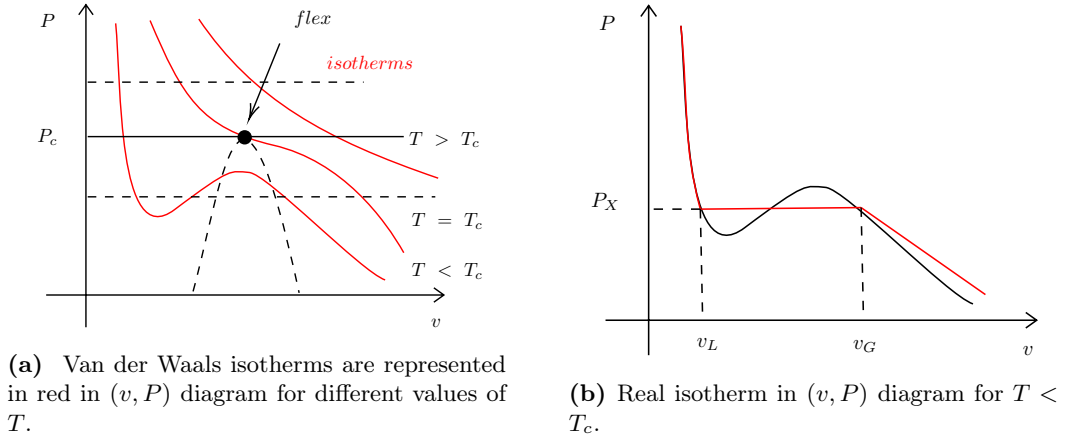


Figure 9.2

- First of all, from the representation of the isotherms we can see that the critical point is a flex for the critical isotherm (i.e. the one with $T = T_c$); in other words, we can determine the critical point from the equations:

$$\frac{\partial P}{\partial v} = 0, \quad \frac{\partial^2 P}{\partial v^2} = 0$$

The second in particular means that there is a flex point. Let us pay attention to it, indeed it is a standard way to find critical points. We obtain

$$v_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad k_B T_c = \frac{8a}{27b}$$

- Another way to find the critical point consists in noticing that at $T = T_c$, the 3 solutions coincide. In fact, we can note that the equation $P(v) = P = \text{const}$ is cubic in v . Let us rewrite the Van der Waals equation

$$P = \frac{v^2 k_B T - a(v - b)}{v^2(v - b)}$$

as

$$v^3 - \left(b + \frac{k_B T}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0 \quad (9.10)$$

For $T > T_c$ this equation has one real solution and two imaginary ones, and for $T < T_c$ three distinct real solutions; when $T = T_c$ the three solutions of the equation coincide. This means that at the critical point $T = T_c$ this last equation Eq.(9.10) must be written in the form:

$$(v - v_c)^3 = 0 \Rightarrow v^3 - 3v^2 v_c + 3v v_c^2 - v_c^3 = 0$$

Equating the coefficients with Eq.(9.10) we get:

$$v_c^3 = \frac{ab}{P_c}, \quad 3v_c^2 = \frac{a}{P_c}, \quad 3v_c = b + \frac{k_B T_c}{P_c}$$

from which we have again:

$$v_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad k_B T_c = \frac{8a}{27b} \quad (9.11)$$

We have found a very interesting result: in fact, if we can measure a and b at high temperatures then we are able to determine the critical point of the system.

This model has also an interesting property, since it predicts that:

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} \approx 0.375$$

which is a universal number, independent of a and b and so of the particular fluid considered. Experimentally this ratio is approximately 0.29 for Argon, 0.23 for water and 0.31 for He⁴. Therefore, even if it is very rough, this model leads to reasonable conclusions.

9.2.2 Law of corresponding states

The universal value of the ratio $\frac{P_c v_c}{k_B T_c}$ suggests a deeper correspondence between different fluid systems. We can also rewrite Van der Waals equation (9.8) in a dimensionless form, rescaling the thermodynamic quantities of the system. In particular, defining:

$$\pi \equiv \frac{P}{P_c} = P \frac{27b^2}{a}, \quad \nu \equiv \frac{v}{v_c} = \frac{v}{3b}, \quad \tau \equiv \frac{T}{T_c} = k_B T \frac{27b}{8a} \quad (9.12)$$

Van der Waals equation becomes:

$$\left(\pi + \frac{3}{\nu^2} \right) (3\nu - 1) = 8\tau \quad (9.13)$$

We have found another very interesting result: when rescaled by their critical thermodynamic properties (by P_c, v_c and T_c), all fluids obey the same state equation. This is the law of corresponding states: this is a form of universality. The law of corresponding states applies everywhere on the phase diagram. It can even be shown that this law is a consequence of dimensional analysis, and is more general than what might seem: experimentally the law of corresponding states is well satisfied also by fluids which do not obey Van der Waals equation.

9.2.3 Region of coexistence and Maxwell's equal area rule

In real fluids, for $T < T_c$ ($\tau < 1$), there is a first order liquid-gas transition with coexistence between vapor and liquid phase and non analyticity of the thermodynamic potential. In particular, a real isotherm for $T < T_c$ is the one in Figure 9.2b. How this is described by the mean-field (i.e. Van der Waals) theory? The Van der Waals isotherm for $T < T_c$ is given by the graphic in Figure 9.3. The liquid phase goes into a phase region that is not thermodynamically stable. How can we remove the non physical regions of the Van der Waals equation of state and describe coexistence? The solution is the Maxwell (or equal area) construction!

Equal area or Maxwell construction

As we have previously anticipated, Maxwell's equal area rule is a method to "manually" remove the unphysical regions of Van der Waals isotherms.

From phase coexistence and general properties of phase transitions we know that at the coexistence of two phases the chemical potentials and the pressures of the two phases must be equal; furthermore, from thermodynamic potentials we also know that the chemical potential is the Gibbs free energy per particle, namely $G = \mu N$, and in general we have also:

$$dG = -S dT + V dP + \mu dN$$

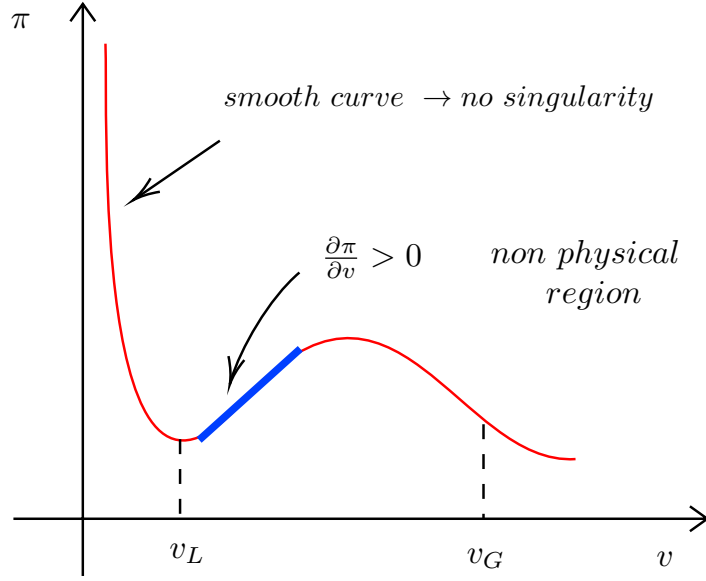


Figure 9.3: Van der Waals isotherm for $T < T_c$.

Now, differentiating $G = \mu N$ and subtracting this last equation we get:

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dP$$

Therefore, since along an isotherm $dT = 0$, we will have:

$$d\mu = \frac{V}{N} dP$$

At the coexistence we have also $dP_{coex} = 0$, hence

$$d\mu = 0$$

is the physical condition. Recall that for Van der Waals $dP \neq 0$! Hence, the physical coexistence condition implies

$$0 = \int_1^2 d\mu = \mu(2) - \mu(1) \stackrel{\text{Van der Waals}}{=} \frac{1}{N} \int_{P_G}^{P_L} dP V$$

Looking also at the Figure 9.4, we see that this means that the horizontal segment of the isotherm must be drawn so that the two regions have the same area (from which the name of the method). The integral can be partitioned in two parts

$$0 = \int_{P_G}^{P_L} V dP \Rightarrow \int_{P_G}^{P_x} V dP = - \int_{P_x}^{P_L} dP V$$

Hence, the equal area condition gives the value of P_x of the coexistence line!

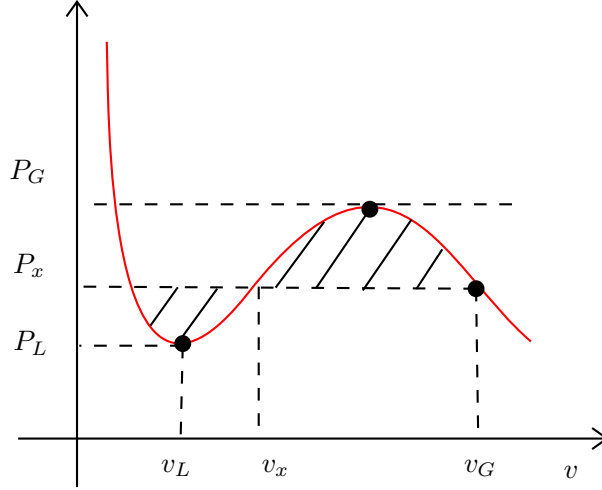


Figure 9.4: Maxwell's equal area rule: Van der Waals isotherm for $T < T_c$.

9.2.4 Critical exponents of Van der Waals equation

Let us now study the behaviour of systems obeying Van der Waals equations near the critical point, computing one of the critical exponents.

β exponent

Let us recall that the equation of state is

$$\left(\pi + \frac{3}{\nu^2}\right)(3\nu - 1) = 8\tau$$

where

$$\pi = \frac{P}{P_c}, \quad \nu = \frac{v}{v_c}, \quad \tau = \frac{T}{T_c}$$

Let us consider

$$\begin{cases} t \equiv \tau - 1 = \frac{T - T_c}{T_c} \\ \Phi \equiv \nu - 1 = \frac{v - v_c}{v_c} \end{cases} \quad (9.14)$$

indeed we want to analyze the deviation from the critical point. Close to the critical point we have $\tau \sim \nu \sim 1$ and $t \sim \Phi \sim 0$.

We now expand the equation of state with respect to t and Φ in the neighbourhood of the critical point:

$$\left(\pi + \frac{3}{(1 + \Phi)^2}\right)(3(\Phi + 1) - 1) = 8(t + 1)$$

By rearranging,

$$\Rightarrow \pi = \frac{8(t + 1)}{2(\Phi + 1) - 1} - \frac{3}{(1 + \Phi)^2}$$

Expanding for $\Phi \sim 0$, since we have

$$(1 + \Phi)^\alpha \simeq 1 + \alpha\Phi + \frac{\alpha(\alpha - 1)}{2!}\Phi^2 + \frac{\alpha(\alpha - 1)(\alpha - 2)}{3!}\Phi^3$$

we obtain

$$\begin{aligned} \pi &\simeq (1 + t) \left(4 - 6\Phi + 9\Phi^2 - \frac{27}{2}\Phi^3 + \dots \right) - (3 - 6\Phi + 9\Phi^2 - 12\Phi^3 + \dots) \\ &\sim 1 + 4t - 6\Phi t + 9\Phi^2 t - \frac{3}{2}\Phi^3 - \frac{27}{2}\Phi^3 t + \dots \end{aligned}$$

Finally, the result is

$$\pi \simeq 1 + 4t - 6t\Phi - \frac{3}{2}\Phi^3 + O(t\Phi^2, \Phi^4) \quad (9.15)$$

where the terms we have neglected are justified a posteriori (i.e. we will see that $\Phi \sim t^{1/2}$; we could have not neglected them, but the result of the computation doesn't change).

The strategy we want to apply is the following: since we want to determine how Φ changes with t , we can determine the relation between the densities Φ_g and Φ_l in the gaseous and liquid phase from Maxwell's equal area rule. This way, from the expression of π we can determine the pressures in the two phases and express them in terms of Φ_g or Φ_l , and since $\pi_l = \pi_g$ at the coexistence we can obtain from this equation the behaviour of Φ in terms of t .

Hence, as said, in order to get the values of $v_G(P)$ and $v_L(P)$ at coexistence, we use the Maxwell construction

$$\int_{P_G}^{P_L} v \, dP = 0$$

and since $v = (\Phi + 1)v_c$ and $dP = P_c \, d\pi$ we have:

$$\int_{liq}^{gas} (\Phi + 1)v_c P_c \, d\pi = 0 \quad (9.16)$$

Let us consider $T < T_c$ fixed (it is true if and only if $t < 0$, but small), hence

$$\pi = \pi(v) = \pi(\Phi)$$

From Eq.(9.15) we have

$$d\pi \simeq -6t \, d\Phi - \frac{9}{2}\Phi^2 \, d\Phi$$

Thus the result of the differential $dP = P_c \, d\pi$ is

$$dP = P_c \left[-6t \, d\Phi - \frac{9}{2}\Phi^2 \, d\Phi \right]$$

Then, from equation (9.16) we have the integral

$$\int_{\Phi_l}^{\Phi_g} \Phi \left(-6t - \frac{9}{2}\Phi^2 \right) d\Phi = 0 \quad (9.17)$$

hence,

$$-3\Phi_g^2 \left[t + \frac{\Phi_g^2}{g} \right] + 3\Phi_l^2 \left[t + \frac{\Phi_l^2}{g} \right] = 0$$

Since t is small we can neglect it, and so:

$$\Phi_g^2 = \Phi_l^2 \quad \Rightarrow \quad \Phi_g = \pm \Phi_l$$

Remembering that:

$$\Phi_g = \frac{v_g - v_c}{v_c}, \quad \Phi_l = \frac{v_l - v_c}{v_c}$$

we see that the only acceptable solution is

$$\Phi_g = -\Phi_l \quad (9.18)$$

(since the volume of a gas is larger than that of a liquid). Therefore, substituting Φ_g and $\rho_l = -\rho_g$ into the expression of π (Eq. (9.15)), we get

$$\begin{aligned}\Phi_g &\rightarrow \pi_g = 1 + 4t - 6t\Phi_g - \frac{3}{2}\Phi_g^3 \\ \Phi_l &\rightarrow \pi_l = 1 + 4t + 6t\Phi_g + \frac{3}{2}\Phi_g^3\end{aligned}$$

The two expression of π must be equal $\pi_g = \pi_l$ since we are at the coexistence. Solving with respect to Φ_g we get

$$3\rho_g(4t + \rho_g^2) = 0$$

and excluding of course the case $\rho_g = 0$, in the end:

$$\Phi_g = 2\sqrt{-t} \sim \left(\frac{T_c - T}{T_c}\right)^{1/2} \quad (9.20)$$

which implies

$$\beta = \frac{1}{2} \quad (9.21)$$

9.3 Theories of weakly interacting fluids

If the gas is not ideal but made by weakly interacting particles, it is possible to follow a *perturbative approach* to compute the partition function of such systems. Let us consider N particles in region Ω of volume V . Particles interact through a generic two-body potential that depends only on the relative distance between the particles:

$$U_2(\vec{\mathbf{r}}_i, \vec{\mathbf{r}}_j) = \Phi(|\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j|)$$

Hence,

$$\Rightarrow U(\{\vec{\mathbf{r}}\}) = \frac{1}{2} \sum_{i,j} \Phi(|\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j|) \quad (9.22)$$

Its Hamiltonian will be:

$$\mathcal{H}_\Omega(\{\vec{\mathbf{r}}\}) = \sum_{i=1}^N \frac{\vec{\mathbf{p}}_i^2}{2m} + \sum_{i,j>i} \Phi(|\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j|) \quad (9.23)$$

and its partition function in the canonical ensamble:

$$Z_\Omega(N, V, T) = \frac{1}{N! \Lambda^{3N}} Q_N(V, T) \quad (9.24)$$

where

$$Q_N(V, T) = \int_V d\vec{\mathbf{r}}_1 \int_V d\vec{\mathbf{r}}_2 \cdots \int_V d\vec{\mathbf{r}}_N \exp[-\beta U(\{\vec{\mathbf{r}}\})] \quad (9.25)$$

Remark. Of course for ideal gases $U = 0$, and so

$$Q_N(V, T) = V^N \rightarrow Z_N^{ideal} = \frac{V^N}{N! \Lambda^{3N}}$$

and the dependence on T is exclusively due to $\Lambda = \Lambda(T)$ (i.e. kinetic energy).

Now, suppose $U \neq 0$, but small! If we consider also the interaction terms we must insert a correction χ in the configurational contribution to the partition function. We can say that our $Q_N(V, T)$ it would be the one of the ideal version times a new function

$$Q_N(V, T) \simeq V^N \chi(N, V, T) \quad (9.26)$$

which (depending on the possible presence of attractive terms in the interaction potential Φ can in general be also a function of the temperature T ; furthermore the correction depends strongly on the gas density: if it is low the particles will not "perceive" the presence of the other ones and the ideal gas approximation is a good one, while for high densities the particles will be closer to each other and corrections to Q_N are necessary.

Remark. If Φ is only repulsive, χ does not depend on T .

Let us note that inserting the correction χ , the free energy of the system will be:

$$F_N = F_N^{ideal} - k_B T \ln \chi \quad (9.27)$$

As previously said, the correction χ due to particle-particle interaction depends on the particle density ρ of the fluid:

$$\begin{cases} \rho_{small} & \Rightarrow U = 0 \\ \rho_{high} & \Rightarrow U \neq 0 \text{ and not negligible} \end{cases} \quad (9.28)$$

This suggests that the equation of state of a weakly interacting gas can be expanded formally in powers of ρ . This is known as *virial expansion*.

In particular, for the ideal gas:

$$\frac{P}{k_B T} = \rho$$

For a non ideal gas, let us add the other terms of the expansion

$$\rightarrow \frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots + O(\rho^n) \quad (9.29)$$

this is a virial expansion and it is one of the most used. The coefficient B are called the *virial coefficients*. The Eq.(9.29) was first introduced as a formula to fit experimental data. Indeed, making a fit, you will obtain the virial coefficients. This is what physicist have done for years. Then, mapping the coefficient with the real world experiments, we can find some macroscopical parameters. The formula (9.29) can be also obtained rigorously from a perturbation approach to the partition function (as we will see later). Now, the question is: which is the virial expansion of a Van der Walls (i.e. mean field) gas?

9.3.1 Van der Walls and virial expansion

Let us see for example the virial expansion of the Van der Waals equation. From Van der Waals equation we have:

$$\frac{P}{k_B T} = \frac{N}{V - bN} - \frac{aN^2}{k_B T V^2}$$

Let us factorize the term (N/V) ,

$$\frac{P}{k_B T} = \left(\frac{N}{V}\right) \left(1 - b\frac{N}{V}\right)^{-1} - \frac{a}{k_B T} \left(\frac{N}{V}\right)^2$$

Then, by expanding in power of (N/V) and defining $\rho = N/V$, we have

$$\begin{aligned} \Rightarrow \frac{P}{k_B T} &= \left(\frac{N}{V}\right) + \left(\frac{N}{V}\right)^2 \left(b - \frac{a}{k_B T}\right) + \left(\frac{N}{V}\right)^3 b^2 + \left(\frac{N}{V}\right)^4 b^3 + \dots \\ &= \rho + \left(b - \frac{a}{k_B T}\right) \rho^2 + b^2 \rho^3 + b^3 \rho^4 + \dots \end{aligned}$$

We can thus immediately identify the first virial coefficient:

$$B_2(T)^{VdW} = b - \frac{a}{k_B T}, \quad B_3^{VdW} = b^2$$

where in $B_2(T)^{VdW}$ the first term is repulsive on excluded volume and the second one is the attraction term. We note also that B_3^{VdW} is always positive.

Boyle's temperature T_B

The Boyle's temperature is the T at which the second coefficient is zero:

$$B_2^{VdW}(T_B) = 0$$

so we have removed the most important coefficient. The competing effects of repulsion and attraction are cancelled out. In this case, the Van der Walls temperature T_B^{VdW} is

$$T_B^{VdW} = \frac{a}{bk_B}$$

to be compared with the critical temperature T_c^{VdW} that is

$$T_c^{VdW} = \frac{8a}{27b^3}$$

We notice that $T_c^{VdW} \ll T_B^{VdW}$. It is clear that the Boyle's temperature must be much greater than the critical one.

Remark. Consider a polymer, the transition point called the θ point is when the second coefficient is zero, as the case described above, but it is interesting in polymer kind of system (lesson).

9.3.2 Cluster expansion technique for weakly interacting gases

We now obtain the formal virial expansion by starting from the microscopic system and performing a perturbation expansion of the Boltzmann weights for small values of U . Let us start from the partition function

$$Q_N = \int_V d\vec{r}_1 \dots \int_V d\vec{r}_N e^{-\beta U(\{\vec{r}\})} = \int_V d\vec{r}_1 \dots \int_V d\vec{r}_N e^{-\beta \sum_{i,j>i} \Phi_{ij}} \quad (9.30)$$

where we have used the short notation

$$\Phi_{ij} \equiv \Phi(|\vec{r}_i - \vec{r}_j|)$$

The idea is to find a "small quantity" in terms of which we can expand Q_N ; this quantity is the so called *Mayer function*.

Definition 8: Mayer function

The *Mayer f-function* is an auxiliary function that often appears in the series expansion of thermodynamic quantities related to classical many-particle systems.

It is defined as

$$f(|\vec{r}|) \equiv e^{-\beta\Phi(|\vec{r}|)} - 1 \quad (9.31)$$

Remark. Note: if $\beta\Phi(r) \ll 1$, we have $f(r) \ll 1$.

In fact, when the gas is ideal $f(\vec{r}) = 0$, and if the particles interact weakly Φ is small, and so is $f(\vec{r})$. In particular, this expansion will work well for low densities (namely $|\vec{r}_i - \vec{r}_j|$ is large and so $\Phi(|\vec{r}_i - \vec{r}_j|) \rightarrow 0$) or high temperatures (namely $\beta \rightarrow 0$): in both cases, in fact, $e^{-\beta\Phi(|\vec{r}_i - \vec{r}_j|)} \rightarrow 1$ and $f(|\vec{r}_i - \vec{r}_j|) \rightarrow 0$. Using the short notations $\Phi_{ij} \equiv \Phi(|\vec{r}_i - \vec{r}_j|)$ and $f_{ij} \equiv f(|\vec{r}_i - \vec{r}_j|)$ we have

$$\begin{aligned} \Rightarrow e^{-\beta \sum_i \sum_{j>i} \Phi_{ij}} &= \prod_i \left(\prod_{j>i} (1 + f_{ij}) \right) \\ &= \underbrace{(1 + f_{12})(1 + f_{13}) \dots (1 + f_{1N})}_{i=1} \dots \underbrace{(1 + f_{23})(1 + f_{24}) \dots (1 + f_{2N})}_{i=2} \dots \\ &= (1 + f_{12} + f_{13} + f_{12}f_{13})(1 + f_{14}) \dots (1 + f_{23}) \\ &= 1 + \sum_i \sum_{j>i} f_{ij} + \sum_{i=1}^N \sum_{k \geq i} \sum_{l > k} \sum_{j>i} \sum_{(ij) \neq (lk)} f_{ik}f_{kl} + O(f^3) \end{aligned}$$

where

$$f_{ij} \equiv e^{-\beta\Phi_{ij}} - 1$$

Higher order terms contain products of $3, 4, \dots f_{ij}$ terms. For simplicity, let us consider first only linear terms. Hence, the solution is given by considering only the linear term. This is the cluster expansion.

As said, this first approximation is reasonable if either

1. ρ is small enough. It implies that $|\vec{r}_i - \vec{r}_j| \gg 1$ and hence $\Phi_{ij} \ll 1$.
2. Sufficiently high T such that $\Phi(|\vec{r}_i - \vec{r}_j|)/k_B T \ll 1$. What is important it is the ration between β and Φ_{ij} .

In either cases we have $\exp(-\beta\Phi_{ij}) \rightarrow 1$ and $f_{ij} \rightarrow 0$. By keeping only linear terms, the configurational contribution to the partition function will be

$$\begin{aligned} Q_N(V, T) &= \int_V d\vec{r}_1 \dots d\vec{r}_N \left(1 + \sum_{i,j>i} f_{ij} + \dots \right) = V^N + \sum_{i,j>i} \int_V d\vec{r}_1 \dots \int_V d\vec{r}_N f_{ij} \\ &= V^N + V^{N-2} \sum_{i,j>i} \int_V d\vec{r}_i d\vec{r}_j f_{ij} + \dots \end{aligned}$$

We are summing up over all configurations ij . Let us try to compute the double integral, with the definition of a new variable $\vec{r} = \vec{r}_i - \vec{r}_j$:

$$\int_V d\vec{r}_i \int_V d\vec{r}_j f_{ij}(|\vec{r}_i - \vec{r}_j|) \stackrel{\text{translational symmetry}}{=} \int_V d\vec{r}_i \int_V d\vec{r} f(\vec{r}) = V \int_V d\vec{r} f(|\vec{r}|) \equiv -2B_2 V$$

Hence,

$$B_2 \equiv -\frac{1}{2} \int_V d\vec{r} f(|\vec{r}|) \quad (9.32)$$

From this we see precisely how the virial coefficient, which as we have already stated can be experimentally measured, is related to the microscopic properties of the interaction between the particles, represented by the Mayer function f . It can also be

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shown that all the virial coefficients can be expressed in terms of integrals of products of Mayer functions: higher order coefficients involve the computation of increasingly difficult integrals, which can however be visualized in terms of graphs.

What we have seen now is how the cluster expansion works in general. Let us now apply it in order to find the virial expansion for real gases. From what we have found, the configurational partition function of the system becomes:

$$Q_N(V, T) = V^N - V^{N-1} B_2(T) \sum_{i,j>i} 1 + \dots$$

The remaining sum is equal to $N(N-1)$: in fact, for any of the N values that i can assume, j can have $N-1$ values. These are all the possible connections (bonds) between pairs of particles (i, j) with $j > i$. Hence,

$$Q_N(V, T) = V^N - V^{N-1} B_2(T) N(N-1) + \dots \quad (9.33)$$

and, considering that $N-1 \approx N$ for large N , the complete partition function of the system will be:

$$Z_N(V, T) = \left(\frac{V^N}{N! \Lambda^{3N}} \right) \left(1 - \frac{N^2}{V} B_2(T) + \dots \right) \quad (9.34)$$

We recognise in this expression that $(1 - B_2 N^2/V + \dots)$ is the correction χ to the ideal gas partition function that we have mentioned earlier; therefore, the free energy of the system will be:

$$F_N = F_N^{ideal} - k_B T \ln \left[1 - \frac{N^2}{V} B_2(T) + \dots \right] \quad (9.35)$$

and its pressure:

$$P_N = - \left(\frac{\partial F_N}{\partial V} \right)_{T,N} = \frac{N k_B T}{V} \left(1 + \frac{\frac{N}{V} B_2}{1 - \frac{N^2}{V} B_2} \right) = \frac{N k_B T}{V} \left(\frac{1 - \frac{N^2}{V} B_2 + \frac{N}{V} B_2}{1 - \frac{N^2}{V} B_2} \right)$$

Expanding the denominator for $\frac{N}{V} B_2 \ll 1$ $\rho \ll 1$, one gets

$$P_N \simeq \frac{N k_B T}{V} \left(1 + \frac{N}{V} B_2 + \dots \right) \quad (9.36)$$

here we see the correction to the ideal gas.

Remark. The equation (9.36) gives an important relation between experimentally accessible observables as P_N and microscopic quantities such as $f(\vec{r})$ (and hence $\Phi(\vec{r})$) through the estimate of B_2 . Therefore, it is important computing B_2 , because one time we have this we have the expansion. Or if we wish, by doing the fit of data at different temperature we obtain B_2 from the experiment and we can see f_{ij} .

The expansion in Eq.(9.36) contains only low-order terms in the density N/V , so strictly speaking it is valid only for low densities. To consider higher order terms in the virial expansion we need to consider higher order products of the f_{ij} . However, we can use a "trick" in order to extend its range; in fact, remembering that the McLaurin expansion $(1-x)^{-1} = 1+x+\dots$, from the Eq.(9.36) we can write:

$$\frac{PV}{N k_B T} \approx 1 + \rho B_2 + \dots \simeq \frac{1}{1 - B_2 \rho}$$

and now re-expand $(1 - B_2\rho)^{-1}$, so that we can express all the virial coefficients in terms of the first one:

$$\frac{1}{1 - B_2\rho} \simeq 1 + B_2\rho + (B_2)^2\rho^2 + (B_2)^3\rho^3 + \dots$$

Hence,

$$\frac{P}{k_B T} = \rho + B_2\rho^2 + (B_2)^2\rho^3 + (B_2)^3\rho^4 + \dots$$

Identifying the coefficients for each power we get, in the end:

$$B_3 \approx (B_2)^2, \quad B_4 \approx (B_2)^3, \quad \dots, \quad B_n \approx (B_2)^{n-1}$$

This is the approximation of higher order virial coefficients with powers of B_2 .

Remark. One question at the exam can be: let us compute virial expansion of a gas in a potential.

9.3.3 Computation of virial coefficients for some interaction potentials Φ

Let us now see this method in action by explicitly computing some coefficients B_2 for particular interaction potentials.

Hard sphere potential

The particles are interacting (it is not ideal!) and there is a size that is the range of the potential. As a first trial, we use a hard sphere potential similar (see Figure 9.5) to the one we have seen for the derivation of the Van der Waals equation:

$$\Phi(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (9.37)$$

(the difference with what we have seen in Van der Waals equation is that now the potential is purely repulsive, and has no attractive component).

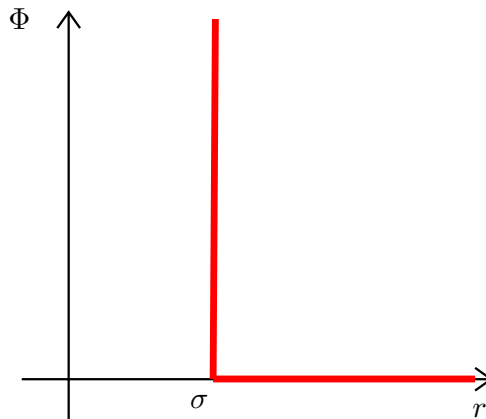


Figure 9.5: Plot of the hard sphere potential $\Phi(r)$.

In this case,

$$f(\vec{r}) = e^{-\beta\Phi(r)} - 1 = \begin{cases} -1 & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (9.38)$$

Therefore, from the definition of B_2 and shifting to spherical coordinates:

$$B_2(T) = -\frac{1}{2} \int_V d\vec{r} f(|\vec{r}|) = -\frac{1}{2} 4\pi \int_0^{+\infty} dr r^2 [e^{-\beta\Phi(r)} - 1] = 2\pi \int_0^\sigma dr r^2 = \frac{2}{3} \pi \sigma^3$$

Hence,

$$\Rightarrow B_2^{HS}(T) = \frac{2}{3} \pi \sigma^3 \quad (9.39)$$

this is the second virial coefficient for a hard sphere gas. As expected B_2^{HS} does not depend on temperature (purely repulsive interaction). Finally, for hard spheres we have:

$$PV = Nk_B T \left(1 + \frac{2}{3} \pi \sigma^3 \frac{N}{V} \right) \quad (9.40)$$

Note that the excluded volume interaction (hard sphere term) increases the product PV with respect to the ideal gas.

Square wall potential

We now use a slight refinement of the previous potential:

$$\Phi(\vec{r}) = \begin{cases} +\infty & |\vec{r}| < r_0 \\ -\varepsilon & r_0 < |\vec{r}| < r_0 + \delta \\ 0 & |\vec{r}| > r_0 + \delta \end{cases} \quad (9.41)$$

This can be seen as a hard sphere potential where the spheres have an attractive shell of thickness δ . We thus have:

$$f(\vec{r}) = \begin{cases} -1 & |\vec{r}| < r_0 \\ e^{\beta\varepsilon} - 1 & r_0 < |\vec{r}| < r_0 + \delta \\ 0 & |\vec{r}| > r_0 + \delta \end{cases} \quad (9.42)$$

so that:

$$\begin{aligned} B_2 &= -\frac{1}{2} \int f(|\vec{r}|) d\vec{r} = -\frac{1}{2} \int 4\pi r^2 f(r) dr = \\ &= -2\pi \left[\int_0^{r_0} (-r^2) dr + \int_{r_0}^{r_0+\delta} (e^{\beta\varepsilon} - 1) r^2 dr \right] = \\ &= -2\pi \left\{ -\frac{r_0^3}{3} + \frac{e^{\beta\varepsilon} - 1}{3} [(r_0 + \delta)^3 - r_0^3] \right\} = B_2^{\text{h.s.}} - \frac{2}{3} \pi (e^{\beta\varepsilon} - 1) [(r_0 + \delta)^3 - r_0^3] \end{aligned}$$

where B_2^{HS} is the first virial coefficient of the hard sphere potential we have previously seen. Now, if the temperature is sufficiently high, namely $\beta\varepsilon \ll 1$, we can approximate $e^{\beta\varepsilon} - 1 \approx \beta\varepsilon$, so that:

$$B_2 = B_2^{HS} - \frac{2}{3} \pi \beta \varepsilon r_0^3 \left[\left(1 + \frac{\delta}{r_0} \right)^3 - 1 \right] \quad (9.43)$$

For the sake of simplicity, defining:

$$\lambda \equiv \left(1 + \frac{\delta}{r_0} \right)^3 - 1$$

we will have, in the end:

$$\frac{PV}{Nk_B T} = 1 + B_2 \rho = 1 + \left(B_2^{HS} - \frac{2}{3} \frac{\pi \varepsilon}{k_B T} r_0^3 \lambda \right) \rho \quad (9.44)$$

so in this case B_2 actually depends on the temperature.

Lennard-Jones potential

This potential is a quite realistic representation of the interatomic interactions. It is defined as:

$$\Phi = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (9.45)$$

which contains a long-range attractive term (the one proportional to $1/r^6$, which can be justified in terms of electric dipole fluctuations) and a short-range repulsive one (proportional to $1/r^{12}$, which comes from the overlap of the electron orbitals, i.e. Pauli excluded principle). This potential is plotted in Figure 9.6. The minimum is in $r_{min} = 2^{1/\sigma}$. We can play with the range of attraction by changing σ or by changing the ϵ .

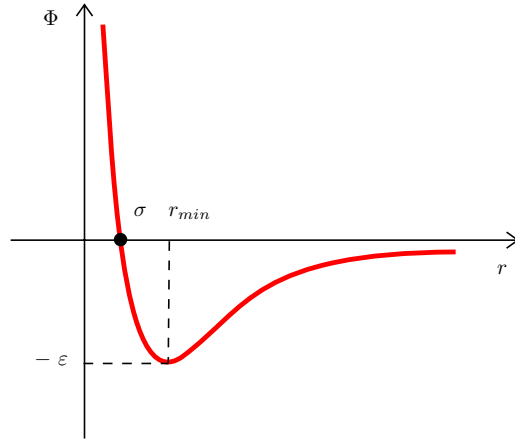


Figure 9.6: Plot of the Lennard-Jones potential Φ .

With this interaction potential, the first virial coefficient is:

$$B_2(T) = -2\pi \int_0^\infty r^2 \left[e^{-\frac{4\epsilon}{k_B T} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]} - 1 \right] dr$$

which is not analytically computable. However, it can be simplified defining the variables

$$x = \frac{r}{\sigma}, \quad \tau = \frac{k_B T}{\epsilon}$$

so that, integrating by parts $\int f'g = fg - \int g'f$ where $f' = x^2g = \exp[-()]$, we obtain

$$\begin{aligned} B_2(T^*) &= \frac{2}{3}\pi\sigma^3 \frac{4}{\tau} \int_0^\infty x^2 \left(\frac{12}{x^{12}} - \frac{6}{x^6} \right) e^{-\frac{4}{\tau} \left(\frac{1}{x^{12}} - \frac{1}{x^6} \right)} dx \\ &= A \int_0^\infty \left(\frac{12}{x^{16}} - \frac{6}{x^4} \right) e^{-\frac{4}{\tau} \left(\frac{1}{x^{12}} - \frac{1}{x^6} \right)} dx \end{aligned}$$

Now, we can expand the exponential and integrate term by term; this gives an expression of B_2 as a power series of $1/\tau$:

$$B_2(\tau) = -2A' \sum_{n=0}^\infty \frac{1}{4n!} \Gamma\left(\frac{2n-1}{4}\right) \left(\frac{1}{\tau}\right)^{\frac{2n+1}{4}} \quad (9.46)$$

where Γ is the Euler function and A' is a constant. Note that the attractive part of the Lennard-Jones potential has introduced in B_2 a dependence on the temperature.

9.3.4 Higher order terms in the cluster expansion

Let us consider again the formal expansion

$$\prod_i \left(\prod_{j>i} (1 + f_{ij}) \right) = 1 + \sum_{i,j>i} f_{ij} + \sum_{\substack{i,j>i \\ l>k \\ k>i \\ (ij) \neq (kl)}} f_{ij} f_{kl} + \dots$$

The problem with this expansion is that it groups terms quite different from one another. For example the terms $f_{12}f_{23}$ and $f_{12}f_{34}$. Indeed the first term corresponds to a diagram as in Figure 9.7a, while the second to two disconnected diagrams as in Figure 9.7b.



Figure 9.7

Another problem of the above expansion is that it does not recognize identical clusters formed by different particles. For example the terms $f_{12}f_{23}$ and $f_{12}f_{14}$ contribute in the same way to the partition function. It is then convenient to follow a diagrammatic approach similar to the Feynmann approach in the reciprocal space.

For the linear term f_{ij} the only diagram is given by Figure 9.8. As we have seen this has multiplicity

$$\frac{N(N-1)}{2}$$

and the integral is of the form

$$\int f_{12} d\vec{r}_1 d\vec{r}_2 = V \int f(\vec{r}) d\vec{r} = -2VB_2$$

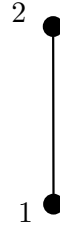


Figure 9.8

For the term $f_{ij}f_{kl}$ we can have the case as in Figure 9.9, that has multiplicity

$$\frac{N(N-1)}{2} \frac{(N-1)(N-3)}{2} \frac{1}{2}$$

and the integral is of the form

$$\int f_{12}f_{34} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

i.e. involving 4-particles

$$\begin{aligned} & \int f(|\vec{r}_1 - \vec{r}_2|) f(|\vec{r}_3 - \vec{r}_4|) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 = \\ & = V^2 \left(\int f(\vec{r}) d\vec{r} \right)^2 = 4V^2 B_2^2 \end{aligned}$$

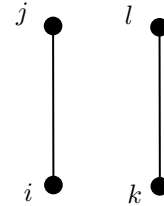


Figure 9.9

The next case is for instance as in Figure 9.10. This involves 3 particles. The multiplicity of this diagram is

$$\frac{N(N-1)(N-2)}{3!} \times 3$$

The integral is of the form

$$\begin{aligned} \int f_{12}f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 &\simeq V \left(\int dr f(r) \right)^2 = \\ &= \int f(|\vec{r}_1 - \vec{r}_2|)f(|\vec{r}_2 - \vec{r}_3|) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \\ &= V \left(\int f(\vec{r}) d\vec{r} \right)^2 = 4VB_2^2 \end{aligned} \quad (9.47)$$

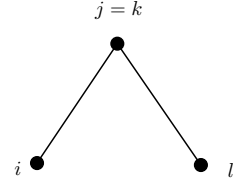


Figure 9.10

Another interesting diagram is the one in Figure 9.11. Its multiplicity is

$$\frac{N(N-1)(N-2)}{3!}$$

The associated integral involves 3 particles and it is of the form

$$\begin{aligned} \int f_{12}f_{23}f_{31} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 &= \\ &= \int f(|\vec{r}_1 - \vec{r}_2|)f(|\vec{r}_2 - \vec{r}_3|)f(|\vec{r}_3 - \vec{r}_1|) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= \int f(|\vec{r}_1 - \vec{r}_2|)f(|\vec{r}_2 - \vec{r}_3|)f(|\vec{r}_3 - \vec{r}_1|) d\vec{r}_2 d\vec{r}_{21} d\vec{r}_{23} \end{aligned}$$

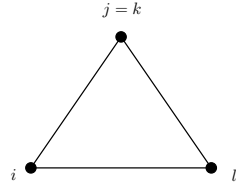


Figure 9.11

On the other hand $\vec{r}_{13} = \vec{r}_{23} - \vec{r}_{21}$, which implies

$$f(|\vec{r}_3 - \vec{r}_1|) = f(|\vec{r}_{23} - \vec{r}_{21}|)$$

Hence,

$$\int f(|\vec{r}_{12}|)f(|\vec{r}_{23}|)f(|\vec{r}_{31}|) d\vec{r}_{21} d\vec{r}_{23} d\vec{r}_2 = \int f(|\vec{r}_{12}|)f(|\vec{r}_{23}|)f(|\vec{r}_{23} - \vec{r}_{21}|) d\vec{r}_{21} d\vec{r}_{23} d\vec{r}_2$$

Let us call this integral

$$\int f_{12}f_{23}f_{31} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \equiv 3!V(B_3 - 2B_2^2) \quad (9.48)$$

The configurational partition function with the terms in Eq.9.47 and Eq.9.48 becomes

$$\begin{aligned} Q_N(V, T) &= V^N - V^N \frac{N(N-1)}{V} B_2 + V^N \frac{N(N-1)(N-2)(N-3)}{8V^2} (4B_2^2) + V^N \frac{N(N-1)(N-2)}{2V^2} 4B_2^2 \\ &= V^N \left(1 + \frac{N(N-1)}{V} B_2 + \frac{N(N-1)(N-2)(N-3)}{2V^2} B_2^2 + \frac{N(N-1)(N-3)}{V^2} B_3 \right) \end{aligned} \quad (9.49)$$

Let us now face the problem in a slightly different ways. Let us remind that

$$Q_N(V, T) = \sum_{\text{diagrams}} \int \prod_{kl} f_{kl} d^{3N}r \quad (9.50)$$

where the sum is over all possible diagrams, i.e. all possible ways in which ones can draw edges between pairs of points (k, l) . For each such diagrams I have to product between all edge and then integrate over the configurational space (N points).

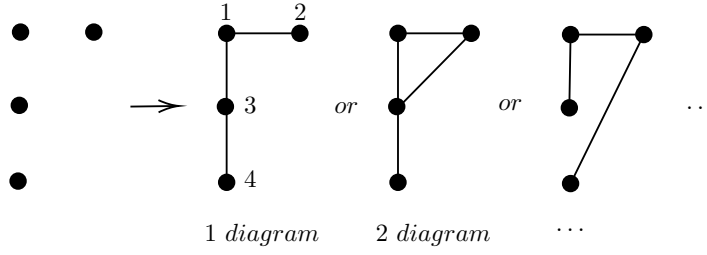


Figure 9.12: Example of connected diagrams for $i = 4$ sites.

Let us now consider only *connected* diagrams for i sites. In other words given i points (i particles) from a system of N points and I consider all the possible ways I can connect these i points (an example is shown in Figure 9.12).

For each diagram we take the product $\prod_{kl} f_{kl}$ and then integrate over the position of the i points (i particles). For a fixed diagram:

$$\int \prod_{kl \in \text{diagram}} f_{kl} d\vec{r}_1 \dots d\vec{r}_i$$

Example 29: Diagram for $i = 4$ sites

For example the diagram 1 in Figure 9.12 gives the contribution

$$\int f_{12} f_{13} f_{34} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

The diagram 2 gives

$$\int f_{12} f_{13} f_{23} f_{34} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

and so on.

Finally, we sum over all these connected diagrams of i points:

$$\sum_{\text{connected diagrams}} \int \prod_{lk \in \text{diagram}} f_{kl} d\vec{r}_1 \dots d\vec{r}_i$$

the results is what we call $(i!VB_i)$ and defines B_i . Let us analyze what happens for different values of i points:

- case $i = 1$: clearly $B_1 = 1$;
- case $i = 2$: just one edge, hence we have just one connected diagram. The integral becomes:

$$\int f_{12} d\vec{r}_1 d\vec{r}_2 = -2VB_2$$

- case $i = 3$: the connected diagrams are shown in Figure 9.13.

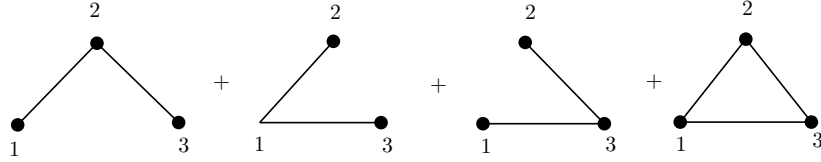


Figure 9.13: Connected diagrams for $i = 3$ points.

$$\begin{aligned}
 & \sum_{\substack{\text{connected diagrams} \\ \text{of } i = 3 \text{ points}}} \int \prod_{kl \in \text{diagram}} f_{kl} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \\
 & = \underbrace{\int f_{12}f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 + \int f_{12}f_{13} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 + \int f_{13}f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3}_{3V(\int f(\vec{r})d\vec{r})^2} \\
 & + \underbrace{\int f_{12}f_{23}f_{13} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3}_{3!V(B_3-2B_2^2)}
 \end{aligned}$$

Hence,

$$\begin{aligned}
 \sum_{\substack{\text{connected diagrams} \\ \text{of } i = 3 \text{ points}}} \int \prod_{kl \in \text{diagram}} f_{kl} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 &= 3V(-2B_2)^2 + 6V(B_3 - 2B_2^2) \\
 &= 6VB_3 = 3!VB_3
 \end{aligned}$$

Eventually, for the partition function we have to sum over all possible clusters. One possible procedure is:

1. given the N points we can partition them into connected clusters. For all i points we can make m_i clusters of that size i .

$$\sum_i i m_i = N$$

For each cluster of size i we have a term $(i!VB_i)$. If there are m_i of them we have a weight $(i!VB_i)^{m_i}$.

2. Now, we have to count in how many ways we can make the partition of N in a set of $\{m_i\}$ clusters. Clearly if we permute the label of the N vertices we have possible different clusters. In principle, this degeneracy is proportional to $N!$

On the other hand, if one changes the order of the labels within a cluster (in $i!$ ways) this does not change the cluster and since there are m_i clusters of size i we have to divide by $(i!)^{m_i}$.

Moreover, since there are m_i clusters one can swap them (in $m_i!$ ways). The degeneracy is $\frac{N!}{m_i!(i!)^{m_i}}$. Therefore,

$$Q_N(V, T) = \sum_{\{m_i\}} \prod_i \frac{N!}{m_i!(i!)^{m_i}} (i!VB_i)^{m_i} \quad (9.51)$$

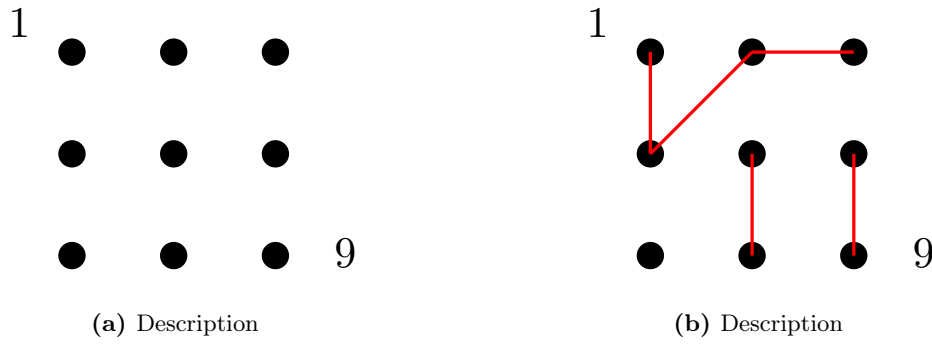


Figure 9.14

Exercise 7: $N = 9$ points

Consider the $N = 9$ points in Figure 9.14a.

1. Partition these points into clusters, as in Figure 9.14b.

For this partition $\{m_i\}$ we have $m_4 = 1, m_2 = 2, m_1 = 1$. Now, the cluster of size 4 can be connected in a given different ways $(4!VB_4)^1$.

2. Compute the degeneracy of this case (More on Huang chapter 10).

Chapter 10

Landau theory of phase transition for homogeneous systems

10.1 Introduction to Landau theory

Landau theory is a phenomenological mean field theory of phase transitions that aims at describing the occurrence of phase transitions in a unitary framework (no spatial variation of the order parameter). Landau theory is based on some assumptions, which we now introduce:

1. Existence of an uniform order parameter η . Remember the definition of the order parameter:

$$\eta = \begin{cases} 0 & T \geq \bar{T} \text{ (disordered phase)} \\ \neq 0 & T < \bar{T} \text{ (ordered phase)} \end{cases}$$

Well known examples are

$$\begin{cases} \eta \rightarrow m \\ \eta \rightarrow \rho_L - \rho_G \end{cases}$$

2. There exists a function \mathcal{L} called Landau free energy¹, which is an analytic function of the coupling constants $\{K_i\}$ of the system and of the order parameter η :

$$\mathcal{L} = \mathcal{L}(\eta)$$

3. The form of \mathcal{L} must satisfy the underlying symmetry of the system.
4. The equilibrium states of the system are the global minima of \mathcal{L} with respect to η .

We also assume that the thermodynamic properties of the system can be obtained by differentiating \mathcal{L} , just like we can do with thermodynamic potentials².

Note also that the general formulation of the Landau theory does not depend on the dimensionality of the system (although we will see that once a system has been chosen some details can depend on it).

Remark. Since \mathcal{L} is analytic it can be formally expanded in power of η , for $\eta \sim 0$.

$$\mathcal{L}(\eta) \approx a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + \dots \quad (10.1)$$

¹To be more precise, \mathcal{L} is the Landau free energy density; the "real" Landau free energy should be $L = V\mathcal{L}$.

²Strictly speaking, Landau free energy is not really a thermodynamic potential: the correct interpretation of \mathcal{L} is that it is a coarse grained free energy (not the exact one).

10.2 Landau theory for the Ising model

To make things more clear, let us now consider the Ising model without any external field and see how we can determine the form of \mathcal{L} from the general assumptions we have introduced. In this case η is a scalar (magnetization).

10.2.1 Costruction of \mathcal{L}

First of all, since the equilibrium configurations of the system must be minima of \mathcal{L} :

$$\frac{\partial \mathcal{L}}{\partial \eta} = a_1 + 2a_2\eta + 3a_3\eta^2 + \dots = 0$$

where we have chosen to stop the expansion at the three order. Now, since this equation must hold for all T and for $T > \bar{T}$ ³ we have $\eta = 0$, we see that $a_1 = 0$.

Considering now the constraint on the symmetries of the system, in absence of phase transitions for finite systems we have seen that the Ising model is invariant under parity (\mathbb{Z}^2 symmetry), i.e. its Hamiltonian is simultaneously even in H and $\{S_i\}$:

$$\mathcal{H}(H, \{S_i\}) = \mathcal{H}(-H, \{-S_i\})$$

Thus, in absence of external fields ($H = 0$) the Hamiltonian of the Ising model is even; this means that also \mathcal{L} must be invariant under parity, namely an even function of η :

$$\mathcal{L}(-\eta) = \mathcal{L}(\eta)$$

Therefore all the odd terms of the expansion are null:

$$a_{2k+1} = 0 \quad \forall k \in \mathbb{N}$$

Finally, since we have assumed that \mathcal{L} is an analytic function of η then its expansion cannot contain terms proportional to $|\eta|$.

In conclusion, the minimal expression for $\mathcal{L}(\eta)$ that describes the equilibrium phase diagram of an Ising-like system is:

$$\mathcal{L}(\eta) \simeq a_0(J, T) + a_2(J, T)\eta^2 + a_4(J, T)\eta^4 + O(\eta^6) \quad (10.2)$$

where the coefficients of the expansion a_0, a_2, a_4, \dots are functions of the physical parameters, J and T . However, \mathcal{L} can be further simplified and we can also explicitly show its dependence on the temperature. In fact, first of all we can note that a_0 is the value of \mathcal{L} in the paramagnetic state (when $T > \bar{T}$, $\eta = 0$):

$$\mathcal{L}(\eta = 0) = a_0$$

and so for simplicity we can set $a_0 = 0$ (it's just a constant shift in the energy, what matters is the free-energy difference).

Moreover, in order to have $\eta = \bar{\eta} \neq 0 < \infty$ for $T < \bar{T}$ (thermodynamic stability) we should impose that the coefficient of the highest power of η is always positive. In this case:

$$a_4(J, T) > 0$$

Indeed if this condition is violated \mathcal{L} reaches its absolute minimum for $\eta \rightarrow \pm\infty$, which makes no sense physically! The Landau free energy results

$$\mathcal{L}(\eta) \simeq a_2\eta^2 + a_4\eta^4, \quad \text{with } a_4 > 0 \quad (10.3)$$

³For $T > \bar{T}$ (critical point) we expect a paramagnetic phase.

Finally, fixing J and expanding the coefficients a_2 and a_4 as a function of the reduced temperature $t \equiv \frac{T-\bar{T}}{\bar{T}}$ (in T near \bar{T}), we obtain

$$a_2 \sim a_2^0 + \frac{T-\bar{T}}{\bar{T}} \frac{a}{2} + \dots, \quad a_4 \sim \frac{b}{4} + \dots$$

in the expansion of a_4 we have neglected any explicit dependence on $T - \bar{T}$ because as we will see it will not dominate the behaviour of the thermodynamics near \bar{T} . Moreover, by choosing $a_2^0 = 0$ the sign of a_2 is determined by the one of t . In particular, at $T = \bar{T}$, one has $a_2 = 0$.

We finally have that the form of the Landau free energy for the Ising model is given by:

$$\mathcal{L} = \frac{a}{2} t \eta^2 + \frac{b}{4} \eta^4 + O(\eta^6) \quad (10.4)$$

Remark. Does not matter the coefficient in green in front, so in the next part of the course we will change it. If it is written in this way we have always $a > 0$. We have also $b > 0$.

Note that, in presence of an external magnetic field h , one should consider the Legendre transform of \mathcal{L} obtaining its Gibbs version:

$$\mathcal{L}_G = \frac{a}{2} t \eta^2 + \frac{b}{4} \eta^4 - h \eta \quad (10.5)$$

we have inserted a field coupled with the order parameter.

10.2.2 Equilibrium phases

Let us now see what does the Landau theory for the Ising model predict. First of all, in the absence of external fields we have that the equilibrium states are determined by:

$$\frac{\partial \mathcal{L}}{\partial \eta} = 0 \quad \Rightarrow \quad at\eta + b\eta^3 = \eta(at + b\eta^2) = 0 \quad (10.6)$$

Hence, the minima are

$$\bar{\eta} = \begin{cases} 0 & t > 0 \text{ (i.e. } T > \bar{T}) \\ \pm \sqrt{\frac{-at}{b}} & t < 0 \text{ (i.e. } T < \bar{T}) \end{cases} \quad (10.7)$$

and at $T = \bar{T}$ the 3 solutions coincide!

Let us consider the two different cases:

- Case $t > 0$ ($T > \bar{T}$): the only global minimum of \mathcal{L} is the solution $\bar{\eta} = 0$. The second derivative of \mathcal{L} with respect to η is

$$\frac{\partial^2 \mathcal{L}}{\partial \eta^2} = at + 3b\eta^2$$

which results ≥ 0 for $\bar{\eta} = 0$ and in the case $t > 0$. It implies that $\eta = \bar{\eta}$ is a global minima, as in Figure 10.1a.

- Case $t < 0$ ($T < \bar{T}$): there are 3 solutions, $\bar{\eta} = 0$ and $\bar{\eta} = \pm \sqrt{-\frac{at}{b}}$. Let us see wheter they are minima or local maxima.

$$\left. \frac{\partial^2 \mathcal{L}}{\partial \eta^2} \right|_{\bar{\eta}=0} = at < 0 \quad \Rightarrow \quad \bar{\eta} = 0 \text{ local maxima (no equilibrium)}$$

$$\left. \frac{\partial^2 \mathcal{L}}{\partial \eta^2} \right|_{\bar{\eta} = \pm \sqrt{-\frac{at}{b}}} = at + 3b \left(-\frac{at}{b} \right) = -2at$$

since $t < 0$, we have $-2at > 0$ and hence $\bar{\eta} = \pm \sqrt{-\frac{at}{b}}$ are two minima!

$$\mathcal{L} \left(\bar{\eta} = \pm \sqrt{-\frac{at}{b}} \right) = -\frac{a^2 t^2}{2b} + \frac{a^2 t^2}{4b} = -\frac{a^2 t^2}{4b} < 0$$

Hence, the two minima have the same value are related by the group symmetry \mathbb{Z}^2 ($\bar{\eta} \rightarrow -\bar{\eta}$).

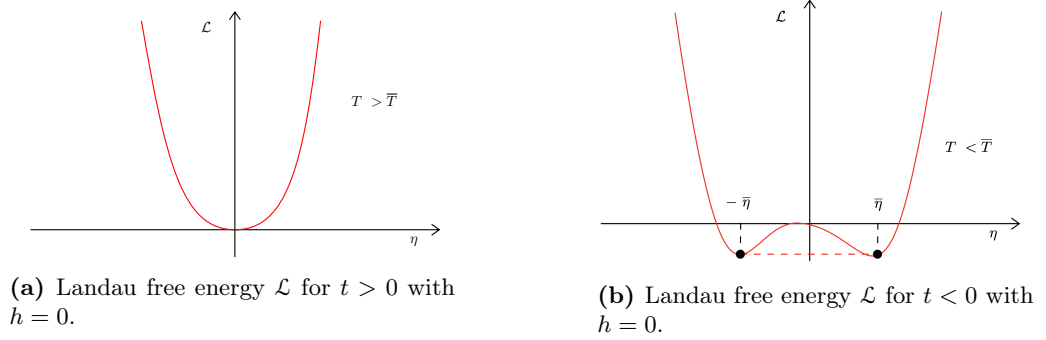


Figure 10.1

10.3 Critical exponents in Landau's theory

Let us therefore see what critical exponents does the Landau theory for the Ising model predict. Let us define $t \equiv \frac{T - \bar{T}}{T}$.

Exponent β

This is immediately determined from what we have just seen: in fact, $\eta \sim t^\beta$ for $h = 0$, $t \rightarrow 0^-$. Since $t < 0$, the minima of \mathcal{L} are

$$\bar{\eta} = \pm \sqrt{-\frac{at}{b}} \Rightarrow \beta = \frac{1}{2}$$

as expected.

Exponent α

The specific heat at zero field of the system is $C_H = -T \frac{\partial^2 \mathcal{L}}{\partial T^2}$. In particular, we have $C_H \sim t^{-\alpha}$ for $h = 0$, $|t| \rightarrow 0$. As we have seen:

- if $t > 0$: $\mathcal{L}(\bar{\eta} = 0) = 0$.
- if $t < 0$: $\mathcal{L}_{min} = \mathcal{L}(\bar{\eta} = \pm \sqrt{-\frac{at}{b}}) = -\frac{a^2 t^2}{4b}$.

Hence,

$$\mathcal{L}_{min} = \begin{cases} 0 & t > 0 \\ -\frac{a^2 t^2}{4b} & t < 0 \end{cases}$$

Therefore:

$$c_H = -T \frac{\partial^2 \mathcal{L}}{\partial T^2} = -T \frac{\partial^2}{\partial T^2} \left(-\frac{a^2}{4b\bar{T}^2} (T - \bar{T})^2 \right)$$

We have

$$\begin{aligned} \frac{\partial}{\partial T} \left[-\frac{a^2}{4b\bar{T}^2} (T - \bar{T})^2 \right] &= -\frac{a^2}{2b\bar{T}^2} (T - \bar{T}) \\ \frac{\partial^2}{\partial T^2} &= \frac{\partial}{\partial T} \left[-\frac{a^2}{2b\bar{T}^2} (T - \bar{T}) \right] = -\frac{a^2}{2b\bar{T}^2} \end{aligned}$$

Hence, the specific heat at zero field results

$$c_H = \begin{cases} 0 & T > \bar{T} \\ \frac{a^2}{2b\bar{T}^2} T & T < \bar{T} \end{cases}$$

We have $t \rightarrow 0^-$ if and only if $T \rightarrow \bar{T}^-$, which implies $c_H \rightarrow \frac{a^2}{2b\bar{T}}$ that is constant. Hence, in both cases:

$$\alpha = 0$$

Exponent δ

Let us remind that $h \sim \eta^\delta$ at $T = \bar{T}$. Considering now also an external field, the state equation of the system will be given by the differentiation of \mathcal{L} :

$$\frac{\partial \mathcal{L}}{\partial \eta} = a\eta + b\eta^3 - h = 0$$

Hence, the condition of equilibrium is

$$h = a\eta + b\eta^3 \quad (10.8)$$

This tells us that, for fixed h , the extreme points of \mathcal{L} are given by the values of η that satisfies Eq.(10.8) (see Figure 10.2).

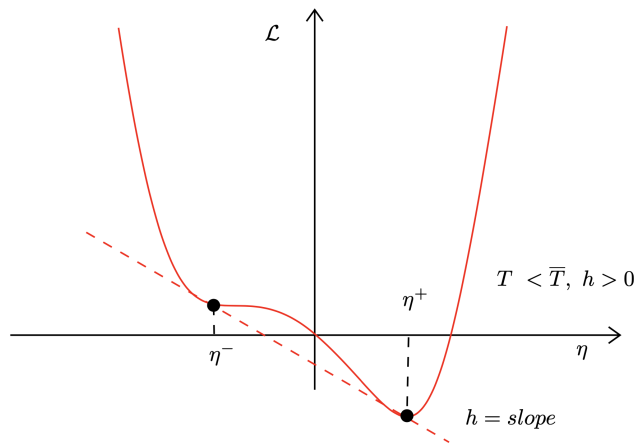


Figure 10.2: Plot of the Landau free energy for $t < 0$ with an external field $h > 0$.

At the critical point $T = \bar{T}$ ($t = 0$) we have $h \sim \eta^3$. Therefore:

$$\delta = 3$$

Exponent γ

Let us remind that $\chi_T \sim t^{-\gamma}$ for $h = 0$, $|t| \rightarrow 0$. If we now differentiate the state equation (10.8) with respect to h we get:

$$at \frac{\partial \eta}{\partial h} + 3b\eta^2 \frac{\partial \eta}{\partial h} = 1$$

Since $\chi = \frac{\partial \eta}{\partial h}$, we have

$$\chi = \frac{1}{at + 3b\eta^2}$$

If we now set $h = 0$, then for:

- $t > 0$: we will have $\bar{\eta} = 0$ and thus $\chi_T = \frac{1}{at}$.
- $t < 0$: we will have $\bar{\eta} = \pm \left(-\frac{at}{b}\right)^{1/2}$ and thus $\chi_T = -\frac{1}{2at}$.

In both cases $\chi_T \sim 1/t$ and thus:

$$\gamma = \gamma' = 1$$

Summary

In summary, the Landau theory for the Ising model gives the following (mean field) values of the critical exponents

$$\beta = \frac{1}{2}, \quad \alpha = 0, \quad \delta = 3, \quad \gamma = 1 \quad (10.9)$$

which, as we expected, are identical to those we have found within Weiss mean field theory. Moreover, Landau theory does not depend on the system dimension d (as expected since is a mean field theory) but only on its symmetries.

Remark. For a $O(n)$ (vector) model the order parameter η becomes a vector field $\vec{\eta}$ with n components and

$$\mathcal{L}_G(\vec{\eta}) = \frac{a}{2} t \vec{\eta} \cdot \vec{\eta} + \frac{b}{4} (\vec{\eta} \cdot \vec{\eta})^2 - \vec{h} \cdot \vec{\eta} + O((\vec{\eta} \cdot \vec{\eta})^3) \quad (10.10)$$

10.4 First-order phase transitions in Landau theory

Lecture 16.

Friday 6th

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As we have seen, Landau theory is based on the assumption that the order parameter is small near the critical point, and we have seen in the example of the Ising model how it can describe a continuous phase transition (in fact, for $t \rightarrow 0$ we have $\eta \rightarrow 0$). However, because of the symmetry properties of the Ising model we have excluded any possible cubic term; what we now want to do is to consider a more general form of \mathcal{L} which includes also a cubic term in η (in the case in which the symmetry is not violated), and see that this leads to the occurrence of a first-order phase transition. In fact, we want to generalize to include multicritical points, or phase transitions. Let us remember that in the Ising model we have phase transition derived by symmetry breaking, while now we have another type of phase transitions.

We have seen that since the order parameter is null for $T > \bar{T}$ the Landau free energy cannot contain any linear term in η . Let us therefore consider the simplest Landau free energy that depends on a particular field:

$$\mathcal{L}(\eta, t, h) = at\eta^2 - w\eta^3 + \frac{b}{4}\eta^4 - h\eta \quad (10.11)$$

where $t \equiv \frac{T-T^*}{2}$ and w is an additional parameter that we fix to be positive, $w > 0$; as in the previous case, we must have $b > 0$ so that η has finite values in the equilibrium configurations. In addition,

$$at = \frac{a}{2}(T - T^*) \quad \begin{cases} > 0 & \text{if } T > T^* \\ < 0 & \text{if } T < T^* \end{cases}$$

Remark. For $w < 0$ the results are the same, but in the $\eta < 0$ diagram.

The temperature T^* is the one at which we have the continuous transition if $w = 0$, but as we will see it doesn't have great significance now. The equilibrium configurations of the system, will be given by:

$$\frac{\partial \mathcal{L}_G}{\partial \eta} = 0 \quad \Rightarrow \quad h = 2at\eta - 3w\eta^2 + b\eta^3$$

In absence of external fields ($h = 0$), the equilibrium states becomes

$$h = 0 \quad \Rightarrow \quad \eta(2at - 3w\eta + b\eta^2) = 0$$

The solutions of this equation are

$$\begin{cases} \bar{\eta} = 0 & \text{disordered phase} \\ \bar{\eta}_{\pm} = \frac{1}{2b} \left(3w \pm \sqrt{9w^2 - 8abt} \right) & \text{ordered phases} \end{cases} \quad (10.12)$$

Let us rewrite the ordered solutions as

$$\bar{\eta}_{\pm} = \frac{1}{2b} \left(3w \pm \sqrt{9w^2 - 8abt} \right) = c \pm \sqrt{c^2 - \frac{2at}{b}} \quad (10.13)$$

with

$$c = \frac{3w}{2b}$$

However, these two last solutions are possible only if:

$$\bar{\eta}_{\pm} \in \mathbb{R} \iff c^2 - \frac{2at}{b} > 0 \iff t = \frac{T - T^*}{2} < \frac{c^2 b}{2a} \equiv t^{**} \equiv \frac{T^{**} - T^*}{2}$$

Hence, we have

$$T^{**} = T^* + \frac{c^2 b}{a} = T^* + 2t^{**}$$

so, since t^{**} is positive, this will occur at temperatures higher than T^* . Let us consider different cases:

- If $t > t^{**}$ ($T > T^{**}$), then the system will be in the disordered phase and we have $\bar{\eta}_{\pm} \notin \mathbb{R}$. The only real solution is $\bar{\eta} = 0$ that is also the absolute minimum of \mathcal{L} . The plot is shown in Figure 10.3.
- If $t \leq t^{**}$ ($T \leq T^{**}$), we have $\bar{\eta}_{\pm} = c \pm \sqrt{c^2 - \frac{at}{b}} \in \mathbb{R}$ are both possible solutions. One will be a local maximum and the other a local minimum.
 - At $T = T^{**}$, we have $\bar{\eta}_- = \bar{\eta}_+$ (flex point), as shown in Figure 10.4.
 - For $T_t < T < T^{**}$, a new minimum appears at $\eta = \bar{\eta}_+$, but we will have $\mathcal{L}(\bar{\eta}_+) > 0$, so this is only a local minimum (since $\mathcal{L}(0) = 0$): in this range of temperatures the ordered phase is metastable. The plot is shown in Figure 10.5.

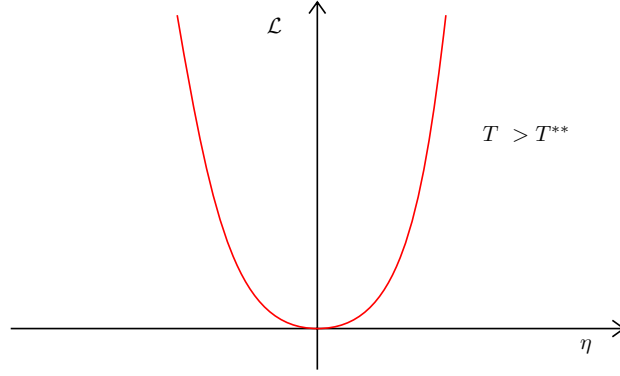


Figure 10.3: Landau free energy for $t > t^{**}$ ($T > T^{**}$). The point $\bar{\eta} = 0$ is the absolute minimum.

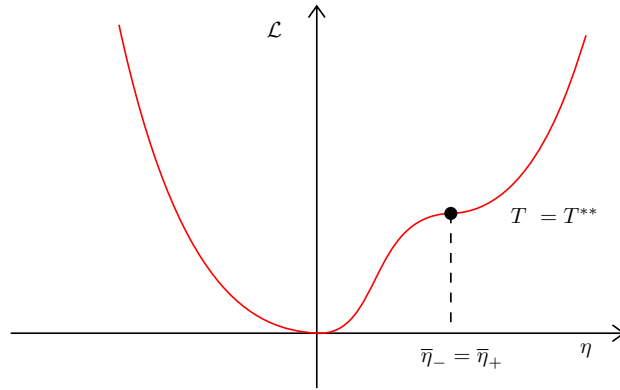


Figure 10.4: Landau free energy for $t \leq t^{**}$ ($T = T^{**}$). The point $\bar{\eta}_- = \bar{\eta}_+$ is a flex one.

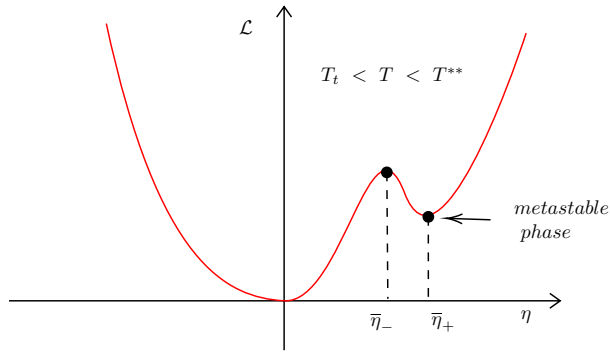


Figure 10.5: Landau free energy for $t \leq t^{**}$ ($T_t < T \leq T^{**}$). The point $\bar{\eta}_+$ is a local minimum.

- If we further decrease the temperature T , we will reach a temperature $T = T_t$ for which $\mathcal{L}(\bar{\eta}_+) = 0 = \mathcal{L}(0)$: at this point the ordered and disordered phase coexist, so this is the temperature of a new transition! The plot is shown in Figure 10.6. T_t is given by the coexistence condition

$$\mathcal{L}(\bar{\eta}_+) = \mathcal{L}(0)$$

that is the coexistence between the disordered and ordered phases. In fact, in the plot of Figure 10.6 we see that there are two minima in the same line, this is a first order transition.

- Finally for $T^* < T < T_t$, $\bar{\eta}_+$ becomes negative and so now $\eta = \bar{\eta}_+$ is the global minimum of \mathcal{L} : the ordered phase becomes stable and the disordered

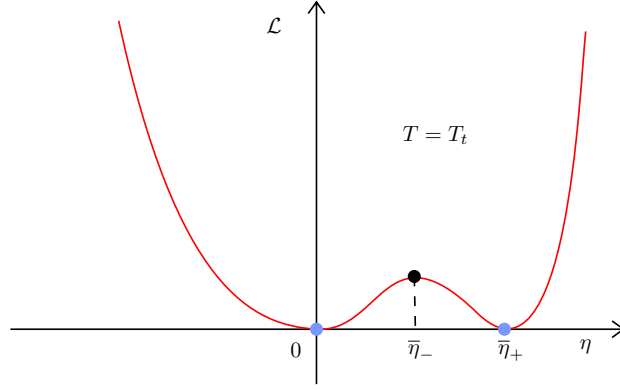


Figure 10.6: Landau free energy for $t \leq t^{**}$ ($T = T_t$). The point $\bar{\eta}_+$ is a minimum. The ordered and disordered phase coexist.

phase metastable, indeed now $\eta = 0$ is only a local minimum (see Figure 10.7).

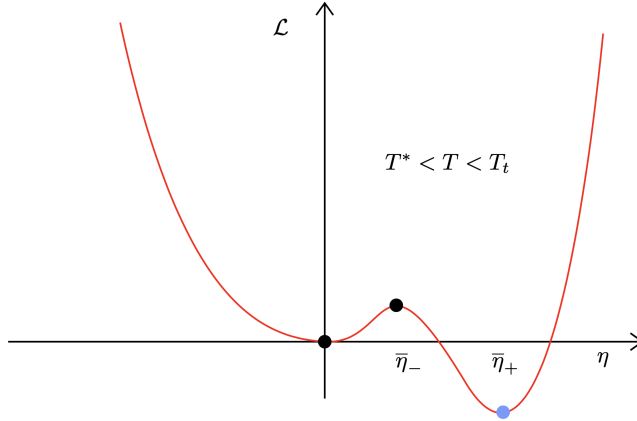


Figure 10.7: Landau free energy for $t \leq t^{**}$ ($T^* < T < T_t$). The point $\bar{\eta}_+$ is the global minimum.

- If now $T < T^*$, \mathcal{L} develops a new minimum for $\eta < 0$, but it is only a local minimum (the asymmetry introduced by $-w\eta^3$ ensures that $\bar{\eta}_+$ is always the global minimum). This means that also for $T < T^*$ the disordered phase with $\bar{\eta}_+$ continues to be the stable one, and so no phase transition occurs at T^* any more; this is what we meant when we said that T^* is not a relevant temperature any more.

Therefore, we have seen that lowering the temperature of the system, the value of η for which \mathcal{L} has a global minimum changes discontinuously from $\eta = 0$ to $\bar{\eta}_+$: this is a first-order transition. All the results obtained are shown in Figure 10.8.

As we said, at $T = T_t$ the system undergoes a first order transition. It is defined by two conditions: it must be a minimum of \mathcal{L} and such that the value of \mathcal{L} in that minimum is zero. Thus we can determine T_t as follows:

$$\begin{cases} \frac{\partial \mathcal{L}}{\partial \eta} = 0 = \eta(2at - 3w\eta + b\eta^2) & \text{extreme condition} \\ \mathcal{L}(0) = \mathcal{L}(\eta_+) = 0 = \eta^2(at - w\eta + \frac{b}{4}\eta^2) & \text{coexistence condition} \end{cases}$$

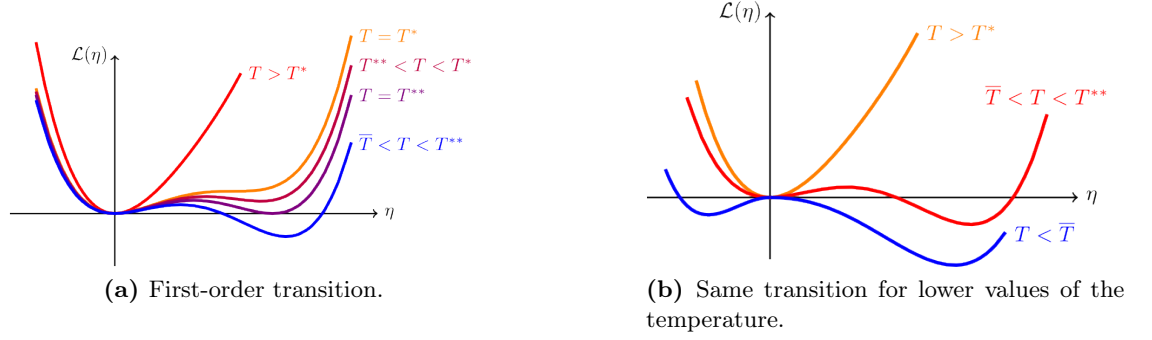


Figure 10.8: The notation in this plot is different from the one used previously. Here $\bar{T} \equiv T^*$, $T^* \equiv T^{**}$ and $T^{**} \equiv T_t$.

Therefore, for $\eta \neq 0$:

$$\Rightarrow \begin{cases} 2at - 3w\eta + b\eta^2 = 0 \\ at - w\eta + \frac{b}{4}\eta^2 = 0 \end{cases}$$

Solving with respect to η and t , we get

$$\begin{cases} \bar{\eta}_t = +\frac{2w}{b} > 0 \\ t_t = \frac{2w^2}{ab} \end{cases}$$

Since by the definition $t = (T - T^*)/2$, we have:

$$T_t = T^* + \frac{4w^2}{ab} \quad (10.14)$$

Remark. Let us note that $T_t > T^*$.

Since at $T = T_t$ there is a first order transition does the system display latent heat?

$$s = -\frac{\partial \mathcal{L}}{\partial T} \Big|_{\eta_t} = -\frac{1}{2}a\bar{\eta}_t^2 = -\frac{a}{2}\left(\frac{2w}{b}\right)^2$$

Hence, there is an entropy jump. The latent heat absorbed to go from the ordered to the disordered phase is

$$q = -T_t s = \frac{a}{2}T_t \left(\frac{2w}{b}\right)^2 \quad (10.15)$$

10.4.1 Phase stability and behaviour of χ_T

Finally, we can also determine the susceptibility of the system:

$$\chi_T \equiv \frac{\partial \eta}{\partial h}$$

In the presence of an external field, let us derive the equation of state with respect to h :

$$\frac{\partial}{\partial h} \left(\frac{\partial \mathcal{L}_G}{\partial \eta} = 0 \right) = \frac{\partial}{\partial h} (2at\eta - 3w\eta^2 + b\eta^3 = h)$$

Hence, since $\chi_T \equiv \frac{\partial \eta}{\partial h}$,

$$\chi(2at - 6w\eta + 3b\eta^2) = 1$$

The result is

$$\chi_T = \frac{1}{2at - 6w\eta + 3b\eta^2} \quad (10.16)$$

We now make use of equation (10.16) to compute the limit of stability of the phases we have found.

10.4.2 Computation of T^{**}

As said, $T = T^{**}$ is the value below which the ordered phase becomes a metastable state (local minima). In particular, since for $T = T^{**}$ the point $\bar{\eta}_- = \bar{\eta}_+$ is a flex point, we have the condition

$$\frac{\partial^2 \mathcal{L}}{\partial \eta^2} = 0$$

thus:

$$\frac{\partial}{\partial \eta}(2at\eta - 6w\eta^2 + b\eta^3 = h) = 0 \Rightarrow 2at - 6w\eta + 3b\eta^2 = \frac{\partial h}{\partial \eta} = \chi^{-1} = 0$$

Remember that at $T = T^{**}$ the two solutions $\bar{\eta}_{\pm}$ coincide, hence from Eq.(10.13) we have

$$c^2 - \frac{2at}{b} = 0 \Rightarrow \bar{\eta}_{\pm} = \eta_2 = \frac{3w}{2b}$$

Inserting in the expression with $\chi^{-1} = 0$, we have

$$\chi^{-1} = 0 = 2at^{**} - 6w\bar{\eta}_2 + 3b\bar{\eta}_2^2$$

Hence,

$$\Longleftrightarrow t^{**} = \frac{9w^2}{8ab} = \frac{1}{2}(T^{**} - T^*) \quad (10.17)$$

Remind that for $T_t < T < T^{**}$ the ordered phase $\bar{\eta}_+$ is metastable.

10.4.3 Computation of T^*

The instability of the disordered phase $\eta = 0$ is when \mathcal{L} presents a flex point at $\eta = 0$. Therefore, from the condition

$$\left. \frac{\partial^2 \mathcal{L}}{\partial \eta^2} \right|_{\bar{\eta}=0} = 0$$

we have

$$\chi^{-1} = 2at - 6w\eta + 3b\eta^2 = \frac{\partial h}{\partial \eta} = 0 \Rightarrow 2at = 0 \Rightarrow t = 0$$

Hence, we have

$$\Rightarrow T = T^* \quad (10.18)$$

thus no phase transition occurs at T^* any more. The plot of the Landau free energy in the case $T = T^*$ is shown in Figure 10.9.

10.5 Multicritical points in Landau theory

It is possible for a system to have more "disarranging parameters" than the only temperature T ; let us call one such field Δ . In this case the phase diagram of the system becomes richer, with coexistence and critical lines that intersect in points called multicritical points; one of the most common examples of a multicritical point is the *tricritical point*, which divides a first-order transition line from a second-order one. An example of a system of the type we are considering is the Blume-Emery-Griffiths model, which we have studied in Mean field theory for the Blume-Emery-Griffiths model. In that case the additional "disarranging field" was the concentration x of He^3 , and the tricritical point is the one we called (x_t, T_t) .

Such a phenomenology can be obtained within Landau theory also with terms different from a simple cubic one; in particular, we can have first order phase transitions

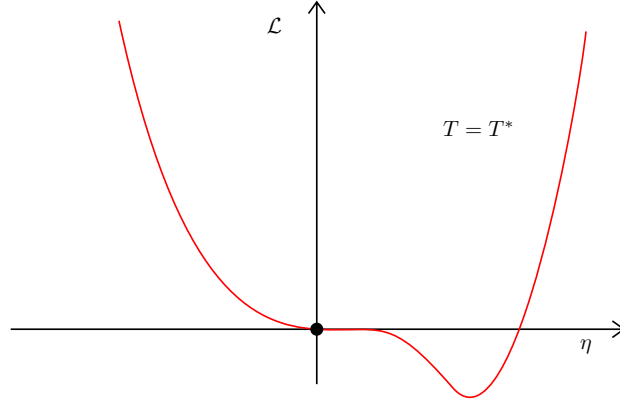


Figure 10.9: Landau free energy for $t \leq t^{**}$ ($T = T^*$). The point $\bar{\eta}_+$ is the global minimum, while the point $\bar{\eta} = 0$ is a flex point.

even when the system is invariant under parity, like in the case of the Ising model. In fact in that situation we required the coefficient of η^4 to be always positive, but if this is not true then \mathcal{L} will be:

$$\mathcal{L}(T, \Delta, \eta) = \frac{a(t, \Delta)}{2} \eta^2 + \frac{b(t, \Delta)}{4} \eta^4 + \frac{c}{6} \eta^6 - h\eta \quad (10.19)$$

where a, b and c are functions of two parameters (T, Δ) and $c > 0$ positive for the stability of the system (otherwise, like in the case previously considered, the minimization of \mathcal{L} leads η to infinity); Δ is the disordered field (in the BEG model Δ was the % He³ atoms).

Remark. To allow the coefficient of η^4 to change sign, we need the η^6 term.

Let us study the phenomenology of Δ (Δ_c is a critical value):

- If $\Delta < \Delta_c$: as T decreases, $a(T, \Delta)$ decreases and, at $T = T_c(\Delta)$, becomes zero. In this region $b(T, \Delta) > 0$ and the system displays the standard (η^4) critical point. At $T = T_c$ we have:

$$T = T_c(\Delta) \Rightarrow \begin{cases} a(T_c, \Delta) = 0 \\ b(T_c, \Delta) > 0 \end{cases}$$

If a changes sign and b is kept positive (which can be done varying the values of T and Δ in a way such that a goes to zero faster than b , depending of course on their explicit expressions) then a critical transition occurs since in this case $\eta = 0$ becomes a local maximum for \mathcal{L} , and it develops two new global minima. Therefore, the solution of the equation $a(T, \Delta) = 0$ will give a line of critical points in (T, Δ) plane.

- If $\Delta > \Delta_c$: as T decreases, $b(T, \Delta)$ becomes zero before $a(T, \Delta)$. At $T = T_c$ we have

$$T = T_c(\Delta) \Rightarrow \begin{cases} a(T_c, \Delta) > 0 \\ b(T_c, \Delta) = 0 \end{cases}$$

Hence, if b becomes negative while a is still positive (which again can be done varying T and Δ so that b vanishes faster than a) then something rather different happens: in this case, one can show that as b approaches zero \mathcal{L} develops two new symmetric local minima at $\bar{\eta}_{\pm}$ (similarly to the case analysed before, with

the difference that now the situation is perfectly symmetric since \mathcal{L} is even) and they will become the new global minima as $\mathcal{L}(\bar{\eta}_{\pm}) = 0$, which happens when b changes sign: this way the equilibrium value of the order parameter change discontinuously from zero to a non-zero quantity so a first-order transition has indeed happened.

In this case, we have

$$\mathcal{L} = a\eta^2 + c\eta^6, \quad a > 0$$

The equilibrium states are

$$\frac{\partial \mathcal{L}}{\partial \eta} = 2a\eta + 6c\eta^5 = 0$$

so, the solutions are

$$\begin{cases} \eta = 0 \\ \eta_{1,2,3,4} \end{cases}$$

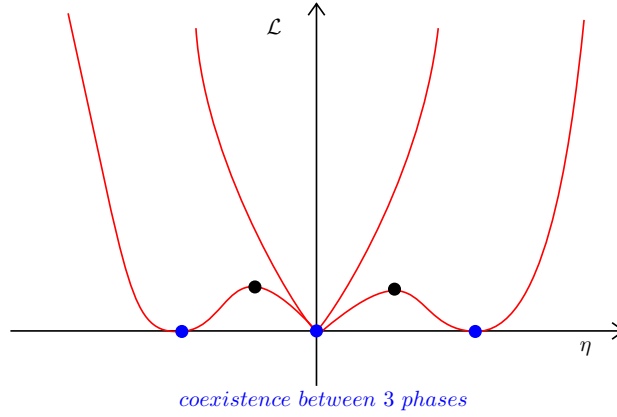


Figure 10.10: Landau free energy for $\Delta > \Delta_c$. There is coexistence between three phases, in fact there are 3 global minima.

- Case $\Delta = \Delta_t$: the tricritical point is given by the values of $\Delta = \Delta_t$ and $T = T_c$ such that

$$a(\Delta_t, T_t) = b(\Delta_t, T_t) = 0$$

This means that when both a and b are null the system goes from exhibiting a continuous critical transition to a discontinuous first-order one; in other words, the tricritical point (T_c, Δ_c) can be determined from the solution of the equations $a(T, \Delta) = 0$ and $b(T, \Delta) = 0$.

At the tricritical point the system is described by the following Landau free-energy:

$$\mathcal{L}_t = c\eta^6 - h\eta$$

The equation of state is

$$\frac{\partial \mathcal{L}_t}{\partial \eta} = 0 \quad \Rightarrow \quad h = 6c\eta^5$$

The first-order transition with an even \mathcal{L} are shown in Figure 10.11.

To conclude let us consider again a system with an Ising-like Landau free energy, where $c > 0$ and a, b are in general functions of the reduced temperature t (and also

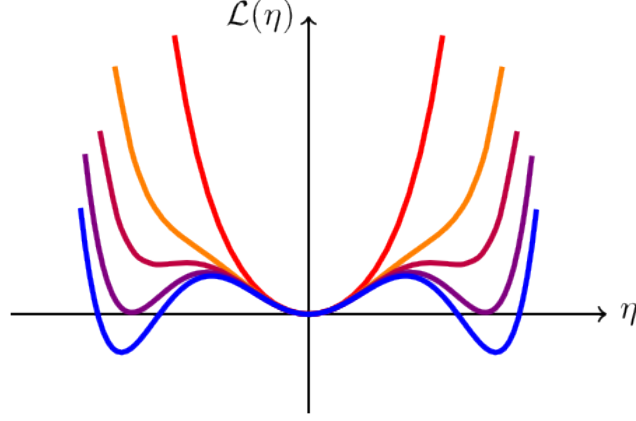


Figure 10.11: First-order transition with an even \mathcal{L} .

of the other "disarranging" parameter Δ , which we now neglect). The Landau free energy is again

$$\mathcal{L} = \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + \frac{c}{6}\eta^6 - h\eta$$

We now want to show that we can understand how the phase diagram of the system is in (a, b) space, i.e. that we can draw where the phase transition lines are and so we are able to visually represents where the various phases of the system are in (a, b) plane.

First of all, we can note that when $a, b > 0$ the only minimum of \mathcal{L} is $\bar{\eta} = 0$, so the system is in the paramagnetic phase. Furthermore if $a < 0$ and $b > 0$ the system is in the magnetic phase, and a second order transition has occurred; therefore we can surely say that the half-line $a = 0, b > 0$ is a second order transition line.

We must thus determine where the first order transition line lies in (a, b) space. In order to do so, we first note that the extrema of \mathcal{L} are given by:

$$0 = \frac{\partial \mathcal{L}}{\partial \eta} = \eta(a + b\eta^2 + c\eta^4) \Rightarrow \bar{\eta}_{\pm}^2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2c}$$

(and of course they exist only when the temperature is such that $b^2 - 4ac > 0$) and since:

$$\frac{\partial^2 \mathcal{L}}{\partial \eta^2} \Big|_{\bar{\eta}_{\pm}} = \pm \bar{\eta}_{\pm}^2 \cdot 2\sqrt{b^2 - 4ac}$$

we have that $\pm \bar{\eta}_{+}$ are maxima while $\pm \bar{\eta}_{-}$ are minima. The first order transition happens when $\mathcal{L}(\pm \bar{\eta}_{\pm}) = \mathcal{L}(0) = 0$, so:

$$\frac{a}{2}\bar{\eta}_{+}^2 + \frac{b}{4}\bar{\eta}_{+}^4 + \frac{c}{6}\bar{\eta}_{+}^6 = 0 \Rightarrow \frac{a}{2} + \frac{b}{4}\bar{\eta}_{+}^2 + \frac{c}{6}\bar{\eta}_{+}^4 = 0$$

Now, from the condition $\partial \mathcal{L} / \partial \eta = 0$ we can express $\bar{\eta}_{+}^4$ as a function of $\bar{\eta}_{+}^2$, and we get $\bar{\eta}_{+}^4 = -(a + b\bar{\eta}_{+}^2)/c$. Substituting we get:

$$\bar{\eta}_{+}^2 = -4\frac{a}{b}$$

and substituting again in $\bar{\eta}_{+}^2 = (-b + \sqrt{b^2 - 4ac})/(2c)$ in the end we get:

$$b = -4\sqrt{\frac{ac}{3}}$$

so the first order transition line is a parabola in (a, b) plane (in particular it will lie in the fourth quadrant). In the end the situation is as in Figure 10.12. As we can see the tricritical point of the system, being the point that divides the first-order from the second-order transition line, is the origin $(0, 0)$ of the parameter space.

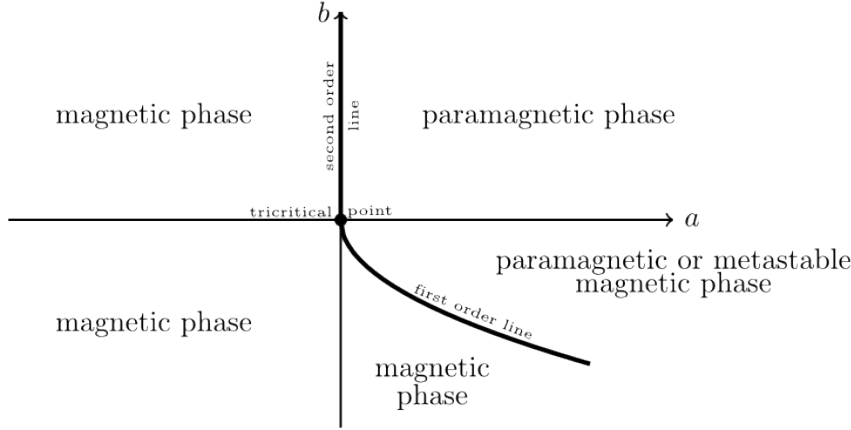


Figure 10.12: Phase diagram of the system in (a, b) space.

10.6 Liquid crystals

We now proceed to study a particular physical system, liquid crystals, to which we will apply Landau theory of phase transitions. As we will see the symmetries of the system will allow the Landau free energy to include a cubic term in the order parameter (which we will properly define), and so we will be able to describe the first-order transition from an isotropic to a nematic phase (which we are now going to introduce).

10.6.1 What are liquid crystals?

Liquid crystals phase (LC) can be seen as an intermediate phase between a liquid and a solid: they are liquid like any other conventional fluid, but also have internal orientational order like solid crystals. This orientational order provides them particular anisotropic properties from an optical, electric and magnetic point of view. The most common structural characteristics of the molecules that constitute liquid crystals are the following:

- They have an elongated, anisotropic shape.
- Their axes can be considered rigid with good approximation.
- They have strong electric dipoles or easily polarizable groups.

Furthermore, it seems that the groups located at the extremities of a molecule are not relevant for the formation of phases.

The vast majority of the interesting phenomenology of liquid crystals concerns the geometry and dynamics of the preferred axis of orientation $\vec{n}(\vec{r})$, called *director*. This is a 'two arrow vector' that gives the local average alignment of the elementary constituents. In this description the amplitude of $\vec{n}(\vec{r})$ is irrelevant and one takes $\vec{n}(\vec{r})$ such that is unitary (i.e. $|\vec{n}(\vec{r})| = 1$). Since there is no head-tail symmetry (apolar order), $\vec{n} = -\vec{n}$ (i.e. $+\vec{n}(\vec{r})$ and $-\vec{n}(\vec{r})$ are physically equivalent). There is a plethora of possible liquid crystal phases; the most common are:

- **Nematic:** this phase is characterized by a very strong long-ranged orientational order: the main axes of the molecules tend to orientate along a preferred direction (see Figure 10.14), determined by the director. There is no long-ranged translational order of the molecular centers of mass, even if a short-ranged one can exist.

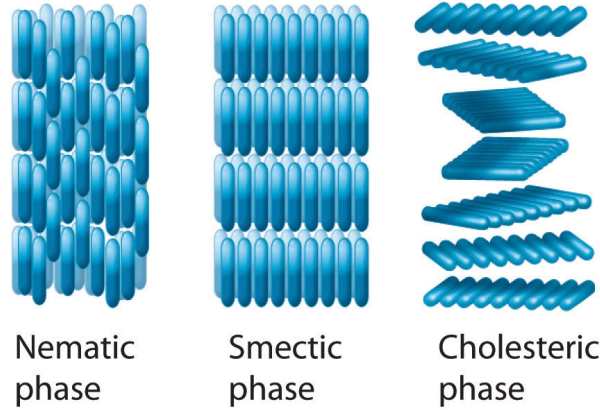


Figure 10.13: Graphical representation of the nematic, smectic and cholesteric phases of a liquid crystal.

From optical point of view the Nematic phase is birifrangent, i.e. they exhibit two different refractive indexes: one parallel to the director \vec{n} (called ordinary refractive index) and one orthogonal to it (special refractive index). These optical properties of the nematic phase are used to build devices like LCDs.

- **Smectic:** also in this phase the molecules are aligned along a preferred direction, but contrarily to the nematic one this phase has also a spatial periodic order: the molecules are organised in layers. Furthermore, differently from nematic phases, smectic liquid crystals have non-uniform density and are generally more viscous.
- **Cholesteric:** It is similar to the nematic phase since it has a long-ranged orientational order, but the direction of \vec{n} changes regularly in space; the typical configuration of a cholesteric liquid crystal has a director $\vec{n}(\vec{r})$ that rotates when \vec{r} varies along a particular direction: for example, in a three-dimensional reference frame the molecules are orientated along the y direction in xy plane, but this direction roteates if z changes.

The structure of a cholesteric liquid crystal is characterised by the spatial distance along the torsion axis, called pitch, after which the director has rotated by an angle of 2π . The pitch of the most common cholesteric liquid crystals is of the order of several hundred nanometers, so comparable with the wavelength of visible light; furthermore, it can also be very sensitive to changes in temperature, chemical composition, or external electromagnetic fields. Note also that a nematic liquid crystal can be seen as a cholesteric one with infinite pitch; these two phases in fact are not independent from each other, and there is no real phase transition between them.

10.6.2 Definition of an order parameter for nematic liquid crystals

What we now want to do is to apply Landau theory to liquid crystals in order to study the transition from an isotropic to a nematic phase (Figure 10.14); therefore, we must define an order parameter for such a system. This is absolutely not trivial, and there are two ways to do it a microscopic and a macroscopic one. We will use a macroscopic approach.

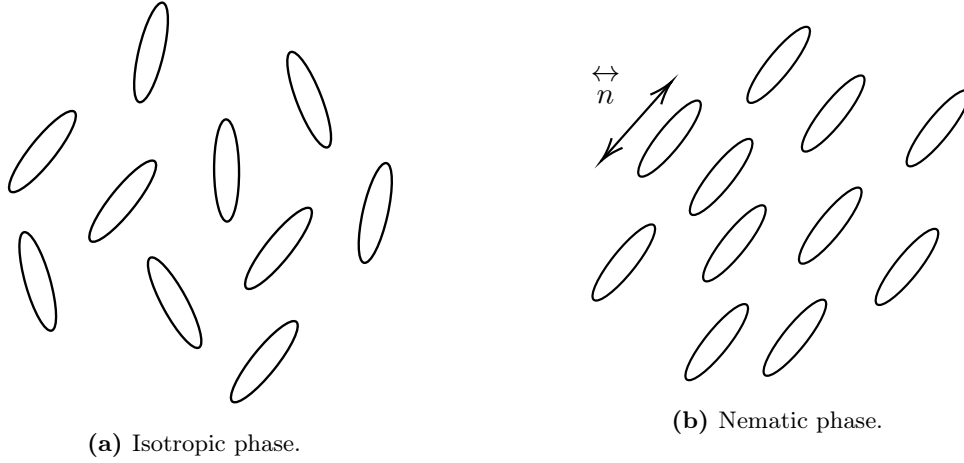


Figure 10.14

Macroscopic approach

From a macroscopic point of view we have already stated that an important difference between the disordered and nematic phases consists in the response functions when the liquid crystal is subjected to magnetic or electrical fields. Hence, a macroscopic definition of an order parameter for LC phase is based on the system response when subject to fields. For instance, supposing that we have a liquid crystal subject to an external magnetic field \vec{H} , the diamagnetic response of the system will be measurable in terms of its magnetization \vec{M} , and in particular:

$$\vec{M} = \bar{\chi} \vec{H} \quad (10.20)$$

where $\bar{\chi}$ is the response function matrix, namely the magnetic susceptibility of the system. In components we have:

$$M_\alpha = \chi_{\alpha\beta} H_\beta \quad (10.21)$$

where the indexes α, β stands for x, y, z . If \vec{H} is static, then χ is symmetric, i.e.

$$\chi_{\alpha\beta} = \chi_{\beta\alpha}$$

In the isotropic phase χ will also be diagonal, namely

$$\chi_{\alpha\beta} = \chi \delta_{\alpha\beta}$$

while in the nematic phase For a LC in the neumatic one has

$$\chi_{\alpha\beta} = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix} \quad (10.22)$$

where, as before, we have supposed that the director \vec{n} is parallel to the z direction.

Therefore we could build an order parameter in terms of the susceptibility χ , and this parameter will necessarily have a tensorial nature (since χ itself is in general a tensor), so it will not be a simple scalar like in the previous case. Since we want our order parameter to vanish in the disordered phase, we can define it "removing" from χ its isotropic component. In other words, in components we can define:

$$Q_{\alpha\beta} = A \left(\chi_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \text{Tr } \bar{\chi} \right) \quad (10.23)$$

where A is a constant. In this way Q is a good tensorial order parameter. In particular, the order parameter is a second rank traceless tensor. Let us note that its definition is completely general, and in fact it is useful also to describe other kinds of phases, not only the uniaxial nematic one.

It is possible to show that $Q_{\alpha\beta}$ can be written in terms of the local average orientational order of the elementary constituents, $\overleftrightarrow{n}(\vec{r})$ and the degree of local order given by a scalar $S(\vec{r})$. Hence, we can define

$$Q_{\alpha\beta}(\vec{r}) = S(\vec{r}) \left(n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) - \frac{1}{3} \delta_{\alpha\beta} \right) \quad (10.24)$$

The advantage of this definition of the order parameter (which is the one we will use in the following) is that it also takes into account the degree of orientation and the mean direction. By definition Q is symmetric and traceless⁴, so in general way we can write it as:

$$Q = \begin{pmatrix} q_1 & q_2 & q_3 \\ q_2 & q_4 & q_5 \\ q_3 & q_5 & -q_1 - q_4 \end{pmatrix} \quad (10.25)$$

10.6.3 Landau-de Gennes theory for nematic liquid crystals

Since we now have a proper order parameter, we can formulate the Landau theory for the phase transitions of nematic liquid crystals (also called Landau-de Gennes theory). In particular we want to study the transition between the isotropic and nematic phase, and we call T_{n-i} the temperature at which it occurs.

As we have already stated, the Landau free energy \mathcal{L} must be consistent with the symmetries of the system, so in this case it must be invariant under rotations. Now, since Q transforms as a tensor under rotations and \mathcal{L} must be a scalar, it will contain terms of the form $\text{Tr } \bar{Q}^P$; to the fourth order we will have (the linear term is absent because by definition Q is traceless, i.e. $\text{Tr}(Q) = 0$):

$$\mathcal{L} = \mathcal{L}_0 + \frac{1}{2} A(T) \text{Tr } \bar{Q}^2 + \frac{1}{3} B(T) \text{Tr } \bar{Q}^3 + \frac{1}{4} C(T) \left[\left(\text{Tr } \bar{Q}^2 \right)^2 + \text{Tr } \bar{Q}^4 \right]$$

In reality this expression, and in particular the quartic term, can be simplified: in fact it is a property (which we will not prove) of any $n \times n$ symmetric matrix that $\text{Tr } \bar{Q}^s$ with $s > n$ can be expressed as a polynomial of $\text{Tr } \bar{Q}^p$ with $p < n$, so in our case any $\text{Tr } \bar{Q}^s$ with $s \geq 4$ can be expressed in terms of $\text{Tr } \bar{Q}^2$ and $\text{Tr } \bar{Q}^3$ (we are automatically neglecting $\text{Tr } \bar{Q}$ since in our case it vanishes, but in general it must be considered). Therefore, we can write the Landau free energy as:

$$\mathcal{L} = \mathcal{L}_0 + \frac{1}{2} A(T) \text{Tr } \bar{Q}^2 + \frac{1}{3} B(T) \text{Tr } \bar{Q}^3 + \frac{1}{4} C(T) \left(\text{Tr } \bar{Q}^2 \right)^2 \quad (10.26)$$

or, in components:

$$\mathcal{L} = \mathcal{L}_0 + \frac{1}{2} A(T) Q_{\alpha\beta} Q_{\beta\alpha} + \frac{1}{3} B(T) Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{1}{4} C(T) (Q_{\alpha\beta} Q_{\beta\alpha})^2 \quad (10.27)$$

Remark. Since each 3×3 matrix satisfies the relation

$$\text{Tr } \bar{Q}^4 = \frac{1}{2} \left(\text{Tr } \bar{Q}^2 \right)^2$$

the term proportional to $C(T)$ can be written as $\frac{1}{2} C(T) \text{Tr } \bar{Q}^4$.

⁴A matrix whose trace is zero is said to be traceless.

Let us note that since our order parameter is a tensor its invariance under rotations does not exclude the possible existence of terms with odd powers of Q in \mathcal{L} , in particular the cubic one.

For the most general case of a *biaxial* nematic phase $\bar{\bar{Q}}$ can be diagonalized giving

$$Q_{\alpha\beta} = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}(S+\eta) & 0 \\ 0 & 0 & -\frac{1}{3}(S-\eta) \end{pmatrix} \quad (10.28)$$

where we remind that S is the degree of local order. If $\eta = 0$ we have the standard *uniaxial* nematic phase and the order parameter becomes

$$Q_{\alpha\beta} = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}S & 0 \\ 0 & 0 & -\frac{1}{3}S \end{pmatrix} \quad (10.29)$$

Now, from the expression of Q in the case of a uniaxial nematic liquid crystal (Eq.(10.29)) we have:

$$\text{Tr } \bar{\bar{Q}}^2 = \frac{2}{3}S^2, \quad \text{Tr } \bar{\bar{Q}}^3 = \frac{2}{9}S^3, \quad (\text{Tr } \bar{\bar{Q}}^2)^2 = \frac{4}{9}S^4$$

Hence, for uniaxial nematic liquid crystal the Landau free energy becomes

$$\mathcal{L} = \mathcal{L}_0 + \frac{A(T)}{3}S^2 + \frac{2}{27}B(T)S^3 + \frac{C(T)}{9}S^4 \quad (10.30)$$

so that, supposing that B and C do not depend on the temperature (i.e. $B(T) = B$ and $C(T) = C$), while $A(T) \simeq A(T - T^*)$, we have:

$$\mathcal{L} = \mathcal{L}_0 + \frac{A}{3}(T - T^*)S^2 + \frac{2}{27}BS^3 + \frac{C}{9}S^4 \quad (10.31)$$

This Landau free energy has exactly the same form of the one we studied in first-order phase transitions in Landau theory (Eq.(10.11)), with the substitutions:

$$a = \frac{2}{3}A, \quad w = -\frac{2}{27}B, \quad b = \frac{4}{9}C$$

Applying the results we have already found (Eq.(10.14)), we will have that the first-order transitions between the isotropic and nematic phases occurs at the temperature:

$$T_{n-i} = T^* + \frac{4w^2}{ba} = T^* + \frac{2B^2}{27AC} \quad (10.32)$$

Chapter 11

Role of fluctuations in critical phenomena: Ginzburg criterium, Coarse-graining and Ginzburg-Landau theory of phase transitions

11.1 Importance of fluctuations: the Ginzburg criterium

As we have seen, the main assumption (and the most important problem) of mean field theories is that the fluctuations of the order parameter are completely neglected in the computation of the partition function Z ; this approximation breaks down in the neighbourhoods of critical points, where as we have seen in long range correlations the correlation length becomes comparable with the size of the system:

$$\xi \stackrel{T \rightarrow T_c}{\sim} |T - T_c|^{-\nu}$$

What we would now like to do is to include these fluctuations in a mean field theoretical framework; this will lead to the so called Ginzburg-Landau theory.

Overall, mean field is not a very good approximation in proximity of the critical point, and the question is: how bad is the mean field approximation in proximity of it? As a first approach we can try to estimate how big is the error we make in mean field theories neglecting the fluctuations of the order parameter near a critical point, so that we can understand under which conditions mean field theories are actually a good approximations.

To make things explicit, let us use the Ising model as a base for our considerations. We have seen in Weiss mean field theory for the Ising model that the Weiss mean field theory for the Ising model is based on the assumption that

$$\langle S_i S_j \rangle \xrightarrow{MF} \langle S_i \rangle \langle S_j \rangle$$

i.e. that the spins are statistically independent; therefore, a possible estimate of the error for each pair of spin (S_i, S_j) made with this assumption can be:

$$E_{ij} = \frac{|\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle|}{\langle S_i \rangle \langle S_j \rangle} \quad (11.1)$$

The numerator of E_{ij} is, by definition, the two-point connected correlation function:

$$G_c(i, j) \equiv \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \rangle \quad (11.2)$$

Assuming *translational invariance*, we have

$$G_c(i, j) \rightarrow G_c(|\vec{r}_i - \vec{r}_j|) \rightarrow G_c(r)$$

In order to compute $G_c(r)$ we cannot assume homogeneity since $\langle S_i \rangle = \langle S_j \rangle = m$. It implies that $G_c = 0$ identically, and if we want to compute the error in the mean field, is always zero. Therefore, in order to have non-null correlation functions we need that the system exhibits some kind of inhomogeneity, not necessarily due to thermal fluctuations. In fact, the connected correlation function G_c describes not only the spatial extension of the fluctuations of the order parameter, but also, through the linear response theory, the way in which m varies in space in response to an external inhomogeneous magnetic field. Within a mean field theory this is the only way to compute G_c ! Let us see this explicitly. We know that from the partition function of the Ising model in an inhomogeneous external field \vec{H}_i , i.e.:

$$Z[H_i] = \text{Tr}_{\{S\}} \left(e^{-\beta(-J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i)} \right) \quad (11.3)$$

we have the definition of the thermal average

$$\langle S_i \rangle = \frac{\text{Tr}_{\{S\}} \left(S_i e^{-\beta(-J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i)} \right)}{Z[H_i]} = \frac{1}{\beta Z} \frac{\partial Z}{\partial H_i} = \beta^{-1} \frac{\partial \ln Z}{\partial H_i} = - \frac{\partial F}{\partial H_i} \quad (11.4)$$

Similarly, one can show that

$$\langle S_i S_j \rangle = \frac{\beta^{-2}}{Z} \frac{\partial^2 Z}{\partial H_i \partial H_j} \quad (11.5)$$

and thus:

$$\begin{aligned} G_c(i, j) &= \frac{\beta^{-2}}{Z} \frac{\partial^2 Z}{\partial H_i \partial H_j} - \left(\frac{\beta^{-1}}{Z} \frac{\partial Z}{\partial H_i} \right) \left(\frac{\beta^{-1}}{Z} \frac{\partial Z}{\partial H_j} \right) \\ &= \beta^{-2} \frac{\partial^2 \ln Z}{\partial H_i \partial H_j} = - \frac{\partial^2 F(\{H_i\})}{\partial H_i \partial H_j} \end{aligned} \quad (11.6)$$

Therefore, the response in i due to a variation of H in j is

$$\frac{\partial}{\partial H_j} \langle S_i \rangle = \frac{\partial}{\partial H_j} \left[\beta^{-1} \frac{\partial \ln Z}{\partial H_i} \right] = \frac{\partial}{\partial H_j} \left[- \frac{\partial F}{\partial H_i} \right] = \beta G_c(i, j)$$

so $G_c(i, j)$ can indeed be seen as a response function. The *generating functions* are:

- $Z[H_i]$: generating function of $G(i, j)$.
- $\ln Z[H_i] = -\beta F$: generating function of $G_c(i, j)$.

If we now call:

$$M = \sum_i \langle S_i \rangle$$

we will have

$$\frac{\partial M}{\partial H_j} = \sum_i \frac{\partial \langle S_i \rangle}{\partial H_j} = \beta \sum_i G_c(i, j)$$

If our system is invariant under translations and subject to a uniform field, then:

$$\frac{\partial M}{\partial H} = \sum_j \frac{\partial M}{\partial H_j} \frac{\partial H_j}{\partial H} = \beta \sum_{ij} G_c(i, j)$$

and since $\chi_T = \partial M / \partial H$ we get:

$$\chi_T = \beta \sum_{i,j} G_c(i, j) = \beta \sum_{i,j} (\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle) \quad (11.7)$$

which is a version of the *fluctuation-dissipation theorem*.

11.1.1 Fluctuation-dissipation relation

The fluctuation–dissipation theorem (FDT), or fluctuation–dissipation relation (FDR), is a powerful tool in statistical physics for predicting the behavior of systems that obey detailed balance. It is a general result of statistical thermodynamics that quantifies the relation between the fluctuations in a system that obeys detailed balance and the response of the system to applied perturbations.

More specifically, the fluctuation–dissipation theorem says that when there is a process that dissipates energy, turning it into heat (e.g., friction), there is a reverse process related to thermal fluctuations.

For instance, let us consider the Brownian motion: if an object is moving through a fluid, it experiences drag (air resistance or fluid resistance). Drag dissipates kinetic energy, turning it into heat. The corresponding fluctuation is Brownian motion. An object in a fluid does not sit still, but rather moves around with a small and rapidly-changing velocity, as molecules in the fluid bump into it. Brownian motion converts heat energy into kinetic energy—the reverse of drag.

Now, let us consider the partition function with an homogeneous magnetic field $H_i = H, \forall i$:

$$Z_N = \text{Tr}_{\{S\}} e^{\beta J \sum_{\langle ij \rangle} S_i S_j + H \sum_i S_i}$$

The magnetization is thus:

$$M = \sum_i \langle S_i \rangle = \frac{1}{Z} \text{Tr}_{\{S\}} \sum_i S_i e^{\beta J \sum_{\langle ij \rangle} S_i S_j + H \sum_i S_i} = \frac{1}{\beta Z_N} \frac{\partial Z_N}{\partial H}$$

Similarly, we have

$$\sum_{ij} \langle S_i S_j \rangle = \frac{1}{\beta^2 Z_N} \frac{\partial^2 Z_N}{\partial H^2}$$

Recall that

$$\frac{1}{N} F = -\frac{1}{N} k_B T \ln Z$$

Hence, the magnetic susceptibility is:

$$\begin{aligned} \chi_T &= \frac{\partial m}{\partial H} = \frac{\partial}{\partial H} \left[-\frac{1}{N} \frac{\partial F}{\partial H} \right] = \frac{\partial}{\partial H} \left[\frac{1}{N} k_B T \frac{\partial \ln Z}{\partial H} \right] \\ &= \frac{1}{N} k_B T \left[\frac{\partial^2 \ln Z}{\partial H^2} \right] = \frac{1}{N} k_B T \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial H^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial H} \right)^2 \right] \\ &= \frac{1}{N \beta} \left[\beta^2 \sum_{ij} \langle S_i S_j \rangle - \beta^2 \left(\sum_i \langle S_i \rangle \right)^2 \right] \\ &= \frac{\beta}{N} \sum_{ij} G_c(i, j) = \frac{\beta}{N} \sum_{ij} G_c(\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j) \\ &= \beta \sum_i G_c(\vec{\mathbf{x}}_i) \end{aligned}$$

where we have defined $\vec{\mathbf{x}}_i \equiv \vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j$. Therefore:

$$\Rightarrow \chi_T = (a^d k_B T)^{-1} \int_{\Omega} d^d \vec{\mathbf{r}} G_c(\vec{\mathbf{r}}) \quad (11.8)$$

this is the fluctuation dissipation relation.

11.1.2 Computation of E_{TOT}

Let us now try to understand when the error E_{ij} done in mean field theories is negligible. Now, in general terms if we formulate a mean field theory for a system we will make the error E_{ij} in the region where correlations are relevant, namely if $|\vec{r}|$ is the distance between two points of the system the error is made for $|\vec{r}| \leq \xi$, with ξ the correlation length. The total relative error is the $E_R(r)$ integrated over the region of radius $|\vec{r}| \leq \xi$, i.e. where correlations are not negligible:

$$E_{TOT} = \frac{\int_{|\vec{r}| \leq \xi} G_c(r) d^d \vec{r}}{\int_{|\vec{r}| \leq \xi} \langle S_i \rangle \langle S_j \rangle d^d \vec{r}} \quad (11.9)$$

where we have called d the dimensionality of our system. Supposing $T < T_c$, so that the order parameter η is non null, i.e. $\eta(r) = \eta \neq 0$, we have:

$$\langle S_i \rangle \langle S_j \rangle \approx \eta^2$$

is uniform in the region $|\vec{r}| < \xi$. Hence, our mean field theory will be a good approximation if $E_{TOT} \ll 1$:

$$E_{TOT} \sim \frac{\int_{|\vec{r}| \leq \xi} G_c(\vec{r}) d^D \vec{r}}{\int_{|\vec{r}| \leq \xi} \eta^2 d^D \vec{r}} \ll 1 \quad (11.10)$$

known as Ginzburg criterion. If it is satisfied, then the mean field theory is a valid approximation.

11.1.3 Estimation of E_{TOT} as $t \rightarrow 0^-$

In order to express Eq.(11.10) in a useful fashion, let us write it in terms of critical exponents; using also the version we have just found of the fluctuation-dissipation theorem (Eq.(11.8)) we get (supposing our system is continuous) that the numerator of Eq.(11.10) can be approximated as

$$\int_{|\vec{r}| \leq \xi} G_c(r) d^d r \stackrel{\text{fluctuation dissipation}}{\sim} k_B T_c \chi_T \sim t^{-\gamma}$$

On the other hand, the denominator can be approximated as

$$\int_{|\vec{r}| \leq \xi} \eta^2 d^d r \sim \xi^d |t|^{2\beta} \sim t^{2\beta - \nu d}$$

Therefore, the Ginzburg criterion can be reformulated as:

$$E_{TOT} \stackrel{t \rightarrow 0^-}{\sim} t^{-\gamma + \nu d - 2\beta} \ll 1$$

and in the limit $t \rightarrow 0^-$ this is possible only if $-\gamma + \nu d - 2\beta > 0$, i.e.:

$$d > \frac{\gamma + 2\beta}{\nu} \equiv d_c \quad (11.11)$$

This means that Ginzburg criterion allows us to determine the *upper critical dimension* d_c of a system, namely the dimension above which mean field theories are good approximations. Let us consider three different cases:

- Case $d < d_c$: fluctuations are relevant and mean field is no a good approximation.
- Case $d > d_c$: fluctuations are less important and mean field describes properly the critical point.

- Case $d = d_c$: mean field critical exponents ok but strong correction to the scaling expected. For a Ising-like systems (in the mean field) we have

$$\beta = \frac{1}{2}, \quad \gamma = 1 \quad \Rightarrow \quad d_c = \frac{2}{\nu}$$

In order to compute d_c we need to compute ν withing the mean field approximation. Let us note that since it depends on the critical exponents, the upper critical dimension d_c ultimately depends on the universality class of the system considered; furthermore, in order to actually be able to compute d_c we must generalize Landau theory to systems with spatial inhomogeneities so that we are able to compute the critical exponent ν .

Remark. Remind that within the mean field theory the ν exponent it is not defined. In fact, the ν exponent define the divergence of the correlation length, but in the mean field we neglect correlation between fluctuations.

We have $\nu_{MF} = 1/2$, hence the upper critical dimension for the mean field is $d > 4$.

11.2 Functional partition function and coarse graining

Since in proximity of the critical point the correlation length ξ diverges, there is no point in which we can see small scales. It is convenient to rewrite the microscopic partition function as an effective partition function obtained by integrating out the degrees of freedom over regions of linear size $l \gg a$ but still $l \ll \xi$. Indeed, a possible way to overcome the limitations of mean field theories can be the following: we could regard the profile of the order parameter $m(\vec{r})$ to be the "degree of freedom" of our system and compute the partition function as a functional integral; in other words from the microscopic configuration of our system we can obtain $m(\vec{r})$ with a *coarse graining procedure* (we will immediately see what we mean by this) and then determine Z as a trace over all the possible configurations of our system, i.e. over all the possible forms of $m(\vec{r})$:

$$Z = \text{Tr}_{\{S\}} e^{-\beta \mathcal{H}[\{S\}]} = \int \mathcal{D}[m(\vec{r})] \left[\sum_{\substack{\{S\} \\ \text{compatible with the} \\ \text{profile } m(\vec{r})}} e^{-\beta \mathcal{H}[\{S\}]} \right] \quad (11.12)$$

where we traced over all the possible microscopic configurations $\{S\}$ compatible with the order parameter profile $m(\vec{r})$. Let us define the effective Hamiltonian \mathcal{H}_{eff} :

$$\sum_{\substack{\{S\} \\ \text{compatible with the} \\ \text{profile } m(\vec{r})}} e^{-\beta \mathcal{H}[\{S\}]} = e^{-\beta \mathcal{H}_{eff}(m(\vec{r}))} \quad (11.13)$$

How, in practice, can we perform the coarse graining procedure and obtain \mathcal{H}_{eff} ? We therefore must understand how to determine $m(\vec{r})$; the idea of coarse graining procedures is the following: for a given microscopic configuration $\{S\}$ we average the order parameter $m(\vec{r})$ over sufficiently wide "blocks", i.e. portions of the system with linear dimension l much greater than its microscopic scale, which we call a (in the case of the Ising model, for example, a can be taken as the lattice constant), but still microscopic and in particular much smaller than the correlation length ξ , so that the

Lecture 17.
Wednesday 11th
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order parameter is uniform in every block. In other words, coarse graining a system means dividing it into cells of linear dimension l , with l such that:

$$a \ll l \ll \xi(T) < L \quad (11.14)$$

(L being the linear dimension of our system) and averaging the order parameter $m(\vec{r})$. This way we can obtain an expression for $m(\vec{r})$ (since l is anyway microscopic with respect to the size of the system, so we can regard \vec{r} as a continuous variable).

Remark. Hence, we partition the configurations according to the magnetization profile. For example, if we have a configuration with half spin up and half down, we obtain a profile with 1 and -1.

11.3 Coarse graining procedure for the Ising model

To make things more clear, let us see how the coarse graining procedure works for the Ising model. For instance, see the two dimensional system represented in Figure 11.1, where we have many spins in each square in which the system is divided.

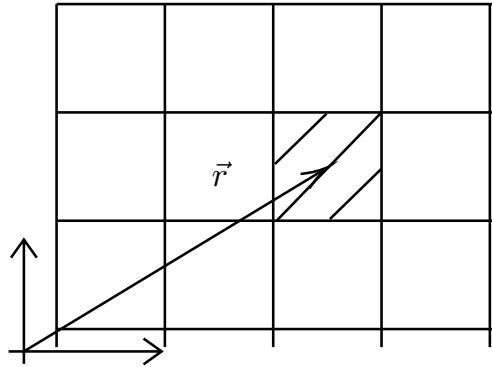


Figure 11.1: Two dimensional system divided into cells with a huge number of spins.

If we call $m_i = \langle S_i \rangle$ the local magnetization at the i -th and d the dimensionality of the system, once we have chosen the linear dimension l , every "block" will have volume l^d ; we replace what it is inside every block of the system centered in \vec{r} , with the coarse grained magnetization:

$$m_l(\vec{r}) = \frac{1}{N_l} \sum_{i \in \vec{r}} S_i \quad (11.15)$$

where $N_l = (l/a)^d$ is the number of spins in each cell.

Remark. Since close to the critical point T_c , we have that the correlation length diverges $\xi \gg a$, we can always choose $l \ll \xi$ but still $l \gg a$ such that the number N_l is large enough. In this way, $m(\vec{r})$ can be made to be a regular function of \vec{r} .

Moreover, since it has been built as an average, $m_l(\vec{r})$ does not fluctuate much on microscopic scales but varies smoothly in space. Of course, in general we need to specify l in order to determine m_l , but the coarse graining procedure we are applying will be useful only if the final results are independent of l (at least in the spatial scales considered).

Remark. In the reciprocal space (Fourier transform), the bound in Eq.(11.14) implies the following cut off on the wave vector \vec{q} :

$$|\vec{q}| > \Lambda = l^{-1}$$

Hence, this theory cannot develop ultraviolet divergences!

We now must express the partition function in terms of $m_l(\vec{\mathbf{r}})$:

$$Z = \sum_{m_l(\vec{\mathbf{r}})} \left(\sum_{\substack{\{S\} \\ \text{compatible with the} \\ \text{profile } m(\vec{\mathbf{r}})}} e^{-\beta \mathcal{H}(\{S\})} \right) = \sum_{m_l(\vec{\mathbf{r}})} e^{-\beta \mathcal{H}_{eff}[m(\vec{\mathbf{r}})]}$$

If $m(\vec{\mathbf{r}})$ is regular, the sum converges to a functional integral:

$$Z_{GL} = \int \mathcal{D}[m_l(\vec{\mathbf{r}})] e^{-\beta \mathcal{H}_{eff}[m(\vec{\mathbf{r}})]} \quad (11.16)$$

so we must compute $\mathcal{H}_{eff}[m(\vec{\mathbf{r}})]$. First let us notice that Eq.(11.13):

$$\sum_{\substack{\{S\} \\ \text{compatible with the} \\ \text{profile } m(\vec{\mathbf{r}})}} e^{-\beta \mathcal{H}(\{S\})} = e^{-\beta \mathcal{H}_{eff}(m(\vec{\mathbf{r}}))}$$

is proportional to the probability that the system displays a configuration with a profile $m_l(\vec{\mathbf{r}})$.

11.3.1 Computation of $\mathcal{H}_{eff}[m(\vec{\mathbf{r}})]$

Since we now have a system made up of "blocks" this effective Hamiltonian will be composed of two parts: a bulk component relative to the single blocks and an interface component relative to the interaction between the blocks; let us consider them individually.

- **Bulk component:** suppose that every block of volume l^d is separate from the rest of the system; inside every one of them the magnetization is uniform (since the linear dimension of the blocks is much smaller than the correlation length $l \ll \xi$), so we can use Landau theory for uniform systems. In the case of the Ising model, it led to the free energy:

$$\mathcal{L} = atm^2 + \frac{\bar{b}}{4} m^4$$

The total bulk energy is thus obtained summing over all the blocks:

$$\beta \mathcal{H}_{eff}^{bulk}[m] = \sum_{\vec{\mathbf{r}}} \bar{a} t m^2(\vec{\mathbf{r}}) + \frac{\bar{b}}{2} m^4(\vec{\mathbf{r}}) \quad (11.17)$$

Hence, the probability that the system displays a configuration with a profile $m_l(\vec{\mathbf{r}})$ is proportional to

$$P^{cell}(m_l(\vec{\mathbf{r}})) \simeq e^{-\beta \mathcal{H}_{eff}^{bulk}(m(\vec{\mathbf{r}}))} = e^{-\sum_{\vec{\mathbf{r}}} \bar{a} t m^2(\vec{\mathbf{r}}) + \frac{\bar{b}}{2} m^4(\vec{\mathbf{r}})} \quad (11.18)$$

- **Interaction component:** we now must take into account the fact that adjacent blocks do interact. In particular, since as we have stated m does not vary much on microscopic scales, the interaction between the blocks must be such that strong variations of magnetization between neighbouring blocks is energetically unfavourable. If we call $\vec{\mu}$ a vector of magnitude l ($|\vec{\mu}| = l$) that

points from one block to a neighbouring one (see Figure 11.2), the most simple analytic expression that we can guess for such a term can be a harmonic one:

$$- \beta \mathcal{H}_{eff}^{int} = \sum_{\vec{r}} \sum_{\vec{\mu}} \frac{\bar{k}}{2} (m(\vec{r} + \vec{\mu}) - m(\vec{r}))^2 + O((m(\vec{r} + \vec{\mu}) - m(\vec{r}))^4) \quad (11.19)$$

(the factor $1/2$ multiplying \bar{k} , just like the numeric factors multiplying \bar{a} and \bar{b} , have been inserted for future convenience). We can also think of this as a first approximation of a general interaction between the blocks, namely as the first terms of a Taylor expansion of the real interaction energy.

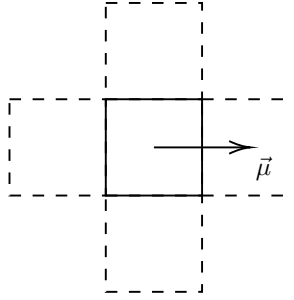


Figure 11.2: Two dimensional system divided into block. The vector $\vec{\mu}$ points from one block to a neighbouring one.

The total energy is thus obtained by summing the two terms. Now, since the linear dimension of the blocks l is much smaller than the characteristic length L of the system we can treat \vec{r} as a continuous variable and thus substitute the sum over \vec{r} with an integral:

$$\sum_{\vec{r}} \xrightarrow{\frac{l}{L} \ll 1} \frac{1}{l^d} \int d^d \vec{r}$$

(while the sum over $\vec{\mu}$ remains a sum, since for every \vec{r} there is only a finite number of nearest neighbours). Therefore:

- **Bulk component:**

$$\beta \mathcal{H}_{eff}^{bulk}[m] = \frac{1}{l^d} \int \left(\bar{a} t m^2(\vec{r}) + \frac{\bar{b}}{2} m^4(\vec{r}) \right) d^d \vec{r} \quad (11.20)$$

Thus, if we now define for the sake of simplicity:

$$a \equiv \frac{\bar{a}}{l^d}, \quad b \equiv \frac{\bar{b}}{l^d}$$

we will have:

$$\beta \mathcal{H}_{eff}^{bulk}[m] = \int \left(a t m^2(\vec{r}) + \frac{b}{2} m^4(\vec{r}) \right) d^d \vec{r}$$

- **Interaction component:**

$$- \beta \mathcal{H}_{eff}^{int} = \frac{1}{l^d} \int \sum_{\vec{\mu}} \frac{\bar{k}}{2} (m(\vec{r} + \vec{\mu}) - m(\vec{r}))^2 d^d \vec{r} \quad (11.21)$$

Keeping in mind that $|\vec{\mu}| = l$, the interaction term can be rewritten in terms of $\vec{\nabla}m$:

$$\begin{aligned} \frac{1}{l^D} \int \sum_{\vec{\mu}} \frac{\bar{k}}{2} (m(\vec{r} + \vec{\mu}) - m(\vec{r}))^2 d^d \vec{r} &= \frac{1}{l^{d-2}} \int \frac{\bar{k}}{2} \sum_{\vec{\mu}} \left(\frac{m(\vec{r} + \vec{\mu}) - m(\vec{r})}{l} \right)^2 d^d \vec{r} \\ &= \frac{\bar{k}}{2l^{d-2}} \int \sum_{\vec{\mu}} \left(\frac{\partial m}{\partial \chi_\mu} \right)^2 d^d \vec{r} \\ &\xrightarrow{\frac{a}{L} \ll \frac{l}{L} \ll 1} \int \frac{k}{2} (\vec{\nabla}m)^2 d^d \vec{r} \end{aligned}$$

where we have called χ_μ the components of $\vec{\mu}$ and we have rescaled the elastic constant by l^{d-2} :

$$k \equiv \frac{\bar{k}}{l^{d-2}}$$

In this way the result is independent on l .

• **Total energy:**

$$\beta \mathcal{H}_{eff}[m] = \int \left[atm^2(\vec{r}) + \frac{b}{2} m^4(\vec{r}) + \frac{k}{2} (\vec{\nabla}m(\vec{r}))^2 \right] d^d \vec{r} \quad (11.22)$$

Therefore, the (functional) partition function of the system will be as in Eq.(11.16):

$$Z_{GL} = \int \mathcal{D}[m(\vec{r})] e^{-\beta \mathcal{H}_{eff}[m(\vec{r})]} = \int \mathcal{D}[m(\vec{r})] e^{-\int \left[atm^2(\vec{r}) + \frac{b}{2} m^4(\vec{r}) + \frac{k}{2} (\vec{\nabla}m(\vec{r}))^2 \right] d^d \vec{r}} \quad (11.23)$$

Let us now make a couple of considerations:

- If $m(\vec{r}) = m$ (uniform system) the energy of the system has the same structure of the one used in Landau theory.
- The term proportional to $(\vec{\nabla}m(\vec{r}))^2$ is completely new but we could have introduced it intuitively to a Landau-like mean field functional, since the introduction of spatial variations in the order parameter has an energetic cost which must depend on how it varies in space, i.e. it depends on the gradient of m . This term can be also added directly to the Landau theory by simply assuming that, when $m \rightarrow m(\vec{r})$ (one has to consider an additional energy cost due to small variation of m).

Why we take $(\vec{\nabla}m)^2$ and not something else? The choice is first of all a consequence of the isotropy of the system (all directions are equivalent). Since the system is isotropic and \mathbb{Z}^2 -invariant, we must use combinations of derivatives that are invariant under rotations and parity, and, among all the possible combinations, $(\vec{\nabla}m(\vec{r}))^2$ is the simplest one.

Remark. Let us consider the cases in which $m \rightarrow \vec{m}$ ($O(n)$ models); we have:

$$(\nabla \vec{m})^2 = \sum_{i=1}^n \sum_{\alpha=1}^d \partial_\alpha m_i \partial_\alpha m_i$$

Higher order terms are:

$$(\nabla^2 \vec{m})^2 = \sum_{i=1}^n \sum_{\alpha=1}^d \sum_{\beta=1}^d (\partial_\alpha \partial_\alpha m_i) (\partial_\beta \partial_\beta m_i)$$

and

$$\vec{m}^2 (\nabla \vec{m})^2 = \sum_{i=1}^n \sum_{j=1}^n \sum_{\alpha=1}^d m_i m_j \partial_\alpha m_j \partial_\alpha m_j$$

In most cases it is sufficient to consider only the lowest order term.

11.3.2 Magnetic non-homogeneous field

If there is also an external magnetic field

$$\vec{h}(\vec{r}) = \beta \vec{H}(\vec{r})$$

we must add to the Hamiltonian the term (Legendre transform):

$$- \int \vec{h}(\vec{r}) \cdot \vec{m}(\vec{r}) d^d \vec{r}$$

so that the partition function becomes:

$$Z_{GL} = \int \mathcal{D}[m(\vec{r})] e^{-\int [atm^2(\vec{r}) + \frac{b}{2}m^4(\vec{r}) + \frac{k}{2}(\vec{\nabla}m(\vec{r}))^2 - \vec{h}(\vec{r}) \cdot \vec{m}(\vec{r})] d^d \vec{r}} \quad (11.24)$$

which is a functional of $m(\vec{r})$ and $\vec{h}(\vec{r})$. As usual, all the thermodynamics of the system can be obtained from Z_{GL} , provided that now we take functional derivatives instead of usual derivatives. Moreover, the free energy functional is defined as

$$F[m, h] = \int d^d \vec{r} \left[atm^2(\vec{r}) + \frac{b}{2}m^4(\vec{r}) + \frac{k}{2}(\vec{\nabla}m(\vec{r}))^2 - h(\vec{r})m(\vec{r}) \right] \quad (11.25)$$

11.3.3 Functional derivatives

In the calculus of variations, a field of mathematical analysis, the functional derivative relates a change in a functional to a change in a function on which the functional depends. Functionals are usually expressed in terms of an integral of functions, their arguments, and their derivatives.

Definition 9: Functional derivative

Given a manifold M representing (continuous/smooth) functions h (with certain boundary conditions etc.), and a functional G defined as $G : M \rightarrow \mathbb{R}$. The functional derivative of $G[h]$, denoted $\delta G/\delta h$, is defined by

$$\int \frac{\delta G}{\delta h}(x) \Phi(x) dx = \lim_{\varepsilon \rightarrow 0} \frac{G(h + \varepsilon \Phi) - G(h)}{\varepsilon} = \left[\frac{d}{d\varepsilon} G[h + \varepsilon \Phi] \right]_{\varepsilon=0}$$

where Φ is an arbitrary function. In physics, it is common to use the Dirac delta function $\delta(x - y)$ in place of a generic test function $\Phi(x)$, for yielding the functional derivative at the point y :

$$\frac{\delta G[h(x)]}{\delta h(y)} = \lim_{\varepsilon \rightarrow 0} \frac{G[h(x) + \varepsilon \delta(x - y)] - G[h(x)]}{\varepsilon}$$

or, in many dimensions:

$$\frac{\delta G[h(\vec{r})]}{\delta h(\vec{r}')} = \lim_{\varepsilon \rightarrow 0} \frac{G[h(\vec{r}) + \varepsilon \delta(\vec{r} - \vec{r}')] - G[h(\vec{r})]}{\varepsilon} \quad (11.26)$$

Properties

Like the derivative of a function, the functional derivative satisfies the following properties, where $F[h]$ and $G[h]$ are functionals:

- Linearity:

$$\frac{\delta(\lambda F + \mu G)[h]}{\delta h(x)} = \lambda \frac{\delta F[h]}{\delta h(x)} + \mu \frac{\delta G[h]}{\delta h(x)}$$

where λ, μ are constants.

- Product rule:

$$\frac{\delta(FG)[h]}{\delta h(x)} = \frac{\delta F[h]}{\delta h(x)} G[\rho] + F[h] \frac{\delta G[h]}{\delta h(x)}$$

- Chain rules: if F is a functional and G another functional, then

$$\frac{\delta F[G[h]]}{\delta h(y)} = \int dx \frac{\delta F[G]}{\delta G(x)} \Big|_{G=G[h]} \cdot \frac{\delta G[h](x)}{\delta h(y)}$$

If G is an ordinary differentiable function (local functional) g , then this reduces to:

$$\frac{\delta F[g(h)]}{\delta h(y)} = \frac{\delta F[g(h)]}{\delta g[h(y)]} \frac{dg(h)}{dh(y)}$$

Let us consider some examples.

Example 30: Functional derivative of a function

A function can be written in the form of an integral like a functional. For example,

$$f(\vec{r}) \equiv F[f] = \int f(\vec{r}') \delta^d(\vec{r} - \vec{r}') d^d \vec{r}'$$

Since the integrand does not depend on derivatives of f , the functional derivative of $f(\vec{r})$ is,

$$\frac{\delta f(\vec{r})}{\delta f(\vec{r}')} \equiv \frac{\delta F}{\delta f(\vec{r}')} = \frac{\partial}{\partial f(\vec{r}')} [f(\vec{r}') \delta^d(\vec{r} - \vec{r}')] = \delta^d(\vec{r} - \vec{r}') \quad (11.27)$$

Example 31: Functional derivative of interaction component of \mathcal{H}_{eff}

The functional derivative of the interaction component of $\mathcal{H}_{eff}[m(\vec{r})]$ is

$$\frac{\delta}{\delta m(\vec{r})} \left[\int \frac{k}{2} (\vec{\nabla} m(\vec{r}'))^2 d^d \vec{r}' \right] = -k (\vec{\nabla}^2 m) \quad (11.28)$$

Taking into account the result Eq.(11.28), we have:

$$\langle m(\vec{r}) \rangle = -\frac{\delta F}{\delta h(\vec{r})} = -\frac{\delta \ln Z[h]}{\delta h(\vec{r})} \quad (11.29)$$

and one can show that the magnetic susceptibility is

$$\begin{aligned} \chi(\vec{r}, \vec{r}') &= \frac{\delta^2 F}{\delta h(\vec{r}) \delta h(\vec{r}')} = \beta^{-1} \frac{\delta^2 \ln Z[h]}{\delta h(\vec{r}) \delta h(\vec{r}')} \\ &= \beta^{-1} [\langle m(\vec{r}) m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle] = \beta^{-1} G_c(\vec{r}, \vec{r}') \end{aligned} \quad (11.30)$$

The problem is again try to approximate this term as much as we can. Let us do it.

11.4 Saddle point approximation: Landau theory for non-homogeneous systems

We can now compute Z , as a first approach, using the saddle point approximation; as we will see this will reproduce a Landau-like mean field theory which will also take into account the presence of inhomogeneities. In particular thanks to the new term involving $\vec{\nabla} m(\vec{r})$ we will be able to compute the fluctuation correlation function and

so also to determine the critical exponents η and ν . Let us recall the results previously obtained:

$$Z_{GL} = \int \mathcal{D}[m(\vec{r})] e^{-\beta \mathcal{H}_{eff}[m(\vec{r})] + \int \vec{h}(\vec{r}) \cdot \vec{m}(\vec{r}) d^d \vec{r}}$$

where $h(\vec{r}) = \beta H(\vec{r})$ and

$$\beta \mathcal{H}_{eff}[m] = \int \left[atm^2(\vec{r}) + \frac{b}{2} m^4(\vec{r}) + \frac{k}{2} (\vec{\nabla} m(\vec{r}))^2 \right] d^d \vec{r}$$

Therefore we approximate Z with the leading term of the integral, i.e. we must determine the function m_0 that maximizes the exponent, namely minimizes:

$$L(m, \vec{\nabla} m, h) = \beta \mathcal{H}_{eff} - \int \vec{h} \cdot \vec{m} d^d \vec{r} = \int \left[atm^2 + \frac{b}{2} m^4 + \frac{k}{2} (\vec{\nabla} m)^2 - \vec{h} \cdot \vec{m} \right] d^d \vec{r} \quad (11.31)$$

Let $m_0(\vec{r})$ be the profile for which $L(m_0(\vec{r}), h(\vec{r}))$ is minimum, then compute Z_{GL} as

$$Z_{GL}[h] \stackrel{\text{saddle point}}{\simeq} Z_{GL}^0[h] = e^{-L[m_0(\vec{r})]} \quad (11.32)$$

In order to find the minimum $m_0(\vec{r})$, one has to impose the stationarity condition of the functional L :

$$\delta L = 0 \quad (11.33)$$

Now, let us define \mathfrak{h} the integrand of $\beta \mathcal{H}_{eff}$:

$$\mathfrak{h} = atm^2 + \frac{b}{2} m^4 + \frac{k}{2} (\vec{\nabla} m)^2$$

By considering δL with respect to the variations δm and $\delta(\vec{\nabla} m)$, one gets the equation of state

$$h(\vec{r}) = - \left[\vec{\nabla} \left(\frac{\partial \mathfrak{h}}{\partial (\vec{\nabla} m)} \right) - \frac{\partial \mathfrak{h}}{\partial m} \right] \quad (11.34)$$

Hence, by using the definition of \mathfrak{h} , we obtain the state equation:

$$h(\vec{r}) = -k \vec{\nabla}^2 m_0(\vec{r}) + 2atm_0(\vec{r}) + 2bm_0^3(\vec{r}) \quad (11.35)$$

this is the mean field solution of the Gibbs-Landau. It is more general than the one found before, indeed it has the additional term $\vec{\nabla}^2$. Let us note that:

- If $h = 0$: Eq.(11.34) reduces to the *Euler-Lagrange equation*

$$\frac{\partial \mathfrak{h}}{\partial m} = \vec{\nabla} \left(\frac{\partial \mathfrak{h}}{\partial (\vec{\nabla} m)} \right) \quad (11.36)$$

- If $h(\vec{r}) = h$ (homogeneous field) and $m_0(\vec{r}) = m_0$: Eq.(11.35) reduces to the equation of state of the Landau theory of uniform systems

$$h = 2atm_0 + 2bm_0^3$$

Remark. Moreover, note that a mean field theory of systems with spatial disomogeneity can start directly by considering the free energy functional defined in Eq.(11.25):

$$F[m, h] = \int \left[atm^2(\vec{r}) + \frac{b}{2} m^4(\vec{r}) + \frac{k}{2} (\vec{\nabla} m)^2 - h(\vec{r})m(\vec{r}) \right] d^d \vec{r}$$

Example 32: Show relation (11.36)

Let us consider the case $h = 0$, we want to obtain the Euler-Lagrange equation:

$$\frac{\partial \mathfrak{h}}{\partial m} = \vec{\nabla} \left(\frac{\partial \mathfrak{h}}{\partial(\vec{\nabla} m)} \right)$$

In order to do that, we define

$$L[m, \vec{\nabla} m, h] = \int \mathcal{L}(m, \vec{\nabla} m, h) d^d \vec{r}$$

Supposing $h = 0$ and looking for the variation of L with respect to the variations of m , δm , and the variation of $\vec{\nabla} m$, $\delta(\vec{\nabla} m)$, we have:

$$\begin{aligned} \delta L[m, \vec{\nabla} m, 0] &= \int \mathcal{L}(m + \delta m, \vec{\nabla} m + \delta(\vec{\nabla} m)) d^d \vec{r} - \int \mathcal{L}(m, \vec{\nabla} m) d^d \vec{r} \\ &= \int \left[\mathcal{L}(m + \delta m, \vec{\nabla} m + \delta(\vec{\nabla} m)) - \mathcal{L}(m, \vec{\nabla} m) \right] d^d \vec{r} \\ &= \int \left[\frac{\partial \mathcal{L}}{\partial m} \delta m + \frac{\partial \mathcal{L}}{\partial(\vec{\nabla} m)} \delta(\vec{\nabla} m) \right] d^d \vec{r} \end{aligned}$$

where in the last step we did a Taylor expansion around $(m, \vec{\nabla} m)$. We now integrate by parts (i.e. $\int f g' = f g - \int f' g$) the red term, obtaining

$$\begin{aligned} \delta L &= \int \left[\frac{\partial \mathcal{L}}{\partial m} \delta m - \vec{\nabla} \frac{\partial \mathcal{L}}{\partial(\vec{\nabla} m)} \delta m \right] d^d \vec{r} + \int \left[\frac{\partial \mathcal{L}}{\partial \vec{\nabla} m} \delta m \right] d^d \vec{r} \\ &= \int \left[\frac{\partial \mathcal{L}}{\partial m} \delta m - \vec{\nabla} \frac{\partial \mathcal{L}}{\partial(\vec{\nabla} m)} \delta m \right] d^d \vec{r} + \int_V \vec{\nabla} \left[\frac{\partial \mathcal{L}}{\partial \vec{\nabla} m} \delta m \right] d^d \vec{r} \end{aligned}$$

where for the blue term we have used the divergence theorem $\int_{\partial \Omega} F = \int_V \vec{\nabla} F$. Moreover, the blue term vanishes at the boundary of the integration. Hence, we have

$$\delta L = \int \delta m \left[\frac{\partial \mathcal{L}}{\partial m} - \vec{\nabla} \frac{\partial \mathcal{L}}{\partial(\vec{\nabla} m)} \right] d^d \vec{r}$$

The stationarity condition $\delta L = 0$ (Eq.(11.33)) is true $\forall \delta m \neq 0$ if and only if the integrand is zero, thus we obtain the *Euler-Lagrange equation*:

$$\frac{\partial \mathcal{L}}{\partial m} - \vec{\nabla} \left(\frac{\partial \mathcal{L}}{\partial(\vec{\nabla} m)} \right) = 0$$

Hence, when $h = 0$, we have $\mathcal{L} \rightarrow \mathfrak{h}$.

11.5 Correlation function in the saddle point approximation for non-homogeneous systems

We can now proceed to compute the correlation function within our approximations. In order to do that, we take the (functional!) derivative of the state equation

(11.35) with respect to $h(\mathbf{r}')$. Remembering that

$$\chi_T(\mathbf{r}, \mathbf{r}') = \frac{\delta m(\mathbf{r})}{\delta h(\mathbf{r}')}$$

and that from Eq.(11.27):

$$\frac{\delta h(\mathbf{r})}{\delta h(\mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}')$$

The functional derivative becomes

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{\delta h(\mathbf{r})}{\delta m(\mathbf{r})} \frac{\delta m(\mathbf{r})}{\delta h(\mathbf{r}')} = \left[-k\vec{\nabla}^2 + 2at + 6bm_0^2(\mathbf{r}) \right] \chi_T(\mathbf{r} - \mathbf{r}') \quad (11.37)$$

where we have assumed translational invariance (i.e. uniform systems). Now, from fluctuation-dissipation theorem we know that:

$$G_c(\mathbf{r} - \mathbf{r}') = k_B T \chi_T(\mathbf{r} - \mathbf{r}')$$

so that

$$\beta \left[-k\vec{\nabla}^2 + 2at + 6bm_0^2 \right] G_c(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (11.38)$$

Note that this means that the correlation function $G_c(\mathbf{r} - \mathbf{r}')$ can be interpreted as the Green's function of the operator D written between the square brackets:

$$D \equiv -k\vec{\nabla}^2 + 2at + 6bm^2$$

the equation (11.38) is also known as *Fundamental Equation* and $G_c(\mathbf{r} - \mathbf{r}')$ as *Fundamental Solution*, or Green's function of the differential operator D .

As said, in case of translationally invariant (i.e. uniform) systems, m is constant and equal to the equilibrium values given by the Landau theory for the Ising model; in particular, depending on the sign of t there are two possible situations:

- Case $t > 0$ ($T > T_c$): in this case the mean field solution is $m(\mathbf{r}) = m_0 = 0$, so the last equation becomes:

$$(-k\vec{\nabla}^2 + 2at) G_c(\mathbf{r} - \mathbf{r}') = k_B T \delta(\mathbf{r} - \mathbf{r}') \quad (11.39)$$

Defining:

$$\xi_>(t) \equiv \left(\frac{k}{2at} \right)^{1/2}$$

this can be rewritten as:

$$(-\vec{\nabla}^2 + \xi_>^{-2}(t)) G_c(\mathbf{r} - \mathbf{r}') = \frac{k_B T}{k} \delta(\mathbf{r} - \mathbf{r}')$$

- Case $t < 0$ ($T < T_c$): in this case the magnetization is:

$$m_0 = \pm \left(-\frac{at}{b} \right)^{1/2}$$

so the differential equation for G_c becomes:

$$(-k\vec{\nabla}^2 - 4at) G_c(\mathbf{r} - \mathbf{r}') = k_B T \delta(\mathbf{r} - \mathbf{r}') \quad (11.40)$$

Defining:

$$\xi_<(t) \equiv \left(-\frac{k}{4at} \right)^{1/2}$$

this can be written as

$$(-\vec{\nabla}^2 + \xi_<^{-2}(t)) G_c(\mathbf{r} - \mathbf{r}') = \frac{k_B T}{k} \delta(\mathbf{r} - \mathbf{r}')$$

We will shortly see that $\xi_>$ and $\xi_<$ are the expressions of the correlation length for $T > T_c$ and $T < T_c$, respectively. We can therefore see that in both cases we get:

$$\xi \sim t^{-1/2} \Rightarrow \nu = \frac{1}{2} \quad (11.41)$$

that is the mean field value of ν !

Remark. Since $\nu = 1/2$, the upper critical dimension of a critical point belonging to the Ising universality class is

$$d_c = \frac{2}{\nu} = 4$$

as previously anticipated.

We have seen that for both the cases, $t > 0$ and $t < 0$, the correlation function can be obtained by solving the differential equation:

$$(-\nabla^2 + \xi^{-2})G_c(\vec{r} - \vec{r}') = \frac{k_B T}{k} \delta(\vec{r} - \vec{r}') \quad (11.42)$$

which can be solved with the Fourier transform and by using spherical coordinates.

11.5.1 Solution of (11.42) by Fourier transform

Let us do the Fourier transform of Eq.(11.42):

$$(-\nabla^2 + \xi^{-2}(t))G_c(\vec{r} - \vec{r}') = \frac{k_B T}{k} \delta(\vec{r} - \vec{r}')$$

If we define $\vec{x} \equiv \vec{r} - \vec{r}'$ and we use the following convention for the Fourier transform $\tilde{G}(q)$ of G :

$$\tilde{G}(q) = \int_{-\infty}^{+\infty} G_c(|\vec{x}|) e^{-i\vec{q} \cdot \vec{x}} d^d |\vec{x}|$$

then transforming both sides of the equation we get:

$$(q^2 + \xi^{-2})\tilde{G}(q) = \frac{k_B T}{k} \Rightarrow \tilde{G}(q) = \frac{k_B T}{k} \frac{1}{q^2 + \xi^{-2}} \quad (11.43)$$

where $q = |\vec{q}|$. From this last equation we can also see that when $T = T_c$, since $\xi \rightarrow \infty$ we have $\tilde{G}(q) \simeq \frac{1}{q^2}$ and so performing the inverse Fourier transform one gets

$$G_c(|\vec{x}|) = |\vec{x}|^{2-d}$$

from which we have that the critical exponent η is null (we will see that explicitly once we have computed G). In fact, at $T = T_c$ we have previously defined

$$G(r) \sim |\vec{x}|^{2-d-\eta}$$

hence, in this case we have $\eta = 0$. Therefore, reminding that $\vec{x} \equiv \vec{r} - \vec{r}'$ we can now determine $G(\vec{x})$ with the Fourier antitransform:

$$G(\vec{x}) = \int \frac{d^d \vec{q}}{(2\pi)^d} \frac{e^{i\vec{q} \cdot \vec{x}}}{q^2 + \xi^{-2}} \quad (11.44)$$

This integral is a bit tedious to compute, and in general its result depends strongly on the dimensionality d of the system; the general approach used to solve it is to shift to spherical coordinates in \mathbb{R}^d and then complex integration for the remaining

Lecture 18.
 Friday 13th
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part, which involves $|\vec{q}|$. In order to do some explicit computations, let us consider the case $d = 3$; we will then have:

$$G(\vec{x}) = \int \frac{d^3 \vec{q}}{(2\pi)^3} \frac{e^{i\vec{q} \cdot \vec{x}}}{q^2 + \xi^{-2}} \stackrel{\text{spherical coordinates}}{=} \frac{1}{(2\pi)^3} \int_0^\infty \frac{q^2}{q^2 + \xi^{-2}} dq \int_{-1}^{+1} e^{iq|\vec{x}| \cos \theta} d(\cos \theta) \int_0^{2\pi} d\varphi$$

$$\stackrel{z \equiv \cos(\theta)}{=} \frac{2\pi}{(2\pi)^3} \int_0^\infty \frac{q^2}{q^2 + \xi^{-2}} dq \left[\frac{e^{iq|\vec{x}|z}}{iq|\vec{x}|} \right]_{-1}^1 = \frac{1}{(2\pi)^2 |\vec{x}|} \int_0^\infty \frac{q \sin(q|\vec{x}|)}{q^2 + \xi^{-2}} dq$$

This last integral can be computed, using the residue theorem, extending it to the complex plane:

$$I = \int_0^\infty \frac{q \sin(q|\vec{x}|)}{q^2 + \xi^{-2}} dq = \frac{1}{2} \int_{-\infty}^{+\infty} \frac{q \sin(q|\vec{x}|)}{q^2 + \xi^{-2}} dq = \frac{1}{2} \text{Im} \oint \frac{ze^{iz|\vec{x}|}}{(z^2 + \xi^{-2})} dz$$

There are two poles at $z_P = \pm i\xi^{-1}$; we choose as the contour of integration γ which contains only the pole at $+i\xi^{-1}$ (see Figure 11.3) and so using the residue theorem we will have:

$$I = \frac{1}{2} \text{Im} \oint_\gamma \frac{ze^{iz|\vec{x}|}}{(z + i\xi^{-1})(z - i\xi^{-1})} dz \stackrel{\text{residue theorem}}{=} \frac{1}{2} \text{Im} [2\pi i \text{Res}(i\xi^{-1})]$$

Since,

$$\text{Res}(i\xi^{-1}) = \frac{i\xi^{-1}e^{-\xi^{-1}|\vec{x}|}}{2i\xi^{-1}} = \frac{e^{-|\vec{x}|/\xi}}{2}$$

we obtain

$$I = \frac{1}{2} \text{Im} [2\pi i \text{Res}(i\xi^{-1})] = \frac{\pi}{2} e^{-|\vec{x}|/\xi} \quad (11.45)$$

Therefore, in the end we have:

$$G(|\vec{x}|) = \frac{1}{8\pi} \frac{e^{-|\vec{x}|/\xi}}{|\vec{x}|} \quad (11.46)$$

We see now clearly that the correlation function has indeed an exponential behaviour (as we have stated also in long range correlations) and that ξ is really the correlation length; furthermore, $G(\vec{x}) \sim 1/|\vec{x}|$ and from the definition of the exponent η we have $G(\vec{x}) \sim 1/|\vec{x}|^{d-2+\eta}$, so since $d = 3$ we indeed have $\eta = 0$.

One can also solve the equation for $G(\vec{r} - \vec{r}')$ by using the spherical coordinates and use the Bessel functions.

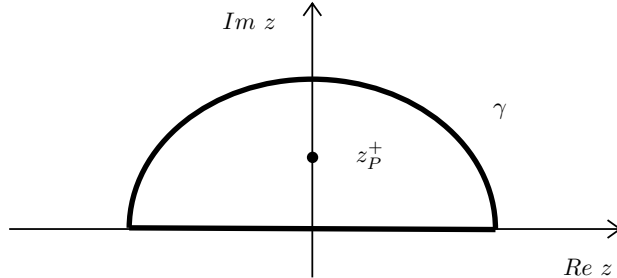


Figure 11.3: Positive integration contour γ in the complex plane for the integral I . It contains only the pole at $+i\xi^{-1}$.

Therefore, we have seen that for the Ising model $\nu = 1/2$. If we also consider the values of the other critical exponents we see that the upper critical dimension for this model is $d = 4$. In other words, mean field theories are actually good approximations for the Ising model if $d \geq 4$. We will later see some other confirmations of this fact.

11.6 Including fluctuations at the Gaussian level (non interacting fields)

Until now even if we have introduced Ginzburg-Landau theory we are still neglecting the effects of the fluctuations since we are regarding the mean field theory approximation for non-homogeneous systems as a saddle point approximation of a more general theory; in other words, since we are approximating

$$Z_{GL}[h] \stackrel{\text{saddle point}}{\simeq} Z_{GL}^0[h] = e^{-L[m_0(\vec{r})]}$$

we are still regarding the magnetization m as non fluctuating over the system. In order to include the fluctuations we must do more and go further the simple saddle point approximation. The simplest way we can include fluctuations in our description is expanding Z expressed as a functional integral around the stationary solution and keeping only quadratic terms; this means that we are considering fluctuations that follow a normal distribution around the stationary value. The important thing to note, however, is that in this approximation these fluctuations are independent, i.e. they do not interact with each other. As we will see, with this assumption the values of some critical exponents will differ from the "usual" ones predicted by mean field theories.

Hence, let us introduce fluctuations at the Gaussian level. Consider consider $h = 0$ and $m_0(\vec{r}) = m_0$ be the solution of the saddle point approximation. Let us expand the general expression

$$\beta \mathcal{H}_{eff}[m(\vec{r})] = \int \left(atm^2 + \frac{b}{2}m^4 + \frac{k}{2}(\vec{\nabla}m)^2 \right) d^d\vec{r}$$

by using

$$m(\vec{r}) = m_0 + \delta m(\vec{r})$$

If we assumed that the fluctuations $\delta m(\vec{r})$ are small, we would obtain:

$$\begin{aligned} (\vec{\nabla}m)^2 &= (\vec{\nabla}(m_0 + \delta m))^2 = (\vec{\nabla}(\delta m))^2 \\ m^2 &= m_0^2 + 2m_0\delta m + (\delta m)^2 \\ m^4 &= m_0^4 + 4m_0^3\delta m + 6m_0^2(\delta m)^2 + 4m_0\delta m^3 + (\delta m)^4 \end{aligned}$$

Hence, we have

$$\beta \mathcal{H}_{eff} = V \underbrace{\left(atm_0^2 + \frac{b}{2}m_0^4 \right)}_{A_0} + \int \left(\frac{k}{2}(\vec{\nabla}(\delta m))^2 + (at + 3bm_0^2)\delta m^2 + 2bm_0\delta m^3 + \frac{b}{2}\delta m^4 \right) d^d\vec{r} \quad (11.48)$$

where V is the volume of the system and the term proportional to δm , $(2atm_0 + 2bm_0^3)$, is zero since m_0 is the solution of the extremal condition (m_0 is the stationary solution)

$$\left. \frac{\delta \mathcal{H}_{eff}}{\delta m} \right|_{m=m_0} = 0$$

For simplicity let us first consider $T > T_c$; in this case, we know that $m_0 = 0$ and hence,

$$m(\vec{r}) = m_0 + \delta m(\vec{r}) = \delta m(\vec{r})$$

We have also $A_0 = 0$, $3bm_0^2\delta m^2 = 0$ and $2bm_0\delta m^3 = 0$. Taking all of this into account, we obtain:

$$\beta \mathcal{H}_{eff}^{T>T_c}(\delta m) = \int d^d\vec{r} \left(\frac{k}{2}(\vec{\nabla}\delta m)^2 + at(\delta m)^2 + \frac{b}{2}(\delta m)^4 \right)$$

The Gaussian approximation consists in neglecting the quartic term $(\delta m)^4$, hence we finally obtain:

$$\beta \mathcal{H}_{eff}^{G,T>T_c}(\delta m) \simeq \int d^d \vec{r} \left(\frac{k}{2} (\vec{\nabla} \delta m)^2 + at(\delta m)^2 \right) \quad (11.49)$$

Remark. It is important to understand that these are fluctuations with respect to the solution m_0 .

In order to compute this integral it is more convenient to shift to Fourier space.

11.6.1 Gaussian approximation for the Ising model in Ginzburg-Landau theory

For simplicity, consider the case $T > T_c$; now, let us compute the partition function

$$Z_G(\delta m) = \int \mathcal{D}[\delta m] e^{-\int d^d r \left(\frac{k}{2} (\vec{\nabla} \delta m)^2 + at(\delta m)^2 \right)} \quad (11.50)$$

in the Fourier space. Let us make some remarks on what happens when we apply Fourier transformations in this case. If our system is enclosed in a cubic box of volume $V = L^d$ (with periodic boundary conditions), we can define the Fourier components of the magnetization as:

$$\delta m_{\vec{k}} = \int_V \delta m(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d^d \vec{r} \quad (11.51)$$

where $\vec{k} = k_1, \dots, k_d = \frac{2\pi \vec{n}}{L}$ with $k_\alpha = \frac{2\pi}{L} n_\alpha$ and $n_\alpha = 0, \pm 1, \dots$. We can therefore expand the magnetization in a Fourier series:

$$\delta m(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} (\delta m_{\vec{k}}) \quad (11.52)$$

Substituting this expression of m in $\delta m_{\vec{k}}$ we obtain an integral representation for the Kronecker delta; in fact:

$$\delta m_{\vec{k}} = \sum_{\vec{k}'} \delta m_{\vec{k}'} \left(\frac{1}{V} \int_V e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} d^d \vec{r} \right)$$

and this is true only if:

$$\frac{1}{V} \int_V e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} d^d \vec{r} = \delta_{\vec{k}, \vec{k}'} \quad \Rightarrow \quad \int_V e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} d^d \vec{r} = V \delta_{\vec{k}, \vec{k}'}$$

Let us now make an observations; since $\delta m(\vec{r}) \in \mathbb{R}$ (is real) we have that

$$\delta m_{\vec{k}}^* = \delta m_{-\vec{k}}$$

Useful relations

- Sometimes it is useful to convert the sum over \vec{k} by an integral by using the density of states in the \vec{k} space that is $V/(2\pi)^d$, hence one useful relation is

$$\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^d} \int_{\mathbb{R}^d} d^d \vec{k} \quad (11.53)$$

- From the relation Eq.(11.53), we have:

$$\frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}(\vec{r}-\vec{r}')} \rightarrow \frac{1}{\mathcal{V}} \frac{\mathcal{V}}{(2\pi)^d} \int_{\mathbb{R}^D} d^d \vec{k} e^{i\vec{k}(\vec{r}-\vec{r}')} = \delta(\vec{r} - \vec{r}')$$

Hence, another useful relation is:

$$\frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}(\vec{r}-\vec{r}')} \rightarrow \delta(\vec{r} - \vec{r}') \quad (11.54)$$

- As previously shown, by inserting $m(\vec{r})$ into the expression for $m_{\vec{k}}$

$$m(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} m_{\vec{k}}, \quad m_{\vec{k}} = \int_V m(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d^d \vec{r}$$

one gets

$$\int_V e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d^d \vec{r} = V \delta_{\vec{k}\vec{k}'} \quad (11.55)$$

- Finally, since

$$\int_V e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d^d \vec{r} = V \delta_{\vec{k}\vec{k}'} \xrightarrow{V \rightarrow \infty} (2\pi)^d \delta(\vec{k} - \vec{k}')$$

We get the last useful relation:

$$V \delta_{\vec{k}\vec{k}'} \xrightarrow{V \rightarrow \infty} (2\pi)^d \delta(\vec{k} - \vec{k}') \quad (11.56)$$

Remark. Our coarse graining procedure is based on the construction of blocks which have a linear dimension that cannot be smaller than a , the characteristic microscopic length of the system; this means that not all the \vec{k} are allowed, and in particular we must have

$$|\vec{k}| \leq \frac{\pi}{a} = \Lambda$$

It is the ultraviolet cut-off!

Gaussian Hamiltonian in Fourier space

We want to compute Eq.(11.49) in the Fourier space. For simplicity, let us change notation as follows

$$\delta m(\vec{r}) \leftrightarrow \varphi(\vec{r}), \quad k \leftrightarrow c$$

Hence, Eq.(11.49) becomes

$$\beta \mathcal{H}_{eff}^{G,T>T_c}[\varphi] = \int \left[\frac{c}{2} (\nabla \varphi)^2 + at \varphi^2 \right] d^d \vec{r} \quad (11.57)$$

with

$$\varphi(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \varphi_{\vec{k}}, \quad \varphi_{\vec{k}} \in \mathbb{C}$$

Let us consider the terms of expression (11.57) separately:

- Term $at\varphi^2$: the integral we are considering is

$$\int at\varphi^2(\vec{r}) d^d\vec{r} = \frac{at}{V^2} \sum_{\vec{k}, \vec{k}'} \int_{\mathbb{R}^d} e^{i(\vec{k}+\vec{k}')\cdot\vec{r}} \varphi_{\vec{k}} \varphi_{\vec{k}'} d^d\vec{r} \stackrel{(11.55), (11.56)}{=} \frac{at}{V^2} \sum_{\vec{k}, \vec{k}'} \varphi_{\vec{k}} \varphi_{\vec{k}'} (2\pi)^d \delta(\vec{k}+\vec{k}')$$

On the other hand,

$$(2\pi)^d \delta(\vec{k} + \vec{k}') \xrightarrow{V \gg 1} V \delta_{\vec{k}, -\vec{k}'}$$

Hence, the term becomes

$$\int at\varphi^2(\vec{r}) d^d\vec{r} \xrightarrow{V \gg 1} \frac{1}{2V} \sum_{\vec{k}} 2at\varphi_{\vec{k}} \varphi_{-\vec{k}} \quad (11.58)$$

- Term $\frac{c}{2}(\nabla\varphi)^2$: consider the integral

$$\begin{aligned} \int \frac{c}{2}(\nabla\varphi)^2 d^d\vec{r} &= \frac{c}{2} \frac{1}{V^2} \int \left(\nabla \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \varphi_{\vec{k}} \right) \left(\nabla \sum_{\vec{k}'} e^{i\vec{k}'\cdot\vec{r}} \varphi_{\vec{k}'} \right) d^d\vec{r} \\ &= \frac{c}{2V^2} \sum_{\vec{k}, \vec{k}'} \left(-\vec{k} \cdot \vec{k}' \right) \varphi_{\vec{k}} \varphi_{\vec{k}'} \underbrace{\int e^{i(\vec{k}+\vec{k}')\cdot\vec{r}} d^d\vec{r}}_{(2\pi)^d \delta(\vec{k}+\vec{k}') \rightarrow V \delta_{\vec{k}, -\vec{k}'}} = \frac{c}{2V} \sum_{\vec{k}} |\vec{k}|^2 \varphi_{\vec{k}} \varphi_{-\vec{k}} \end{aligned}$$

Hence, the term becomes

$$\int \frac{c}{2}(\nabla\varphi)^2 d^d\vec{r} \xrightarrow{V \gg 1} \frac{c}{2V} \sum_{\vec{k}} |\vec{k}|^2 \varphi_{\vec{k}} \varphi_{-\vec{k}} \quad (11.59)$$

In conclusion, the Gaussian Hamiltonian in Eq.(11.49) in the Fourier space is the sum of the two terms in Eq.(11.58) and Eq.(11.59):

$$\beta\mathcal{H}_{eff}^{G, T>T_c}[\varphi] \xrightarrow{V \gg 1} \frac{1}{2V} \sum_{\vec{k}} \left(2at + c|\vec{k}|^2 \right) \varphi_{\vec{k}} \varphi_{-\vec{k}} \quad (11.60)$$

Now, thinking about the functional integral form of the partition function, what does the measure $\int \mathcal{D}[\varphi]$ become in Fourier space?

Since $\varphi(\vec{r})$ is expressed in terms of the Fourier modes $\varphi_{\vec{k}}$, which are in general complex,

$$\varphi(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} \varphi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}, \quad \varphi_{\vec{k}} \in \mathbb{C}$$

the measure of the integral becomes:

$$\int \mathcal{D}[\varphi(\vec{r})] \rightarrow \int_{-\infty}^{+\infty} \prod_{|\vec{k}| < \Lambda} d(\text{Re}\{\varphi_{\vec{k}}\}) d(\text{Im}\{\varphi_{\vec{k}}\}) \quad (11.61)$$

However, since $\varphi(\vec{r})$ is real (i.e. $\varphi_{\vec{k}}^* = \varphi_{-\vec{k}}$) the real and imaginary parts of the Fourier modes are not independent, because we have:

$$\begin{cases} \text{Re}\{\varphi_{\vec{k}}\} = \text{Re}\{\varphi_{-\vec{k}}\} \\ \text{Im}\{\varphi_{\vec{k}}\} = -\text{Im}\{\varphi_{-\vec{k}}\} \end{cases}$$

This means that if we use the measure we have written above (Eq.(11.61)) we would integrate twice on the complex plane; we must therefore change the measure so as

to avoid this double counting. We can for example simply divide everything by 2, or restrict the integration on the region where for example the last coordinate of $\vec{\mathbf{k}}$, let us call it k_z , is positive. Therefore:

$$\begin{aligned} \text{Tr} &\equiv \int \mathcal{D}[\varphi(\vec{\mathbf{r}})] = \int_{-\infty}^{+\infty} \prod_{\substack{|\vec{\mathbf{k}}| < \Lambda \\ k_z > 0}} d\text{Re}\{\varphi_{\vec{\mathbf{k}}}\} d\text{Im}\{\varphi_{\vec{\mathbf{k}}}\} \\ &= \frac{1}{2} \int_{-\infty}^{+\infty} \prod_{|\vec{\mathbf{k}}| < \Lambda} d\text{Re}\{\varphi_{\vec{\mathbf{k}}}\} d\text{Im}\{\varphi_{\vec{\mathbf{k}}}\} \end{aligned} \quad (11.62)$$

For sake of brevity, we define:

$$\text{Tr} \equiv \int_{-\infty}^{+\infty} \prod'_{\vec{\mathbf{k}}} d\varphi_{\vec{\mathbf{k}}}, \quad \prod'_{\vec{\mathbf{k}}} d\varphi_{\vec{\mathbf{k}}} \equiv \prod_{\substack{|\vec{\mathbf{k}}| < \Lambda \\ k_z > 0}} d\text{Re}\{\varphi_{\vec{\mathbf{k}}}\} d\text{Im}\{\varphi_{\vec{\mathbf{k}}}\} \quad (11.63)$$

In the end, in the Fourier space we have:

$$\tilde{Z}_G^{T > T_c} = \int \mathcal{D}[\varphi(\vec{\mathbf{r}})] e^{-\beta \tilde{\mathcal{H}}_{eff}^{T > T_c}[\varphi_{\vec{\mathbf{k}}}] } = \int_{-\infty}^{+\infty} \left(\prod'_{\vec{\mathbf{k}}} d\varphi_{\vec{\mathbf{k}}} \right) e^{-\beta \tilde{\mathcal{H}}_{eff}^{G, T > T_c}[\varphi_{\vec{\mathbf{k}}}] } \quad (11.64)$$

where

$$-\beta \tilde{\mathcal{H}}_{eff}^{G, T > T_c}[\varphi_{\vec{\mathbf{k}}}] = -\frac{1}{2V} \sum_{\vec{\mathbf{k}}} \left(2at + c|\vec{\mathbf{k}}|^2 \right) |\varphi_{\vec{\mathbf{k}}}|^2 \quad (11.65)$$

Free energy in Gaussian approximation

Let us consider again the case $T > T_c$ (for which we have $(m_0 = 0)$) and $h = 0$. In this case, the partition function of the system in the Fourier space is the one in Eq.(11.64):

$$\tilde{Z}_G^{T > T_c} = \prod_{\substack{|\vec{\mathbf{k}}| < \Lambda \\ k_z > 0}} \int_{-\infty}^{+\infty} d\text{Re}\{\varphi_{\vec{\mathbf{k}}}\} d\text{Im}\{\varphi_{\vec{\mathbf{k}}}\} e^{-\frac{1}{2V} \sum_{\vec{\mathbf{k}}} (2at + c|\vec{\mathbf{k}}|^2) |\varphi_{\vec{\mathbf{k}}}|^2}$$

Since $|\varphi_{\vec{\mathbf{k}}}|^2 = \text{Re}^2 \varphi_{\vec{\mathbf{k}}} + \text{Im}^2 \varphi_{\vec{\mathbf{k}}}$, changing variables to:

$$x \equiv \text{Re} \varphi_{\vec{\mathbf{k}}}, \quad y \equiv \text{Im} \varphi_{\vec{\mathbf{k}}}$$

Thus, we have

$$\int_{-\infty}^{+\infty} dx dy e^{-A(x^2 + y^2)} = \frac{\pi}{A}, \quad A \equiv \frac{2at + c|\vec{\mathbf{k}}|^2}{2V}$$

Hence,

$$\tilde{Z}_G^{T > T_c} = e^{-\beta \tilde{F}_G^{T > T_c}} = \prod_{\substack{|\vec{\mathbf{k}}| < \Lambda \\ k_z > 0}} \frac{2\pi V}{2at + c|\vec{\mathbf{k}}|^2} = \exp \left[\frac{1}{2} \sum_{|\vec{\mathbf{k}}| < \Lambda} \log \left(\frac{2\pi V}{2at + c|\vec{\mathbf{k}}|^2} \right) \right]$$

We therefore have that the free energy of the system is:

$$\tilde{F}_G^{T > T_c} = -\frac{k_B T}{2} \sum_{|\vec{\mathbf{k}}| < \Lambda} \log \left(\frac{2\pi V}{2at + c|\vec{\mathbf{k}}|^2} \right) \quad (11.66)$$

Remark. For $T < T_c$ we have $m_0 = \pm(-at/b)^{1/2} \neq 0$. In addition, we have to redefine the quadratic term $(at + 3bm_0^2)$ (in Eq.(11.48)), that for $m_0^2 = -at/b$, becomes $-2at$. Moreover, we have also the term $VA_0 = V(atm_0^2 + \frac{b}{2}m_0^4)$. Therefore, in the case $T < T_c$ the free energy of the system is

$$\tilde{F}_G^{T < T_c} = VA_0 - \frac{k_B T}{2} \sum_{|\vec{k}| < \Lambda} \log \left(\frac{2\pi V}{2at + c|\vec{k}|^2} \right) \quad (11.67)$$

Specific heat in the Gaussian approximation

We can now compute the specific heat of the system, and so determine its critical exponent α . We therefore want to compute:

$$c_V^G = -T \frac{\partial^2}{\partial T^2} \frac{F_{GL}}{V}$$

The derivatives are straightforward, and in the end we get:

$$c_V^G = \underbrace{\frac{A}{V} \sum_{|\vec{k}| < \Lambda} \frac{1}{\left(2at + c|\vec{k}|^2\right)^2}}_{1^{st}} - \underbrace{\frac{B}{V} \sum_{|\vec{k}| < \Lambda} \frac{1}{2at + c|\vec{k}|^2}}_{2^{st}}$$

One can show that

$$1^{st} \propto \begin{cases} \xi^{4-d} \sim t^{-\nu(4-d)} & d < 4 \\ < \infty & d > 4 \end{cases}$$

and

$$2^{nd} \propto \begin{cases} \xi^{2-d} \sim t^{-\nu(2-d)} & d < 2 \\ < \infty & d > 2 \end{cases}$$

Therefore for $d < 2$ the 2^{nd} contribution to c_V^{GL} diverges, but in the same range of d the divergence of the first contribution is more relevant; on the other hand, for $2 \leq d < 4$ only the first contribution diverges. It is therefore the 1^{st} term that determines the divergence of the specific heat, and in particular for $d < 4$ we have $c_V^G \sim t^{-\nu(4-d)}$; in summary:

$$c_V^G \sim \begin{cases} t^{-\nu(4-d)} & d < 4 \\ < \infty & d > 4 \end{cases} \quad (11.68)$$

and so we see that in the Gaussian approximation the inclusion of the fluctuations has changed the behaviour of c_V at the transition point; in particular, has changed the value of the critical exponent α ($c_V \sim t^{-\alpha}$) to:

$$\alpha_G = \nu(4-d) \quad \text{for } d < 4 \quad (11.69)$$

In order to compute it, however, we still must determine ν so we now proceed to compute the two-point correlation function in order to determine both η and ν .

Two-point correlation function in the Gaussian approximation

We have to compute the 2-point correlation function for $\mathcal{H}_{eff}^G(\varphi)$. We know that the (simple) correlation function is defined as:

$$G(\vec{r}, \vec{r}') = \langle \varphi(\vec{r}) \varphi(\vec{r}') \rangle$$

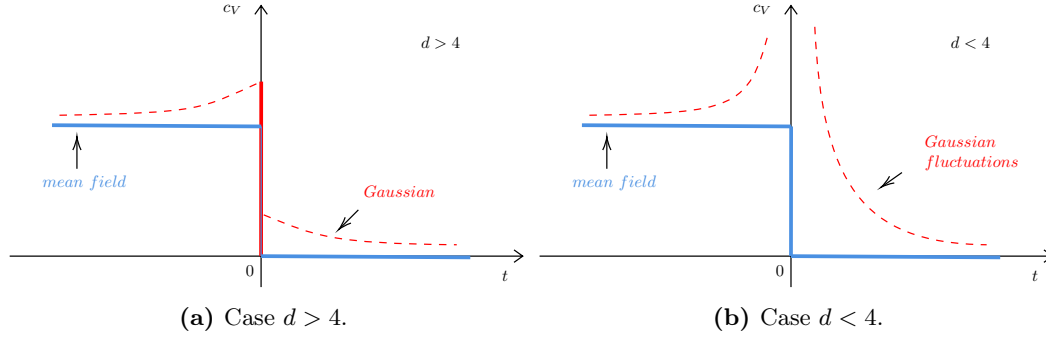


Figure 11.4: Behaviour of the specific heat c_V as a function of the rescaled temperature t . In blue it is represented its behaviour in the mean field theory, while in red the one with Gaussian approximations. We see that in the case $d < 4$ with Gaussian approximations the specific heat diverges near $t \sim 0$.

so we first have to determine:

$$\varphi(\vec{r})\varphi(\vec{r}') = \frac{1}{V^2} \sum_{\vec{k}, \vec{k}'} e^{i(\vec{k} \cdot \vec{r} + \vec{k}' \cdot \vec{r}')} \varphi_{\vec{k}} \varphi_{\vec{k}'}$$

Shifting to Fourier space, we have (the subscript G stands for Gaussian):

$$\langle \varphi_{\vec{k}} \varphi_{\vec{k}'} \rangle_G = \frac{\int_{-\infty}^{+\infty} d\varphi_{\vec{k}_1} \dots d\varphi_{\vec{k}} d\varphi_{\vec{k}'} \varphi_{\vec{k}} \varphi_{\vec{k}'} e^{-\beta \mathcal{H}_{eff}}}{\int_{-\infty}^{+\infty} d\varphi_{\vec{k}_1} \dots d\varphi_{\vec{k}} d\varphi_{\vec{k}'} e^{-\beta \mathcal{H}_{eff}}}$$

where, as we said,

$$\beta \mathcal{H}_{eff}^G = V A_0 + \frac{1}{2V} \sum_{\vec{k}} \left(2at + c |\vec{k}|^2 \right) |\varphi_{\vec{k}}|^2$$

It is clear that in $\langle \varphi_{\vec{k}} \varphi_{\vec{k}'} \rangle_G$ all the integrals factorize since the Fourier modes are all independent (they are decoupled); therefore, all the integrals in the numerator that don't involve \vec{k} or \vec{k}' simplify with the same integrals in the denominator. Taking this into account, it is possible to show

$$\langle \varphi_{\vec{k}} \varphi_{\vec{k}'} \rangle_G = \frac{V}{2at + c |\vec{k}|^2} \delta_{\vec{k}, -\vec{k}'}$$

that, in the limit $V \rightarrow \infty$ (Eq.(11.56)) becomes

$$\langle \varphi_{\vec{k}} \varphi_{\vec{k}'} \rangle_G \xrightarrow{V \rightarrow \infty} \frac{(2\pi)^d}{2at + c |\vec{k}|^2} \delta(\vec{k} + \vec{k}') \quad (11.70)$$

Going back to real space, by antitransforming, we have:

$$\begin{aligned} \langle \varphi(\vec{r}) \varphi(\vec{r}') \rangle_G &= \frac{1}{V^2} \sum_{\vec{k}, \vec{k}'} e^{i(\vec{k} \cdot \vec{r} + \vec{k}' \cdot \vec{r}')} \langle \varphi_{\vec{k}} \varphi_{\vec{k}'} \rangle_G = \frac{1}{V^2} \sum_{\vec{k}, \vec{k}'} e^{i(\vec{k} \cdot \vec{r} + \vec{k}' \cdot \vec{r}')} \frac{V}{2at + c |\vec{k}|^2} \delta_{\vec{k}, -\vec{k}'} \\ &= \frac{1}{V} \sum_{\vec{k}} \frac{e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}}{2at + c |\vec{k}|^2} \end{aligned}$$

We see that defining:

$$\xi(t) = \left(\frac{c}{2at} \right)^{1/2}$$

we get

$$\langle \varphi(\vec{r})\varphi(\vec{r}') \rangle_G = \frac{1}{V} \sum_{\vec{k}} \frac{1}{c} \frac{e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}}{|\vec{k}|^2 + \xi^{-2}} = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{x}} \hat{G}(\vec{k}) \quad (11.71)$$

where we have defined the correlation function

$$\hat{G}(\vec{k}) = \frac{1}{c} \frac{1}{|\vec{k}|^2 + \xi^{-2}} \quad (11.72)$$

this correlation function acquires the same form of the one computed in mean field theory. This means that the critical exponents ν and η now have the same values predicted by mean field theory (see Sec.(11.5) and Sec.(11.5.1)), namely:

$$\Rightarrow \begin{cases} \nu_G = \frac{1}{2} \\ \eta_G = 0 \end{cases} \quad (11.73)$$

hence, there are no changes with Gaussian fluctuations! Interactions between $\varphi_{\vec{k}}$ are needed!

Chapter 12

Widom's scaling theory. Block-spin Kadanoff's transformation

12.1 Introduction

We have seen that as a given system approaches a critical point $T \rightarrow T_c^\pm$, the distance ξ over which the fluctuations of the order parameter are correlated becomes comparable to the size of the whole system L and the microscopic aspects of the system become irrelevant. This means that near a critical point the system has no longer characteristic lengths (a, L) , besides ξ of course that becomes the only relevant length scale of the problem. We can therefore expect that if we "move" a little bit from a critical point ($t \sim 0$), for example changing the temperature by a small amount, the free energy of the system as a function will not change its shape, hence it is invariant in form by a change of scale.

This hypothesis is also suggested by experimental data such as the ones shown by Guggenheim for the gas phase diagrams and the ones shown for ferromagnetic materials at different temperatures. Let us consider the experiment in Figure 12.2 ([4] pag. 119); we can see that data from different temperatures, if scaled properly, collapse into two (one for $t < 0$ and one for $t > 0$) unique curves. It is clearly illustrated in Figure 12.1. At the origin, the Widom's static scaling theory was introduced also to explain this collapse.

Lecture 19.
Wednesday 18th
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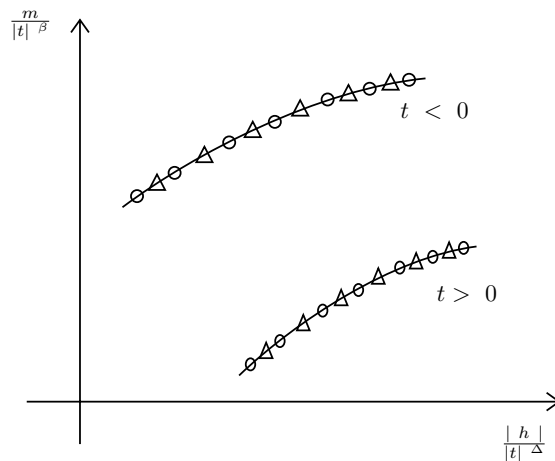


Figure 12.1: Scaled magnetization m is plotted against scaled magnetic field h .

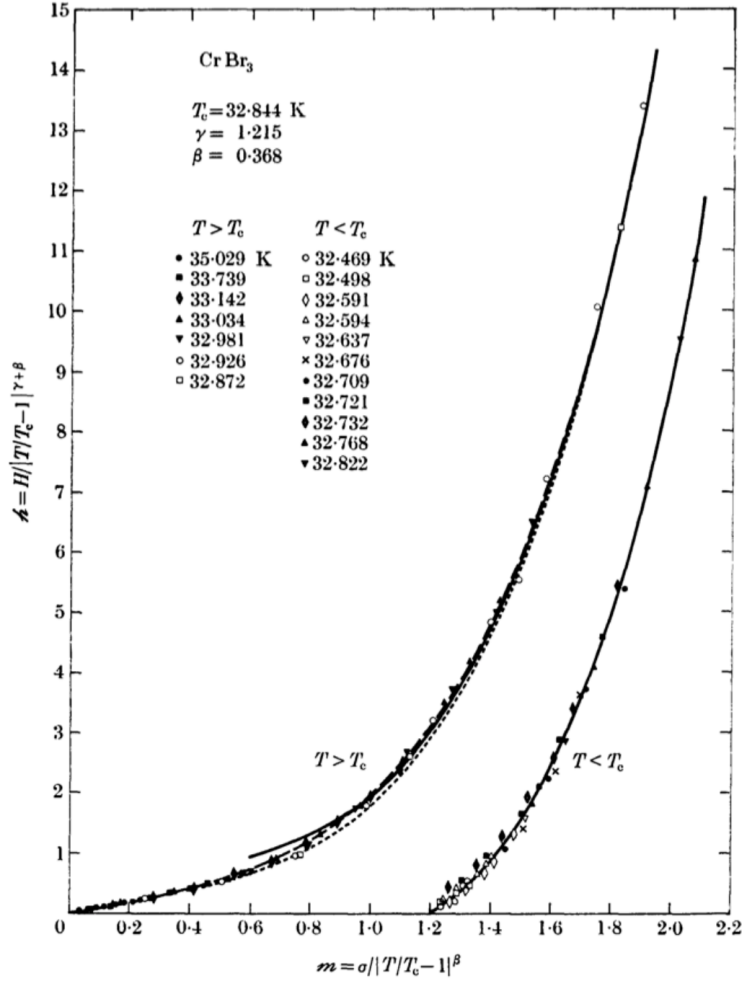


Figure 12.2: Scaled magnetic field h is plotted against scaled magnetization m for the insulating ferromagnet CrBr_3 , using data from seven supercritical ($T > T_c$) and from eleven subcritical $T < T_c$ isotherms. Here $\sigma \equiv M/M_0$. (1969) [4]

12.2 Widom's static scaling theory

We have seen that when a phase transition occurs the free energy of the system is such that the response functions exhibit singularities, often in the form of divergences. To make a concrete example (but of course all our statements are completely general) if we consider a magnetic system we can suppose to write its free energy density as:

$$f(T, H) = f_r(T, H) + f_s(T, H)$$

where $t = (T - T_c)/T_c$ and $h = (H - H_c)/k_B T$, f_r is the "regular" part of the free energy (which does not significantly change near a critical point, it is an analytic function), while f_s is the "singular" one, which contains the non-analytic behaviour of the system near a critical point (i.e. $t \sim 0$ and $h \sim 0$).

Widom's static scaling hypothesis consists in assuming that the singular part f_s of the free energy is a generalized homogeneous function, i.e.:

$$f_s(\lambda^{p_1} t, \lambda^{p_2} h) = \lambda f_s(t, h), \quad \forall \lambda \in \mathbb{R}$$

Note that assuming that one thermodynamic potential is a generalized homogeneous function implies that all the other thermodynamic potentials are so.

Therefore, in order to properly define the scaling hypothesis, we should rely on the mathematical concept of homogeneous functions and now we discuss the main properties of such functions.

12.2.1 Homogeneous functions of one or more variables

Single variable

Let us begin with the definition of homogeneous function for a single variable r .

Definition 10: Homogeneous function

A function $f(r)$ is said to be homogeneous in r if

$$f(\lambda r) = g(\lambda)f(r), \quad \forall \lambda \in \mathbb{R} \quad (12.1)$$

where g is, for the moment, an unspecified function (we will shortly see that it has a precise form).

Example 33: Parabola $f(r) = Br^2$

An example of homogeneous function is

$$f(r) = Br^2$$

in fact

$$f(\lambda r) = B(\lambda r)^2 = \lambda^2 f(r)$$

and so in this case $g(\lambda) = \lambda^2$.

A very interesting property of an homogeneous functions is that, once its value in a point r_0 (i.e. $f(r_0)$) and the function $g(\lambda)$ are known, the entire $f(r)$ can be reconstructed for all $r \in \mathbb{R}$; indeed, any r can be written in the form $r = \lambda r_0$ (of course with $\lambda = r/r_0$), so that

$$f(r) = f(\lambda r_0) = g(\lambda)f(r_0) \quad (12.2)$$

We now want to show that $g(\lambda)$ has a precise form.

Theorem 3

The function $g(\lambda)$ is not arbitrary, but it must be of the form

$$g(\lambda) = \lambda^p \quad (12.3)$$

where p is the degree of the homogeneity of the function.

Proof. From the definition of homogeneous function, for $\lambda, \mu \in \mathbb{R}$ we have on one hand that:

$$f(\lambda\mu r) = f(\lambda(\mu r)) = g(\lambda)f(\mu r) = g(\lambda)g(\mu)f(r)$$

on the other hand,

$$f((\lambda\mu)r) = g(\lambda\mu)f(r)$$

and so:

$$g(\lambda\mu) = g(\lambda)g(\mu)$$

If we now suppose g to be differentiable¹, then differentiating with respect to μ this last equation we get:

$$\frac{\partial}{\partial \mu}[g(\lambda\mu)] = \frac{\partial}{\partial \mu}[g(\lambda)g(\mu)] \Rightarrow \lambda g'(\lambda\mu) = g(\lambda)g'(\mu)$$

¹Actually $g(\lambda)$ continuous is sufficient, but proof becomes more complicated.

Setting $\mu = 1$ and defining $p \equiv g'(\mu = 1)$, we have:

$$\lambda g'(\lambda) = g(\lambda)p \Rightarrow \frac{g'(\lambda)}{g(\lambda)} = \frac{p}{\lambda}$$

which yields:

$$\frac{d}{d\lambda}(\ln g(\lambda)) = \frac{p}{\lambda} \Rightarrow \ln g(\lambda) = p \ln \lambda + c \Rightarrow g(\lambda) = e^c \lambda^p$$

Now, $g'(\lambda) = p e^c \lambda^{p-1}$, so since $g'(1) = p$ by definition we have $p = p e^c$ and thus $c = 0$. Therefore:

$$g(\lambda) = \lambda^p$$

A homogeneous function such that $g(\lambda) = \lambda^p$ is said to be homogeneous of degree p . ■

Generalized homogeneous functions (more variables)

Let us now define homogeneous functions for more than only one variable:

$$f(\lambda x, \lambda y) = \lambda^p f(x, y), \quad \forall \lambda \in \mathbb{R}$$

The function $f(x, y)$ is a *generalized homogeneous function* if has as more general form

$$f(\lambda^a x, \lambda^b y) = \lambda f(x, y), \quad \forall \lambda \in \mathbb{R} \quad (12.4)$$

Remark. If we consider instead

$$f(\lambda^a x, \lambda^b y) = \lambda^p f(x, y)$$

we can always choose $\lambda^p \equiv s$ such that

$$f(s^{a/p} x, s^{b/p} y) = s f(x, y)$$

and choosing $a' = a/p$ and $b' = b/p$ we are back to (12.4). Hence, it is the most general form an homogeneous function can have.

Remark. Since λ is arbitrary, we can choose $\lambda = y^{-1/b}$, thus we get

$$f(x, y) = y^{1/b} f\left(\frac{x}{y^{a/b}}, 1\right)$$

in that way f depends on x and y only through the ratio $\frac{x}{y^{a/b}}$! Similarly, for x , one can choose $\lambda = x^{-1/a}$, obtaining

$$f(x, y) = x^{1/a} f\left(1, \frac{y}{x^{b/a}}\right)$$

Example 34

The function $f(x, y) = x^3 + y^7$ is an homogeneous one. Indeed, we have:

$$f(\lambda^{1/3} x, \lambda^{1/7} y) = \lambda x^3 + \lambda y^7 = \lambda f(x, y)$$

Instead, examples of non-homogeneous functions are:

$$f(x) = e^{-x}, \quad f(x) = \log x$$

12.2.2 Widom's scaling hypothesis

As said, the Widom's static scaling hypothesis consists in assuming that the singular part of the free energy, f_s , is a generalized homogeneous function, i.e.:

$$f_s(\lambda^{p_1}t, \lambda^{p_2}h) = \lambda f_s(t, h), \quad \forall \lambda \in \mathbb{R} \quad (12.5)$$

where p_1 and p_2 are the degrees of the homogeneity.

The exponents p_1 and p_2 are not specified by the scaling hypothesis; however, we are shortly going to show that all the critical exponents of a system can be expressed in terms of p_1 and p_2 ; this also implies that if two critical exponents are known, we can write p_1 and p_2 in terms of them (since in general we will have a set of two independent equations in the two variables p_1 and p_2 and therefore determine all the critical exponents of the system. In other words, we just need to know two critical exponents to obtain all the others.

Remark. Since f_s is a generalized homogeneous function, it is always possible to choose λ to remove the dependence on one of their arguments; for example, one can choose $\lambda = h^{-1/p_2}$ to obtain

$$f_s(t, h) = h^{1/p_2} f_s(h^{-p_1/p_2}t, 1)$$

where

$$\Delta \equiv \frac{p_2}{p_1}$$

is called the *gap exponent*.

12.3 Relations between critical exponents

Let us now explore the consequences of Widom's assumption on the critical exponents of a system, again on a magnetic one for concreteness. Indeed, let us see how this simple hypothesis allow us, by simple differential calculus, to obtain relations between the thermodynamic critical exponents.

12.3.1 Exponent β (scaling of the magnetization)

Let us start from the scaling hypothesis

$$f_s(\lambda^{p_1}t, \lambda^{p_2}h) = \lambda f_s(t, h)$$

Since

$$M = \frac{\partial f}{\partial H}$$

deriving both sides of Widom's assumption with respect to h^2 we get:

$$\lambda^{p_2} \frac{\partial f_s}{\partial h}(\lambda^{p_1}t, \lambda^{p_2}h) = \lambda \frac{\partial f_s}{\partial h}$$

and thus:

$$\lambda^{p_2} M_s(\lambda^{p_1}t, \lambda^{p_2}h) = \lambda M_s(t, h)$$

On the other hand, we know that, for $h = 0$ and $t \rightarrow 0^-$, $M_s(t) \sim (-t)^\beta$. Hence, in order to determine β , we set $h = 0$ so that this becomes

$$M_s(t, 0) = \lambda^{p_2-1} M_s(\lambda^{p_1}t, 0)$$

²We should in principle derive with respect to H , but since $h \propto \beta H$, the β factors simplify on both sides.

Since λ is arbitrary, using the properties of generalized homogeneous functions, we set

$$\lambda^{p_1} t = -1 \quad \Rightarrow \quad \lambda = (-t)^{-1/p_1}$$

to eliminate the dependence on t . Hence, we get

$$M_s(t, 0) = (-t)^{(1-p_2)/p_1} M_s(-1, 0)$$

By definition of the β critical exponent, we have:

$$\beta = \frac{1 - p_2}{p_1} \quad (12.6)$$

12.3.2 Exponent δ

Let us consider again the relation

$$\lambda^{p_2} M_s(\lambda^{p_1} t, \lambda^{p_2} h) = \lambda M_s(t, h)$$

We can determine the exponent δ by setting $t = 0$ ($T = T_c$), obtaining:

$$M(0, h) = \lambda^{p_2-1} M(0, \lambda^{p_2} h)$$

Now, using again the same property of generalized homogeneous functions we set

$$\lambda^{p_2} h = 1 \quad \Rightarrow \quad \lambda = h^{-1/p_2}$$

and we get:

$$M_s(0, h) = h^{(1-p_2)/p_2} M_s(0, 1)$$

Since $M_s \stackrel{h \rightarrow 0^+}{\sim} h^{1/\delta}$, we have:

$$\delta = \frac{p_2}{1 - p_2} \quad (12.7)$$

Now we can also express p_1 and p_2 in terms of β and δ from the two relations Eq.(12.6) and Eq.(12.7). The result is:

$$p_1 = \frac{1}{\beta(\delta + 1)}, \quad p_2 = \frac{\delta}{\delta + 1} \quad (12.8)$$

from which we see that the gap exponent is:

$$\Delta \equiv \frac{p_2}{p_1} = \beta\delta \quad (12.9)$$

12.3.3 Exponent γ

In order to obtain the magnetic susceptibility, we derive twice the expression of Widom's assumption with respect to h , to get:

$$\lambda^{2p_2} \chi_T(\lambda^{p_1} t, \lambda^{p_2} h) = \lambda \chi_T(t, h)$$

The exponent γ describes the behaviour of χ_T for $t \rightarrow 0$ when no external field is present ($h = 0$). What we can now see is that the scaling hypothesis leads to the equality of the exponents for $t \rightarrow 0^+$ and $t \rightarrow 0^-$.

- Case $t \rightarrow 0^-$: setting $h = 0$ and $\lambda = (-t)^{-1/p_1}$ we get

$$\chi_T(t, 0) = (-t)^{-\frac{2p_2-1}{p_1}} \chi_T(-1, 0)$$

and if we call γ^- the critical exponent for $t \rightarrow 0^-$, we see that, since

$$\chi_T(t, 0) \stackrel{t \rightarrow 0^-}{\sim} (-t)^{-\gamma_-}$$

we get

$$\gamma_- = \frac{2p_2 - 1}{p_1} = \beta(\delta - 1)$$

- Case $t \rightarrow 0^+$: setting $h = 0$ and $\lambda = (t)^{-1/p_1}$ we get

$$\chi_T(t, 0) = t^{-\frac{2p_2-1}{p_1}} \chi_T(1, 0)$$

and if we call γ^+ the critical exponent for $t \rightarrow 0^+$, we see that, since

$$\chi_T(t, 0) \stackrel{t \rightarrow 0^+}{\sim} t^{-\gamma_+}$$

we get

$$\gamma_+ = \frac{2p_2 - 1}{p_1} = \beta(\delta - 1)$$

We therefore see explicitly that:

$$\gamma_- = \gamma_+ \equiv \gamma = \frac{2p_2 - 1}{p_1} = \beta(\delta - 1) \quad (12.10)$$

12.3.4 Exponent α (scaling of the specific heat)

In order to determine the behaviour of the specific heat (at constant external field) near the critical point, we derive the expression of Widom's assumption twice with respect to the temperature t , so that:

$$\lambda^{2p_1} c_H(\lambda^{p_1} t, \lambda^{p_2} h) = \lambda c_H(t, h)$$

We want to see again that the scaling hypothesis leads to the equality of the exponents for $t \rightarrow 0^+$ and $t \rightarrow 0^-$.

- Case $t \rightarrow 0^-$: setting $h = 0$ and $\lambda = (-t)^{-1/p_1}$ we get

$$c_H(t, 0) = (-t)^{-\left(2 - \frac{1}{p_1}\right)} c_H(-1, 0)$$

and if we call α^- the critical exponent for $t \rightarrow 0^-$, we see that, since

$$c_H(t, 0) \stackrel{t \rightarrow 0^-}{\sim} (-t)^{-\alpha_-}$$

we get

$$\alpha_- = 2 - \frac{1}{p_1}$$

- Case $t \rightarrow 0^+$: setting $h = 0$ and $\lambda = (t)^{-1/p_1}$ we get

$$c_H(t, 0) = t^{-\left(2 - \frac{1}{p_1}\right)} c_H(1, 0)$$

and if we call α^+ the critical exponent for $t \rightarrow 0^+$, we see that, since

$$c_H(t, 0) \stackrel{t \rightarrow 0^+}{\sim} t^{-\alpha_+}$$

we get

$$\alpha_+ = 2 - \frac{1}{p_1}$$

We have again:

$$\alpha_- = \alpha_+ \equiv \alpha = 2 - \frac{1}{p_1} \quad (12.11)$$

12.3.5 Griffiths and Rushbrooke's equalities

If we now substitute $p_1 = \frac{1}{\beta(\delta+1)}$ into $\alpha = 2 - \frac{1}{p_1}$, we get:

$$\alpha + \beta(\delta + 1) = 2 \quad (12.12)$$

This is the *Griffiths equality*, which we have already encountered in inequalities between critical exponents as an inequality (see Sec.2.7.4).

On the other hand, *Rushbrooke's equality* is obtained by combining Griffith equality with the relation $\gamma = \beta(\delta - 1)$:

$$\alpha + 2\beta + \gamma = 2 \quad (12.13)$$

We therefore see, as anticipated in Sec.2.7.4, that the static scaling hypothesis allows to show that they are indeed exact equalities.

12.3.6 An alternative expression for the scaling hypothesis

We can re-express Widom's assumption in another fashion often used in literature. Let us consider the Widom's assumption

$$f_s(\lambda^{p_1} t, \lambda^{p_2} h) = \lambda f_s(t, h)$$

If we set $\lambda = t^{-1/p_1}$, then:

$$f_s(1, t^{-p_2/p_1} h) = t^{-1/p_1} f_s(t, h)$$

From $\Delta = \frac{p_2}{p_1}$ and $\alpha = 2 - \frac{1}{p_1}$, we can rewrite this as:

$$f_s(t, h) = t^{2-\alpha} f_s\left(1, \frac{h}{t^\Delta}\right) \quad (12.14)$$

which is the most used form of the scaling hypothesis in statistical mechanics.

As we can notice, we have not considered the critical exponents η and ν ; this will be done shortly in Kadanoff's scaling and correlation lengths.

12.3.7 Scaling of the equation of state

Besides the relations between critical exponents, Widom's static scaling theory allows us to make predictions on the shape of the state equation of a given system. By predicting the scaling form of the equation of state, we can explain the collapse of the experimental data. Let us now see how, again for a magnetic system. We start from the relation

$$M_s(t, h) = \lambda^{p_2-1} M_s(\lambda^{p_1} t, \lambda^{p_2} h)$$

Using the property of generalized homogeneous functions we set $\lambda = |t|^{-1/p_1}$. Hence,

$$M_s(t, h) = |t|^{\frac{1-p_2}{p_1}} M_s\left(\frac{t}{|t|}, \frac{h}{|t|^{p_2/p_1}}\right)$$

Since $\beta = (1 - p_2)/p_1$ and $\Delta = p_2/p_1$, we have

$$\frac{M_s(t, h)}{|t|^\beta} = M_s\left(\frac{t}{|t|}, \frac{h}{|t|^\Delta}\right) \quad (12.15)$$

Hence, we can define the *scaled magnetization* and *scaled magnetic field* as

$$\bar{m} \equiv |t|^{-\beta} M(t, h), \quad \bar{h} \equiv |t|^{-\Delta} h(t, M) \quad (12.16)$$

and

$$F_{\pm}(\bar{h}) \equiv M_s(\pm 1, \bar{h}) \quad (12.17)$$

where $+1$ corresponds to $t > 0$ (namely $T > T_c$) and -1 to $t < 0$ (i.e. $T < T_c$). Using these definitions, Eq.(12.15) becomes

$$\bar{m} = F_{\pm}(\bar{h}) \quad (12.18)$$

The meaning of this equation is that if we measure M and h and rescale them as we have just seen, all the experimental data should fall on the same curve independently of the temperature T ; there are of course two possible curves (not necessarily equal), one for $T > T_c$ and one for $T < T_c$ (which correspond to $M(1, h)$ and $M(-1, h)$). These predictions are in perfect agreement with experimental results shown in Figure 12.2, and are one of the greatest successes of Widom's static scaling theory.

12.4 Kadanoff's block spin and scaling of the correlation function

As we have seen, Widom's static scaling theory allows us to determine exact relations between critical exponents, and to interpret the scaling properties of systems near a critical point. However, this theory is based upon the following equation:

$$f(T, H) = f_r(T, H) + f_s(T, H)$$

but gives no physical interpretation of it; in other words, it does not tell anything about the physical origin of scaling laws. Furthermore, as we have noticed Widom's theory does not involve correlation lengths, so it tells nothing about the critical exponents ν and η .

We know that one of the characteristic traits of critical phenomena is the divergence of the correlation length ξ , which becomes the only physically relevant length near a critical point. However, by now we are unable to tell if and how this is related to Widom's scaling hypothesis; everything will become more clear within the framework of the Renormalization Group, in which we will see that Widom's assumption is a consequence of the divergence of correlation length.

Nonetheless, before the introduction of the Renormalization Group, Kadanoff (1966) proposed a plausibility argument for his assumption applied to the Ising model, which we are now going to analyse. We will see that Kadanoff's argument, which is based upon the intuition that *the divergence of ξ implies a relation between the coupling constants of an effective Hamiltonian \mathcal{H}_{eff} and the length on which the order parameter m is defined*, is correct in principle but not in detail because these relations are in reality more complex than what predicted by Kadanoff; furthermore, Kadanoff's argument does not allow an explicit computation of critical exponents. We will have to wait for the Renormalization Group in order to solve these problems.

12.4.1 Kadanoff's argument for the Ising model

Let us consider a d -dimensional Ising model with hypercubic lattice with lattice constant a ; assuming nearest-neighbour interactions the Hamiltonian of the system will be:

$$-\beta\mathcal{H}_{\Omega} = K \sum_{\langle ij \rangle} \sigma_i \sigma_j + h \sum_{i=1}^N \sigma_i \quad (12.19)$$

where $\sigma_i = \pm 1$, $K = \beta J$ and $h = \beta H$, as usual.

The Kadanoff's argument is based on a coarse-grained operation on the system and on two basic assumptions.

Coarse graining operation

Since the values of the spin variables are correlated on lengths of order $r < \xi(t)$, we partition the system into blocks of size la (l is an adimensional scale) such that

$$a \ll la \ll \xi(t)$$

The spins contained in this regions of linear dimension la will behave, statistically, as a single unit. We can therefore imagine to carry out, similarly to what we have seen for the Ginzburg-Landau theory, a coarse graining procedure where we substitute the spins σ_i inside a "block" of linear dimension la (which will therefore contain l^d spins) with a single *block spin* (or *superspin*) S_I ; the total number of blocks will of course be:

$$N_l = \frac{N}{l^d}$$

Considering the I -th block, we can define the block spin S_I as:

$$S_I \equiv \frac{1}{|m_l|} \frac{1}{l^d} \sum_{i \in I} \sigma_i \quad (12.20)$$

where the mean magnetization of the I -th block m_l is:

$$m_l \equiv \frac{1}{l^d} \sum_{i \in I} \langle \sigma_i \rangle \quad (12.21)$$

Remark. The division by $|m_l|$ in equation (12.20) is crucial because it rescales the new variables S_I to assume only the values ± 1 , just like the original ones (rescaling of the fields).

In the end we are left with a system of block spins on a hypercubic lattice with lattice constant la . We can therefore rescale the spatial distances between the degrees of freedom of our system:

$$\vec{r}_l = \frac{\vec{r}}{l}$$

In other words, since la is now the characteristic length of the system we are measuring the distances in units of la (just like in the original one we measured distances in units of a). The coarse graining procedure we have just seen is described by Figure 12.3 for a two-dimensional Ising model.

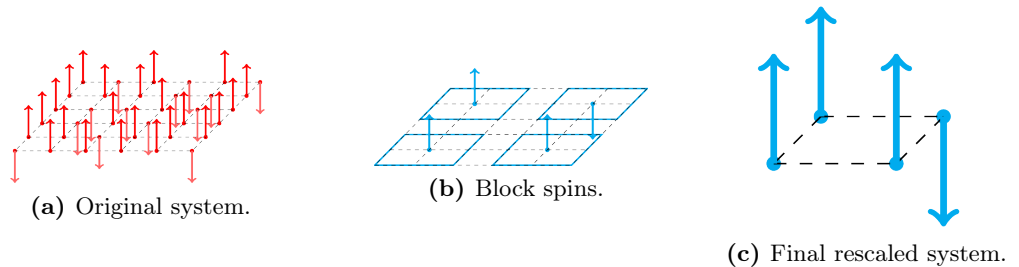


Figure 12.3: Coarse graining procedure for a two-dimensional Ising model.

Kadanoff's argument now proceeds with two assumptions.

1st crucial assumption

The first assumption states that, in analogy to what happens in the original system, we assume that the block spins interact with the nearest neighbours and an external effective field (just like the original ones do). Hence, the Hamiltonian of the

new system \mathcal{H}_l is equal in form to \mathcal{H}_Ω , the original one, of course provided that the spins, coupling constants and external fields are redefined. If we call K_l and h_l these new constants, the new effective Hamiltonian is:

$$-\beta\mathcal{H}_l = K_l \sum_{\langle IJ \rangle}^{N_b} S_I S_J + h_l \sum_{I=1}^{N_b} S_I \quad (12.22)$$

Remark. This assumption is in general wrong!

Since in the new system the lengths have been rescaled by a factor l , this means that in the new system all the lengths will be measured in units of la . Hence, also the correlation length has to be measured in units of la , and in particular we will have:

$$\xi_l = \frac{\xi}{l}$$

This means that the new system has a lower correlation length $\xi_l < \xi$, and so the system described by \mathcal{H}_l is more distant from the critical point than the original one \mathcal{H}_Ω . Hence, we will have a new effective temperature:

$$t_l > t$$

Similarly, in the coarse grained system the magnetic field h_l will be rescaled to an effective one:

$$h \sum_i \sigma_i = h \sum_I \sum_{i \in I} \sigma_i = h \sum_I |m_l| l^d S_I = \underbrace{h|m_l|l^d}_{h_l} \sum_I S_I = h_l \sum_I S_I$$

which implies that there is a relation between the new magnetic field and the mean magnetization:

$$h_l = h|m_l|l^d$$

Since the Hamiltonian of the block spin system \mathcal{H}_l has the same form of the original one \mathcal{H}_Ω , the same will be true also for the partition function Z_l and the free energy, provided that h, K and N are substituted with h_l, K_l and N/l^d ; in particular, considering the singular part f_s of the free energy density we will have:

$$N_l f_s(t_l, h_l) = \frac{N}{l^d} f_s(t_l, h_l) = N f_s(t, h)$$

and so

$$\Rightarrow f_s(t_l, h_l) = l^d f_s(t, h)$$

Remark. Note that the homogeneity condition is recovered with $\lambda \equiv l^d$.

2st crucial assumption

In order to proceed, we should ask how t and h change under the block spin transformation; hence, we now need the second assumption. We assume that:

$$t_l = t l^{y_t}, \quad h_l = h l^{y_h}, \quad y_t, y_h > 0 \quad (12.23)$$

where the y_t, y_h are called *scaling exponents* and are for now unspecified, apart from the fact that they must be positive (so that the coarse grained system is indeed farther from the critical point with respect to the original one).

The justification of this assumption lies in the fact that we are trying to understand the scaling properties of our system near a critical point, and these are the simplest possible relations between (t, h) and (t_l, h_l) that satisfy the following symmetry requirements:

- when $h \rightarrow -h$, then $h_l \rightarrow -h_l$;
- when $h \rightarrow -h$, then $t_l \rightarrow t_l$;
- when $t = h = 0$, then $t_l = h_l = 0$.

If we use this assumption in the free energy equation

$$f_s(t_l, h_l) = l^d f_s(t, h)$$

we get:

$$f_s(t, h) = l^{-d} f_s(tl^{y_t}, hl^{y_h}) \quad (12.24)$$

This is very similar to Widom's scaling hypothesis (Eq.(12.5)), but with the parameter λ that is the inverse of the block volume l^d . Since l has no specified value, we can choose the one we want and again we use the properties of generalized homogeneous functions to eliminate one of the arguments of f_s . In particular, setting

$$l = |t|^{-1/y_t}$$

we get:

$$f_s(t, h) = |t|^{d/y_t} f_s(1, h|t|^{-y_h/y_t}) \quad (12.25)$$

where the gap exponent is now

$$\Delta = \frac{y_h}{y_t} \quad (12.26)$$

comparing this equation with the alternative expression of the scaling hypothesis (Eq.(12.14)) we have:

$$2 - \alpha = \frac{d}{y_t} \quad (12.27)$$

12.4.2 Kadanoff's argument for two-point correlation functions

Let us now compute the two-point correlation function of the block spin system:

$$G_{IJ}(\vec{r}_l, t_l) \equiv \langle S_I S_J \rangle - \langle S_I \rangle \langle S_J \rangle \quad (12.28)$$

where \vec{r}_l is the vector of the relative distance between the centers of the I -th and J -th block (measured in units of la , as stated before). We want now to see how this correlation length is related to the one of the original system $G(\vec{r}, t)$. Since from the first assumption we have

$$h_l = h|m_l|l^d \Rightarrow |m_l| = \frac{h_l l^{-d}}{h}$$

Using the second assumption, for which $h_l = h l^{y_h}$, we obtain:

$$|m_l| = l^{y_h - d}$$

Since

$$S_I = \frac{1}{|m_l|} \frac{1}{l^D} \sum_{i \in I} \sigma_i$$

the two-point correlation function becomes

$$\begin{aligned} G_{IJ}(\vec{r}_l, t_l) &= \langle S_I S_J \rangle - \langle S_I \rangle \langle S_J \rangle = \frac{1}{l^{2(y_h - d)} l^{2d}} \sum_{i \in I} \sum_{j \in J} \left[\underbrace{\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle}_{G_{ij}} \right] \\ &= \frac{l^d l^d}{l^{2(y_h - d)} l^{2d}} [\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle] \end{aligned}$$

where in the last step we have made the assumption that, since $la \ll \xi$, G_{ij} inside a block is fairly constant, we can bring it outside the sum. Hence, the sum over i, j becomes l^{2d} . Hence, we have:

$$G_{IJ}(\vec{r}_l, t_l) = l^{2(d-y_h)} G_{ij}(\vec{r}, t) \quad (12.29)$$

Introducing also the dependence on h , we have:

$$G_{IJ}\left(\frac{\vec{r}}{l}, tl^{y_t}, hl^{y_h}\right) = l^{2(d-y_h)} G_{ij}(\vec{r}, t, h) \quad (12.30)$$

Again, we can remove the dependence on t by setting $l = t^{-1/y_t}$ so that:

$$G(\vec{r}, t, h) = t^{\frac{2(d-y_h)}{y_t}} G(\vec{r}t^{1/y_t}, 1, ht^{-y_h/y_t}) \quad (12.31)$$

Now, \vec{r} scales with l as all the lengths of our system, and since we have set $l = t^{-1/y_t}$ we have

$$|\vec{r}|t^{1/y_t} = 1 \quad \Rightarrow \quad t = |\vec{r}|^{-y_t}$$

Therefore, inserting in (12.31):

$$G(\vec{r}, t, h) = |\vec{r}|^{-2(d-y_h)} F_G\left(ht^{-y_h/y_t}\right) \quad (12.32)$$

where we have defined

$$F_G\left(ht^{-y_h/y_t}\right) \equiv G(1, 1, ht^{-y_h/y_t}) \quad (12.33)$$

Let us remember that the power law behaviour of G in proximity of the critical point is

$$G \sim |\vec{r}|^{2-d-\eta}$$

we get

$$2(d - y_h) = d - 2 + \eta \quad (12.34)$$

With the choice $l = t^{-1/y_t}$ we further have that the correlation length scales as:

$$\xi = l\xi_l = \xi_l t^{-1/y_t}$$

and remembering that the correlation length diverges as

$$\xi \sim t^{-\nu}$$

we also have:

$$\nu = \frac{1}{y_t} \quad (12.35)$$

The Eq.(12.35) together with Eq.(12.27) leads to the *hyperscaling relation*:

$$\Rightarrow 2 - \alpha = \nu d \quad (12.36)$$

Hyperscaling relations are known to be less robust than the normal scaling relations between critical exponents (for example, for Hamiltonians with long-ranged power law interactions hyperscaling relations don't hold).

Chapter 13

Renormalization group theory. Universality

13.1 Renormalization group (RG)

Lecture 20.
Friday 20th
December, 2019.
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Kadonoff: the block spin transformations justifies the Widom scaling with $\lambda \iff l$,

$$\begin{cases} f_s(t, h) = l^{-D} f_s(tl^{Y_t}, hl^{Y_h}) \\ G(\vec{r}, t, h) = l^{-2(D-Y_h)} G\left(\frac{\vec{r}}{l}, tl^{Y_t}, hl^{Y_h}\right) \\ t_l = tl^{Y_t}, \quad h_l = hl^{Y_h} \end{cases} \quad (13.1)$$

We do two crucial assumptions:

1.

$$\mathcal{H}_l = \mathcal{H}_1 \quad (13.2)$$

2.

$$\begin{cases} t_l = tl^Y \\ h_l = hl^h \end{cases} \quad (13.3)$$

Remark. An open problem is: how an iterative procedure of coarse-graining can produce the second assumption?

How this can give rise to the singular behaviour of f_s ? How can we explain universality of the critical points?

13.1.1 Main goals of RG

1. To furnish an algorithm way to perform systematically the coarse graining procedure.

Achieved by integrating the degrees of freedom at smaller length scales and obtain a new hamiltonian describing the system at larger length scales.

This will be equivalent to find a transformation between the coupling constants $k \rightarrow k'$.

2. Identify the origin of the critical behaviour.

The coarse graining procedure will give rise to a system with

$$\xi_l = \frac{\xi}{l} \quad (13.4)$$

more distant from criticality.

Let us start from a generic hamiltonian $\mathcal{H} = \mathcal{H}([k])$, where $[k] = (k_1, k_2, \dots, k_n)$. For example, for the standard Ising model $k \equiv k_1$ and $h \equiv k_2$. In general we can have n coupling constants.

Suppose we apply a coarse-graining procedure in which we integrate the degree of freedom within distance l with $a \leq la \leq L$.

There are many ways (for example the Kadanoff's block spin)

$$[k'] = \mathcal{R}_l[k], \quad l > 1 \quad (13.5)$$

where \mathcal{R}_l is the transformation of the RG. The relation (13.5) gives rise to a recursive relation.

The properties of \mathcal{R}_l are:

1. \mathcal{R}_l is analitic! (Sum of a finite number of degrees of freedom).
2. The set of \mathcal{R}_l , labeled by l forms a semigroup.

Let \mathcal{R}_{l_1} and \mathcal{R}_{l_2} be two transformations

$$\begin{cases} [k'] = \mathcal{R}_{l_1}[k] \\ [k''] = \mathcal{R}_{l_2}[k'] = \mathcal{R}_{l_2} \circ \mathcal{R}_{l_1}[k] \end{cases} \quad (13.6)$$

Hence,

$$\mathcal{R}_{l_2 l_1}[k] = \mathcal{R}_{l_2} \circ \mathcal{R}_{l_1}[k] \quad (13.7)$$

Remark. Is not a group since does not exist the inverse element ($l > 1$ always!).

Remark. There is no a unique way to define \mathcal{R}_{l_1} but all of them result in the integration of the degrees of freedom at smaller length scales.

The procedure can be carried out either in real space or in the momentum space. \mathcal{R}_{l_1} but all of them result in the integration of the degrees of freedom at smaller negth scales.

Given $\mathcal{H}[k]$ we can define

$$Z_N[k] = \text{Tr } e^{-\beta \mathcal{H}[k]} \quad (13.8)$$

and

$$f_N[k] = -\frac{k_B T}{N} \log Z_N[k] \quad (13.9)$$

After the coarse graining between a and la , the number N of degrees of freedom is reduced by

$$N_l = \frac{N}{l^D} \quad (13.10)$$

3. The new hamiltonian $\mathcal{H}_l[k']$ can be (and in general it is) different from the previous one: $\mathcal{H}[k]$ (main difference with Kadanoff) but its symmetry cannot change!

For example, if we start from

$$\mathcal{H}_N = Nk_0 + k_2 \sum_{ij} S_i S_j \quad (13.11)$$

we cannot produce

$$\mathcal{H}_{N'} = N'k'_0 + k'_1 \sum_I S_I + k'_2 \sum_{IJ} S_I S_J + k'_3 \sum_{IJK} S_I S_J S_K \quad (13.12)$$

Remark. If $km = 0$, it is possible that $k'm \neq 0$ as long as the symmetry of \mathcal{H}' is equal to the one of \mathcal{H} .

4. The invariance condition is not in \mathcal{H} (as in Kadanoff) but in Z !

$$Z_{N'}[k'] = Z_N[k] \quad (13.13)$$

Condition (13.13) must be satisfied by the coarse-graining procedure. Which is the consequence of (13.13) on the free-energy?

$$f_N[k] \simeq \frac{1}{N} \log Z_N[k] \simeq \frac{l^D}{l^D N} \log Z_{N'}[k'] \simeq l^{-D} \frac{1}{N'} \log Z_{N'}[k'] \quad (13.14)$$

Hence,

$$f[k] \propto l^{-D} f[k'] \quad (13.15)$$

Remark. Since a single \mathcal{R}_l involves the integration of a finite number of degrees of freedom, it cannot develop the singularity behaviour we are looking for.

Question: if \mathcal{R}_l is analitic, what is the origin of the singular behaviour in the RG approach?

13.1.2 Singular behaviour in RG

The point is that, in order to integrate a thermodynamic number of degrees of freedom, one has to apply an infinite number of RG transformations.

After n iterations we have $l \rightarrow l^n$ and $[k] \rightarrow [k^{(n)}]$. As n changes, the coupling constants perform a trajectory in the parameter space $[k]$.

By varying the initial conditions (i.e. either the starting model or the values of the physical parameters) one obtains a *flux of trajectories*. A part from some pathological cases (cycle limits, attractors) these trajectories are attracted towards fixed points.

The scaling behaviour introduced by Widom is related to the behaviour of the trajectories close to same fixed points.

13.1.3 Zoology of the fixed points

A fixed point k^* of $\mathcal{R}_l[k]$ satisfies

$$[k^*] = \mathcal{R}_l[k^*] \quad (13.16)$$

On the other hand, we know that

$$\xi[k'] = \frac{\xi[k]}{l} \equiv \xi_l \quad (13.17)$$

At the fixed point

$$\xi[k^*] = \frac{\xi[k^*]}{l} \quad (13.18)$$

There are two cases:

$$\xi[k^*] = \begin{cases} 0 & \text{trivial} \\ \infty & \text{critical} \end{cases} \quad (13.19)$$

Each fixed point has its own basin of attraction. This is defined as the set $\{[k]\}$ such that

$$\mathcal{R}_l^{(n)}[k] \xrightarrow{n \rightarrow \infty} [k^*] \quad (13.20)$$

Theorem 4

All the points $[k]$ belonging to a basin of attraction of a critical fixed point have their correlation length $\xi = \infty$.

Proof.

$$\xi[k] = l\xi[k^{(1)}] = \dots l^n \xi[k^{(n)}] \quad (13.21)$$

If $[k]$ is in basin of attraction of $[k^*]$, we have

$$[k^{(n)}] \xrightarrow{n \rightarrow \infty} [k^*] \quad (13.22)$$

On the other hand, $\xi[k^*] = \infty$, so

$$\Rightarrow \xi[k] = l^n \xi[k^*] = \infty \quad (13.23)$$

■

Definition 11: Critical manifold

Set of $[k]$ that forms the basin of attraction of a critical fixed point.

Universality

All the critical models that belong to the critical manifold, have the same critical behaviour of the corresponding critical fixed point. Study the behaviour of \mathcal{R}_l close to the fixed points.

13.1.4 Linearization of RG close to the fixed points and critical exponents

Let $[k^*]$ be a fixed point of \mathcal{R}_l and consider

$$\vec{k} = \vec{k}^* + \delta\vec{k} \quad (13.24)$$

In components, the RG transformation is

$$k'_j = (\mathcal{R}_l)_j(\vec{k}^* + \delta\vec{k}) = k_j^* + \sum_i \left(\frac{\partial k'_j}{\partial k_i} \right)_{\vec{k}^*} \delta k_i + O(\delta k_i^2) \quad (13.25)$$

The linearized transformation is

$$\delta\vec{k}' = \bar{\pi} \delta\vec{k} \quad (13.26)$$

where

$$(\bar{\pi})_{ij} = \left(\frac{\partial k'_j}{\partial k_i} \right)_{\vec{k}^*} \quad (13.27)$$

is a square matrix

1. $\bar{\pi}$ is in general not symmetric. One has to distinguish between left and right eigenvectors.
2. $\bar{\pi}$ is not always diagonalizable or sometimes the eigenvalues are complex. For most of the physical system, however, $\bar{\pi}$ can be diagonalized and the eigenvalues are real.

Let $\lambda_l^{(\sigma)}$ be the σ -esim eigenvalue and $\vec{\mathbf{l}}^{(\sigma)}$ the corresponding eigenvector

$$\Rightarrow \bar{\pi}_{ij}^{(l)} l_j^{(\sigma)} = \lambda_l^{(\sigma)} l_i^{(\sigma)} \quad (13.28)$$

this is the eigenvalue equation. Since the \mathcal{R}_l 's form a semi-group

$$\bar{\pi}^{(l)} \bar{\pi}^{(l')} = \bar{\pi}^{(ll')} \quad (13.29)$$

and

$$\lambda_l^{(\sigma)} \lambda_{l'}^{(\sigma)} = \lambda_{ll'}^{(\sigma)} \quad (13.30)$$

By solving (13.30) one can show

$$\lambda_l^{(\sigma)} = l^{(Y_\sigma)} \quad (13.31)$$

where Y_σ is the critical exponent to be determined.

How $\delta \vec{\mathbf{k}}$ behaves under the linearized transformation $\bar{\pi}$?

Let us expand $\delta \vec{\mathbf{k}}$ in terms of $\vec{\mathbf{l}}^{(\sigma)}$ (that is a complete orthonormal base)

$$\delta \vec{\mathbf{k}} = \sum_{\sigma} a^{(\sigma)} \vec{\mathbf{l}}^{(\sigma)} \quad (13.32)$$

where

$$a^{(\sigma)} = \vec{\mathbf{l}}^{(\sigma)} \cdot \delta \vec{\mathbf{k}} \quad (13.33)$$

Remark. Ortonormality is not always true since in general $\bar{\pi}$ is not symmetric!

$$\delta \vec{\mathbf{k}}' = \bar{\pi} \delta \vec{\mathbf{k}} = \sum_{\sigma} a^{(\sigma)} \bar{\pi}(\vec{\mathbf{l}}^{(\sigma)}) = \sum_{\sigma} a^{(\sigma)} \lambda^{(\sigma)} \vec{\mathbf{l}}^{(\sigma)} = \sum_{\sigma} a^{(\sigma)'} \vec{\mathbf{l}}^{(\sigma)} \quad (13.34)$$

where $a^{(\sigma)'}$ is the projection of $\delta \vec{\mathbf{k}}'$ on $\vec{\mathbf{l}}^{(\sigma)}$.

Same components of $\delta \vec{\mathbf{k}}$ grow under the action of $\bar{\pi}$ while same others shrink. If we order the eigenvalues in descending order

$$|\vec{\lambda}_1| \geq |\vec{\lambda}_2| \geq |\vec{\lambda}_3| \geq \dots |\vec{\lambda}_\sigma| \quad (13.35)$$

three cases can occur

1. Case $|\lambda^{(\sigma)}| > 1$ (i.e. $y^\sigma > 0$): implies that $a^{(\sigma)}$ grows under $\bar{\pi}$. There are relevant eigenvalues/eigenvectors.
2. Case $|\lambda^{(\sigma)}| < 1$ (i.e. $y^\sigma < 0$): implies that $a^{(\sigma)}$ decreases under $\bar{\pi}$. There are irrelevant eigenvalues/eigenvectors.
3. Case $|\lambda^{(\sigma)}| = 1$ (i.e. $y^\sigma = 0$): implies that $a^{(\sigma)}$ remains constant under $\bar{\pi}$. There are marginal eigenvalues/eigenvectors.

Starting from a point close to a critical fixed point $\vec{\mathbf{k}}^*$ (but not on the critical manifold), the trajectory will abandau $[k^*]$ along the relevant directions whereas it will approach $[k^*]$ along the irrelevant directions.

- *Irrelevant eigenvectors* form the local basis of the basin of attraction of $[k^*]$.
- *Relevant eigenvectors* codimension C of the basin of attraction.

Remark. The eigenvalues and the corresponding eigenvectors depend on the chosen fixed point $[k^*]$.

13.2 RG and scaling

Let

$$\begin{cases} k_1 \rightarrow k_1(T) = T \\ k_2 \rightarrow k_2(H) = H \end{cases} \quad (13.36)$$

for simplicity. Suppose to perform a RG transformation \mathcal{R}_l such that

$$\begin{cases} T' = \mathcal{R}_l^T(T, H) \\ H' = \mathcal{R}_l^H(T, H) \end{cases} \quad (13.37)$$

The critical fixed point is defined as

$$\begin{cases} T^* = \mathcal{R}_l^T(T^*, H^*) \\ H^* = \mathcal{R}_l^H(T^*, H^*) \end{cases} \quad (13.38)$$

with $\xi(T^*, H^*) = \infty$.

Remark. Remember that $\vec{\mathbf{k}}^* \equiv (T^*, H^*)$.

For standard magnetic systems $H^* = 0$. By linearising around the fixed point $\delta\vec{\mathbf{k}} = (t, h)$ where

$$\begin{cases} t = \frac{(T-T^*)}{T^*} \\ h = \frac{(H-H^*)}{H^*} \end{cases} \quad (13.39)$$

we obtain

$$\begin{pmatrix} t' \\ h' \end{pmatrix} = \bar{\pi} \begin{pmatrix} t \\ h \end{pmatrix} \quad (13.40)$$

with

$$\bar{\pi} = \begin{pmatrix} \frac{\partial \mathcal{R}_l^T}{\partial T} & \frac{\partial \mathcal{R}_l^T}{\partial H} \\ \frac{\partial \mathcal{R}_l^H}{\partial T} & \frac{\partial \mathcal{R}_l^H}{\partial H} \end{pmatrix}_{T^*, H^*} \quad (13.41)$$

In general the eigenvectors $\vec{\mathbf{l}}^{(\sigma)}$ are linear combinations of t and h . When $\bar{\pi}$ can be diagonalized, t and h are not mixed. Suppose this is the case and let

$$\lambda_l^{(t)} = l^{Y_t}, \quad \lambda_l^{(h)} = l^{Y_h} \quad (13.42)$$

A linear transformation is

$$\begin{pmatrix} t' \\ h' \end{pmatrix} = \begin{pmatrix} \lambda_l^{(t)} & 0 \\ 0 & \lambda_l^{(h)} \end{pmatrix} \begin{pmatrix} t \\ h \end{pmatrix} \quad (13.43)$$

After n iterations, we have

$$\begin{cases} t^{(n)} = (l^{Y_t})^n t \\ h^{(n)} = (l^{Y_h})^n h \end{cases} \quad (13.44)$$

On the other hand,

$$\xi' \equiv \xi(t', h') = \frac{\xi(t, h)}{l} \quad (13.45)$$

and, hence, after n iterations

$$\xi(t, h) = l^n \xi(l^{nY_t} t, l^{nY_h} h) \quad (13.46)$$

Idea (lesson): we are very close to the critical point (infinite) and we want to go a little bit away in order to not to be anymore infinite. In such a way after n iterations we obtain the previous result. Let $h = 0$ ($H = H^*$), hence

$$\xi(t, 0) = l^n \xi(l^{nY_t} t, 0) \quad (13.47)$$

Since l is arbitrary, we can choose it such that

$$tl^{nY_t} = b \gg 1, \quad b \in \mathbb{R}^+ \quad (13.48)$$

In such a way we go away from the critical point!

Remark. l is not an integer any more.

$$\Rightarrow l^n = \left(\frac{b}{t}\right)^{1/Y_t} \quad (13.49)$$

so, for $t \rightarrow 0$

$$\xi(t) = \left(\frac{t}{b}\right)^{-1/Y_t} \xi(b) \quad (13.50)$$

On the other hand, $\xi \sim t^{-\nu}$, $t \rightarrow 0$

$$\Rightarrow \nu = \frac{1}{Y_t} \quad (13.51)$$

where

$$Y_t = \frac{1}{l} \ln \lambda_l^t \quad (13.52)$$

The equation (13.52) is an important result since it gives a recipe, based on \mathcal{R}_l , to compute Y_t explicitly!

Similarly,

$$\begin{aligned} f_s(t, h) &= l^{-D} f_s(t', h') = l^{-nD} f_s(t^{(n)}, h^{(n)}) \\ &= l^{-nD} f_s(l^{nY_t} t, l^{nY_h} h) \end{aligned} \quad (13.53)$$

Hence, we get the free energy of the original system, by using the renormalization group!

Let l such that $l^{nY_t} t = b \gg 1$, hence

$$l^n = \left(\frac{b}{t}\right)^{1/Y_t} \quad (13.54)$$

$$f_s(t, h) = t^{D/Y_t} b^{-D/Y_t} f_s\left(b, \frac{b^{Y_h/Y_t} h}{t^{Y_h/Y_t}}\right) \quad (13.55)$$

that is of the form

$$f_s(t, h) = \bar{b} t^{2-\alpha} f_s\left(b, \frac{\bar{b} h}{t^\Delta}\right) \quad (13.56)$$

with

$$\begin{cases} 2 - \alpha = D\nu = \frac{D}{Y_t} \\ \Delta = \frac{Y_h}{Y_t} \end{cases} \quad (13.57)$$

where Y_h and Y_t can be computed as

$$Y_h = \frac{1}{l} \log \lambda_l^{(h)} \quad (13.58)$$

Hence, we have all we need for the computation!

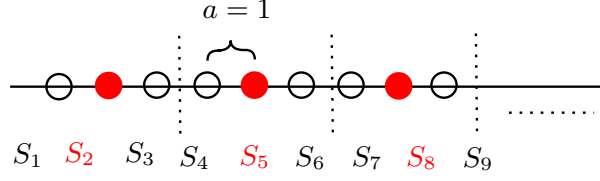


Figure 13.1: Description.

13.3 Real space renormalization group on 1D Ising model ($H = 0$)

13.3.1 Decimation procedure for $D = 1$

Decimation means summing up over all spins. $D = 1$ the procedure is clearly exact. Idea: pass from a N - spins system to one with $\frac{N}{b}$ spins by summing the remaining $N - \frac{N}{b}$ spins.

Case $b=3$ (see Figure 13.1).

Sum over the spins with the empty circle at the border of each clock, keeping the spins full circle untouched. We obtain Figure 13.2.

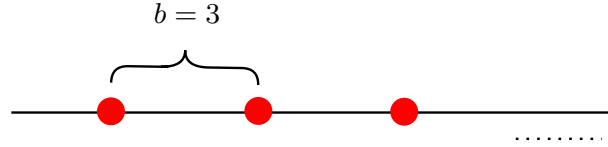


Figure 13.2: Description.

Let us see how it works for the two blocks $[S_1, S_2, S_3]$ and $[S_4, S_5, S_6]$. Let us call

$$S_2 \equiv S'_1, \quad S_5 = S'_2 \quad \text{fixed} \quad (13.59)$$

$$\sum_{S_3=\pm 1} \sum_{S_4=\pm 1} \exp[kS'_1 S_3 + kS_3 S_4 + kS_4 S'_2] \quad (13.60)$$

Since

$$e^{kS_3 S_4} = \cosh(k)(1 + xS_3 S_4) \quad (13.61)$$

with

$$x \equiv \tanh k \quad (13.62)$$

we have

$$\sum_{S_3, S_4} (\cosh k)^3 (1 + xS'_1 S_3)(1 + xS_3 S_4)(1 + xS_4 S'_2) \quad (13.63)$$

Performing the expansion and summing over S_3, S_4 it is easy to show that (to do)

$$Z'_{N'}(k') = \text{Tr}_{\{S'_I\}} \left[2^{2N'} (\cosh k)^{3N'} (1 + x^3 S'_I S'_{I+1}) \right] \quad (13.64)$$

This must have the same form of $Z_N(k)$. Hence, we should rewrite equation (13.64) as

$$Z'_{N'}(k') = \text{Tr}_{\{S'_I\}} \exp[-\beta \mathcal{H}'(k')] \quad (13.65)$$

with

$$-\beta \mathcal{H}' = N' g(k, k') + k' \sum_I S'_I S'_{I+1} \quad (13.66)$$

We note that

$$\begin{aligned}
 2^2(\cosh k)^3(1 + x^3 S'_I S'_{I+1}) &= 2^2 \frac{\cosh k'}{\cosh k'} (\cosh k)^3 (1 + x^3 S'_I S'_{I+1}) \\
 &= 2^2 \frac{(\cosh k)^3}{\cosh k'} (\cosh k') (1 + x' S'_I S'_{I+1}) \\
 &= 2^2 \frac{(\cosh k)^3}{\cosh k'} \exp(k' S'_I S'_{I+1}) \\
 &= \exp \left[2 \ln 2 + \ln \left[\frac{(\cosh k)^3}{\cosh k'} \right] + k' S'_I S'_{I+1} \right]
 \end{aligned} \tag{13.67}$$

It is ok with

$$\begin{cases} g(k, k') = 2 \ln 2 + \ln \left[\frac{(\cosh k)^3}{\cosh k'} \right] \\ x' = x^3 \iff k' = \tanh^{-1} [(\tanh k)^3] \Rightarrow k' = R_{b=3}(k) \\ N' = \frac{N}{b} \end{cases} \tag{13.68}$$

For $x' = x^3$, we have two fixed points

$$\begin{cases} x^* = 0 \iff k \rightarrow 0 \iff T \rightarrow \infty \\ x^* = 1^- \iff k \rightarrow \infty \iff T \rightarrow 0 \end{cases} \tag{13.69}$$

For $\forall x_0 < 1$, we have $R^{(n)} \xrightarrow{n \rightarrow \infty} 0^+$, $x = 1$ is an unstable fixed point, as shown in Figure 13.3. We have

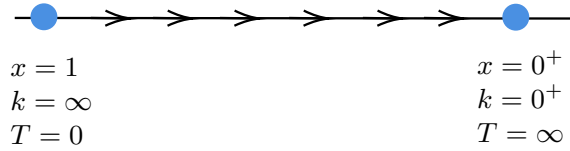


Figure 13.3: Description.

$$\xi(x') = \frac{\xi(x)}{b}, \quad \text{with } x' = x^b \tag{13.70}$$

where b is arbitrary. Let us choose $b = c / \ln x$:

$$\xi(x^b) = \xi(e^{b \ln x}) = \xi(e^c) = \frac{\xi(x)}{b} = \left(\frac{c}{\ln x} \right)^{-1} \xi(x) \tag{13.71}$$

Finally,

$$\xi(e^c) = \frac{\ln x}{c} \xi(x) \Rightarrow \xi(x) = \frac{c \xi(e^c)}{\ln x} = \frac{\text{const}}{\ln x} \tag{13.72}$$

$$\xi(k) = \frac{\text{const}}{\ln(\tanh k)} \tag{13.73}$$

equal to the exact model in $D = 1$. $k \rightarrow \infty$ ($x \rightarrow 1$), we have

$$\xi \sim e^{\text{const}/T} \tag{13.74}$$

finite $\forall k \neq \infty$.

13.3.2 Decimation procedure for $D > 1$ (proliferation of interactions)

Doing on a square lattice, block transformation (length b). There are problems with the spins at the boundaries. In order to get $Z'_{N'}(k') = Z_N(k)$, at least an additional term in the Hamiltonian must be introduced

$$\mathcal{H} \rightarrow \mathcal{H}' = \mathcal{H}'(k', k'_2) \quad (13.75)$$

This unfortunately occurs at each iteration! There is an uncontrolled proliferation and approximations are necessary.

Example 35: Decimation of Ising on square lattice

x : spin to sum over

$$\begin{cases} k' = \frac{1}{4} \ln \cosh 4k \\ L' = \frac{1}{8} \ln \cosh 4k \\ Q' = \frac{1}{8} \ln \cosh 4k - \frac{1}{2} \ln \cosh 2k \end{cases} \quad (13.76)$$

(4 spins). The approximations are:

1. Neglect Q' term.
2. Omit explicit dependence on L' . Hence, assuming $k' + L' \rightarrow k'$. 1 recursion

$$k' = \frac{3}{8} \ln \cosh 4k \quad (13.77)$$

$$\begin{cases} k^{(n)} \xrightarrow{n \rightarrow \infty} \infty & k_0 > k_c \\ k^{(n)} \xrightarrow{n \rightarrow \infty} 0 & k_0 < k_c \end{cases} \quad (13.78)$$

where $\infty, 0$ are stable fixed point.

$$\delta k' = \lambda_t \delta k = l^{Y_t} \delta k \quad (13.79)$$

where

$$\lambda_t = \left. \frac{dk'}{dk} \right|_{k=k_c} \quad (13.80)$$

For $l = \sqrt{2}$,

$$\begin{aligned} Y_t &= \frac{\ln \lambda_t}{\ln l} = \frac{1}{\ln \sqrt{2}} \ln \left(\frac{dk'}{dk} \right)_{k=k_c} \\ &= \frac{1}{\ln \sqrt{2}} \ln \left(\frac{d}{dk} \left(\frac{3}{8} \ln (\cosh 4k) \right) \right) = 1.070 \end{aligned} \quad (13.81)$$

so, this is actual a relevant eigenvalue. We have also the critical exponents

$$\nu = \frac{1}{Y_t} = 0.9345, \quad \alpha = 2 - \frac{d}{Y_t} = 0.1313 \quad (13.82)$$

Chapter 14

Spontaneous symmetry breaking

14.1 Spontaneous symmetry breaking

When we talk about a broken symmetry, we oftene refer to a situation as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \quad (14.1)$$

where \mathcal{H}_0 is invariant under the group \mathcal{G} and \mathcal{H}_1 is invariant under a subgroup $\mathcal{G}' \subset \mathcal{G}$.

Example 36: Ising with magnetic field

$$\mathcal{H} = J \sum_{\langle ij \rangle} S_i S_j + \sum_i H_i S_i \quad (14.2)$$

The second term, \mathcal{H}_1 , breaks the \mathbb{Z}^2 symmetry satisfied by the 1st alone.

Example 37

In quantum mechanics: hydrogen atom in presence of an electric field $\vec{\mathbf{E}}$ (Stark effect) or a magnetic one, $\vec{\mathbf{B}}$, (Zeeman effect). If \mathcal{H}_1 is small, the original symmetry is weakly violated and perturbative approaches are often used.

In all the above examples, one says that the symmetry is broken explicitly.

Definition 12: Spontaneous symmetry breaking

The Hamiltonian maintains the original symmetry but the variables used to describe the system become asymmetric.

At this point it is convenient to distinguish between

- Discrete symmetries: examples are \mathbb{Z}^2 , \mathbb{Z}_q .
- Continuous symmetries: examples are xy , $O(n)$.

Let us consider first the discrete ones by focusing on \mathbb{Z}^2 (Ising).

If $H = 0$, \mathcal{H}_{Ising} is invariant with respect to the change $S_i \rightarrow -S_i$, hence the discrete group is

$$\mathcal{G} = \mathbb{Z}^2 \quad (14.3)$$

A Ginzburg-Landau theory of the Ising is given by

$$-\beta \mathcal{H}(\Phi) = \int d^D \vec{x} \left[\frac{1}{2} (\nabla \Phi)^2 + \frac{r_0}{2} \Phi^2 + \frac{u_0}{4} \Phi^4 - h \Phi \right] \quad (14.4)$$

and

$$Z(r_0, u_0, h) = \int D\Phi e^{-\beta \mathcal{H}(\Phi)} \quad (14.5)$$

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The symmetry is $\Phi \rightarrow -\Phi$ if $h = 0$. Consider the saddle point equation of state

$$-\nabla^2\Phi + r_0\Phi + u_0\Phi^3 = h \quad (14.6)$$

If h does not depend on \vec{x} , uniform solution ($\nabla\Phi = 0$).

The saddle point is equivalent to find the uniform value Φ_0 that is the extrema of the potential

$$V(\Phi) = \frac{1}{2}r_0\Phi^2 + \frac{u_0}{4}\Phi^4 - h\Phi \quad (14.7)$$

For $h = 0$, $V' = (r_0 + u_0\Phi^2)\Phi = 0$. Remembering that $r_0 \propto (T - T_c)$, we have two cases

1. Case $T > T_c$ ($r_0 > 0$): there is only one solution $\Phi_0 = 0$.

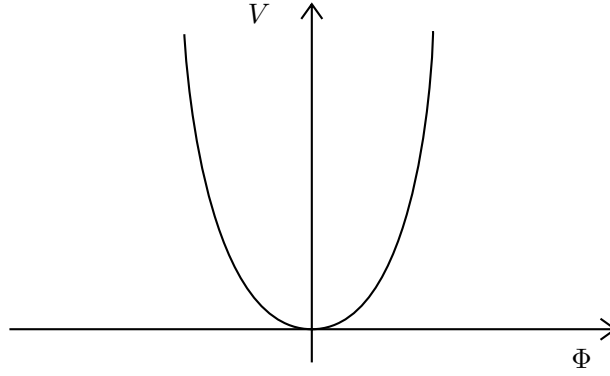


Figure 14.1: Description.

2. Case $T < T_c$ ($r_0 < 0$): there are two solutions $\Phi_0 = \pm\sqrt{-\frac{r_0}{u_0}}$.

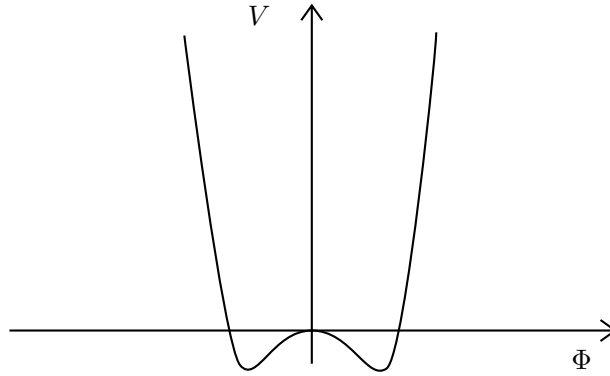


Figure 14.2: Description.

Remark. The two solution $\pm\Phi_0$ are related by the transformation $\in \mathbb{Z}^2$: $\Phi \rightarrow -\Phi$.

Remark. For $T < T_c$ the two states (phases) $\pm\Phi_0$ have a lower symmetry than the state $\Phi_0 = 0$.

Remark. If the thermal fluctuations $\delta\Phi$ are sufficiently strong to allow passages between the two states $\pm\Phi_0$ at $T < T_c$, we have $\langle\Phi\rangle = 0$ (preserves states).

However, for $T < T_c$ and $N \rightarrow +\infty$, transition between the two states will be less and less probable and the system will be trapped into one of the two states ($\pm\Phi_0$).

The system choose spontaneously one of the two less symmetric state. Therefore, its physics is not any more described by Φ but the fluctuations $\delta\Phi$ around the chosen minimum Φ_0 . There is spontaneous symmetry breaking.

The variable Φ is not any more symmetric and one has to look at $\Phi \rightarrow \Phi_0 + \delta\Phi$, where $\delta\Phi$ is a new variable!

14.2 Spontaneous breaking of continuous symmetries and the anset of Goldstone particles

Let us start with a simple model in which the order parameter is a scalar complex variable

$$\Phi = \frac{\Phi_1 + i\Phi_2}{\sqrt{2}} \quad (14.8)$$

and with an \mathcal{H} that is invariant with respect to a global continuous transformation.

The simplest model in statistical mechanics is the XY model with $O(2)$ symmetry or a GL model for a superfluid or superconductor (no magnetic field)

$$\mathcal{H}_{eff} = \int d^D \vec{x} \left[\nabla \Phi \cdot \nabla \Phi^* + \frac{r_0}{2} \Phi^* \Phi + \frac{u_0}{4} (\Phi^* \Phi)^2 \right] \quad (14.9)$$

where

$$\Phi(\vec{x}) = \frac{1}{\sqrt{2}} [\Phi_1(\vec{x}) + i\Phi_2(\vec{x})] \quad (14.10)$$

or

$$\Phi(\vec{x}) = \psi(\vec{x}) e^{i\alpha(\vec{x})} \quad (14.11)$$

- Superfluid: Φ macroscopic wave function of the Bose condensate (density of superfluid $n = |\Phi|^2$).
- Superconductor: Φ single particle wave function describing the position of the centre of mass of the Cooper pair.

14.2.1 Quantum relativistic case (field theory)

The analog of \mathcal{H} is the action

$$S(\Phi) = \int d^D \vec{x} \mathcal{L}(\Phi) \quad (14.12)$$

where

$$\mathcal{L}(\Phi) = -\frac{1}{2} \partial_\mu \Phi \partial^\mu \Phi^* - \frac{r_0}{2} \Phi \Phi^* - \frac{u_0}{4} (\Phi \Phi^*)^2 \quad (14.13)$$

It describes a scalar complex (i.e. charged) muonic field with mass m . Note that in this case $r_0 > 0$ and $m \equiv \sqrt{r_0}$. The term $(\Phi \Phi^*)^2$ means self-interaction with strenght $\lambda \equiv u_0$.

In all cases, the original symmetry is $U(1)$, i.e. both \mathcal{H} and \mathcal{L} are invariant with respect to the transformation

$$\Phi \rightarrow e^{i\theta} \Phi, \quad \Phi^* \rightarrow e^{-i\theta} \Phi^* \quad (14.14)$$

Remark. The phase θ does not depend on \vec{x} (global symmetry).

In components (14.14) become

$$\begin{cases} \Phi_1 \rightarrow \Phi_1 \cos \theta - \Phi_2 \sin \theta \\ \Phi_2 \rightarrow \Phi_2 \cos \theta + \Phi_1 \sin \theta \end{cases} \quad (14.15)$$

$$(\Phi'_1, \Phi'_2) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix} \quad (14.16)$$

Let us focus first on the statistical mechanics model and to the most interesting case of $r_0 < 0$.

In components \mathcal{H} becomes

$$\mathcal{H} = \int d^D \vec{x} \left[(\nabla \Phi_1)^2 + (\nabla \Phi_2)^2 \right] + \int d^D \vec{x} V(\Phi_1, \Phi_2) \quad (14.17)$$

where

$$V(\Phi_1, \Phi_2) = \frac{r_0}{2} (\Phi_1^2 + \Phi_2^2) + \frac{u_0}{4} (\Phi_1^2 + \Phi_2^2)^2 \quad (14.18)$$

It is the mexican hat potential, shown in Figure 14.3

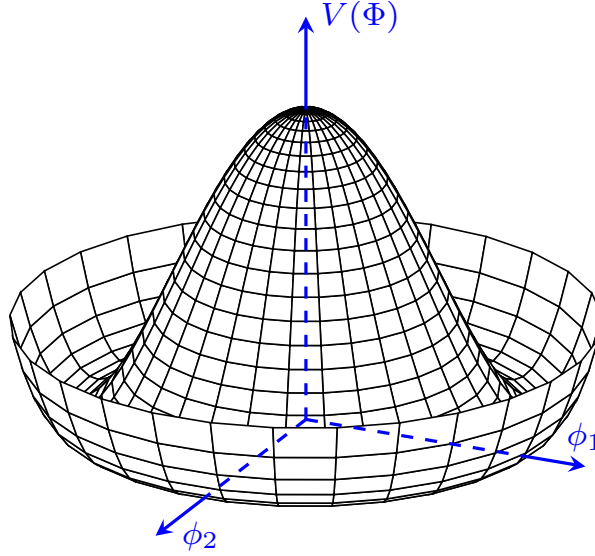


Figure 14.3: Case $r_0 < 0$.

For $r_0 < 0$, there is a uniform solution ($\nabla \Phi_1 = \nabla \Phi_2 = 0$). Let $S = \sqrt{\Phi_1^2 + \Phi_2^2}$,

$$V(S) = \frac{r_0}{2} S^2 + \frac{u_0}{4} S^4 \quad (14.19)$$

$$\frac{dV(S)}{dS} = r_0 S + u_0 S^3 = 0 \quad (14.20)$$

There is 1 maximum at $S = 0$ and minima for $S^2 = -\frac{r_0}{u_0}$

For $r_0 < 0$, \mathcal{H} displays minima when

$$\Phi_1^2 + \Phi_2^2 \equiv v^2 = -\frac{r_0}{u_0} \quad (14.21)$$

On the $2D$ plane (Φ_1, Φ_2) the minima lie on the circle of radius

$$v = \sqrt{-\frac{r_0}{u_0}} \quad (14.22)$$

The spontaneous symmetry breaking occurs when the system "chooses" one of the infinite available minima.

In our example, suppose that the chosen minimum is

$$\Phi_1 = v = \sqrt{-\frac{r_0}{u_0}}, \quad \Phi_2 = 0 \quad (14.23)$$

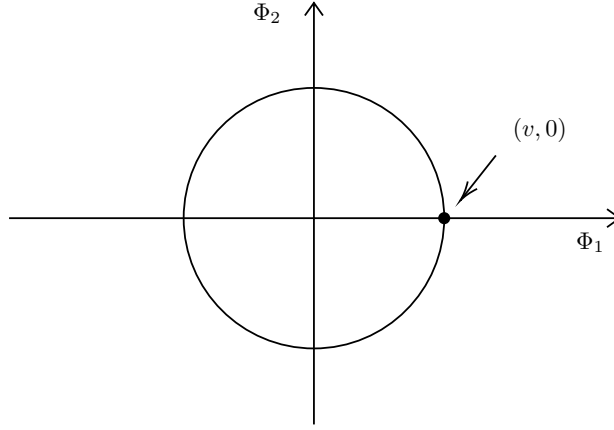


Figure 14.4: Description.

14.3 Interpretation in relativistic quantum mechanics

1. $r_0 < 0$ corresponds to an imaginary mass. This is because to move away from $\Phi = 0$, the system experiences a negative resistance in both directions, being $\Phi = 0$ a relative local minimum.
2. The minimum has the lowest energy and therefore it must correspond to the empty state. In this case, however, there is an infinite number of empty states!

Summarizing: the starting Hamiltonian (or Lagrangian) is invariant with respect to $U(1)$ but the one that describes the fluctuation dynamics around one of the chosen minimum state is not invariant with respect to $U(1)$.

Let us now write the Lagrangian with respect to the fluctuations of Φ_1 and Φ_2 around the chosen state

$$\begin{cases} \Phi_1 = v + \delta\Phi_1 \\ \Phi_2 = 0 + \delta\Phi_2 \end{cases} \quad (14.24)$$

or

$$\Phi = v + (\delta\Phi_1 + i\delta\Phi_2) \quad (14.25)$$

Note that, since

$$\begin{cases} \delta\Phi_1 = \Phi_1 - v \\ \delta\Phi_2 = \Phi_2 \end{cases} \quad (14.26)$$

we have

$$\langle \delta\Phi_1 \rangle_{\Phi_0} = \langle \delta\Phi_2 \rangle_{\Phi_0} = 0 \quad (14.27)$$

As expected the expectation of the empty state is back to be zero.

For the quantum relativistic Lagrangian, let us write

$$r_0 \rightarrow m^2, \quad u_0 \rightarrow \lambda, \quad v^2 = -\frac{m^2}{\lambda} \quad (14.28)$$

$$\begin{aligned}
\mathcal{L} &= -\frac{1}{2}\partial_\mu(\delta\Phi_1 + i\delta\Phi_2)\partial_\mu(\delta\Phi_1 - i\delta\Phi_2) \\
&\quad -\frac{m^2}{2}(v + \delta\Phi_1 + i\delta\Phi_2)(v + \delta\Phi_1 - i\delta\Phi_2) \\
&\quad -\frac{\lambda}{4}[(v + \delta\Phi_1 + i\delta\Phi_2)(v + \delta\Phi_1 - i\delta\Phi_2)]^2 \\
&= -\frac{1}{2}(\partial_\mu\delta\Phi_1\partial^\mu\delta\Phi_1) - \frac{1}{2}(\partial_\mu\delta\Phi_2\partial^\mu\delta\Phi_2) \\
&\quad -\frac{m^2}{2}(v^2 + 2v\delta\Phi_1 + \delta\Phi_1^2 + \delta\Phi_2^2) \\
&\quad -\frac{\lambda}{4}(v^2 + 2v\delta\Phi_1 + \delta\Phi_1^2 + \delta\Phi_2^2)^2
\end{aligned} \tag{14.29}$$

Since $m^2 = -v^2\lambda$,

$$\begin{aligned}
\mathcal{L} &= -\frac{1}{2}(\partial_\mu\delta\Phi_1\partial^\mu\delta\Phi_1) - \frac{1}{2}(\partial_\mu\delta\Phi_2\partial^\mu\delta\Phi_2) \\
&\quad + \frac{\lambda v^2}{2}(v^2 + 2v\delta\Phi_1 + \delta\Phi_1^2 + \delta\Phi_2^2) \\
&\quad - \frac{\lambda}{4}(v^4 + 4v^2\delta\Phi_1^2 + (\delta\Phi_1^2 + \delta\Phi_2^2)^2 + 4v^3\delta\Phi_1 + 2v^2(\delta\Phi_1^2 + \delta\Phi_2^2) + 4v\delta\Phi_1(\delta\Phi_1^2 + \delta\Phi_2^2))
\end{aligned} \tag{14.30}$$

Neglecting the constant terms in v

$$\begin{aligned}
\mathcal{L}(\delta\Phi_1, \delta\Phi_2) &= -\frac{1}{2}(\partial_\mu\delta\Phi_1)^2 - \frac{1}{2}(\partial_\mu\delta\Phi_2)^2 \\
&\quad -\lambda v^2\delta\Phi_1^2 - v\lambda\delta\Phi_1((\delta\Phi_1)^2 + (\delta\Phi_2)^2) \\
&\quad -\frac{\lambda}{4}((\delta\Phi_1)^2 + (\delta\Phi_2)^2)^2
\end{aligned} \tag{14.31}$$

Remark. The term $-\lambda v^2\delta\Phi_1^2$ indicates that the field $\delta\Phi_1$ (related to the transversal fluctuations) has a null empty state ($\langle\delta\Phi_1\rangle = 0$) and a mass M such that:

$$M^2 = 2\lambda v^2 = -2r_0 \tag{14.32}$$

Therefore, it represents a real, massive, mesonic scalar field that is physically acceptable.

However, \mathcal{L} is not any more invariant under the transformation $\delta\Phi_1 \rightarrow -\delta\Phi_1$.

Remark. The field $\delta\Phi_2$ has no mass! It describes the fluctuations along the circle where the potential V is in its minimum which implies no dynamical inertia, that implies no mass!

So, starting with one complex scalar field $\Phi(\vec{x})$ having mass m , when $m^2 < 0$ one gets a real scalar field $\delta\Phi_1$ with mass $M = \sqrt{-2m^2}$ and a second scalar field $\delta\Phi_2$ that is massless. This is called the *Goldstone boson*.

Theorem 5

If a continuous symmetry is spontaneously broken and there are no long range interactions, exists an elementary excitation with zero momentum or particle of zero mass called Goldstone boson.

More generally, let \mathcal{P} be a subgroup of \mathcal{G} . If \mathcal{G} has N independent generators and \mathcal{P} has M independent generators, if \mathcal{P} is the new (lower) symmetry, therefore $N - M$ Goldstone bosons exist.

In the previous case $\mathcal{G} = U(1) \Rightarrow N = 1$ whereas $M = 0$ (we have chosen a specific minimum).

Example 38

XY model in statistical mechanics:

- $\delta\Phi_1$: fluctuation of the modulus of m .
- $\delta\Phi_2$: fluctuations of the spin directions \Rightarrow spin waves.

Remark. In particle physics the presence of Goldstone bosons brings a serious problem in field theory since the corresponding particles are not observed!

Higgs-Englert-Brout (1964)

Higgs mechanism gives back the mass to the Goldstone particles. The basic idea is that the Goldstone theorem that works for a continuous global symmetry it can fail for local gauge theories!

14.4 Spontaneous symmetry breaking in Gauge symmetries

Statistical mechanics, G1 model for superconductors in presence of a magnetic field (*Meissner effect*, i.e. the magnetic induction $\vec{B} = 0$ inside the superconductor).

$$\mathcal{H}(\Phi) = \int d^D \vec{x} \left[\frac{1}{2} B^2 + \left| \left(\vec{\nabla} - 2i\vec{A} \right) \Phi \right|^2 \right] + \frac{r_0}{2} \Phi^* \Phi + \frac{u_0}{4} (\Phi^* \Phi)^2 - \vec{B} \cdot \vec{H} \quad (14.33)$$

where $\frac{B^2}{2}$ is the energy of the magnetic field \vec{B} and $\vec{\nabla} \rightarrow [\vec{\nabla} + iq\vec{A}]$ is the minimal coupling. Consider \vec{H} the external magnetic field

$$\vec{B} = \vec{H} + \vec{M} \quad (14.34)$$

is the induction field.

Normal conductor corresponding to $\Phi_0 = 0$, that implies $\vec{B} = \vec{H}$. For a superconductor we have $\Phi \neq 0$, a spontaneous symmetry breaking.

14.5 Fiedl theory analog

Scalar charged mesonic fields selfinteracting and in presence of an electromagnetic field with potential quadrivector $A_\mu(\vec{x})$.

$$\partial_\mu \rightarrow D_\mu = [\partial_\mu + iqA_\mu] \quad (14.35)$$

$$\Phi = \frac{1}{\sqrt{2}}(\Phi_1 + i\Phi_2), \quad \Phi^* = \frac{1}{\sqrt{2}}(\Phi_1 - i\Phi_2) \quad (14.36)$$

Remark. Because of the presence of $A_\mu(\vec{x})$, we should consider a theory that satisfies symmetry $U(1)$ locally! The transformations are

$$\begin{cases} \Phi(\vec{x}) \rightarrow e^{i\alpha(\vec{x})} \Phi(\vec{x}) \\ \Phi^*(\vec{x}) \rightarrow e^{-i\alpha(\vec{x})} \Phi^*(\vec{x}) \end{cases} \quad (14.37)$$

hence, exists $A_\mu(\vec{x})$ interacting with $\Phi(\vec{x})$.

The Lagrangian is

$$\mathcal{L} = -\frac{1}{4} F_{\mu\nu}(\vec{x}) F^{\mu\nu}(\vec{x}) + (D_\mu \Phi(\vec{x}))^* (D_\mu \Phi(\vec{x})) - V(\Phi, \Phi^*) \quad (14.38)$$

where

$$D_\mu \Phi = (\partial_\mu + iqA_\mu)\Phi \quad \text{Gauge-covariant derivative} \quad (14.39a)$$

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu \quad \text{field strength tensor} \quad (14.39b)$$

$$V(\Phi, \Phi^*) = \frac{m^2}{2} \Phi \Phi^* + \frac{\lambda}{4} (\Phi \Phi^*)^2 \quad (14.40)$$

- Case $m^2 > 0$: the minimum is in $\Phi = 0$.
- Case $m^2 < 0$: the minimum is in $\Phi = \sqrt{-\frac{m^2}{\lambda}} \equiv v$ (circle of radius $|\Phi| = v$).

Let us choose the state

$$\bar{\Phi}_1 = v, \quad \bar{\Phi}_2 = 0 \quad (14.41)$$

and consider

$$\Phi(x) = (v + \delta\Phi_1) + i\delta\Phi_2 \quad (14.42)$$

Inserting in the Lagrangian and keeping in mind $-m^2 = v^2\lambda$

$$\begin{aligned} \mathcal{L} = & -\frac{1}{4}F_{\mu\nu}F^{\mu\nu} + \frac{1}{2}(\partial_\mu\delta\Phi_1)^2 + \frac{1}{2}(\partial_\mu\delta\Phi_2)^2 \\ & -\lambda v^2\delta\Phi_1^2 + q^2v^2A_\mu A^\mu - qvA^\mu\partial_\mu\delta\Phi_2 + \text{higher order terms} \end{aligned} \quad (14.43)$$

1. Term $\lambda v^2\delta\Phi_1^2$: the field $\delta\Phi_1$ is massive with mass $m = v\sqrt{2}$ (Higgs boson).
2. Term $q^2v^2A_\mu A^\mu$: this terms means that the Gauge boson A_μ , the photon, has got a mass

$$M_A = 2qv \quad (14.44)$$

Remark. Since now A_μ is massive, it has three independent polarization states.

3. Term $qvA^\mu\partial_\mu\delta\Phi_2$: the field $\delta\Phi_2$ is not massive (no term $\propto \delta\Phi_2^2$) and is mixed with A_μ . Dynamically this means that a propagating photon can transform itself into a field $\delta\Phi_2$ (photon r Goldstone boson).

Since $\delta\Phi_2$ does not seem to be a physical field it should be eliminated by a Gauge transformation.

Indeed a gauge transformation is also characterized by the transformation

$$A_\mu(\vec{x}) \rightarrow A_\mu(\vec{x}) + \frac{1}{qv}\partial_\mu\delta\Phi_2(x) \quad (14.45)$$

Inserting (14.45) in the Lagrangian, we eliminate the mixed term $qvA^\mu\partial_\mu\delta\Phi_2$ and $\frac{1}{2}(\partial_\mu\delta\Phi_2)^2$.

$$\mathcal{L} = -\frac{1}{4}F_{\mu\nu}F^{\mu\nu} + \frac{1}{2}(\partial_\mu\delta\Phi_1)^2 - \lambda v^2\delta\Phi_1^2 + q^2v^2A_\mu A^\mu + \text{higher order terms} \quad (14.46)$$

Remark. Among the higher order terms there are

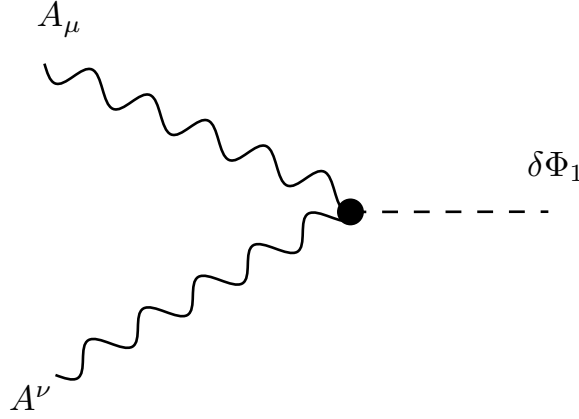
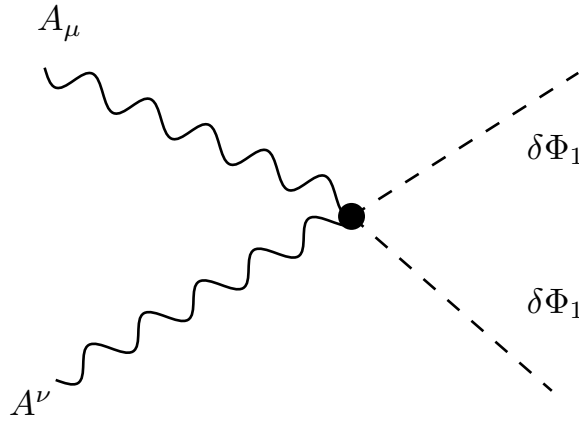
- $\propto \delta\Phi_1 A_\mu A^\mu$.
- $\propto \delta\Phi_1^2 A_\mu A^\mu$.

The new Lagrangian contains two fields: one is a massive photon with spin 1 and the second field $\delta\Phi_1$ is massive too, but has spin 0 (scalar).

The Goldstone boson has been "laten" by the Gauge boson that now is massive!

The mechanics trough which the gauge boson becomes massive is the so called *Higgs mechanism*.

In summary: (according to the degrees of freedom)

**Figure 14.5:** Description.**Figure 14.6:** Description.

- Global $U(1) \Rightarrow 2$ scalar fields with mass $1+1 \xrightarrow{\text{symmetry breaking}} 1$ scalar field massive and 1 scalar field not massive $1+1$.
- Local gauge $U(1) \Rightarrow 2$ massive scalar fields + 1 photon $(2+2)$ two polarizations $\xrightarrow{\text{symmetry breaking}} 1$ massive scalar field, 1 massive photon $1 + 3$ polarization.

Remark. The presence of the massive photon $m_A^2 = q^2 v^2$, $q = 2l$ in superconductivity, gives rise to the experimental drop

$$B(x) = B(0) \exp\left(-\frac{x}{l}\right) \quad (14.47)$$

inside the system.

- We cannot introduce by hand a massive photon i.e. a term like $\frac{1}{2}m_A^2 A_\mu A^\mu$ in the Lagrangian because we would violate explicitly the gauge symmetry!
- The Lagrangian is gauge invariant.
- Symmetry breaking occurs at the level of the vacuum state.
- A gauge symmetry that is explicitly broken is not renormalizable.

14.5.1 Non abelian gauge theories

Example 39

Electro-weak interactions theory (Glashow-Weinberg-Salam) (theory of leptons).

Lagrangian has $\underbrace{SU(2)}_{\text{weak interactions}} \times \underbrace{U(1)}_{\text{electromagnetian}}$

Example 40: Quantum chromodynamic (quarks+gluons)

In this case, one has a term that is $SU(3)$ invariant + the GWS lagrangian with symmetry $SU(2) \times U(1)$, implies

$$SU(3) \times SU(2) \times U(1) \quad (14.48)$$

Because of the groups $SU(2)$ and $SU(3)$ the symmetries above are not abelian. (For example in $SU(2)$ two matrices $U(\alpha)$ and $U(\beta)$ do not commute in general).

14.6 Extension of Higgs mechanism to non abelian theories

14.6.1 GWS model

Complex field $SU(2)$

$$\Phi = \frac{1}{\sqrt{2}} \begin{pmatrix} \Phi_1 + i\Phi_2 \\ \Phi_3 + i\Phi_4 \end{pmatrix} = \begin{pmatrix} \Phi_a(\vec{x}) \\ \Phi_b(\vec{x}) \end{pmatrix} \quad (14.49)$$

where Φ_a, Φ_b are complex fields.

Gauge transformation $SU(2) \times U(1)$:

$$\begin{pmatrix} \Phi_a(\vec{x}) \\ \Phi_b(\vec{x}) \end{pmatrix} \rightarrow e^{\frac{i}{2}\alpha_0(\vec{x})} e^{\frac{i}{2}\vec{\tau} \cdot \vec{\alpha}(\vec{x})} \begin{pmatrix} \Phi_a(\vec{x}) \\ \Phi_b(\vec{x}) \end{pmatrix} \quad (14.50)$$

where $\vec{\tau}$ are Pauli matrices, $\alpha_0, \alpha_1, \alpha_2, \alpha_3$ are four real functions (4 vectorial mesons).

$$\vec{\alpha}(\vec{x}) \rightarrow W_\mu^a(\vec{x}) = \left(W_\mu^{(1)}(\vec{x}), W_\mu^{(2)}(\vec{x}), W_\mu^{(3)}(\vec{x}) \right) \quad (14.51)$$

The scalar gauge field is

$$\alpha_0(\vec{x}) \rightarrow B_\mu(\vec{x}) \quad (14.52)$$

with B_μ is a linear combination of A_μ and $W_\mu^{(3)}$.

Lagrangian:

$$\mathcal{L} = (D_\mu \Phi)^\dagger (D^\mu \Phi) - \mu^2 \Phi^* \Phi - \lambda (\Phi^* \Phi)^2 - \frac{1}{4} b^{\mu\nu} b_{\mu\nu} - \frac{1}{4} f_a^{\mu\nu} f_{\mu\nu}^a \quad (14.53)$$

$$D_\mu \rightarrow \partial_\mu - \frac{1}{2} i g \tau^a W_\mu^a - \frac{i}{2} g' B_\mu \quad (14.54)$$

$$f_{\mu\nu}^a = \partial_\mu W_\nu^a - \partial_\nu W_\mu^a - g \varepsilon^{abc} W_\mu^b W_\nu^c \quad (14.55)$$

$$b_{\mu\nu} = \partial_\mu B_\nu - \partial_\nu B_\mu \quad (14.56)$$

$$W_\mu^a \rightarrow W_\mu^a - \varepsilon^{abc} \alpha_b(\vec{x}) W_\mu^c(\vec{x}) + \frac{1}{g} \partial_\mu \alpha^a(\vec{x}) \quad (14.57a)$$

$$B_\mu \rightarrow B_\mu + \frac{1}{g'} \frac{\partial \alpha_0}{\partial x_\mu} \quad (14.57b)$$

$$\nu \sim \Phi_1^2 + \Phi_2^2 + \Phi_3^2 + \Phi_4^2 = v^2 \quad (14.58)$$

Choosing the direction on the sphere in \mathbb{R}^4 , 3 symmetries are broken a 3 Goldstone bosons.

14.6.2 Higgs mechanism

Higgs scalar field

$$\delta\Phi = \begin{pmatrix} \Phi^+ \\ \Phi_0 \end{pmatrix} \quad (14.59)$$

such that

$$\langle 0 | \Phi | 0 \rangle = \begin{pmatrix} 0 \\ v \end{pmatrix} \quad (14.60)$$

$$\Rightarrow \mathcal{L}_{Higgs} = \frac{1}{2} (g\nu)^2 W_\mu^+ W^{-\mu} + \frac{1}{2} v^2 \left(g W_\mu^{(3)} - g' B_\mu \right)^2 \quad (14.61)$$

where

$$W_\mu^{(1)} = \frac{1}{\sqrt{2}} (W_\mu^+ + W_\mu^-) \quad (14.62a)$$

$$W_\mu^{(2)} = \frac{1}{\sqrt{2}} (W_\mu^+ - W_\mu^-) \quad (14.62b)$$

Mass of the W^+ particle and its antiparticle

$$M_W^2 = \frac{1}{2} (gv)^2 \quad (14.63)$$

The 2^{nd} term is a linear combination of W_μ^3 and B_μ which corresponds to Z^0 , the field for a third weak gauge boson.

To make Z_μ^0 and A_μ orthogonal we should consider

$$A_\mu = (\cos \theta_W) B_\mu + (\sin \theta_W) W_\mu^3 \quad (14.64a)$$

$$Z_\mu^0 = (-\sin \theta_W) B_\mu + (\cos \theta_W) W_\mu^3 \quad (14.64b)$$

where θ_W is the Weiberg angle:

$$\tan \theta_W = \frac{g'}{g} \quad (14.65)$$

$$M_{Z^0}^2 = \frac{1}{2} \left(\frac{vg}{\cos \theta_W} \right)^2 = \frac{Mw^2}{\cos^2 \theta_W} \quad (14.66)$$

Conclusions

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