

# Chapter 1

## Statistical mechanics and numerical simulation

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## 1.1 Brief History of simulation

Numerical simulation started in the fifties when computers were used for the first time for peaceful purposes. In particular, the computer MANIAC started in 1952<sup>1</sup> at Los Alamos. Simulation provides a complementary approach to theoretical methods<sup>2</sup>. Areas of physics where the perturbative approaches are efficient (dilute gases, vibrations in quasi-harmonic solids) do not require simulation methods. Conversely, liquid state physics, where few exact results are known and where the theoretical developments are not always under control, has been developed largely through simulation. The first Monte Carlo simulation of liquids was performed by Metropolis *et al.* in 1953<sup>3</sup>.

The first Molecular Dynamics was realized on the hard disk model by Alder and Wainwright in 1957[1]. The first Molecular Dynamics of a simple liquid (Argon) was performed by Rahman in 1964.

In these last two decades, the increasing power of computers associated with their decreasing costs allowed numerical simulations with personal computers. Even if supercomputers are necessary for extensive simulations, it becomes possible to perform simulations on low cost computers. In order to measure the power of computers, the unit of performance is the GFlops (or billion of floating point operations per second). Nowadays, a Personal computer PC (for instance, Intel Core i7) has a processor with four cores (floating point unit) and offers a power of 24 Gflops. Whereas the frequency of processors seems to have plateaued last few years, power of computers continues to increase because the number of cores within a processor grows. Nowadays, processors with 6 or 8 cores are available. In general, the power of a computer is not a linear function of cores for many programs. For scientific codes, it is possible to exploit this possibility by developing scientific programs incorporating libraries which perform parallel computing (OpenMP, MPI). The gnu compilers are free softwares allowing for parallel computing. For massive parallelism, MPI (message passing interface) is a library which

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<sup>1</sup>The computer MANIAC is the acronym of "mathematical and numerical integrator and computer". MANIAC I started March 15, 1952.

<sup>2</sup>Sometimes, theories are in their infancy and numerical simulation is the sole manner for studying models

<sup>3</sup>Metropolis, Nicholas Constantine (1915-1999) both mathematician and physicist of education was hired by J. Robert Oppenheimer at the Los Alamos National Laboratory in April 1943. He was one of scientists of the Manhattan Project and collaborated with Enrico Fermi and Edward Teller on the first nuclear reactors. After the war, Metropolis went back to Chicago as an assistant professor, and returned to Los Alamos in 1948 by creating the Theoretical Division. He built the MANIAC computer in 1952, then 5 years later MANIAC II. He returned from 1957 to 1965 to Chicago and founded the Computer Research division, and finally, returned to Los Alamos.

spreads the computing load over many cores.

Table 1.1 gives the characteristics and power of most powerful computers in the world

Ranking	Vendor /Cores.	(TFlops)	Pays
1	Cray XTS / 224162	1759 2331	Oak Ridge Nat. Lab. USA 2009
2	Dawning / 120640	1271 2984	NSCS (China)2010
3	Roadrunner /122400	1042 1375	Doe USA 2009
4	Cary XTS /98928	831 1028	NICST USA 2009
5	Blue GeneP 212992	825 1002	FZJ Germany 2009
...	...	...	...
18	SGI /23040	237 267	France 2010

Table 1.1: June 2009 Ranking of supercomputers

It is worth noting that the rapid evolution of the power of the computers. In 2009, only one computer exceeded the TFlops, while they are 4 this year. In the same period, the IDRIS computer went from 9 last year to 38 this year. Note that China owns the second most powerful computer in the world. The last remark concerns the operating system of the 500 fastest computers: Linux and associated distributions 484, Windows 5, others 11.

## 1.2 Ensemble averages

Knowledge of the partition function of a system allows one to obtain all thermodynamic quantities. First, we briefly review the main ensembles used in Statistical Mechanics. We assume that the thermodynamic limit leads to the same quantities, a property for systems where interaction between particles are not long ranged or systems without quenched disorder.

For finite size systems (which correspond to those studied in computer simulation), there are differences that we will analyze in the following.

### 1.2.1 Microcanonical ensemble

The system is characterized by the set of macroscopic variables: volume  $V$ , total energy  $E$  and the number of particles  $N$ . This ensemble is not appropriate for experimental studies, where one generally has

- a fixed number of particles, but a fixed pressure  $P$  and temperature  $T$ . This corresponds to a set of variables  $(N, P, T)$  and is the isothermal-isobaric ensemble,

- a fixed chemical potential  $\mu$ , volume  $V$  and temperature  $T$ , ensemble  $(\mu, V, T)$  or grand canonical ensemble,
- a fixed number of particles, a given volume  $V$  and temperature  $T$ , ensemble  $(N, V, T)$  or canonical ensemble.

There is a Monte Carlo method for the micro canonical ensemble, but it is rarely used, in particular for molecular systems. Conversely, the micro-canonical ensemble is the natural ensemble for the Molecular Dynamics of Hamiltonian systems where the total energy is conserved during the simulation.

The variables conjugated to the global quantities defining the ensemble fluctuate in time. For the micro-canonical ensemble, this corresponds to the pressure  $P$  conjugate to the volume  $V$ , to the temperature  $T$  conjugate to the energy  $E$  and to the chemical potential  $\mu$  conjugate to the total number of particles  $N$ .

### 1.2.2 Canonical ensemble

The system is characterized by the following set of variables: the volume  $V$ ; the temperature  $T$  and the total number of particles  $N$ . If we denote the Hamiltonian of the system  $\mathcal{H}$ , the partition function reads

$$Q(V, \beta, N) = \sum_{\alpha} \exp(-\beta\mathcal{H}(\alpha)) \quad (1.1)$$

where  $\beta = 1/k_B T$  ( $k_B$  is the Boltzmann constant). The sum runs over all configurations of the system. If this number is continuous, the sum is replaced with an integral.  $\alpha$  denotes the index of these configurations. The free energy  $F(V, \beta, N)$  of the system is equal to

$$\beta F(V, \beta, N) = -\ln(Q(V, \beta, N)). \quad (1.2)$$

One defines the probability of having a configuration  $\alpha$  as

$$P(V, \beta, N; \alpha) = \frac{\exp(-\beta\mathcal{H}(\alpha))}{Q(V, \beta, N)}. \quad (1.3)$$

One easily checks that the basic properties of a probability are satisfied, i.e.  $\sum_{\alpha} P(V, \beta, N; \alpha) = 1$  and  $P(V, \beta, N; \alpha) > 0$ .

The derivatives of the free energy are related to the moments of this probability distribution, which gives a microscopic interpretation of the macroscopic thermodynamic quantities. The mean energy and the specific heat are then given by

- Mean energy

$$U(V, \beta, N) = \frac{\partial(\beta F(V, \beta, N))}{\partial \beta} \quad (1.4)$$

$$= \sum_{\alpha} \mathcal{H}(\alpha) P(V, \beta, N; \alpha) \quad (1.5)$$

$$= \langle \mathcal{H}(\alpha) \rangle \quad (1.6)$$

- Specific heat

$$C_v(V, \beta, N) = -k_B \beta^2 \frac{\partial U(V, \beta, N)}{\partial \beta} \quad (1.7)$$

$$= k_B \beta^2 \left( \sum_{\alpha} \mathcal{H}^2(\alpha) P(V, \beta, N; \alpha) - \left( \sum_{\alpha} \mathcal{H}(\alpha) P(V, \beta, N; \alpha) \right)^2 \right) \quad (1.8)$$

$$= k_B \beta^2 (\langle \mathcal{H}(\alpha)^2 \rangle - \langle \mathcal{H}(\alpha) \rangle^2) \quad (1.9)$$

### 1.2.3 Grand canonical ensemble

The system is then characterized by the following set of variables: the volume  $V$ , the temperature  $T$  and the chemical potential  $\mu$ . Let us denote the Hamiltonian  $\mathcal{H}_N$  the Hamiltonian of  $N$  particles, the grand partition function  $\Xi(V, \beta, \mu)$  reads:

$$\Xi(V, \beta, \mu) = \sum_{N=0}^{\infty} \sum_{\alpha_N} \exp(-\beta(\mathcal{H}_N(\alpha_N) - \mu N)) \quad (1.10)$$

where  $\beta = 1/k_B T$  ( $k_B$  is the Boltzmann constant) and the sum run over all configurations of  $N$  particles and over all configurations for systems having a number of particles going from 0 to *infinity*. The grand potential is equal to

$$\beta \Omega(V, \beta, \mu) = -\ln(\Xi(V, \beta, \mu)) \quad (1.11)$$

In a similar way, one defines the probability (distribution)  $P(V, \beta, \mu; \alpha_N)$  of having a configuration  $\alpha_N$  (with  $N$  particles) by the relation

$$P(V, \beta, \mu; \alpha_N) = \frac{\exp(-\beta(\mathcal{H}_N(\alpha_N) - \mu N))}{\Xi(V, \beta, \mu)} \quad (1.12)$$

The derivatives of the grand potential can be expressed as moments of the probability distribution

- Mean number of particles

$$\langle N(V, \beta, \mu) \rangle = - \frac{\partial(\beta\Omega(V, \beta, \mu))}{\partial(\beta\mu)} \quad (1.13)$$

$$= \sum_N \sum_{\alpha_N} NP(V, \beta, \mu; \alpha_N) \quad (1.14)$$

- Susceptibility

$$\chi(V, \beta, \mu) = \frac{\beta}{\langle N(V, \beta, \mu) \rangle \rho} \frac{\partial \langle N(V, \beta, \mu) \rangle}{\partial \beta \mu} \quad (1.15)$$

$$= \frac{\beta}{\langle N(V, \beta, \mu) \rangle \rho} \left[ \sum_N \sum_{\alpha_N} N^2 P(V, \beta, \mu; \alpha_N) - \left( \sum_N \sum_{\alpha_N} NP(V, \beta, \mu; \alpha_N) \right)^2 \right] \quad (1.16)$$

$$= \frac{\beta}{\langle N(V, \beta, \mu) \rangle \rho} (\langle N^2(V, \beta, \mu) \rangle - \langle N(V, \beta, \mu) \rangle^2) \quad (1.17)$$

### 1.2.4 Isothermal-isobaric ensemble

The system is characterized by the following set of variables: the pressure  $P$ , the temperature  $T$  and the total number of particles  $N$ . Because this ensemble is generally devoted to molecular systems and not used for lattice models, one only considers continuous systems. The partition function reads:

$$Q(P, \beta, N) = \frac{\beta P}{\Lambda^{3N} N!} \int_0^\infty dV \exp(-\beta PV) \int_0^V d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N)) \quad (1.18)$$

where  $\beta = 1/k_B T$  ( $k_B$  is the Boltzmann constant).

The Gibbs potential is equal to

$$\beta G(P, \beta, N) = -\ln(Q(P, \beta, N)). \quad (1.19)$$

One defines the probability  $\Pi(P, \beta, \mu; \alpha_V)$ <sup>4</sup> of having a configuration  $\alpha_V \equiv \mathbf{r}^N$  (particle positions  $\mathbf{r}^N$ ), with a temperature  $T$  and a pressure  $P$ .

$$\Pi(P, \beta, \mu; \alpha_V) = \frac{\exp(-\beta V) \exp(-\beta(U(\mathbf{r}^N)))}{Q(P, \beta, N)}. \quad (1.20)$$

The derivatives of the Gibbs potential are expressed as moments of this probability distribution. Therefore,

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<sup>4</sup>In order to avoid confusion with the pressure, the probability is denoted  $\Pi$ .

- Mean volume

$$\langle V(P, \beta, N) \rangle = \frac{\partial(\beta G(P, \beta, N))}{\partial \beta P} \quad (1.21)$$

$$= \int_0^\infty dV V \int_0^V d\mathbf{r}^N \Pi(P, \beta, \mu; \alpha_V). \quad (1.22)$$

This ensemble is appropriate for simulations which aim to determine the equation of state of a system.

Let us recall that a statistical ensemble can not be defined from a set of intensive variables only. However, we will see in Chapter 7 that a technique so called Gibbs ensemble method is close in spirit of such an ensemble (with the difference we always consider in simulation finite systems).

## 1.3 Model systems

### 1.3.1 Introduction

We restrict the lecture notes to classical statistical mechanics, which means that the quantum systems are not considered here. In order to provide many illustrations of successive methods, we introduce several basic models that we consider several times in the following

### 1.3.2 Simple liquids

A *simple liquid* is a system of  $N$  point particles labeled from 1 to  $N$ , of identical mass  $m$ , interacting with an external potential  $U_1(\mathbf{r}_i)$  and among themselves by a pairwise potential  $U_2(\mathbf{r}_i, \mathbf{r}_j)$  (i.e. a potential where the particles only interact by pairs). The Hamiltonian of this system reads:

$$\mathcal{H} = \sum_{i=1}^N \left[ \frac{\mathbf{p}_i^2}{2m} + U_1(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} U_2(\mathbf{r}_i, \mathbf{r}_j), \quad (1.23)$$

where  $\mathbf{p}_i$  is the momentum of the particle  $i$ .

For instance, in the grand canonical ensemble, the partition function  $\Xi(\mu, \beta, V)$  is given by

$$\Xi(\mu, \beta, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{(d^d \mathbf{p}_i)(d^d \mathbf{r}_i)}{h^{dN}} \exp(-\beta(\mathcal{H} - \mu N)) \quad (1.24)$$

where  $h$  is the Planck constant and  $d$  the space dimension.

The integral over the momentum can be obtained analytically, because there is factorization of the multidimensional integral on the variables  $\mathbf{p}_i$ . The one-dimensional integral of each component of the momentum is a Gaussian integral. Using the thermal de Broglie length

$$\Lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}, \quad (1.25)$$

one has

$$\int_{-\infty}^{+\infty} \frac{d^d p}{h^d} \exp(-\beta p^2/(2m)) = \frac{1}{\Lambda_T^d}. \quad (1.26)$$

The partition function can be reexpressed as

$$\Xi(\mu, \beta, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{e^{\beta\mu}}{\Lambda_T^d} \right)^N Z_N(\beta, N, V) \quad (1.27)$$

where  $Z_N(\beta, N, V)$  is called the configuration integral.

$$Z_N(\beta, N, V) = \int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N)) \quad (1.28)$$

One defines  $z = e^{\beta\mu}$  as the fugacity.

The thermodynamic potential associated with the partition function,  $\Omega(\mu, \beta, V)$ , is

$$\Omega(\mu, \beta, V) = -\frac{1}{\beta} \ln(\Xi(\mu, \beta, V)) = -PV \quad (1.29)$$

where  $P$  is the pressure.

Note that, for classical systems, only the part of the partition function with the potential energy is non-trivial. Moreover, there is decoupling between the kinetic part and potential part, contrary to the quantum statistical mechanics.

### 1.3.3 Ising model and lattice gas. Equivalence

The Ising model is a lattice model where sites are occupied by particles with very limited degrees of freedom. Indeed, the particle is characterized by a spin which is a two-state variable  $(-1, +1)$ . Each spin interacts with its nearest neighbors and with an external field  $H$ , if it exists. The Ising model, initially introduced for describing the behavior of para-ferromagnetic systems, can be used in many physical situations. This simple model can be solved analytically in several situations (one and two dimensions) and accurate results can be obtained in higher dimensions.

The Hamiltonian reads

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j \quad (1.30)$$

where  $\langle i, j \rangle$  denotes a summation over nearest-neighbor sites and  $J$  is the interaction strength. If  $J > 0$ , the interaction is ferromagnetic and conversely, if  $J < 0$ , the interaction is antiferromagnetic. The analytical solution of the system in one dimension shows that there is no phase transition at a finite temperature. In two dimensions, Onsager (1944) obtained the solution in the absence of an external field. In three dimensions, no analytical solution has been obtained, but theoretical developments and numerical simulations give the properties of the system in the phase diagram magnetization-temperature.

The lattice gas model was introduced by Lee and Yang. The basic idea, greatly extended later, consists of assuming that the macroscopic properties of a system with a large number of particles do not crucially depend on the microscopic details of the interaction. By performing a coarse-graining of the microscopic system, one builds an effective model with a smaller number of degrees of freedom. This idea is often used in statistical physics, because it is often necessary to reduce the complexity of the original system for several reasons: 1) practical: In a simpler model, theoretical treatments are more tractable and simulations can be performed with larger system sizes. 2) theoretical: macroscopic properties are almost independent of some microscopic degrees of freedom and a local average is an efficient method for obtaining an effective model for the physical properties of the system. This method underlies the existence of a certain universality, which is appealing to many physicists.

From a Hamiltonian of a simple liquid to a lattice gas model, we proceed in three steps. The first consists of rewriting the Hamiltonian by introducing a microscopic variable: this step is exact. The second step consists of performing a local average to define the lattice Hamiltonian; several approximations are performed in this step and it is essential to determine their validity. In the third step, several changes of variables are performed in order to transform the lattice gas Hamiltonian into a spin model Hamiltonian: this last step is exact again.

## Rewriting of the Hamiltonian

First, let us reexpress the Hamiltonian of the simple liquid as a function of the microscopic<sup>5</sup> density

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (1.31)$$

By using the property of the Dirac distribution

$$\int f(x)\delta(x - a)dx = f(a) \quad (1.32)$$

one obtains

$$\sum_{i=1}^N U_1(\mathbf{r}_i) = \sum_{i=1}^N \int_V U_1(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_i)d^d\mathbf{r} = \int_V U_1(\mathbf{r})\rho(\mathbf{r})d^d\mathbf{r} \quad (1.33)$$

in a similar way

$$\sum_{i \neq j} U_2(\mathbf{r}_i, \mathbf{r}_j) = \sum_{i \neq j} \int_V U_2(\mathbf{r}, \mathbf{r}_j)\delta(\mathbf{r} - \mathbf{r}_i)d^d\mathbf{r} \quad (1.34)$$

$$= \sum_{i \neq j} \int_V \int_V U_2(\mathbf{r}, \mathbf{r}')\delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j)d^d\mathbf{r}d^d\mathbf{r}' \quad (1.35)$$

$$= \int_V \int_V U_2(\mathbf{r}', \mathbf{r})\rho(\mathbf{r})\rho(\mathbf{r}')d^d\mathbf{r}d^d\mathbf{r}' \quad (1.36)$$

## Local average

The area ("volume")  $V$  of the simple liquid is divided into  $N_c$  cells such that the probability of finding more than one particle center per cell is negligible<sup>6</sup> (typically, this means that the diagonal of each cell is slightly smaller than the particle diameter, see Fig. 1.1). Let us denote by  $a$  the linear length of the cell, then one has

$$\int_V \prod_{i=1}^N d^d\mathbf{r}_i = a^d \sum_{\alpha=1}^{N_c} \quad (1.37)$$

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<sup>5</sup> The local density is obtained by performing a local average that leads to a smooth function

<sup>6</sup>The particle is an atom or a molecule with its own characteristic length scale.

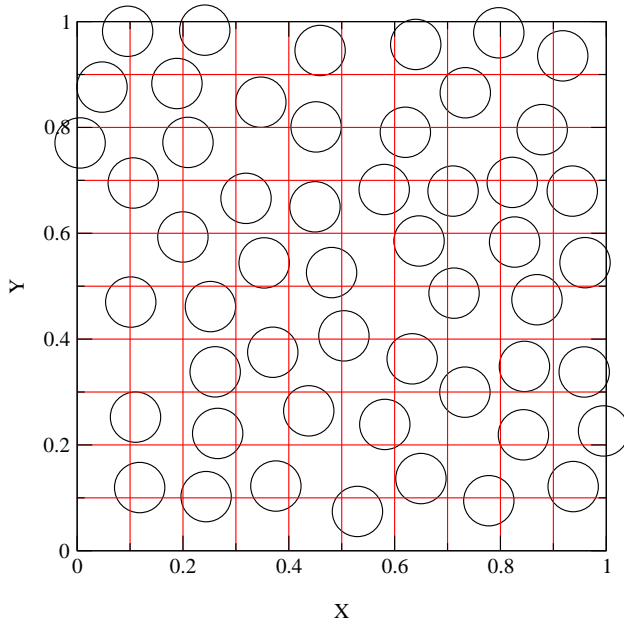


Figure 1.1: Particle configuration of a two-dimensional simple liquid. The grid represents the cells used for the local average. Each cell can accommodate zero or one particle center.

which gives  $N_c = V/a^d$ . The lattice Hamiltonian is

$$\mathcal{H} = \sum_{\alpha=1}^{N_c} U_1(\alpha) n_{\alpha} + 1/2 \sum_{\alpha, \beta}^{N_c} U_2(\alpha, \beta) n_{\alpha} n_{\beta} \quad (1.38)$$

where  $n_{\alpha}$  is a Boolean variable, namely  $n_{\alpha} = 1$  when a particle center is within a cell  $\alpha$ , and 0 otherwise. Note that the index  $\alpha$  of this new Hamiltonian is associated with cells whereas the index of the original Hamiltonian is associated with the particles. One obviously has  $U(\alpha, \alpha) = 0$ , no self-energy, because there is no particle overlap. Since the interaction between particles is short range,  $U_2(r)$  is also short range, and is replaced with an interaction between nearest neighbor cells:

$$\mathcal{H} = \sum_{\alpha=1}^{N_c} U_1(\alpha) n(\alpha) + U_2 \sum_{\langle \alpha \beta \rangle} n_{\alpha} n_{\beta} \quad (1.39)$$

The factor  $1/2$  does not appear because the bracket  $\langle \alpha\beta \rangle$  only considers distinct pairs.

### **Equivalence with the Ising model**

We consider the previous lattice gas model in a grand canonical ensemble. The relevant quantity is then

$$\mathcal{H} - \mu N = \sum_{\alpha} (U_1(\alpha) - \mu) n_{\alpha} + U_2 \sum_{\langle \alpha, \beta \rangle} n_{\alpha} n_{\beta}. \quad (1.40)$$

Let us introduce the following variables

$$S_i = 2n_i - 1. \quad (1.41)$$

As expected, the spin variable is equal to  $+1$  when a site is occupied by a particle ( $n_i = 1$ ) and  $-1$  when the site is unoccupied ( $n_i = 0$ ). One then obtains

$$\sum_{\alpha} (U_1(\alpha) - \mu) n_{\alpha} = \frac{1}{2} \sum_{\alpha} (U_1(\alpha) - \mu) S_{\alpha} + \frac{1}{2} \sum_{\alpha} (U_1(\alpha) - \mu) \quad (1.42)$$

and

$$U_2 \sum_{\langle \alpha, \beta \rangle} n_{\alpha} n_{\beta} = \frac{U_2}{4} \sum_{\langle \alpha, \beta \rangle} (1 + S_{\alpha})(1 + S_{\beta}) \quad (1.43)$$

$$= \frac{U_2}{4} \left( \frac{N_c c}{2} + c \sum_{\alpha} S_{\alpha} + \sum_{\langle \alpha, \beta \rangle} S_{\alpha} S_{\beta} \right) \quad (1.44)$$

where  $c$  is the coordination number (number of nearest neighbors) of the lattice. Therefore, this gives

$$\mathcal{H} - \mu N = E_0 - \sum_{\alpha} H_{\alpha} S_{\alpha} - J \sum_{\langle \alpha, \beta \rangle} S_{\alpha} S_{\beta} \quad (1.45)$$

with

$$E_0 = N_c \left( \langle U_1(\alpha) \rangle - \frac{\mu}{2} + \frac{U_2 c}{8} \right) \quad (1.46)$$

where  $\langle U_1(\alpha) \rangle$  corresponds to the average of  $U_1$  over the sites.

$$H_{\alpha} = \frac{\mu - U(\alpha)}{2} - \frac{cU_2}{4} \quad (1.47)$$

and

$$J = -\frac{U_2}{4} \quad (1.48)$$

where  $J$  is the interaction strength. Finally, one gets

$$\Xi_{gas}(N, V, \beta, U(r)) = e^{-\beta E_0} Q_{Ising}(H, \beta, J, N_c). \quad (1.49)$$

This analysis confirms that the partition function of the Ising model in the canonical ensemble has a one-to-one map with the partition function of the lattice gas in the grand canonical ensemble. One can easily show that the partition function of the Ising model with the constraint of a constant total magnetization corresponds to the partition function in the canonical ensemble of the lattice gas model.

Some comments on these results: first, one checks that if the interaction is attractive,  $U_2 < 0$ , one has  $J > 0$ , which corresponds to a ferromagnetic interaction. Because the interaction is divided by 4, The critical temperature of the Ising model is four times higher than of the lattice gas model. Note also that the equivalence concerns the configuration integral and not the initial partition function. This means that, like for the Ising model, the lattice gas does not own a microscopic dynamics, unlike to the original liquid model. By performing a coarse-graining, one has added a symmetry between particles and holes, which does not exist in the liquid model. This leads for the lattice gas model a symmetrical coexistence curve and a critical density equal to  $1/2$ . A comparison with the Lennard-Jones liquid gives a critical packing fraction equal to 0.3 in three dimensions. In addition, the coexistence curves of liquids are not symmetric between the liquid phase and the gas phase, whereas the lattice gas due to its additional symmetry  $\rho_{liq} = 1 - \rho_{gas}$ , leads to a symmetric coexistence curve.

Before starting a simulation, it is useful to have an estimate of the phase diagram in order to correctly choose the simulation parameters. The mean-field theory gives a first approximation, for instance, of the critical temperature. For the Ising model (lattice gas), one obtains

$$T_c = cJ = \frac{cU_2}{4} \quad (1.50)$$

As expected, the mean-field approximation overestimates the value of the critical temperature because the fluctuations are neglected. This allows order to persist to a temperature higher than the exact critical temperature of the system. Unlike to the critical exponents which do not depend on the lattice, the critical temperature depends on the details of the system. However, larger the coordination number, the closer the mean-field value to the exact critical temperature.

## 1.4 Conclusion

In this chapter, we have drawn the preliminary scheme before the simulation: 1) Select the appropriate ensemble for studying a model 2) When the microscopic model is very complicated, perform a coarse-graining procedure which leads to an effective model that is more amenable for theoretical treatments and/or more efficient for simulation. As we will see in the following chapters, refined Monte Carlo methods consists of including more and more knowledge of the Statistical Mechanics, which finally leads to a more efficient simulation. Therefore, I recommend reading of several textbooks on the Statistical Physics[12, 5, 11, 33]. In addition to these lecture notes, several textbooks or reviews are available on simulations[10, 20, 21, 4].

## 1.5 Exercises

### 1.5.1 ANNNI Model

Frustrated systems are generally characterized by a large degeneracy of the ground state. This property can be illustrated through a simple model, the ANNNI model (Axial Next Nearest Neighbor Ising). One considers a lattice in one dimension, of unit step and of length  $N$ , on which, with periodic boundary conditions, an Ising variable exists on each lattice point. Spins interact with a ferromagnetic nearest neighbor interaction  $J_1 > 0$  and an antiferromagnetic next nearest neighbor interaction  $J_2 < 0$ . The Hamiltonian reads

$$\mathcal{H} = -J_1 \sum_{i=1}^N S_i S_{i+1} - J_2 \sum_{i=1}^N S_i S_{i+2} \quad (1.51)$$

such that  $S_{N+1} = S_1$  and  $S_{N+2} = S_2$ .

♣ **Q. 1.5.1-1** One considers a staggered configuration of spins.  $S_i = (-1)^i$ . Calculate the energy per spin of this configuration. Infer that this configuration cannot be the ground state of the ANNNI model whatever the values of  $J_1$  and  $J_2$ . The calculation should be done for a lattice with a number of even.

♣ **Q. 1.5.1-2** Calculate the energy per spin for a configuration of aligned (configuration A) and for a periodic configuration pour a configuration of alternated spins of period 4 (configuration B) , corresponding to a sequence of two spins up and two spins down, and two spins up, etc. . . The calculation will be done for a lattice of length multiple of 4.

♣ **Q. 1.5.1-3** Show that the configuration  $A$  has a lower energy than the configuration  $B$  for a ratio  $\kappa = -J_2/J_1$  to be determined.

In the case where  $\kappa = 1/2$ , one admits that the ground-state is strongly degenerated and that the configurations associated are sequences of spins of length  $k \geq 2$ .

♣ **Q. 1.5.1-4** From one of these configurations on a lattice of length  $L - 1$ , one inserts at the end of the lattice one site with a spin  $S_L$ . What sign must this spin be with respect to  $S_{L-1}$  in order that the new configuration belongs to the ground state of a lattice of length  $L$ ?

♣ **Q. 1.5.1-5** From one of these configurations on a lattice of length  $L - 2$ , one inserts two sites at the end of the lattice with two spins  $S_{L-1}$  and  $S_L$  of same sign. What sign must be these two spins with respect to  $S_{L-2}$  in order that the new configuration belongs to the ground state of a lattice of length  $L$  and is different from a configuration generated by the previous process?

♣ **Q. 1.5.1-6** Let us denote by  $D_L$  the degeneracy of a lattice of size  $L$ . By using previous results, justify the relation

$$D_L = D_{L-1} + D_{L-2} \quad (1.52)$$

♣ **Q. 1.5.1-7** Show that for large values of  $L$ , one has

$$D_L \sim (a_F)^L \quad (1.53)$$

where  $a_F$  is a constant to be determined.

The entropy per spin of the ground state in the thermodynamic limit is defined as

$$S_0 = \lim_{L \rightarrow \infty} \frac{k_B}{L} \ln(D_L). \quad (1.54)$$

♣ **Q. 1.5.1-8** Calculate numerically this value.

♣ **Q. 1.5.1-9** Justify that  $S_0$  is less than  $\ln(2)$ . What can one say about the degeneracy of the ground state for a value of  $\kappa = 1/2$ ?

## 1.6 Blume-Capel model

The Blume-Capel model describes a lattice spin system where the spin variables can take 3 values :  $-1, 0$  and  $+1$ . This model describes metallic ferromagnetism and superfluidity in a Helium  $\text{He}^3\text{-He}^4$  mixture. Here, we consider a mean-field approach, that allows tractable calculations, by assuming that lattice spins interact all together (long ranged interactions). The Hamiltonian is

$$H = \Delta \sum_{i=1}^N S_i^2 - \frac{1}{2N} \left( \sum_{i=1}^N S_i \right)^2 \quad (1.55)$$

where the second term of the Hamiltonian describes a ferromagnetic coupling and  $\Delta > 0$  is the difference between ferromagnetic states ( $S_i = \pm 1$ ) and paramagnetic states ( $S_i = 0$ ).

♣ **Q. 1.6.0-10** Determine the ground states and the associated energies. Verify that the ground state energy is extensive. Infer a phase transition at  $T = 0$  for a value  $\Delta$  to be determined.

♣ **Q. 1.6.0-11** Let us denote by  $N_+$ ,  $N_-$  and  $N_0$  the number of sites occupied by spins  $+1$ ,  $-1$  and  $0$  respectively. Show that the total energy of the system can be expressed as a function of  $\Delta$ ,  $N$ ,  $M = N_+ - N_-$  and  $Q = N_+ + N_-$ .

♣ **Q. 1.6.0-12** Justify that the number of available microstates is given by

$$\Omega = \frac{N!}{N_+!N_-!N_0!}. \quad (1.56)$$

♣ **Q. 1.6.0-13** Using a Stirling's formula, show that the microcanonical entropy per spin  $s = S/N$  can be written as a function of  $m = M/N$  and  $q = Q/N$  (One sets  $k_B = 1$ ).

♣ **Q. 1.6.0-14** By introducing  $\epsilon = E/N$ , show that the energy per site is given by

$$q = 2K\epsilon + Km^2 \quad (1.57)$$

where  $K$  is a parameter to be determined.

♣ **Q. 1.6.0-15** Show that the entropy per spin reads

$$\begin{aligned} s(m, \epsilon) = & -(1 - 2K\epsilon - Km^2) \ln(1 - 2K\epsilon - Km^2) - \frac{1}{2}(2K\epsilon + Km^2 + m) \ln(2K\epsilon + Km^2 + m) \\ & - \frac{1}{2}(2K\epsilon + Km^2 - m) \ln(2K\epsilon + Km^2 - m) + (2K\epsilon + Km^2) \ln 2. \end{aligned} \quad (1)$$

In the following, we determine the transition line in the diagram  $T - \Delta$ .

**♣ Q. 1.6.0-16** Show that expansion of the entropy per spin to 4th order in  $m$  can be written as

$$s = s_0 + Am^2 + Bm^4 + O(m^6) \quad (1.59)$$

with

$$A = -K \ln \left( \frac{K\epsilon}{1 - 2K\epsilon} \right) - \frac{1}{4K\epsilon} \quad (1.60)$$

and

$$B = -\frac{K}{4\epsilon(1 - 2K\epsilon)} + \frac{1}{8K\epsilon^2} - \frac{1}{96(K\epsilon)^3}. \quad (1.61)$$

**♣ Q. 1.6.0-17** When  $A$  and  $B$  are negative, what is the value of  $m$  for which the entropy is maximum? Which is the corresponding phase?

**♣ Q. 1.6.0-18** By using the definition of the microcanonical temperature, show that in the same phase

$$\beta = 2K \ln \left( \frac{1 - 2K\epsilon}{K\epsilon} \right). \quad (1.62)$$

**♣ Q. 1.6.0-19** The transition line corresponds to  $A = 0$  and  $B < 0$ . Infer that the transition temperature is given by the implicit equation

$$\beta = \frac{\exp\left(\frac{\beta}{2K}\right)}{2} + 1. \quad (1.63)$$

**♣ Q. 1.6.0-20** The transition line ends in a tricritical point when the coefficient  $B$  is equal to zero. Show for this point that the temperature is given by

$$\frac{K^2}{2\beta^2} \left[ 1 + 2 \exp \left( \frac{-\beta}{2K} \right) \right] - \frac{K}{2\beta} + \frac{1}{12} = 0. \quad (1.64)$$

**♣ Q. 1.6.0-21** For lower temperature, where it is necessary to perform the expansion beyond the 4th order, explain why the transition line becomes first order.

### 1.6.1 Potts model

The Potts model is a lattice model where the spin variables are denoted  $\sigma_i$  where  $\sigma_i$  goes from 1 to  $q$ . The interaction between nearest neighbor sites is given by the Hamiltonian:

$$H = -J \sum_{\langle i,j \rangle} \delta_{\sigma_i \sigma_j} \quad (1.65)$$

where  $\delta_{ij}$  denotes the Kronecker symbol and is equal to 1 when  $i = j$  and 0 when  $i \neq j$ .

♣ **Q. 1.6.1-1** For  $q = 2$ , show that this model is equivalent to a Ising model ( $H = -J_I \sum_{\langle i,j \rangle} S_i S_j$ ) with a coupling constant equal to  $J = 2J_I$ .

To estimate the phase diagram of this model, one can use a mean-field approach. Let  $x_i$  is the fraction of spins in the state  $i$  where  $i$  runs  $i = 1, 2, \dots, q$ .

♣ **Q. 1.6.1-2** Assuming that the spins are independent, give a simple expression for the entropy per site  $s$  as a function of  $x_i$  and the Boltzmann constant.

♣ **Q. 1.6.1-3** Assuming that the spins are independent, justify that the energy per site is given by

$$e = -\frac{cJ}{2} \sum_i x_i^2. \quad (1.66)$$

where  $c$  is the lattice coordination number.

♣ **Q. 1.6.1-4** Infer the dimensionless free energy per site  $\beta f$ .

♣ **Q. 1.6.1-5** A guess is  $x_1 = \frac{1}{q}(1 + (q-1)m)$  and  $x_i = \frac{1}{q}(1 - m)$  for  $i = 2, \dots, q$ . Infer the difference  $\beta f(m) - \beta f(0)$

♣ **Q. 1.6.1-6** Show that  $m = 0$  is always solution of the previous equation when  $\beta f(m) - \beta f(0) = 0$ .

♣ **Q. 1.6.1-7** Consider first the case  $q = 2$ . Determine the temperature of transition by calculating  $\frac{\partial \beta f(m)}{\partial m} = 0$ .

♠ **Q. 1.6.1-8** For  $q > 2$ , show that

$$c\beta Jm = \ln \left( \frac{1 + (q-1)m}{1-m} \right) \quad (1.67)$$

One admits that  $m_c = \frac{q-2}{q-1}$ , determine the “temperature” of transition  $1/\beta_c$ . Show that  $\beta f(m_c) = \beta f(0)$ . Show that the order of the transition changes for  $q > q_c$  with  $q_c$  to be determined.

♠ **Q. 1.6.1-9** Calculate the latent heat of the transition when the transition becomes first order..

One wishes to perform the simulation of the two dimensional Potts model. It was shown that in two dimensions the critical value of  $q$  is 4.

♣ **Q. 1.6.1-10** Write a Metropolis algorithm for the simulation of the  $q$ -state Potts model.

♣ **Q. 1.6.1-11** Describe briefly the convergence problems of the Metropolis algorithm for  $q \leq 4$  and  $q > 4$

♣ **Q. 1.6.1-12** Give a method adapted for studying the transition in the two cases. Justify your answer.

## 1.7 Modèle de Spins à longue portée

On considère un système modèle (introduit par H. Touchette) pour illustrer l'inéquivalence entre les ensembles thermodynamiques quand on est en présence d'interactions à longue portée. Soit un système de  $N$  spins avec  $N$  pair dont l'Hamiltonien est le suivant

$$\mathcal{H} = \sum_{i=1}^{N/2} \sigma_i + \frac{N}{2} \sigma_0 \quad (1.68)$$

où  $\sigma_0$  et  $\sigma_i$  sont des variables d'Ising usuels. Ce système est donc un ensemble de  $N/2$  spins sans interaction (sous système 1) et  $N/2$  spins interagissant très fortement (sous-système 2 car le retournement de ces spins ne peut être que global.

On cherche à calculer l'entropie moyenne par spin  $s(e)$  dans l'ensemble microcanonique avec  $e$  l'énergie moyenne par spin. Pour cela, on considère d'abord le groupe des  $N/2$  spins sans interaction.

♣ **Q. 1.7.0-13** Si on note  $N_+$  et  $N_-$ , le nombre de spins orientés vers le haut et orientés vers le bas, respectivement. Que vaut l'énergie du sous-système  $E_1$  en fonction  $N_+$  et  $N_-$ .

♣ **Q. 1.7.0-14** Calculer le nombre de configurations disponibles de ce sous-système  $\Omega(E_1)$  en fonction de  $N_+$  et de  $N_-$ ?

♣ **Q. 1.7.0-15** Pour le système complet, justifier le fait que le nombre total de configurations accessibles  $\Omega(E)$  est donné par la relation

$$\Omega(E) = \Omega_1(E + N/2) + \Omega_1(E - N/2) \quad (1.69)$$

où  $\Omega_1(E)$  est le nombre de configurations du sous-système 1 ayant l'énergie  $E$ .

♣ **Q. 1.7.0-16** En déduire que l'entropie par spin  $s(e)$  avec  $e = E/N$  est donnée par la relation

$$\begin{aligned} s(e) &= \frac{1}{2} s_\sigma(2e + 1) && \text{pour } e \in [-1, 0[ \\ &= \frac{1}{2} s_\sigma(2e - 1) && \text{pour } e \in [1, 0] \end{aligned} \quad (1.70)$$

avec

$$s_\sigma(e) = - \left( \frac{1-e}{2} \right) \ln \left( \frac{1-e}{2} \right) - \left( \frac{1+e}{2} \right) \ln \left( \frac{1+e}{2} \right) \quad (1.71)$$

♣ **Q. 1.7.0-17** On cherche à déterminer l'allure de cette fonction. Déterminer les valeurs de l'énergie où l'entropie est maximale, puis celle où l'entropie s'annule. Montrer que l'entropie est symétrique par rapport à l'énergie zéro.

♣ **Q. 1.7.0-18** Donner les quatre configurations où l'entropie s'annule.

♣ **Q. 1.7.0-19** Proposer un algorithme Wang-Landau pour ce modèle sur l'intervalle d'énergie  $[-1, 1]$ . Expliquer pourquoi on doit traiter les deux sous-systèmes différemment.

On cherche maintenant à calculer les grandeurs thermodynamiques dans l'ensemble canonique.

♣ **Q. 1.7.0-20** Calculer la fonction de partition du système pour  $N$  spins à une température inverse  $\beta$

♣ **Q. 1.7.0-21** Montrer que l'énergie libre par spin du système  $f(\beta)$  à la limite thermodynamique est donnée par la relation

$$f(\beta) = -\frac{|\beta|}{2\beta} - \frac{\ln(2 \cosh \beta)}{2\beta} \quad (1.72)$$

♣ **Q. 1.7.0-22** Montrer que l'énergie moyenne par spin  $u(\beta)$  du système est donnée par la relation  $u = \frac{d\beta f(\beta)}{d\beta}$ .

♣ **Q. 1.7.0-23** Calculer l'énergie moyenne par spin du système  $u(\beta)$ .