4th exam item

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June 1, 2020

Abstract

Thermodynamic simulations, Ising-model and the Metropolis algorithm

Contents

1 Introduction

Not only do thermodynamic simulations have important practical applications, but they also give us insight into what is "dynamic" in thermodynamics. In the following few pages we are going to dwelve into how to calculate thermodynamic properties of complex systems, give a brief summary of the Metropolis algorithm and its applications. The theory forms the basis for field- theoretic calculations of quantum chromodynamics, some of the most fundamental and most time-consuming computations in existence. [1]

2 The Ising-model

Ferromagnets contain finite-size domains in which the spins of all the atoms point in the same direction. When an external magnetic field is applied to these materials, the different domains align and the materials become "magnetized." Yet as the temperature is raised, the total mag- netism decreases, and at the Curie temperature the system goes through a phase transition beyond which all magnetization vanishes.

To handle this behaviour we can develop the most simple model: a **chain of spins**. As our model we consider N magnetic dipoles fixed in place on the links of a linear chain. Because the particles are fixed, their positions and momenta are not dynamic variables, and we need worry only about their spins. We assume that the particle at site i has spin s_i , which is either up or down:

$$s_i \equiv s_{z,i} = \pm\frac{1}{2}$$

Each configuration of the N particles is described by a quantum state vector:

$$|\alpha_j\rangle = |s_1, s_2, ..., s_N\rangle = \Big\{ \pm\frac{1}{2}, \pm\frac{1}{2}, ... \Big\}, \quad j = 1, ..., 2^N$$

Since fixed particles cannot be interchanged, we do not need to concern ourserlves with the symmtery of the wave function.

The energy of the system arises from the interaction of the spins with each other and with the external magnetic field B . We know from quantum mechanics that an electron's spin and magnetic moment are proportional to each other, so a magnetic dipole–dipole interaction is equivalent to a spin–spin interaction. We assume that each dipole interacts with the external magnetic field and with its nearest neighbor through the potential:

$$V_i = -J\vec{s_i}\vec{s_{i+1}} - gB\mu_B\vec{s_i}$$

Here the constant J is called the *exchange energy* and is a measure of the strength of the spin– spin interaction. The constant g is the *gyromagnetic ratio*, that is, the proportionality constant between a particle's angular momentum and magnetic moment. The constant $\mu_B = e\hbar/(2m_e c)$ is the Bohr magneton, the basic measure for magnetic moments.

Even for small numbers of particles, the 2^N possible spin configurations gets to be very large ($2^{20} > 10^6$), and it is expensive for the computer to examine them all. Realistic samples with $\approx 10^{23}$ particles are beyond imagination. Consequently, statistical approaches are usually assumed, even for moderate values of N.

The energy of the system in state α_k is the expectation value of the sum of the potential V over the spins of the particles:

$$E_{\alpha_k} = \langle \alpha_k | \sum_i V_i \, | \alpha_k \rangle = -J \sum_{i=1}^{N-1} s_i s_{i+1} - gB\mu_B \sum_{i=1}^{N} s_i \tag{1}$$

If we turn off the external magnetic field there will be no preferred direction in space and the average magnetization should vanish even though energetically most adventageous state would be all spins aligned. To resolution of the paradox is that the system is unstable at $B = 0$. Some properties must be calculated differently. For example magnetization should be calculated $\langle | \sum_i s_i | \rangle$ and not $\langle \sum_i s_i \rangle$, with no preferred direction.

The equilibrium alignment of the spins depends critically on the sign of the exchange energy J . If $J > 0$, the lowest energy state will tend to have neighboring spins aligned. If the temperature is low enough, the ground state will be a ferromagnet with all the spins aligned. If $J < 0$, the lowest energy state will tend to have neighbors with opposite spins. If the temperature is low enough, the ground state will be a antiferromagnet with alternating spins.

A fascinating aspect of magnetic materials is the existence of a critical temperature, the *Curie temperature*, above which the gross magnetization essentially vanishes. Below the Curie temperature the quantum state of the material has long-range order extending over macroscopic dimensions; above the Curie temperature there is only short-range order extending over atomic dimensions. Even though the 1-D Ising model predicts realistic temperature dependences for the thermodynamic quantities, the model is too simple to support a phase transition. However, the 2-D and 3-D Ising models do support the Curie temperature phase transition. [1]

3 Some statistical mechanics

Statistical mechanics starts with the elementary interactions among a system's particles and constructs the macroscopic thermodynamic properties such as specific heats. The essential assumption is that all configurations of the system consistent with the constraints are possible. In some simulations the problem is set up such that the energy of the system is fixed. The states of this type of system are described by what is called a *microcanonical ensemble*. In contrast, when the temperature, volume, and number of particles remain fixed, we have what is called a *canonical ensemble*.

When we say that an object is at temperature T , we mean that the object's atoms are in thermodynamic equilibrium at temperature T such that each atom has an average energy proportional to T . Although this may be an equilibrium state, it is a dynamic one in which the object's energy fluctuates as it exchanges energy with its environment (it is thermodynamics after all). Indeed, one of the most illuminating aspects of the simulation we shall develop is its visualization of the continual and random interchange of energy that occurs at equilibrium.

The energy E_{α_j} of state α_j in a canonical ensemble is not constant but is distributed with probabilities $P(\alpha_j)$ given by the Boltzmann distribution:

$$P(E_{\alpha_j}, T) = \frac{e^{-E_{\alpha_j}/k_B T}}{Z(T)}$$

$$Z(T) = \sum_{\alpha_j} e^{-E_{\alpha_j}/(k_B T)}$$

Here k is Boltzmann's constant, T is the temperature, and $Z(T)$ is the partition function, a weighted sum over states. Note that the sums $Z(T)$ are over the individual states or configurations of the system. Another formulation is to sum over the energies of the states of the system and includes a density-of-states factor $g(E_i)$ to account for degenerate states with the same energy. While the present sum over states is a simpler way to express the problem (one less function), we shall see that the sum over energies is more efficient numerically. In fact, in this section we even ignore the partition function $Z(T)$ because it cancels out when dealing with the ratio of probabilities. [1]

3.1 Analytical solution of Ising-chain

In order to solve the 1D Ising model analitically we need to understand the partition function properly [2]. $Z(T)$ is summed over all states $|\alpha_k\rangle$ which means all the spin position realization of the system. If periodic conditions are given ($s_1 \equiv s_N$) we can actually calculate the sum analitically since we already have the formulare eq. 1 where in the case of periodic boundary conditions all sums go to N:

$$Z = \sum_{\alpha_k} e^{-E_{\alpha_k}\beta}$$

This can be written as:

$$Z = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} e^{\sum_{i=1}^{N} (-J s_i s_{i+1} - gB\mu_B \frac{s_i + s_{i+1}}{2})\beta}$$

Where the sums for spin i are sums for ± 1. We made a nice trick by introducing instead of $\sum_i s_i$, $\sum_i \frac{s_i + s_{i+1}}{2}$ which will make life simpler later on. Now we can happily realize that the sum in the exponential results in a separable form:

$$Z = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} e^{\sum_i E_i(s_i, s_{i+1})\beta}$$

This can easilly be deconstructed to spin pairs:

$$Z = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} e^{E_1(s_1,s_2)\beta} e^{E_2(s_2,s_3)\beta} \cdot \dots e^{E_N(s_N,s_1)\beta}$$

We can introduce the matrix $t_{s_i,s_{i+1}} = e^{E_i(s_i,s_{i+1})\beta}$. Since spins can only take values ± 1, it takes the following form:

$$t = \begin{pmatrix} e^{\beta E(\uparrow,\uparrow)} & e^{\beta E(\downarrow,\uparrow)} \\ e^{\beta E(\uparrow,\downarrow)} & e^{\beta E(\downarrow,\downarrow)} \end{pmatrix} = \begin{pmatrix} e^{\beta J + B\beta g\mu_B} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta B g\mu_B} \end{pmatrix} \tag{2}$$

Therefore the partition function simplifies to:

$$Z = \sum_{\{s_i\}_{i=1}^N} t_{s_1,s_2} t_{s_2,s_3} \cdot \ldots \cdot t_{s_N,s_1} = \sum_{s_1} [t^N]_{s_1,s_2} = Tr(t^N)$$

To calculate the trace we need the eigenvalues and eigenstates of the t matrix.

$$\begin{aligned} t\,|t_+\rangle &= \lambda_+\,|t_+\rangle \qquad & t^N\,|t_+\rangle &= \lambda_+^N\,|t_+\rangle \\ t\,|t_-\rangle &= \lambda_-\,|t_-\rangle \qquad & t^N\,|t_-\rangle &= \lambda_-^N\,|t_-\rangle \end{aligned}$$

Since the eigenstates with the eigenvalues give the decompostion of t:

$$\begin{aligned} t &= \lambda_+\,|t_+\rangle\langle t_+| + \lambda_-\,|t_-\rangle\langle t_-| \\ t^N &= \lambda_+^N\,|t_+\rangle\langle t_+| + \lambda_-^N\,|t_-\rangle\langle t_-| \end{aligned}$$

Given the above equations the trace of t^N is $\lambda_+^N + \lambda_-^N$. Calculating these is simple since we have eq. 2:

$$\lambda_\pm = e^{\beta J} ch(\beta B g\mu_B) \pm \sqrt{e^{-2\beta J} + e^{2\beta J} sh^2(\beta B g\mu_B)} \overset{(B=0)}{=} 2ch(\beta J) \tag{3}$$

Given that $\lambda_+ > \lambda_-$ and we take the $N \to \infty$ limit the partition function is:

$$Z = \lambda_+^N + \lambda_-^N = \lambda_+^N \cdot \left(1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right) \to \lambda_+^N$$

Since $U = \langle E \rangle = -\frac{\partial ln Z}{\partial \beta}$, if we take it at $B = 0$ given eq. 3 it becomes:

$$\frac{U}{J} = -Nth(\beta J) = \begin{cases} N, & k_B T \to 0 \\ 0, & k_B T \to \infty \end{cases}$$

Specific heat and magnetization can be calculated as [1]:

$$C = \frac{1}{N}\frac{dU}{dT} = \frac{(J/k_B T)^2}{ch^2(J/k_B T)}$$

$$M = -\frac{\partial F}{\partial H} = \frac{N e^{J/k_B T} sh(B/k_B T)}{\sqrt{e^{2J/k_B T} sh^2(B/k_B T) + e^{-2J/k_B T}}}$$

Where F is the free energy of the system and can be calculated as $-k_BTlnZ$. This calculation can be reproduced for 2 dimensions as well but it becomes more cumbersome and tireing so we introduce a general algoritm in order to be able to simulate the system in finite time and proper precision.

4 The Metropolis algorithm

In trying to devise an algorithm that simulates thermal equilibrium, it is important to understand that the Boltzmann distribution does not require a system to remain in the state of lowest energy but says that it is less likely for the system to be found in a higher-energy state than in a lower-energy one. Of course, as $T \to 0$, only the lowest energy state will be populated. For finite temperatures we expect the energy to fluctuate by approximately k_BT about the equilibrium value.

In their simulation of neutron transmission through matter, Metropolis, Rosenbluth, Teller, and Teller invented an algorithm to improve the Monte Carlo calculation of averages. This Metropolis algorithm is now a cornerstone of computational physics. The sequence of configurations it produces (a Markov chain) accurately simulates the fluctuations that occur during thermal equilibrium. The algorithm randomly changes the individual spins such that, on the average, the probability of a configuration occurring follows a Boltzmann distribution.

The Metropolis algorithm is a combination of the variance reduction technique (subtracting a well-chosen function to reduce the variance of ours thus acquireing more precise results) and the von Neumann rejection technique. Now we would like to have spins flip randomly, have a system that can reach any energy in a finite number of steps (ergodic sampling), have a distribution of energies described by a Boltzmann distribution, yet have systems that equilibrate quickly enough to compute in reasonable times.

The Metropolis algorithm is implemented via a number of steps. We start with a fixed temperature and an initial spin configuration and apply the algorithm until a thermal equilibrium is reached (equilibration). Continued application of the algorithm generates the statistical fluctuations about equilibrium from which we deduce the thermodynamic quantities such as the magnetization $M(T)$. Then the temperature is changed, and the whole process is repeated in order to deduce the T dependence of the thermodynamic quantities. The accuracy of the deduced temperature dependences provides convincing evidence for the validity of the algorithm. Because the possible 2^N configurations of N particles can be a very large number, the amount of computer time needed can be very long. Typically, a small number of iterations $\approx 10N$ is adequate for equilibration. The explicit steps of the algortihms are:

1. Take an arbitrary spin configuration $\alpha_k = \{s_1, s_2, ..., s_N\}$
2. Generate a trial configuration α_{trial}:
   (a) choose a particle randomly [1]
   (b) flip its spin

[1] in large-scale not just one particle is updated but a random sweep is applied through the system to remove any auto-correlations

3. Calculate the energy of the trial configuration $E_{\alpha_{trail}}$
4. If $\alpha_{trial} \leq E_{\alpha_k}$, accept the trial by setting $\alpha_{k+1} = \alpha_{trial}$
5. If $\alpha_{trial} > E_{\alpha_k}$, accepts the trial with relative probability $R = e^{-\Delta E/k_B T}$
   (a) choose a uniform random number $r_i \in [0, 1]$
   (b) set $\alpha_{k+1} = \{\alpha_{trail},\ if\ R \geq r_i \quad | \quad \alpha_k,\ if\ R < r_j$

The heart of this algorithm is its generation of a random spin configuration α_j with probability

$$P(E_{\alpha_j}, T) \propto e^{-E_{\alpha_j}/k_B T}$$

The technique is a variation of von Neumann rejection in which a random trial configuration is either accepted or rejected depending upon the value of the Boltz- mann factor. Explicitly, the ratio of probabilities for a trial configuration of energy E t to that of an initial configuration of energy E_i is

$$R = \frac{P_{trial}}{P_i} = e^{-\Delta E/k_B T}, \qquad \Delta E = E_{trial} - E_{\alpha_i}$$

If the trial configuration has a lower energy, the relative probability will be greater than 1 and we will accept the trial configuration as the new initial configuration without further ado. However, if the trial configuration has a higher energy, we will not reject it out of hand but instead accept it with relative probability. To accept a configuration with a probability, we pick a uniform random number between 0 and 1 , and if the probability is greater than this number, we accept the trial configuration; if the probability is smaller than the chosen random number, we reject it. When the trial configuration is rejected, the next configuration is identical to the preceding one.

It is possible to start with random values of spins, which is often referred to as hot start. Another choise is a cold start in which the system is started with all spins parallel ($J > 0$) or antiparallel ($J < 0$). In general the system is let to run for a few iterations ($\approx 10N$) before calculating the equilibrium. Similair results of numerical simulations should come from cold, hot or arbitrary starts. [1]

5 Beyond all this

This process can be trivially extended to 2 and 3 dimensions as well, also one can take into account not just nearest-neighbors but next-nearest-neighbors as well. A recently popular method is the Wang-Landau sampling which has similair steps as described in the Metropolis algortihms but buildson the densitiy-of-states function $g(E)$.

The metropolis algorithm is used in many parts of physics, in calculating Feymann path-integrals one should do the following. Express the Green's function as a path integral that requires integration of the Hamiltonian along paths and a summation over all the paths. We

evaluate this path integral as the sum over all the trajectories in a space-time lattice. Each trial path occurs with a probability based on its action, and we use the Metropolis algorithm to include statistical fluctuation in the links, as if they are in thermal equilibrium. This is similar to our work with the Ising model, however now, rather than reject or accept a flip in spin based on the change in energy, we reject or accept a change in a link based on the change in energy. The more iterations we let the algorithm run for, the more time the deduced wave function has to equilibrate to the ground state.

References

[1] Rubin H Landau, Manuel José Páez Mejía, José Páez, and Cristian C Bordeianu. A survey of computational physics: introductory computational science, 2008.

[2] Ludwig Ridderstolpe. Exact solutions of the ising model. 2017.