

STATISTICAL PHYSICS: A PRIMER

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Abstract

I. FUNDAMENTAL PRINCIPLES OF STATISTICAL MECHANICS

This section provides a brief review of the fundamental principles of statistical physics based on two existing textbooks: L. D. Landau and E. M. Lifshitz, *Statistical Physics (Part 1)* and C. Kittel, *Elementary Statistical Physics*.

A. Introduction

Macroscopic systems have a very large number ($\sim 10^{23}$) degrees of freedom. The actual application of the methods of mechanics involves the necessity of setting up and solving the same number of differential equations, which is impracticable. Furthermore, it is completely impossible to provide initial conditions of all the coordinates and momenta.

At first sight we may conclude that, as the number of particles increases, the behavior of a macroscopic system becomes less and less predictable. This is not true. It is an important experimental fact that we can simply answer many questions concerning systems in or near thermodynamic equilibrium without detailed knowledge of the motions of individual particles.

A system is called in equilibrium when it has been placed in contact with a heat reservoir for sufficiently long time. A large isolated system will also in time reach equilibrium. The time within which the system reaches equilibrium is called the relaxation time. It describes

approximately the time required for fluctuation in properties of the system to damp out. The term “sufficiently long time” essentially refers to time intervals that are long in comparison to the relaxation time.

Statistical mechanics and thermodynamics are formulated in accordance with the experimental fact that, when the number of particles is very large, new types of regularity appear in the behavior of macroscopic systems in or near thermodynamic equilibrium. The statistical laws result from the presence of a large number of particles in the system. They cannot in any way be reduced to purely mechanical laws.

B. Review of Classical Mechanics

1. The Lagrangian

The mechanical state of a system is described by specifying its generalized coordinates q_i and velocities \dot{q}_i . The Lagrangian of the system, usually denoted by L , is a function of the generalized coordinates q_i and velocities \dot{q}_i :

$$L = L(q_i, \dot{q}_i, t).$$

For a system of particles with s degrees of freedom, the Lagrangian takes the form of

$$L = \sum_{i=1}^s \frac{1}{2} m_i \dot{q}_i^2 - U(q).$$

Here L shows no explicit dependence on t , and the potential U depends on q only. (We use q to represent all q_i 's.)

2. Hamilton's least action principle

The action, usually denoted by S , is defined by the integral

$$S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt,$$

under the condition that $q(t_1) = q^{(1)}$ and $q(t_2) = q^{(2)}$ are fixed. The action S can be evaluated along any path $q(t)$ which connects the given initial coordinate(s) $q(t_1) = q^{(1)}$ and final coordinate(s) $q(t_2) = q^{(2)}$ in the time interval from t_1 to t_2 . The actual path $q(t)$ is the path along which S takes the least possible value. This statement is called the principle of least action or Hamilton's principle, which may be expressed as $\delta S/\delta q = 0$ at $q(t)$.

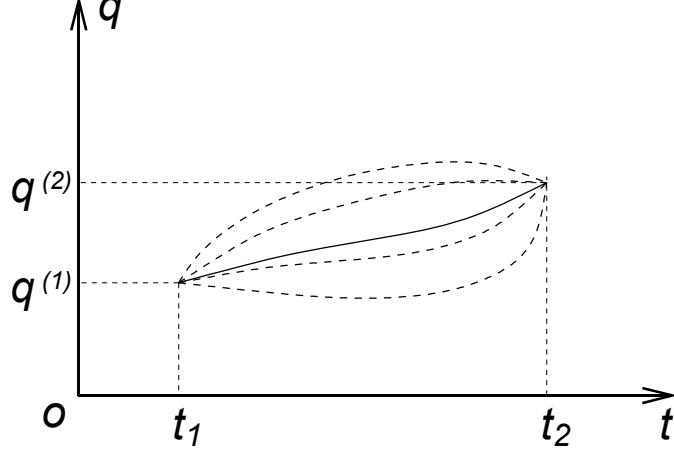


Fig. Among infinite number of possible paths, the actual path (solid line) is the one along which the action takes the least possible value.

3. Lagrange's equations

The equation of motion for the actual path $q(t)$ is derived from the condition

$$\delta S = \delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t) dt = \int_{t_1}^{t_2} \sum_i \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) dt = 0.$$

From $\delta \dot{q}_i = d\delta q_i/dt$, we obtain

$$\delta S = \left[\sum_i \frac{\partial L}{\partial \dot{q}_i} \delta q_i \right]_{t_1}^{t_2} + \int_{t_1}^{t_2} \sum_i \left(\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i dt = 0.$$

Since the varied path has fixed ends $q(t_1) = q^{(1)}$ and $q(t_2) = q^{(2)}$, $\left[\sum_i \frac{\partial L}{\partial \dot{q}_i} \delta q_i \right]_{t_1}^{t_2} = 0$. The variation δq is arbitrary, and δq_i 's are independent of each other. Therefore, the condition $\delta S = 0$ leads to totally s equations of motion

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0, \quad i = 1, 2, \dots, s,$$

if the system has s degrees of freedom. These equations derived from $\delta S = 0$ are called Lagrange's equations.

Hamilton's principle uses the δ -variation of S . The varied path in configuration space \mathbf{q} , over which the action integral $S = \int_{t_1}^{t_2} L dt$ is evaluated, always terminates at fixed endpoints $q^{(1)}$ and $q^{(2)}$ in the fixed time interval from t_1 to t_2 : $q(t_1) = q^{(1)}$ and $q(t_2) = q^{(2)}$. For such δ -variation of $q(t)$, the variation of $S = \int_{t_1}^{t_2} L(q, \dot{q}) dt$ is given by

$$\delta S = \int_{t_1}^{t_2} \sum_i \left(\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i dt,$$

with $\delta q(t_1) = \delta q(t_2) = 0$. Hamilton's principle states that $\delta S = 0$ at the actual path. This leads to Lagrange's equations.

4. Hamilton's equations

Instead of describing the state of a mechanical system by q and \dot{q} , we introduce generalized momenta through the definition

$$p_i = \frac{\partial L(q_i, \dot{q}_i, t)}{\partial \dot{q}_i},$$

and then describe the mechanical state by q and p . (Similarly, we use p to represent all p_i 's.)

The variation of the Lagrangian $L(q, \dot{q})$ (as a function of q and \dot{q}) is

$$\delta L = \sum_i \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right),$$

which may also be written as

$$\delta L = \sum_i (\dot{p}_i \delta q_i + p_i \delta \dot{q}_i)$$

by using the definition of p and Lagrange's equations. Note that $\delta L = \dot{p} \delta q + p \delta \dot{q}$ is true at the actual path only.

Now we define the Hamilton's function or Hamiltonian of the system as a function of q and p :

$$H(q, p) = \sum_i p_i \dot{q}_i - L(q, \dot{q}),$$

where \dot{q} is regarded as a function of q and p based on the definition of $p = \partial L(q, \dot{q})/\partial \dot{q}$. The variation of H (as a function of q and p) is

$$\delta H = \sum_i (\dot{q}_i \delta p_i + p_i \delta \dot{q}_i) - \delta L = - \sum_i \dot{p}_i \delta q_i + \sum_i \dot{q}_i \delta p_i.$$

Note that this expression is true at the actual path only.

From the expression for $\delta H(q, p)$ at the actual path, we obtain Hamilton's equations:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}.$$

They are also called canonical equations. We want to point out that for δL the two independent variations are δq and $\delta \dot{q}$ while for δH the two independent variations are δq and δp .

5. The law of conservation of energy

For $L(q, \dot{q})$ not explicitly depending on time, H is also independent of time. Then the time variation of H is given by

$$\frac{dH}{dt} = \sum_i \frac{\partial H}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial H}{\partial p_i} \dot{p}_i = - \sum_i \dot{p}_i \dot{q}_i + \sum_i \dot{q}_i \dot{p}_i = 0.$$

This expresses the conservation of energy.

C. Phase Space and Statistical Distribution Function

1. Phase space

Consider a macroscopic system with s degrees of freedom. Let q_i denote the s coordinates and p_i denote the s momenta, where the subscripts i take the values 1, 2, ..., s . The phase space of the system, spanned by $\{q_i, p_i\}$, is $2s$ -dimensional. Any microscopic state of the system can be represented mathematically by a point in the phase space. Consequently, the time-evolution of the state of the system is described by a curve in the phase space, called the phase trajectory.

2. Statistical distribution function

The statistical distribution function is defined as follows. Let $\Delta q \Delta p$ denote some small volume element of the phase space, corresponding to many microscopic states with $\{q_i, p_i\}$ lying in the short intervals Δq_i and Δp_i . In a sufficiently long time, due to the extremely large number of degrees of freedom and the extremely complex interaction with the surrounding environment, the phase trajectory of the system passes many times through each volume element $\Delta q \Delta p$ of the phase space¹. Let Δt be the part of the total time T during which the time-varying state stays in a given volume element $\Delta q \Delta p$. When the total time T increases infinitely, the ratio $\frac{\Delta t}{T}$ converges to some limit

$$\Delta w = \lim_{T \rightarrow \infty} \frac{\Delta t}{T},$$

which can be regarded as the probability that, if the system in thermodynamic equilibrium is observed at an arbitrary instant, it will be found in the given volume $\Delta q \Delta p$ of the phase space². Taking the limit of infinitesimal phase volume $dq dp$, we define the statistical distribution function $f(q, p) \equiv f(q_1, \dots, q_s, p_1, \dots, p_s)$ as

$$dw = f(q, p) dq dp.$$

Apparently, $f(q, p)$ must satisfy the normalization condition

$$\int dq dp f(q, p) = 1.$$

¹Hypothesis I

²Hypothesis II

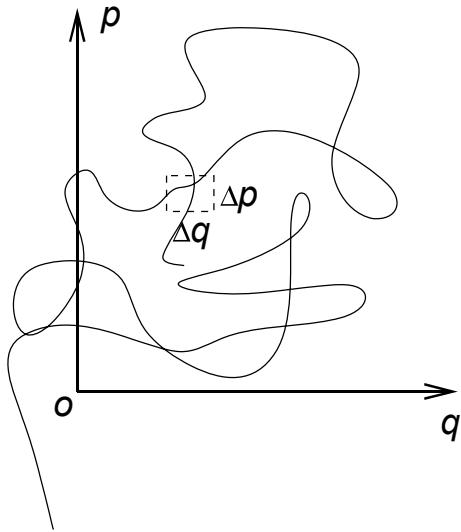


Fig. Schematic illustration of a phase trajectory passing through a volume element $\Delta q\Delta p$ in the phase space.

3. Statistical mean value

The mean value of any physical quantity C which depends on the microscopic state of the system (i.e., on the values of q_i and p_i , $C = C(q, p)$) can be expressed as

$$\langle C \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int dt C[q(t), p(t)],$$

for a sufficiently long observation period. With the help of the statistical distribution function $f(q, p)$, the above time averaging can be obtained in the statistical averaging

$$\langle C \rangle = \int dq dp f(q, p) C(q, p).$$

D. Statistical Ensemble and Liouville's Theorem

1. Statistical ensemble

The physical quantities of interest to us for a system in thermodynamic equilibrium are mostly time averages over a sufficiently long time in a segment of the phase trajectory. J.

Willard Gibbs made a great advance in the problem of calculating average values of physical quantities. He suggested that instead of taking time averages we imagine a group of similar systems, but suitably randomized, and take averages over this group at one time. The group of similar systems is called an ensemble of systems and is to be viewed as an intellectual construction to simulate and represent at one time the properties of the actual system as developed in the course of time.

An ensemble of systems is composed of many systems all constructed alike. Each system in the ensemble is a replica of the actual system and is equivalent for all practical purposes to the actual system; it satisfies all external requirements placed on the actual system. The ensemble is randomized suitably in the sense that every phase point accessible to the actual system in the course of time is represented in the ensemble by one or more systems at one instant of time³.

The scheme introduced by Gibbs is to replace time averages over a single system by ensemble averages, which are averages at a fixed time over all systems in an ensemble. The problem of demonstrating the equivalence of the two types of averages is the subject of ergodic theory. It is certainly plausible that the two averages might be equivalent, but it has not been proved in general that they are exactly equivalent. It may be argued that the ensemble average really corresponds better to the actual situation than does the time average. For a closed system, we never really know the initial conditions, so we do not know exactly how to take the time average. For a system in contact with a heat reservoir, we never really know the interaction between the system and the reservoir (because detailed knowledge of motions of individual particles in a large composite system is not available), so we do not know exactly how to take the time average either. The ensemble average describes our ignorance appropriately.

In summary, instead of considering points representing states of one system at different

³Hypothesis III

instants t_1, t_2, \dots , we may consider a collection of many identical systems, which at some instant t , are in different microscopic states represented by phase points in phase space. In this way we introduce a statistical ensemble, which is geometrically represented by a distribution of representative points in phase space. The normalized distribution function $f(q, p, t)$ is defined as the relative density of representative points in phase space at instant t .

2. Time evolution of distribution function: Liouville's theorem

The phase points represent the microscopic states of the identical systems in ensemble. They move in the phase space according to the canonical equations of motion. Consequently, given a distribution function $f(q, p, 0)$ at a time instant $t = 0$, the distribution function $f(q, p, t)$ at later time instants $t > 0$ can be determined. With the equations of motion in Hamilton's form:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i},$$

where $H = H(q, p)$ is the Hamiltonian for the system considered, and the equation of continuity in the phase space

$$\frac{\partial f}{\partial t} + \nabla_{2s} \cdot (f \mathbf{v}_{2s}) = 0,$$

where ∇_{2s} and \mathbf{v}_{2s} are the $2s$ -dimensional gradient operator and velocity in the phase space, respectively, we obtain Liouville's Theorem

$$\begin{aligned} \frac{df}{dt} &= \frac{\partial f}{\partial t} + \sum_{i=1}^s \left(\frac{\partial f}{\partial q_i} \dot{q}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right) \\ &= \frac{\partial f}{\partial t} + \sum_{i=1}^s \left(\frac{\partial f}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \\ &= 0, \end{aligned}$$

which states that the density of phase points is constant along phase trajectories. Hence the distribution of phase points moves in the phase space like an incompressible fluid. [$\nabla_{2s} \cdot \mathbf{v}_{2s} = 0$ follows from the canonical equation of motion. Combining $\nabla_{2s} \cdot \mathbf{v}_{2s} = 0$ with the continuity equation yields $df/dt = 0$.]

E. Statistical Equilibrium

1. Mechanical invariants

We have defined the statistical distribution function $f(q, p)$ from $\Delta w = \lim_{T \rightarrow \infty} \frac{\Delta t}{T}$ and $dw = f(q, p) dq dp$. For an ensemble to be a satisfactory representation of the actual system in equilibrium, we require that the distribution function $f(q, p, t)$ be independent of time, i.e., given $f(q, p, 0) = f(q, p)$ as the initial condition at $t = 0$, then $f(q, p, t) = f(q, p)$ at $t > 0$ as well⁴. It follows from Liouville's theorem $\frac{df}{dt} = 0$ that

$$\mathbf{v}_{2s} \cdot \nabla_{2s} f = \sum_{i=1}^s \left(\frac{\partial f}{\partial q_i} \dot{q}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right) = 0,$$

which means that $f(q, p)$ is a mechanical invariant or an integral of the motion, and that phase points move on surfaces of constant $f(q, p)$. Therefore, the equilibrium distribution function $f(q, p)$ must be a function of some physical quantities which remain constant when the system moves as a closed system. These quantities are all mechanical invariants or integrals of the motion.

2. Statistical independence

A macroscopic system may be imagined to be divided into many subsystems. Each of them is still a mechanical system but not a closed one. Since these subsystems, being parts of the whole system, are themselves macroscopic bodies, we can still assume that over not too long intervals of time they behave approximately as closed systems. For each subsystem, the particles which interact with the surrounding parts are those near the surface of the subsystem; the relative number of such particles, compared with the total number of particles in the subsystem, decreases rapidly as the size of the subsystem increases. Therefore, if the subsystem is sufficiently large, the interaction energy with the surrounding parts will be

⁴Hypothesis IV

negligibly small compared with its internal energy. Thus we may claim that the subsystems are quasi-closed.

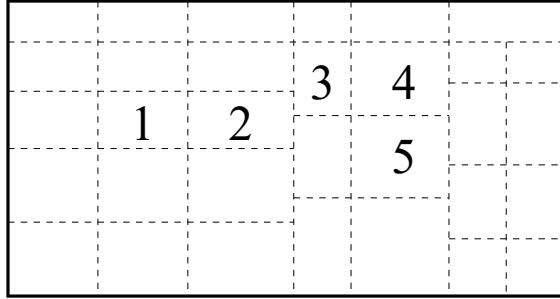


Fig. A macroscopic system can be virtually divided into many macroscopic quasi-closed subsystems.

The fact that different subsystems may be regarded as weakly interacting indicates that they may also be regarded as statistically independent. By statistical independence we mean that the state of one subsystem does not affect the probabilities of various states of other subsystems⁵. Let us consider any two subsystems, and let $dq^{(1)}dp^{(1)}$ and $dq^{(2)}dp^{(2)}$ be volume elements in their phase spaces respectively. If we regard the two subsystems together as one composite subsystem, then the statistical independence signifies mathematically that the probability of the composite subsystem being in its phase volume element $dq^{(12)}dp^{(12)} = dq^{(1)}dp^{(1)}dq^{(2)}dp^{(2)}$ is the product of the probabilities of the two subsystems being respectively in $dq^{(1)}dp^{(1)}$ and $dq^{(2)}dp^{(2)}$, i.e.,

$$f^{(12)}dq^{(12)}dp^{(12)} = f^{(1)}dq^{(1)}dp^{(1)} \cdot f^{(2)}dq^{(2)}dp^{(2)},$$

or

$$f^{(12)} = f^{(1)}f^{(2)},$$

where $f^{(12)} = f^{(12)}(q^{(1)}, p^{(1)}, q^{(2)}, p^{(2)})$ is the distribution function of the composite subsystem and $f^{(1)} = f^{(1)}(q^{(1)}, p^{(1)})$ and $f^{(2)} = f^{(2)}(q^{(2)}, p^{(2)})$ are the distribution functions of the two subsystems, respectively.

⁵Hypothesis V

The statistical independence has a very important consequence regarding the magnitude of fluctuation. Consider a system made of N statistically independent subsystems of equal size. We denote an additive quantity of the system by G , with $G = \sum_{i=1}^N g_i$, where each g_i is contributed by a subsystem. The average of G , \bar{G} , is given by $\bar{G} = \langle \sum_{i=1}^N g_i \rangle = N\bar{g}$, where \bar{g} is the average of g_i in a subsystem. The mean square fluctuation of G , $\langle (\Delta G)^2 \rangle$, is defined as

$$\langle (\Delta G)^2 \rangle = \langle (G - \bar{G})^2 \rangle = \left\langle \left[\sum_{i=1}^N (g_i - \bar{g}) \right]^2 \right\rangle.$$

With the help of the statistical independence, it can be shown that of the N^2 terms from $[\sum_{i=1}^N (g_i - \bar{g})]^2$, only N terms of the form $(g_i - \bar{g})^2$ survive during the averaging process indicated by $\langle \cdot \cdot \cdot \rangle$. As a result,

$$\langle (\Delta G)^2 \rangle = N \langle (\Delta g)^2 \rangle,$$

where $\langle (\Delta g)^2 \rangle = \langle (g_i - \bar{g})^2 \rangle$ is the mean square fluctuation of g_i in the subsystem. Therefore, root-mean-square (r.m.s.) fluctuation of G , $\sqrt{\langle (\Delta G)^2 \rangle}$, is related to that of g_i , through $\sqrt{\langle (\Delta G)^2 \rangle} = \sqrt{N} \sqrt{\langle (\Delta g)^2 \rangle}$. As for the relative fluctuation, we have

$$\frac{\sqrt{\langle (\Delta G)^2 \rangle}}{\bar{G}} = \frac{1}{\sqrt{N}} \frac{\sqrt{\langle (\Delta g)^2 \rangle}}{\bar{g}}.$$

3. The significance of energy

The statistical independence asserts that the distribution function $f^{(12)}$ of a combination of two subsystems is equal to the product of the distribution functions $f^{(1)}$ and $f^{(2)}$ of the two subsystems: $f^{(12)} = f^{(1)}f^{(2)}$. Hence

$$\log f^{(12)} = \log f^{(1)} + \log f^{(2)},$$

from which we conclude that the logarithm of the distribution function is an additive quantity. Therefore, the logarithm of the distribution function is not merely an integral of the motion, but an additive integral of motion.

There are only seven independent additive integrals of the motion: the energy $E(q, p)$, the three components of the momentum $\mathbf{P}(q, p)$, and the three components of the angular momentum $\mathbf{M}(q, p)$. The only additive combination of these additive quantities is of the form

$$\log f^{(i)}(q^{(i)}, p^{(i)}) = \alpha^{(i)} - \beta E^{(i)}(q^{(i)}, p^{(i)}) + \boldsymbol{\gamma} \cdot \mathbf{P}^{(i)}(q^{(i)}, p^{(i)}) + \boldsymbol{\delta} \cdot \mathbf{M}^{(i)}(q^{(i)}, p^{(i)}),$$

where i is the subsystem index and β , $\boldsymbol{\gamma}$, and $\boldsymbol{\delta}$ must be the same for all subsystems in a given closed system. The momentum and angular momentum are related to the motion of a system as a whole. Since we are interested in the internal state of the system, we imagine the system to be enclosed in a “box” such that the momentum and angular momentum are no longer integrals of the motion, and the only remaining additive integral of the motion is the energy. Hence,

$$\log f^{(i)}(q^{(i)}, p^{(i)}) = \alpha^{(i)} - \beta E^{(i)}(q^{(i)}, p^{(i)}).$$

This distribution actually corresponds to the so-called canonical ensemble, which is suitable for describing a macroscopic subsystem in thermal equilibrium with its environment. Here we emphasize that this important ensemble has been derived from only two basic assumptions: (1) f is a time-independent solution of the Liouville equation, i.e., f is a mechanical invariant, and (2) $\log f$ is an additive mechanical invariant due to the statistical independence.

4. Microcanonical and canonical distributions

With the help of the above results, we are ready to set up two distribution functions, namely, the microcanonical distribution function and the canonical distribution function.

The microcanonical distribution function is given by

$$f(q, p) = \text{constant}, \text{ for } E_0 \leq E(q, p) \leq E_0 + \Delta E,$$

$$f(q, p) = 0, \text{ for } E(q, p) < E_0 \text{ or } E(q, p) > E_0 + \Delta E.$$

It is a time-independent solution of Liouville's equation $\frac{df}{dt} = 0$. In the limit of $\Delta E \rightarrow 0$, it can be formally expressed as

$$f(q, p) = \text{constant} \times \delta[E(q, p) - E_0].$$

Regarding the microcanonical distribution function as the true distribution function for a closed system is equivalent to asserting that, in the course of a sufficiently long time, the phase trajectory of a closed system passes arbitrarily close to every point of the manifold defined by $E(q, p) = E_0$ in the phase space⁶. This assertion, called the ergodic hypothesis, is not true in general.

The canonical distribution function is given by

$$f(q, p) = \text{constant} \times \exp[-\beta E(q, p)],$$

where the constant is a normalization factor. It is a time-independent solution of Liouville's equation $\frac{df}{dt} = 0$, and is of the same form as the distribution function

$$\log f^{(i)}(q^{(i)}, p^{(i)}) = \alpha^{(i)} - \beta E^{(i)}(q^{(i)}, p^{(i)}),$$

which is derived for the weakly interacting subsystems from the general requirement of statistical independence. Therefore, the canonical ensemble describes systems in thermal contact with a heat reservoir⁷. A detailed discussion of the canonical distribution function will be given after we introduce the concept of entropy. Here we point out only the following. The coefficient α is just a normalization constant while the coefficient β is a parameter determined by the condition of thermodynamic equilibrium. Note that β must be the same for all the subsystems in equilibrium (otherwise $\log f$ is not additive).

⁶Hypothesis VI

⁷Hypothesis VII

F. Quantum Mechanical Considerations

We consider the transcription into quantum mechanical language of some of the statements about classical mechanics which we have been using.

A. The classical equations of motion in Hamiltonian form are

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p}.$$

In the Schrödinger formulation of quantum mechanics we use the equation

$$i\hbar \frac{\partial}{\partial t} \Psi(q, t) = \hat{H}\Psi(q, t),$$

where $\hbar = h/2\pi$, \hat{H} is the Hamiltonian operator, and Ψ is the wave function.

B. The classical assumption that all accessible regions of phase space have equal *a priori* probabilities is replaced in quantum statistical mechanics by the statement that all accessible states have equal *a priori* probabilities and random phases.

C. Classical integrals of the form $\int A(q, p)d\Gamma$ in phase space are replaced by sums $\sum_i A_i$ over all eigenstates i of the Hamiltonian operator, where A_i denotes the expectation value of quantity A in the i th eigenstate. An integral of particular importance which we shall encounter later is the *partition function* for the canonical ensemble:

$$Z = \int e^{-E(q,p)/k_B T} d\Gamma;$$

in quantum statistical mechanics the partition function for the canonical ensemble is

$$Z = \sum_i e^{-E_i/k_B T}.$$

In quantum statistical mechanics, the number of eigenstates of the Hamiltonian operator can be counted. We now consider how we may find an absolute definition of the number of states for classical systems which will agree quantitatively with that for quantum systems, for problems where the classical and quantum solutions are similar. We wish to show that the volume in phase space equivalent to one quantum state is \hbar^{3N} , for an N particle system. The uncertainty principle

$$\Delta q_i \Delta p_i \approx \hbar$$

for each of the $3N$ degrees of freedom suggests a result of the type stated.

According to the semiclassical quantum theory,

$$\oint pdq = nh.$$

This tells us that the area in phase space swept out by the orbit in a one-dimensional problem is an integral multiple of h . The volume associated with each quantum state is h ; for N particles in three dimensions the volume in phase space would be h^{3N} , which is the natural unit for measuring $\Delta\Gamma = \int d\Gamma$.

Let us consider a free particle in quantum mechanics. The wave equation for stationary states (eigenstates of \hat{H}) is

$$\hat{H}\Psi = -\frac{\hbar^2}{2m} \frac{d^2}{dq^2} \Psi = E\Psi.$$

The plane wave solution is of the form $\Psi \sim e^{ikq}$, for which the energy is given by

$$E = \frac{\hbar^2}{2m} k^2.$$

Here $k = 2\pi/\lambda$ is called the wave vector and λ is the corresponding wavelength. The de Broglie relation can be written as $p = \hbar k$, so $E = p^2/2m$ as in classical mechanics. To quantize the particle motion, we consider that the particle is confined to a ring of length L . This ring geometry requires that the wave function be periodic in L :

$$\Psi(q + L) = \Psi(q),$$

which means that

$$k(q + L) = kq + 2\pi n,$$

where n is an integer. Therefore, the wave vector is given by

$$k_n = \frac{2\pi}{L}n, \quad n = \pm 1, \pm 2, \pm 3, \dots$$

Each value of n specifies an energy eigenstate of the system. The equivalent volume of phase space associated with a single state is

$$\delta\Gamma = L\delta p = L\hbar\delta k = L\hbar\frac{2\pi}{L} = h,$$

which is exactly the result we mentioned earlier.

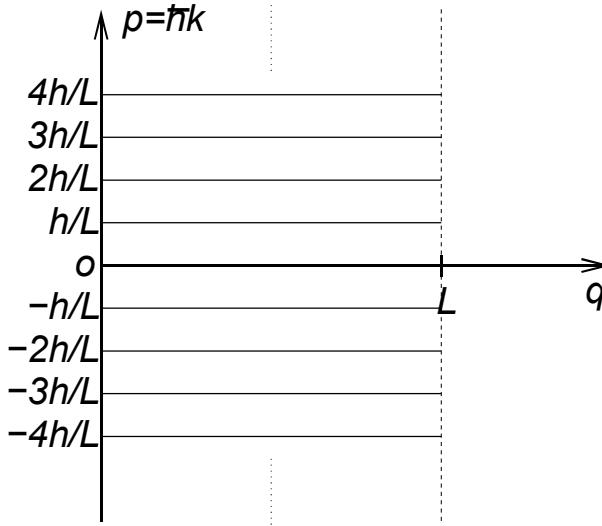


Fig. Schematic illustration of the energy eigenstates (represented by solid-line bars, discretely distributed along the p axis) obtained for a free particle confined to a ring of length L . The phase volume associated with a single state is h .

We can understand the result $\delta\Gamma = h$ in some generality by considering the quantization condition $\oint pdq = nh$ of semiclassical quantum theory. This tells us as noted above that the volume in phase space associated with the conjugate coordinates q and p is divided into cells of volume h . The argument is easily extended to an N particle system of $3N$ pairs of conjugate coordinates: the phase space is divided into cells of volume h^{3N} . Therefore, a volume $\Delta\Gamma$ in phase space corresponds to the number Δn of quantum states, where Δn is given by $\Delta n = \Delta\Gamma/h^{3N}$.

Now consider that the N particles are identical. Physically, for any two cells in the $6N$ -dimensional phase space, if they differ only by an interchange of particles in 3-dimensional real space, then they correspond to the same physical state. It is noted that for N particles, there are totally $N!$ permutations. Therefore, in calculating the number of states Δn corresponding to the phase-space volume $\Delta\Gamma$, we must use

$$\Delta n = \frac{\Delta\Gamma}{N!h^{3N}},$$

which takes the factor of $\frac{1}{N!}$ into account.

G. Entropy and The Law of Increase of Entropy

1. Entropy

For a system in thermodynamic equilibrium (the system itself can be a closed system or a subsystem of a closed system), an additive thermodynamic quantity can be defined as

$$S = -k_B \sum_n w_n \log w_n,$$

where k_B is the Boltzmann constant and w_n is the distribution function for the system, satisfying $\sum_n w_n = 1$, with n being the set of all quantum numbers which denote the various stationary states of the system. This means that the interaction of the system with the surrounding environment is entirely neglected. Otherwise, the stationary states do not exist.

Let us consider two weakly interacting subsystems whose distribution functions are given by $w_{n^{(1)}}^{(1)}$ and $w_{n^{(2)}}^{(2)}$ respectively. Here $n^{(1)}$ and $n^{(2)}$ are the two sets of quantum numbers which denote the various stationary states of the two subsystems respectively. We emphasize once again that introducing the quantum numbers $n^{(1)}$ and $n^{(2)}$ means that the interaction of either subsystem with its surrounding environment is entirely neglected. According to the statistical independence, the distribution function of the composite system formed by the two subsystems is given by

$$w_{n^{(12)}}^{(12)} = w_{n^{(1)}}^{(1)} w_{n^{(2)}}^{(2)},$$

where $n^{(12)}$ is simply a combination of $n^{(1)}$ and $n^{(2)}$. From $w^{(12)} = w^{(1)}w^{(2)}$ and the normalization conditions $\sum_{n^{(12)}} w_{n^{(12)}}^{(12)} = 1$, $\sum_{n^{(1)}} w_{n^{(1)}}^{(1)} = 1$, and $\sum_{n^{(2)}} w_{n^{(2)}}^{(2)} = 1$, it is readily seen that $S^{(12)} = -k_B \sum_{n^{(12)}} w_{n^{(12)}}^{(12)} \log w_{n^{(12)}}^{(12)}$, $S^{(1)} = -k_B \sum_{n^{(1)}} w_{n^{(1)}}^{(1)} \log w_{n^{(1)}}^{(1)}$, and $S^{(2)} = -k_B \sum_{n^{(2)}} w_{n^{(2)}}^{(2)} \log w_{n^{(2)}}^{(2)}$ satisfy

$$S^{(12)} = S^{(1)} + S^{(2)}.$$

Hence S is an additive quantity.

The quantity S defined above is called the entropy. It is of central importance in both the statistical physics and the thermodynamics. The physical meaning of the entropy can be seen clearly if the microcanonical or the canonical distribution function is substituted into $S = -k_B \sum_n w_n \log w_n$. For the microcanonical distribution, $w_n = \frac{1}{\Delta\Gamma}$, where $\Delta\Gamma$ is the number of stationary states with energy distributed between E_0 and $E_0 + \Delta E$. It follows

$$S = k_B \log \Delta\Gamma.$$

For the canonical distribution, $w_n = \frac{\exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)}$, and

$$S = -k_B \log w(\langle E \rangle),$$

where $\langle E \rangle$ is the mean energy $\sum_n w_n E_n$ and $w(\langle E \rangle) = \frac{\exp(-\beta \langle E \rangle)}{\sum_n \exp(-\beta E_n)}$ is the occupation probability for any stationary state of energy $E_n = \langle E \rangle$. Since the energy probability distribution is very sharp around the mean energy $\langle E \rangle$, the inverse of $w(\langle E \rangle)$, $\frac{1}{w(\langle E \rangle)}$, can be regarded as the “degree of broadening” of the macroscopic state of the system with respect to its microscopic states. Therefore $\Delta\Gamma = \frac{1}{w(\langle E \rangle)}$ is the number of microscopic states corresponding to the canonical distribution and

$$S = k_B \log \Delta\Gamma.$$

The above results can be readily applied to classical statistics. With the help of the quantum mechanical uncertainty principle, we use the relations

$$\sum_n \rightarrow \int \frac{dq dp}{(2\pi\hbar)^s}$$

and

$$w_n \rightarrow (2\pi\hbar)^s f(q, p)$$

to define the entropy as

$$S = -k_B \int dq dp f(q, p) \log[(2\pi\hbar)^s f(q, p)].$$

For the microcanonical distribution, $f(q, p) = \frac{1}{\Delta q \Delta p}$, where $\Delta q \Delta p$ is the phase volume for $E(q, p)$ between E_0 and $E_0 + \Delta E$. It follows $S = k_B \log \Delta\Gamma$, where $\Delta\Gamma = \frac{\Delta q \Delta p}{(2\pi\hbar)^s}$ is

the number of quantum states “contained” in the phase volume $\Delta q\Delta p$. For the canonical distribution,

$$f(q, p) = \frac{\exp[-\beta E(q, p)]}{\int dq dp \exp[-\beta E(q, p)]},$$

and

$$S = -k_B \log[(2\pi\hbar)^s f(\langle E \rangle)],$$

where $\langle E \rangle$ is the mean energy $\int dq dp f(q, p)E(q, p)$ and $f(\langle E \rangle)$ is the phase-space probability density at any phase point (q, p) of energy $E(q, p) = \langle E \rangle$. Since the energy probability distribution is very sharp around the mean energy $\langle E \rangle$, the inverse of $f(\langle E \rangle)$, $\frac{1}{f(\langle E \rangle)}$, can be regarded as the “degree of broadening” of the macroscopic state of the system with respect to its microscopic states. Therefore $\Delta q\Delta p = \frac{1}{f(\langle E \rangle)}$ is the phase volume of the corresponding microscopic states, $\Delta\Gamma = \frac{\Delta q\Delta p}{(2\pi\hbar)^s}$ is the number of quantum states which are “contained” in the phase volume $\Delta q\Delta p$, and $S = k_B \log \Delta\Gamma$.

2. Partial equilibrium

So far the entropy has been defined for systems in complete equilibrium. Now we show that the entropy can be defined as well for systems in arbitrary macroscopic states (which are in general inhomogeneous).

The time within which a system will reach equilibrium is called the relaxation time. Obviously, to define the entropy for arbitrary macroscopic states, we have to consider the system over time intervals Δt which are small compared with the relaxation time. Physically, the relaxation time in general decreases with decreasing size of the system. Bearing this in mind, we divide the system in inhomogeneous macroscopic state into many small parts; each part is so small that its own relaxation time is much smaller than Δt . Therefore the inhomogeneous macroscopic system can be regarded as being composed of many small subsystems, each is homogeneous and already in its own equilibrium state according to certain distribution function $w_{n^{(i)}}^{(i)}$. Such an inhomogeneous macroscopic system is said to be

in partial equilibrium. We then apply the equation of definition $S = -k_B \sum_n w_n \log w_n$ to calculate the entropy $S^{(i)} = -k_B \sum_n w_{n^{(i)}}^{(i)} \log w_{n^{(i)}}^{(i)}$ for each part. The entropy of the whole system is given by $S = \sum_i S^{(i)}$. We emphasize that the statistical independence is implied in defining the entropy for systems in partial equilibria.

Multiple time scales: *Here we have three distinct time scales, the relaxation time of the whole system T_r , the time interval Δt over which the entropy is defined (first for the subsystems in partial equilibria and then for the whole system based on the additivity of entropy), and the relaxation time of a subsystem τ_r . Obviously, to validate the above argument, we require (1) $\tau_r \ll \Delta t$ for defining the entropy of subsystems in partial equilibria; (2) $\Delta t \ll T_r$ for defining the entropy of the whole system which may in general vary in time. Essentially, the time interval Δt is deemed to be microscopically long ($\tau_r \ll \Delta t$ to allow partial equilibria) but macroscopically short ($\Delta t \ll T_r$ to allow time resolution). This separation of different time scales is essential to the theory of regression of fluctuations (Onsager 1931).*

We want to point out that the above description of partial equilibrium is consistent with the earlier discussion about the quasi-closed subsystems: For each subsystem, the particles which take part in the interaction with the surrounding parts are those near the surface of the subsystem; the relative number of such particles, compared with the total number of particles in the subsystem, decreases rapidly as the size of the subsystem increases. Therefore when the subsystem is sufficiently large, the energy of its interaction with the surrounding parts will be negligibly small compared with its internal energy. That the inter-subsystem interaction is much weaker than the intra-subsystem interaction leads to partial equilibria: each subsystem has already reached its own equilibrium but the whole system has not yet.

3. The law of increase of entropy

Complete statistical equilibrium is specified by some statistical distribution function that gives the maximum possible value of entropy. Examples include microcanonical, canonical,

and grandcanonical distributions, which give the maximum entropy for closed systems, systems of given average energy, and systems of given average energy and average particle number, respectively. The law of increase of entropy states that if a closed system is not in statistical equilibrium, then its macroscopic state will vary in time and the entropy will increase, until ultimately the system reaches the complete equilibrium. (Remember how a time-varying entropy is defined for a nonequilibrium macroscopic state.) According to the statistical meaning of entropy, the increase of entropy in a closed system approaching complete equilibrium means that more and more microscopic states become accessible by the evolving macroscopic state.

II. EQUILIBRIUM STATISTICAL MECHANICS

This section is concerned with two most important statistical ensembles: the microcanonical ensemble and the canonical ensemble. The microcanonical ensemble is of fundamental value while the canonical ensemble is more widely used. For more details, see C. Kittel, *Elementary Statistical Physics*.

A. The Microcanonical Ensemble

The energy is a constant of motion for a conservative system. If the energy of the system is prescribed to be in the range δE at E_0 , we may, according to the preceding section, form a satisfactory ensemble by taking the density as equal to zero except in the selected narrow range δE at E_0 : $P(E) = \text{constant}$ for energy in δE at E_0 and $P(E) = 0$ outside this range. This particular ensemble is known as the microcanonical ensemble. It is appropriate to the discussion of an isolated system because the energy of an isolated system is a constant.

Let us consider the implications of the microcanonical ensemble. We are given an isolated classical system with constant energy E_0 . At time t_0 the system is characterized by definite values of position and velocity for each particle in the system. The macroscopic average physical properties of the system could be calculated by following the motion of the particles over a reasonable interval of time. We do not consider the time average, but consider instead an average over an ensemble of systems each at constant energy within δE at E_0 . The microcanonical ensemble is arranged with constant density in the region of phase space accessible to the system. Here we have made as a fundamental postulate the assumption of *equal a priori probabilities for different accessible regions of equal volume in phase space*.

1. Entropy

The entropy of the microcanonical ensemble is

$$S = k_B \log \Delta\Gamma,$$

where $\Delta\Gamma$ is the number of states with energy distributed between E_0 and $E_0 + \Delta E$. Remember that the general definition of the entropy is $S = -k_B \sum_n w_n \log w_n$, where k_B is the Boltzmann constant and w_n is the distribution function for the system, satisfying $\sum_n w_n = 1$, with n being the set of all quantum numbers which denote the various stationary states of the system. The entropy of the microcanonical ensemble is obtained from a maximization of $S = -k_B \sum_n w_n \log w_n$ with respect to w_n , subject to the normalization condition $\sum_n w_n = 1$ and the energy condition that w_n is nonzero only if the corresponding energy is in the selected narrow range δE at E_0 .

2. Conditions for equilibrium

The entropy is a maximum when a closed system is in equilibrium. The value of S for a system in equilibrium depends on the energy U of the system; on the number N_i of each molecular species i of the system; and on external variables x_ν , such as volume, strain, magnetization. In other words,

$$S = S(U, x_\nu, N_i).$$

We consider the condition for equilibrium in a system made up of two interconnected subsystems. Initially the subsystems are separated from each other by a rigid, insulating, non-permeable barrier.

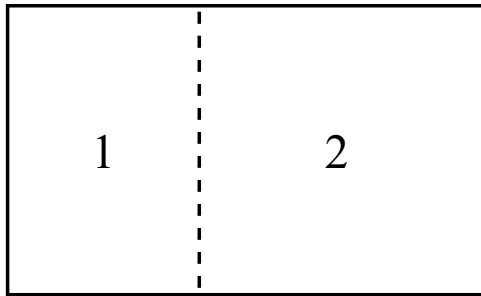


Fig. A closed system made up of two interconnected subsystems.

Weakly interacting quasi-closed subsystems: *In the following discussion, we consider two weakly interacting quasi-closed subsystems 1 and 2. On the one hand, the two*

subsystems are quasi-closed and hence $S = S_1 + S_2$ from the statistical independence. On the other hand, weak coupling is assumed between the two subsystems. This allows the whole (closed) system to relax towards complete equilibrium (e.g., via energy transfer between the two subsystems) if the total entropy is not maximized.

Thermal equilibrium

Imagine that the barrier is allowed to transmit energy (beginning at one instant of time), with other inhibitions remaining in effect. If the conditions of the two subsystems 1 and 2 do not change, then they are in *thermal equilibrium* and the entropy of the total system must be a maximum with respect to small transfer of energy from one subsystem to the other. Using the additive property of the entropy,

$$S = S_1 + S_2,$$

we have in equilibrium

$$\delta S = \delta S_1 + \delta S_2 = 0,$$

or

$$\delta S = \left(\frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left(\frac{\partial S_2}{\partial U_2} \right) \delta U_2 = 0.$$

Because the total system is thermally closed and the total energy is constant, i.e., $\delta U = \delta U_1 + \delta U_2 = 0$, we have

$$\delta S = \left[\left(\frac{\partial S_1}{\partial U_1} \right) - \left(\frac{\partial S_2}{\partial U_2} \right) \right] \delta U_1 = 0.$$

As δU_1 is an arbitrary variation, we obtain in thermal equilibrium

$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}.$$

Defining the *temperature* T by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{x_\nu, N_i},$$

we obtain $T_1 = T_2$ as the condition for thermal equilibrium.

Suppose that the two subsystems were not originally in thermal equilibrium, but that $T_2 > T_1$. When thermal contact is established to allow energy transmission, the total entropy

S will increase. (The removal of any constraint can only increase the volume of phase space accessible to the system.) Thus, after thermal contact is established, $\delta S > 0$, or

$$\left[\left(\frac{\partial S_1}{\partial U_1} \right) - \left(\frac{\partial S_2}{\partial U_2} \right) \right] \delta U_1 > 0,$$

and

$$\left[\frac{1}{T_1} - \frac{1}{T_2} \right] \delta U_1 > 0.$$

Assuming $T_2 > T_1$, we have $\delta U_1 > 0$. This says that energy passes from the system of high T to the system of low T . So T is indeed a quantity that behaves qualitatively like a temperature.

Mechanical equilibrium

Now imagine that the wall is allowed to move and also passes energy, but does not pass particles. The volumes V_1 and V_2 of the two subsystems can readjust to (further) maximize the entropy. In mechanical equilibrium

$$\delta S = \left(\frac{\partial S_1}{\partial V_1} \right) \delta V_1 + \left(\frac{\partial S_2}{\partial V_2} \right) \delta V_2 + \left(\frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left(\frac{\partial S_2}{\partial U_2} \right) \delta U_2 = 0.$$

After thermal equilibrium has been established, we have

$$\left(\frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left(\frac{\partial S_2}{\partial U_2} \right) \delta U_2 = 0.$$

As the total volume $V = V_1 + V_2$ is constant, we have $\delta V = \delta V_1 + \delta V_2 = 0$, and

$$\delta S = \left[\left(\frac{\partial S_1}{\partial V_1} \right) - \left(\frac{\partial S_2}{\partial V_2} \right) \right] \delta V_1 = 0.$$

As δV_1 is an arbitrary variation, we obtain in mechanical equilibrium

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}.$$

Defining the *pressure* Π by

$$\frac{\Pi}{T} = \left(\frac{\partial S}{\partial V} \right)_{U, N_i},$$

we see that for a system in thermal equilibrium ($T_1 = T_2$), $\Pi_1 = \Pi_2$ is the condition for mechanical equilibrium. In general we define a generalized force X_ν related to the coordinate x_ν by the equation

$$\frac{X_\nu}{T} = \left(\frac{\partial S}{\partial x_\nu} \right)_{U,N_i}.$$

Suppose that the two subsystems in thermal equilibrium were not originally in mechanical equilibrium, but that $\Pi_1 > \Pi_2$. When the wall is allowed to move, the total entropy S will increase. (The removal of any constraint can only increase the volume of phase space accessible to the system.) From

$$\delta S = \left[\left(\frac{\partial S_1}{\partial V_1} \right) - \left(\frac{\partial S_2}{\partial V_2} \right) \right] \delta V_1 = \frac{1}{T} [\Pi_1 - \Pi_2] \delta V_1 > 0,$$

we see that $\Pi_1 > \Pi_2$ requires $\delta V_1 > 0$: the subsystem of the higher pressure expands in volume. So Π is indeed a quantity that behaves qualitatively like a pressure.

Particle equilibrium

Now imagine that the wall allows diffusion through it of molecules of the i th chemical species. Suppose thermal equilibrium and mechanical equilibrium have already been established. From $\delta N_{i1} + \delta N_{i2} = 0$ and

$$\delta S = \left[\left(\frac{\partial S_1}{\partial N_{i1}} \right) - \left(\frac{\partial S_2}{\partial N_{i2}} \right) \right] \delta N_{i1} = 0,$$

we obtain

$$\frac{\partial S_1}{\partial N_{i1}} = \frac{\partial S_2}{\partial N_{i2}},$$

as the condition for particle equilibrium. Defining the *chemical potential* μ_i by

$$-\frac{\mu_i}{T} = \left(\frac{\partial S}{\partial N_i} \right)_{U,x_\nu},$$

we see that for a system in both thermal equilibrium ($T_1 = T_2$) and mechanical equilibrium ($\Pi_1 = \Pi_2$), $\mu_{i1} = \mu_{i2}$ is the condition for particle equilibrium. It is easy to show that particles tend to move from a region of higher chemical potential to that of a lower chemical potential as the system approaches equilibrium ($\delta S > 0$).

3. Connection between statistical and thermodynamical quantities

For a system in equilibrium, $S = S(U, x_\nu, N_i)$, where U is the energy, x_ν denotes the set of external parameters describing the system, and N_i is the number of molecules of the several species present. If the conditions are changed slightly, but reversibly in such a way that the resulting system is also in equilibrium, we have

$$dS = \left(\frac{\partial S}{\partial U} \right) dU + \sum_\nu \left(\frac{\partial S}{\partial x_\nu} \right) dx_\nu + \sum_i \left(\frac{\partial S}{\partial N_i} \right) dN_i = \frac{dU}{T} + \frac{1}{T} \sum_\nu X_\nu dx_\nu - \frac{1}{T} \sum_i \mu_i dN_i,$$

which may be rewritten as

$$dU = TdS - \sum_\nu X_\nu dx_\nu + \sum_i \mu_i dN_i.$$

Consider that the number of particles is fixed and the volume is the only external parameter: $dN_i = 0$; $x_\nu \equiv V$; $X_\nu \equiv \Pi$. Then,

$$dU = TdS - \Pi dV.$$

We see that the change of internal energy consists of two parts. The term TdS represents the change in U when the external parameters are kept constant ($dV = 0$). This is what meant by *heat*. Thus

$$DQ = TdS$$

is the quantity of heat added to the system in a *reversible* process. The symbol D is used instead of d because DQ is not an exact differential — that is, Q is not a state function. The term $-\Pi dV$ is the change in internal energy caused by the change in external parameters; this is what we mean by mechanical work, and

$$DW = -\Pi dV$$

is the work done on the system through the volume change dV . By elementary mechanics $DW = -pdV$, hence $\Pi \equiv p$. Therefore the change in internal energy may be expressed as

$$dU = DQ + DW,$$

which is the *First Law of Thermodynamics*.

That $dS = DQ/T$ is an exact differential in a reversible process is a statement of the *Second Law of Thermodynamics*. That is, DQ/T is a differential of a state function, entirely defined by the state of the system. Now we know that state function is the entropy.

On $S = S(U, V)$: Here the discussion on various thermodynamic quantities starts from $S = S(U, V)$ in equilibrium and $dS = dU/T + pdV/T$ for reversible processes. The evaluation of S as a function of U and V can be carried out using the microcanonical ensemble which is characterized by U and V . This will be done for the ideal gas.

We are ready to express U as a function of S and V : $U = U(S, V)$. Other quantities of interest are then obtained from $U(S, V)$:

$$dU = TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV,$$

from which

$$T = \left(\frac{\partial U}{\partial S}\right)_V;$$

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_S.$$

However, S and V are often inconvenient independent variables; it is more convenient to work with T, V or T, p . For this purpose we introduce some *thermodynamic potentials*: F and G .

Helmholtz free energy

The Helmholtz free energy F is defined as

$$F(T, V) \equiv U - TS,$$

where $T = \left(\frac{\partial U}{\partial S}\right)_V$ has been used to replace S by T as an independent variable. From $dU = TdS - pdV$ and

$$dF = dU - TdS - SdT = -SdT - pdV = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV,$$

we obtain

$$-S = \left(\frac{\partial F}{\partial T} \right)_V,$$

and

$$-p = \left(\frac{\partial F}{\partial V} \right)_T.$$

Therefore, if the Helmholtz free energy F is expressed as a function of independent variables T and V , then S and p are readily calculated.

On the Helmholtz free energy F : *While the definition of $F \equiv U - TS$ is applicable to arbitrary macroscopic states (so long as there is partial equilibrium and hence the entropy can be defined), the total differential $dF = -SdT - pdV$ is obtained for reversible processes only. That is, $-S = (\partial F / \partial T)_V$ and $-p = (\partial F / \partial V)_T$ are relations for equilibrium states only. It will be shown that for an equilibrium system of fixed T and V , $F(T, V)$ can be obtained from the partition function of canonical ensemble.*

Consider a thermodynamic process at constant temperature T . The change in F is given by $\Delta F = \Delta U - T\Delta S = (\Delta Q - T\Delta S) + \Delta W$. For a reversible process, $\Delta Q = T\Delta S$, and hence $\Delta F = \Delta W$. For an irreversible process, however, $\Delta Q < T\Delta S$ according to the second law of thermodynamics, and hence $\Delta F < \Delta W$. That $-\Delta W \leq -\Delta F$ means the maximum work which can be done by the system is the decrease of F . If the volume is fixed, then $\Delta W = 0$ and $\Delta F \leq 0$. That is, at constant temperature and volume, the Helmholtz free energy varies towards a minimum, which is just $F(T, V)$ for the final equilibrium state.

On $\Delta Q \leq T\Delta S$: *Consider a system in contact with a large heat bath such that a constant temperature T is maintained. If ΔQ is the heat received by the system from the heat bath, then the heat received by the heat bath from the system is $-\Delta Q$. Assuming that the change in the heat bath is reversible, we have $-\Delta Q/T$ as the change of its entropy. That the total entropy tends to increase means $-\Delta Q/T + \Delta S \geq 0$, i.e., $\Delta Q \leq T\Delta S$.*

Gibbs free energy

The Gibbs free energy G is defined as

$$G(T, p) \equiv U - TS + pV,$$

where $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $p = -\left(\frac{\partial U}{\partial V}\right)_S$ has been used to replace S and V by T and p as the two independent variables. From $dU = TdS - pdV$ and

$$dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp,$$

we obtain

$$-S = \left(\frac{\partial G}{\partial T}\right)_p ,$$

and

$$V = \left(\frac{\partial G}{\partial p}\right)_T .$$

Therefore, if the Gibbs free energy G is expressed as a function of independent variables T and p , then S and V are readily calculated.

Consider a thermodynamic process at constant temperature T and pressure p . The change in G is given by $\Delta G = \Delta U - T\Delta S + p\Delta V = (\Delta Q - T\Delta S) + \Delta W + p\Delta V = \Delta Q - T\Delta S$. For a reversible process, $\Delta Q = T\Delta S$, and hence $\Delta G = 0$. For an irreversible process, $\Delta Q < T\Delta S$, and hence $\Delta G < 0$. Therefore, at constant temperature and pressure, the Gibbs free energy tends to a minimum.

4. Calculation of the entropy of a perfect gas using the microcanonical ensemble

Consider the microcanonical ensemble for N non-interacting point particles of mass m confined in the volume V with total energy in δU at U . The accessible volume of phase space is

$$\Delta\Gamma = \int dq_1 \cdots dq_{3N} \int dp_1 \cdots dp_{3N} = V^N \int dp_1 \cdots dp_{3N},$$

where the $3N$ -dimensional momentum space integral is to be evaluated subject to the constraint that

$$U - \delta U \leq \frac{1}{2m} \sum_{i=1}^{3N} p_i^2 \leq U.$$

The accessible volume in momentum space is that of a shell of thickness $\delta U \sqrt{m/2U}$ on a hypersphere of radius $\sqrt{2mU}$. We can prove that, for a system of particle number $N \sim 10^{23}$,

the value of $\log \Delta\Gamma$ is not sensitive to the value of δU , and we may replace the shell of thickness $\delta U \sqrt{m/2U}$ by the entire sphere of radius $\sqrt{2mU}$.

The volume of a ν -dimensional hypersphere of radius R can be written as

$$V(R) = CR^\nu,$$

from which the volume of a shell of thickness s at the surface of this hypersphere is

$$V_s = V(R) - V(R-s) = C[R^\nu - (R-s)^\nu] = V(R) \left[1 - \left(1 - \frac{s}{R}\right)^\nu \right].$$

Therefore, if ν is large enough so that $s\nu \gg R$, V_s is practically given by the volume $V(R)$ of the whole sphere. Since $\nu = 3N \sim 10^{23}$ for a macroscopic system, the momentum space integral in $\Delta\Gamma$ is then replaced by the volume of the $3N$ -dimensional sphere of radius $\sqrt{2mU}$.

To evaluate this volume, consider the integrals

$$\mathcal{J} = \int_{-\infty}^{\infty} e^{-(x_1^2 + x_2^2 + \dots + x_\nu^2)} dx_1 dx_2 \dots dx_\nu = \left(\int_{-\infty}^{\infty} e^{-x^2} dx \right)^\nu = \pi^{\nu/2},$$

and

$$\mathcal{J} = \int_0^{\infty} e^{-r^2} r^{\nu-1} S_\nu dr = \frac{S_\nu}{2} \int_0^{\infty} e^{-t} t^{(\nu-2)/2} dt = \frac{S_\nu}{2} \left(\frac{\nu}{2} - 1 \right)!,$$

where $r^{\nu-1} S_\nu$ denotes the surface area of the ν -dimensional sphere. It follows

$$S_\nu = \frac{2\pi^{\nu/2}}{(\nu/2 - 1)!},$$

from which the volume of the sphere of radius R is obtained as

$$\Omega = \int_0^R S_\nu r^{\nu-1} dr = \frac{\pi^{\nu/2}}{(\nu/2)!} R^\nu.$$

Then the volume of the accessible region in phase space is obtained as

$$\Delta\Gamma = V^N \frac{\pi^{3N/2}}{(3N/2)!} (2mU)^{3N/2},$$

from which the entropy $S = k_B \log \Delta\Gamma$ is also obtained:

$$\begin{aligned} S &= Nk_B \log [V\pi^{3/2} (2mU)^{3/2}] - \frac{3Nk_B}{2} \log \frac{3N}{2} + \frac{3Nk_B}{2} \\ &= Nk_B \log [V (4\pi m/3)^{3/2} (U/N)^{3/2}] + \frac{3Nk_B}{2}, \end{aligned}$$

using the Stirling approximation ($\ln n! \approx n \ln n - n$) for large N .

However, the entropy obtained above is not additive. Now consider that the N particles are identical. Physically, for any two points in the $6N$ -dimensional phase space, if they differ only by an interchange of particles in real space, then they correspond to the same state. Therefore, in calculating $\Delta\Gamma$, we must use $\frac{1}{N!} \int dq_1 \cdots dq_{3N}$ instead of $\int dq_1 \cdots dq_{3N}$. Taking the factor of $\frac{1}{N!}$ into account and introducing h^{3N} as the unit of volume in phase space, we obtain the entropy

$$S = k_B \log \frac{\Delta\Gamma}{N! h^{3N}} = Nk_B \log \left[\frac{(2\pi m)^{3/2} e(V/N)(U/N)^{3/2}}{(3/2)^{3/2} h^3} \right] + \frac{3Nk_B}{2},$$

which is additive. Here h is Planck's constant.

According to the definition of the temperature, we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{3Nk_B}{2} \frac{\partial}{\partial U} \log U = \frac{3Nk_B}{2U},$$

so that the internal energy of a perfect monatomic gas is related to the temperature through

$$U = \frac{3Nk_B T}{2}.$$

According to the definition of the pressure, we have

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N} = Nk_B \frac{\partial}{\partial V} \log V = \frac{Nk_B}{V},$$

so that the equation of state is

$$pV = Nk_B T.$$

Substituting $U/N = 3k_B T/2$ into the expression of S , we obtain

$$S = Nk_B \log \left[\left(2\pi m k_B T / h^2 \right)^{3/2} e(V/N) \right] + \frac{3Nk_B}{2}.$$

The *thermal de Broglie wavelength* λ associated with a molecule is defined by

$$\lambda = \frac{h}{(2\pi m k_B T)^{1/2}},$$

and in terms of λ , the entropy may be expressed as

$$S = Nk_B \log \left[e(V/N) / \lambda^3 \right] + \frac{3Nk_B}{2}.$$

B. The Canonical Ensemble

The microcanonical ensemble is a general statistical method, but usually it is very difficult to use because of the difficulty in evaluating the volume of phase space accessible to the system. The canonical ensemble invented by Gibbs avoids some of the difficulties, and leads us easily to the Boltzmann factor $\exp(-\Delta E/k_B T)$ for the ratio of populations of two states differing by ΔE in energy. We shall see that the canonical ensemble describes systems in thermal contact with a heat reservoir; the microcanonical ensemble describes systems which are perfectly insulated.

Consider a microcanonical ensemble representing a very large system. We imagine that each system of the ensemble is divided into a large number of subsystems which are in mutual thermal contact and can exchange energy with each other. The subsystems will have the same physical constitution as the large system (neglecting interaction effects between subsystems). We focus on the distribution function for one subsystem denoted by s ; the rest of the system is denoted by r and referred to as a heat reservoir. The total system is denoted by t .

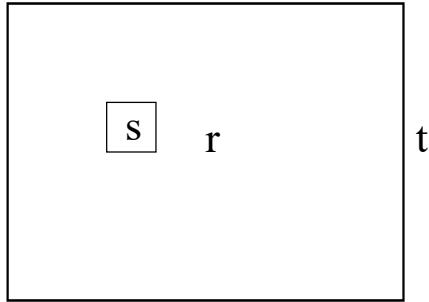


Fig. The total system (t) formed by a subsystem (s) and a heat reservoir (r).

Let dw_t denote the probability that the total system is in an element of volume $d\Gamma_t$ of the appropriate phase space. The total system is described by the microcanonical ensemble, thus

$$dw_t = C d\Gamma_t,$$

if the energy is in δE_t at E_t , and $dw_t = 0$ otherwise; here C is a normalization constant. We

write

$$d\Gamma_t = d\Gamma_s d\Gamma_r,$$

factorizing the elements of the total phase space into a factor containing coordinates and momenta belonging to the subsystem s and a similar factor for the heat reservoir r . Thus

$$dw_t = Cd\Gamma_t = Cd\Gamma_s d\Gamma_r,$$

if $d\Gamma_t = d\Gamma_s d\Gamma_r$ is accessible, and $dw_t = 0$ otherwise.

Now we introduce the probability dw_s that the subsystem is in $d\Gamma_s$, *without specifying the condition of the reservoir*, but still requiring that the total energy be in δE_t at E_t . Then

$$dw_s = \int_{\Delta\Gamma_r} dw_t = Cd\Gamma_s \int_{\Delta\Gamma_r} d\Gamma_r = Cd\Gamma_s \Delta\Gamma_r,$$

where $\Delta\Gamma_r$ is the volume of the accessible phase space of the reservoir r , determined by the condition that the energy of the total system is in δE_t at E_t . Our task is to evaluate $\Delta\Gamma_r$; that is, given that the subsystem is in $d\Gamma_s$ and that the total energy $E_s + E_r$ is δE_t at E_t , how much phase space is accessible to the reservoir?

The entropy of the reservoir is $S_r = k_B \log \Delta\Gamma_r$, so that

$$\Delta\Gamma_r = e^{S_r/k_B},$$

where $\Delta\Gamma_r$ and S_r are both functions of the energy of the reservoir E_r . We note that $E_r = E_t - E_s$ and $E_s \ll E_t$ because the subsystem is assumed to be small in comparison to the total system. Using the expansion

$$S_r(E_r) = S_r(E_t - E_s) = S_r(E_t) - \frac{\partial S_r(E_t)}{\partial E_t} E_s + \dots,$$

we have

$$\Delta\Gamma_r(E_r) = e^{S_r(E_r)/k_B} = e^{S_r(E_t)/k_B} \exp \left[-\frac{\partial S_r(E_t)}{\partial E_t} \frac{E_s}{k_B} \right] = e^{S_r(E_t)/k_B} \exp \left[-\frac{E_s}{k_B T} \right],$$

where the definition $1/T = \partial S_r(E_t)/\partial E_t$ has been used. Here the temperature T applies to both the reservoir and the subsystem, which are in thermal contact.

Finally, the probability for the subsystem in $d\Gamma_s$ is obtained:

$$dw_s = Cd\Gamma_s \Delta\Gamma_r = Ce^{S_r(E_t)/k_B} \exp\left[-\frac{E_s}{k_B T}\right] d\Gamma_s = A \exp\left[-\frac{E_s}{k_B T}\right] d\Gamma_s,$$

where $A = Ce^{S_r(E_t)/k_B}$ is a quantity for normalization:

$$\int dw_s = A \int \exp\left[-\frac{E_s}{k_B T}\right] d\Gamma_s = 1.$$

Therefore, for the subsystem the probability density is given by the *canonical ensemble*

$$\rho(E) = Ae^{-E/k_B T},$$

where here and henceforth the subscript s is dropped, and E is the energy of the entire subsystem. The average value of a quantity $Q(q, p)$ over a canonical distribution is given by

$$\bar{Q} = \int Q(q, p) \rho(q, p) d\Gamma = \frac{\int Q(q, p) e^{-E(q, p)/k_B T} d\Gamma}{\int e^{-E(q, p)/k_B T} d\Gamma}.$$

Weak interaction between the subsystem and the heat reservoir: *In the above discussion, the reservoir is regarded as quasi-closed. On the one hand, it is regarded as a closed system for which the formulae $\Delta\Gamma_r = e^{S_r/k_B}$ and $1/T = \partial S_r(E_t)/\partial E_t$ have been used. (The first relation is for the entropy of a microcanonical ensemble, and the second is for the definition of temperature in the microcanonical ensemble.) On the other hand, the reservoir is not entirely closed because it has energy exchange with the subsystem (via some weak interaction). Of course, the interaction is assumed to be so weak that the presence of the “small” subsystem does not affect the closedness of the reservoir.*

Principle of equipartition of energy

Consider one of the variables in the energy, say the variable p_j . A situation of particular importance occurs when p_j is an additive quadratic term in the energy:

$$E = bp_j^2 + \text{other terms not containing } p_j.$$

We then calculate the average energy associated with p_j :

$$\overline{\epsilon(p_j)} = \overline{bp_j^2} = \frac{\int bp_j^2 e^{-bp_j^2/k_B T} dp_j}{\int e^{-bp_j^2/k_B T} dp_j} = \frac{1}{2} k_B T,$$

as the other terms in the exponent are canceled in the numerator and denominator. We have obtained an important result: in a classical problem the average energy associated with each variable which contributes a *quadratic* term to the energy has the value $\frac{1}{2}k_B T$ in thermal equilibrium. This is known as the principle of equipartition of energy. For a free atom the Hamiltonian is $H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$, a total of three quadratic terms. The thermal energy is therefore $U = N\bar{H} = \frac{3Nk_B T}{2}$ for N atoms. This is the internal energy for a perfect gas of N atoms.

1. Elementary example of energy distribution

Consider a system of N independent particles, each bearing a magnetic momentum μ which may be directed either parallel or antiparallel to an external field H . The energy of each particle is $\pm\mu H$, depending on the orientation of the magnetic moment.

Number of states

We first derive the number of states in which there are $(N+n)/2$ moments being positive and $(N-n)/2$ moments being negative, such that the net moment is $n\mu$ and the total energy is $-n\mu H$. This number is given by

$$W(n) = \frac{N!}{[(N+n)/2]![(N-n)/2]!},$$

which satisfies

$$\sum_{n=-N}^N W(n) = 2^N,$$

where 2^N is the total number of different arrangements. Using the Stirling approximation, we write $W(n)$ as

$$W(n) \approx B \exp \left[-\frac{n^2}{2N} \right],$$

where B is a constant for normalization: $\sum_{n=-N}^N W(n) = 2^N$.

Energy distribution

We then represent the system of N moments by a canonical ensemble. The probability of finding the system in a particular state of net moment $n\mu$ is $\rho(n) = Ae^{-E/k_B T}$, where

$E = -n\mu H$. It follows that the probability of finding the system in any state of net moment $n\mu$ is

$$p(n) = W(n)\rho(n) \approx C \exp \left[-\frac{n^2}{2N} + \frac{n\mu H}{k_B T} \right],$$

where $C = AB$ is a quantity for normalization: $\sum_{n=-N}^N p(n) = 1$. In equilibrium the average moment $\bar{n}\mu$ is given by

$$\bar{n} = \sum_{n=-N}^N np(n) \approx \int np(n)dn = \frac{\mu H}{k_B T} N,$$

which is also the most probable value of n : $[\partial p(n)/\partial n]|_{\bar{n}} = 0$.

The probability $p(n)$ may be rewritten as

$$p(n) \approx C' \exp \left[-\frac{(n - \bar{n})^2}{2N} \right].$$

That is, n has a Gaussian distribution about \bar{n} with variance N :

$$\int (n - \bar{n})^2 p(n)dn = N,$$

which implies that the width of energy distribution δE is

$$\delta E = \sqrt{\int (E - \bar{E})^2 p(n)dn} = \sqrt{N} \mu H.$$

It follows that

$$\frac{\delta E}{|\bar{E}|} = \frac{\sqrt{N}}{\bar{n}} = \frac{1}{\sqrt{N}} \frac{k_B T}{\mu H},$$

which suggests that *the energy of a large system is very well defined indeed*. Here the large system means that the number of degrees of freedom is very large. From the narrow energy distribution in canonical ensemble, we expect that the microcanonical ensemble and the canonical ensemble are equivalent in describing a macroscopic system. Nevertheless, the canonical ensemble is much easier to work with because we do not have to arrange to keep the total energy constant or within bounds.

2. Thermodynamic functions for the canonical ensemble

Let $\Gamma(E)$ denote the volume of phase space corresponding to energies less than E . Then the volume of phase space corresponding to energies between \bar{E} and $\bar{E} + \delta E$ is

$$\Delta\Gamma = \left(\frac{\partial\Gamma(E)}{\partial E} \right)_{\bar{E}} \delta E.$$

Here \bar{E} is the average value of energy:

$$\bar{E} = \frac{\int E(q, p)e^{-E(q,p)/k_B T} d\Gamma}{\int e^{-E(q,p)/k_B T} d\Gamma}.$$

We define the entropy of the canonical ensemble by $S = k_B \log \Delta\Gamma$, in which δE is the range of reasonably probable values of energy in the canonical ensemble. Let $p(E)dE$ be the canonical ensemble probability that the system will have energy in the range dE at E . Then, $p(E)dE = \rho(E)d\Gamma(E)$, and hence

$$p(E) = \rho(E) \frac{\partial\Gamma(E)}{\partial E},$$

where $\rho(E)$ is the normalized probability density in phase space: $\rho(E) = Ae^{-E/k_B T}$. In many problems, the density of states $\partial\Gamma(E)/\partial E$ increases monotonically with increasing energy, and $p(E)$ is a sharply peaked distribution. We estimate the breadth δE by $p(\bar{E})\delta E = 1$, i.e., by

$$\rho(\bar{E}) \left(\frac{\partial\Gamma(E)}{\partial E} \right)_{\bar{E}} \delta E = 1.$$

Note that $p(E)$ is normalized: $\int p(E)dE = \int \rho(E)d\Gamma(E) = 1$. This lead to

$$\Delta\Gamma = 1/\rho(\bar{E}) = A^{-1}e^{\bar{E}/k_B T} = A^{-1}e^{U/k_B T},$$

and

$$S = k_B \log \Delta\Gamma = -k_B \log A + U/T,$$

from which we have

$$k_B T \log A = U - TS.$$

Recall that the Helmholtz free energy F is defined by $F \equiv U - TS$. It follows that in the canonical ensemble, the equilibrium Helmholtz free energy is given by

$$F = k_B T \log A = -k_B T \log Z,$$

where Z is the *partition function*, defined by

$$Z \equiv \int e^{-E(q,p)/k_B T} d\Gamma$$

in classical physics or

$$Z \equiv \sum_i e^{-E_i/k_B T}$$

in quantum physics. (In classical problems involving N identical spinless particles, $Z \equiv \frac{1}{N!h^{3N}} \int e^{-E(q,p)/k_B T} d\Gamma$, where $\frac{1}{N!h^{3N}} \int d\Gamma$ may be regarded as a summation over discrete quantum states.)

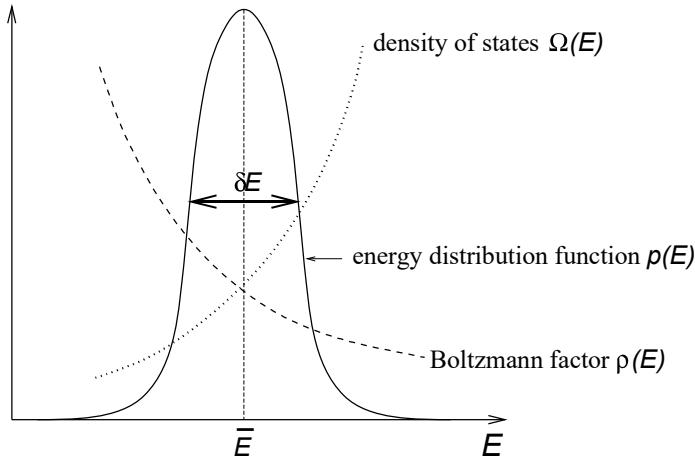


Fig. The Boltzmann factor $\rho(E)$ ($\sim e^{-E/k_B T}$) is a fast decreasing function of the energy E , the density of states $\Omega(E) = \partial\Gamma(E)/\partial E$ is a fast increasing function of E , and as a consequence, the energy distribution function $p(E) = \rho(E)\Omega(E)$ is sharply peaked around the mean energy \bar{E} .

Peaked energy distribution: According to the general discussion based on the statistical independence of (macroscopic) subsystems, the energy, being itself an additive quantity, has the relative fluctuation $\sim 1/\sqrt{N}$, in which N is a measure of the system size. This

means the energy distribution is indeed very peaked in a macroscopic system. The fact that the density of states is a fast increasing function of the energy can also be viewed as a consequence of the statistical independence of macroscopic subsystems: higher energy can be realized by more combinations of the energy states of the subsystems whereas lower energy can be realized by less combinations. In essence, the narrow distribution of the energy is due to the statistical independence and the additivity of the energy.

3. Perfect gas

We now treat the classical perfect gas using the canonical ensemble. We start from the partition function

$$Z = \frac{1}{N!h^{3N}} \int e^{-E/k_B T} d\Gamma = \frac{V^N}{N!h^{3N}} \left(\int_{-\infty}^{\infty} e^{-p_i^2/2mk_B T} dp_i \right)^{3N} = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2},$$

where

$$\begin{aligned} E &= \sum_{i=1}^{3N} \epsilon_i = \sum_{i=1}^{3N} \frac{p_i^2}{2m}; \\ d\Gamma &= \prod_{i=1}^{3N} d\Gamma_i = \prod_{i=1}^{3N} dq_i dp_i. \end{aligned}$$

Recalling the definition of λ , the thermal de Broglie wavelength, $\lambda = \frac{h}{(2\pi m k_B T)^{1/2}}$, we obtain the partition function:

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N,$$

from which the free energy F is also obtained:

$$F = -k_B T \log Z = -Nk_B T \log \left[\frac{eV}{N\lambda^3} \right].$$

Other properties such as entropy and internal energy can also be derived. The entropy is given by

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk_B \log \left[\frac{eV}{N\lambda^3} \right] + \frac{3}{2} Nk_B,$$

in agreement with the expression derived from the microcanonical ensemble. The pressure is given by

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{Nk_B T}{V},$$

also in agreement with the microcanonical ensemble result. The internal energy, defined as the average value of energy in the canonical ensemble, may be expressed by

$$U = \bar{E} = \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} = -Z^{-1} \frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} (\beta F),$$

where $\beta \equiv 1/k_B T$. Substituting $F = -Nk_B T \log \left[\frac{eV}{N\lambda^3} \right]$ into this equation yields

$$U = \frac{\partial}{\partial \beta} (\beta F) = \frac{3N}{2\beta}.$$

Comparing the two ensembles: *For the microcanonical ensemble approach, the entropy S is first evaluated as a function of U , V , and N : $S = S(U, V, N)$, from which the temperature T and the pressure p are derived from appropriate partial derivatives. For the canonical ensemble approach, the Helmholtz free energy F is first evaluated as a function of T , V , and N : $F = F(T, V, N)$, from which the entropy S , the pressure p , and the internal energy U are derived.*

4. Entropy of a system in a canonical ensemble

Let E_s be the s -th energy eigenvalue of a system, and let $p_s = \frac{e^{-E_s/k_B T}}{\sum_s e^{-E_s/k_B T}} = \frac{e^{-E_s/k_B T}}{Z}$ be the probability that the system will be found in the state s . The entropy $S = (U - F)/T$ may be expressed in the instructive form

$$S = -k_B \sum_s p_s \log p_s.$$

The proof is simple. Using $U = \sum_s p_s E_s$ and $F = -k_B T \log Z$, we have

$$S = \frac{U - F}{T} = \sum_s p_s \frac{E_s}{T} + k_B \log Z = k_B \sum_s p_s \left(\frac{E_s}{k_B T} + \log Z \right) = -k_B \sum_s p_s \log p_s.$$

The present expression for S also applies to the microcanonical ensemble:

$$S = -k_B \sum_s p_s \log p_s = -k_B \sum_{s=1}^{\hat{N}} \frac{1}{\hat{N}} \log \frac{1}{\hat{N}} = k_B \log \hat{N},$$

where \hat{N} is the number of accessible states.

Exercise: Assume that a system has a probability p_s of being in state s , which has energy E_s . Further, let the system have a given average value of the energy U . Then show that, if the entropy is defined as $S = -k_B \sum_s p_s \log p_s$, the entropy is *maximized* when p_s is a canonical distribution.

C. Ising Model

1. Introduction

The Ising model grew out of attempts to explain ferromagnetism, which results from the interaction among electron spins. Ferromagnetism is the existence of spontaneous magnetization in a certain temperature range. Here “spontaneous” means magnetization in the absence of applied magnetic field. In the Ising model only the z component of spin is considered. A more complete model, the Heisenberg model, takes into account all three components of spin.

The Ising model consists of a lattice of N fixed sites. There is a spin, denoted by S_i ($i = 1, 2, \dots, N$), attached to each site, and each spin interacts with its nearest neighbors. The Hamiltonian of the Ising model is

$$E(\{S_i\}) = - \sum_{\langle i,j \rangle} J_{ij} S_i S_j - H \sum_i S_i,$$

where $\langle i,j \rangle$ denotes nearest-neighbor pairs, J_{ij} is the coupling constant for pair $\langle i,j \rangle$, and H is the applied magnetic field. The spin variable S_i takes the value 1 for spin up, or -1 for spin down. For a system of N lattice sites, there are totally 2^N spin configurations. If $J_{ij} = J$, then

$$E(\{S_i\}) = -J \sum_{\langle i,j \rangle} S_i S_j - H \sum_i S_i,$$

which describes a spin system of ferromagnetic coupling when $J > 0$, or describes a spin system of antiferromagnetic coupling when $J < 0$. It is readily seen that, when $J > 0$, the lowest energy configuration is that all spins are up or down, while when $J < 0$, antiparallel spins ($S_i S_j = -1$) in nearest-neighbor pair helps lower the energy. For a one-dimensional chain of Ising spins, the lowest energy configuration is $\cdots \uparrow\uparrow\uparrow\uparrow\uparrow\cdots$ or $\cdots \downarrow\downarrow\downarrow\downarrow\downarrow\cdots$ for $J > 0$, but $\cdots \uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\cdots$ for $J < 0$.

We will focus on the one-dimensional Ising model of ferromagnetic coupling. The energy function is

$$E(\{S_i\}) = -J \sum_i S_i S_{i+1} - H \sum_i S_i,$$

and the partition function is

$$Q(H, T) = \sum_{\{S_i\}} e^{-\beta E(\{S_i\})},$$

which involves a summation over 2^N configurations. Here $\beta \equiv 1/k_B T$. The Helmholtz free energy is

$$A = -\frac{1}{\beta} \log Q,$$

from which a few thermodynamic quantities can be obtained:

$$U = \frac{1}{Q} \sum_{\{S_i\}} E(\{S_i\}) e^{-\beta E(\{S_i\})} = -\frac{\partial}{\partial \beta} \log Q = \frac{\partial}{\partial \beta} (\beta A)$$

for internal energy,

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

for heat capacity, and

$$M = \frac{1}{Q} \sum_{\{S_i\}} \left(\sum_i S_i \right) e^{-\beta E(\{S_i\})} = \frac{1}{\beta Q} \frac{\partial}{\partial H} Q = -\frac{\partial}{\partial H} A$$

for magnetization. Spontaneous magnetization means $M = \langle \sum_i S_i \rangle \neq 0$ at $H = 0$.

2. Transfer matrix method

We study the one-dimensional Ising model

$$-\beta E(\{S_i\}) = \beta J \sum_i S_i S_{i+1} + \beta H \sum_i S_i,$$

with the periodic boundary condition $S_{N+1} = S_1$. That is, the model is defined on a ring of N sites. The partition function can be written as

$$\begin{aligned} Q &= \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{\beta J \sum_i S_i S_{i+1} + \beta H \sum_i S_i} \\ &= \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} \exp \left[\beta J \sum_i S_i S_{i+1} + \frac{1}{2} \beta H \sum_i (S_i + S_{i+1}) \right]. \end{aligned}$$

We define a 2×2 transfer matrix P :

$$P = \begin{bmatrix} P_{++} & P_{+-} \\ P_{-+} & P_{--} \end{bmatrix} = \begin{bmatrix} e^{\beta J + \beta H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta H} \end{bmatrix},$$

with entries $P_{SS'} = \exp[\beta J S S' + \frac{1}{2} \beta H (S + S')]$. Then the partition may be expressed as

$$Q(H, T) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} P_{S_1 S_2} P_{S_2 S_3} \cdots P_{S_N S_1} = \sum_{S_1} (P^N)_{S_1 S_1} = \text{Tr}(P^N).$$

The two eigenvalues of P are

$$\lambda_{\pm} = e^{\beta J} \left[\cosh(\beta H) \pm \left(\sinh^2(\beta H) + e^{-4\beta J} \right)^{1/2} \right],$$

and the partition function becomes

$$Q(H, T) = \lambda_+^N + \lambda_-^N.$$

As $\lambda_+ > \lambda_-$ for any H , $(\lambda_-/\lambda_+)^N \rightarrow 0$ when $N \rightarrow \infty$, thus

$$Q(H, T) = \lambda_+^N,$$

from which we obtain the Helmholtz free energy per spin (free energy density):

$$\frac{A}{N} = -\frac{1}{N\beta} \log Q = -\frac{1}{\beta} \log \lambda_+ = -J - \frac{1}{\beta} \log \left[\cosh(\beta H) + \left(\sinh^2(\beta H) + e^{-4\beta J} \right)^{1/2} \right].$$

For $H = 0$ and $\beta J \rightarrow 0$ (high temperature),

$$\frac{A}{N} = -J - \frac{1}{\beta} \log \left(1 + e^{-2\beta J} \right) \simeq -J - \frac{1}{\beta} \log (2 - 2\beta J) = -\frac{1}{\beta} \log 2.$$

Physically, at extremely high temperature, all spin configurations have the same probability to appear, thus $U = 0$ and $S = k_B \log 2^N$, where 2^N is the total number of configurations. Consequently, $A = U - TS = -k_B T \log 2^N$.

The magnetization per spin (magnetization density) is given by

$$\begin{aligned}\frac{M}{N} &= -\frac{\partial}{\partial H} \frac{A}{N} = -\frac{\partial}{\partial H} \left(-J - \frac{1}{\beta} \log \left[\cosh(\beta H) + \left(\sinh^2(\beta H) + e^{-4\beta J} \right)^{1/2} \right] \right) \\ &= \frac{\sinh(\beta H)}{\left(\sinh^2(\beta H) + e^{-4\beta J} \right)^{1/2}},\end{aligned}$$

whose magnitude is always smaller than 1. For $H = 0$, $M = 0$, so there is no spontaneous magnetization. There is no finite-temperature order-disorder phase transition.

3. Renormalization group

For the one-dimensional Ising model

$$-\beta E(\{S_i\}) = \beta J \sum_i S_i S_{i+1} + \beta H \sum_i S_i,$$

the partition function may be expressed as

$$\begin{aligned}Q_N &= \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} \exp \left[\beta J \sum_i S_i S_{i+1} + \frac{1}{2} \beta H \sum_i (S_i + S_{i+1}) \right] \\ &= \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} P_{S_1 S_2} P_{S_2 S_3} \cdots P_{S_N S_1} = \text{Tr} (P^N),\end{aligned}$$

where P is the transfer matrix

$$P = \begin{bmatrix} P_{++} & P_{+-} \\ P_{-+} & P_{--} \end{bmatrix} = \begin{bmatrix} e^{\beta J + \beta H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta H} \end{bmatrix} = \begin{bmatrix} e^{j+h} & e^{-j} \\ e^{-j} & e^{j-h} \end{bmatrix} = \begin{bmatrix} \frac{1}{\mu\nu} & \mu \\ \mu & \frac{\nu}{\mu} \end{bmatrix},$$

in which $\mu = e^{-j} = e^{-\beta J}$ and $\nu = e^{-h} = e^{-\beta H}$. We rewrite Q_N for N spins as

$$Q_N = \text{Tr} (P^N) = \text{Tr} \left[(P^2)^{N/2} \right] = \text{Tr} (P_2^{N/2}),$$

where $P_2 = P^2$ is given by

$$P_2 = \begin{bmatrix} \mu^2 + \frac{1}{\mu^2\nu^2} & \nu + \frac{1}{\nu} \\ \nu + \frac{1}{\nu} & \mu^2 + \frac{\nu^2}{\mu^2} \end{bmatrix} = c \begin{bmatrix} \frac{1}{\mu'\nu'} & \mu' \\ \mu' & \frac{\nu'}{\mu'} \end{bmatrix}.$$

Here c is introduced to allow a solution for μ' and ν' :

$$\mu' = \left(\nu + \frac{1}{\nu} \right)^{1/2} \left(\mu^4 + \frac{1}{\mu^4} + \nu^2 + \frac{1}{\nu^2} \right)^{-1/4};$$

$$\begin{aligned}\nu' &= \left(\mu^4 + \nu^2\right)^{1/2} \left(\mu^4 + \frac{1}{\nu^2}\right)^{-1/2}; \\ c &= \left(\nu + \frac{1}{\nu}\right)^{1/2} \left(\mu^4 + \frac{1}{\mu^4} + \nu^2 + \frac{1}{\nu^2}\right)^{1/4}.\end{aligned}$$

Now we write P_2 as

$$P_2 = c \begin{bmatrix} \frac{1}{\mu'\nu'} & \mu' \\ \mu' & \frac{\nu'}{\mu'} \end{bmatrix} = c \begin{bmatrix} e^{j'+h'} & e^{-j'} \\ e^{-j'} & e^{j'-h'} \end{bmatrix},$$

and this P_2 can be regarded as the transfer matrix for a system with

$$-\beta E'(\{S_i\}) = j' \sum_i S_i S_{i+1} + h' \sum_i S_i + \sum_i \log c.$$

With the help of above results, we are ready to do partial summation for the partition function of N spins. This leads to an equivalent model that consists of $N/2$ block spins, with effective coupling constant J' and field H' determined from $j' = \beta J'$ and $h' = \beta H'$. For a large even number N , the partial summation is carried out over $S_2, S_4, \dots, S_{2i}, \dots, S_N$:

$$\begin{aligned}Q_N &= \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} P_{S_1 S_2} P_{S_2 S_3} \cdots P_{S_N S_1} \\ &= \sum_{S_1} \sum_{S_3} \cdots \sum_{S_{2i-1}} \cdots \sum_{S_{N-1}} (\sum_{S_2} P_{S_1 S_2} P_{S_2 S_3}) (\sum_{S_4} P_{S_3 S_4} P_{S_4 S_5}) \\ &\quad \cdots (\sum_{S_{2i}} P_{S_{2i-1} S_{2i}} P_{S_{2i} S_{2i+1}}) \cdots (\sum_{S_N} P_{S_{N-1} S_N} P_{S_N S_1}) \\ &= \sum_{S_1} \sum_{S_3} \cdots \sum_{S_{2i-1}} \cdots \sum_{S_{N-1}} (P_2)_{S_1 S_3} (P_2)_{S_3 S_5} \cdots (P_2)_{S_{2i-1} S_{2i+1}} \cdots (P_2)_{S_{N-1} S_1} \\ &= \sum_{S_1} \sum_{S_3} \cdots \sum_{S_{2i-1}} \cdots \sum_{S_{N-1}} \prod_{i=1}^{N/2} (P_2)_{S_{2i-1} S_{2i+1}} \\ &= \sum_{S_1} \sum_{S_3} \cdots \sum_{S_{2i-1}} \cdots \sum_{S_{N-1}} \prod_{i=1}^{N/2} \exp[j' S_{2i-1} S_{2i+1} + \frac{1}{2} h' (S_{2i-1} + S_{2i+1}) + \log c] \\ &= \sum_{S_1} \sum_{S_3} \cdots \sum_{S_{2i-1}} \cdots \sum_{S_{N-1}} e^{-\beta E'},\end{aligned}$$

where the energy function

$$-\beta E'(\{S_i\}) = j' \sum_{i=1}^{N/2} S_{2i-1} S_{2i+1} + \frac{1}{2} h' \sum_{i=1}^{N/2} (S_{2i-1} + S_{2i+1}) + \sum_{i=1}^{N/2} \log c,$$

is for an equivalent Ising model of $N/2$ block spins, with effective coupling constant J' and field H' determined from $j' = \beta J'$ and $h' = \beta H'$. The above partial summation is a coarse graining, reducing a model of N spins to an equivalent model of $N/2$ spins:

$$Q_N(J, H) = Q_{N/2}(J', H'),$$

with an appropriate change of parameters:

$$(\mu, \nu) \rightarrow (\mu', \nu').$$

This is called a *renormalization group (RG) transformation*. The fixed point of (μ, ν) is defined by

$$(\mu, \nu) \rightarrow (\mu', \nu') = (\mu, \nu).$$

The first fixed point is $\mu = e^{-\beta J} = 0$ and $\nu = e^{-\beta H} = 1$, corresponding to a perfectly ordered state at $T = 0$ with vanishing external field. The second fixed point is $\mu = e^{-\beta J} = 1$ and $\nu = \text{any positive value}$, corresponding to a completely disordered state at $T = \infty$.

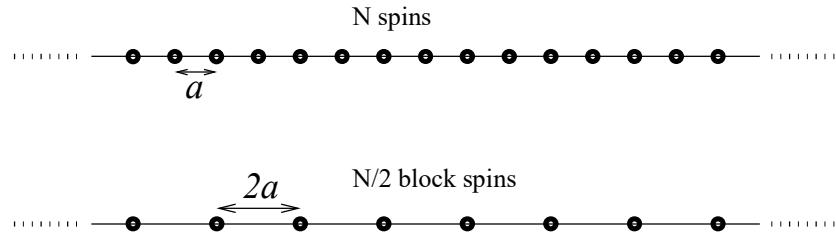


Fig. Schematic illustration for the RG transformation which changes the lattice spacing by a factor of 2.

Physical interpretation of RG transformation: *Physically, the RG transformation changes the minimum length scale over which a model is defined: the above RG transformation for the Ising model changes the minimum length scale from one lattice constant to two. (Originally, N spins are defined on a lattice of lattice constant a , and after the RG transformation, the $N/2$ block spins are defined with lattice constant $2a$). Measured by the new lattice spacing, the same physical correlation length of the (same) system appears to be shortened: Let ξ be the correlation length measured by the original lattice constant a and ξ' the correlation length measured by the new lattice constant $2a$, then $\xi' = \xi/2$, and in this sense the system appears to be more disordered as short-range correlation shows a smaller correlation length (in the unit of $2a$). More explicitly, ξ can be obtained from j and h while ξ' from j' and h' in the same way, i.e., $\xi = f(j, h)$ and $\xi' = f(j', h')$. $\xi' = \xi/2$ means that, by measuring the system with a larger length scale ($2a$), the system shows a shortened*

short-range correlation. The fixed point corresponds to either the ordered state of $\xi = \infty$ or the completely disordered state of $\xi = 0$. If we start from a disordered state of some finite correlation length, then by performing the RG transformation repeatedly, the system will be driven further away from the unstable fixed point $(\mu, \nu) = (0, 1)$ and approach the stable fixed point of $\mu = 1$.

A simple observation: Let's focus on the case of zero external field. We start from a point (μ, ν) close to the unstable fixed point $(0, 1)$. That is, μ is close to 0^+ and $\nu = 1$. According to the expressions for the RG transformation $(\mu, \nu) \rightarrow (\mu', \nu')$, we have $\mu' = \sqrt{2}\mu/\sqrt{\mu^4 + 1}$ and $\nu' = 1$. Obviously, if this RG transformation is performed repeatedly, then μ will gradually approach 1 while ν will stay at 1. It can be shown that the correlation length ξ is given by $\xi \approx \frac{1}{2}e^{2\beta J}$ in the low temperature regime ($\xi \rightarrow \infty$ as $T \rightarrow 0$). It follows that for μ close to 0^+ , $\mu \rightarrow \mu' \approx \sqrt{2}\mu$ and $\xi \approx \frac{1}{2\mu^2} \rightarrow \xi' \approx \frac{1}{2\mu'^2}$, with $\xi' \approx \frac{1}{2}\xi$ as generally expected.

4. Curie-Weiss molecular-field theory

Most of realistic models cannot be solved exactly. Therefore, various approximate methods have been developed. The mean-field theory is an approximate method that is not only simple but also particularly suitable for the study of order-disorder phase transitions. Here we introduce the Curie-Weiss molecular-field theory for the ferromagnetic systems.

Consider N noninteracting spins in an external field H :

$$E^{(0)} = -H \sum_{i=1}^N S_i.$$

The partition function is

$$Z_N^{(0)}(H) = \sum_{S_1} \cdots \sum_{S_N} e^{\beta H \sum_{i=1}^N S_i} = \prod_{i=1}^N \sum_{S_i} e^{\beta H S_i} = [2 \cosh(\beta H)]^N,$$

from which the magnetization per site is

$$m = \frac{M}{N} = \frac{1}{N\beta Z_N^{(0)}} \frac{\partial}{\partial H} Z_N^{(0)} = \tanh(\beta H).$$

Now we write the interaction term in the Ising model as

$$-JS_iS_j = -JS_i\langle S_j \rangle - JS_i(S_j - \langle S_j \rangle).$$

For a finite system of translational symmetry (say, a ring) or an infinite system, $\langle S_j \rangle$ is independent of j , and hence $\langle S_j \rangle = M/N = m$. According to

$$-JS_iS_j = -JmS_i - JS_i(S_j - m),$$

the $\langle i, j \rangle$ spin-spin interaction leads to an effective field $Jm + J(S_j - m)$ acting on spin S_i , in which Jm is the average part and $J(S_j - m)$ is the fluctuating part which depends on the fluctuating spin configurations. The molecular-field theory keeps the average field Jm only. Therefore, under the molecular-field approximation, the energy function of N interacting spins becomes that of N noninteracting spins, all in an effective field

$$H_{eff} = Jzm + H,$$

where H is the externally applied field, z is the number of nearest neighbors, and Jzm is the average internal field due to interaction. Accordingly, the partition function is given by

$$Z_N(J, H) = Z_N^{(0)}(H_{eff}) = Z_N^{(0)}(Jzm + H),$$

and the magnetization is given by

$$m = \frac{M}{N} = \frac{1}{N\beta Z_N} \frac{\partial}{\partial H} Z_N = \tanh[\beta(Jzm + H)].$$

That m appears in both sides of this equation makes it an implicit equation for m . This approach is called the *self-consistent mean-field theory*, because m is determined by H_{eff} , which depends on m itself. The magnetization m is an *order parameter* that describes the spin orientational order of the system.

Under the molecular-field approximation, the energy is given by

$$\begin{aligned} E &= -J \sum_{\langle i,j \rangle} \langle S_i \rangle \langle S_j \rangle - H \sum_i \langle S_i \rangle \\ &= -N(\frac{1}{2}Jzm^2 + Hm), \end{aligned}$$

where z is the number of nearest neighbors.

In the absence of the external field H , the equation for determining m is

$$m = \tanh(\beta J z m).$$

At $T = 0$, the solutions are $m = \pm 1$, depending on the sign of m . That is, at zero temperature, there is a perfect ordering of spin orientation in the system, corresponding to either of the two lowest energy configurations (spins either all up or all down). As the temperature is raised above zero, the two solutions of m , differing in sign only, show that $|m|$ decreases with increasing T . In particular, when a critical temperature T_c is reached, the two solutions of m both vanish. To see the behavior of m near T_c , expand $\tanh(\beta J z m)$ for small m : $\tanh(\beta J z m) \approx \beta J z m - \frac{1}{3}(\beta J z m)^3$. This leads to the equation

$$m = \beta J z m - \frac{1}{3}(\beta J z m)^3,$$

for m , which has three solutions:

$$m = 0; \quad m = \pm \frac{\sqrt{3}}{\beta J z} \left(1 - \frac{1}{\beta J z}\right)^{1/2}.$$

The critical temperature is determined by $\beta_c J z = 1$, and hence $T_c = J z / k_B$. For $T > T_c$, $m = 0$ is the only solution, corresponding to the disordered paramagnetic phase. For $T \leq T_c$, the solutions $m = \pm \frac{\sqrt{3}}{\beta J z} \left(1 - \frac{1}{\beta J z}\right)^{1/2}$ are relevant, corresponding to the ordered ferromagnetic phase. For $T \leq T_c$ but close to T_c , we have

$$m = \pm \sqrt{3} \sqrt{1 - \frac{T}{T_c}},$$

which shows a singularity in $\frac{\partial m}{\partial T}$ at T_c . The power $\frac{1}{2}$ for the temperature dependence of m is called a critical exponent.

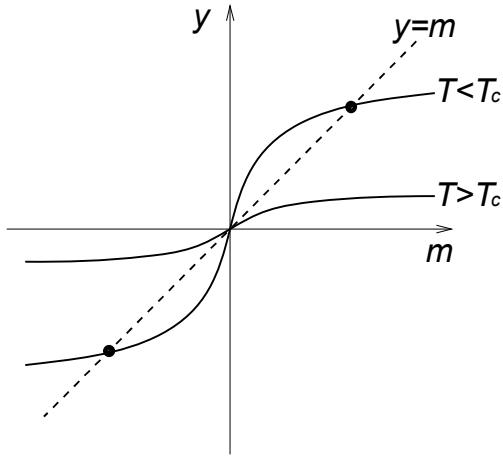


Fig. Solutions of the mean-field equation $m = \tanh(\beta J z m)$ for spontaneous magnetization. The dashed line represents $y = m$ and the solid lines represent $y = \tanh(\beta J z m)$. Nonzero solutions appear for $\beta J z > 1$, i.e., $T < T_c = J z / k_B$.

The mean-field theory predicts an order-disorder phase transition for the ferromagnetic Ising model in any space dimension. Obviously, the mean-field theory totally fails in one dimension, where there is no finite-temperature phase transition. For the two-dimensional model, while there is a finite-temperature phase transition, the mean-field theory is not able to predict the critical exponents quantitatively correctly. Physically, mean-field theory makes quantitatively correct predictions about some aspects of phase transitions (e.g. critical exponents) in high spatial dimensions where each particle or spin has many nearest neighbors to justify a mean-field approximation.

Critical point

For the d -dimensional Ising model ($d \geq 2$), two ferromagnetic phases of spontaneous magnetization $m = \pm|m|$ coexist in the absence of the external field H , for temperature ranging from $T = 0$ to $T = T_c$. At a temperature lower than T_c , as the field H passes through zero from $H = 0^-$ to $H = 0^+$, the system undergoes a first-order phase transition, with m jumping from $m = -|m|$ to $m = |m|$. According to

$$m = \frac{1}{N\beta Z} \frac{\partial}{\partial H} Z = -\frac{\partial}{\partial H} \frac{A}{N},$$

there is a singularity in the partition function $Z(H, T)$ and the free energy $A(H, T) =$

$-\frac{1}{\beta} \log Z$ at $H = 0$ for $T < T_c$. The magnitude of spontaneous magnetization depends on temperature and vanishes at T_c following $|m| \propto (1 - T/T_c)^\beta$. (Here β denotes a critical exponent whose mean-field value is $\frac{1}{2}$.) Therefore, the two ferromagnetic phases become identical at T_c . Above T_c there is no singularity, and the system is in a single paramagnetic phase. The point $(H = 0, T = T_c)$ at which the two ordered phases become identical is called a *critical point*, and the phase transition taking place at the critical point is called a *critical transition* or a *continuous transition*.

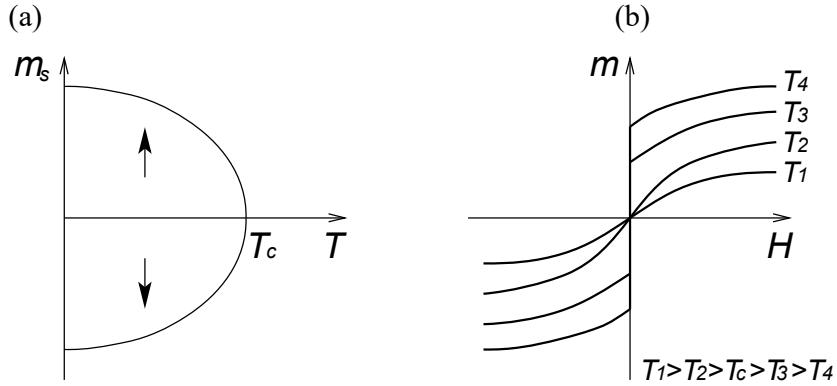


Fig. (a) Spontaneous magnetization (in the absence of an external magnetic field) as a function of temperature. Note that spontaneous magnetization appears for temperature below the Curie point T_c , which is also called the critical point. (b) Magnetization as a function of applied field for different temperatures. At temperatures above T_c , the magnetization is a continuous function of H , whereas at temperatures below T_c , the magnetization curve shows a discontinuity at $H = 0$.

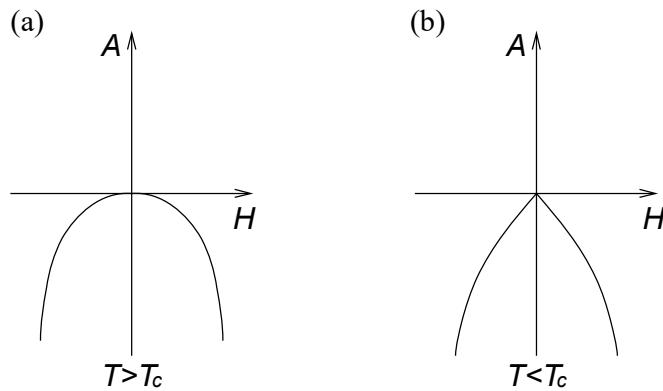


Fig. At temperatures above T_c , the magnetization is a continuous function of H , whereas at

temperatures below T_c , the magnetization curve shows a discontinuity at $H = 0$. According to $m = -\frac{\partial}{\partial H} \frac{A}{N}$, the free energy $A(H, T)$ is differentiable for $T > T_c$, as illustrated in (a). For $T < T_c$, the discontinuity of m from $H = 0^-$ to $H = 0^+$ implies that $A(H, T)$ is not differentiable at $H = 0$, as illustrated in (b).

Similarity between ferromagnetic phase transition and liquid-gas phase transition: *Magnetic field $H \longleftrightarrow$ pressure P ; spontaneous magnetization $M_s \longleftrightarrow$ density difference between the gas and liquid $\rho_L - \rho_G$ (M_s and $\rho_L - \rho_G$ both vanish for temperatures above critical point); M - H phase diagram \longleftrightarrow ρ - P phase diagram (ρ is the density) below/above the critical point (with/without discontinuity); Curie-Weiss molecular-field theory \longleftrightarrow Van der Waals equation $\left[P + \left(\frac{N}{V} \right)^2 a \right] (V - Nb) = Nk_B T$, which predicts a critical point $T_c = 8a/27bk_B$, $P_c = a/27b^2$, and $V_c = 3Nb$.*

5. Spontaneous symmetry breaking and ergodicity breaking

This is a descriptive outline of the concepts of spontaneous symmetry breaking and ergodicity breaking. For more details, see N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group*.

Impossibility of phase transitions

The Hamiltonian of the Ising model

$$E(J, H, \{S_i\}) = - \sum_{\langle i,j \rangle} J_{ij} S_i S_j - H \sum_i S_i$$

shows the up-down symmetry (more precisely, the time-reversal symmetry or Z_2 symmetry):

$$E(J, H, \{S_i\}) = E(J, -H, \{-S_i\}).$$

Thus

$$\begin{aligned} Z_N(J, -H, T) &= \sum_{\{S_i\}} \exp [-\beta E(J, -H, \{S_i\})] \\ &= \sum_{\{S_i\}} \exp [-\beta E(J, H, \{-S_i\})] \\ &= \sum_{\{S_i\}} \exp [-\beta E(J, H, \{S_i\})] \\ &= Z_N(J, H, T) \end{aligned}$$

That is, the free energy density $f(J, H, T) = \frac{A_N(J, H, T)}{N} = -\frac{1}{N\beta} \log Z_N(J, H, T)$ is even in H :

$$f(J, H, T) = f(J, -H, T).$$

It follows that the magnetization density

$$m(H) = \frac{M(H)}{N} = -\frac{\partial}{\partial H} \frac{A_N(J, H, T)}{N} = -\frac{\partial}{\partial H} f(J, H, T)$$

is odd in H :

$$m(H) = -m(-H).$$

At $H = 0$, we must have $m(0) = -m(0) = 0$: the magnetization in zero external field must be zero! This is the “impossibility theorem” for phase transitions. What has gone wrong?

Spontaneous symmetry breaking

The argument above that $m(0) = 0$ is indeed correct *for a finite system*. It fails in the thermodynamic limit ($N \rightarrow \infty$), because $f(H)$ can develop a discontinuity in its first derivative $\partial f(H)/\partial H$. We can evade the consequence of the “impossibility theorem” if the behavior near $H = 0$ is

$$f(H) = f(0) - m_s |H| + O(H^\sigma), \quad \sigma > 1.$$

This $f(H)$ is not differentiable at $H = 0$:

$$-\frac{\partial f}{\partial H} = \begin{cases} +m_s + O(H^{\sigma-1}), & H > 0 \\ -m_s + O(H^{\sigma-1}), & H < 0 \end{cases}.$$

As $|H| \rightarrow 0$,

$$-\frac{\partial f}{\partial H} = \begin{cases} +m_s, & H > 0 \\ -m_s, & H < 0 \end{cases}.$$

Therefore, the spontaneous magnetization is given by

$$m_s = \lim_{H \rightarrow 0^+} -\frac{\partial f}{\partial H}$$

and

$$-m_s = \lim_{H \rightarrow 0^-} -\frac{\partial f}{\partial H}.$$

It is noted that the limits $N \rightarrow \infty$ and $H \rightarrow 0$ do *not* commute:

$$\lim_{N \rightarrow \infty} \lim_{H \rightarrow 0} -\frac{1}{N} \frac{\partial A_N(H)}{\partial H} = 0$$

whereas

$$\lim_{H \rightarrow 0} \lim_{N \rightarrow \infty} -\frac{1}{N} \frac{\partial A_N(H)}{\partial H} \neq 0.$$

In order to possibly get a spontaneous magnetization, the limit $N \rightarrow \infty$ must be taken first to allow a discontinuity to be developed in $\partial f(H)/\partial H$.

This set of phenomena is referred to as *spontaneous symmetry breaking*. When $H = 0$, $E(\{S_i\}) = E(\{-S_i\})$. Even though the Hamiltonian is invariant under $\{S_i\} \rightarrow \{-S_i\}$, the statistical expectation value of $\sum_i S_i$ is *not* invariant under time-reversal transformation: $\langle \sum_i S_i \rangle \neq -\langle \sum_i S_i \rangle$ because

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle \sum_i S_i \rangle \neq 0.$$

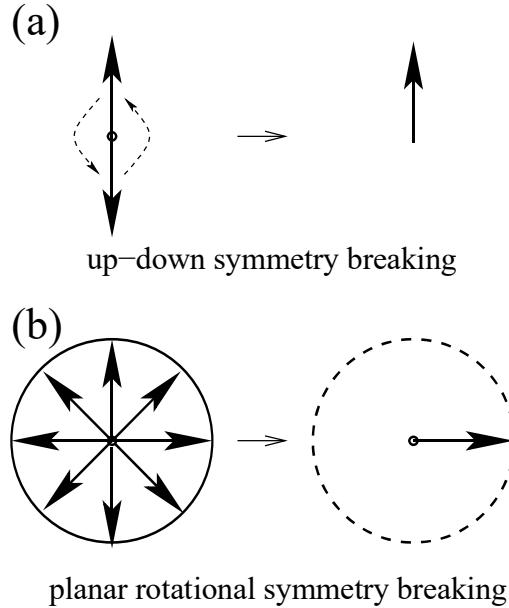


Fig. Schematic illustration of discrete (a) and continuous (b) symmetry breaking. Although the Hamiltonian of the spin system is invariant under certain symmetry operation (rotation), the ensemble average of the total spin does not vanish, thus breaking the symmetry.

Ergodicity breaking

Statistical mechanics is intended to represent the actual dynamical behavior of a system in equilibrium. What are the consequences of spontaneous symmetry breaking for the dynamics? To answer this, let us recall how the actual dynamics of a system enters the statistical mechanics.

Usually, statistical mechanics is justified by identifying time averages with ensemble averages. To be more precise, for any observable $A(\{\eta_i\})$, where $\eta_i(t)$ are the dynamical degrees of freedom as a function of time, the time average is given by

$$\langle A \rangle \equiv \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A[\{\eta_i(t')\}] dt'$$

and in statistical mechanics it is hypothesized that

$$\langle A \rangle = \int \prod_i d\eta_i P_{eq}(\{\eta_i\}) A(\{\eta_i\}),$$

where $P_{eq}(\{\eta_i\})$ is the equilibrium probability density for variables $\{\eta_i\}$. These variables constitute the phase space for the system.

The basic assumption of statistical mechanics is that these two averages give the same result. This hypothesis is the *ergodic hypothesis*: as $t \rightarrow \infty$, $\{\eta_i(t)\}$ comes arbitrarily close to every possible configuration of the $\{\eta_i\}$ allowed by energy conservation.

When $H = 0$ and $T < T_c$, regions of configuration space (or phase space) with $M = +Nm_s$ and $M = -Nm_s$ are sampled equally for a finite system. An observer of the system would notice that at first the system had a net (e.g.) positive magnetization. After a while, a large cluster of down spins might form and then grow, eventually causing the system to have a net negative magnetization. The rate R at which the whole system might switch from positive to negative magnetization is expected to be of the Arrhenius form

$$R \propto e^{-\beta \Delta F},$$

where ΔF is the energy barrier for the switching. For a system of N spins in d -dimensional space, ΔF is proportional to the surface area of the system, and hence $\Delta F \propto N^{(d-1)/d}$. Therefore, the *lifetime* of a state with a given magnetization, τ , is roughly $1/R$, i.e.,

$$\tau \propto \exp [\beta \gamma N^{(d-1)/d}],$$

where γ is the energy per unit area of the domain wall, formed during switching between the positive- and negative-magnetization domains.

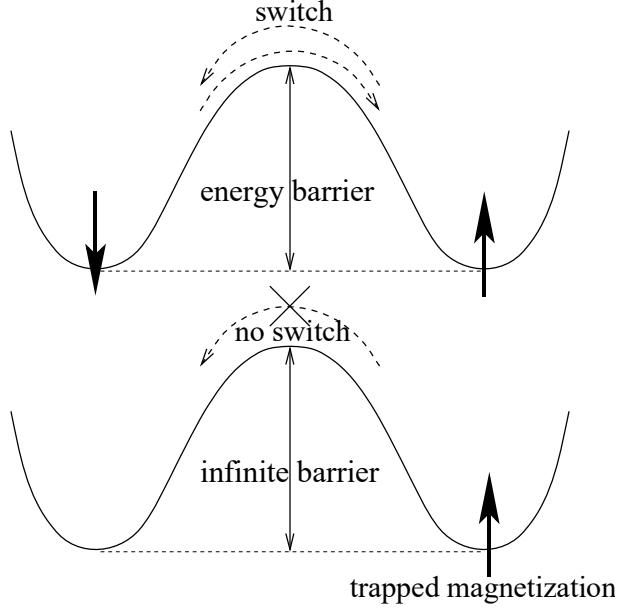


Fig. Schematic illustration of ergodicity breaking. The lifetime of positive-magnetization state goes to infinity in the thermodynamic limit, leaving the system trapped in this state.

In the thermodynamic limit, the lifetime will rapidly grow very large, so that the *initial condition* determines whether or not the magnetization is positive or negative. Thus, in the thermodynamic limit, the system is effectively trapped in one or the other region of configuration or phase space. This is known as *ergodicity breaking*.

An important feature of this form of ergodicity breaking is that the configuration space has been fragmented into two regions corresponding to positive and negative magnetization. Thus, for every state of the system in one region, there is a corresponding time-reversed state in the other region, i.e., there is a one-to-one mapping between states of the system in the two disjoint regions of configuration space. The two regions are said to be related by symmetry, the same symmetry that has been spontaneously broken. Recall that, by first taking the thermodynamic limit and then letting the field vanish, spontaneous symmetry breaking can be obtained from ensemble average, which is effectively done over only one of the two regions. This ensemble average with spontaneous symmetry breaking is equivalent

to the time average with ergodicity breaking.

D. Monte Carlo Simulations

1. Introduction

Monte Carlo simulations and molecular dynamics simulations are the two main approaches to computer simulations in statistical physics. The aims of these simulations are to study equilibrium and non-equilibrium thermodynamic systems by stochastic computer simulations. Computer simulations allow studies of complicated systems in which analytical solutions are not possible. Computer simulations also have some advantages over experiments, for example, one can calculate and study properties that are difficult to obtain in experiments. Further, one can predict the behavior of the system of interest before expensive and time-consuming experiments are conducted.

There are, of course, also some disadvantages with computer simulations. Firstly, a real system is often very complex and in order to model such a system approximations and simplifications are necessary. The modeling of the system is crucial for the simulations to be good, so that great care must be taken. Secondly, a computer only has a finite memory size, so the simulations must be performed on fairly small systems, typically $N \approx 10^2$ to 10^7 atoms, while a real system has approximately $N \approx 10^{23}$ atoms. Therefore a nontrivial extrapolation to much larger systems has to be performed. Fortunately, there are well developed methods, called the finite size scaling theory, to do this extrapolation. Still, quantitative as well as qualitative knowledge of a real system can be obtained through studies of simplified model systems. The simulations on these model systems are in principle numerically exact, i.e., the results are accurate apart from statistical errors, that can be made as small as desired if only enough computing time is used.

Monte Carlo (henceforth called MC) simulations will be discussed in the following. MC simulations in statistical physics rely on the usage of random numbers to generate a stochas-

tic trajectory through the phase space of the model considered, and to calculate thermal averages if equilibrium properties are desired. The first successful simulation was carried out by Metropolis et al. in 1953. (See N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.M. Teller and E. Teller, J. Chem. Phys. **21**, 1087 (1953).) Since then this technique has been under heavy development which is likely to continue in the future, since better and better computers become available with time. Presently, it is possible to carry out simulations of good quality even on personal computers but the simulations still have to be performed on supercomputers if high accuracy and/or large systems are required. MC simulations can be applied to many different fields, such as diffusion processes in solids, fluid-, surface- and plasma- physics, properties of alloys, crystal growth kinetics, quantum many-body problems, critical phenomena in magnetic systems, kinetics of adsorption on surfaces, and thermal properties of disordered systems. For a more complete survey of MC simulations in statistical physics, see D.P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge Univ. Press (2000).

2. Random number generators

Since MC simulations rely on the usage of random numbers, it is crucial to use random numbers of high quality in order to succeed in the simulations. A digital computer can only produce pseudo random numbers using some suitable algorithm. These pseudo random number sequences are exactly reproducible, because the sequence is started with a user defined integer, called seed.

There are some requirements on the pseudo random numbers: they must be uniformly distributed in the interval $[0,1]$, the sequence must be as less correlated as possible, and they must be generated fast. A limitation due to the finite word length of computers is that the pseudo random numbers have a finite period. For instance, on a 32-bit processor the period is $2^{31} \approx 10^9$ numbers only. This is not enough for most of the simulations, but fortunately there are some ways to get around this problem.

3. Thermodynamic averages

The thermodynamic system of interest consists of N particles in a volume V at a specified temperature T . By these three quantities, an equilibrium canonical ensemble is defined. Now each particle i is described by a set of dynamical variables $\{\alpha_i\}$. In spin models, $\{\alpha_i\}$ corresponds to the spin vector \mathbf{S}_i of particle i . Let \mathbf{X} be a point in phase space Ω :

$$\mathbf{X} = \{\{\alpha_1\}, \{\alpha_2\}, \dots, \{\alpha_N\}\},$$

which fully describes the microscopic state of the system. The total energy of the particles is described by the Hamiltonian $H(\mathbf{X})$ as a function of \mathbf{X} . The probability density P_{eq} at the phase point \mathbf{X} in Ω is given by

$$P_{\text{eq}}(\mathbf{X}) = \frac{1}{Z} \exp[-H(\mathbf{X})/k_{\text{B}}T],$$

where Z is the partition function, k_{B} the Boltzmann constant, and T the temperature. Let $A(\mathbf{X})$ denote a thermodynamic observable. The thermal average (expectation value) of $A(\mathbf{X})$ in equilibrium is given by

$$\langle A \rangle_T = \frac{1}{Z} \int_{\Omega} d\mathbf{X} A(\mathbf{X}) \exp[-H(\mathbf{X})/k_{\text{B}}T].$$

4. Importance sampling and Metropolis algorithm

The basic idea behind MC simulations is to calculate the phase space integrals for thermal average numerically. In principle, standard numerical integration methods could be used, but the problem is that we have to deal with the high dimensionality of the integration space Ω . Another problem is that the exponential Boltzmann factor is always vanishingly small for most of the configurations. This means that, out of all the possible configurations, only very few of them will make significant contribution to the expectation value of $A(\mathbf{X})$. Therefore, a method is needed to *restrict the sampling only to the interesting/important volume in phase space*. Metropolis *et al.* introduced a sampling algorithm based on this

concept, called importance sampling. In this algorithm a configuration \mathbf{X}_ν is not chosen completely at random but with a probability $P_{\text{eq}}(\mathbf{X}_\nu)$ that is proportional to its Boltzmann factor $\exp[-H(\mathbf{X})/k_B T]$. Then the average of A reduces to a simple arithmetic average:

$$\langle A \rangle = \frac{1}{M} \sum_{\nu=1}^M A(\mathbf{X}_\nu)$$

over a (long) sequence of M states. This sequence may be regarded as a numerical realization of the canonical ensemble in which different microscopic states appear according to their respective statistical probabilities. Metropolis proposed a stochastic method to generate such a sequence of states $\mathbf{X}_\nu \rightarrow \mathbf{X}_{\nu+1} \rightarrow \mathbf{X}_{\nu+2} \rightarrow \dots$, where each step has a transition probability $W(\mathbf{X}_\nu \rightarrow \mathbf{X}_{\nu+1})$. This kind of sequence is called *a Markov chain*. From the theory of Markov chains in probability theory, one can show that $P(\mathbf{X}_\nu) \rightarrow P_{\text{eq}}(\mathbf{X}_\nu)$ as $M \rightarrow \infty$, if *the condition of detailed balance* is fulfilled:

$$P_{\text{eq}}(\mathbf{X}_\nu) W(\mathbf{X}_\nu \rightarrow \mathbf{X}_{\nu'}) = P_{\text{eq}}(\mathbf{X}_{\nu'}) W(\mathbf{X}_{\nu'} \rightarrow \mathbf{X}_\nu)$$

A simple choice for W is given in terms of the energy change $\Delta E = H(\mathbf{X}_{\nu'}) - H(\mathbf{X}_\nu)$, as proposed by Metropolis:

$$W(\mathbf{X}_\nu \rightarrow \mathbf{X}_{\nu'}) = \begin{cases} 1 & \Delta E < 0 \text{ (down-hill)} \\ \exp(-\Delta E/k_B T) & \Delta E > 0 \text{ (up-hill)} \end{cases}$$

This is the only place where the temperature enters into the algorithm. Essentially, the Metropolis Monte Carlo method generates a random walk through phase space using rejections to achieve detailed balance and thereby the Boltzmann distribution.

Note that, while the equilibrium properties can be studied in MC simulations, long runs are necessary for obtaining good results: (i) We must wait for a sufficiently long time to let the system reach equilibrium; (ii) The sequence for averaging must be long enough to reduce statistical fluctuations (noises).

From the original paper of Metropolis: *In the original paper of Metropolis, the importance sampling method was proposed for the investigation of a system of interacting molecules. Here we quote: So the method we employ is actually a modified Monte*

Carlo scheme, where, instead of choosing configurations randomly, then weighting them with $\exp(-E/kT)$, we choose configurations with a probability $\exp(-E/kT)$ and weight them evenly. This we do as follows: We place the N particles in any configuration, for example, in a regular lattice. Then we move each of the particles in succession \dots . We then calculate the change in energy of the system ΔE , which is caused by the move. If $\Delta E < 0$, i.e., if the move would bring the system to a state of lower energy, we allow the move and put the particle in its new position. If $\Delta E > 0$, we allow the move with probability $\exp(-\Delta E/kT)$; \dots . Then, whether the move has been allowed or not, i.e., whether we are in a different configuration or in the original configuration, we consider that we are in a new configuration for the purpose of taking our averages.

5. Boundary conditions

In a Monte Carlo simulation a finite system of N particles is studied. If bulk properties are desired, the system needs to be extrapolated to infinite size (thermodynamic limit). Therefore, the boundary condition of the finite system is very important. The usual choice is the periodic boundary conditions. Consider a finite system of the shape of a hyper cubic box defined by the base vectors $\{\mathbf{L}_1, \mathbf{L}_2, \dots, \mathbf{L}_d\}$, where d is the dimensionality of the system. The base vectors are, of course, orthogonal and have the form $\mathbf{L}_q = L_q \mathbf{e}_q$, $q = (1, \dots, d)$, where L_q is the linear size of the system along the q -axis and \mathbf{e}_q is the corresponding unit vector. The periodic boundary conditions are then mathematically defined for any observable A at \mathbf{r} , through the relation

$$A(\mathbf{r}) = A(\mathbf{r} \pm \mathbf{L}_q), \quad q = (1, \dots, d).$$

Obviously, with periodic boundary conditions, an infinite system is obtained as a periodic array of infinitely many identical finite systems. Due to the periodic boundary conditions, the longest wave length of statistical fluctuations is given by the linear size of the finite system.

6. Practical implementation of the Metropolis algorithm

The basic theory behind MC simulations has been outlined. Now we describe how a MC simulation is actually performed. Markov chains has been briefly discussed, but nothing has been said about what the move $\mathbf{X} \rightarrow \mathbf{X}'$ actually means in practice. The condition of detailed balance implies

$$\frac{W(\mathbf{X} \rightarrow \mathbf{X}')}{W(\mathbf{X}' \rightarrow \mathbf{X})} = \exp\left(-\frac{\Delta E}{k_B T}\right),$$

where ΔE is the energy change caused by the move $\mathbf{X} \rightarrow \mathbf{X}'$.

In practice, a MC simulation procedure is performed in the following way. First, one specifies the initial condition for $\mathbf{X} = \{\{\alpha_1\}, \{\alpha_2\}, \dots, \{\alpha_N\}\}$. This choice is arbitrary since it will soon be “forgotten” by the system in approaching the equilibrium, and hence should not influence the equilibrium distribution later on. However, it is good to use different initial conditions to check that this is indeed the case. Then, one particle i is chosen, either randomly or systematically, and its dynamical variable α_i is changed to α'_i . The energy change ΔE associated with this trial move is calculated. From the energy change, the transition probability W is calculated according to

$$W = \begin{cases} 1 & \Delta E < 0 \text{ down-hill} \\ \exp(-\Delta E/k_B T) & \Delta E > 0 \text{ up-hill} \end{cases}$$

Then, a random number r , uniformly distributed in $[0, 1]$, is drawn. If $r > W$ (of probability $1 - W$), the trial move is rejected and the state with the old configuration $\{\alpha_i\}$ is kept, counted once more in the averaging. Otherwise, if $r < W$ (of probability W), the trial move is accepted and the new state with configuration $\{\alpha'_i\}$ is used in averaging. (Down-hill trial move ($W = 1$) is accepted with probability 1 for $r < 1$, up-hill trial move ($W = \exp(-\Delta E/k_B T)$) is accepted with probability W for $r < W$.) This procedure is then repeated. Finally, the averages of the desired quantities are calculated in a long sequence of configurations.

In the procedure outlined above, the success of the trial move $\mathbf{X} \rightarrow \mathbf{X}'$ depends on the energy difference, which should be comparable to $k_B T$. If the energy change is too large,

then it is almost impossible to accept an up-hill trial move ($W \rightarrow 0$), and the stochastic trajectory of the system cannot be efficiently generated. On the other hand, if the energy change is too small, then the system moves very slowly in the phase space and the sampling is not efficient either. For continuous models like the Heisenberg model, It is convenient to limit the allowed change by introducing a control parameter δ . The allowed change then satisfies $|\alpha_i - \alpha'_i| < \delta$. The acceptance ratio, i.e., the ratio of accepted moves to total trial moves, can be tuned via δ and should be close to 0.5. That is, an up-hill ΔE should be comparable to $k_B T$.

The Metropolis algorithm is particularly suitable for running on massive parallel computers for studying very large systems.

7. Monte Carlo simulation of the 2D Ising model (Project for students)

Consider a 2D Ising model defined on a square lattice of $N_G = N \times N$ sites. The energy function is given by

$$E(\{S_{i,j}\}) = -J \sum_{i=1}^N \sum_{j=1}^N (S_{i,j} S_{i+1,j} + S_{i,j} S_{i,j+1}) - H \sum_{i=1}^N \sum_{j=1}^N S_{i,j},$$

where $J > 0$ is the ferromagnetic coupling constant and H is the external field. The periodic boundary condition is applied such that $S_{1,j} = S_{N+1,j}$ and $S_{i,1} = S_{i,N+1}$. That is, the square lattice is in fact a torus without boundaries. The MC simulation is to generate a sequence of spin configurations distributed according to the Boltzmann factor $\exp(-E/k_B T)$, and various thermodynamic quantities can be measured in this sequence. Note that the only control parameter here is $J/k_B T$. Below we will present the results with E measured by J and T measured by J/k_B .

The simulation starts from a randomly prepared spin configuration. To generate a sequence of states according to the canonical distribution one by one, we make a trial move by randomly picking a site on the lattice (i, j) and reversing the spin there ($S_{i,j} \rightarrow S'_{i,j} = -S_{i,j}$).

The energy change caused by this trial move is given by

$$\Delta E = -(S_{i-1,j} + S_{i+1,j} + S_{i,j-1} + S_{i,j+1})(S'_{i,j} - S_{i,j}).$$

The algorithm for Metropolis importance sampling is applied as follows. For a down-hill move of $\Delta E \leq 0$, we allow the trial move and add the new spin configuration to the sequence. For an up-hill move of $\Delta E > 0$, we allow the move with probability $w = \exp(-\Delta E/T) < 1$. A random number between 0 and 1 is generated for comparison with w : if $r < w$, the trial move is accepted and the new configuration is added to the sequence; if $r > w$, the trial move is rejected and the old configuration is kept and counted for one more time in the sequence. A repeated use of trial move followed by acceptance/rejection will generate a long sequence of configurations for the purpose of equilibration and measurement of ensemble averages.

We are mostly interested in the internal energy U , heat capacity C_V , magnetic moment M , and magnetic susceptibility χ . The internal energy U is defined to be the mean energy $\langle E \rangle$:

$$U = \langle E \rangle.$$

The heat capacity is defined by

$$C_V = \frac{\partial U}{\partial T}.$$

It can be shown that the internal energy is given by

$$U = -\frac{\partial}{\partial \beta} \log Q$$

from which we have

$$C_V = \frac{\beta}{T} [\langle E^2 \rangle - \langle E \rangle^2],$$

which allows the evaluation of C_V by measuring the energy fluctuation. Here $\beta = 1/k_B T$ and Q is the canonical partition function. According to the general argument based on the statistical independence, U and C_V are extensive properties, proportional to N_G when it is large enough. Note that $[\langle E^2 \rangle - \langle E \rangle^2]$ is proportional to N_G because of the additivity of E .

The magnetic moment is defined as

$$M = \left\langle \sum_{i,j} S_{i,j} \right\rangle,$$

and the magnetic susceptibility is defined as

$$\chi = \frac{\partial M}{\partial H}.$$

It can be shown that the magnetic moment is given by

$$M = \frac{1}{\beta} \frac{\partial}{\partial H} \log Q$$

from which we have

$$\chi = \beta \left[\left\langle \left(\sum_{i,j} S_{i,j} \right)^2 \right\rangle - \left\langle \sum_{i,j} S_{i,j} \right\rangle^2 \right],$$

which allows the evaluation of χ by measuring the fluctuation of total spin. Similar to U and C_V , M and χ are also extensive properties. In particular, the fluctuation expression for χ indicates that it is proportional to N_G because of the additivity of total spin.

We present the numerical results with U , C_V , M , and χ all normalized by $N_G = N^2$.

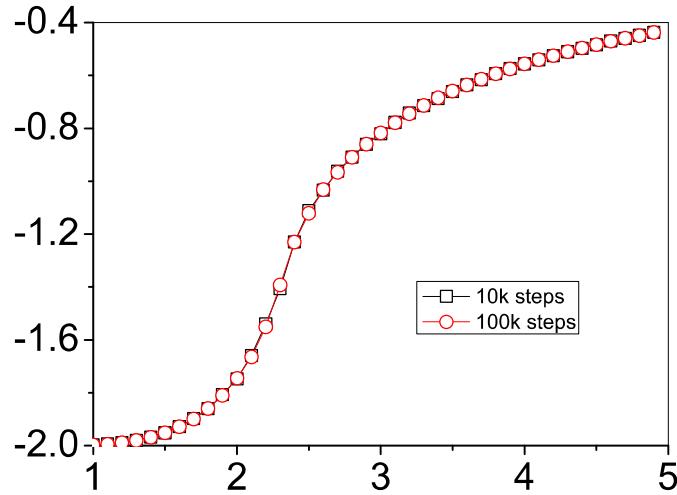


Fig. The internal energy (per site) as a function of temperature. MC steps: 10K and 100K; system size: 20×20 . Here the internal energy is normalized by N_G and measured by J , the temperature is measured by J/k_B .

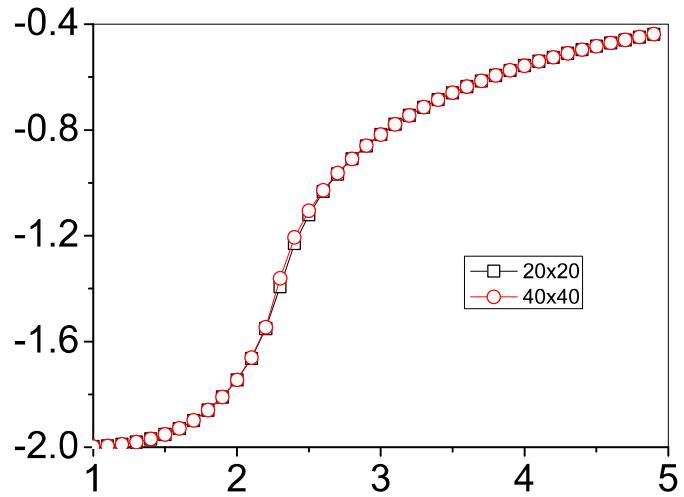


Fig. The internal energy (per site) as a function of temperature. MC steps: 100K; system size: 20×20 and 40×40 .

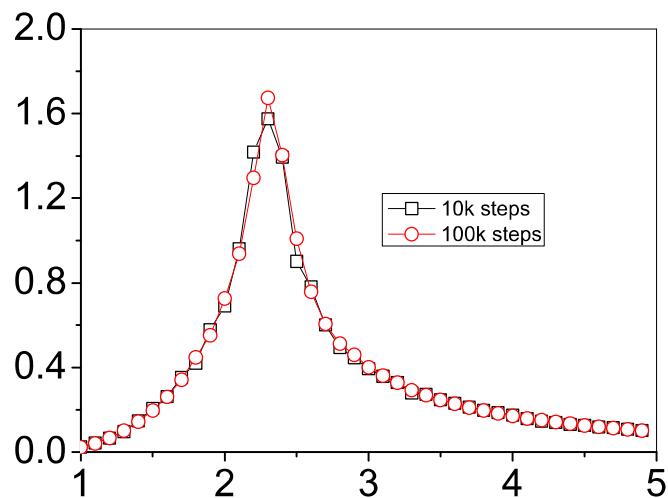


Fig. The heat capacity as a function of temperature. MC steps: 10K and 100K; system size: 20×20 .

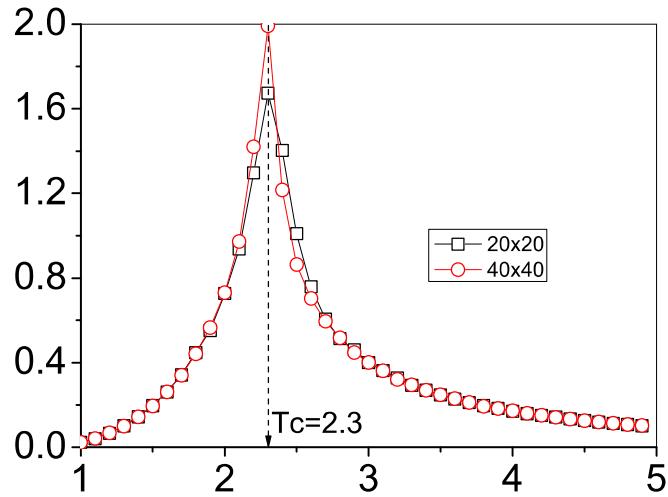


Fig. The heat capacity as a function of temperature. MC steps: 100K; system size: 20×20 and 40×40 .

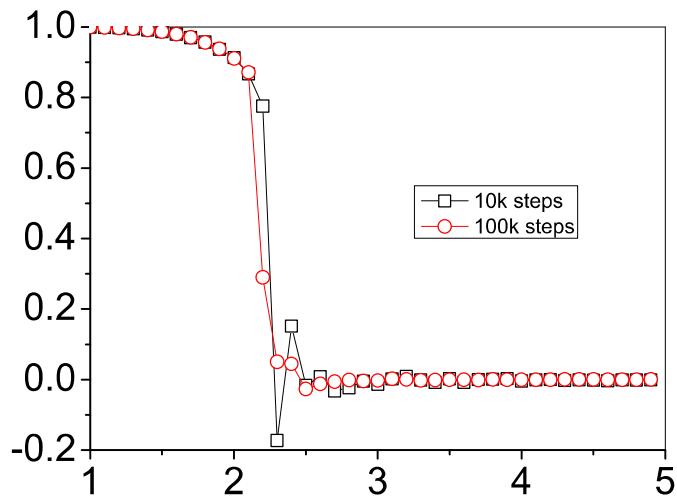


Fig. The magnetic moment (per site) as a function of temperature. MC steps: 10K and 100K; system size: 20×20 . Here $\langle \sum_{i,j} S_{i,j} \rangle$ has been used in averaging.

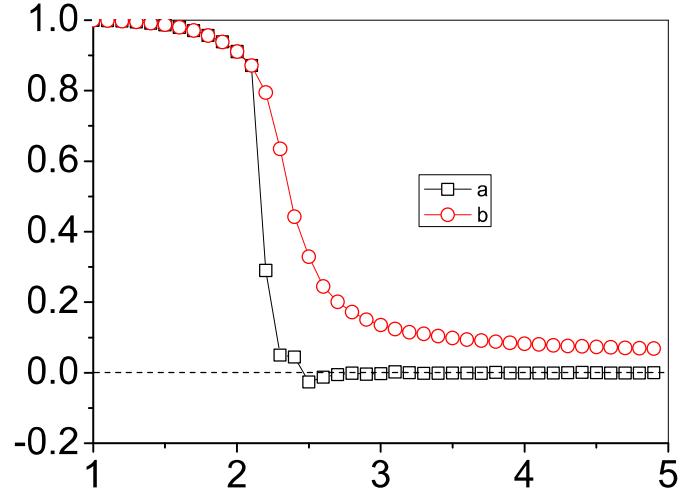


Fig. The magnetic moment (per site) as a function of temperature. MC steps: 100K; system size: 20×20 . Here squares denote the results obtained using $\langle \sum_{i,j} S_{i,j} \rangle$ in averaging; circles denote the results obtained using $\langle | \sum_{i,j} S_{i,j} | \rangle$ in averaging.

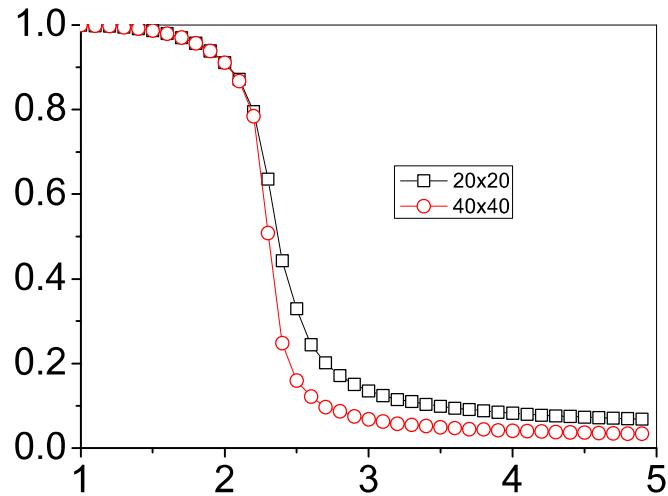


Fig. The magnetic moment (per site) as a function of temperature. MC steps: 100K; system size: 20×20 and 40×40 . Here $\langle | \sum_{i,j} S_{i,j} | \rangle$ has been used in averaging.

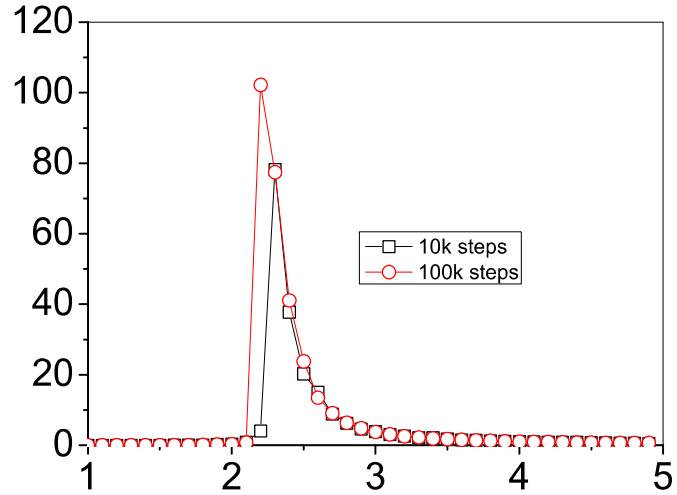


Fig. The magnetic susceptibility (per site) as a function of temperature. MC steps: 10K and 100K; system size: 20×20 . Here $\langle \sum_{i,j} S_{i,j} \rangle$ has been used in averaging.

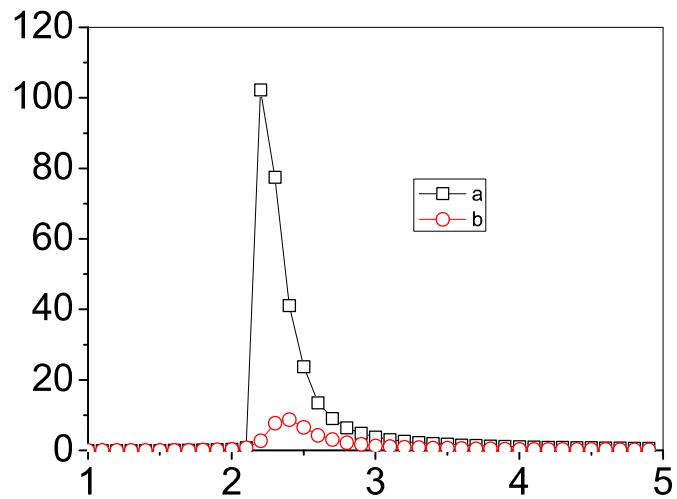


Fig. The magnetic susceptibility (per site) as a function of temperature. MC steps: 100K; system size: 20×20 . Here squares denote the results obtained using $\langle \sum_{i,j} S_{i,j} \rangle$ in averaging; circles denote the results obtained using $\langle |\sum_{i,j} S_{i,j}| \rangle$ in averaging.

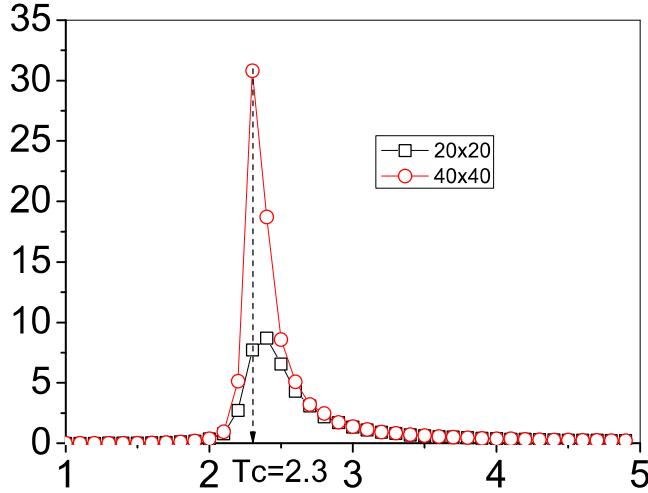


Fig. The magnetic susceptibility (per site) as a function of temperature. MC steps: 100K; system size: 20×20 and 40×40 . Here $\langle |\sum_{i,j} S_{i,j}| \rangle$ has been used in averaging.

We want to point out that, due to the finite size of the simulated system, at temperatures immediately below the critical temperature T_c (which is determined to be 2.3 here, in good agreement with the analytical result $2/\ln(1 + \sqrt{2})$), the system may undergo up-to-down and down-to-up switches in magnetic moment from time to time, because the energy barrier is not that high. This introduces “large” fluctuations associated with the magnetic switch of the whole domain, which are considered to be absent in thermodynamic limit. To avoid the unwanted large fluctuations and keep the small fluctuations associated with a particular sign of average total spin, we replace $\langle \sum_{i,j} S_{i,j} \rangle$ by $\langle |\sum_{i,j} S_{i,j}| \rangle$ in measuring M and χ . This is to let the configurations of total spin up and those of total spin down contribute to M constructively rather than destructively. As a consequence, in the course of measuring M and χ there is effectively no magnetic switch of the whole domain.

Nevertheless, the magnetic switch noted above for finite systems is interesting by itself. The lifetime of a metastable magnetic state depends on the temperature and the system size, as illustrated below.

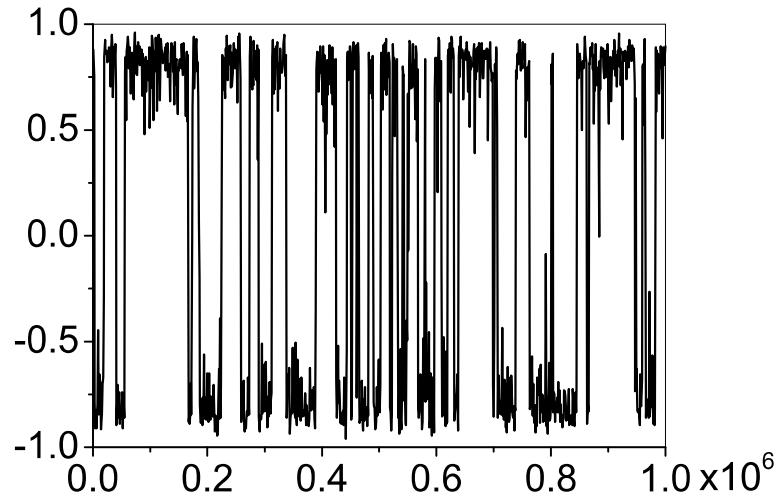


Fig. Instantaneous magnetization ($N_G^{-1} \sum_{i,j} S_{i,j}$) as a function of “time”, with N_G trial moves defined as one MC step. The average lifetime is about 10^5 MC steps for system size 20×20 and $T = 2.2$.

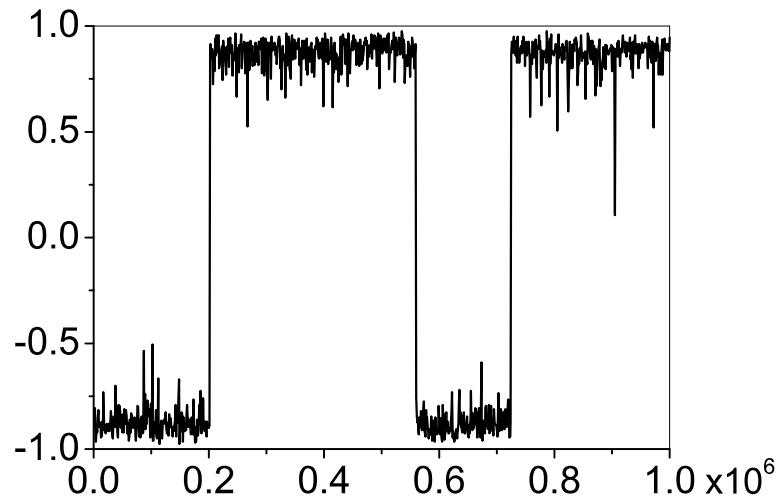


Fig. Instantaneous magnetization ($N_G^{-1} \sum_{i,j} S_{i,j}$) as a function of “time”, with N_G trial moves defined as one MC step. The average lifetime is about 5×10^5 MC steps for system size 20×20 and $T = 2.1$.

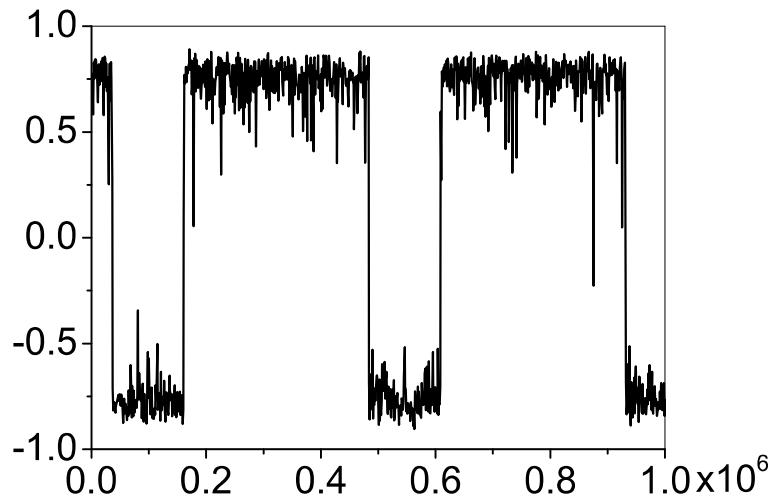


Fig. Instantaneous magnetization ($N_G^{-1} \sum_{i,j} S_{i,j}$) as a function of “time”, with N_G trial moves defined as one MC step. The average lifetime is about 5×10^5 MC steps for system size 40×40 and $T = 2.21$.