

Statistical Mechanics

Hagai Meirovitch

INTRODUCTION

Classical thermodynamics is a **general** methodology that enables one to derive relations among macroscopic properties such as volume (V), pressure (P), temperature (T), energy (E), entropy (S), Helmholtz free energy ($A=E-TS$) etc. without the need to consider the atomic properties of the system: e.g., the equation of state is $PV=NRT$.

Some of other relations:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \quad S = \left(\frac{\partial A}{\partial T}\right)_{V,N} \quad E = -T^2 \left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_{V,N}$$

In **statistical mechanics**, on the other hand, the macroscopic thermodynamic behavior is obtained from the specific microscopic description of a system (atomic interactions, atomic masses, etc.). Therefore, statistical mechanics also provides information that is beyond the reach of classical thermodynamics - **what is the native structure of a protein ?**

It is impossible to know the exact dynamic behavior of a large system (i.e., the atomic coordinates at time t). Appearance of a **3D** configuration is only known with a certain probability.

Thus, statistical mechanics is a probabilistic theory, and computational methods, such as **Monte Carlo** and **molecular dynamics** are based on these probabilistic properties.

Program

- (a) We start by summarizing some properties of basic physics of mechanical systems.
- (b) A very short discussion on classical thermodynamics.
- (c) Derivation of statistical mechanics by demanding compatibility with the theory of classical thermodynamics.
- (d) Statistical mechanics as a probabilistic theory.
- (e) Examples.

Macroscopic Mechanical Systems are Deterministic

Refreshing some basic physics

Examples of forces \mathbf{F} ($F=|\mathbf{F}|$):

- 1) Stretching a spring by a distance x : $\mathbf{F}=-fx$, Hook's Law
 f - spring constant.
- 2) Gravitation force: $\mathbf{F} = kMm/r^2$ - m and M masses with distance r ; k - constant. On earth (R, M large), $\mathbf{g} = kM/R^2$
 $\mathbf{F} = m\mathbf{g}$
- 3) Coulomb law: $\mathbf{F} = kq_1q_2/r^2$ q_1, q_2 charges.

Newton's second law: $\mathbf{F} = m\mathbf{a}$ - \mathbf{a} acceleration

Mechanical work W : if a constant force is applied along distance d , $W = Fd$ ($F = |\mathbf{F}|$). More general, $W = \int \mathbf{F} \cdot d\mathbf{x}$.

Potential energy: If mass m is raised to height, h negative work is done, $W = -mgh$ and the mass gains potential energy, $E_p = -W = +mgh$ - the ability to do mechanical work: when m falls down, E_p is converted into: kinetic energy, $E_k = mv^2/2$, where $v^2/2 = gh$ (at floor).

A spring stretched by d : $E_p = -W = \int f dx = fd^2/2$

In a closed system the total energy, $E_t = E_p + E_k$ is constant but E_p/E_k can change; e.g., oscillation of a mass hung on a spring and distorted from its equilibrium position.

The dynamical state of a mechanical macroscopic system in principle is deterministic in the sense that if the forces are known, and the positions and velocities of the masses at time $t=0$ are known as well, their values at time t can in principle be determined by solving Newton's equations,

$$\mathbf{F}=m\mathbf{a}.$$

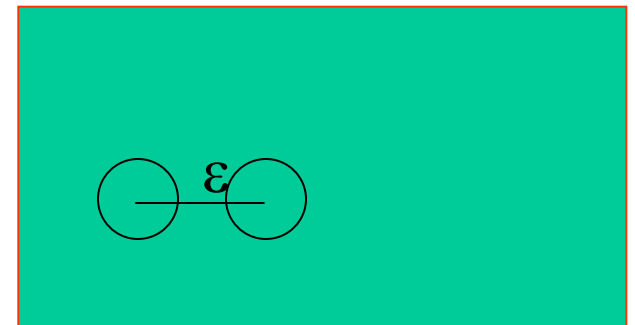
Simple examples: harmonic oscillator (a spring), a trajectory of a projectile, movement of a spaceship, etc. In some cases the solution might be difficult requiring strong computers.

Stability - a system of interacting masses (by some forces) tends to arrange itself in the lowest potential energy structure (which might be degenerate) also called the ground state. The system will stay in the ground state if the kinetic energy is very small - this situation defines maximum order.

The larger the kinetic energy the larger is the disorder - in the sense that at each moment a different arrangement of the masses will occur (no ground state any more). Still, in principle, the trajectories of the masses can be calculated.

Two argon atoms at rest positioned at the lowest energy distance ε - interacting through Lennard-Jones potential. Microscopic system.

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Classical Thermodynamics

Unlike mechanical systems, thermodynamic systems also include transition of heat. Definition of the (dynamic) state by coordinates and velocities of the molecules is impossible.

A state is defined by several macroscopic variables only: volume – V , temperature – T , pressure – P that are not independent - connected by an equation of state

$$f(P, V, T) = 0$$

Equilibrium – external conditions have not changed for a long time and all relaxation processes have occurred.

Reversible transformation from states A  B – very slow, actually composed of many reversible intermediate states.

Very general theory because no microscopic (atomic) information is involved.

The first law of thermodynamics

The first law is the conservation of energy for thermodynamic systems. It states that the variation in energy during any transformation (from state **a** to **b**) is equal to the amount of energy that the system receives from the surrounding, and it depends on states **a** and **b** and not on the intermediate process.

The law implies the existence of internal energy E which is a state function defined up to an additive constant and is an extensive parameter (proportional to the size of the system),

$$E_2 - E_1 = \Delta E = Q - W$$

Q - heat received from the surrounding; W - mechanical work done by the system. T is of surrounding.

The second and third laws of thermodynamics

The law is based on the realization that while mechanical work can be transferred completely to heat, there is a limitation in transferring heat to mechanical work. From the microscopic point of view - molecular motion is not ordered and the kinetic energy cannot be fully harnessed.

The law was introduced initially in terms of engines, perpentum mobile, Carnot cycle, by Kelvin, Clausius and others. will represent a postulate based on entropy. A given thermal equilibrium state a is chosen as standard state. The entropy $S(b)$ of the system in state b is

$$S(b) = \int_a^b \frac{d'Q}{T} \quad \begin{array}{l} \text{Integration over any reversible path } a \longrightarrow b \\ T \text{ is of surrounding, } d'Q \text{ absorbed by system} \end{array}$$

$S(T=0)=0$ (third law). Entropy is an extensive state function;

The second law:

$$\int_a^b \frac{d'Q}{T} \leq S(b) - S(a) \quad \text{equality - for a reversible path}$$

Helmholtz free energy $F(A)$, independent variables T and V

$F = E - TS$ – Helmholtz free energy. $F = F(T, V, N)$

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

Maxwell relation
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

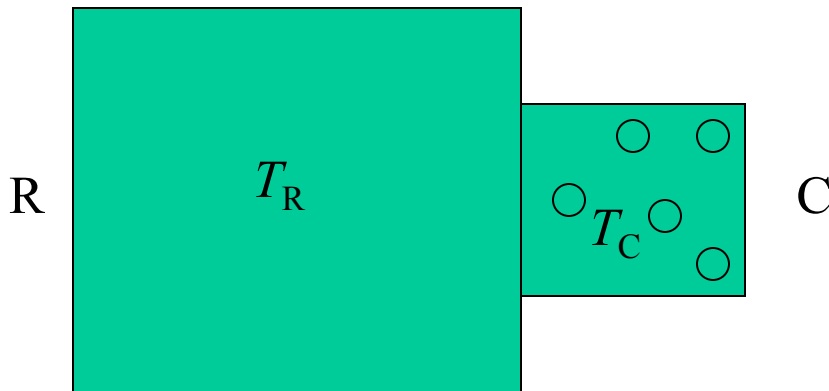
Suppose a system that cannot exchange energy in the form of work (W) with the environment. T is defined by environment. In this case

$$0 = W \leq F(a) - F(b) \qquad F(b) \leq F(a)$$

→ the free energy cannot increase during a transformation. OR If the free energy is a minimum the system is in a state of stable equilibrium. Because any transformation would produce an increase in F - in contradiction to the above inequality.

Thermodynamic systems at equilibrium and equilibrium statistical mechanics

A typical system is described below; examined from a microscopic point of view – non-rigorous treatment



A system **C** of N molecules in a constant volume V is in thermal contact with a large reservoir (**R**) (also called **heat bath**) with a well defined temperature T_R . At equilibrium (after a long time) energy is still exchanged between R and C but the average kinetic energy of a molecule of C is constant and equal to that in R leading to $T_C = T_R$.

However, in contrast to a macroscopic mechanical system, there is no way to know the trajectories of the particles that are changed constantly due to collisions and the energy exchange between C&R, i.e. the random knocks of the R atoms on the interface. However, the averaging E_k & E_p along very long trajectory leads to definite $\langle E_k \rangle$ and $\langle E_p \rangle$, and thus for a snapshot of configuration of N particles $\rightarrow \sim N \langle E_k \rangle$ and $\sim N \langle E_p \rangle$.

Relating kinetic energy to temperature: At high T , E_k is high - dominant, E_p is high— strong random knocks and collisions , large uncertainty related to trajectories \rightarrow large disorder. At low T , E_k is low, the effect of the molecular forces significant - the system arranges itself in a low potential energy state – low disorder.

Therefore, a thermodynamic system at equilibrium cannot be characterized by the positions & velocities of its 10^{23} particles but only by the average values of several macroscopic parameters such as P , T , E (internal energy) and entropy, S .

For example, in measuring T the thermometer feels the average effect of many molecular states $(\mathbf{x}^N, \mathbf{v}^N)$ of the tested system and for a long measurement **all** the microscopic states $(\mathbf{x}^N, \mathbf{v}^N)$ are realized and affect the result of T .

Hence to obtain the average values of macroscopic parameters from microscopic considerations a probability density $P(\mathbf{x}^N, \mathbf{v}^N)$ should be assigned to each system state $(\mathbf{x}^N, \mathbf{v}^N)$ where $(\mathbf{x}^N, \mathbf{v}^N) = (x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N, v_{x1}, v_{y1}, v_{z1}, \dots, v_{xN}, v_{yN}, v_{zN})$ thus assuming that all states contribute.

The space based on $(\mathbf{x}^N, \mathbf{v}^N)$ is called phase space (with P a probability space, or ensemble)

Then a macroscopic parameter M is a statistical average,

$$\langle M \rangle = \int P(\mathbf{x}^N, \mathbf{v}^N) M(\mathbf{x}^N, \mathbf{v}^N) d(\mathbf{x}^N \mathbf{v}^N).$$

The entropy for a discrete and continuous system is (k_B is the Boltzmann constant),

$$S = \langle S \rangle = -k_B \sum P_i \ln P_i \quad \text{and}$$

$$S = -k_B \int P(\mathbf{x}^N \mathbf{v}^N) \ln P(\mathbf{x}^N, \mathbf{v}^N) d(\mathbf{x}^N \mathbf{v}^N) + \\ + \ln \{ \text{const.} [\text{dimension}(\mathbf{x}^N \mathbf{v}^N)] \}$$

Notice, P is a probability density with dimension $1/(\mathbf{x}^N \mathbf{v}^N)$.
The constant is added to make S independent of $(\mathbf{x}^N \mathbf{v}^N)$.

The problem – how to determine P . The correct P should lead to the usual thermodynamic properties. In thermodynamics an N, V, T system is described by the Helmholtz free energy A ,

$$A(T, V, N) = E - TS,$$

which from the second law of thermodynamics should be minimum for a given set of constraints.

We shall determine P by minimizing the statistical free energy with respect to P .

A can be expressed as the average

$$A = \langle A(P) \rangle = \int P(\mathbf{X}) [E(\mathbf{X}) + k_B T \ln P(\mathbf{X})] d\mathbf{X} + \text{const.}$$

$\mathbf{X} = (\mathbf{x}^N, \mathbf{v}^N)$. We take the derivative of A with respect to P and equate to zero; the const. is omitted.

$$A' = \int [E(\mathbf{X}) + k_B T \ln P(\mathbf{X}) + k_B T P(\mathbf{X}) / P(\mathbf{X})] d\mathbf{X} = 0$$

$$E(\mathbf{X}) + k_B T [\ln P(\mathbf{X}) + 1] = 0$$

$$\ln P(\mathbf{X}) = - [E(\mathbf{X}) + k_B T] / k_B T = - [E(\mathbf{X}) / k_B T] + 1$$

$$P(\mathbf{X}) = \text{const} \cdot \exp[-E(\mathbf{X}) / k_B T]$$

The normalization is $Q = \int \exp[-E(\mathbf{X}) / k_B T] d\mathbf{X}$

i.e., $P^B(\mathbf{X}) = \exp[-E(\mathbf{X})/k_B T] / Q$

P^B – the Boltzmann probability (density).

Q – the canonical partition function.

The integrand defining A (p. 18) is $E(\mathbf{X}) + k_B T \ln P^B(\mathbf{X})$

Substituting P^B and taking the \ln gives,

$$E(\mathbf{X}) + k_B T [-E(\mathbf{X})/k_B T - \ln Q] = -k_B T \ln Q$$

$-k_B T \ln Q$ is constant for any \mathbf{X} and can be taken out of the integral of A . Thus,

$$A = \langle E \rangle - T \langle S \rangle = -k_B T \ln Q$$

In summary. Assuming the existence of temperature and that the entropy function is

$$S = -k_B \int P(\mathbf{x}^N, \mathbf{v}^N) \ln P(\mathbf{x}^N, \mathbf{v}^N) d(\mathbf{x}^N, \mathbf{v}^N)$$

We have defined P^B by connecting with thermodynamics.

The relation $A = -k_B T \ln Q$ is very important. It enables calculating A by Q that is based on the microscopic details of the system.

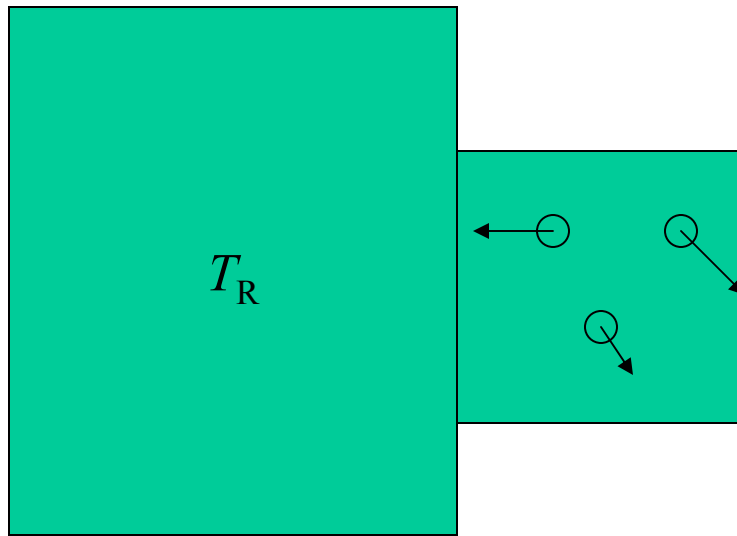
In classical thermodynamics all quantities are obtained as derivatives of A . Hence, with statistical mechanics all these quantities can be obtained by taking derivatives of $\ln Q$.

Also, the probabilistic character of statistical mechanics enables calculating averages even without calculating Q .

These averages can be even geometrical properties that are beyond the reach of thermodynamics, such as the **end-to-end distance** of a polymer, the **radius of gyration** of a protein and many other geometrical or dynamic properties. This is in particular useful in computer simulation.

The ensemble of configurations defined by constant V , T and N and their Boltzmann probabilities is called the canonical ensemble.

Calculation of the partition function Q



Systems at equilibrium

N particles with velocities \mathbf{v}^N and coordinates \mathbf{x}^N are moving in a container in contact with a reservoir of temperature $T_R = T$.

We have seen that the Helmholtz free energy, A is

$$A = E - TS = -k_B T \ln Q \quad \text{where}$$

$$Q = \int \exp[-E(\mathbf{x}^N, \mathbf{v}^N)/k_B T] d(\mathbf{x}^N \mathbf{v}^N)$$

$$E(\mathbf{x}^N, \mathbf{v}^N) = E_k(\mathbf{v}^N) + E_p(\mathbf{x}^N)$$

$E(\mathbf{x}^N, \mathbf{v}^N)$ is the Hamiltonian of the system (for $E_p(\mathbf{x}^N)$ see p. 8).

If the forces do not depend on the velocities (most cases) E_k is independent of E_p and the integrations can be separated. Also, the integrations over the velocities of different particles are independent. Moreover, the integrations over the components v_x , v_y , and v_z are independent. Therefore, we treat first the integration over v_x (denoted v) of a single particle.

To recall: the linear momentum vector $\mathbf{p} = m\mathbf{v}$; therefore, for one component:

$$E_k = mv^2/2 = p^2/2m$$

A useful integral (from table):

$$\int_0^{\infty} \mathbf{exp}(-ax^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

Therefore, for calculating $Q(p)$ our integral is

$$\int_{-\infty}^{\infty} \mathbf{exp}\left(-\frac{p^2}{2mk_B T}\right) dp = \sqrt{2\pi mk_B T}$$

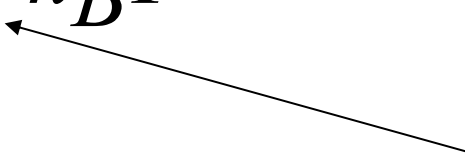
because

$$a = \frac{1}{2mk_B T}$$

The integral over the $3N$ components of the momentum (velocities) is the following product:

$$\left(\sqrt{2\pi mk_B T}\right)^{3N}$$




Q is (h is the Planck constant – see Hill p.74; $\Omega=V^N$),

$$Q = \frac{\left(\sqrt{2\pi mk_B T}\right)^{3N}}{N! h^{3N}} \int_{\Omega} \exp\left(-\frac{E(\mathbf{x}^N)}{k_B T}\right) d\mathbf{x}^N$$


The problem is to calculate the configurational integral

$$\int_{\Omega} \exp\left(-\frac{E(\mathbf{x}^N)}{k_B T}\right) dx^1 dy^1 dz^1 dx^2 dy^2 dz^2 \dots$$

The division by N factorial, $N!=1 \times 2 \times 3 \dots \times N$ is required from quantum mechanical considerations because the particles are independent and indistinguishable (however, introduced by Gibbs!, Hill p.62). Thus, each configuration of the N particles in positions $\mathbf{x}^1, \mathbf{x}^2, \mathbf{x}^3, \dots, \mathbf{x}^N$ can be obtained $N!$ times by exchanging the particles in these positions. For example, for 3 particles there are $3!=6$ possible permutations.

sites			
Particles 1,2,3	1	2	3
	3	2	1
	3	1	2
	1	3	2
	2	1	3
	2	3	1

Stirling approximate formula: $\ln N! \approx N \ln (N/e)$

The Helmholtz free energy $A(N, V, T)$ is:

$$-k_B T N \ln \left\{ \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{e}{N} \right\} - k_B T \ln \int_{\Omega} \exp \left(-\frac{E(\mathbf{x}^N)}{k_B T} \right) d\mathbf{x}^N$$

The **velocities** (momenta) part is completely solved; it contains m and h - beyond classical thermodynamics!

The problem of statistical mechanics is thus to solve the integral. For an ideal gas, $E = 0$ (no interactions) hence $\int = V^N$ trivial!!

$$A(N, V, T) = -k_B T N \ln \left\{ \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{eV}{N} \right\}$$

Thermodynamic derivatives of A of an ideal gas (properties $\sim N$ or $\sim V$ are called extensive):

Pressure:
Intensive
variable $\sim N/V$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = Nk_B T / V \Rightarrow PV = Nk_B T$$

Internal energy:
Extensive variable
 $\sim N$

$$E = -T^2 \left(\frac{\partial \left(\frac{A}{T} \right)}{\partial T} \right)_{V,N} = \frac{3}{2} Nk_B T$$

E is the average kinetic energy (see later) $\sim T$, independent of V ! Each degree of freedom contributes $(1/2)k_B T$. If the forces (interactions) do not depend on the velocities, T is determined by the kinetic energy only (see previous note).

The specific heat C_V is independent of T and V .

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V,N} = \frac{3}{2} Nk_B$$

The entropy is:

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,N} = \frac{E - A}{T} = Nk_B \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right]$$

In thermodynamics one obtains for an ideal gas: $S = C_V \ln T + R \ln V + A$. S contains microscopic parameters (e.g., m) not known in thermodynamics. S increases with N - extensive variable. V/N intensive! S is not defined at $T=0$ – should be 0 according the third law of thermodynamics; the ideal gas picture holds only for high T . $S \sim \ln T$ and $E \sim T$, both increase with T , but $A = E - TS$.

In the case of a **real** gas $E(\mathbf{x}^N) \neq 0$ and the problem is to calculate the configurational partition function denoted Z , where the momentum part is ignored,

$$Z = \int \exp[-E(\mathbf{x}^N)/k_B T] d\mathbf{x}^N$$

Notice: While Q is dimensionless, Z has the dimension of \mathbf{x}^N .
Also,

$$Z = \int \nu(E) \exp[-E/k_B T] dE$$

$\nu(E)$ – the density of states around E ; $\nu(E)dE$ – the volume in configurational space with energy between E and $E + dE$. For a discrete system [$n(E_i)$ is the degeneracy of E]

$$Z = \sum \exp[-E_i/k_B T] = \sum n(E_i) \exp[-E_i/k_B T] \quad 30$$

The contribution of Z to the thermodynamic functions is obtained from derivatives of the configurational Helmholtz free energy, F

$$F = -k_B T \ln Z$$

Calculating Z for realistic models of fluids, polymers, proteins, etc. by analytical techniques is unfeasible. Powerful numerical methods such as Monte Carlo and molecular dynamics are very successful.

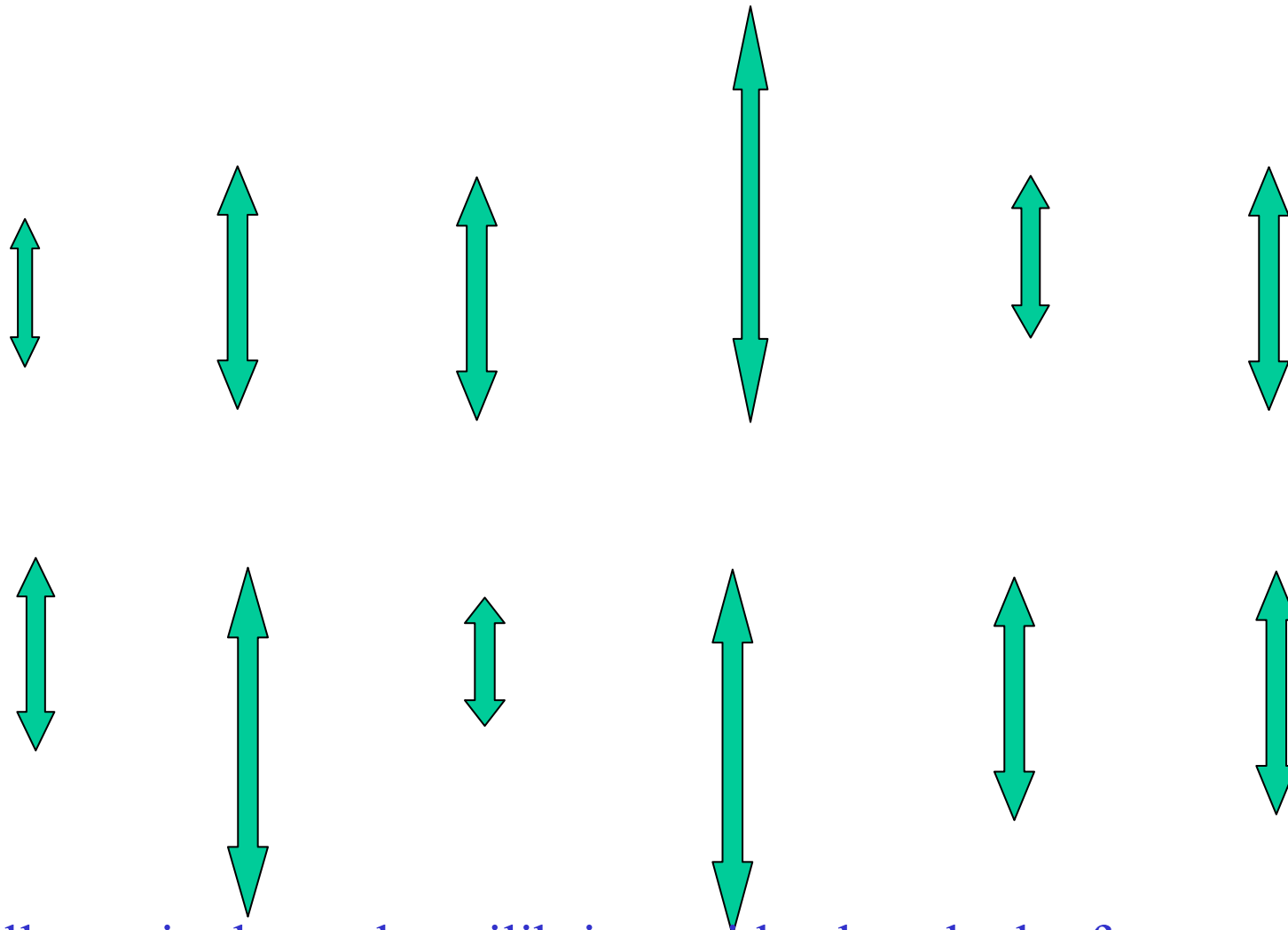
A simple example: N classical harmonic oscillators

They are at equilibrium with a heat bath of temperature T - a good model for a crystal at high temperature, where each atom feels the forces exerted by its neighbor atoms and can approximately be treated as an independent oscillator that does not interact with the neighbor ones.

Therefore, $Q_N = q^N$, where q is the partition function of a **single** oscillator. Moreover, the components (x, y, z) are independent as well; therefore, one can calculate q_x and obtain $Q_N = q_x^{3N}$.

The energy of a **macroscopic** oscillator (e.g., a mass hung on a spring) is determined by its amplitude (the stretching distance) and the position $x(t)$ of the mass is known exactly as a function of t .

The amplitude of a **microscopic** oscillator is caused by the energy provided by the heat bath. This energy changes all the time and the amplitude changes as well but has an **average** value that increases as T increases. Unlike a macroscopic mechanical oscillator, $x(t)$ is **unknown**; we only know $P^B(\mathbf{x})$.



Oscillators in thermal equilibrium with a heat bath of temperature T . A snapshot of their amplitudes at time t . The average amplitude is well defined (or the average amplitude of one oscillator as a function of time)-
canonical ensemble picture.

The kinetic and potential energy (Hamiltonian) of an oscillator are

$$p^2/2m + fx^2/2$$

f is the force constant and the partition function is, $q=q_k q_p$ where q_k was calculated before; ν is the frequency of the oscillator.

$$q_k = \frac{\sqrt{2\pi m k_B T}}{h}$$

$$q_p = \sqrt{\frac{2\pi k_B T}{f}}$$

$$q = 2\pi \sqrt{\frac{m k_B T}{f h}} = \frac{k_B T}{h\nu}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$$

$$E = -T^2 \left(\frac{\partial \left(\frac{A}{T} \right)}{\partial T} \right) = k_B T \quad E_k = E_p = 1/2 k_B T \quad \Rightarrow \quad C_V = k_B$$

The average energy (see later) of one component (e.g., x direction) of an oscillator is twice as that of an ideal gas – effect of interaction. For N , 3D oscillators, $E = 3Nk_B T$ - extensive ($\sim N$) and $C_V = 3Nk_B$ - Dulong-Petit Law. The entropy is also extensive,

$$S = E/T - A/T = 3Nk_B (1 + \ln [k_B T / h\nu])$$

E and S increase with T .

In mechanics the total energy of an oscillator is constant, $fd^2/2$ where d is the amplitude of the motion and at time t the position of the mass is known exactly.

In statistical mechanics a classical oscillator changes its positions due to the random energy delivered by the heat bath. The positions of the mass x are only known with their Gaussian Boltzmann probability;

$$P(x) = \exp[-fx^2/2k_B T]/q_p$$

In principle x can be very large, but for a given T there is an average amplitude & in practice x fluctuates around this value.

When T increases the energy increases meaning that the average amplitude increases and the position of the mass is less defined due to larger fluctuations (in x^2); therefore, the entropy is enhanced.

Notice: A classical oscillator is a valid system only at high T . At low T one has to use the quantum mechanical oscillator.

Thus far we have obtained the macroscopic thermodynamic quantities from a microscopic picture by calculating the partition function Q and taking (thermodynamic) derivatives of the free energy $-kBT \ln Q$. We have discussed two simple examples, ideal gas and classical oscillators.

We shall discuss next the probabilistic significance of statistical mechanics.

The probabilistic character of statistical mechanics

Thus far, the thermodynamic properties were obtained from the relation between the free energy, A and the partition function Q , $A = -k_B T \ln Q$ using known thermodynamics derivatives. However, the theory is based on the assumption that each configuration in **phase space** has a certain probability (or probability density) to occur - the Boltzmann probability,

$$P^B(\mathbf{X}) = \exp[-E(\mathbf{X})/k_B T] / Q$$

where $\mathbf{X} \equiv \mathbf{x}^N \mathbf{v}^N$ is a $6N$ vector of coordinates and velocities. Therefore, any thermodynamic property such as the energy is an expectation value defined with $P^B(\mathbf{X})$.

For example, the statistical average (denoted by $\langle \rangle$) of the energy is:

$$\langle E \rangle = \int P^B(\mathbf{x}^N, \mathbf{v}^N) E(\mathbf{x}^N, \mathbf{v}^N) d(\mathbf{x}^N \mathbf{v}^N),$$

where $E(\mathbf{x}^N, \mathbf{v}^N)$ is a random variable. $\langle E \rangle$ is equal to E calculated by a thermodynamic derivative of the free energy, A . For an ideal gas (pp.22-25) $\langle E \rangle$ is obtained by a Gaussian

$$Q_{IG} = \frac{(\sqrt{2\pi m k_B T})^{3N}}{N! h^{3N}} V^N$$

$$P^B = \frac{\exp\left[-\frac{\mathbf{p}^2}{2m k_B T}\right] / N! h^{3N}}{Q_{IG}} = \frac{\exp\left[-\frac{\mathbf{p}^2}{2m k_B T}\right]}{(\sqrt{2\pi m k_B T})^{3N} V^N}$$

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} \frac{\mathbf{p}^2}{2m} \exp\left[-\frac{\mathbf{p}^2}{2m k_B T}\right] d\mathbf{p} \int_V d\mathbf{x}}{(\sqrt{2\pi m k_B T})^{3N} V^N} = \frac{3}{2} N k_B T$$

This is the same result obtained from thermodynamic derivatives (p. 28). For two degrees of freedom the integral is:

$$\begin{aligned}
 & \frac{\int_{-\infty}^{\infty} \frac{(p_1^2 + p_2^2)}{2m} \exp\left[-\frac{p_1^2 + p_2^2}{2mk_B T}\right] dp_1 dp_2 \int dx_1 dx_2}{(\sqrt{2\pi mk_B T})^2 V^2} = \\
 & \frac{[\sqrt{\pi}(2mk_B T)^{3/2} (\sqrt{2\pi mk_B T})] \cdot 2}{2m \cdot 2} = \frac{3}{2} \cdot 2k_B T
 \end{aligned}$$

$$\int_{-\infty}^{\infty} x^2 \mathbf{exp}[-ax^2] dx = \frac{\sqrt{\pi}}{2a^{3/2}}$$

The **entropy** can also be expressed as a statistical average. For a discrete system,

$$S = \langle S \rangle = -k_B \sum_i P_i \ln P_i$$

If the system populates a **single** state k , $P_k=1$ and $S=0 \Rightarrow$ there is **no** uncertainty. This never occurs at a finite temperature. It occurs for a quantum system at $T=0$ K.

On the other hand, if all states have the same probability, $P_i=1/\Omega$, where Ω is the total number of states, the uncertainty about the state of the system is **maximal** (any state can be populated equally) and the entropy is **maximal** as well,

$$S = -k_B \ln \Omega$$

This occurs at very high temperatures where the kinetic energy is large and the majority of the system's configurations can be visited with the same **random** probability.

It has already been pointed out that the velocities (momenta) part of the partition function is completely solved (pp. 24-26). On the other hand, unlike an ideal gas, in practical cases the potential energy, $E(\mathbf{x}^N) \neq 0$ and the problem of statistical mechanics is to calculate the configurational partition function denoted Z , where the momentum part is ignored (see p. 30)

$$Z = \int \exp[-E(\mathbf{x}^N)/k_B T] d\mathbf{x}^N$$

where Z has the dimension of \mathbf{x}^N . Also,

$$Z = \int \nu(E) \exp[-E/k_B T] dE$$

$\nu(E)$ – the density of states; $\nu(E)dE$ – the volume in configurational space with energy between E and $E + dE$. For a discrete system $n(E_i)$ is the degeneracy and Z is

$$Z = \sum_i \exp[-E_i/k_B T] = \sum_E n(E) \exp[-E/k_B T]$$

The thermodynamic functions can be obtained from derivatives of the configurational Helmholtz free energy, F

$$F = -k_B T \ln Z.$$

From now on we ignore the velocities part and mainly treat Z .
Probability space picture: The configurational space is viewed as a $3N$ dimensional sample space Ω , where to each “point” \mathbf{x}^N (random variable) corresponds the Boltzmann probability density,

$$P^B(\mathbf{x}^N) = \exp[-E(\mathbf{x}^N)]/Z$$

where $P^B(\mathbf{x}^N)d\mathbf{x}^N$ is the probability to find the system between \mathbf{x}^N and $\mathbf{x}^N + d\mathbf{x}^N$. The potential energy $E(\mathbf{x}^N)$ defined for \mathbf{x}^N is also a random variable with an expectation value $\langle E \rangle$

The power of the probabilistic approach is that it enables calculating not only macroscopic thermodynamic properties such as the average energy, pressure etc. of the whole system, but also microscopic quantities, such as the average end-to-end distance of a polymer. This approach is extremely useful in computer simulation, where every part of the system can be treated, hence almost any microscopic average can be calculated (distances between the atoms of a protein, its radius of gyration, etc.).

The entropy can also be viewed as an expectation value, where $\ln P^B(\mathbf{x}^N)$ is a random variable,

$$S = \langle S \rangle = -k_B \int_{\Omega} P^B(\mathbf{x}^N) \ln P^B(\mathbf{x}^N) d\mathbf{x}^N$$

Likewise, the free energy F can formally be expressed as an average of the random variable, $E(\mathbf{x}^N) + k_B T \ln P^B(\mathbf{x}^N)$,

$$F = -k_B T \ln Z = \int_{\Omega} P^B(\mathbf{x}^N) [E(\mathbf{x}^N) + k_B T \ln P^B(\mathbf{x}^N)] d\mathbf{x}^N$$

Fluctuations (variances)

The variance (fluctuation) of the energy is:

$$\begin{aligned} \sigma^2(E) &= \int_{\Omega} P^B(\mathbf{x}^N) [E(\mathbf{x}^N) - \langle E \rangle]^2 d\mathbf{x}^N = \\ &= \langle E(\mathbf{x}^N)^2 \rangle - \langle E(\mathbf{x}^N) \rangle^2 \end{aligned}$$

Notice that the expectation value is denoted by $\langle \rangle$ and E is the energy. It can be shown (Hill p. 35) that the specific heat at

constant volume is: $C_v = (dE/dT)_V = \sigma^2(E) / k_B T^2$

In regular conditions $C_v = \sigma^2(E) / k_B T^2$ is an extensive variable, i.e., it increases $\sim N$ as the number of particles N increases; therefore, $\sigma(E) \sim N^{1/2}$ and the relative fluctuation of E decreases with increasing N ,

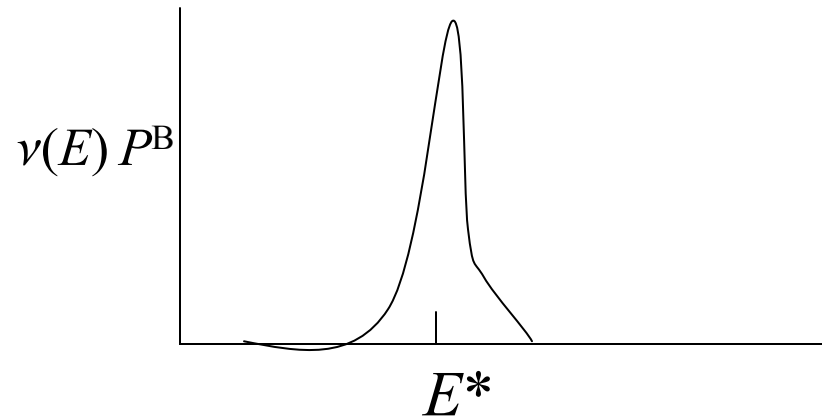
$$\frac{\sigma(E)}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

Thus, in macroscopic systems ($N \sim 10^{23}$) the fluctuation (i.e., the standard deviation) of E can be ignored because it is $\sim 10^{11}$ times smaller than the energy itself \Rightarrow these fluctuations are not observed in macroscopic objects. Like $Z, \langle E \rangle$ can be expressed,

$$\langle E \rangle = \int E(\mathbf{x}^N) P^B(\mathbf{x}^N) d\mathbf{x}^N = \int E \nu(E) P^B(E) dE$$

where $\nu(E)$ is the density of states and $P^B(E)$ is the Boltzmann probability of a configuration with E .

The fact that $\sigma(E)$ is so small means that the contribution to $\langle E \rangle$ comes from a very narrow range of energies around a typical energy $E^*(T)$ that depends on the temperature



Therefore, the partition function can be approximated by taking into account only the contribution related to $E^*(T)$.

$$Z = \int \nu(E) \exp[-E/k_B T] dE \cong f_T(E^*) = \nu(E^*) \exp[-E^*/k_B T] \therefore$$

$$F = -k_B T \ln Z \cong E^*(T) + k_B T \ln \nu(E^*) = E^*(T) - TS$$

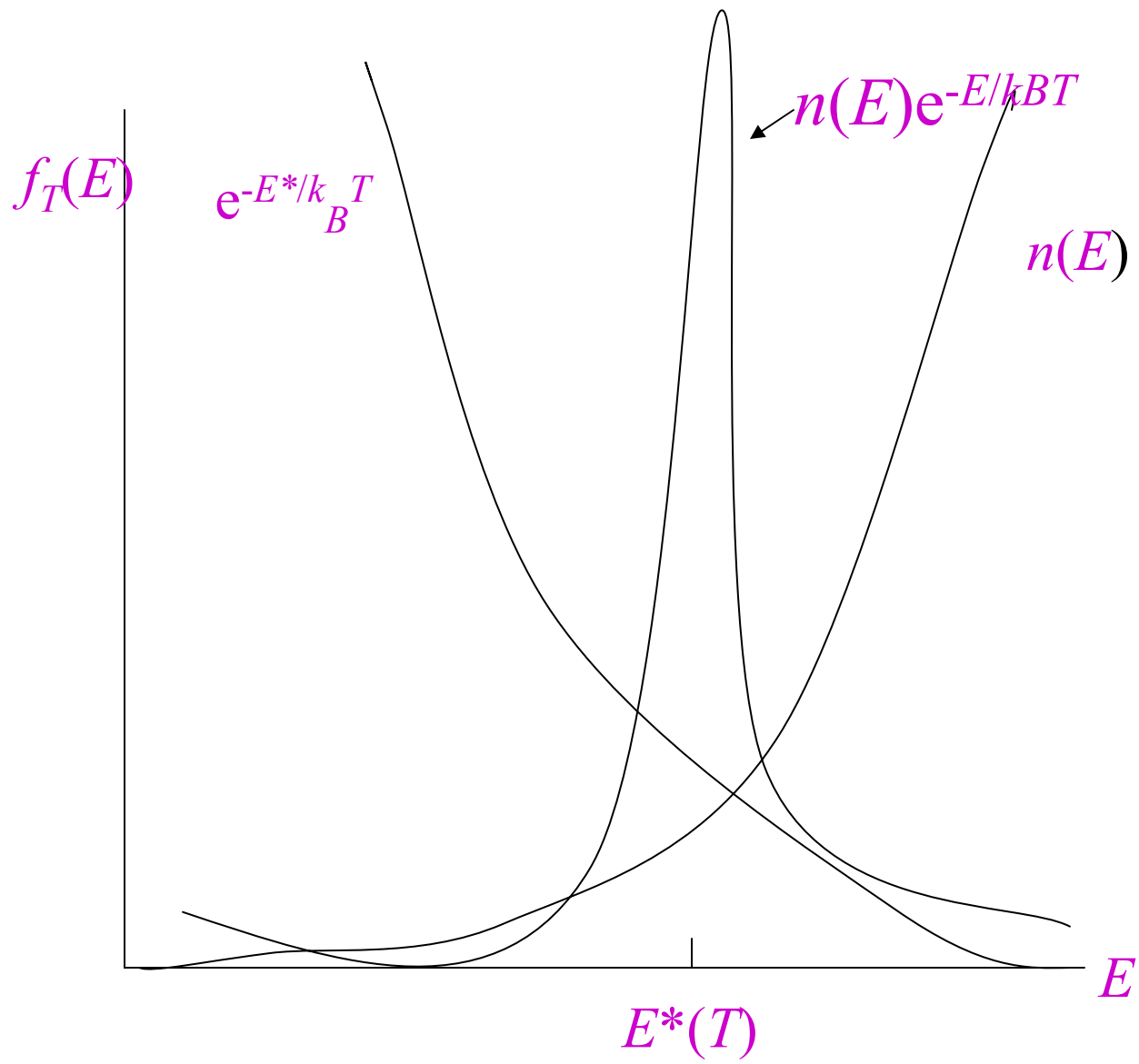
The entropy, $-k_B \ln \nu(E^*)$ is the logarithm of the degeneracy of the most probable energy. For a discrete system

$$Z = \sum n(E_i) \exp [- E_i/k_B T]$$

where E_i are the set of energies of the system and $n(E_i)$ their degeneracies. For a macroscopic system the number of different energies is large ($\sim N$ for a discrete system) while only the maximal term

$$n(E^*) \exp [- E^*/k_B T]$$

contributes. This product consists of two exponentials. At very low T the product is maximal for the ground state energy, where most of the contribution comes from $\exp[- E_{GS}^*/k_B T]$ while $n(E_{GS}^*) \sim 1$ ($S=0$). At very high T the product is maximal for a high energy, where $n(E^*)$ is maximal (maximum degeneracy \Rightarrow maximum entropy) but the exponential of the energy is small. For intermediate T

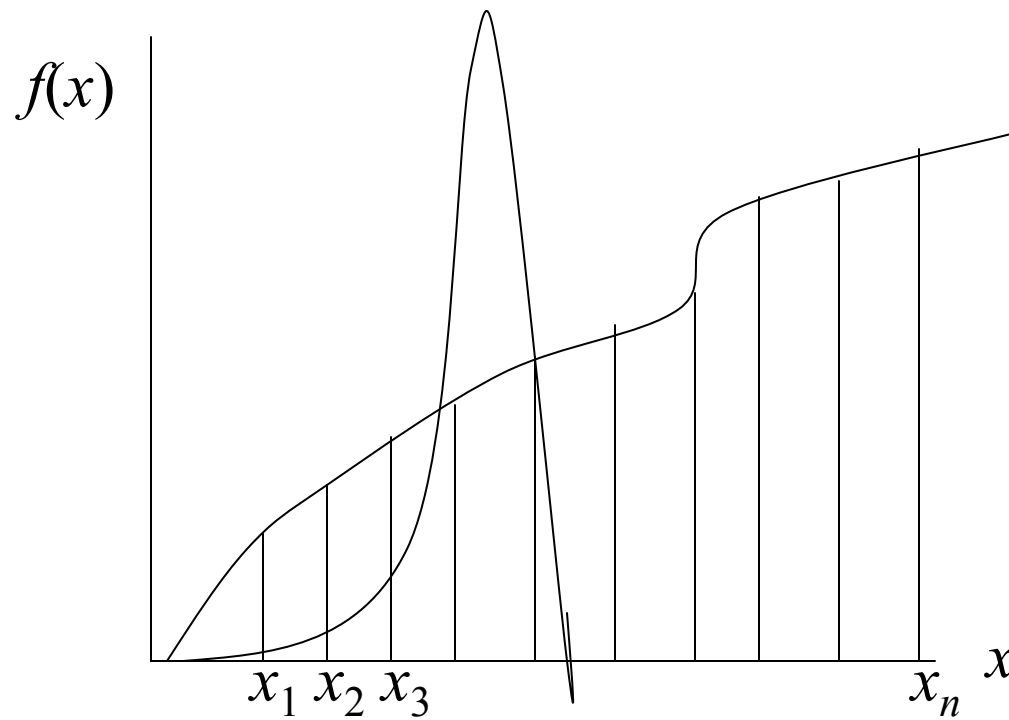


The fact that the contribution to the integrals comes from an extremely narrow region of energies makes it very difficult to estimate $\langle E \rangle$, S and other quantities by numerical integration. This is because the $3N$ dimensional configurational space is huge and the desired **small** region that contributes to the integrals is unknown **a-priori**.

Therefore, dividing the space into small regions (grid) would be impractical and even if done the corresponding integration would contribute **zero** because the small important region would be missed - clearly a waste of computer time.

The success of **Monte Carlo** methods lies in their ability to find the contributing region very efficiently leading to precise estimation of various averages, such as $\langle E \rangle$.

Numerical integration



$$\int f(x) dx \cong \sum_i f(x_i) \Delta x_i \quad \Delta x_i = x_i - x_{i-1}$$

What is the probability to find the system in a certain energy (not \mathbf{x}^N)?

$$P^B(E) = n(E) \exp[-E/k_B T] / Z$$

So, this probability depends not only on the energy but also on the degeneracy $n(E)$. The relative population of two energies is therefore:

$$\frac{P^B(E_1)}{P^B(E_2)} = \frac{n(E_1) \cdot \exp(-E_1/k_B T)}{n(E_2) \cdot \exp(-E_2/k_B T)} = \frac{n(E_1)}{n(E_2)} \cdot \exp(-\Delta E/k_B T)$$

$$\Delta E = E_1 - E_2$$

Solving problems in statistical mechanics

The first step is to identify the states of the system and the corresponding energies (e.g., the configurations of a fluid and their energies). Then, three options are available:

- 1) The **thermodynamic approach**: Calculate the partition function $Z \Rightarrow$ the free energy $F = -k_B T \ln Z$ and obtain the properties of interest as suitable derivatives of F .
- 2) Calculate **statistical averages** of the properties of interest.
- 3) Calculate the **most probable** term of Z and the most dominant contributions of the other properties.

Problem: N independent spins interact with a magnetic field H . the interaction energy (potential) of a spin is μH or $-\mu H$, depending of whether μ , the magnetic moment is positive or negative. Positive μ leads to energy $-\mu H$. Calculate the various thermodynamic functions (E, F, S , etc.) at a given temperature T .

2^N stats of the system because each spin is or $+1(-\mu)$ or $-1(\mu)$.

Potential energy of spin configuration i : $E_i = -N_+ \mu H + N_- \mu H$ or $E_i = -(N - N_-) \mu H + N_- \mu H$ where N_+ and N_- are the numbers of $+1$ and -1 spins. The magnetization of i is:

$$M = N_+ \mu H - N_- \mu H$$

No kinetic energy is defined for this model.

Option 1: Thermodynamic approach

We have to calculate $Z = \sum_i \exp[-E_i/k_B T]$; i runs over all the 2^N different states of the system!

This summation can be calculated by a trick. The spins are independent, i.e., they do not interact with each other \Rightarrow changing a spin does not affect the other spins. Therefore, the summation over the states of N spins can be expressed as the product $Z=(z_1)^N$ where z_1 is the partition function of a single spin (see oscillator!).

$$z_1 = \exp(-\mu H/k_B T) + \exp(+\mu H/k_B T) = 2 \cosh[\mu H/k_B T]$$

$$\cosh(x) = [\exp(x) + \exp(-x)]/2$$

$$Z = [2 \cosh(\mu H/k_B T)]^N$$

$$F = -k_B T \ln Z = -k_B T N \ln [2 \cosh(\mu H / k_B T)]$$

Entropy:

$$S = - \left(\frac{\partial F}{\partial T} \right)_H = N k_B \left[\ln \left\{ 2 \cosh \left(\frac{\mu H}{k_B T} \right) \right\} - \frac{\mu H}{k_B T} \tanh \left(\frac{\mu H}{k_B T} \right) \right]$$

$$T = \infty, S/N = \ln 2 ; T = 0, S = 0$$

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{\sinh(x)}{\cosh(x)}$$

Energy:

$$E = F + TS = -T^2 \frac{\partial \left(\frac{F}{T} \right)}{\partial T} \Bigg|_H = -N \mu H \tanh \left(\frac{\mu H}{k_B T} \right)$$

Magnetization: $M = N_+ - N_-$

$$M = -\left(\frac{\partial F}{\partial H}\right)_T = N\mu \tanh\left(\frac{\mu H}{k_B T}\right)$$

Specific heat:

$$C = -\left(\frac{\partial E}{\partial T}\right)_H = \frac{Nk_B \left(\frac{\mu H}{k_B T}\right)^2}{\cosh^2\left(\frac{\mu H}{k_B T}\right)}$$

Option 2: Statistical approach

Again we can treat first a **single** spin and calculate its average energy. z_1 for a single spin is:

$$z_1 = \exp(-\mu H/k_B T) + \exp(+\mu H/k_B T) = 2 \cosh[\mu H/k_B T]$$

The Boltzmann probability for \pm spin is: $\exp[\pm \mu H/k_B T] / z_1$

The average energy is

$$\langle E \rangle_1 = [-\mu H \exp(+\mu H/k_B T) + \mu H \exp(-\mu H/k_B T)] / z_1$$

$$= -\mu H \{2 \sinh[\mu H/k_B T]\} / \{2 \cosh[\mu H/k_B T]\} =$$

$$= -\mu H \tanh(\mu H/k_B T) \quad ; \quad \langle E \rangle = -\mu H N \tanh(\mu H/k_B T)$$

The entropy s_1 of a single spin is:

$s_1 = -k_B [P^+ \ln P^+ + P^- \ln P^-]$, where P is the Boltzmann probability.

$$\begin{aligned} s_1 &= -k_B \left\{ \exp[+\mu H/k_B T] [\mu H/k_B T - \ln z_1] + \right. \\ &\quad \left. \exp[-\mu H/k_B T] [-\mu H/k_B T - \ln z_1] \right\} / z_1 = \\ &= -k_B \left\{ \mu H/k_B T [e^+ - e^-] / z_1 - \ln z_1 [e^+ + e^-] / z_1 \right\} = \\ &= -k_B \left\{ \mu H/k_B T \tanh[\mu H/k_B T] - \ln z_1 \right\} \end{aligned}$$

The same result as on p. 57.

Option 3: Using the most probable term

$$E = -N_+ \mu H + N_- \mu H \Rightarrow E' = E/\mu H = -N_+ + N_-$$
$$N = N_+ + N_-$$

$$N_- = (N + E')/2 \quad ; \quad N_+ = (N - E')/2$$

$$M = \mu (N_+ - N_-) \quad E = -MH$$

The # of spin configurations with E , $W(E) = N! / (N_+! N_-!)$

The terms of the partition function have the form,

$$f_T(E') = \frac{N!}{\left(\frac{N + E'}{2}\right)! \left(\frac{N - E'}{2}\right)!} \exp[-E' \mu H / k_B T]$$

For a given N , T , and H we seek to find the maximal term. We take $\ln f_T(E)$, derive it with respect to E' , and equate the result to 0, using the Stirling formula, $\ln N! \approx N \ln N$.

$$\ln f_T(E') = N \ln N - \left(\frac{N+E'}{2}\right) \ln \left(\frac{N+E'}{2}\right) - \left(\frac{N-E'}{2}\right) \ln \left(\frac{N-E'}{2}\right) - \frac{\mu H E'}{k_B T}$$

The maximum or minimum of a function $f(x)$ with respect to x , is obtained at the value x^* where $(df/dx)|_{x^*} = f'(x^*) = 0$ and $(d^2f/dx^2)|_{x^*} < 0$ or > 0 , respectively.

$$\frac{\partial f_T(E')}{\partial E'} = -\frac{1}{2} \ln \frac{N+E'}{2} + \frac{1}{2} \ln \frac{N-E'}{2} - \frac{\mu H}{k_B T} = 0$$

$$\frac{1}{2} \ln \frac{N-E'}{N+E'} = \frac{\mu H}{k_B T} \Rightarrow \frac{N-E'}{N+E'} = \exp \frac{2\mu H}{k_B T}$$

$$E' = N \frac{1 - \exp\left(\frac{2\mu H}{k_B T}\right)}{1 + \exp\left(\frac{2\mu H}{k_B T}\right)} = N \frac{\exp\left(\frac{\mu H}{k_B T}\right)}{\exp\left(\frac{\mu H}{k_B T}\right)} \left[\frac{\exp\left(-\frac{\mu H}{k_B T}\right) - \exp\left(\frac{\mu H}{k_B T}\right)}{\exp\left(-\frac{\mu H}{k_B T}\right) + \exp\left(\frac{\mu H}{k_B T}\right)} \right]$$

$$E' = -N \tanh\left[\frac{\mu H}{k_B T}\right]$$

The most probable energy, E^* for given T and H is:

$$E^* = -N\mu H \tanh(\mu H/k_B T)$$

and

$$M = N\mu \tanh(\mu H/k_B T)$$

As obtained before.

<u>degeneracy</u>	<u>energy</u>	<u>typical T</u>	<u>spin configurations</u>
1 (min. $S=0$)	$-N\mu H$ (min.)	$T_0 = 0$	$\uparrow\uparrow\uparrow\uparrow\dots\uparrow\uparrow \quad \uparrow(H)$
N	$-(N-1)\mu H + \mu H$ $= -N\mu H + 2\mu H$	very low (T_0)	$\downarrow\uparrow\uparrow\uparrow \dots \uparrow\uparrow$
$N! / [(N-2)!2!]$ $= N(N-1)/2$	$-N\mu H + 4\mu H$	$T_2 > T_0$	$\downarrow\downarrow\uparrow\uparrow \dots \uparrow\uparrow$
.			$k \downarrow$
$N! / [(N-k)!k!]$	$-N\mu H + 2k\mu H$	$T_k > T_{k-1}$	$\downarrow\downarrow\downarrow\downarrow \dots \uparrow\uparrow$
.			
.			$N/2 \quad N/2$
$N! / [(N/2)!(N/2)!]$ (max. degeneracy $S = N \ln 2$)	$\mu H (N/2 - N/2)$ $= 0$	high T	$\downarrow\downarrow\downarrow\downarrow \dots \uparrow\uparrow \uparrow\uparrow$

$N_- > N_+$ not physical, negative temperature! dE increases, dS decreases.

internal energy, the entropy, the specific heat and the total magnetic moment M of this system with the help of the canonical distribution.

SOLUTION

Since the spins are independent of each other, the partition function of the total system Z_N is equal to the N th power of the partition function for the

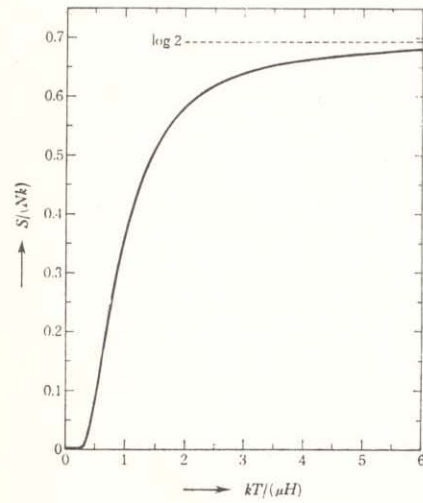


Fig. 1.11.

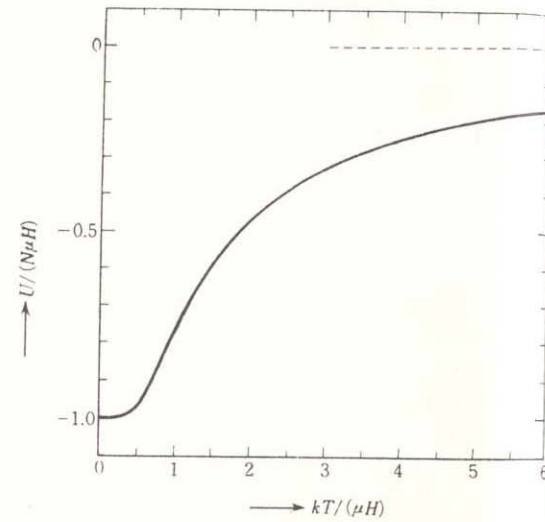


Fig. 1.12.

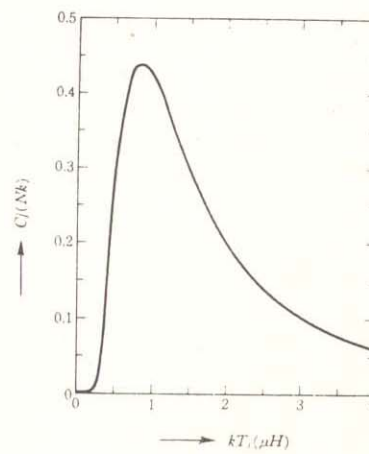


Fig. 1.13.

Several points:

The entropy can be defined in two ways:

1) As a statistical average:

$$S = -k_B \sum_i P_i \ln P_i \quad (P_i - \text{Boltzmann}) \text{ and}$$

2) as: $S \cong k_B \ln n(E^*)$

$n(E^*)$ - degeneracy of the most probable energy. For large systems the two definitions are identical.

As a **mechanical** system the spins “would like” to stay in the ground state (all spins are up; **lowest** potential energy \Rightarrow most stable state), where no uncertainty exists (maximum order) \Rightarrow the entropy is 0.

However, the spins interact with a heat bath at a finite T , where **random** energy flows in and out the spin system. Thus, spins parallel to H (spin **up**) might absorb energy and “**jump**” to their higher energy level (spin **down**), then some of them will release their energy back to the bath by returning to the lower energy state (\uparrow) and vice versa.

For a given T the average number of excited spins (\downarrow) is constant and this number increases (i.e., the average energy increases) as T is increased.

The statistical mechanics treatment of this model describes this physical picture. As T increases the average energy ($= E^*(T)$ - the most probable energy) increases correspondingly.

As $E^*(T)$ increases the number of states $n(E^*)$ with energy $E^*(T)$ increases as well, i.e., the system can populate more states with the same probability \Rightarrow the uncertainty about its location increases $\Rightarrow S$ increases.

So, the increased energy and its randomness provided by the heat bath as T increases, is expressed in the spin system by higher $E^*(T)$ and enhanced disorder, i.e., larger $\ln n(E^*) \Rightarrow$ larger $S(T)$.

The stability of a thermodynamic system is a “**compromise**” between two opposing tendencies: to be in the lowest potential energy and to be in a maximal disorder. At $T=0$ the potential energy wins; it is minimal \Rightarrow complete order $S=0$ (minimal). At $T=\infty$ the disorder wins, S and E^* are both maximal.

At finite T the stability becomes a compromise between the tendencies for order and disorder; it is determined by finding the most probable (**maximal**) term of the partition function [at $E^*(T)$]:

$$n(E^*) \exp-[E^*/k_B T]$$

or equivalently the minimal term of the free energy,

$$E^* + k_B T \ln n(E^*) = E^* - TS^*$$

Notice that while the (macroscopic) energy is known very accurately due to the small fluctuations, the configuration (state) is unknown. We only know that the system can be located with equal probability in any of the $n(E^*)$ states.