Statistical Mechanics

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Program

(a) We start by summarizing some properties of basic physics of mechanical systems.

(b) A short discussion on classical thermodynamics – differences from macroscopic mechanical systems.

(c) Derivation of statistical mechanics by demanding compatibility with classical thermodynamics.

(d) Statistical mechanics as a probabilistic theory.

(e) Examples.

Macroscopic Mechanical Systems are Deterministic

Refreshing some basic physics

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

1) Stretching a spring by a distance x: $\mathbf{F}=-f\mathbf{x}$, 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, $W=$ ✎ $\mathbf{F}\cdot d\mathbf{x}$.

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 dawn, E_p is converted into: kinetic energy, $E_k=m\mathbf{v}^2/2$, where $v^2/2=gh$ (at floor).

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

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.

SUMMARY

(1) The dynamical state of a **mechanical macroscopic system** is **deterministic**, in principle, i.e., 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.

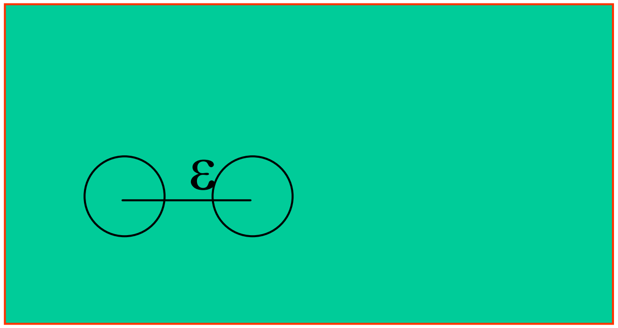
(2) Ignoring friction, kinetic and potential energies and mechanical work can in general be converted without loss.

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.

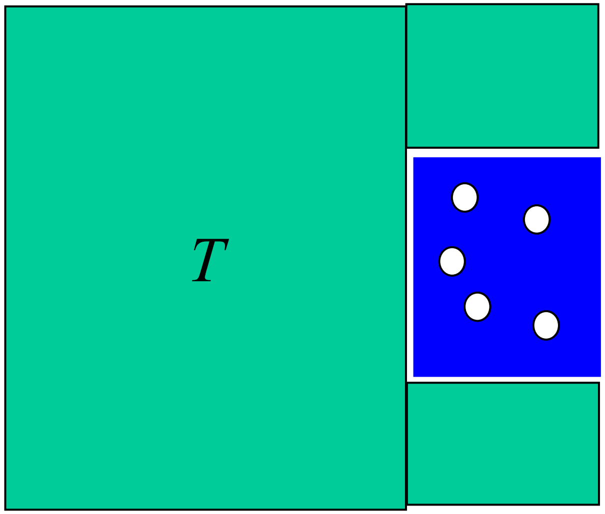
Two argon atoms at rest positioned at the lowest energy distance ε – interacting through Lennard-Jones potential. Microscopic system.

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



Classical thermodynamics

A large system of $N \sim 10^{23}$ particles (blue) is surrounded by a very large (infinite) heat bath with absolute temperature T (green) ➡ $T = T_{\text{system}}$. The system can interact mechanically and thermally with the surroundings.



Example: Ideal gas (dilute; high T)

Described by the equation of state:

$$PV = Nk_B T$$

V – volume

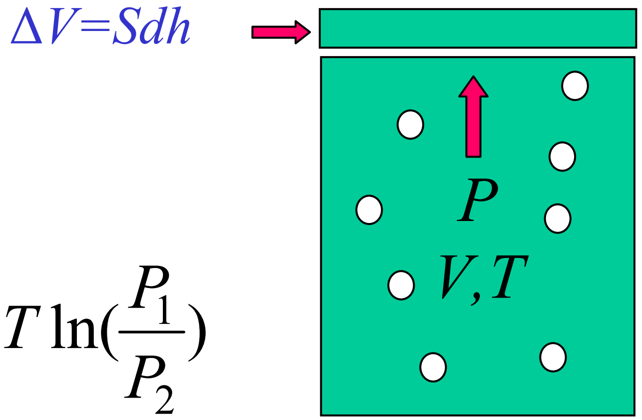
P – pressure

k_B – Boltzmann constant

➡ a very limited description – by only a few macroscopic parameters. The trajectories of particles are not considered.

This limited treatment makes thermodynamics a very general theory

Mechanical work, equilibrium, and reversibility



Ideal gas in a container of V,T,P. If the volume increases by dV the mechanical work is $dW = PSdh = PdV$ and for ideal gas

$$W = \int_{V_1}^{V_2} P(V)dV = \int_{V_1}^{V_2} \frac{Nk_B T}{V} dV = Nk_B T \ln\left(\frac{V_2}{V_1}\right) = Nk_B T \ln\left(\frac{P_1}{P_2}\right)$$

This is correct only if the piston is moved infinitesimally slowly to allow equilibration of the system at each step – i.e. the transformation is reversible.

if ΔV is moved fast there will not be time for the pressure to build at the piston (ΔV will be too dilute) $\Rightarrow P_{\text{fast}} < P$ and $dW_{\text{fast}} < dW$

$\Rightarrow$ Reversible work is maximal.

The theory is developed at equilibrium

Internal energy, heat, and the first law of thermodynamics

E - internal energy of the system; it is a state function defined up to an additive constant and is extensive (proportional to the system size)

q – the amount of heat (energy) absorbed by the system

W- mechanical work done by the system on the surroundings

The **first law** of thermodynamics (conservation of energy):

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

q is a disordered energy added to the system particles. A 19th-century question: can q be converted totally into mechanical work?

Answer – no (**second law**) but maximum W is obtained in reversible transformations (see later)

Entropy, and the second and third laws

It became necessary to define a measure for the randomness involved with heat. $T \sim P$ suggests that the randomness of particles increases with T hence with q. The measure is the entropy S:

$$dS = \frac{dq_{rev}}{T} \qquad S(b) = \int_0^b \frac{dq_{\mathrm{rev}}}{T}$$

Integration over any reversible path from 0, the state of the system at T=0 to b; T is of heat bath.

Third law: $S(T=0)=0$. Entropy is an extensive state function; dS is effective at low T and decreases with increasing T.

Second law:

$$dS \geq \frac{dq}{T} \qquad S(b) - S(a) \geq \int_a^b \frac{dq}{T}$$

Heat absorbed irreversibly (fast) is not spread over the system but is concentrated locally increasing the local T which decreases dq/T.

In an isolated system (q=0 from outside) if $a \longrightarrow b$ $\quad S(b) \geq S(a)$

Maximal entropy in spontaneous (irreversible) processes

$S(b) \geq S(a)$ means that in an isolated system $S(\textit{final state})$ cannot be less than $S(\textit{initial state})$; thus, the state of maximal entropy is the most stable.

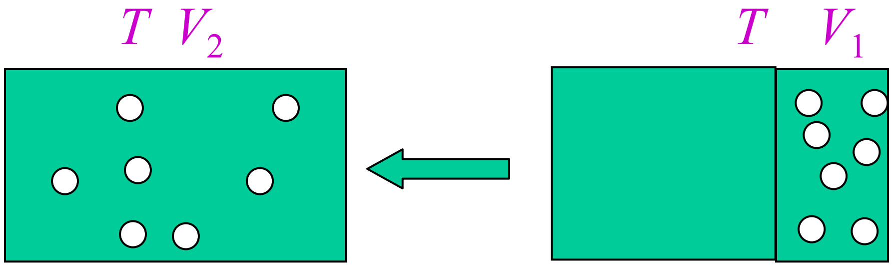
For given E and V the values of other system parameters at equilibrium are those that maximize the entropy $\delta(S)_{E,V} \geq 0$.

Spontaneous processes always go in one direction of increasing entropy.

Spontaneous expansion of ideal gas (IG) at constant T (piston removed)

E_{IG} depends on T but not on V (Joule experiment). No work is done and no heat comes from the bath; One can show, $S_{\mathrm{IG}}=C_v \ln T + k_B N \ln V + const.$ where $C_v = (\partial E/\partial T)_V$ is the specific heat. ⇒

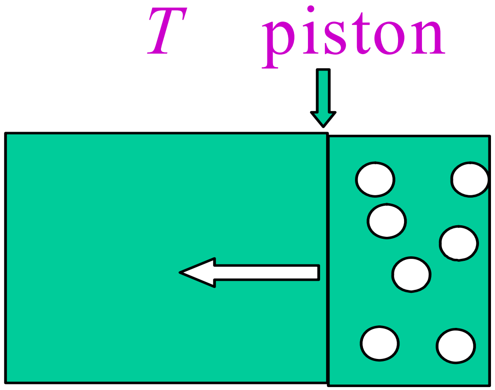
$\Delta S_{\mathrm{IG}} = k_B N \ln(V_2/V_1)$, i.e, the entropy (bath + system) increases in an irreversible process (S_{bath} remains unchanged).



A reversible process

The volume of an ideal gas is increased reversibly, mechanical work is done and heat q is absorbed by the system from the heat bath. The entropy of bath is thus decreased by q/T (T unchanged).

Total change of entropy (in bath +system) is zero: $\Delta S_{tot} = \Delta S_{IG} - q/T = 0$



If the piston is moved fast at each step the amount of work would decrease hence the total of heat q' absorbed from the bath is $q' < q$ and

$$\Delta S_{tot} = \Delta S_{IG} - q'/T > 0$$

The Helmholtz free energy $A(F)$

First law: $dE = dq - dW = TdS - PdV = d(TS) - SdT - PdV$

$$dA = d(E-TS) = -SdT - PdV$$

$A = E-TS$ – Helmholtz free energy. $\mathbf{A = A(T,V,N)}$ $[S(E,V,N)]$

One can show that if $a \rightarrow b$ the maximal work W is gained in a reversible process and less otherwise,

$$W \leq A(a) - A(b) = -\Delta A$$

Thus, if a system cannot exchange work with environment then

$0 = W \leq A(a) - A(b)$ $A(b) \leq A(a) \Longrightarrow$ A cannot increase.

If A is minimum the system is in a stable equilibrium or $\delta(A)_{T,V} \leq 0$ (compare with δS). Thus, minimum A is a compromise between the tendency for maximum entropy and minimum potential energy.

Classical thermodynamics – summary

In a mechanical many-body system one strives to calculate (analytically or numerically) the trajectories of the bodies. In thermodynamics a many-body microscopic system is described by a small number of macroscopic parameters; atomic degrees of freedom are ignored → the theory is general and highly applicable but provides limited information.. The parameters are related via partial derivatives,

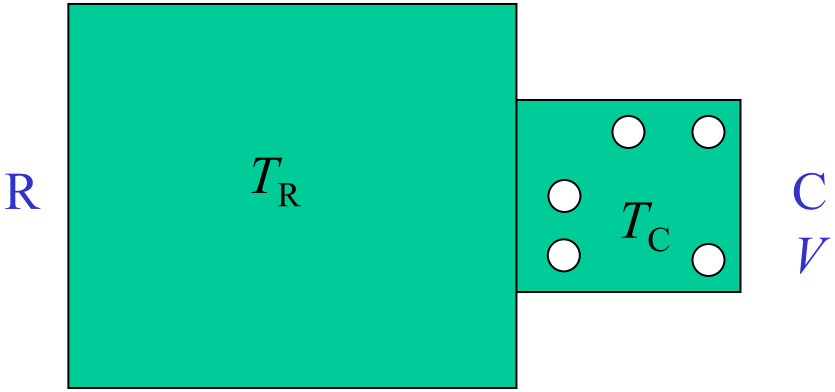
$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P \qquad E = -T^2 \left(\frac{\partial \left(\frac{A}{T}\right)}{\partial T}\right)_{V,N}$$

The notion of entropy expresses the disordered nature of heat, which cannot totally be converted into mechanical work.

Statistical mechanics is a probabilistic theory where classical thermodynamics is derived from a microscopic point of view (involving atomic forces, masses etc); thus, much more information is gained.

Equilibrium statistical mechanics

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



A system C of N (equal) molecules in a constant volume V is in thermal contact with a large reservoir (R) (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, averaging E_k & E_p along a very long trajectory leads to definite $<E_k>$ and $<E_p>$, and thus for a snapshot of configuration of N particles→ $\sim N<E_k>$ and $\sim N<E_p>$.

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 ➡ 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 $(\mathbf{x}^N,\mathbf{v}^N) = (x_1,y_1,z_1,x_2,y_2,z_2, \ldots x_N,y_N,z_N,v_{x1},v_{y1}v_{z1}\ldots\ v_{xN},v_{yN}v_{zN})$ 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,

$$<M> = \text{✎}\, P(\mathbf{x}^N,\mathbf{v}^N)\, M(\mathbf{x}^N,\mathbf{v}^N)\, d(\mathbf{x}^N\mathbf{v}^N).$$

We define the entropy S of a discrete and continuous system (k_B is the Boltzmann constant) as statistical averages,

$$S = <S> = -k_B \quad \Sigma P_i \ln P_i \quad \text{and}$$

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

$$+ \ln\{\text{const.}[\text{dimension } (\mathbf{x}^N\mathbf{v}^N)]\}$$

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 (see p. 13)

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

$A = E - TS$ can be expressed as the average

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

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

$$A' = \int [E(\mathbf{X})+k_BT\ln P(\mathbf{X}) + k_BT\, P(\mathbf{X})\,/P(\mathbf{X})]d\mathbf{X}=0$$

$$E(\mathbf{X})+k_BT[\ln P(\mathbf{X}) + 1]=0 \quad \text{(for any } \mathbf{X}\text{)}$$

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

$$P(\mathbf{X}) = \text{const}\times\exp[-E(\mathbf{X})/k_BT]$$

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

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

P^{B} – the Boltzmann probability (density).

Q – the canonical partition function.

The intgrand defining A (p. 20) is $E(\mathbf{X})+k_BT\ln P^{\mathrm{B}}(\mathbf{X})$

Substituting P^{B} and taking the ln gives,

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

$-k_BT\ln Q$ is constant for any **X** and can be taken out of the integral of A. Thus (we ignore the const.),

$$A=\langle E\rangle-T\langle S\rangle=-k_BT\ln Q+cont.$$

In summary. Using the notion of temperature and assuming that the entropy is

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

P^B was obtained by minimizing A (minimum at constant V,T - from thermodynamics; see p. 13); we also obtained $A = -k_BT\ln Q$

Thermodynamic approach: The relation $A = -k_BT\ln Q$ enables one calculating A from Q that is based on the microscopic details of the system.

In classical thermodynamics all quantities are obtained as derivatives of A. Hence, in statistical mechanics all these quantities can be obtained as derivatives of $-k_BT\ln Q$.

Probabilistic approach: in statistical mechanics a system is modeled by a probability space; thus, the macroscopic parameters can be obtained as expectation values & variances,

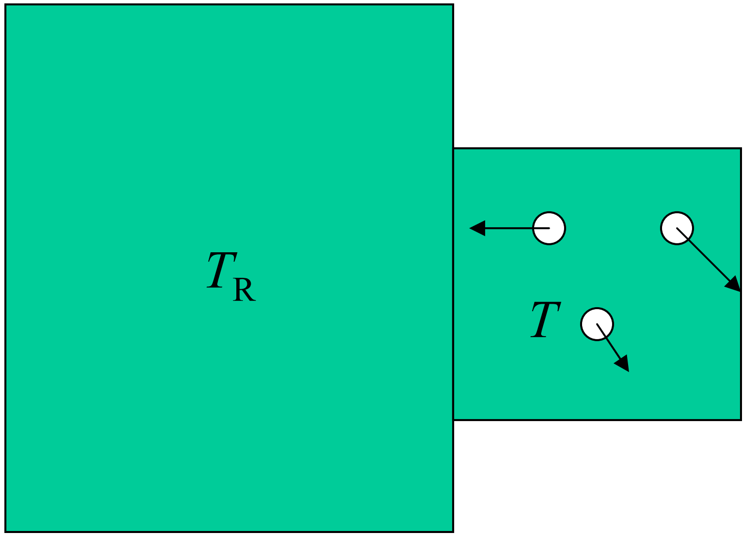
$$<E> = \text{✎}\, P^{\mathrm{B}}(\mathbf{x}^N\mathbf{v}^N)E(\mathbf{x}^N,\mathbf{v}^N)\; d(\mathbf{x}^N\mathbf{v}^N)$$

$$S = -k_B \text{✎}\, P^{\mathrm{B}}(\mathbf{x}^N\mathbf{v}^N)\; \ln P^{\mathrm{B}}(\mathbf{x}^N,\mathbf{v}^N)\; d(\mathbf{x}^N\mathbf{v}^N)$$

Using simulation, one can obtain 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 other properties; they can be obtained without calculating Q, i.e. the values of P_i^{B} are not needed!!

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

Calculating *Q*



A system 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 $T=T_\mathrm{R}$. We have seen that the Helmholtz free energy, A is

$A=E-TS= - k_BT\ln Q$ where

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

and $$E(\mathbf{x}^N,\mathbf{v}^N)= E_\mathrm{k}(\mathbf{v}^N) + E_\mathrm{p}(\mathbf{x}^N)$$

$E(\mathbf{x}^N,\mathbf{v}^N)$ is the Hamiltonian of the system (for $E_\mathrm{p}(\mathbf{x}^N)$ see p. 4).

If the forces <u>do not depend on the velocities</u> (most cases) E_k is independent of E_p and the integrations can be separated. Also, the integrations over the velocities of different particles and even over the components v_x ,v_y, and v_z are independent. Thus, we first integrate over v_x (denoted v) of a single particle.

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

$$E_\mathrm{k}= mv^2/2 = p^2/2m$$

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

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

because

$$a = \frac{1}{2mk_BT}$$

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

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

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

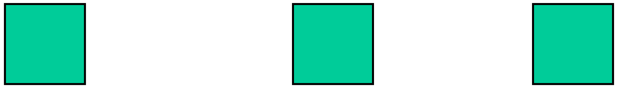
$$Q = \frac{\left(\sqrt{2\pi m k_B T}\right)^{3N}}{N! h^{3N}} \int_{\Omega} \exp\left(-\frac{E(\mathbf{x}^N)}{k_B T}\right) d\mathbf{x}^N$$

The problem is to calculate the configurational integral

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

The division by *N* factorial, *N*!=1 � 2 � 3… � *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 $\mathbf{x}^1$, $\mathbf{x}^2$, $\mathbf{x}^3$,….,$\mathbf{x}^N$ 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 (const. of p.21 is $\ln h^2$)

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

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.

Ideal gas

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:
<u>Intensive</u> variable
$\sim N/V$

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

Internal energy:
<u>Extensive</u> variable $\sim N$
$E = C_v T + const.$ (thermo.)

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

$E \sim T$ is the <u>average</u> kinetic energy (see later); each degree of freedom contributes $(1/2)k_BT$. If the forces do not depend on the velocities, T is determined by the kinetic energy only. E is <u>independent of V!</u> (Joule experiment).

The specific heat C_V is independent of T and V.

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

The entropy is:

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

In thermodynamics, $S_{IG}=C_v \ln T + k_B N \ln V + const.$ (unknown). S contains microscopic parameters (e.g., m) not known in thermodynamics. $S \sim N$ → 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 $A=E-TS$.

Ideal gas results in probability space

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 thermodynamic 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,

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

where $\mathbf{X}$ 🕓 $\mathbf{x}^N\mathbf{v}^N$ is a $6N$ vector of coordinates and velocities (random variables). Therefore, thermodynamic properties (e.g. energy, enropy) are expectation values defined with $P^{\mathrm{B}}(\mathbf{X})$.

For example, the statistical average (denoted by <>) of the energy is:

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

where $E(\mathbf{x}^N,\mathbf{v}^N)$ is a random variable; we show $\langle E\rangle=\frac{3}{2}Nk_BT$ calculated as a derivative of A. For an ideal gas P^{B}~Gaussian

$$Q_{\mathrm{IG}}=\frac{(\sqrt{2\pi mk_BT})^{3N}}{N!h^{3N}}V^N$$

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

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

For two degrees of freedom the integral is:

$$\frac{\int_{-\infty}^{\infty}\frac{(p_1^2+p_2^2)}{2m}\exp-[\frac{p_1^2+p_2^2}{2mk_BT}]dp_1dp_2\int dx_1dx_2}{(\sqrt{2\pi mk_BT})^2V^2}=$$

$$=\frac{\frac{[\sqrt{\pi}(2mk_BT)^{3/2}(\sqrt{2\pi mk_BT})]\cdot 2}{2m\cdot 2}}{(\sqrt{2\pi mk_BT})^2}=\frac{3}{2}\cdot 2k_BT$$

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

The entropy of an ideal gas can be obtained as a statistical average of ln P_i^{B} in a similar manner.

Entropy as a measure of order

For a discrete system,

$$S = \langle S \rangle = -k_B \quad \Sigma_i P_i \ln P_i$$

If the system populates a single state k, $P_k=1$ and $S=0$ ⬇ 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, $P_i=1/$⌖, where ⌖ 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,

$S= -k_B \quad \ln$ ⌖

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

In a continuum system, where the forces do not depend on the velocities (momenta), the velocities part of the partition function is completely solved and the problem is to treat the potential energy part defined over the coordinates, $\mathbf{x}^N$.

For an ideal gas $E(\mathbf{x}^N)=0$ and the Boltzmann probability density over space (volume) is uniform - $1/V$ for a single particle and $1/V^N$ for N particles leading to the total configurational entropy, $\sim N\ln V$ (see p.31).

When $E(\mathbf{x}^N)\neq 0$ one is interested mainly in the configurational partition function denoted Z, where the (solved) momentum part is ignored,

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

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

Also,

$$Z= ✎\ ■(E)\exp[-\ E/k_BT]\ dE$$

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

$$Z = \swarrow_i \exp\ [-\ E_i/k_BT] = \swarrow_l\ n(E_l)\ \exp\ [-\ E_l/k_BT]$$

The thermodynamic functions are obtained from derivatives of the configurational Helmholtz free energy, F (or by averaging)

$$F = -k_BT\ln Z$$

Calculating Z for realistic models of fluids, polymers, proteins, etc. analytically is unfeasible. Powerful numerical methods, e.g., Monte Carlo and molecular dynamics are very successful.

Also, $F=<E>-TS.$

At low T the kinetic energy is low, the interactions (forces) are dominant holding the system close to the ground state - the state of lowest potential energy $<E(\mathbf{X}^N)>$. Thus, the positions of the particles are relatively well defined (ordered state) → significant configurational information → low entropy.

At high T, E_{kinetic} is large → strong movements of particles → high $<E(\mathbf{X}^N)>$ → many states are visited → high disorder → high entropy.

At each T, F is a compromise between the tendencies of maximum S and minimum E where $S(T)$ and $E(T)$ are those that lead to minimum F; at high T, S is dominant and at low T E is dominant. Unlike a mechanical system, the trajectories are unknown. At low T $P^{\mathrm{B}} \sim 1$ for a tiny part of space; at high T, P^{B} ~ same for all configurations.

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.

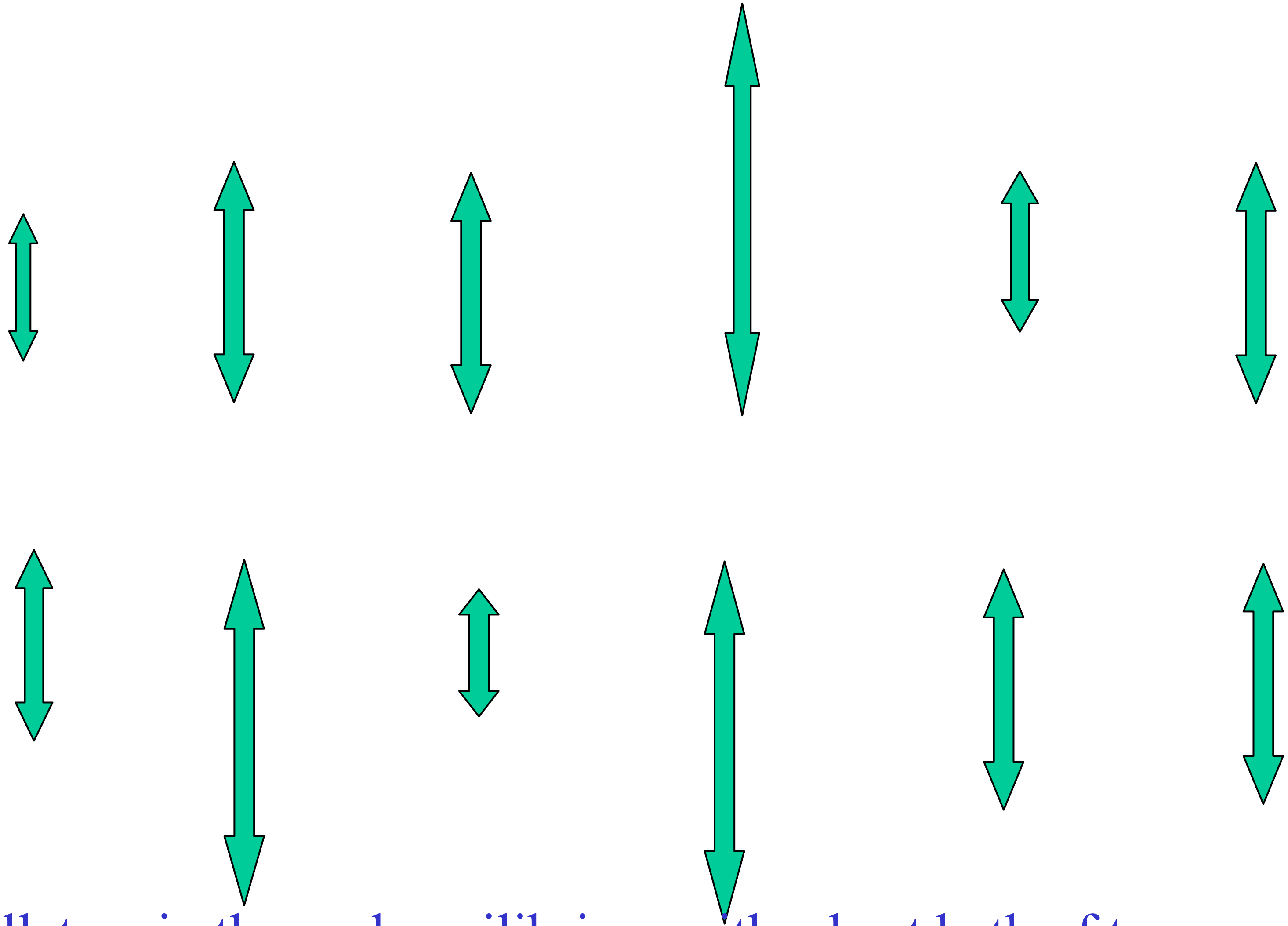
Therefore, $Q_N = q^N$, where q is the partition function of a single oscillator. Moreover, the components (x, y, z) are independent as well; therefore, one can calculate q_x and obtain $Q_N = q_x^{3N}$.

Macroscopic (mechanical) oscillator

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

Microscopic oscillator

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, $q=q_\mathrm{k}q_\mathrm{p}$ where q_k was calculated before; ■ is the frequency of the oscillator.

$$q_\mathrm{k} = \frac{\sqrt{2\pi m k_B T}}{h} \qquad q_\mathrm{p} = \sqrt{\frac{2\pi k_B T}{f}}$$

$$q = 2\pi\sqrt{\frac{m}{f}}\frac{k_B T}{h} = \frac{k_B T}{h\nu} \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}}$$

$$E = -T^2\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right) = k_B T$$ $<E_\mathrm{k}>=<E_\mathrm{p}>= 1/2k_\mathrm{B}T$ ⬇ $C_V = k_B$

The <u>average</u> energy 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, $E= 3Nk\mathrm{B}T$ - extensive ($\sim N$) and $C_V = 3Nk_\mathrm{B}$ - Dulong-Petit Law. The entropy is also extensive,

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

E and S increase with T. S is not defined at T=0

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 force and the random energy delivered by the heat bath. The position of the mass x is only known with the Gaussian Boltzmann probability;

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

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 average energy (and its variance $k_B{}^2T^2$, both increase → the average amplitude increases and the position of the mass is less defined due to larger fluctuations ($<x>=0$ but $<x^2>=k_BT/f$); 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.

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 🕈, where to each "point" $\mathbf{x}^N$ (random variable) corresponds the Boltzmann probability density,

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

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 $<E>$

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 $\ln P^{\mathrm{B}}(\mathbf{x}^N)$ is a random variable,

$$S = <S> = -k_B \int P^{\mathrm{B}}(\mathbf{x}^N) \ln P^{\mathrm{B}}(\mathbf{x}^N)\, d\mathbf{x}^N$$

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

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

Fluctuations (variances)

The variance (fluctuation) of the energy is:

$$\sigma^2(E) = \int_{\Gamma} P^{\mathrm{B}}(\mathbf{x}^N)[E(\mathbf{x}^N) - \langle E \rangle]^2\, d\mathbf{x}^N =$$

$$= \langle E(\mathbf{x}^N)^2 \rangle - \langle E(\mathbf{x}^N) \rangle^2$$

Notice that the expectation value is denoted by <> 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,

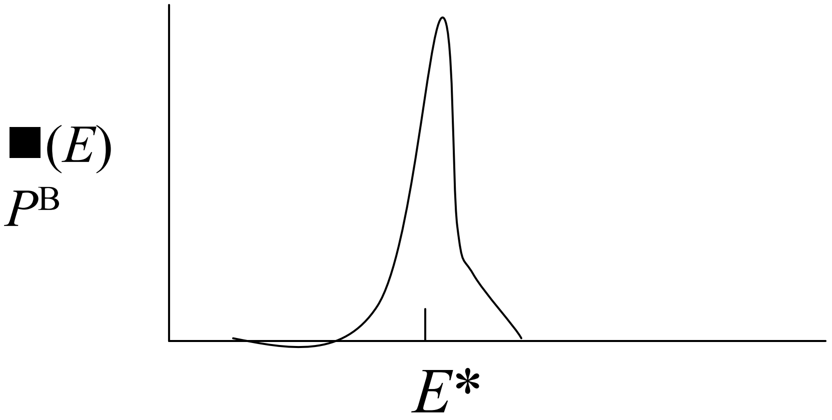
$$\frac{\sigma(E)}{<E>} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

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, $<E>$ can be expressed,

$$<E> = \int E(\mathbf{x}^N) P^{\mathrm{B}}(\mathbf{x}^N) \mathrm{d}\mathbf{x}^N = \int E\,\Omega(E) P^{\mathrm{B}}(E)\mathrm{d}E$$

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

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



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

$Z =$ ✎ ■$(E)\exp[-E/k_BT]\, dE$ ✍ $f_T(E^*) =$ ■$(E^*)\exp[-E^*/k_BT]$ ॐ

$F = -k_BT\ln Z$ ✍ $E^*(T) + k_BT\ln$ ■$(E^*) = E^*(T) - TS$

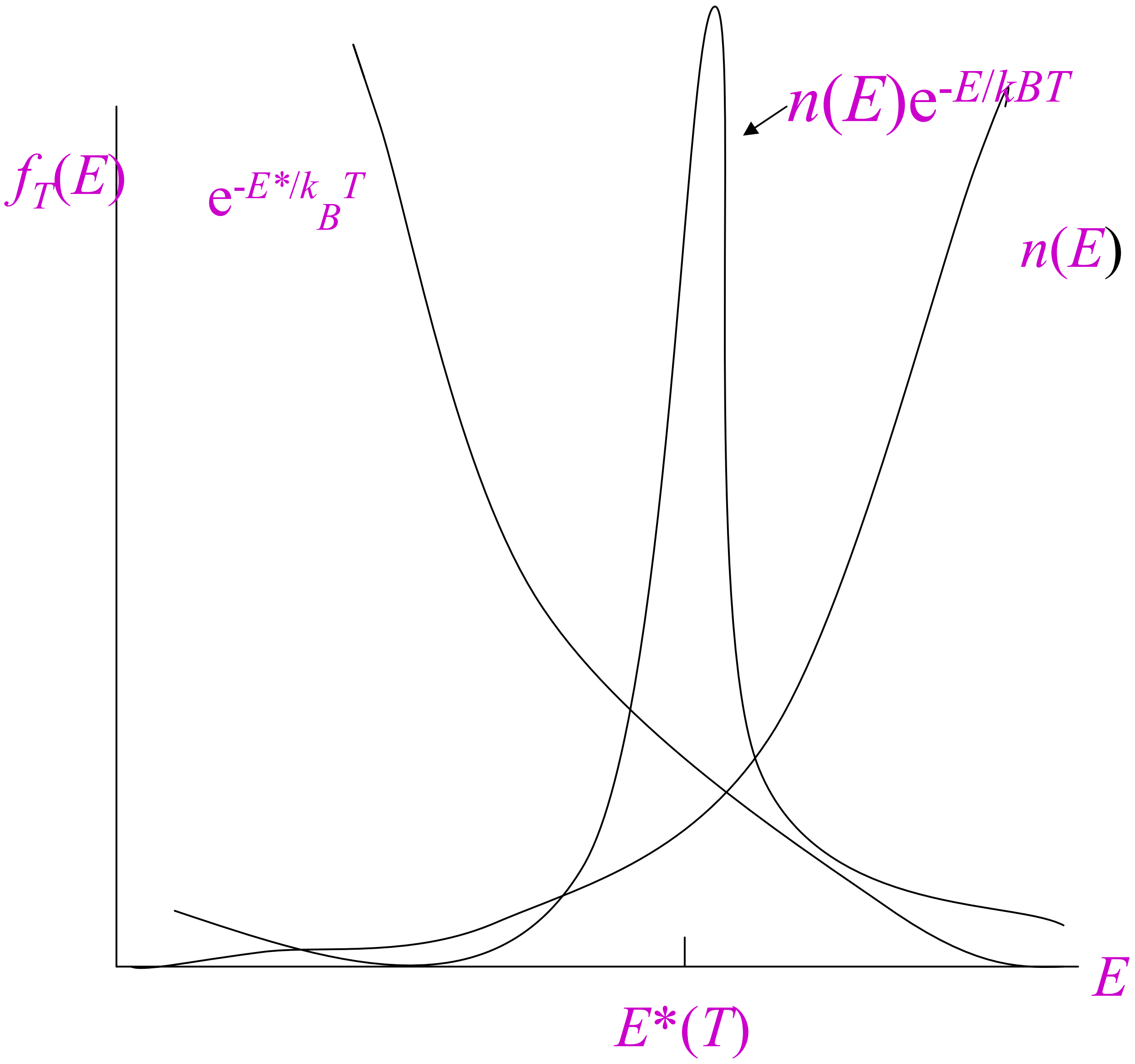
The entropy, $-k_B \ln \blacksquare(E^*)$ is the logarithm of the degeneracy of the most probable energy. For a discrete system

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

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 <u>only the maximal term</u>

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

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 ⬇ maximum entropy) but the exponential of the energy is small. For intermediate T:

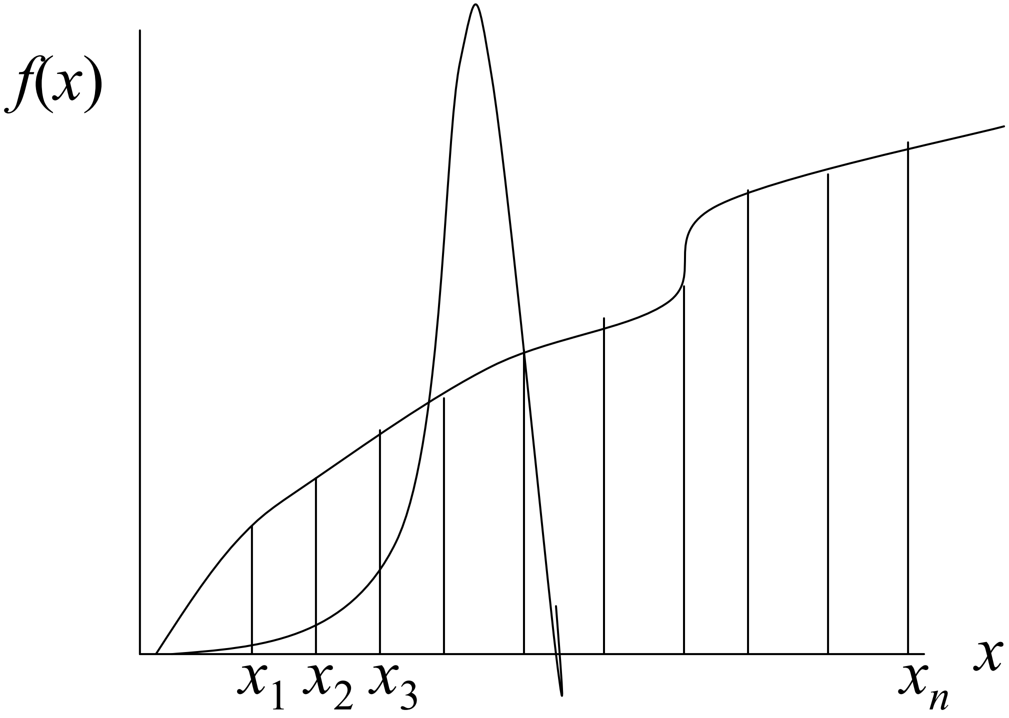

$f_T(E)$
$e^{-E^*/k_B T}$
$n(E)e^{-E/kBT}$
$n(E)$
E
$E^*(T)$

The fact that the contribution to the integrals comes from an extremely narrow region of energies makes it very difficult to estimate $<E>$, 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 $<E>$.

Numerical integration



✏ $f(x)dx$ ✍ ⇙$_i$ $f(x_i)$👎x_i 👎$x_i = x_i - x_{i-1}$

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

$$P^{\mathrm{B}}(E)=n(E)\exp\text{-}[E/k_BT]/Z$$

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

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

$$\Delta E=E_1-E_2$$

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 ⬇ 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 $❍H$ or - $❍H$, depending of whether $❍$, the magnetic moment is positive or negative. Positive $❍$ leads to energy - $❍H$. 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 $+1(-❍)$ or $-1(❍)$.

Potential energy of spin configuration i: $E_i = -N_+ ❍H + N_- ❍H$

or

$E_i = -(N-N_-)❍H + N_- ❍ H$ where N_+ and N_- are the numbers of $+1$ and -1 spins. The magnetization of i is:

$M \quad N ❍H \quad N ❍H$

Option 1: Thermodynamic approach

We have to calculate $Z = \Sigma_i \exp\text{-}[E_i/k_BT]$; 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 ⇒ 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!).

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

$$F=-k_BT\ln Z=-k_BTN\ln[2\cosh(\text{❍}H/k_BT)]$$

Entropy:

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

T=◎, 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:

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

Magnetization: $M=N_+ - N_-$

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

Specific heat:

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

Option 2: Statistical approach

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

$$z_1 = \exp(-❍H/k_BT) + \exp(+❍H/k_BT) = 2\cosh[❍H/k_BT]$$

The Boltzmann probability for ⌖ spin is: $\exp[⌖\ ❍H/k_BT]\ /\ z_1$

The average energy is

$$\langle E\rangle_1 = [-❍H\exp(+❍H/k_BT) + ❍H\exp(-❍H/k_BT)]/z_1$$

$$= -❍H\ \{2\sinh[❍H/k_BT]\}/\ \{2\cosh[❍H/k_BT]\} =$$

$$= -❍H\ \tanh(❍H/k_BT) \quad ; \quad \langle E\rangle = -❍HN\tanh(❍H/k_BT)$$

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.

$$s_1 = -k_B\{\exp[+\mu H/k_BT][\mu H/k_BT - \ln z_1] + \exp[-\mu H/k_BT][-\mu H/k_BT - \ln z_1]\}/z_1 =$$

$$= -k_B\{\mu H/k_BT\,[e^+ - e^-]/z_1 - \ln z_1[e^+ + e^-]/z_1\} =$$

$$= -k_B\{\mu H/k_BT \tanh[\mu H/k_BT] - \ln z_1\}$$

The same result as on p. 59.

Option 3: Using the most probable term

$E = -N_+$ ❍ $H + N_-$ ❍ H ⬇ $E' = E/$❍$H = -N_+ + N_-$

$N = N_+ + N_-$

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

$M =$ ❍ $(N_+ - N_-)$ $E = -MH$

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$N$! 🕔 Nln$N$.

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

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 $(df'/dx)|_{x^*} < 0$ or > 0, respectively.

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

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

$$E' = N\frac{1-\exp(\frac{2\mu H}{k_BT})}{1+\exp(\frac{2\mu H}{k_BT})} = N\frac{\exp(\frac{\mu H}{k_BT})}{\exp(\frac{\mu H}{k_BT})}\left[\frac{\exp(-\frac{\mu H}{k_BT})-\exp(\frac{\mu H}{k_BT})}{\exp(-\frac{\mu H}{k_BT})+\exp(\frac{\mu H}{k_BT})}\right]$$

$$E' = -N\,\mathbf{tanh}[\frac{\mu H}{k_BT}]$$

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

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

and

$$M = N\mu \tanh(\mu H/k_BT)$$

As obtained before.

degeneracy	energy	typical T	spin configurations
1 (min. S=0)	-*N*❍*H* (min.)	$T_0 = 0$	✸✸✸✸…✸✸ ✸(*H*)
N	-(*N*-1)❍*H*+❍*H* = -*N*❍*H*+2❍*H*	very low (T_0)	❊✸✸✸ …✸✸
N!/[(*N*-2)!2!] =*N*(*N*-1)/2	-*N*❍*H*+4❍*H*	$T_2>T_0$	❊❊✸✸ …✸✸
.			
N!/[(*N*-*k*)!*k*!]	-*N*❍*H* +2*k*❍*H*	$T_k>T_{k-1}$	*k* ❊ ❊❊❊❊ …✸✸
.			
.			
N! / [(*N*/2)!(*N*/2)!] (max. degeneracy $S = N \ln 2$)	❍*H* (*N*/2-*N*/2) =0	high T	*N*/2 *N*/2 ❊❊❊❊..✸✸ ✸✸

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 Nth power of the partition function for the

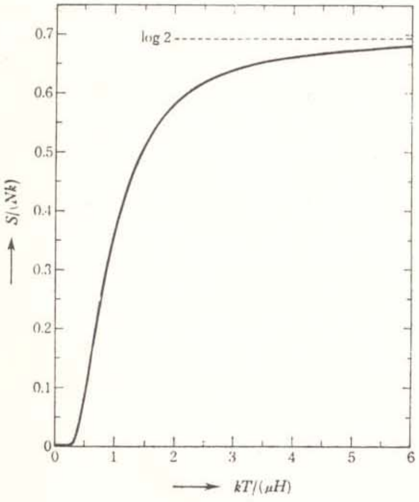


Fig. 1.11.

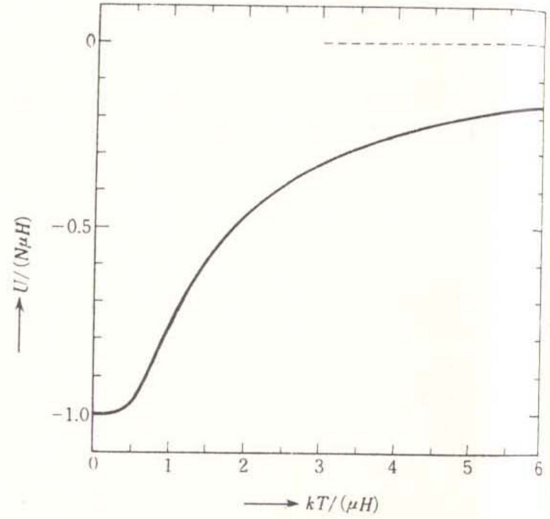


Fig. 1.12.

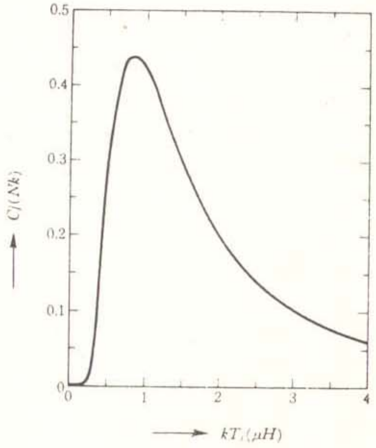


Fig. 1.13.

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: $S \approx k_B \ln n(E^*)$

$n(E^*)$ - 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 ⇒ most stable state), where no uncertainty exists (maximum order) ⇒ 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 (✸) and vice versa.

For a given T the average number of excited spins (❈) 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 ⇓ the uncertainty about its location increases ⇓ 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 $n(E^*)$ ⇓ 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 maximal disorder. At $T=0$ the potential energy wins; it is minimal ⇓ complete order $S=0$ (minimal). At $T=$◎ 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 $E^*(T)$]:

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

or equivalently the minimal term of the free energy,

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

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.