

Statistical Thermodynamics.

Important concepts.

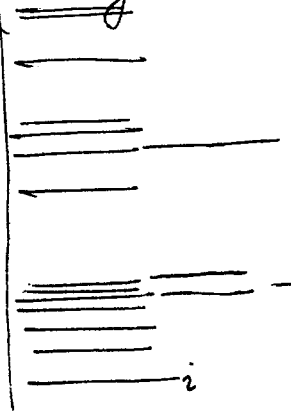
① The energy of any system is discrete, i.e. only individual values are possible and the system has to jump from one "allowed" value to another.

The discrete nature of permitted / allowed energy is only apparent for microscopic systems - i.e. atoms or molecules, but the consequences of this microscopic discrete energy are observable macroscopically and were the source of a lot of puzzles in classical physics.

e.g. spectrum of black body radiation
spectra of atoms
specific heat of metals and diatomic gases

② We will refer to the discrete nature of energy by saying that energy is quantized. The allowed energy levels of a microscopic system (i.e. atom or molecule) are also called the allowed states of the molecule, and should not be confused with the state of the macroscopic system that consists of many (say 10^{10}) molecules.

The ^{quantum} energy levels can be arranged in order of increasing energy like the rungs of a ladder and labelled by an index i . In general, it is possible that some of the distinct states have identical energy. Such states are said to be degenerate. (If they have nearly the same energy, they are said to be nearly degenerate)



Now, although the labelling of states by an ordinal index i is convenient for theoretical purposes, in practice one uses a set of quantum numbers that describe the energy state of the molecule. The quantum numbers take on integer ($0, \pm 1, \pm 2, \dots$) or half-integer ($\pm \frac{1}{2}, \pm \frac{3}{2}, \dots$) values, and the energy of the state is calculated from a ~~very~~ simple (or complex!) formula that is a function of the quantum number.

Example. A simple rigid rotator (or rigid rotor) has a rotational energy $\epsilon_{\text{rot}}(J) = k\theta_r J(J+1)$; $J = 0, 1, 2, 3, \dots$ here. J is the rotational quantum number, the "allowed" values are \rightarrow k is Boltzmann's constant, and θ_r is a characteristic temperature that is specific to the rigid rotator and depends on its moment of inertia. Note that $k\theta_r = \epsilon_0$ a reference/characteristic energy.

It turns out that a rotating quantum rotator requires two quantum numbers (J, M) to completely specify its rotational state. The quantum number M specifies the orientation of the angular momentum of the rotor, and J specifies its magnitude. The energy only depends on the magnitude of the angular momentum vector and not its orientation — provided space is isotropic. The allowed values of M are $M = -J, (-J+1), \dots, -1, 0, 1, \dots, J$; thus there are $(2J+1)$ values of M for any J , and the $(2J+1)$ states characterized by (J, M) fixed J , and varying M are degenerate. We often say that the level ϵ_J is $(2J+1)$ -fold degenerate.

②. Microscopic systems are fundamentally indistinguishable i.e. it is impossible even in principle to distinguish between two identical atoms e.g. H & H or O & O or two electrons, etc.

In consequence any correct description of a system must satisfy certain symmetry properties with respect to exchange of identical particles.

Every microscopic system (for our purposes) consists of a collection of fundamental particles —

electron e

proton p

neutron n

photon ϕ .

e, p, n have intrinsic angular momentum — called "spin"

and their spin quantum number $s = \frac{1}{2}$.

photons ϕ have intrinsic angular momentum, spin, and their spin quantum number $s = 1$.

Any atom in nucleus

Any nucleus consists of neutrons and protons, and any atom is neutrons, protons & electrons.

When fundamental particles are combined in a nucleus or an atom their spins "couple" or add. The resultant spin is either integer (or 0) if there are an even number of fundamental particles, or half-integer if there are an odd number of fundamental particles.

Integer or zero spin collections are called bosons.

Half-integer spin collections are called fermions.

Microstate description: A set of numbers $\{N_i\}$, $i=1, \dots$ describing the population in individual quantum states labelled i . For Fermions $N_i = 0$ or 1 . For Bosons N_i is not restricted.

Macrostate description: A set of numbers $\{N_j\}$, $j=1, 2, \dots$ describing population in groups of quantum states. Groups labelled by j . All states in the group (C_j such states) have the same, or nearly the same, energy ϵ_j .

Because $C_j \gg 1$ typically, one requires a much smaller set of numbers $\{N_j\}$ to describe the state of the macroscopic system (collection of particles).

With there are many microstates (i.e. sets of numbers $\{N_i\}$) associated with each macrostate - set of numbers $\{N_j\}$.

Basic assumption of statistical mechanics - All microstates consistent with the constraints ($\sum_i N_i = N$; $\sum_i \epsilon_i N_i = E$) are equally probable.

This implies that if certain macrostate descriptions have more microstates associated with them, then they are more probable.

Seek: most probable macrostate

Need: Explicit formula for number of microstates associated with any given macrostate - all satisfying constraints

For fermions
macrostate

$$W = \prod_j \frac{C_j!}{(C_j - N_j)! N_j!}$$

For bosons

$$W = \prod_j \frac{(C_j + N_j - 1)!}{(C_j - 1)! N_j!}$$

Example. Suppose in group j , there are 5 distinct quantum states and 3 particles, i.e. $C_j = 5$ $N_j = 3$.

Macrostate description $\{ \dots, 3, \dots \}$
 \uparrow place j

Let us label the states A, B, C, D, E and describe individual arrangements in this group by specifying the occupation number in a string with A first and E last.

The formula for fermions predicts $\frac{5!}{(5-3)! 3!} = \frac{5!}{2! 3!} = 10$

i.e. $\frac{120}{2 \times 6} = 10$ distinct ways of doing this.

Explicitly they are $\{ \overset{1}{1}, \overset{2}{1}, \overset{3}{1}, \overset{4}{0}, \overset{5}{0} \}$, $\{ \overset{1}{1}, \overset{2}{1}, \overset{3}{0}, \overset{4}{1}, \overset{5}{0} \}$, $\{ \overset{1}{1}, \overset{2}{1}, \overset{3}{0}, \overset{4}{0}, \overset{5}{1} \}$
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thus there are 10 possible microstate descriptions consistent with $N_j = 3$. The same procedure must be repeated for each group j , and the total number of microstates for the set $\{N_j\}$ is the product of all these numbers.

If the particles were bosons the formula, ^{for bosons} predicts $\frac{(5+3-1)!}{(5-1)! 3!} = \frac{7!}{4! 3!}$

i.e. $\frac{5040}{24 \times 6} = 35$ possible ways of doing this. In addition to the 10 ways enumerated above, there are 25 other arrangements of the type $\{ 3, 0, 0, 0, 0 \}$, $\{ 0, 3, 0, 0, 0 \}$... 5 of these
 $\{ 2, 1, 0, 0, 0 \}$, $\{ 2, 0, 1, 0, 0 \}$, $\{ 0, 2, 1, 0, 0 \}$ 20 of these

Explicitly for fermions

$$W(\{N_j\}) = \prod_j \frac{C_j!}{(C_j - N_j)! N_j!}$$

$$\ln W(\{N_j\}) = \sum_j \ln C_j! - \ln(C_j - N_j)! - \ln N_j!$$

Use Sterling's approx $\ln z! = z \ln z - z$ for $z \gg 1$

$$\ln W = \sum_j N_j \ln\left(\frac{C_j}{N_j} - 1\right) - C_j \ln\left(1 - \frac{N_j}{C_j}\right).$$

$$\delta(\ln W) = \sum_j \delta N_j \ln\left(\frac{C_j}{N_j} - 1\right).$$

But variations δN_j are constrained by the requirement $\sum_j N_j = N \Rightarrow \sum_j \delta N_j = 0$

$$\sum_j \epsilon_j N_j = E \Rightarrow \sum_j \epsilon_j \delta N_j = 0.$$

Use Lagrange multipliers α, β .

$$\delta(\ln W) = \sum_j \delta N_j \left[\left(\ln \frac{C_j}{N_j} - 1 \right) - \alpha - \beta \epsilon_j \right] = 0. \text{ for a max.}$$

Most probable macrostate - has largest number of microstates associated with it. All microstates are equally probable.

Maximize $W(\{N_j\})$. Easier to maximize $\ln W(\{N_j\})$

$\{N_j\}$ - set of numbers describing populations in groups of states (labelled j). Group j has C_j individual quantum states, each of energy ϵ_j .

$$W(\{N_j\}) = \prod_j \frac{C_j!}{(C_j - N_j)! N_j!} \quad \text{for Fermions}$$

$$= \prod_j \frac{(C_j + N_j - 1)!}{(C_j - 1)! N_j!} \quad \text{for Bosons.}$$

In the Boltzmann limit $C_j \gg N_j \gg 1$.
we find $N_j^* = \frac{C_j}{e^{\alpha + \beta \epsilon_j} + 1}$ for fermions

$$= \frac{C_j}{e^{\alpha + \beta \epsilon_j} - 1} \quad \text{for bosons.}$$

However Boltzmann limit $N_j \ll C_j \Leftrightarrow e^{\alpha + \beta \epsilon_j} \gg 1$.
Hence in this limit

$$N_j^* = \frac{C_j}{e^{\alpha + \beta \epsilon_j}} \quad \text{for either bosons or fermions}$$

Imposing constraint $\sum_j N_j^* = N$ we obtain

$$e^\alpha = \frac{1}{N} \sum_j C_j e^{-\beta \epsilon_j}$$

$$\text{Define } Q \equiv \sum_j C_j e^{-\beta \epsilon_j}$$

$$\frac{N_j^*}{N} = \frac{C_j e^{-\beta \epsilon_j}}{\sum_j C_j e^{-\beta \epsilon_j}} = \frac{C_j e^{-\beta \epsilon_j}}{Q}$$

the partition function

$$\begin{aligned} \ln W_{\max} &= \sum_j N_j^* \left[\ln \frac{C_j}{N_j^*} + 1 \right] \\ &= N \left(1 + \ln \frac{Q}{N} \right) + \beta E \quad \text{finally.} \\ &= N \left(1 + \ln \frac{Q}{N} \right) + \frac{E}{kT} \quad ; \beta = \frac{1}{kT} \end{aligned}$$

$$Q = Q_{tr} Q_{int}$$

Q_{int} is not a function of V .

$$Q_{tr} = \frac{\pi^{3/2}}{8T^3} \quad \tau^2 = \frac{h^2}{8mV^{2/3}} = \frac{h^2}{8mkT} \cdot \frac{1}{V^{2/3}}$$

$$\tau^3 = \left(\frac{h^2}{8mkT} \right)^{3/2} \cdot \frac{1}{V}$$

$$\text{So } Q_{tr} = V \cdot \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$\left(\frac{\partial \ln Q}{\partial V} \right)_E = \left(\frac{\partial \ln Q_{tr}}{\partial V} \right)_E + \left(\frac{\partial \ln Q_{int}}{\partial V} \right)_E \rightarrow 0$$

$$= \frac{1}{V}$$

$$\begin{aligned} \left(\frac{\partial \ln Q}{\partial T} \right)_V &= \left(\frac{\partial}{\partial T} \ln \left\{ \sum_j C_j e^{-\epsilon_j/kT} \right\} \right)_V \\ &= \frac{1}{Q} \frac{\partial}{\partial T} \sum_j C_j e^{-\epsilon_j/kT} \\ &= \frac{1}{Q} \cdot \frac{1}{kT^2} \sum_j C_j \epsilon_j e^{-\epsilon_j/kT} \\ &= \frac{1}{kT^2} \frac{1}{N} \sum_j \epsilon_j N_j = \frac{1}{kT^2} \frac{E}{N} \end{aligned}$$

$$\begin{aligned}
 d(\ln W_{\max}) &= \left(\frac{\partial \ln W_{\max}}{\partial \mathcal{H}} \right)_{E, N} d\mathcal{H} + \left(\frac{\partial \ln W_{\max}}{\partial E} \right)_{\mathcal{H}, N} dE \\
 &= N \left(\frac{\partial \ln Q}{\partial \mathcal{H}} \right)_E d\mathcal{H} + dE \left\{ \frac{1}{kT} + \left(\frac{\partial T}{\partial E} \right)_{\mathcal{H}, N} \left[-\frac{E}{kT^2} + N \left(\frac{\partial \ln Q}{\partial T} \right)_N \right] \right\} \\
 &= N \frac{1}{\mathcal{H}} d\mathcal{H} + \frac{dE}{kT} + \left(\frac{\partial T}{\partial E} \right)_{\mathcal{H}, N} dE \left[-\frac{E}{kT^2} + N \frac{E}{kT^2 N} \right]
 \end{aligned}$$

$$\begin{aligned}
 \text{So } kT d(\ln W_{\max}) &= \frac{NkT}{\mathcal{H}} d\mathcal{H} + dE = p d\mathcal{H} + dE \\
 &= T dS \quad \text{from thermodynamics.}
 \end{aligned}$$

suggests $dS = k d \ln W_{\max}$.

Postulate $S = k \ln \Omega \approx k \ln W_{\max}$