I. Probabilities of being in various states

II. Equilibrium

III. The Fundamental Postulate and Boltzmann's H-Theorem

Please read Stowe Chapter 8 and the electronic page on the H-Theorem.

I. Probabilities of being in various states

(This is Chapter 7, Section B.)

Consider a system with # possible states = Ω_0.

If all states are equally likely, then the probability of being in any particular states is $P_{(1)} = \dfrac{1}{\Omega_0}$.

The probability of being in a subset of them, where the subset includes Ω_i states is

$$P_{(subset\ of\ i)} = \frac{\Omega_i}{\Omega_0}.$$

Example: Consider the system of 1 die (with 6 faces)

$$P_{(\text{any one face})} = \frac{1}{6}$$

$$P_{(\text{a face with} >1 \text{ dot})} = \frac{\#\text{ states with} > 1\text{ dot}}{\text{total \# states}} = \frac{5}{6}$$

To understand how to compute probabilities for larger systems (Stowe Chapter 3, Sect. B), consider a system with N elements. These could be N dice, shaken in a closed box.

$$\text{Each element can either } \underbrace{\text{meet}}_{\frac{1}{6}} \text{ or } \underbrace{\text{not meet}}_{\frac{5}{6}} \; \underbrace{\text{criterion A}}_{\text{"lands with 1 dot up"}}.$$

Define P = the probability of meeting the criterion

Define Q = the probability of not meeting the criterion.

Only choose criteria for which P + Q = 1.

Example for N=2 elements. Use subscripts to index element #.

$$(p_1 + q_1) = 1$$

$$(p_2 + q_2) = 1$$

So $(p_1 + q_1)\cdot(p_2 + q_2) = 1\cdot 1 = 1$. Carry out the multiplication:

$$\underbrace{p_1p_2} + \underbrace{q_1p_2 + \underbrace{p_1q_2}} + \underbrace{q_1q_2} = 1$$

Prob. that both elts. satisfy the criterion.

Prob that one does other does not, with no concern for which is which.

Prob that elt#1 does, and elt#2 does not.

Prob that both elts fail the criterion.

If every element is distinguishable (dice are different colors), then each term in the sum represents a state. If the 2 elements are indistinguishable (same color), then the middle 2 terms describe the same state.

Continue example for 2 dice:

$$P(2\ successes) = \frac{1}{6}\cdot\frac{1}{6} = \frac{1}{36}$$

$$P(2\ failures) = \frac{5}{6}\cdot\frac{5}{6} = \frac{25}{36}$$

$$P(Elt\,\#1\ succeeds,\ Elt\,\#2\ fails) = \frac{1}{6}\cdot\frac{5}{6} = \frac{5}{36}$$

$$P(either\ one\ succeeds,\ other\ fails) = \frac{1}{6}\cdot\frac{5}{6}+\frac{5}{6}\cdot\frac{1}{6} = \frac{10}{36}$$

$$P(at\ least\ one\ succeeds) = \frac{1}{6}\cdot\frac{1}{6}+\frac{1}{6}\cdot\frac{5}{6}+\frac{5}{6}\cdot\frac{1}{6} = \frac{11}{36}$$

We could extend this from 2 $\Rightarrow$ N elements to get

$$\left(p_1+q_1\right)\left(p_2+q_2\right)\ldots\left(p_N+q_N\right)=1 \qquad \text{"Eq 1"}$$

$$p_1p_2\ldots p_N+q_1p_1\ldots p_N+\ldots+q_1q_2\ldots q_N=1$$

Now suppose all of the elements have identical p's and q's:

$$p_1=p_2=\ldots=p_N\equiv p$$

$$q_1=q_2=\ldots=q_N\equiv q$$

then Eq 1 becomes:

$$\left(p+q\right)\left(p+q\right)\ldots\left(p+q\right)=1$$

When $N=2$, this has the form $p^2+2pq+q^2=1$

When $N=3$, this has the form $p^3+3p^2q+3pq^2+q^3=1$

For general N, the left hand side looks like:

$$\left(p+q\right)^N=\sum_{n=0}^{N}\underbrace{\frac{N!}{n!\left(N-n\right)!}}\,p^nq^{N-n}=1$$

This term is called the binomial coefficient. It gives the total number of ways that N objects can combine to give n successes and N-n failures.

An approximation that helps us calculate large factorials is Stirling's Formula (Stowe Appendix 3A):

$$\ln m! = m\ln m - m + \frac{1}{2}\ln(2\pi m)$$

Now suppose that the N elements are tested relative to M independent criteria rather than just one criterion.

So each element could pass or fail each criterion.

The probability that the object is in state i with respect to Criterion 1 and state j with respect to Criterion 2 and...and state k with respect to Criterion M is

$$P(i,j,...k)=p(i)\cdot p(j)\cdot ...\cdot p(k)$$

That is: if the criteria are uncorrelated, just multiply the probabilities associated with meeting them.

Example: suppose a given element (gas particle in a room) could be checked for two criteria. Here functional arguments in parentheses indicate criterion #

Criterion #1: Is it in the front 1/3 of the room? P(1)=1/3, Q(1)=2/3.

Criterion #2: Is it in the top half of the room? P(2)=1/2, Q(2)=1/2.

Then:

$$P(front\ \ 1/3,\ top\ \ 1/2) = \frac{1}{3}\cdot\frac{1}{2} = \frac{1}{6}$$

$$P(front\ \ 1/3,\ bottom\ \ 1/2) = \frac{1}{3}\cdot\frac{1}{2} = \frac{1}{6}$$

$$P(back\ \ 2/3,\ top\ \ 1/2) = \frac{2}{3}\cdot\frac{1}{2} = \frac{1}{3}$$

$$P(back\ \ 2/3,\ bottom\ \ 1/2) = \frac{2}{3}\cdot\frac{1}{2} = \frac{1}{3}$$

II. Equilibrium

Definition: an isolated system is in **thermodynamic equilibrium** when the probabilities of its being in various possible states do not vary with time.

Why they don't change: because it is simultaneously in
mechanical equilibrium (no unbalanced forces)
thermal equilibrium (no temperature differences)
and **chemical equilibrium** (no chemical reactions are taking place within it or around it).

Definition: the **relaxation time** of a system is the characteristic time it takes to return to equilibrium after it has been perturbed.

Definition: if a system undergoes a process (e.g., transfer of heat, work, or particles) that takes significantly longer than the relaxation time, we say that the process is **quasi - static.**

III. The Fundamental Postulate and Boltzmann's H-Theorem

Postulate: An isolated (i.e., non-interacting) system in equilibrium is equally likely to be in any of its accessible states.

This postulate is based on reasonableness and experimental data.

If the system is adequately described by the laws of statistics and (reversible) mechanics, then the postulate is a consequence of the H-Theorem:

Consider a system which could be in any one of a variety of states "r", or some other one "s".

The probability of its being in any particular state "r" at time t is $\mathrm{P}_r(t)$.

Require that the probability be normalized: $\sum_r P_r(t) = 1$.

Define $\mathrm{H} \equiv$ mean value of $\ln(\mathrm{P}_r)$ over all accessible states $= \overline{\ln P_r}$.

This is (see Stowe's definition of the mean, Eq. 3.1): $\sum_r P_r \ln P_r$.

We will show that $\frac{dH}{dt} \le 0$, meaning that the probability of being in any specific state decreases monotonically in time (while maintaining the normalization $\sum_r P_r = 1$, so the probabilities for all states are equalizing), and $\frac{dH}{dt} = 0$ only when all P_r have the same value.

To show this: suppose that several similar states are accessible to the system, and the system can easily transition between them (for example, different arrangements of the air molecules in a room).

Define W_{rs} = rate of transition from state "r" to state "s"

So W_{sr} = rate of transition from state "s" to state "r".

If the effect that causes the transitions is weak, and the states are similar, then $\mathrm{W}_{rs} = W_{sr}$.

Notice that the change per unit time in the probability of the system being in state "r" is:

$$\frac{dP_r}{dt} = \sum_s P_s W_{sr} - \sum_s P_r W_{rs}$$ [transitions into r minus transitions out of r]

Plug in $W_{sr} = W_{rs}$.

Then $\dfrac{dP_r}{dt} = \sum_s W_{rs}\left(P_s - P_r\right)$. "Eq 0"

Now define $H = \overline{\ln P_r} = \sum_r P_r \ln P_r$.

Then $\dfrac{dH}{dt} = \sum_r \left(\dfrac{dP_r}{dt} \ln P_r + P_r \dfrac{d(\ln P_r)}{dt} \right)$

$$= \sum_r \left(\frac{dP_r}{dt} \ln P_r + P_r \frac{1}{P_r} \frac{dP_r}{dt} \right)$$

$= \sum_r \dfrac{dP_r}{dt}\left(\ln P_r + 1\right)$. Plug in Eq 0 to get:

$= \sum_r \sum_s W_{rs}\left(P_s - P_r\right)\left(\ln P_r + 1\right)$ "Eq 1"

Rename the summation indices, r ↔ s, so Eq 1 can be rewritten as:

$$\frac{dH}{dt} = \sum_s \sum_r W_{sr}\left(P_r - P_s\right)\left(\ln P_s + 1\right)$$

Again substitute $W_{sr} = W_{rs}$.

$$\frac{dH}{dt} = \sum_s \sum_r W_{rs}\left(P_r - P_s\right)\left(\ln P_s + 1\right)$$

Change the order of the 2 sums:

$$\frac{dH}{dt} = \sum_r \sum_s W_{sr}\left(P_r - P_s\right)\left(\ln P_s + 1\right) \qquad \text{"Eq 2"}$$

Add Eq 1 + Eq 2:

$$2\frac{dH}{dt} = \sum_r \sum_s W_{rs}\left[\left(P_s - P_r\right)\left(\ln P_r + 1\right) + \left(P_r - P_s\right)\left(\ln P_s + 1\right)\right]$$

$$\downarrow$$

$$\left[-\left(P_r - P_s\right)\left(\ln P_r - \ln P_s\right)\right]$$

So

$$\frac{dH}{dt} = -\frac{1}{2}\sum_r \sum_s W_{rs}\left(P_r - P_s\right)\left(\ln P_r - \ln P_s\right)$$

Notice that if $P_r > P_s$, then $\ln P_r > \ln P_s$, so

$\left(P_r - P_s\right)\left(\ln P_r - \ln P_s\right) \geq 0.$

It only $= 0$ when $P_r = P_s$.

Rewriting:

$$\frac{dH}{dt} = \underset{\text{neg}}{-\frac{1}{2}}\sum_r \sum_s \underbrace{W_{rs}}_{\geq 0}\underbrace{\left(P_r - P_s\right)\left(\ln P_r - \ln P_s\right)}_{\geq 0}$$

So $\frac{dH}{dt} \leq 0$, and $= 0$ only when $P_r = P_s$ for all s.

Restate the fundamental postulate:

An isolated system in equilibrium is equally likely to be in any of its accessible states:

This is the real foundation for use of the probability formula,

$$\text{P(being in any accessible state)} = \frac{1}{\text{total number of accessible states}}.$$

Corollary:

If there are Ω_0 total states, and Ω_i state that all have property "i," then the probability that one will measure the property "i" is

$$\text{P(i)} = \frac{\Omega_i}{\Omega_0}.$$

I. Density of states

I. Density of states

The density of states reflects the environment (potential) that the system encounters.

It is an essential factor in calculating transition rates in quantum mechanics.

Facts about the density of states:

1) Energy levels associated with different states overlap or are spaced very closely in macroscopic systems.

(a) Example: in a room with N air molecules, every permutation of their positions is a different state ("level"), but all have the same energy.

When levels have the same energy, we say they are degenerate.

If n=# levels with identical energy E, we say "the system is n-fold degenerate."

(b) If without permuting any air molecules in a room, we just energize one of them, then we again have a different state, whose energy is slightly higher than the next lower.

2) Since levels are close-packed (or overlapping), approximate them as continuous rather than discrete, and define

$$\text{density of states} = \text{density of "levels"} = \frac{\text{number of accessible states}}{\text{size of energy interval attributed to a single level}}$$

Symbolically, this is:

$$g(E) = \frac{\Omega}{\Delta E}.$$

The argument "(E)" indicates that the density of states depends on the center E of the energy interval.

3) Demonstrate that $g(E) \propto E^{N/2}$, where $N = \#$ degrees of freedom of the system.

(This is Stowe Appendix 7A.)

This is a special case of the fact that in m dimensions, $g \propto E^{N(m-2)/2}$.

The goal is to show that $g(E) \propto E^{\text{a really big number}}$, so, g changes rapidly with E.

Count the number of states of a system:

Suppose a system has N degrees of freedom.

Suppose degree of freedom "i" makes available Ω_i states. Then the total number of states $\Omega_0 = \prod_{i=1}^{N} \Omega_i$.

The symbol $\prod$ means product $\Omega_1 \cdot \Omega_2 \cdot ... \cdot \Omega_N$.

Example: consider a dumbbell lying along the z-axis.

Let i = the degree of freedom (dof) associated with rotation about the x-axis.

The existence of this dof makes possible the set of x-axis angular momentum states.

The dumbbell is free to be in any of these states while simultaneously storing energy in an independent dof (for example, vibrations in $\hat{z}$).

So total #(vibrational and $\hat{x}$-rotational states) =

$\left(\#\text{ vibrational states}\right)\times\left(\#\ \hat{x}\text{-rotational states}\right)$.

We need an expression for a general Ω_i which we can then multiply.

Recall that the # states (dΩ) in the volume $dV_r dV_p$ is $\frac{1}{h^3}\underbrace{dxdydzdp_xdp_ydp_z}_{\text{6 dof's "}dq_i\text{"}}$

So the #states dΩ_i due to any one of those dq$_i$ has proportionality:

$d\Omega_i \propto dq_i$

Integrate over the allowed range of the q_i :

$\Omega_i \propto \int dq_i$ "Eq 1"

Now consider only dof's that store energy in the form bq_i^2 :

$E_i = bq_i^2$

Define $r_i \equiv \sqrt{E_i} = \sqrt{b}q_i$

So $dr_i = \sqrt{b}dq_i$

So $dq_i = \frac{1}{\sqrt{b}}dr_i$

$$\Omega_i \propto \left(\frac{1}{\sqrt{b}}\right)\int dr_i$$

Absorb the $\frac{1}{\sqrt{b}}$ into the proportionality, so

$$\Omega_i \propto \int dr_i$$

Then $\Omega_0 = \prod_{i=1}^{N}\Omega_i \propto \prod_{i=1}^{N}\int dr_i$

Notice $\sum_{i=1}^{N} E_i = E_{tot}$ for N dof

So $\sum_{i=1}^{N} r_i^2 = E_{tot}$

Recall the equation for a sphere of radius ℓ centered on (0,0,0):

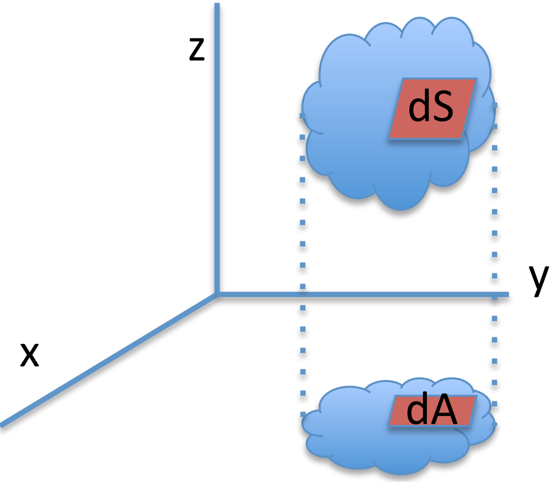
$x^2 + y^2 + z^2 = \ell^2$

So the r_i are the components of an N-dimensional sphere of radius $\sqrt{E_{tot}}$.

Visualize Ω_0 in three dimensions:

$$\Omega_0 \propto \underbrace{\prod_{i=1}^{N} \int dr_i}_{\substack{\Downarrow \\ \iiint dx\,dy\,dz}} \qquad \text{AND} \qquad \underbrace{\sum_{i=1}^{N} r_i^2 = E_{tot} = "E"}_{\substack{\Downarrow \\ x^2 + y^2 + z^2 = E}}$$

Recall from calculus: if a volume in 3-D has a surface S, and we want to find the integral of a function $g(x, y, z)$ over S, if we can write a function $z = f(x, y)$, we can project S onto an area A in the x-y plane and do the integral over A:



$$\int g(x,y,z)\,dS = \int g(x,y,f(x,y))\sqrt{\left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2 + 1}\,dA$$

Here $z = f(x,y) = \left(E - x^2 - y^2\right)^{\frac{1}{2}}$

So $\dfrac{\partial f}{\partial x} = \dfrac{-x}{\left(E - x^2 - y^2\right)^{\frac{1}{2}}}$

$$\frac{\partial f}{\partial y} = \frac{-y}{\left(E - x^2 - y^2\right)^{\frac{1}{2}}}$$

and $g = 1$.

$$\int g(x,y,z)\,dS = \int 1\cdot dS$$

$$\int g\big(x,y,f(x,y)\big) = 2\times\int 1\cdot\left[\frac{x^2}{E-x^2-y^2}+\frac{y^2}{E-x^2-y^2}+1\right]^{1/2} dxdy$$

Factor of 2 because we integrate separately for upper and lower hemispheres, each of which make the same projection A.

$$= 2\int\left[\frac{E}{E-x^2-y^2}\right]dxdy$$

$$= 2\sqrt{E}\int\left[\frac{1}{E-x^2-y^2}\right]dxdy$$

Switch to polar coordinates. Let $\Re^2 = x^2 + y^2$.

Then $dxdy = \Re d\Re d\theta$

$$= 2\sqrt{E}\int_0^{\sqrt{E}}\frac{\Re d\Re}{\left(E-\Re^2\right)^{1/2}}\int_0^{2\pi} d\theta$$

$$= 2\sqrt{E}\cdot\sqrt{E}\cdot 2\pi = 4\pi E$$

Notice $4\pi E$ can be written as $4\pi\left(\sqrt{E}\right)^2 = 4\pi\left(\text{sphere's radius}\right)^{\text{#dimensions-1}}$

Generalize to the N-dimensional sphere. There we expect

$\Omega_0 = \prod_{i=1}^{N} \Omega_i \propto \prod_{i=1}^{N} \int dr_i$ should be proportional to $\left(\text{radius}\right)^{N-1}$

$$\left(\sqrt{E}\right)^{N-1}$$

$$E^{(N-1)/2}$$

$$\approx E^{N/2}$$

We see that $\Omega_0 \propto E^{N/2}$. We need one more argument to show that Ω_0 is also proportional to ΔE.

The number of states Ω_0 is an analytic (well behaved) function, so it can be written as a Taylor Series in ΔE:

$$\Omega(E) = \Omega(0) + \Omega'(0)\Delta E + \Omega''\frac{(\Delta E)^2}{2!} + \ldots$$

As $\Delta E \to 0$, $\Omega \to 0$, so $\Omega(0) = 0$.

Now consider ΔE very small, $\Delta E \to dE$, so $(\Delta E)^2 \to 0$ and higher orders

We are left with $\Omega(E) \propto \Delta E$

Now we have $\Omega_0 \propto E^{N/2}\Delta E$.

But also, $\Omega_0 = g(E)\Delta E$. (Look back at page 62)

So $g(E) \propto E^{N/2}$

Example of the large numbers involved in calculations of everyday situations:

Consider a room full of air.

$N \approx 5 \times 10^{28}$ molecules

#states = $\Omega_0 \propto E^{N/2} = E^{5\times10^{28}/2} = E^{2.5\times10^{28}}$.

This is $E^{(25 \text{ followed by 27 zeroes})}$.

Demonstrate that a small change of E produces a large change in Ω_0 :

Suppose temperature $T_1 = 300$ K (this is room temperature).

Allow it to rise by 1 degree:

$T_2 = 301$ K.

Find $\dfrac{\Omega(301\text{K})}{\Omega(300\text{K})}$, using the fact that energy E $\propto$ temperature T:

$$\frac{\Omega(301\text{K})}{\Omega(300\text{K})} = \frac{E_{301K}^{N/2}}{E_{300K}^{N/2}} = \left(\frac{E_{301K}}{E_{300K}}\right)^{N/2} = (1.0033)^{N/2}.$$

For $N \approx 5 \times 10^{28}$, the ratio is $(1.0033)^{2.5\times10^{28}}$.

That is: the number of states increases by a **factor** of $(1.0033)^{2.5\times10^{28}}$

which is $10^{(36 \text{ followed by 25 zeroes})}$.

I. Refresher on logarithms

II. Why do we observe only the most probable state?

III. Entropy

Please read Stowe Chapter 9.

I. Refresher on logarithms

Suppose $x = b^y$

Then $y = \log_b x$

So a logarithm is just an exponent. The base b is the number being raised to the power.

When x is too large to be easily manageable, y is often easier to use because it is smaller.

Requirements on the base:

$b > 0$

$b \neq 1$

Example problem: Find $\log_2 32$.

Translation: $2^x = 32$, find x.

Solution: $x = 5,\ 5 = \log_2 32$.

Useful properties of logs:

$$\log_b 1 = 0$$

$$\log_b b = 1$$

$$\log_b \left(b^x\right) = x$$

$$\log xy = \log x + \log y$$

$$\log\left(\frac{x}{y}\right) = \log x - \log y$$

$$\log\left(x^y\right) = y \log x$$

Notice there are NO formulas for:

$$\log(x \pm y)$$

$$\log x \log y$$

$$\frac{\log x}{\log y}$$

$$\left(\log x\right)^y$$

To change base from b to a:

$$\log_b x = \frac{\log_a x}{\log_a b}, \qquad a > 0,\ a \neq 1.$$

This leads to:

$$\log_b a = \frac{1}{\log_a b}$$

and

$$\ln x = \log_{10} x \cdot \ln 10$$

Here "ln" just means the base b is $e = 2.718...$

and ln10=2.30...

II. If the elements of a system are free to choose any accessible state, why do we never observe any but the most probable state?

Preview of the answer: the most probable state is zillions of times more probable than even the next-most-probable.

To show this, we calculate the relative probabilities of observing possible states of an example system.

Consider 2 systems that interact (thermally, mechanically, and/or diffusively).

The total energy of the combined system = E = "5 units".

E is conserved for the combined system but can pass between the 2 component systems.

E is quantized, so each component system can have $E_1 = 0, 1, 2, 3, 4$, or 5.

Then the other component must have $(5\text{-}E_1)$.

Allow subsystem 1 to have 6 dof

and subsystem 2 to have 10 dof.

	Subsystem 1	Subsystem 2
#dof (N)	6	10
Energy	E_1	$E_2=5-E_1$
#accessible states Ω_0	$(E_1)^{6/2}=(E_1)^3$	$(E_2)^{10/2}=(E_2)^5$

Tabulate the # accessible states Ω_0 for the combined system, for different options of energy partition between the 2 subsystems. Recall $\Omega_0 = \Omega_1 \cdot \Omega_2$.

E_1	E_2	$\Omega_1=(E_1)^3$	$\Omega_2=(E_2)^5$	$\Omega_0=\Omega_1\Omega_2$	Ω_0/Ω_{tot}
0	5	0	3125	0	0
1	4	1	1024	1024	0.26
2	3	8	243	1944	0.50
3	2	27	32	864	0.22
4	1	64	1	64	0.02
5	0	125	0	0	0

$$\Omega_{tot} = 3896$$

Recall the fundamental postulate: the system is equally likely to be in any of its accessible states.

This system has 3896 accessible states.

Half (1944) of all accessible states have ($E_1 = 2$, $E_2 = 3$).

So half of the time we probe the system, we will find ($E_1 = 2$, $E_2 = 3$).

Half of the time we will find one of the other states.

Now let us redo this example for interacting 1-liter volumes of water:

	Subsystem 1	Subsystem 2
#dof (N)	4×10^{24}	8×10^{24}

E_1	E_2	$\Omega_1=(E_1)^{N(1)/2}$	$\Omega_2=(E_2)^{N(2)/2}$	$\Omega_0=\Omega_1\Omega_2$
0	5	0	$10^{2.8\times10^\wedge24}$	0
1	4	1	$10^{2.4\times10^\wedge24}$	$10^{2.4\times10^\wedge24}$
2	3	$10^{0.6\times10^\wedge24}$	$10^{1.9\times10^\wedge24}$	$10^{2.5\times10^\wedge24}$
3	2	$10^{1.0\times10^\wedge24}$	$10^{1.2\times10^\wedge24}$	$10^{2.2\times10^\wedge24}$
4	1	$10^{1.2\times10^\wedge24}$	1	$10^{1.2\times10^\wedge24}$
5	0	$10^{1.4\times10^\wedge24}$	0	0

Consider one example from this table.

When $E_2 = 5$ and $N_2 = 8\times10^{24}$,

$$\Omega_2 = (5)^{8\times10^{24}/2} = (5)^{4\times10^{24}} = \left(5^4\right)^{10^{24}} = (625)^{10^{24}}.$$

Method to convert this to a power of 10, for easier comparisons:

Let $625=10^n$

so $n = \log_{10} 625 = 2.8$

so $\Omega_2 = \left(10^{2.8}\right)^{10^{24}} = 10^{2.8\times10^{24}}$

Notice how strongly the $(E_1 = 2,\ E_2 = 3)$ state is most probable:

$$\frac{\text{Most probable}}{\text{Next most probable}} = \frac{(E_1 = 2,\ E_2 = 3)}{(E_1 = 1,\ E_2 = 4)} = \frac{10^{2.5\times10^{24}}\ \text{states}}{10^{2.4\times10^{24}}\ \text{states}} = 10^{0.1\times10^{24}}$$

This ratio is $10^{(\text{1 followed by 23 zeroes})}$.

Conclusion:

i) the system is equally likely to be in any of its accessible states

ii) in the absence of constraints, the probability (of any quality) = $\dfrac{\text{\# states with that quality}}{\text{total \# accessible states}}$

iii) we see empirically that for macroscopic systems, it is often the case that:

  a) many states have the same value for a particular quality (many rearrangements of the system yield the same quality, and each rearrangement is a different state)

  b) one value of that quality has by far the most states

  c) statistically that value of that quality will appear in essentially all measurements of the system. The likelihood of a deviation from it is 1 out of $10^{(\text{1 followed by 24 zeroes})}$.

[About the rearrangements: for example, there are more ways to select 2 out of 5 objects, than there are to select 1 out of 5.]

Another way to say this is:

"When 2 interacting macroscopic systems (for example, air in the right half and the left half of a room) are in equilibrium, the values of the various system variables (number of molecules in each half, volume, and other things that affect qualities like energy) will be such that the number of states available to the combined system is a maximum."

That statement concerns a system IN EQUILIBRIUM. As a corollary:

As 2 interacting systems approach equilibrium, the changes that their system variables undergo will be such as to cause the number of states available to the combined system to increase.
i.e., if $\Omega_0 =$ total # states accessible to the combined system,

$\Delta\Omega_0 > 0.$ This is the Second Law of Thermodynamics.

III. Entropy S

Definition: Entropy $S \equiv k \ln \Omega$

#states accessible to a macroscopic system

Boltzmann's constant, $1.381 \times 10^{-23} J / K$

Why does the equation include *k*?

Historically entropy was recognized as a useful descriptor of systems, on the basis of their thermal behavior alone---i.e., before the statistical counting of states, Ω, was investigated. So the first definition of S (which is still used and still correct) was indirectly through its change, with no absolute reference:

$$\Delta S = \frac{\Delta Q}{T}.$$

T had already been related to energy through $E \propto kT$ (this will come up in Chapter 9). So to preserve the historical units of entropy, one needs

$$\Delta S = \frac{\Delta Q}{T} = \frac{\Delta Q}{\frac{E}{k}} \propto k.$$

Facts about this definition of entropy:

1) if we combine 2 systems, their entropies add.

Recall if System 1 has Ω_1 accessible states

and System 2 has Ω_2 accessible states

then $\text{System}_{total} = \text{System 1} + \text{System 2}$ has $\Omega_{total} = \Omega_1 \cdot \Omega_2$ accessible states.

$$\begin{aligned} S_{tot} = k\ln\Omega_{tot} = k\ln\left(\Omega_1 \cdot \Omega_2\right) &= k\left[\ln\Omega_1 + \ln\Omega_2\right] \\ &= k\ln\Omega_1 + k\ln\Omega_2 \\ &= S_1 + S_2 \end{aligned}$$

2) i) The Second Law says: Ω increases as systems approach equilibrium.

ii) Since $S = k\ln\Omega$, as Ω increases, S also increases.

iii) At equilibrium, $\Omega = \Omega_{\max}$, so $S = S_{\max}$.

iv) The Fundamental Postulate says all states are equally probable, so it is highly improbable that S will decrease after reach $S_{\max}$.

Combine these 4 facts into an Alternative Form of the Second Law:

$\Delta S \geq 0$ for ALL systems.

$\Delta S > 0$ for those *approaching* equilibrium, and
$\Delta S = 0$ for those *a*t equilibrium.

"For any two interacting systems, the entropy of the combined system cannot decrease."

3) This can be generalized for > 2 interacting systems because of the additivity of S.

I. Definition of temperature
II. Relationship between temperature and internal energy
III. Relationship between temperature and direction of heat flow
IV. The Zeroth Law of Thermodynamics

Please read Stowe Chapter 4, Sections A and B only.

I. Definition of temperature

How are entropy, heat, and temperature related?

Consider how the entropy S of a system changes in response to heat flowing into or out of a system. We will find that the rate of change $\propto \dfrac{1}{Temperature}$.

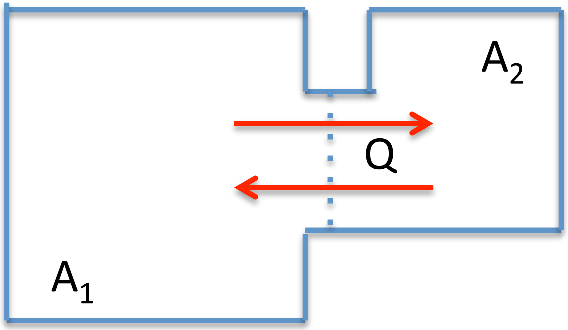
Recall the First Law: $dE = dQ - dW + \mu dN$

So we want to examine: $\dfrac{dS}{dQ} \Rightarrow \left.\dfrac{dS}{dE}\right|_{V,N}$

"V" means constant volume: no work

"N" means constant particles: no diffusion

Consider 2 systems A_1 and A_2 in thermal contact. The combined system is called $A_0 \equiv A_1 + A_2$



Name their entropies:

S_1 of A_1

S_2 of A_2

S_0 of $A_0 = A_1 + A_2$

Name their energies:

E_1

E_2

$E_0 = E_1 + E_2$

Recall the Second Law:

$\Delta S > 0$ approaching equilibrium, and $\Delta S = 0$ at equilibrium.

So when $A_1 + A_2$ are in equilibrium, their combined entropy is maximized.

At equilibrium, $\left.\dfrac{\partial S_0}{\partial E_1}\right|_{V,N} = 0$ or $\left.\dfrac{\partial S_0}{\partial E_2}\right|_{V,N} = 0$

Suppose $\left.\frac{\partial S_0}{\partial E_1}\right|_{V,N} = 0$

Use $S_0 = S_1 + S_2$

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{V,N} + \left.\frac{\partial S_2}{\partial E_1}\right|_{V,N} = 0$$

Use energy conservation: $dE_1 = -dE_2$

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{V,N} - \left.\frac{\partial S_2}{\partial E_2}\right|_{V,N} = 0$$

So at equilibrium,

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{V,N} = \left.\frac{\partial S_2}{\partial E_2}\right|_{V,N}$$

Thus equilibrium is characterized by the fact that the 2 systems have equal values of the property $\left.\frac{\partial S_i}{\partial E_i}\right|_{V,N}$. Name this $\frac{1}{T_i} \equiv \left.\frac{\partial S_i}{\partial E_i}\right|_{V,N}$.

Thus at equilibrium:

$$\frac{1}{T_1} = \frac{1}{T_2}.$$

So:

At equilibrium, $T_1 = T_2$.

II. Relationship between temperature and internal energy

Recall the definition:

$$\frac{1}{T_i} = \left.\frac{\partial S_i}{\partial E_i}\right|_{V,N}$$

Use $S = k \ln \Omega$, where $\Omega = \#$ of states

$$\frac{1}{T_i} = k \frac{\partial \ln \Omega}{\partial E}$$

Recall that "E" here means $\mathrm{E}_{\text{internal}}$.

We showed that when $\mathrm{E}_{\text{internal}}$ is stored in a degree of freedom as

$\mathrm{E}_{\text{internal}} = bq^2$, then $\Omega = (const) \times E_{\text{internal}}^{\mathbb{N}/2}$, where $\mathbb{N}$ is #dof

$$\frac{1}{T_i} = k \frac{\partial \ln\left[(const) \times E_{\text{int}}^{\mathbb{N}/2}\right]}{\partial E_{\text{int}}}$$

$$= k \frac{\partial\left[\ln const + \ln E_{\text{int}}^{\mathbb{N}/2}\right]}{\partial E_{\text{int}}}$$

$$\frac{1}{T_i} = k \cdot \frac{\mathbb{N}}{2} \cdot \frac{1}{E_{\text{int}}}$$

Conclude:

$\mathrm{E}_{\text{int}} = \frac{1}{2}\mathbb{N}kT$ when stored as ~bq^2.

In this case, call it $\mathrm{E}_{thermal}$

thus $\mathrm{kT} \propto \frac{E_{thermal}}{\mathbb{N}}$.

Generalize this to:

$\mathrm{E}_{\text{int}} = \chi\mathbb{N}kT$

to include the more general case for different dimensionality.

(Recall $g(E) \propto \mathbb{N}\left(m-2\right)/2$ where m = dimensions.

This would cover cases in which energy is not stored as bq^2,

for example relativistic $E = pc$.)

So temperature is a direct measure of internal energy.

Recap:

Temperature measures internal energy (internal energy above the ground state) per dof.

We sense that when 2 non-identical systems come into equilibrium, they are optimizing or equalizing something.

They are NOT equalizing energy or #particles.

They ARE equalizing $\frac{\mathrm{E}_{thermal}}{\mathbb{N}}$, thermal energy per degree of freedom.

Recall $\mathrm{E}_{\substack{total\\internal}} = E_{thermal} + \mu N$

μ is the chemical potential: height of the ground state above the absolute energy reference.

Plug in $\mathrm{E}_{thermal} = \frac{1}{2}\mathbb{N}kT$

$$\mathrm{E}_{\substack{total\\internal}} = \frac{1}{2}\mathbb{N}kT + \mu N$$

If there are N particles, each with ν dof, then $\mathbb{N}=\nu$N.

$$\mathrm{E}_{\substack{total\\internal}} = \frac{1}{2}\nu NkT + \mu N = N\left(\frac{\nu}{2}kT + \mu\right)$$

III. Relationship between the temperature of 2 objects and the direction of energy flow between them

Here we show mathematically that heat flows from the body of higher T to the one of lower T.

Consider 2 systems, A_1 and A_2, in thermal contact, but not yet in equilibrium.

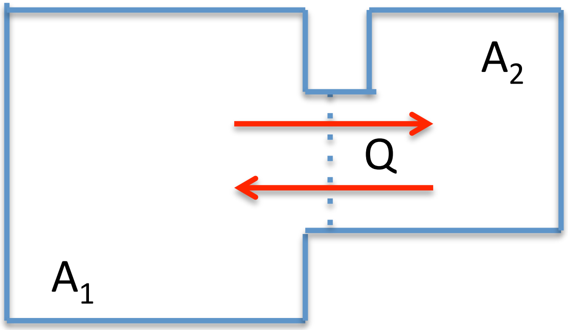
Again define $S_1, E_1, S_2, E_2, S_0 = S_1 + S_2, E_0 = E_1 + E_2$

"Not in equilibrium" means:

$\Delta S_1 \neq 0$ (could be increasing or decreasing)

$\Delta S_2 \neq 0$ (could be increasing or decreasing)

$\Delta S_0 > 0$ (MUST be increasing, according to the Second Law)



The proof has 2 parts. Part 1:

For each system, a change in energy (ΔE) results in a change in entropy:

$$\Delta S = \left.\frac{\partial S}{\partial E}\right|_{V,N} \cdot \Delta E$$

$$= \frac{1}{T} \cdot \Delta E$$

Thus

$$\Delta S = \frac{\Delta E}{T} \qquad \text{"Eq 1"}$$

Now Part 2: Begin with the Second Law:

$$\Delta S_0 > 0$$

Plug in $S_0 = S_1 + S_2$:

$$\Delta S_1 + \Delta S_2 > 0$$

Substitute Eq 1:

$$\frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} > 0$$

Use energy conservation: $\Delta E_1 = -\Delta E_2$

$$\frac{\Delta E_1}{T_1} - \frac{\Delta E_1}{T_2} > 0$$

$$\Delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) > 0$$

This is a combined requirement on ΔE_1 and $\left(\frac{1}{T_1} - \frac{1}{T_2} \right)$:

1) If $T_2 > T_1$, then $\frac{1}{T_1} - \frac{1}{T_2}$ is positive, so ΔE_1 must also be positive.

"If System 1 is the one with lower temperature, then it will gain energy."

2) If $T_1 > T_2$, then $\frac{1}{T_1} - \frac{1}{T_2}$ is negative, so ΔE_1 must also be negative.

"If System 1 is the one with higher temperature, then it will lose energy."

IV. The Zeroth Law of Thermodynamics

Arithmetically, if

$a = c$ and $b = c$ then $a = b$.

This is true of temperatures since they are just numbers, so if

$T_1 = T_3$ and $T_2 = T_3$ then $T_1 = T_2$.

"If 2 systems are each in equilibrium with a third system, then they are in equilibrium with each other."

This is the Zeroth Law of Thermodynamics.

The "test system" (3) with which they are both in equilibrium is called **a thermometer.**

Properties of a thermometer:

1) it tests whether 2 systems will or will not remain in equilibrium when brought into thermal contact with each other.

2) it is any object that has a macroscopic parameter θ that varies considerably with temperature when all other macroscopic parameters are held fixed.
θ is called "the thermodynamic parameter". It could be length, volume, pressure, resistance,....

3) it is much smaller (i.e. has many fewer dof's) than the systems that it is designed to test, so as not to significantly alter them.

I. Temperature scales and the Boltzmann constant
II. Phase transitions
III. The thermodynamic definition of energy
IV. Mathematical detour #1: mean values

Please read Stowe Chapter 10.

I. Temperature scales and the Boltzmann constant

Before absolute temperature was fully understood, the Celsius scale was defined by:

$0^\circ\mathrm{C} \equiv$ the temperature of a state in which ice is in equilibrium with air-saturated water @ atmospheric pressure.

$100^\circ\mathrm{C} \equiv$ the temperature of a state in which water is in equilibrium with water vapor @ atmospheric pressure.

After the concept of absolute zero (Kelvin) was discovered, one could work backward to find that based on the Celsius definition, $0^0\mathrm{C} \cong 273.15\ \mathrm{K}$ at atmospheric pressure. The Celsius definition environments are difficult to reproduce experimentally because they involve controlling both water and air.

What is easier to do---consider water, no air: When liquid, steam, and ice are in simultaneous equilibrium, call the $\mathrm{T} \equiv 273.15\ \mathrm{K}$ exactly.

This happens at pressure 0.006 atm.

It is called water's "triple point."

Given this definition, if the pressure is increased from 0.006 atm to 1 atm, the water remains frozen up to $T = 273.15\ K$, so the Celsius result is recovered. The size of the Celsius and Kelvin degrees remain the same.

Note $E = \frac{1}{2}\mathbb{N}kT$

T (temperature) is measurable, once the triple point is defined.

$\mathbb{N}$ (#dof) is measurable through spectroscopy.

E (energy) is measurable (for example energy causes ionization).

So k is fixed by the choice of the triple point to be $k = 1.381\times 10^{-23} J / K$.

II. Phase transitions

Recall we have said there are occasions when we add energy to a system but the temperature does not change---e.g. boiling, melting.

Show this mathematically:

Recall $\frac{1}{T} \equiv \frac{\partial S}{\partial E}$

Plug in $S = k \ln \Omega$

$$= k \ln\left(E_{thermal}^{\mathbb{N}/2}\right)$$

But $\mathrm{E}_{thermal} = E - \mu N$

So $S = k \ln\left[\left(E - \mu N\right)^{\mathbb{N}/2}\right]$

Then $\frac{1}{T} = \frac{\partial\left\{k \ln\left[\left(E - \mu N\right)^{\mathbb{N}/2}\right]\right\}}{\partial E}$

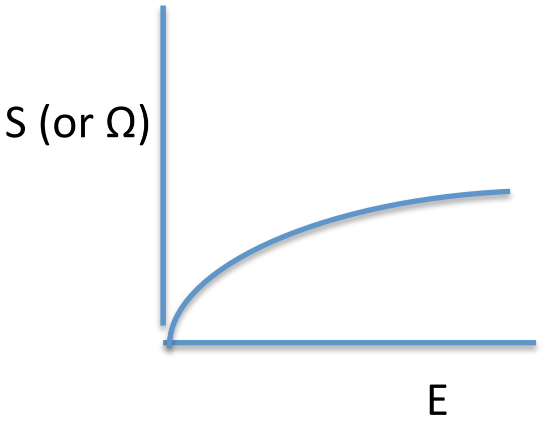
$$\frac{1}{T} = k \cdot \frac{1}{E - \mu N} \cdot \frac{\mathbb{N}}{2}$$

Thus: if E changes, but due to a change in μ, so that $E - \mu N$ stays constant, then T does not change.

The μ is the reference point. It changes if the environment (the potential well) changes.

How to see a phase change graphically:

suppose we measure S (or Ω) directly, and E. Graph them:



The general slope of the curve is a natural logarithm because

$S \propto \ln E^{\mathbb{N}/2}$

Because $\frac{1}{T} = \frac{\partial S}{\partial E}$, when T=constant, we expect $\frac{\partial S}{\partial E}$ to be constant.

Thus: local straight (linear) regions in this curve indicate phase transitions.

How to measure S? Ω?

Macroscopically: use spectroscopy, infer #states from all possible transitions

III. The thermodynamic definition of entropy

(where $S = k\ln\Omega$ is the *statistical* definition of entropy)

Consider a system with energy E. Its entropy is S(E). Add a small amount of heat dQ to it, with no other changes. How does this heat affect S?

Taylor expand:

$$S(E+dQ)=S(E)+\left.\frac{\partial S}{\partial E}\right|_{V,N} dQ+\underbrace{\frac{1}{2}\left.\frac{\partial^2 S}{\partial E^2}\right|_{V,N}(dQ)^2+\ldots}_{\substack{\Downarrow \\ \text{neglect, for infinitesimal } dQ}}$$

Then

$$\underbrace{S(E+dQ)-S(E)}_{\substack{\Downarrow \\ \text{by def, } dS}}=\underbrace{\left.\frac{\partial S}{\partial E}\right|_{V,N}}_{\substack{\Downarrow \\ \frac{1}{T}}} dQ$$

Recap:

$$dS = \frac{dQ}{T}$$

So $dQ = TdS$. Later we will use this in the First Law, making the replacement:

$$dE = \underset{TdS}{\cancel{dQ}} - dW + \mu dN$$

Notice:

dQ is an inexact differential.

dS is an exact differential because $S = k\ln\Omega$. Ω, the number of states, is a measurable (path independent) property.

So $\dfrac{dQ}{T}$ is an exact differential.

IV. Mathematical detour #1: mean values

Let u be a variable that can take any of M discrete values $u_1, u_2, \ldots, u_M$, with respective probabilities $P(u_1), P(u_2), \ldots, P(u_M)$.

Define: the mean (average) value of u as

$$\overline{\mathrm{u}} \equiv \frac{\sum_{i=1}^{M} P(u_i)\cdot u_i}{\sum_{i=1}^{M} P(u_i)} \quad .$$

Normalize it, so that the denominator =1:

$$\overline{\mathrm{u}} \equiv \sum_{i=1}^{M} P(u_i)\cdot u_i$$ when the $P(u_i)$ are normalized.

Now generalize to functions $f(u_i)$:

$$\overline{f(u)} = \sum_{i=1}^{M} P(u_i)\cdot f(u_i)$$ when the $P(u_i)$ are normalized.

Consequences.

(Assume for all cases below that the P are normalized.)

i) If f(u) and g(u) are functions of u,

$$\overline{f(u)+g(u)} = \sum_{i=1}^{M} P(u_i)\left[f(u_i)+g(u_i)\right]$$

$$= \sum_{i=1}^{M} P(u_i)f(u_i) + \sum_{i=1}^{M} P(u_i)g(u_i)$$

Thus:

$$\overline{f(u)+g(u)} = \overline{f(u)} + \overline{g(u)}$$

ii) If c is any constant,

$$\overline{cf(u)} = c \cdot \overline{f(u)}$$

iii) Define the deviation Δu of any particular u_i from the mean $\overline{u}$:

$\Delta u \equiv u_i - \overline{u}$.

Then: $\overline{\Delta u} \equiv \overline{\left(u_i - \overline{u}\right)} = \overline{u} - \overline{\overline{u}} = \overline{u} - \overline{u} = 0$.

Thus: $\overline{\Delta u}$ is always zero.

iv) Define the dispersion $\overline{(\Delta u)^2}$ of u as:

$$\sigma^2 \equiv \overline{(\Delta u)^2} = \sum_i P(u_i)\left(u_i - \bar{u}\right)^2$$

σ^2 is also called "the second moment of u"

σ is called the standard deviation.