

Notes for Chapter 6

Consider a gas or liquid of N molecules and of total energy E in a volume V . Suppose the volume V is isolated — surrounded by a fixed, hard wall that lets no heat or energy in or out of V . If we let this system sit for a long while, then it will eventually come to equilibrium.

Due to the constant stream of collisions between pairs of molecules and between the molecules and the wall, the precise velocities \vec{v}_i and locations \vec{r}_i of the N molecules keep changing. In fact, the microstate $\{ \vec{v}_i, \vec{r}_i \}$ changes from nanosecond to nanosecond.

The sum of the energies

$$\sum_{i=1}^N \frac{1}{2} m \vec{v}_i^2 = E$$

in each microstate is the total energy E .

All of the \vec{v}_i are within the volume V .

How many microstates are there?

Suppose there are Ω of them. Then the entropy S is defined as

$$S = k \ln \Omega. \quad (6.5)$$

We shall assume that all the Ω microstates at equilibrium are equally likely. The entropy S is a measure of our lack of knowledge of the exact microstate of the system.

Why the logarithm?

To see why our uncertainty should be measured by a logarithm of the total number Ω of microstates, let us consider two independent, isolated systems with Ω_1 and Ω_2 microstates. The total number Ω of microstates for the combined system is

$$\Omega = \Omega_1 \Omega_2.$$

Thus the entropy of the combined system is

$$\begin{aligned} S &= k \ln \Omega = k \ln \Omega_1 \Omega_2 \\ &= k (\ln \Omega_1 + \ln \Omega_2) \\ &= k \ln \Omega_1 + k \ln \Omega_2 \\ &= S_1 + S_2. \end{aligned}$$

The logarithm makes entropy additive.

Additive physical quantities are called extensive. The logarithm makes entropy extensive.

Let's estimate Ω and S for an ideal gas of N molecules and total energy E isolated and in equilibrium in a volume V . For each microstate $\{ \vec{v}_i, \vec{r}_i \}$, the energy E is the sum of the kinetic energies of the N molecules

$$E = \sum_{i=1}^N \frac{1}{2} m \vec{v}_i^2 = \sum_{i=1}^N \sum_{j=1}^3 \frac{1}{2} m v_{ij}^2$$

since $\vec{v}_i^2 = v_{i1}^2 + v_{i2}^2 + v_{i3}^2$ (Here x, y, z have morphed into $1, 2, 3$). Thus, the momenta p_{ij} are the $3N$ components of a vector of length R

$$\frac{1}{2m} \sum_{i=1}^N \sum_{j=1}^3 p_{ij}^2 = E = \frac{R^2}{2m}$$

$$R = \sqrt{2mE} = \sqrt{\sum_{i=1}^N \sum_{j=1}^3 p_{ij}^2}$$

This $3N$ -dimensional vector lies on the surface of a sphere. Different points on that sphere of radius $R = \sqrt{2mE}$ correspond to different microstates.

In a space of 3 dimensions, the area of a sphere of radius R is $4\pi R^2$.

In a space of $3N$ dimensions, the area of a sphere of radius $R = \sqrt{2mE}$ is

$$\begin{aligned} A_{\text{area}}^{3N} &= \frac{2}{\left(\frac{3N}{2} - 1\right)!} \pi^{\left(\frac{3N}{2}\right)} R^{3N-1} \\ &= \frac{2}{\left(\frac{3N}{2} - 1\right)!} \pi^{\left(\frac{3N}{2}\right)} (2mE)^{\frac{3N-1}{2}} \end{aligned}$$

Each molecule can be anywhere in the box V . So the number Ω of microstates for one molecule must be proportional to V , for two $\Omega \propto V^2$, and for N molecules

$$\Omega \propto V^N.$$

So

$$\Omega = \text{constant} \times (2mE)^{\frac{3N-1}{2}} \times V^N.$$

Thus the entropy S is with constant $= c'$

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln \left(c' \times (2mE)^{\frac{3N-1}{2}} \times V^N \right) \\ &= k \left[\ln c' + \frac{3N-1}{2} \ln 2mE + N \ln V \right]. \end{aligned}$$

Set c When $N=10$, the -1 in $3N-1$ is important, but when N is more than a few thousand, let alone 6×10^{23} , the -1

can be dropped. Now S looks nicer:

$$\begin{aligned} S &= k \ln \left(c' (2mE)^{\frac{3N}{2}} V^N \right) \\ &= k \ln \left(c'' E^{\frac{3N}{2}} V^N \right) \\ &= k \left[\ln c'' + N \ln E^{\frac{3}{2}} + N \ln V \right] \end{aligned}$$

or

$$S = kN \left(\frac{3}{2} \ln E + \ln V \right) + \text{constant.}$$

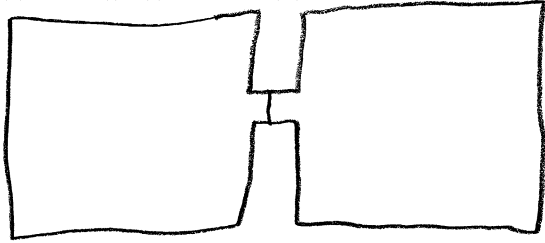
The Sakur-Tetrode formula is

$$S = k \ln \left[\frac{2}{(\frac{3N}{2} - 1)!} \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}} V^N \frac{1}{N! (2\pi h)^{\frac{3N}{2}}} \right].$$

The two new things here are the $N!$ and

$h = h / 2\pi$ where h is Planck's constant.

The $N!$ is there because the molecules are indistinguishable: if you've seen one nitrogen molecule N_2 , you've seen them all.


 N_A, E_A, V_A
 N_B, E_B, V_B

$$S = k \ln \Omega = k \ln \Omega_A \Omega_B$$

$$= k \ln \Omega_A + k \ln \Omega_B$$

$$= k \left[N_A \left(\frac{3}{2} \ln E_A + \ln V_A \right) + N_B \left(\frac{3}{2} \ln E_B + \ln V_B \right) \right] + \text{constant}$$

But $E = E_A + E_B$, so

$$S = k \left[N_A \left(\frac{3}{2} \ln E_A + \ln V_A \right) + N_B \left(\frac{3}{2} \ln (E - E_A) + \ln V_B \right) \right] + C$$

The most probable S is

$$0 = \frac{dS}{dE_A} = \frac{3}{2} \frac{N_A}{E_A} - \frac{3}{2} \frac{N_B}{E_B}$$

or

$$\frac{E_A}{N_A} = \frac{E_B}{N_B}$$

so the two systems have the same $\langle \frac{1}{2} m \vec{v}^2 \rangle$ per molecule.

This is the zeroth law of thermodynamics:

Two systems in thermal contact come to the same temperature.

$$\frac{3}{2} k T_A = \frac{E_A}{N_A} = \frac{3}{2} k T_B = \frac{E_B}{N_B}.$$

We define temperature T as

$$T = \left(\frac{dS}{dE} \Big|_V \right)^{-1} = \left(\frac{dS}{dQ} \right)^{-1}. \quad (6.9)$$

6 A (a) Do the units work in (6.9)?

$$[S] = [k] = \text{E K}^{-1} \text{ so } \left[\frac{dS}{dE} \right] = \frac{\text{E K}^{-1}}{\text{E}} = \text{K}^{-1}$$

so

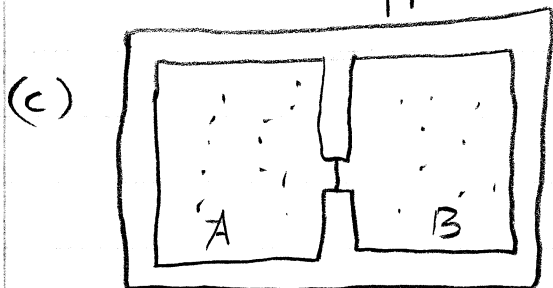
$$\left[\left(\frac{dS}{dE} \right)^{-1} \right] = \text{K}, \text{ degrees Kelvin.}$$

$$(b) \quad S = k \frac{3N}{2} \ln E + k N \ln V$$

$$T = \left(\frac{dS}{dE} \right)^{-1} = \left(k \frac{3N}{2E} \right)^{-1} = \frac{2E}{3kN}$$

$$\text{or } \frac{E}{N} = \frac{3}{2} kT \quad \text{as expected.}$$

(There's a typo in the 1st & 2d printings.)



$S = S_A + S_B$ is maximal when

$$0 = \frac{dS}{dE_A} = \frac{dS_A}{dE_A} + \frac{dS_B}{dE_A}$$

But $E = E_A + E_B$, so $E_B = E - E_A$,

$$\text{so } \frac{d}{dE_A} = \frac{dE_B}{dE_A} \frac{d}{dE_B} = - \frac{d}{dE_B}$$

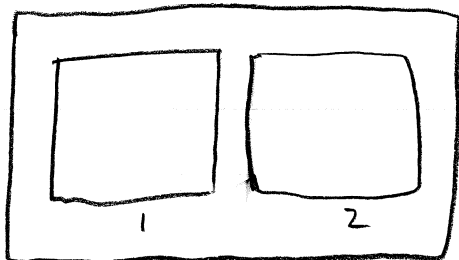
Thus, the condition $0 = dS/dE_A$ gives

$$0 = \frac{dS_A}{dE_A} - \frac{dS_B}{dE_B} = \frac{1}{T_A} - \frac{1}{T_B}$$

So $T_A = T_B$ is condition (6.10)

as follows from the 0th law of thermodynamics.

16B



$$\begin{aligned} E_1 &= E_2 \\ N_1 &= N_2 \\ T_1 &= T_2 \end{aligned}$$

We add dE to the combined system with entropy

$$S = S_1 + S_2 = 2S_1$$

We put αdE in \square_1 and $(1-\alpha)dE$ in \square_2 .

$$S(E+dE) = S_1(E+dE) + S_2(E+(1-\alpha)dE)$$

$$= S_1(E) + \frac{dS_1}{dE} \alpha dE + S_2(E) + \frac{dS_2}{dE} (1-\alpha)dE$$

$$= S_1(E) + \frac{\alpha dE}{T_1} + S_2(E) + \frac{(1-\alpha)dE}{T_2}$$

$$= 2S_1(E) + \frac{\alpha dE + (1-\alpha)dE}{T_1}$$

$$= 2S_1(E) + \frac{dE}{T_1}$$

Now T is given by

$$\frac{1}{T} = \frac{dS}{dE} = \frac{1}{T_1} = \frac{1}{T_2}$$

So $T = T_1 = T_2$ as long as $dE \ll E$.

Thus when a system is duplicated, S doubles but T stays constant.

S is extensive, T is intensive.

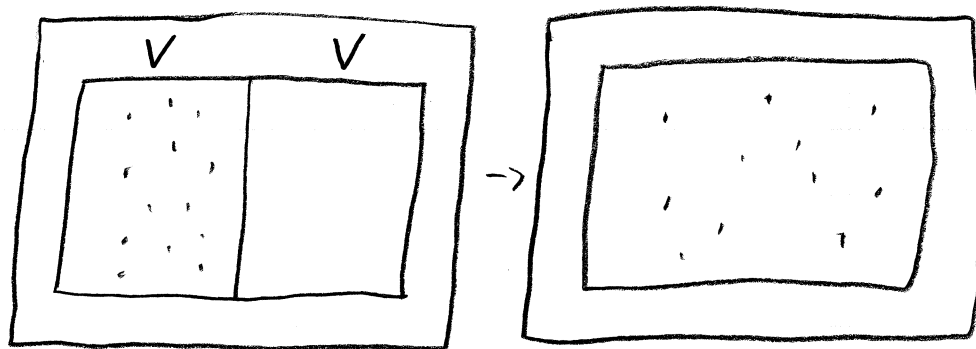
Two systems brought into contact will assume the same T eventually; the total energy & entropy will be the sum of those of the two systems after equilibration.

The first law of thermodynamics is the conservation of energy, including heat.

The second law of thermodynamics:

If we release a constraint on an isolated system, then some states become accessible, and the number Ω of states increases, and so $S = k \ln \Omega$ goes up.

Example:



Suppose we remove a baffle that keeps N Argon atoms on one side of a volume $2V$. By removing this constraint, we make many more microstates accessible.

The change ΔS in the entropy S is

$$\Delta S = k \left[\ln E^{\frac{3N}{2}} (2V)^N - \ln E^{\frac{3N}{2}} V^N \right]$$

in which the final and initial energies are both E , since we did no work on the gas as we allowed it to expand into the volume $2V$. So

$$\begin{aligned} \Delta S &= k (\ln(2V)^N - \ln V^N) \\ &= kN \ln 2. \end{aligned}$$

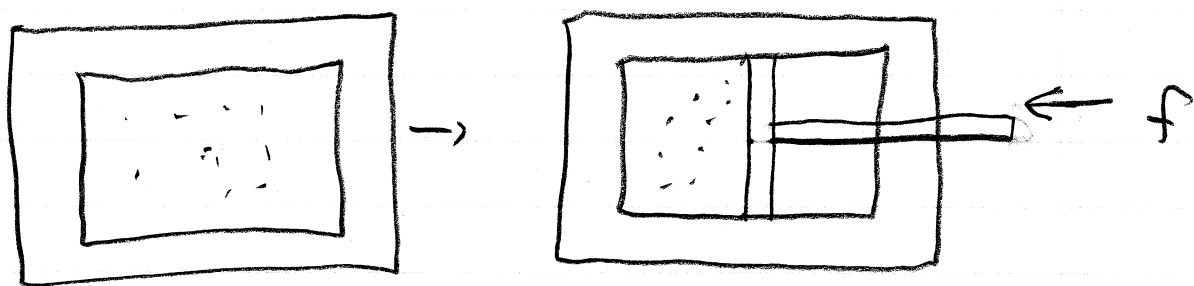
Our uncertainty about the system —

or its disorder — has increased by

$$\Delta I = \frac{\Delta S}{k \ln 2} = N$$

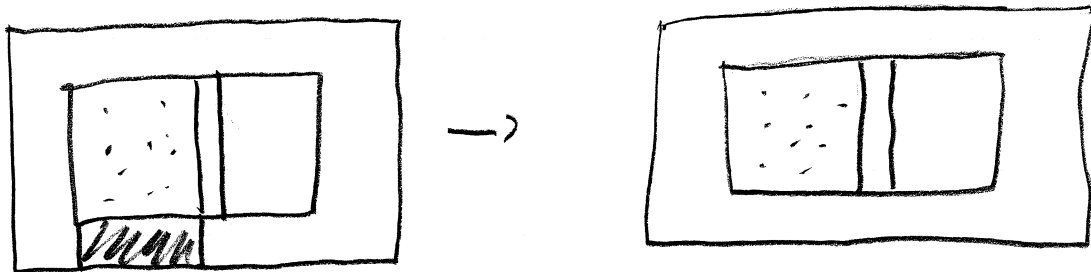
bits of information because we once knew that all N atoms were in the left V and not merely in the whole $2V$.

To restore this system to its original state, we could compress the gas in to the left V by



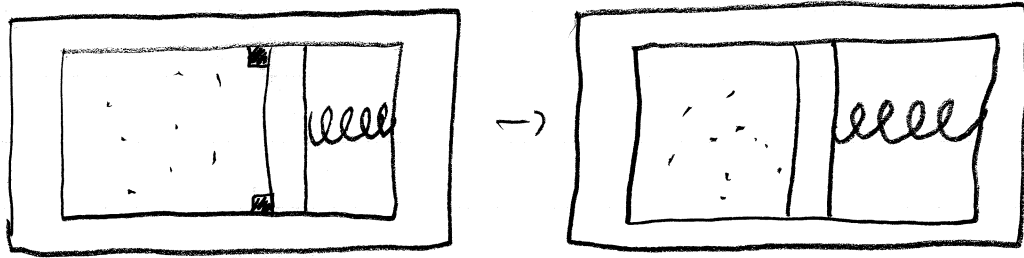
pushing a piston from the right.

The gas would get hotter. We then could cool the gas by replacing



some of the insulation by a conductor and allowing the extra heat to escape until the temperature and energy of the gas returned to their initial values. The cost of releasing the constraint (removing the baffle) would be the transformation of some ordered energy (mechanical work) into disordered energy (heat).

Example:



We release two stops (■) and the spring pushes the piston a distance δ compressing the gas with force f . The work

$\Delta W = f\delta$ done by the spring increases

the kinetic energy E of the gas by

the same amount

$$\Delta E = f\delta,$$

The change ΔS in the entropy of

the gas is

$$\Delta S = k \left(\Delta \ln E^{\frac{3N}{2}} + \Delta \ln V^N \right)$$

$$= \frac{3N}{2} k \frac{\Delta E}{E} + Nk \frac{\Delta V}{V}.$$