2. Entropy and Temperature

Read: Chapter 2

Do: All problems — 1, 2, 3, 4, 5, 6

For next week

Read: Chapter 3

Do: Prob. 1, 2, 3, 4, 8, 11

Recall our fundamental assumption:

For a closed system, all accessible states are equally likely

"Closed" means e.g. total energy U, total number of particles N are specified and held constant

In practice energy $= U \pm \delta U$, number $= N \pm \delta N$ } may not be precisely known, may fluctuate a little —

But $\delta U/U$, $\delta N/N \ll 1$

"Accessible" means allowed by macroscopic specification (e.g. U, N) and the time scale considered

- E.g. graphite might "fluctuate" to diamond
- $H_2 \rightarrow D^{+} + e^{+} + \nu_e$ (molecular $H_2 \Rightarrow$ atomic ^2D)

(Gas in box → black hole)

Don't include these if fluctuation will not occur over a reasonable timescale

If $g \equiv$ "multiplicity" $\equiv$ no. of accessible states

probability of a state $P = \frac{1}{g}$

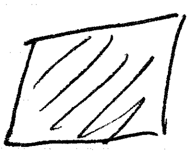
then $\sum_{\text{states}} P(\text{state}) = 1$

We predict how system behaves by averaging over all states

$$\langle X \rangle = \sum_{\text{state}} X(\text{state})\, P(\text{state})$$

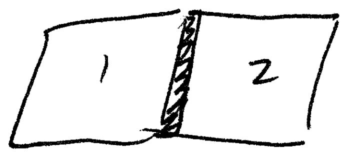
— "Ensemble average" (Ensemble = {all access. states})

Thermal Contact



Consider e.g. gas in a closed box
N = total no of particles
U = total energy

Imagine putting two such boxes in "thermal contact" — can exchange energy but not particles



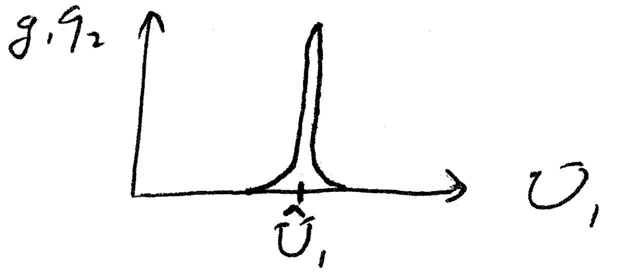
For combined ① + ②, before contact (two isolated systems)

$$\underbrace{g(N, U)}_{\substack{N = N_1 + N_2 \\ U = U_1 + U_2}} = g_1(N_1, U_1)\, g_2(N_2, U_2)$$

Now — establish contact. Boxes can share the fixed total energy U any way they like.

$$g(N, U) = \sum_{0 \le U_1 \le U} g_1(N_1, U_1)\, g_2(N_2, U-U_1)$$

The main idea of statistical mechanics is that for $N_{1,2} \gg 1$, $g_1(N_1, U_1)\, g_2(N_2, U-U_1)$ is a sharply peaked function of U_1



Peak occurs at $U_1 = \hat{U}_1$, "Most probable configuration"

(Not a single state, but a preferred way of sharing U between the two systems)

Also called: "equilibrium configuration"

Where is the peak?

$$dg = \left(\frac{\partial g_1}{\partial U_1}\Big|_{N_1} dU_1 \right) g_2 + g_1 \left(\frac{\partial g_2}{\partial U_2}\Big|_{N_2} dU_2 \right)$$

and $U = U_1 + U_2 = \text{constant}$

$$\Rightarrow \quad dU_2 = -dU_1$$

Notation:

partial derivative $\displaystyle \frac{\partial g_1}{\partial U_1}\Big|_{N_1} = \lim_{\epsilon \to 0} \frac{g_1(U_1+\epsilon, N_1) - g_1(U_1, N_1)}{\epsilon}$

— differentiate with N_1 held fixed

Peak occurs where $dg = 0$, or

$$dg = \left(\frac{\partial g_1}{\partial U_1}\Big|_{N_1} g_2 - g_1 \frac{\partial g_2}{\partial U_2}\Big|_{N_2} \right) dU_1 = 0$$

$$\Rightarrow \quad \frac{\partial g_1}{\partial U_1}\Big|_{N_1} g_2 = g_1 \frac{\partial g_2}{\partial U_2}\Big|_{N_2}$$

Divide by $g_1 g_2 \Rightarrow$

$$\frac{1}{g_1}\frac{\partial g_1}{\partial U_1}\Big|_{N_1} = \frac{1}{g_2}\frac{\partial g_2}{\partial U_2}\Big|_{N_2}$$

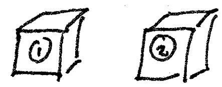
or $$\frac{\partial \ln g_1}{\partial U_1}\Big|_{N_1} = \frac{\partial \ln g_2}{\partial U_2}\Big|_{N_2}$$

<u>Definition</u>:

<u>entropy</u> of the system —

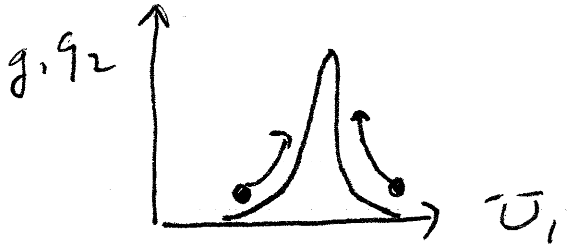
$$\boxed{\sigma(N, U) = \ln g(N, U)}$$

(Nice feature: for isolated systems, entropy is additive

$$g = g_1 g_2 \Rightarrow \sigma = \sigma_1 + \sigma_2 \,)$$ 

Then most probable configuration is given by $$\frac{\partial \sigma_1}{\partial U_1}\Big|_{N_1} = \frac{\partial \sigma_2}{\partial U_2}\Big|_{N_2}$$

which occurs at $U_1 = \hat{U}_1$, $U_2 = \hat{U}_2 = U - \hat{U}_1$.



Suppose U_1, U_2 are energies of the two boxes before contact.

then, if $\frac{\partial}{\partial U_1} g_1 g_2 > 0$ or $\left.\frac{\partial \sigma_1}{\partial U_1}\right|_{N_1} - \left.\frac{\partial \sigma_2}{\partial U_2}\right|_{N_2} > 0$,

U_1 wants to increase; energy wants to flow from ② to ①

Conversely $\left.\frac{\partial \sigma_1}{\partial U_1}\right|_{N_1} - \left.\frac{\partial \sigma_2}{\partial U_2}\right|_{N_2} < 0$

$\Rightarrow$ energy flow from ② to ①

cf the experience that heat flows from a hot body to a cold body

suggests a definition of temperature τ

$$\boxed{\frac{1}{\tau} = \left.\frac{\partial \sigma}{\partial U}\right|_N}$$

$d(\sigma_1 + \sigma_2) = \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) dU_1$

then
- in equilibrium $\tau_1 = \tau_2$
- If $\tau_2 > \tau_1$, then heat flows from ② to ① upon contact, until equilibrium is attained

our τ has dimensions of energy. Conventional temperature is related to τ by a conversion factor.

$\tau = k_B T\ (°\text{Kelvin})$

$k_B \cong 1.4 \times 10^{-16}$ ergs/°K (Boltzmann constant)

— defines °K

In practice — how sharp is peak about most probably configuration (how much does U_1 fluctuate about $\hat{U}_1$)?

Fluctuations

Consider, again, model of a magnet

$$g(N,s) = g(N,0)\, e^{-2s^2/N}$$

If we turn on a magnetic field,

$$U(s) = -2mBs$$

So — thermal contact means that total spin excess s is fixed, but s_1, s_2 are allowed to vary subject to $s = s_1 + s_2$ = constant

$$g_1 g_2 = g_1(N_1,0)\, g_2(N_2,0) \exp\left[-2s_1^2/N_1 - 2s_2^2/N_2\right]$$

$$\sigma = \ln(g_1 g_2) = \ln[g_1(N_1,0)\, g_2(N_2,0)] - 2s_1^2/N_1 - 2s_2^2/N_2$$

Maximize σ to find most probably configuration

$$\sigma = \text{constant} - 2s_1^2/N_1 - 2(s-s_1)^2/N_2$$

$$\frac{\partial \sigma}{\partial s_1} = \frac{-4s_1}{N_1} + \frac{4(s-s_1)}{N_2} = 0 \quad \text{determines } \hat{s}_1$$

$$\Rightarrow \quad \hat{s}_1/N_1 = \hat{s}_2/N_2 \quad \text{and} \quad \hat{s}_1\left(\frac{1}{N_1}+\frac{1}{N_2}\right) = s/N_2$$

$$\sigma_{max} = \text{const} - 2\left[N_1\left(\frac{s_1}{N_1}\right)^2 + N_2\left(\frac{s_2}{N_2}\right)^2\right] \quad \Rightarrow \hat{s}_1/N_1 = \frac{s}{N_1+N_2} = s/N$$

and $$\sigma_{max} = -2(N_1+N_2)(s/N)^2 = -2s^2/N$$

(ignoring constant)

To find how narrow the peak is,
expand

$$s_1 = \hat{s}_1 + \delta$$

$$\frac{\partial^2\sigma}{\partial^2 s_1} = -4\left(1/N_1 + \frac{1}{N_2}\right) = -4\,\frac{N_1+N_2}{N_1N_2}$$

Write $$\sigma(\hat{s}_1+\delta) = \sigma(\hat{s}_1) + \underbrace{\sigma'(\hat{s}_1)}_{0}\,\delta + \tfrac{1}{2}\sigma''(\hat{s}_1)\,\delta^2 + \cdots$$

or $$\sigma = \overset{\text{const}}{1} - 2s^2/N - 2\,\frac{N}{N_1N_2}\,\delta^2$$

and so $$g_1 g_2 = e^{\sigma} = [g_1(N_1,0)\,g_2(N_2,0)] \times e^{-2s^2/N} \exp\left[-2\frac{N}{N_1N_2}\,\delta^2 + \cdots\right]$$

E.g. suppose $N_1 = N_2 = \frac{1}{2}N \sim 10^{22}$

$$\sim \exp\left[-4\delta^2/N_1\right]$$

How likely is $\delta/N_1 = 10^{-10}$?

Prob $\sim e^{-400} \sim 10^{-174}$

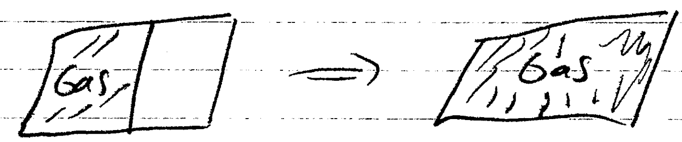
— this large a fluctuation <u>never</u> happens

E.g. a trial every 10^{-12} sec for 10^{18} sec (age of universe)

$\Rightarrow 10^{30}$ trials — <u>much</u> less than 10^{174}

We now understand the origin of <u>irreversibility</u> in system with many degrees of freedom.

- Heat flows from hot body to cold body — not reversible

- 

— not reverse

When isolated systems are brought into contact, the <u>entropy</u> <u>increases</u>

"Law of increase of entropy" — because system seeks the most probable configuration

— "Conventional" entropy $S = k_B \sigma$

then $\frac{1}{\tau} = \frac{\partial \sigma}{\partial U}\Big|_N \Rightarrow \frac{1}{T} = \frac{\partial S}{\partial U}\Big|_N$

or $\Delta(S_1 + S_2) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U_1$

The Laws of Thermodynamics

(These were formulated before their foundations were understood in terms of statistical mech.)

0th: Thermal equilibrium is "transitive"
If ① in equilibrium with ②, and ② with ③,
then ① with ③

1st: Energy conservation
If ① and ② in thermal contact,
$$d(U_1 + U_2) = 0$$

2nd: Increase of entropy
when ① and ② brought into contact,
$$\Delta(S_1 + S_2) \geq 0$$

3rd: $S \to$ constant as $T \to 0$
(ground state has finite multiplicity)