# Foundations of Physics 2B/3C          2019-2020

## Thermodynamics – Lecture 12 Recap

- Looked at adiabatic cooling, both via expansion and demagnetization.
- Were introduced to the Third Law of Thermodynamics.
- Looked at example of Thermodynamics in action, including elastic rods and real gases:

$$pV \to xY \quad ; \quad \delta W = -pdV \to \delta W = xdY$$

$$\delta W = +fdx, mdB, \dots$$

$$pV = RT \to f(p,V,T) = 0$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \dots \quad \left(\frac{\partial p}{\partial V}\right)_T = \cdots$$

## Thermodynamics – Lecture 13 Aims

- To review Thermodynamics.
- To introduce Statistical Mechanics.
- To consider distinguishable particles.
- To consider how we can define entropy and temperature statistically.
- To see how the Boltzmann distribution, for thermal equilibrium arises.

Three Laws + Zeroth

0 — Temperature + thermal equilibrium

1 — Energy conservation          $dU = \delta Q + \delta W$

2 — Entropy of the Universe increases [Engines aren't 100%]

3 — Can't get to absolute zero

2). Statistical Mechanics

Considered bulk properties — impossible to look at the individual behaviour of all atoms
— statistical methods

Macrostate — how a system behaves on average

Microstate — most detailed description of a system we can imagine

## Example 21.1    Flip 4 coins, get Head or Tail

Macrostate = number of heads + number of tails
Microstate = individual arrangement

| Macro | Micro | |
|-------|-------|---|
| 4H | HHHH | 1 |
| 3H 1T | HHHT, HHTH, HTHH, THHH | 4 |
| 2H 2T | | 6 |
| 3T 1H | | 4 |
| 4T | | 1 |

Particles are distinguishable, the number of microstates in
the macrostate

$$\Omega = \frac{N!}{n! \, (N-n)!}$$

$N$ = Total number of particles

$n$ = Number of particles in state 1

$N-n$ = Number of particles in state 2

$$\Omega(2H, 2H) = \frac{4!}{2! \, 2!} = 6$$

Total number of arrangements $\sum \Omega = 2^N$

$\uparrow$ Two possible outcomes

More generally, $N$ particles in total with $n_j$ particles
in a state energy $e_j$

$$N = \sum_j n_j \qquad\qquad \Omega = \frac{N!}{\prod_j n_j!}$$

$$\prod_j n_j! = n_1! \times n_2! \times \ldots \times n_m! \quad \begin{bmatrix} \text{Extended} \\ \text{product} \end{bmatrix}$$

$$N! = N \times (N-1) \times (N-2) \times \ldots \times 1$$

N is large, and often taking natural logs

$$S = k_B \ln \Omega$$

Stirling approximation $\qquad \ln X! \simeq X \ln X - X$

$$\ln X! = \ln X + \ln(X-1) + \ln(X-2) + \ldots + \ln 1$$

$$= \sum_{x=1}^{X} \ln x \simeq \int_1^X \ln x \, dx$$

$$= [x \ln x - x]_1^X \sim X \ln X - X$$

## Thermodynamics – Handout 13

**21.2** 100 coins in a box, can be arranged in one of $2^{100} \approx 10^{30}$ ways, each equally likely,

$$p \sim \frac{1}{10^{30}}$$

Macro $x\,H, y\,T\;(x+y=100)$,   Micro   H T H H T T T H......

Particular microstate requires each coin to be individually labelled – simpler to measure macrostate!

| Macrostate | Number of Microstates |
|---|---|
| 50 $H$ and 50 $T$ | $100!/50!\,50! \sim 4 \times 10^{27}$ |
| 53 $H$ and 47 $T$ | $100!/53!\,47! \sim 3 \times 10^{27}$ |
| 90 $H$ and 10 $T$ | $100!/90!\,10! \sim 1 \times 10^{13}$ |
| 99 $H$ and 1 $T$ | $100!/99!\,1! \sim 100$ |

**21.3** 7 potential wells with energy levels of $0, \varepsilon, 2\varepsilon, 3\varepsilon, 4\varepsilon$. What arrangements of particles give total energy of $4\varepsilon$?
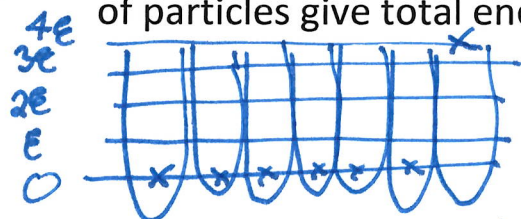


Any one well has energy $4\varepsilon$, 7
Other wells have energy 0

$$\Omega = \frac{N!}{\prod_j n_j!}, \quad N = 7$$

$$\Omega = \frac{7!}{(6!\,0!\,0!\,0!\,1!)} = 7$$

$$\Omega = \frac{7!}{4!\,2!\,1!\,0!\,0!} = 105$$

$n_j$ depend on the internal arrangement.

| Energy | 0 | $\varepsilon$ | $2\varepsilon$ | $3\varepsilon$ | $4\varepsilon$ |
|---|---|---|---|---|---|
| $n_j$ | 6 | 0 | 0 | 0 | 1 |
|  | 4 | 2 | 1 | 0 | 0 |
|  | 5 | 1 | 0 | 1 | 0 |

**21.4**  $\ln 5! = \ln 120 = 4.79$.  Stirling, $5\ln 5 - 5 = 3.04$,   ~40% under

$\ln 100! = 364$, Stirling= 361     1% underestimate

$\ln 1000! = 5912$, Stirling $= 5908$     0.1% underestimate

$N \sim 10^{23}$ for one mole, error in Stirling approx is negligible

## 22. Temperature + Entropy Statistically

Thermal equilibrium defined by some temperature
- Macrostate you see will most likely have the most associated microstates

[Ergodic hypothesis, microstates are continually changing]

### Proof 22.1

Two systems thermally isolated from World

$$E = E_1 + E_2 \quad [\text{Fixed total energy}]$$

First system has $\quad \Omega_1(E_1)$ microstates
Second " $\quad\quad \Omega_2(E_2)$ "

Total Microstates $\quad \Omega_1(E_1)\, \Omega_2(E_2)$

Slightly change energy $E_1$, maximise # of microstates

$$\frac{d}{dE_1}(\Omega_1(E_1)\Omega_2(E_2)) = \Omega_2(E_2)\frac{d\Omega_1(E_1)}{dE_1} + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}\frac{dE_2}{dE_1}$$

$$dE = dE_1 + dE_2 = 0 \quad \text{as total energy fixed}$$
$$\therefore \frac{dE_1}{dE_2} = -1$$

$$\frac{1}{\Omega_1(E_1)}\frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2(E_2)}\frac{d\Omega_2(E_2)}{dE_2}$$

$$\frac{d\ln\Omega_1(E_1)}{dE_1} = \frac{d\ln\Omega_2(E_2)}{dE_2} = \frac{1}{k_B T}$$

Must be a temperature — thermal equilibrium

## Proof 22.2 $\qquad S = k_B \ln \Omega$

1st Law $\qquad dU = TdS - pdV$

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \quad ; \quad \frac{1}{k_B T} = \frac{d \ln \Omega}{dE}$$

Statisically Energy $E$ corresponds to internal energy, $U$

$$\Rightarrow \quad dS = k_B \, d \ln \Omega \Rightarrow S = k_B \ln \Omega$$
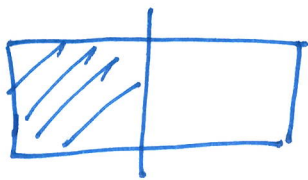
## 23. Boltzmann distribution

Canonical distribution — an ensemble of systems, which exchange energy with a heat reservoir

Thermal equilibrium for distinguishable particles
 — System at same temperature as the reservoir

$$P(\varepsilon_j) = \frac{\exp\left(-\frac{\varepsilon_j}{k_B T}\right)}{\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)}$$

$$\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right) = Z \quad , \quad \text{Normalisation}$$

Partiton function.

Remove partition
$$V \rightarrow 2V$$

Joule expansion, with volume doubling for one mole ideal gas isothermally.

$U = U(T)$, so $dU = 0$, and the first law $(dU = \delta Q + \delta W)$ is $TdS = pdV$

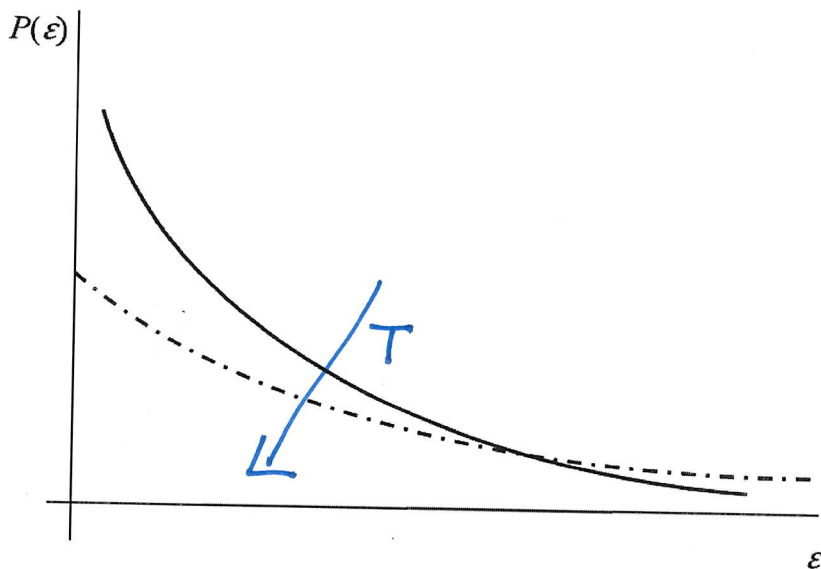$$\Delta S = \int_V^{2V} \frac{p}{T} dV = \int_V^{2V} \frac{R}{V} dV = R \ln 2.$$

Any single molecule now in two places, either left or right

Statistically the number of possible microstates becomes larger by a multiplicative factor of $2^{N_A}$

$$\Omega_{After} = 2^{N_A} \Omega_{Before}$$

$$S_{After} = k_B \ln \Omega_{After} = k_B \ln(2^{N_A} \Omega_{Before}) = k_B \ln(2^{N_A}) + \ln \Omega_{Before}$$

$$= N_A k_B \ln 2 + k_B \ln \Omega_{Before}.$$

$$\Delta S = N_A k_B \ln 2 = R \ln 2.$$



$$P(\varepsilon_j) \propto \exp\left(-\frac{\varepsilon_j}{k_B T}\right).$$

Increase temperature, distribution has more chance of finding a particle with higher energy

For a given temperature, energy takes a probability distribution 'System has' reasonable chance of having $\varepsilon < k_B T$
The exponential quickly reduces the chance of $\varepsilon > k_B T$