8.21 The Physics of Energy
Fall 2009

8.21 Lecture 8

Thermodynamics I: Entropy and Temperature

September 25, 2009

3 concepts for today

1. Entropy = randomness in system

   $\Rightarrow$ thermodynamics, second law, thermal E conversion

2. Temperature:

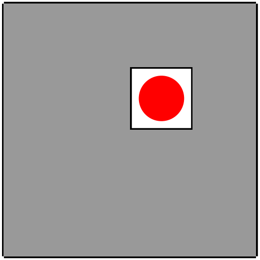
   Can define precisely using entropy, quantum states

   Entropy + Second law + Temperature $\Rightarrow$ Carnot limit

3. Statistical Mechanics: probability distribution on states at temp. T

   — Explain change in C_V, blackbody radiation, nuclear reactions, ...

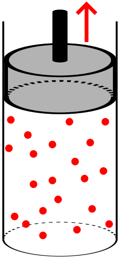
Entropy = ignorance



Have 4 bits info

How many bits (0/1) of information
do you need to find the state?

Answer: 4 $S = k_B \ln 16 = 4 k_B \ln 2$

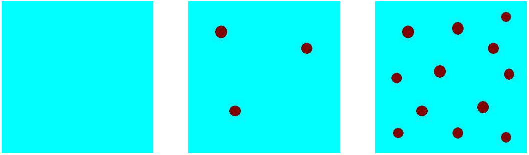


Heat $\longrightarrow$ Mechanical Energy:

Energy loss seems unavoidable.

Why? {
- hot gas: many possible states
- cold gas: fewer possible states
- But laws of physics reversible

To quantify: need Entropy   Can we quantify randomness?   Yes



(a) 462 bytes   (b) 617 bytes   (c) 1045 bytes

.gif file sizes $\sim 450 + 50 * \#$spots

Shannon (information) entropy

Given a (long) random sequence of symbols *e.g.* ADCCBAD...

chosen according to a given probability distribution on symbols

σ = minimal # of bits needed to encode each symbol on average

Example: independent coin flips 50% H, 50% T

HTHHT . . . $\Rightarrow \sigma = 1$ bit/symbol (01001)

Example: A: 25%, B: 25%, C: 25%, D: 25%

A	D	C	C	B	A	$\cdots$
00	11	10	10	01	00	$\cdots$

$\Rightarrow \sigma = 2$

A: 00
B: 01
C: 10
D: 11

k bits can encode 2^k symbols!

$\Rightarrow$ if 2^k symbols each w/ $p = \frac{1}{2^k}$, $\sigma = k = -\log_2 p$

So far pretty straightforward— but what if probabilities differ?

A: 50%, B: 25%, C: 25%

Use variable numbers of bits!

First bit: A→ 0, B *or* C→ 1. Then B→ 10, C→ 11

···	A	B	A	C	A	B	C	···
···	0	10	0	11	0	10	11	···

Probability 0.5: 1 bit, 0.25 + 0.25: 2 bits ⇒ $\sigma = 1.5$.

General distribution: info entropy

$$\sigma = -\sum_i p_i \log_2 p_i$$

Limit to compression efficiency–*e.g.* English, $\sigma \sim 3.2$ bits/character

Entropy (S) in physics: A measure of ignorance.

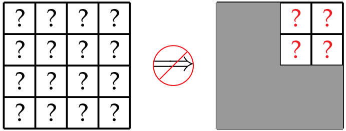
Often only have partial information about a system (*e.g.*, $p, V, T, \ldots$)

Characterize by *ensemble* of states, probability p_i

Given a physical system about which we have only partial info

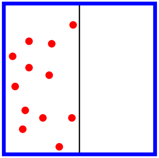
$$\begin{aligned} S &= k_B \ln 2 \times \#\text{ of bits to specify (micro)state} \\ &= -k_B \sum_i p_i \ln p_i \quad (= k_B \ln n \text{ if all } p_i = 1/n) \end{aligned}$$

- Entropy is a state variable, additive (*extensive*)
- Reversibility $\Rightarrow$ S cannot decrease
  (for isolated system/universe)



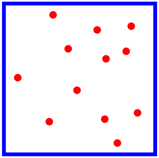
$k_B \ln 16$ $k_B \ln 4$

But entropy can increase



$\Longrightarrow$

$\Delta S = N k_B \ln 2$



Many systems are Mixing

Over a long time, samples all states equally (*ergodic*).

Small initial differences $\Rightarrow$ large changes in small t

Second law of thermodynamics

Entropy of an isolated physical system tends to increase over time, approaching a maximum associated with thermal equilibrium

For isolated system in thermal equilibrium at fixed E, all states equally likely ($p_i = 1/N_E$)

$$\Rightarrow S = k_B \ln N_E$$

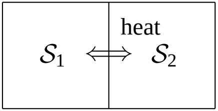
- Dynamics samples states equally over time
- Maximizes $-\sum_i p_i \ln p_i$ when $p_i = 1/N_E$

Example: two quantum SHO's with frequency ω, $E = E_0 + 5\hbar\omega = 6\hbar\omega$

$$S = k_B \ln 6$$

Can now define TEMPERATURE

Thermally couple two systems



Heat can flow back and forth

$U = U_1 + U_2$ fixed,
$S = S_1 + S_2$

$\frac{\partial S_1}{\partial U_1} > \frac{\partial S_2}{\partial U_2}$: heat $\Leftarrow \delta S > 0$

$\frac{\partial S_1}{\partial U_1} < \frac{\partial S_2}{\partial U_2}$: heat $\Rightarrow \delta S > 0$

Systems are in thermal equilibrium when entropy maximized:

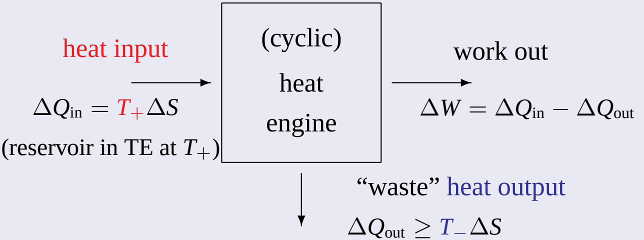
$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}$$

Define temperature:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial U}$$

- Obeys all properties expect of temperature (0th law)
- Agrees with other definitions, more powerful

$1/T = \partial S/\partial U$ & second law $\Rightarrow$ limit to efficiency



$$\Delta W = \Delta Q_{\text{in}} - \Delta Q_{\text{out}} \leq (T_{+} - T_{-})\Delta S$$

$$\Rightarrow \eta = \frac{\Delta W}{\Delta Q_{\text{in}}} = \frac{\Delta Q_{\text{in}} - \Delta Q_{\text{out}}}{\Delta Q_{\text{in}}} \leq \frac{(T_{+} - T_{-})\,\Delta S}{T_{+}\Delta S} = \frac{(T_{+} - T_{-})}{T_{+}}$$

Carnot efficiency limit $(T_+ - T_-)/T_+$

- Engines: next week.
- Most real engine cycles $<$ Carnot efficiency. (Exception: Stirling!)

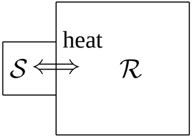
type	T_+	η_C	η_{real}
OTEC	$\Delta T \sim 25$ K	8%	3%
auto engine (Otto cycle)	2300 K	87%	25%
steam turbine coal plant	800 K	62%	40%
combined cycle gas turbine	1800 K	83%	60%

Carnot and actual efficiencies of various heat engines ($T_- \approx 300$ K)

For system at temperature T what is $p(\text{state})$?

$\mathcal{S}$ in thermal eq. with large reservoir $\mathcal{R}$,
$U = E_S + E_R$ fixed

- Energy of $\mathcal{S}$ not fixed, small fluctuations



2 states of $\mathcal{S}$:

E_1: # states $\mathcal{R}$, $E_R = U - E_1$: $p_1 \propto e^{S(U-E_1)/k_B}$
E_2: # states $\mathcal{R}$, $E_R = U - E_2$: $p_2 \propto e^{S(U-E_2)/k_B}$

$$\Rightarrow \frac{p_i}{p_j} = e^{[S(U-E_i)-S(U-E_j)]/k_B}$$

Expand $S(U - E_i) = S(U - E_j) + (E_j - E_i)\partial S/\partial U + \cdots \Rightarrow \frac{p_i}{p_j} = e^{\frac{E_j - E_i}{k_B T}}$

$p_i = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$ (*Boltzmann distribution*)
Z is partition function $Z = \sum_i e^{-\frac{E_i}{k_B T}}$

Boltzmann distribution $p_i = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$

- Determines probability of state for system at temperature T
- Useful for understanding thermal behavior of quantum systems

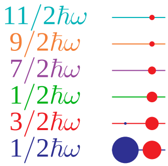
— "Turning on" degrees of freedom as T increases

— Nuclear reactions

— Electron motion in photovoltaics

— Blackbody radiation

“Freezing out DOF”: vibrational mode of hydrogen gas



Boltzmann: $p_n = e^{-(n+1/2)\hbar\omega/k_b T}/Z$

H_2 vibration: $\hbar\omega \cong 0.516$ eV $\cong 8.26 \times 10^{-20}$ J

$\hbar\omega/k_B \cong 6000$ K $\quad \Rightarrow \quad p_n \propto x^n \equiv \left(e^{-6000\mathrm{K}/T}\right)^n$

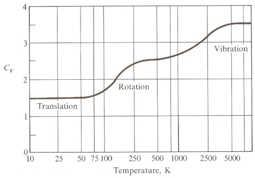
T = 1000 K: $x = e^{-6} \cong 0.002$

$\Rightarrow p_0 \cong 0.998, p_1 \cong 0.002, \ldots$

T = 10,000 K: $x = e^{-0.6} \cong 0.55$

$\Rightarrow p_0 \cong 0.45, p_1 \cong 0.25, p_2 \cong 0.14, \ldots$

Recall specific heat capacity $C_V = \partial U/\partial T$ as function of T



SUMMARY

- Entropy is ignorance of system details, $S = k_B \sigma \ln 2 = -k_B \sum_i p_i \ln p_i$
- Second law: entropy tends to increase,
  approaching maximum at thermal equilibrium
- Isolated system at fixed E, $p_i = 1/N_E$, $S = k_B \ln N_E$
- Temperature defined by $\frac{1}{T} \equiv \frac{\partial S}{\partial U}$
- Maximum efficiency is Carnot efficiency $\eta_C = (T_+ - T_-)/T_+$
- Boltzmann: $p_i = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$, $Z = \sum_i e^{-\frac{E_i}{k_B T}}$