



Statistical Mechanics

3. Entropy, equilibrium and the second law



Principle of equal a-priori probabilities

Start with axioms (see lecture notes for more discussion):

- *Key point 5: Postulate that an **isolated** system is equally likely to be found in any one of its allowed microstates.*
- *Key point 6: The probability that an isolated system, of energy E , will be found in a **macrostate** $N, E, \{\alpha\}$ is proportional to the weight $\Omega(N, E, \{\alpha\})$, ie. the number of microstates associated with the macrostate.*
- Thus different macrostates generally have different **probabilities**.



Principle of equal a-priori probabilities

- Since weight functions are typically exponentially large in N , the maximum for the weight function is extremely sharp.
- Thus macrostates in which the (free) macroscopic variables $\{\alpha\}$ maximise the weight function are overwhelming more probable than other possible values.
- These are the 'equilibrium' values of the macrostates
- *Key point 7: The equilibrium values $\{\alpha^*\}$ of the macroscopic properties $\{\alpha\}$ of an isolated system are those that maximise the weight function $\Omega(N, E, \{\alpha\})$*

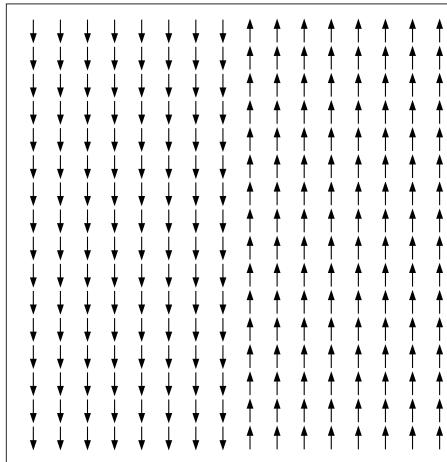
It follows that

- *Key point 8: The equilibrium entropy of an isolated system of N constituents with energy E is $S(N, E) = k \ln \Omega(N, E, \{\alpha^*\})$*

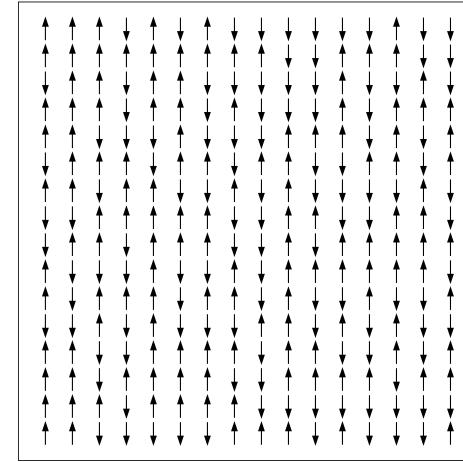
The second law (of thermodynamics)



- Consider again case where free macrovariable is n_L for our model magnet. Fix $E = 0$



Time
→



Initial microstate of macrostate with
 $n = N/2, E = 0, n_L = N/2$.

$$\Omega(N,0,n_L) = 1$$

Typical final microstate of macrostate with:
 $n = N/2, E = 0, n_L = N/4$.

$$\Omega(N,0,n_L) \simeq \exp[Ns(n_L/(N/2))]$$

- “Equilibration”: An isolated system evolves through macrostates with greater and greater weight until it reaches the macrostate with the largest weight and stays there.
- Key point 8 then implies: *The entropy of an isolated system can only increase*



Entropy and disorder

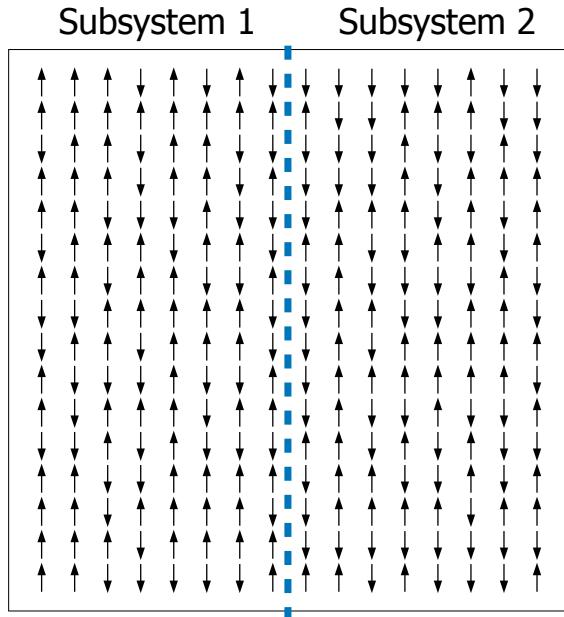
- Entropy is often referred to as a measure of disorder.
- For something to be 'disordered' it may be so in many different ways, whereas 'order' places many restrictions on the ways things can exist.



- Problems 2.5 and 2.6 consider the entropy change of order/disorder transitions in real systems: melting of ice crystals and a copper/gold alloy.



Additivity of entropy



- Consider system to comprise two equal subsystems 1 and 2 having $N_1 = N_2 = N/2$ that can exchange energy.
- Total of n excited dipoles in the system.
- Total fixed energy E
- Saw previously, weight for the macrostate where n_1 of the dipoles in the left half are excited is a product of weight functions for the two halves:

$$\Omega(N, E, n_1) = \Omega_1(N_1, E_1, n_1)\Omega_2(N_2, E_2, n - n_1)$$

- Then from Planck equation (kp 4) the entropies of the two subsystems are **additive**

$$S(N, E, n_1) = S_1(N_1, E_1, n_1) + S_2(N_2, E_2, n_2)$$



Entropy and temperature

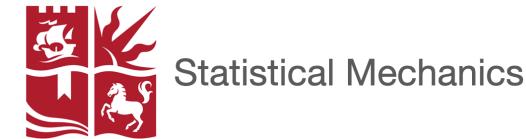
- For our two subsystems in thermal equilibrium we have

$$S(E) = S_1(E_1) + S_2(E_2) \quad E = E_1 + E_2 \quad (\text{assume } N \text{ fixed, so suppress it in notation})$$

- Consider the effect of changing $E_1 \rightarrow E_1 + dE_1$. Since total E is fixed
 $\Rightarrow dE_1 = -dE_2$.
- Now consider the effect on the entropy

$$\begin{aligned} dS &= dS_1 + dS_2 \\ &= \left(\frac{\partial S_1}{\partial E_1} \right) dE_1 + \left(\frac{\partial S_2}{\partial E_2} \right) dE_2 \\ &= \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 \end{aligned}$$

Entropy and temperature



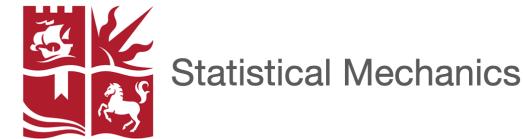
- But at equilibrium the entropy is an extremum (i.e. maximised w.r.t. changes in E_1 and E_2) $\Rightarrow dS = 0$. Hence

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

- **Zeroth law of thermodynamics:** "two systems in thermal equilibrium share the same temperature".
- Deduce that $\frac{\partial S_1}{\partial E_1} = \text{some function of } T$
- In fact (see later) the correct identification is:

- *Key point 9:* $\frac{1}{T} = \frac{\partial S}{\partial E}$

Entropy and temperature



- If we put two systems at **different** temperatures T_1 and T_2 with $T_1 > T_2$ in thermal contact, we expect them to equilibrate to a common temperature.
- From the second law we expect that during this process $dS > 0$
- But $dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1$ implies dE_1 is negative, so energy (heat) flows from the hotter to the colder system in accord with experience.