



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 have different probabilities.
- Macrostates in which the (free) macroscopic variables maximise the weight function are overwhelming more probable than other possible values.



# 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.
- *Key point 7: The equilibrium values  $\{\alpha^*\}$  of the macroscopic properties  $\{\alpha\}$  of an isolated system are those that maximise the weight function  $\Omega(N, E, \{\alpha\})$*

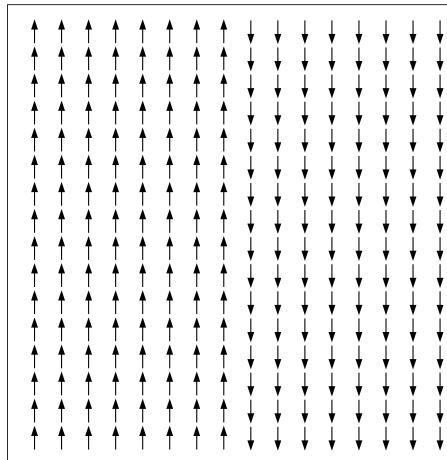
It follows that

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

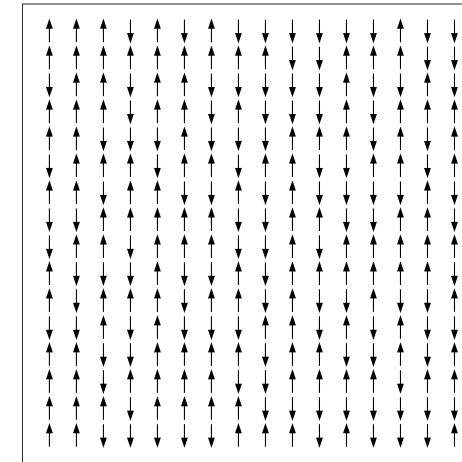
# The second law (of thermodynamics)



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



Time  
→



Initial macrostate of macro state 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.

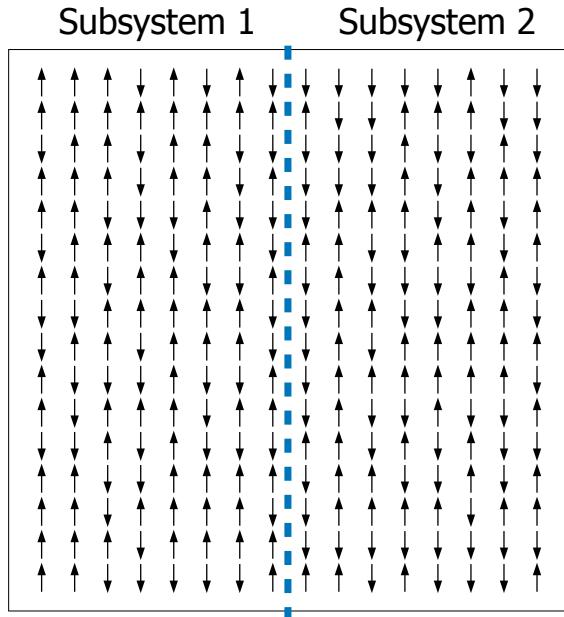


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- Questions 2.5 and 2.6 considers the entropy change of order/disorder transitions in real systems: melting of ice crystals and a copper/gold alloy.



# Additivity of entropy



- Total of  $n$  excited dipoles in the system.
- Total fixed energy  $E$
- Consider system to comprise two equal subsystems 1 and 2 having  $N_1 = N_2 = N/2$  that can exchange energy.
- 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



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- 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

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

- Recall zeroth law: 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:*  $\frac{1}{T} = \frac{\partial S}{\partial E}$
- If we put two systems at **different** temperatures  $T_1$  and  $T_2$  with  $T_1 > T_2$  in thermal contact, expect from the second law that  $dS > 0$
- 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.