

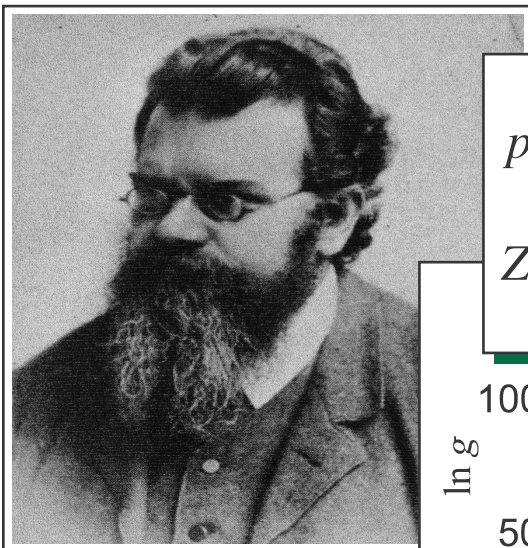
Lecture 3:

Boltzmann distribution

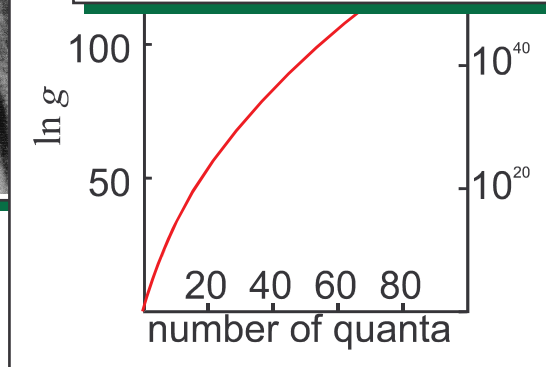
Statistical mechanics: concepts

♦ Aims:

- ▶ Derivation of Boltzmann distribution:
 - ▣ Basic postulate of statistical mechanics.
 - ▣ All states equally likely.
 - ▣ Equal a-priori probability:
 - ▣ Statistical view of thermal equilibrium
 - ▣ Quantum system sharing energy with a reservoir
 - ▣ The canonical ensemble.
 - ▣ Partition function



$$p(\epsilon_i) = \frac{e^{-\beta_{res}\epsilon_i}}{Z(\beta_{res})}$$
$$Z(\beta_{res}) = \sum_i e^{-\beta_{res}\epsilon_i}$$



Equal a-priori probability

◆ Basic Principle of Statistical Mechanics

▶ All microscopic quantum states are equally likely.

▶ Probability of a macroscopic state is proportional to the number of micro-states that can give rise to it (that is, to the quantum-mechanical degeneracy).

◆ Arguments in favour:

▶ Given enough time, the system will explore all the accessible states.

Ergodic hypothesis.

▶ Quantum mechanical principle of detailed balance. Quantum transitions equalise occupation (See problem 5, sheet 1)

▶ Predictive: it gives good results.

▶ We cannot think of anything better (and it is beautifully simple).

Difficulties

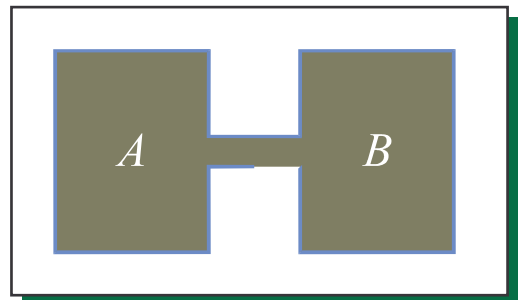
◆ Historical note:

- ▶ Contrary to the prevailing, “positivist” orthodoxy around 1900, e.g. Mach (1838-1916) *paraphrased..*
“*Statements in physics must relate to observables*”.
- ▶ Current view: e.g. Weinberg (1993) *paraphrased..*
“*The positivists mistake was not recognising success when it happens*”.

◆ Difficulties with a-priori probability:

◆ Time to explore all degenerate states:

- ▶ Example: N gas atoms in a container. How long will it take to explore all configurations when atoms are in either left or right half?
- ▶ N molecules
 2^N states (left or right)
- ▶ Transition time
 $\sim 10^{-4}$ s/per molecule
 $\sim 10^{-4}/N$ s for the system.
- ▶ Time of explore all the states, $T = 2^N \times 10^{-4}/N$ s.
- ▶ Take $T = T_{universe} \approx 10^{18}$ s $\Rightarrow N \approx 70$.

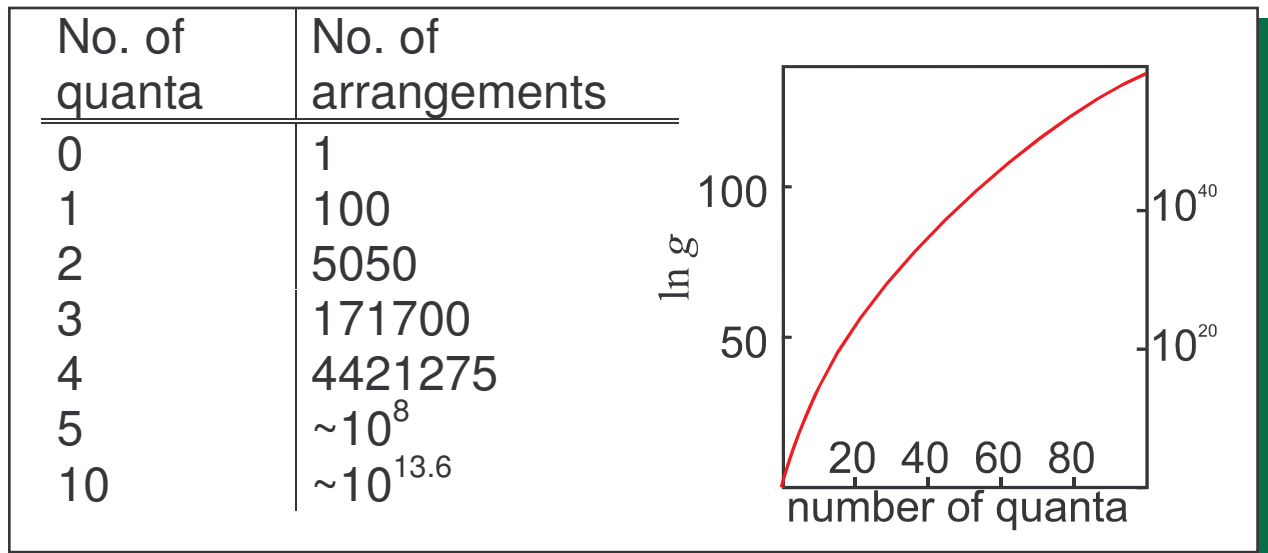


◆ Eigenstates are stationary (by definition) so there can be no transitions.

How to overcome the difficulties

♦ Time to explore all states:

- ▶ We do not need to explore “all” the states. Most microstates group around the most probable state. Also, the number (density) of states increases enormously as the size of the system increases. e.g. 100 oscillators;



♦ Stationary states

- ▶ Switching on an interaction to cause transitions does not help it simply generates a new set of non-degenerate quantum states.
- ▶ Again, we are saved by the huge “density” of states. Given a small spread of energy $\Delta u \sim \hbar/T_{trans}$ there are lots of accessible states.

Ludwig Boltzmann

(1844-1906)

- ▶ Much criticised in his lifetime:
“I am conscious of being only an individual struggling weakly against the stream of time” (1898)
- ▶ Eight years later depressed and suffering headaches he committed suicide.
- ▶ Recognition followed soon afterwards.



“Equilibrium” and “Temp.”

♦ Two systems in contact (i.e. sharing energy)

- ▶ Total energy fixed: $u = u_1 + u_2$.
 - ▣ $g_1(u_1)$ - degeneracy of 1st system
 - ▣ $g_2(u_2)$ - degeneracy of 2nd system
- ▶ For the whole system
 - ▣ $g(u) = g_1(u_1) g_2(u_2) = g_1(u_1) g_2(u-u_1)$
- ▶ Equilibrium state maximises $g(u)$, so evaluate $d\ln(g(u))/du_1$.

$$\frac{d\ln(g_1(u_1))}{du_1} + \frac{d\ln(g_2(u-u_1))}{du_1} = 0$$

$$\frac{d\ln(g_1(u_1))}{du_1} = \frac{d\ln(g_2(u_2))}{du_2}$$

Condition for
thermal equilibrium

- ▶ It follows that the “Temperature” of a system is related to

$$\beta = \frac{d\ln g(u)}{du}$$

so β is some function of thermodynamic temp.

Link between β and temperature

♦ Is β a reasonable measure of T ?

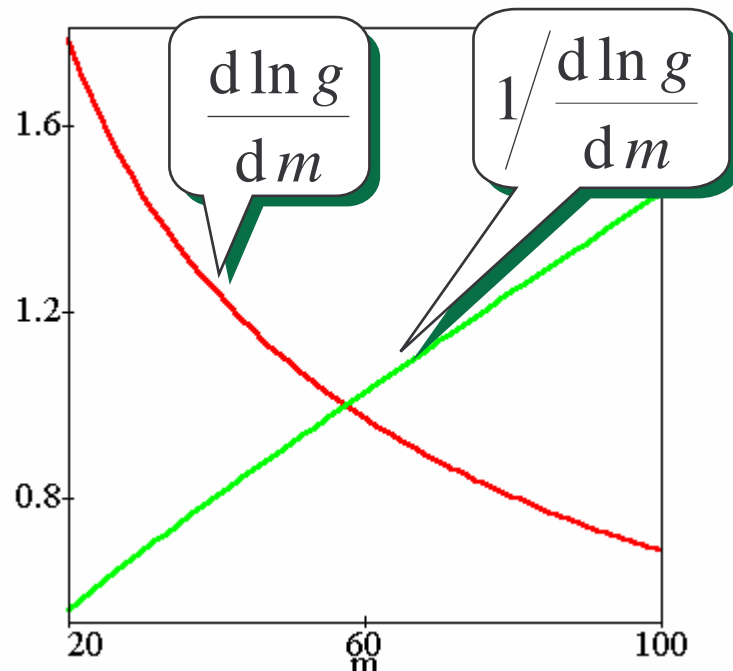
- Take N oscillators with m quanta.

$$g(m) = \frac{(N + m - 1)}{(N - 1)!m!}$$

$$\ln g \approx (N + m - 1) \ln(N + m - 1) - (N - 1) \ln(N - 1) - m \ln m$$

$$\frac{d \ln g}{d m} = \ln(N + m - 1) + 1 - \ln m - 1$$

$$= \ln\left(\frac{N + m - 1}{m}\right) = \ln\left(1 + \frac{N - 1}{m}\right) > 0$$

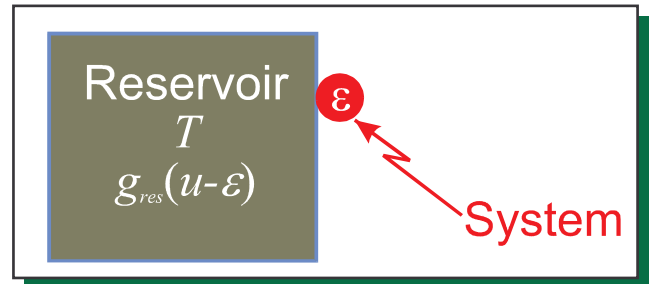


- $1/\beta$ increases steadily with Temperature

Boltzmann distribution

◆ System in contact with a reservoir.

- ▶ Total energy u .
Energy in system, ϵ .



- ▶ Probability of system being in state of energy ϵ :
 $\propto g_{res}(u-\epsilon) \times 1$

Degeneracy of system

$$\begin{aligned}\ln g_{res}(u-\epsilon) &= \ln g_{res}(u) - \epsilon \frac{d \ln g_{res}}{d u} \\ &= \ln g_{res}(u) - \epsilon \beta_{res}\end{aligned}$$

$$p(\epsilon_i) = g_{res}(u-\epsilon_i) = g_{res}(u) e^{-\epsilon_i \beta_{res}} = A e^{-\beta_{res} \epsilon_i}$$

$$\stackrel{=1}{=} = \frac{A e^{-\beta_{res} \epsilon_i}}{\sum_i A e^{-\beta_{res} \epsilon_i}} = \frac{e^{-\beta_{res} \epsilon_i}}{\sum_i e^{-\beta_{res} \epsilon_i}}$$

$$p(\epsilon_i) = \frac{e^{-\beta_{res} \epsilon_i}}{Z(\beta_{res})} \quad ; \quad Z(\beta_{res}) = \sum_i e^{-\beta_{res} \epsilon_i}$$

Boltzmann distribution

Partition function

Partition function, Z

♦ Canonical ensemble

- ▶ Systems in equilibrium with a reservoir are said to be in their canonical state (standard state).
- ▶ The distribution for a number of such systems is the **canonical ensemble**.

♦ Boltzmann distribution

- ▶ Our proof shows “how” the Boltzmann distribution arises.
- ▶ The probability of the systems having a given energy, ϵ , decreases exponentially with ϵ because the degeneracy of the reservoir increases exponentially with ϵ .

♦ Partition function

- ▶ Many thermodynamic properties follow from Z .
- ▶ Example: Average energy in our system

$$\langle \epsilon \rangle = \frac{\sum_i \epsilon_i e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} = -\frac{1}{Z} \frac{dZ}{d\beta}$$

$$\boxed{\langle \epsilon \rangle = -\frac{d \ln Z}{d\beta}}$$

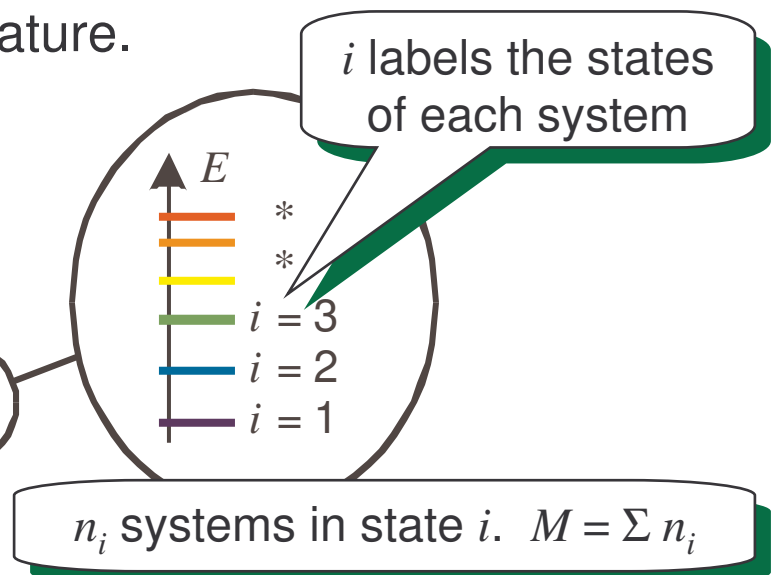
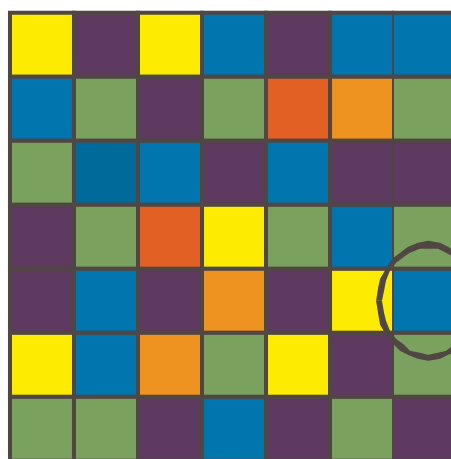
Boltzmann – Gibbs Entropy, I

♦ Boltzmann entropy ($S = k \ln g$)

- ▶ Our discussion has been for an isolated system, i.e. at constant energy, U , say. At fixed energy all the g microstates resulting in a total energy, U , were equally likely.
- ▶ What is the formula for the entropy of a system in contact with a reservoir, i.e. at constant temperature, T ?

♦ The canonical ensemble

- ▶ Consider an ensemble of a sufficiently large number, M , of identical systems so that, for each system, the others act as a heat reservoir. The ensemble is isolated (with fixed energy) but each member of the ensemble is at the same temperature.



Boltzmann – Gibbs entropy, II

♦ Boltzmann – Gibbs entropy

- ▶ Apply the Boltzmann entropy to the ensemble as a whole. The number of ways of arranging n_1 systems (in state 1), plus n_2 systems in (state 2) etc.. is

Entropy of all M systems

$$g = \frac{M!}{n_1! n_2! \dots}$$

N.B. $M = \sum n_i$

$$S_M = k \ln(g)$$

$$\approx k \left(M \ln M - \sum_i n_i \ln n_i \right)$$

Using Stirling's approximation

$$S_M = kM \left(\sum_i \left(\frac{n_i}{M} \right) \ln \left(\frac{n_i}{M} \right) \right)$$

Entropy of one system, $S = S_M/M$

$$p_i = n_i/M$$

$$S = -k \sum_i p_i \ln p_i$$

- ▶ Entropy given in terms of the probability of occupation of each quantum state, i .
- ▶ Often this form is more useful than the original Boltzmann form, especially for small systems.

Bridge to classical thermodynamics

♦ Partition function and the free energy

- ▶ The Boltzmann –Gibbs equation allows us to determine the Free energy, using the Boltzmann distribution to give us the probabilities, p_i .

- ▶ Recall, $F = U - TS$.

Boltzmann probabilities are

$$p_i = \exp(-\epsilon_i / kT) / Z$$

$$\ln(p_i) = -\epsilon_i / kT - \ln(Z)$$

$$S = k \sum_i p_i \left(\frac{\epsilon_i}{kT} + \ln(Z) \right)$$

$$S = \frac{1}{T} \sum_i p_i \epsilon_i + \ln(Z) \sum_i p_i$$

$$U = \sum_i p_i \epsilon_i$$

$$\sum_i p_i = 1$$

$$S = U / T + k \ln(Z)$$

$$U - TS = -kT \ln(Z)$$

Free Energy
in terms of the
Partition Function

$$F = -kT \ln(Z)$$