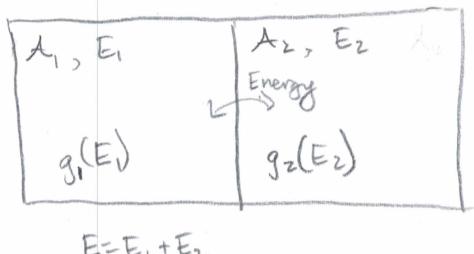


- 1). What does it mean for two systems to be in thermal equilibrium?



E.g. cold beer can placed into hot trunk of car (Reif).

Eventually reach the same "temperature" (and beer tastes less good).

But what is temperature?



What we know is that the composite system $A_1 + A_2$ tends to a state of maximum entropy
 \hookrightarrow highest multiplicity of microstates.

- a) If we know only the total energy E , how many microstates are possible for the combined system?

$$g(E) = \sum_{E_1} g_1(E_1) g_2(E - E_1)$$

Good Question from last worksheet:

"Why can we factor the subspaces if there is correlation?"

* We are assuming that the eigenstates of the two subsystems are to very good approximation determined by external parameters (e.g. B-field for magnet; size of beer can above) and negligible altered by the coupling between them.

EXERCISE 2B: THERMAL EQUILIBRIUM*Objectives:*

- Arrive at a definition of **temperature**, a quantity that is the same for two systems in **thermal equilibrium**.
- Understand the meaning of "hot" and "cold."
- Derive the **Boltzmann factor**

Reference: Kittel & Kroemer, Ch. 2 + beginning of Ch. 3 (Eqs. 1-9)

1. Two systems in thermal equilibrium are said to be at equal temperature. But what exactly is temperature? To arrive at a definition, consider a generic composite system $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$ formed by allowing two subsystems $\mathcal{A}_1, \mathcal{A}_2$ to equilibrate at fixed total energy E .

- a. Write down an expression for the multiplicity $g(N, E)$ of microstates of the total system \mathcal{A} by summing the multiplicities for configurations of variable energy E_1 in subsystem \mathcal{A}_1 . (Let us assume that each subsystem has a discrete energy spectrum; otherwise, you could replace the sum by an integral.)

$$g(E) = \sum_{E_1} g_1(E_1) g_2(E - E_1)$$

- b. The most probable configuration is found by maximizing the summand in part a. Show that the summand is maximized when

$$\frac{d\sigma_1}{dE_1} = \frac{d\sigma_2}{dE_2}, \quad (1)$$

where the **entropy** $\sigma_i = \ln g(N_i, E_i)$ represents the amount of information that would be required to specify the microstate of subsystem \mathcal{A}_i given its energy E_i .

$$\text{Maximizing } g_1(E_1) g_2(E_2) \iff \text{Maximize } \underbrace{\ln[g_1(E_1) g_2(E_2)]}_{\sigma_1(E_1) + \sigma_2(E_2)}$$

$$\begin{aligned} 0 &= \frac{d}{dE_1} [\sigma_1(E_1) + \sigma_2(E_2)]_{E=E} \\ &= \frac{d\sigma_1}{dE_1} + \frac{d\sigma_2}{dE_1} = \frac{d\sigma_1}{dE_1} + \frac{d\sigma_2}{dE_2} \cdot \frac{dE_2}{dE_1} \\ &= \frac{d\sigma_1}{dE_1} - \frac{d\sigma_2}{dE_2} \implies \boxed{\frac{d\sigma_1}{dE_1} = \frac{d\sigma_2}{dE_2}} \end{aligned}$$

$$E_2 = E - E_1$$

- c. Based on your result in Equation 1, propose a definition of **temperature**.

Define temperature s.t. systems in thermal equilibrium are @ equal temperature.

$$\Rightarrow \beta_1 = \beta_2, \text{ where } \beta = \frac{\partial \tau}{\partial E}$$

$$[\beta] = \frac{1}{\text{Energy}} \Rightarrow \text{Define temperature } T = 1/\beta \text{ s.t. } [\tau] = [\text{Energy}]$$

* We often instead use arbitrary Kelvin scale, defined s.t. difference between freezing & boiling is a nice, round number.

* Will use T to denote temperature in Kelvin. Then:

$$\tau = k_B T$$

Boltzmann constant
 $1.38 \times 10^{-23} \text{ J/K}$

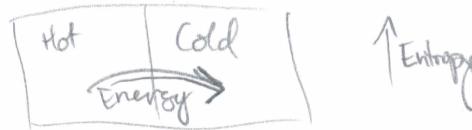
- d. Explain in words the relation between temperature and energy. What does it mean for a system to be "hot" or "cold"?

Cold: $\frac{d\tau}{dE}$ is large \Rightarrow adding a small amount of energy produces a large increase in entropy.

vs. Hot: adding energy only slightly increases (decreases) entropy.
 (removing)

Hence: overall entropy is increased by taking energy out of the hot system and transferring it to the cold one.

\therefore Energy always flows from hot to cold.



(*) See side note on negative temperature... (+ problem set).

- e. What is the entropy σ of the composite system $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$ with known total energy E ?

- i. First, write σ in terms of the sum from part a.

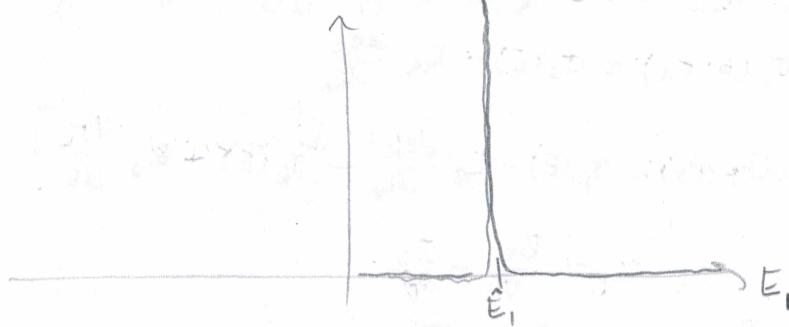
$$\sigma = \ln \sum_{E_1} g_1(E_1) g_2(E - E_1)$$

- ii. How does your expression in i. simplify in the thermodynamic limit? Explain.

Hint: It may help to sketch the typical behavior of the multiplicity $g(E_1, E_2 = E - E_1)$ of states with energy E_1 in subsystem \mathcal{A}_1 .

$$g(E_1, E - E_1) = g_1(E_1) g_2(E - E_1)$$

We previously showed that this function is sharply peaked about most probable configuration \hat{E}_1 :



⇒ To a very good approximation, can neglect all other terms in sum:

$$\sigma \approx \ln g_1(\hat{E}_1) + \ln g_2(E - \hat{E}_1) = \sigma_1(\hat{E}_1) + \sigma_2(E - \hat{E}_1)$$

∴ Entropy is additive, as we claimed it should be

You will examine in the homework just how well this approximation holds.

2. Very often, we are interested in the properties of a system \mathcal{A} that is in thermal equilibrium with a much larger reservoir \mathcal{R} . Let us take the system to be a single spin with two energy states E_\uparrow, E_\downarrow and the reservoir to be its surrounding environment at temperature τ . Calculate the ratio of probabilities P_\uparrow/P_\downarrow for finding the spin in the $|\uparrow\rangle$ or $|\downarrow\rangle$ state, as follows:

- a. Write down an expression for $\ln(P_\uparrow/P_\downarrow)$, noting that the probability of finding the spin in a given state is proportional to the multiplicity of available microstates for the composite system including the reservoir.

$$g_A(E_\uparrow) = g_A(E_\downarrow) = 1$$

Multiplicity of $A+R$ is just $g_R(E-E_A)$

$$\therefore \frac{P_\uparrow}{P_\downarrow} = \frac{g_R(E-E_\uparrow)}{g_R(E-E_\downarrow)}$$

$$\ln(P_\uparrow/P_\downarrow) = \sigma_R(E-E_\uparrow) - \sigma_R(E-E_\downarrow)$$

- b. Express your result from part a. in terms of temperature τ and use it to evaluate P_\uparrow/P_\downarrow . Hint: assume σ_R is smoothly varying & changes only slightly:

$$\sigma_R(E-E_A) \approx \sigma_R(E) - E_A \frac{d\sigma_R}{dE}$$

$$\therefore \ln(P_\uparrow/P_\downarrow) \approx \sigma_R(E) - E_\uparrow \frac{d\sigma_R}{dE} - \left[\sigma_R(E) - E_\downarrow \frac{d\sigma_R}{dE} \right]$$

$$\approx -\frac{E_\uparrow}{\tau} + \frac{E_\downarrow}{\tau}$$

$$\frac{P_\uparrow}{P_\downarrow} = e^{- (E_\uparrow - E_\downarrow)/\tau}$$

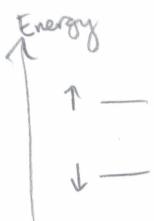
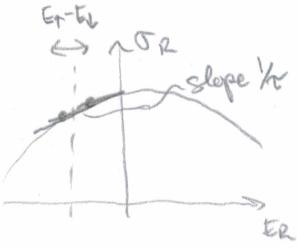
- c. What are the limiting values of P_\uparrow/P_\downarrow as $\tau \rightarrow 0$ and as $\tau \rightarrow \infty$? Assume $E_\uparrow > E_\downarrow$. Are the results consistent with your physical intuition? Why or why not?

$$\tau \rightarrow 0: \frac{P_\uparrow}{P_\downarrow} \rightarrow 0$$

ground state at low temperature

$$\tau \rightarrow \infty: \frac{P_\uparrow}{P_\downarrow} \rightarrow 1$$

not: equally likely to be in either state
(adding even more energy no longer
changes entropy, which is already max.)



- d. To familiarize yourself with more common notational conventions, reexpress your result from b. in terms of
- The temperature T (which has units of Kelvin)
 - The inverse temperature $\beta \equiv 1/\tau$

i) $\tau = k_B T \Rightarrow \frac{P_\uparrow}{P_\downarrow} = e^{-(E_\uparrow - E_\downarrow)/(k_B T)}$

ii) $\tau = 1/\beta \Rightarrow \frac{P_\uparrow}{P_\downarrow} = e^{-\beta(E_\uparrow - E_\downarrow)}$

* τ used in K&K is non-standard notation, but it really is the most natural definition

* In conventional units:

$$\left(\frac{1}{k_B}\right) \frac{1}{T} = \left(\frac{1}{k_B}\right) \frac{dS}{dE} \quad \leftarrow \text{Entropy}$$

$$\rightarrow \frac{S}{k_B} = \sigma \quad \leftarrow \boxed{S = k_B \sigma} \quad \text{units: J/Kelvin}$$

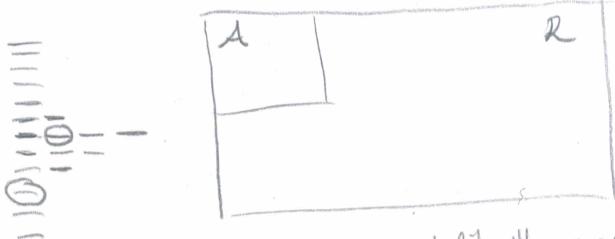
σ vs $[S] = \text{dimensionless}$

Speaking of notation:

I use E for energy (as in Reif & 171), whereas K&K uses U .

3. Boltzmann factor. Consider a generic system \mathcal{A} in thermal equilibrium with a reservoir \mathcal{R} , and consider two microstates of the system with energies E_1 and E_2 . Show that the probabilities of finding the system in these two microstates are related by the Boltzmann factor

$$\frac{P_1}{P_2} = e^{-\beta(E_1 - E_2)}. \quad (2)$$



This is just like the case of the single spin:

$$\ln \frac{P_1}{P_2} = \ln \left[\frac{g_R(E-E_1)}{g_R(E-E_2)} \right] \text{ because we are considering two specific microstates.}$$

$$= \sigma_E(E-E_1) - \sigma_E(E-E_2) \approx -\beta(E_1 - E_2) \quad // \beta = \frac{d\sigma_E}{dE_E}$$

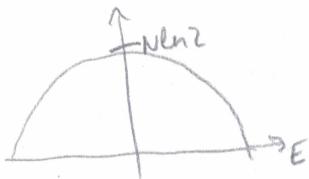
$$\Rightarrow \frac{P_1}{P_2} = e^{-\beta(E_1 - E_2)}$$

* If we want to compare probabilities of finding system at these energies, also need to account for multiplicities or density of states

4. A closer look at multiplicity and entropy. We have been somewhat sloppy in treating the multiplicity $g(E)$ sometimes as a function defined for only a discrete set of energy levels E and sometimes as a continuous function.
- Why might it be a good approximation to regard $g(E)$ as a continuous function in the thermodynamic limit?
- * Suppose the reservoir is a large room... eigenstates for each gas atom are those of a particle in a box... $E_n \propto \frac{n^2}{L^2}$ size of room
 - * Generally, the larger we make the reservoir & the more different degrees of freedom the more finely spaced are the levels.
 - * Even if we are dealing with a simple system like paramagnet w/ discrete energy level spacing Z_{UB} , we rarely have the measurement resolution to resolve a single spin flip
- b. Suppose that our system has a discrete energy spectrum, but the spacing ϵ between energy levels is smaller than some resolution δE quantifying the smallest energy difference that we can measure. How much does the energy uncertainty δE change our lack of knowledge of the microstate, as quantified by the entropy?
- Let $\bar{g}(E)$ represent the multiplicity of states with energies between E and $E + \delta E$. How is $\bar{g}(E)$ related to the multiplicity $g(E)$, in terms of ϵ and δE ? (approximately)
- $$\bar{g}(E) \approx \frac{\delta E}{\epsilon} \cdot g(E)$$
- How is the entropy $\bar{\sigma} = \ln \bar{g}$ related to $\sigma = \ln g$?

$$\bar{\sigma} = \ln \bar{g} = \ln g + \ln(\delta E / \epsilon) = \sigma + \ln(\delta E / \epsilon)$$

- iii. Consider the case of a paramagnet, where $\epsilon = 2\mu B$. Suppose that $\delta E = n\epsilon$ is the change in energy when n spins are flipped, with $1 \ll n < N$. How does the fractional correction $(\bar{\sigma} - \sigma)/\sigma$ to the entropy scale with N and n ?



$$\sigma \sim N$$

$$\frac{\bar{\sigma} - \sigma}{\sigma} \sim \frac{\ln(\delta E/\epsilon)}{N} \sim \frac{\ln(n)}{N}$$

- iv. Suppose $N = 10^{23}$ and $n = 10^{20}$. Give an order-of-magnitude estimate for $(\bar{\sigma} - \sigma)/\sigma$. Does the finite resolution $\delta E = n\epsilon$ matter?

$$\frac{\bar{\sigma} - \sigma}{\sigma} \approx \frac{20 \ln 10}{10^{23}} \sim 10^{-21} \dots \text{so it really doesn't}$$

matter how exactly we count the states. Finite energy resolution adds negligibly to our lack of knowledge of the microstate in the thermodynamic limit. Just a few more bits on top of $\sim 10^{23}$...

When the energy spectrum is best approximated as continuous, it is often useful to refer not to the multiplicity but to the density of states $\mathcal{D}(E)$ per unit energy, defined such that $\bar{g}(E) = \mathcal{D}(E)\delta E$. We shall return to this concept later in the course.