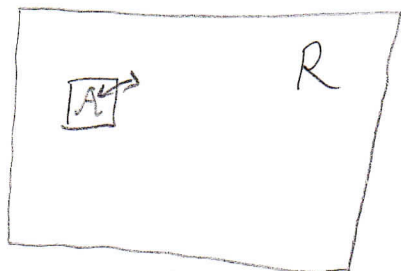


1. Last time: Helmholtz free energy  $F \equiv \langle E \rangle_A - T \sigma_A$

-  $F$  has the same extrema as the combined entropy when  $T$  is fixed.

- Today: verify that  $F$  is minimized when the combined entropy is maximized

(\*)



•  $A$  has energy  $E$

•  $A + R$  has energy  $E_{\text{tot}}$

• Part a: simplify  $\frac{g_R(E_{\text{tot}} - E)}{g_R(E_{\text{tot}})}$  to get  $g_{A+R}(E)$ .

2. b. (ii). when would this assumption break down?

3. Simple model of a solid: Einstein model

• Atoms sit in 3D harmonic potential, frequency  $\omega$ .

• Atoms are all independent (non-interacting).

• Goal: use canonical ensemble, calculate partition function.

b. (iii). History: Einstein wanted to explain why  $C_V \rightarrow 0$  as  $T \rightarrow 0$ .

- First quantum mechanical model of a solid. (1907).

- Einstein used energy levels of harmonic oscillator long before modern QM (1920s).

- Issues with model: wrong behavior as  $T \rightarrow 0$ . Should be  $\sim T^3$ , not exponentially.

- How to improve it? Quantize vibrational modes, not individual atoms. (Debye model).

**EXERCISE 3C: FREE ENERGY, ENSEMBLES, AND THE EINSTEIN MODEL***Objectives:*

- Show that minimizing the free energy of a system maximizes entropy
- Clarify the distinction between the microcanonical and canonical ensembles
- Introduce the Einstein model of a solid

Useful equations:

- Helmholtz free energy:  $F \equiv \langle E \rangle - \tau \sigma$
- Average energy in the canonical ensemble:  $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$
- Heat capacity at constant volume:  $C_V \equiv \left(\frac{\partial E}{\partial \tau}\right)_V$

1. Verify that minimizing the Helmholtz free energy maximizes the total entropy  $\sigma_{A+R}$  of the system and reservoir.

- a. Write down the multiplicity  $g_{A+R}(E)$  of states of the composite system that have energy  $E$  in system  $A$ . Express  $g_{A+R}(E)$  in terms of the multiplicity  $g_A(E)$  of states of  $A$  at energy  $E$ , a Boltzmann factor, and an overall constant  $C$  that is independent of  $E$ .

$$g_{A+R}(E) = g_A(E) g_R(E_{\text{tot}} - E) = g_A(E) \cdot C e^{-\beta E}$$

since  $\frac{g_R(E_{\text{tot}} - E)}{g_R(E_{\text{tot}})} = e^{\ln g_R(E_{\text{tot}} - E) - \ln g_R(E_{\text{tot}})} = e^{\sigma_R(E_{\text{tot}} - E) - \sigma_R(E_{\text{tot}})}$

$$= e^{\sigma_R(E_{\text{tot}}) + \frac{d\sigma_R}{dE} \cdot -E - \sigma_R(E_{\text{tot}})} = e^{-\beta E}, \quad [C \equiv g_R(E_{\text{tot}})]$$

- b. Express the total entropy  $\sigma_{A+R}$  in terms of the temperature  $\tau$  and the energy  $E_{(A)}$  and entropy  $\sigma_{(A)}$  of  $A$ . (We will ordinarily omit the subscript  $A$ .)

$$\sigma_{A+R} = \sigma_A(E) + \ln C - \beta E$$

- c. Find the infinitesimal change  $d\sigma_{A+R}$  in entropy of  $A + R$  associated with an infinitesimal transfer of energy  $dE$  from the reservoir  $R$  to system  $A$  at fixed temperature.

$$d\sigma_{A+R} = d\sigma_A - \beta dE = d\sigma_A - \frac{dE}{\tau}.$$

- d. Express  $d\sigma_{A+R}$  in terms of the corresponding change  $dF$  in free energy.

$$dF = dE - \tau d\sigma_A$$
$$\Rightarrow d\sigma_{A+R} = -\tau dF$$

- e. Based on your expression in d., explain why the most probable energy  $\hat{E}$  of the system  $A$  is that which minimizes the Helmholtz free energy.

The most probable energy  $\hat{E}$  occurs where  $\sigma_{A+R}$  is maximized, i.e. where  $F$  is minimized.

2. Recall that the **microcanonical ensemble** refers to a system at fixed energy, while the **canonical ensemble** refers to a system at fixed temperature.

a. Suppose we have an isolated system of  $N$  interacting particles with multiplicity  $g(E)$ .

i. What ensemble would we use to describe the entire system? What physical law allows us to use this description?

Microcanonical ensemble - fixed energy  $E$ .  
We can use this description because of energy conservation.

ii. What is the probability that the system is in a given microstate  $s$  with energy  $E_s$ ?

$$P(E_s) = \begin{cases} \frac{1}{g(E)} & E_s = E \\ 0 & E_s \neq E \end{cases}$$

b. Consider a subsystem of  $n \ll N$  particles.

i. Is energy conserved in this subsystem? Why or why not?

Energy is not conserved because the subsystem can interact with other parts of the system.

ii. What is the probability that the *subsystem* is in a given microstate  $q$  with energy  $\epsilon_q$ ? What assumptions did we need to make in order to arrive at this result?

$$P(q) = \frac{e^{-\beta \epsilon_q}}{Z} \quad \text{where} \quad \begin{cases} \beta \equiv \frac{d \ln \Omega_{N-n}}{dE} \\ Z = \sum_q e^{-\beta \epsilon_q} \end{cases}$$

We assumed that the entropy of the  $N-n$  particles doesn't change much, so  $\frac{d \ln \Omega_{N-n}}{dE}$  is constant.

iii. What is the probability that the subsystem has energy  $\epsilon_q$ ?

$$P(\epsilon_q) = g_n(\epsilon_q) \frac{e^{-\beta \epsilon_q}}{Z}$$

3. The **Einstein model** of a solid treats each degree of freedom as a (quantized) simple harmonic oscillator. The oscillators are assumed to be independent and to have frequency  $\omega$ .

a. We begin by calculating the partition function of an Einstein solid with  $N$  atoms. Since the oscillators are independent, it is sufficient to calculate the partition function of one oscillator.

i. How many 1D oscillators are there? What are the allowed energy levels of each oscillator?

- $3N$  oscillators (3 per particle, one for each dimension).
- $E_n = \hbar\omega \left(n + \frac{1}{2}\right)$ ,  $n = 0, 1, 2, \dots$

ii. Calculate the partition function of the 1D simple harmonic oscillator.

$$\begin{aligned}
 Z_1 &= \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} = e^{-\beta \hbar \omega / 2} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n \\
 &= \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} = \frac{1}{e^{\beta \hbar \omega / 2} - e^{-\beta \hbar \omega / 2}} = \frac{1}{2 \sinh\left(\frac{\beta \hbar \omega}{2}\right)}.
 \end{aligned}$$

iii. What is the partition function of the Einstein solid?

$$Z = Z_1^{3N} = \left( \frac{1}{2 \sinh\left(\frac{\beta \hbar \omega}{2}\right)} \right)^{3N}.$$



b. Now that we have the partition function, we would like to calculate the heat capacity of the Einstein solid at constant volume.

i. What is the average energy of the solid as a function of temperature  $\tau$ ?

$$\begin{aligned}\langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \ln (Z_1^{3N}) = -3N \frac{\partial}{\partial \beta} \ln Z_1 \\ &= 3N \cdot -\frac{1}{Z_1} \frac{\partial}{\partial \beta} Z_1 \\ &= -3N \cdot 2 \sinh\left(\frac{\beta \hbar \omega}{2}\right) \cdot \frac{-1}{2} \cdot \frac{1}{\sinh^2\left(\frac{\beta \hbar \omega}{2}\right)} \cdot \cosh\left(\frac{\beta \hbar \omega}{2}\right) \cdot \frac{\hbar \omega}{2} \\ &= 3N \cdot \frac{\hbar \omega}{2} \coth\left(\frac{\beta \hbar \omega}{2}\right).\end{aligned}$$

ii. What is the heat capacity  $C_V$  of the solid as a function of  $\tau$ ?

$$\begin{aligned}C_V &= \left(\frac{\partial E}{\partial \tau}\right)_V = \frac{d\beta}{d\tau} \frac{\partial E}{\partial \beta} = -\frac{1}{\tau^2} \frac{\partial E}{\partial \beta} \\ &= -\frac{3N \hbar \omega}{2 \tau^2} \cdot \frac{-1}{\sinh^2\left(\frac{\beta \hbar \omega}{2}\right)} \cdot \frac{\hbar \omega}{2} \\ &= 3N \left(\frac{\hbar \omega}{2 \tau}\right)^2 \cdot \frac{1}{\sinh^2\left(\frac{\hbar \omega}{2 \tau}\right)}.\end{aligned}$$

iii. Sketch  $C_V(\tau)$ . What is the limiting behavior of  $C_V$  as  $\tau \rightarrow \infty$ ? As  $\tau \rightarrow 0$ ?

$$\frac{1}{\sinh^2\left(\frac{\hbar \omega}{2 \tau}\right)} = \frac{4}{e^{\hbar \omega / \tau} - 2 + e^{-\hbar \omega / \tau}}.$$

$$\begin{aligned}\tau \rightarrow \infty: C_V(\tau) &\rightarrow 3N \left(\frac{\hbar \omega}{2 \tau}\right)^2 \cdot \frac{4}{(1 + \frac{\hbar \omega}{\tau} + \frac{1}{2}(\frac{\hbar \omega}{\tau})^2) - 2 + (1 - \frac{\hbar \omega}{\tau} + \frac{1}{2}(\frac{\hbar \omega}{\tau})^2)} \\ &= \frac{3N}{4} \left(\frac{\hbar \omega}{\tau}\right)^2 \cdot \frac{4}{(\frac{\hbar \omega}{\tau})^2} = 3N.\end{aligned}$$

$$\tau \rightarrow 0: C_V(\tau) \rightarrow 3N \left(\frac{\hbar \omega}{2 \tau}\right)^2 \cdot \frac{4}{e^{\hbar \omega / \tau}} = 3N \left(\frac{\hbar \omega}{\tau}\right)^2 \cdot e^{-\hbar \omega / \tau} \rightarrow 0.$$

