THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 6 –BOLTZMANN DISTRIBUTION AND HELMHOLTZ FREE ENERGY

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Outline

In this chapter, we develop the principles to estimate the values of physical properties of a system as temp when the system **S** is in thermal equilibrium with a very large system R, called **reservoir**.

- Boltzmann Factor:
  - Partition Function
  - Energy and Heat Capacity of a Two State System
- Pressure: Thermodynamics Identity.
- Helmholtz Free Energy
  - Ideal Gas: atoms in a box, Equipartition of Energy, and Entropy of Mixing

Canonical Ensemble and Boltzmann Probability

- A key goal of statistical mechanics is to determine the probability that a system occupies a specific quantum state ss with energy ε_s .
- This probability is given by the Boltzmann factor.

From Microcanonical to Canonical Ensemble

- Previously: systems with fixed energy U is microcanonical ensemble
- Now consider a system in contact with a thermal reservoir

Canonical Ensemble

Canonical Ensemble

A canonical ensemble is a collection of identical copies of a system S

- Each copy is in a different accessible microstate
- The system can exchange energy with a reservoir

Constraints:

- Number of particles N is fixed
- Temperature T is fixed (set by the reservoir)
- Energy U can fluctuate

Canonical Ensemble and Boltzmann Probability

Physical Picture

- System S is in thermal contact with a large reservoir
- Energy flows between them, but:
  - The reservoir remains at constant temperature
  - The system explores states with different energies

Key

- The probability of a state depends on its energy and is determined by the Boltzmann distribution.

Probability of a State in the Canonical Ensemble

Consider system S at equilibrium with reservoir $\mathcal{R}$ and system is in a state energy ε

- **$\mathcal{R} + S$ is a closed system**: total energy is fixed.

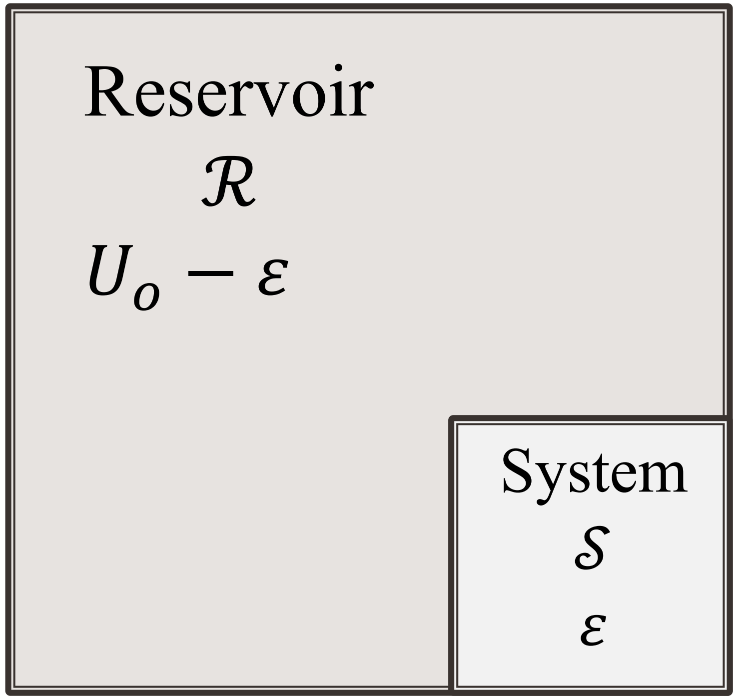
$$U_o = U_{R+S} = U_R + U_s$$

Since the reservoir R is much larger than S

$$U_S \ll U_{\mathcal{R}} \quad \text{and} \quad N_S \ll N_{\mathcal{R}}$$

and N_s and $N_{\mathcal{R}}$ are individually fixed. Here, **S (energy) is not a closed system**.

- Fractional effect of entropy change of reservoir is small for a larger reservoir when it transfers energy ϵ
- We need to find the probability of states of system S is in a specific value of the energy, not the combined system $S + \mathcal{R}$.



Reservoir

$\mathcal{R}$

$U_o - \varepsilon$

System

$\mathcal{S}$

ε

Probability of a State in the Canonical Ensemble

- Let's consider a particular state λ and it has energy ε_λ, energy of reservoir is:

$$U_{\mathcal{R}} = U_o - \varepsilon_\lambda$$

- The total number of microstate of combined system $S + \mathcal{R}$ is:

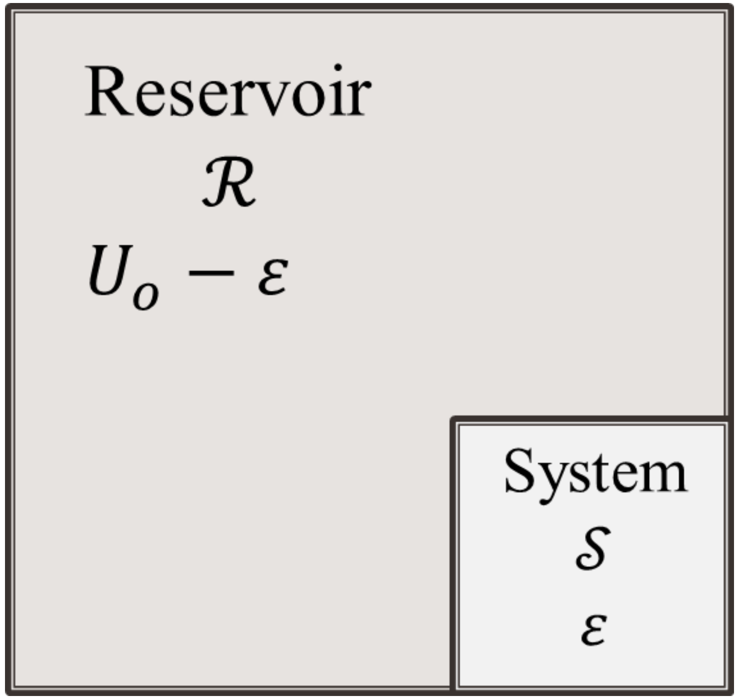
$$g_{total} = g(S\ in\ state\ \lambda) \bullet g(\mathcal{R}, U_{\mathcal{R}} = U_o - \varepsilon_\lambda)$$

Since the system is fixed in state λ, there is only one way for system to be in that exact state.

$$g(S\ in\ state\ \lambda) = 1$$

Therefore

$$g_{total} = g(\mathcal{R}, U_{\mathcal{R}} = U_o - \varepsilon_\lambda)$$



Probability and Reservoir Multiplicity

The probability that the system is in state λ and energy ε_λ is proportional to

$$P(\lambda) \propto g(\mathcal{R}, U_\mathcal{R} = U_o - \varepsilon_\lambda)$$

$$P_{\lambda,\varepsilon_\lambda} \propto g_\mathcal{R}(\mathcal{R}, U_\mathcal{R} = U_o - \varepsilon_\lambda)$$

$$P_{\varepsilon_\lambda} \,\alpha\, g_\mathcal{R}\,(U_o - \varepsilon_\lambda) \qquad [Simplify\ the\ notation]$$

The probability that the system S is in a given state λ, which has energy ε_λ, is proportional to the number of accessible states to the reservoir, $\mathcal{R}$, when the reservoir has the remainder of the energy, $g_\mathcal{R}\,(U_o - \varepsilon_\lambda)$).

Boltzmann Factor

$$P_{\varepsilon_\lambda} \,\alpha\, g_{\mathcal{R}}\,(U_o - \varepsilon_\lambda) = exp[Ln\big(g_{\mathcal{R}}(U_o - \varepsilon_\lambda)\big)]$$

With $Ln(g_{\mathcal{R}}\,(U_o - \varepsilon_\lambda) = \sigma_{\mathcal{R}}\,(U_o - \varepsilon_\lambda)$, We can identify that

$$P_{\varepsilon_\lambda} \,\alpha\, \exp[\sigma\,(U_o - \varepsilon_\lambda)]$$

Where $U_o \gg \varepsilon_\lambda$ and approximate $\sigma(U_o - \varepsilon_\lambda)$ by a Taylor expansion about U_o.

$$f(x_o + a) \approx f(x)|_{x=x_o} + a\left(\frac{\partial f}{\partial x}\right)|_{x=x_o} + \frac{1}{2!}a^2\left(\frac{\partial^2 f}{\partial x^2}\right)|_{x=x_o} + \cdots$$

for small a, we drop terms of order a^2 and higher-order terms

$$\sigma(U_o - \varepsilon_\lambda) \approx \sigma_{\mathcal{R}}(U)\Big|_{U=U_o} - \varepsilon_\lambda\left(\frac{\partial \sigma_{\mathcal{R}}}{\partial U}\right)\Bigg|_{U=U_o} + \cdots$$

Note $\left(\frac{\partial \sigma}{\partial U}\right)\Big|_{U=U_o} = \frac{1}{\tau}$

Boltzmann Factor

$$\sigma_R(Uo - \varepsilon\lambda) \approx \sigma_{\mathcal{R}}(U_o) - \frac{\varepsilon_\lambda}{\tau} + \cdots$$

With all of this:

$$P_{\varepsilon_\lambda} \quad \alpha \; exp(\sigma_{\mathcal{R}}(U_o - \varepsilon_\lambda) \; = \; exp\left(\sigma_{\mathcal{R}}(U_o\,) - \frac{\varepsilon_\lambda}{\tau}\right)$$

$$P_{\varepsilon_\lambda} = C\; exp\left(-\frac{\varepsilon_\lambda}{\tau}\right)$$

Where C is constant, In text “probability that a system S in thermal contact with a reservoir at temperature τ, is in a particular state λ that has energy ε_λ is proportional to $exp\left(-\frac{\varepsilon_\lambda}{\tau}\right)$.”

- The quantity $\boldsymbol{exp\left(-\frac{\varepsilon_\lambda}{\tau}\right)}$ **known as Boltzmann factor** that defines the probability of finding the system in a given state.

Partition Function

We need to determine the constant C

$$\sum_{all\ states\ s} P_s = 1 \rightarrow \sum_{all\ states\ s} P_s = \sum_{all\ states\ s} Cexp\left(-\frac{\mathcal{E}_s}{\tau}\right) = 1$$

So, the constant C is

$$C = \frac{1}{\sum_{all\ states\ s} Cexp\left(-\frac{\mathcal{E}_s}{\tau}\right)}$$

and with this the probability P_s is given by:

$$P_s = \frac{exp\left(\frac{-\varepsilon_s}{\tau}\right)}{\sum_{all\ states\ s} exp\left(-\frac{\mathcal{E}_s}{\tau}\right)}$$

Partition Function

The quantity:

$$\sum_{all\ states\ s} exp\left(-\frac{\mathcal{E}_s}{\tau}\right)$$

is called the "partition function" of the system, $Z(\tau)$.

$$Z(\tau) = \sum_{all\ states\ s} exp\left(-\frac{\mathcal{E}_s}{\tau}\right)$$

Once we have the partition function for a system, we can obtain all of the thermodynamic quantities of interest for that system (average energy, entropy, pressure, specific heat at constant volume or at constant pressure, etc., etc.) by simple calculus and arithmetic.

when solving a statistical mechanics problem, we need to correctly define and compute the partition function of the system. Then, except for a few mathematical operations

Average Value of the Energy of a System

Let's begin with average value of energy:

$$\langle \varepsilon \rangle = \sum_{\substack{all\ states \\ s}} P_s \cdot \varepsilon_s = \sum_{\substack{all\ states \\ s}} \frac{exp\left(-\frac{\varepsilon_s}{\tau}\right)}{Z(\tau)} \cdot \varepsilon_s$$

Let's consider the following:

$$\frac{\partial Ln\big(Z(\tau)\big)}{\partial \tau} = \frac{1}{Z(\tau)} \cdot \frac{\partial Z(\tau)}{\partial \tau} = \frac{1}{Z(\tau)} \frac{\partial \left(\sum_{all\ s} exp\left(-\frac{\varepsilon_s}{\tau}\right)\right)}{\partial \tau}$$

$$= \frac{1}{Z(\tau)} \sum_{\substack{all\ states \\ s}} exp\left(-\frac{\varepsilon_s}{\tau}\right) \frac{\varepsilon_s}{\tau^2} = \frac{1}{\tau^2} \langle \varepsilon \rangle$$

Average Value of the Energy of a System

$$\frac{\partial Ln\big(Z(\tau)\big)}{\partial\tau} = \frac{1}{\tau^2}\langle\varepsilon\rangle$$

$$U = \langle\varepsilon\rangle = \tau^2\frac{\partial Ln\big(Z(\tau)\big)}{\partial\tau}$$

Other properties can be also similarly calculated. For example, the heat capacity at constant volume.

$$C_V = \left(\frac{dU}{\mathrm{d}\tau}\right)_V$$

Heat Capacity at Constant Volume

$$C_V = \left(\frac{\partial\langle\varepsilon\rangle}{\partial\tau}\right)_V = \left(\frac{\partial\left[\tau^2\frac{\partial Ln\left(Z(\tau)\right)}{\partial\tau}\right]}{\partial\tau}\right)_V$$

$$C_V = \left(2\tau\frac{\partial Ln\left(Z(\tau)\right)}{\partial\tau} + \tau^2\frac{\partial^2 Ln\left(Z(\tau)\right)}{\partial\tau^2}\right)_V$$

This is the general expression for the heat capacity at constant volume in terms of mathematical operations with the partition function Z(τ).

The same approach can be used quite generally. For example, could similarly obtain $\langle\varepsilon^2\rangle$ and then from it and from the value of $\langle\varepsilon\rangle$ we could calculate the mean square deviation of the value of the average energy of the system.

Example 6-01

Consider a very simple system, consisting of a single particle in equilibrium with a large reservoir at temperature τ. Our particle can be in one of only two states: it either has energy 0 or it has energy ε. Use the partition function approach to calculate:

a. Thermal average value of the energy of our system, $\langle \varepsilon \rangle$.

b. Heat capacity C_V of system at constant volume.

Example 6-01

Solution:

a. We first calculate Z(τ) = $\sum_{\substack{all\ states \\ s}} exp\left(-\frac{\varepsilon_s}{\tau}\right)$

$$Z(\tau) = exp(0) + exp\left(-\frac{\varepsilon}{\tau}\right) = 1 + exp\left(-\frac{\varepsilon}{\tau}\right)$$

The average energy becomes:

$$\langle\varepsilon\rangle = \tau^2 \frac{\partial Ln\left(Z(\tau)\right)}{\partial\tau}$$

$$\langle\varepsilon\rangle = \tau^2 \frac{\partial Ln\left(1 + exp\left(-\frac{\varepsilon}{\tau}\right)\right)}{\partial\tau} = \tau^2 \cdot \frac{1}{\left(1 + exp\left(-\frac{\varepsilon}{\tau}\right)\right)} exp\left(-\frac{\varepsilon}{\tau}\right)\left(\frac{\varepsilon}{\tau^2}\right)$$

Example 6-1: Solution

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$$\langle\varepsilon\rangle = \frac{\varepsilon}{\left(exp\left(\frac{\varepsilon}{\tau}\right) + 1\right)}$$

Example 6-1: Solution

We can calculate directly from the definition of the average value:

$$\langle \varepsilon \rangle = \sum_{\substack{all\ states \\ s}} P_s \cdot \varepsilon_s = \sum_{\substack{all\ states \\ s}} \frac{exp\left(-\frac{\varepsilon_s}{\tau}\right)}{Z(\tau)} \cdot \varepsilon_s$$

$$\langle \varepsilon \rangle = \frac{exp\left(-\frac{0}{\tau}\right) . 0 + exp\left(-\frac{\varepsilon}{\tau}\right) . \varepsilon}{Z(\tau)}$$

$$\langle \varepsilon \rangle = \frac{\varepsilon \cdot exp\left(-\frac{\varepsilon}{\tau}\right)}{1 + exp\left(-\frac{\varepsilon}{\tau}\right)}$$

$$\langle \varepsilon \rangle = \frac{\varepsilon}{exp\left(\frac{\varepsilon}{\tau}\right) + 1}$$

Example 6-1: Solution

Note: if the two-state energy is $-\frac{1}{2}\varepsilon$ and $\frac{1}{2}\varepsilon$ (we shifted) instead of 0, ε the result would be different:

$$Z = \exp\left(\frac{\varepsilon}{2\tau}\right) + \exp\left(-\frac{\varepsilon}{2\tau}\right) = 2\cosh\left(\frac{\varepsilon}{2\tau}\right)$$

$$\langle\varepsilon\rangle = \sum_{\substack{all\ states\\ s}} \frac{exp\left(-\frac{\mathcal{E}_s}{\tau}\right)}{Z(\tau)} \cdot \varepsilon_s = \frac{\left(-\frac{1}{2}\varepsilon\right)\exp\left(\frac{\varepsilon}{2\tau}\right) + \left(\frac{1}{2}\varepsilon\right)\exp\left(-\frac{\varepsilon}{2\tau}\right)}{Z} = -\frac{1}{2}\varepsilon\tanh\left(\frac{\varepsilon}{2\tau}\right)$$

Or

$$\langle\varepsilon\rangle = \tau^2\frac{\partial Ln\left(Z(\tau)\right)}{\partial\tau} = \tau^2\frac{\partial Ln\left(2\cosh\left(\frac{\varepsilon}{2\tau}\right)\right)}{\partial\tau} = -\frac{1}{2}\varepsilon\tanh\left(\frac{\varepsilon}{2\tau}\right)$$

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heat capacity at constant volume, C_V:

$$C_V = \left(\frac{\partial\langle\varepsilon\rangle}{\partial\tau}\right)_V = \left(\frac{\partial}{\partial\tau}\left[\frac{\varepsilon}{exp\left(\frac{\varepsilon}{\tau}\right)+1}\right]\right)_V = \left(\frac{\varepsilon}{\tau}\right)^2\cdot\frac{exp\left(\frac{\varepsilon}{\tau}\right)}{\left(exp\left(\frac{\varepsilon}{\tau}\right)+1\right)^2}$$

We could have calculated the heat capacity using our expression in terms of the partition function (of course we would get the same expression),

For very large τ, $\left(\frac{\epsilon}{\tau}\right) \to 0$

$$C_V = 0\cdot\frac{1}{(1+1)^2} = 0$$

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In the opposite limit, τ → 0, so $exp\left(\frac{\epsilon}{\tau}\right) \gg 1$and the expression can be approximated by:

$$C_V = \left(\frac{\varepsilon}{\tau}\right)^2 \cdot \frac{exp\left(\frac{\varepsilon}{\tau}\right)}{\left(exp\left(\frac{\varepsilon}{\tau}\right)+1\right)^2} \approx \frac{\left(\frac{\varepsilon}{\tau}\right)^2}{exp\left(\frac{\varepsilon}{\tau}\right)}$$

$$exp\left(\frac{\varepsilon}{\tau}\right) = \sum_{n=1}^{\infty} \frac{1}{n!}\left(\frac{\varepsilon}{\tau}\right)^n = 1 + \left(\frac{\varepsilon}{\tau}\right) + \frac{1}{2!}\left(\frac{\varepsilon}{\tau}\right)^2 + \frac{1}{3!}\left(\frac{\varepsilon}{\tau}\right)^3 + \frac{1}{4!}\left(\frac{\varepsilon}{\tau}\right)^4 + \cdots$$

We need to keep all the terms, because τ → 0 means that each one of them (after the first) will blow up.

$$C_V \approx \frac{\left(\frac{\varepsilon}{\tau}\right)^2}{exp\left(\frac{\varepsilon}{\tau}\right)} \approx \frac{\left(\frac{\varepsilon}{\tau}\right)^2}{1 + \left(\frac{\varepsilon}{\tau}\right) + \frac{1}{2!}\left(\frac{\varepsilon}{\tau}\right)^2 + \frac{1}{3!}\left(\frac{\varepsilon}{\tau}\right)^3 + \frac{1}{4!}\left(\frac{\varepsilon}{\tau}\right)^4 + \cdots}$$

$$C_V \approx \frac{1}{\left(\frac{\tau}{\varepsilon}\right)^2 + \left(\frac{\tau}{\varepsilon}\right) + \frac{1}{2} + \frac{1}{6}\left(\frac{\varepsilon}{\tau}\right) + \frac{1}{24}\left(\frac{\varepsilon}{\tau}\right)^2 + \cdots.} \approx 0$$

Example 6-1: Solution

C_V goes to 0 at both high and low τ and has a maximum somewhere between these two limits.

The maximum is determined setting $\frac{\partial C_V}{\partial \tau} = 0$ and obtaining from the resulting equation the value of τ that makes the equation true.

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We need to keep all the terms, because τ → 0 means that each one of them (after the first) will blow up.

$$C_V \approx \frac{\left(\frac{\varepsilon}{\tau}\right)^2}{exp\left(\frac{\varepsilon}{\tau}\right)} \approx \frac{\left(\frac{\varepsilon}{\tau}\right)^2}{1+\left(\frac{\varepsilon}{\tau}\right)+\frac{1}{2!}\left(\frac{\varepsilon}{\tau}\right)^2+\frac{1}{3!}\left(\frac{\varepsilon}{\tau}\right)^3+\frac{1}{4!}\left(\frac{\varepsilon}{\tau}\right)^4+\cdots}$$

$$C_V \approx \frac{1}{\left(\frac{\tau}{\varepsilon}\right)^2+\left(\frac{\tau}{\varepsilon}\right)+\frac{1}{2}+\frac{1}{6}\left(\frac{\varepsilon}{\tau}\right)+\frac{1}{24}\left(\frac{\varepsilon}{\tau}\right)^2+\cdots.} \approx 0$$

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Partition Function

Up to this point, we have written the partition function as a sum over all accessible microstates:

$$Z(\tau) = \sum_{all\ states\ s} exp\left(-\frac{\mathcal{E}_s}{\tau}\right)$$

In many situations, it is more convenient to sum over **energy levels** rather than individual states.

- Multiple microstates can share the same energy
- We must account for this using the **degeneracy** $g(\varepsilon)$,i.e., the number of states with energy ε

Partition Function in terms of Energy

$$Z(\tau) = \sum_{\substack{all\ energies \\ \varepsilon_s}} g(\varepsilon_s) \cdot exp\left(-\frac{\mathcal{E}_s}{\tau}\right)$$

The two sums express exactly the same quantity, the partition function for the system.

Key Insight

- Both expressions are completely equivalent
- They represent the same physical quantity: the partition function
- The second form is often more practical when degeneracy is known

Probability of a Given Energy Level

The probability Expression:

$$P(system\ has\ energy\ \varepsilon_s) = \frac{g(\mathcal{E}_s)\cdot exp\left(-\frac{\mathcal{E}_s}{\tau}\right)}{Z(\tau)}$$

Comparison between Microcanonical and Canonical ensembles

Microcanonical	**Canonical**
Fixed E, N. Closed system.	Fixed N, T and E is variable. System in thermal contact with reservoir.
$P(\varepsilon_s) = (1/g)$ Where g is the number of accessible states. All are equally likely.	$P(\varepsilon_s) = \frac{exp\left(-\frac{\mathcal{E}_s}{\tau}\right)}{Z(\tau)}$ $\mathrm{Z}(\tau) = \sum_{\substack{all\ states \\ s}} exp\left(-\frac{\mathcal{E}_s}{\tau}\right)$ $Z(\tau)$ is the partition function.

Thank you very much for your attention