Introduction to Statistical Mechanics and Microcanonical Ensembles

PHYS 301 – Prof. Cyr-Racine

1 Introduction and Motivation

The primary goal of statistical mechanics is to translate the microscopic laws of physics into a description of nature on a macroscopic scale.

1.1 The Scale Problem

Typical macroscopic systems contain approximately 10^{23} particles. Even if one knew the microscopic laws perfectly, it is impossible to solve the Schrödinger equation for that many particles. Furthermore, even if you could solve it, doing so might not be interesting or useful.

Instead, we seek answers to more basic macroscopic questions, such as:

- Is the system hot or cold?
- Is it a solid, a liquid, or a gas?
- What is the pressure?

1.2 Emergent Concepts

New concepts emerge when simultaneously considering 10^{23} particles. For example, temperature: it does not make sense to consider the temperature of a single electron, but it is impossible to discuss the macroscopic world without talking about temperature.

This leads to the realization that the language needed to describe physics on one scale is very different from that needed on other scales. This is one of the most important ideas in all of physics. Historically, statistical mechanics has played a crucial role in developing a deeper understanding of the laws of physics (e.g., the development of quantum mechanics was deeply influenced by statistical mechanics arguments).

2 Thermodynamics vs. Statistical Mechanics

Thermodynamics makes no reference to the microscopic nature of a system. It aims to describe a system solely in terms of its macroscopic characteristics (temperature, pressure, magnetization, etc.) and their mutual relationships.

- Thermodynamics predates the development of statistical mechanics and the knowledge that macroscopic materials are made of atoms and molecules.
- It relies on empirical laws; often, the discoverers did not know the physical mechanisms behind them.

Statistical Mechanics provided the tools to explain these laws from first principles. As such, statistical mechanics is considered more fundamental than thermodynamics.

However, since thermodynamics never references the microscopic nature of the system, it is more universal and general, giving it distinct and important uses.

3 The Microcanonical Ensemble

3.1 Definitions

- **Ensemble:** A collection of N particles, molecules, or degrees of freedom, where N is a very large number.
- **Microcanonical Ensemble:** An ensemble with a fixed total energy E.

3.2 Quantum Description

In quantum mechanics, such a system can be described by a Hamiltonian with energy eigenstates $|\Psi_n\rangle$:

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle \tag{1}$$

For an ensemble with $N \sim 10^{23}$ particles, the wavefunction is extremely complicated as it describes what each particle is doing. Each $|\Psi_n\rangle$ describes a **microstate**.

The number of microstates is generally huge. For example, for an ensemble of two-state degrees of freedom (e.g., spin up or spin down), the number of microstates is $2^N = 2^{10^{23}}$. This number is so large that it is essentially meaningless to track specific states.

3.3 Probability and Mixed States

Given this large number, it is impossible to know the exact microstate the system is in. There are generally many microstates all with the same total energy E. Therefore, the system is in a **mixed state** rather than a pure quantum state.

We denote by $|\Psi_n\rangle$ all states with total energy E, and use $p(n)$ to denote the probability that the system is in a specific state $|\Psi_n\rangle$. The expectation value of an operator is given by:

$$\langle \hat{O} \rangle = \sum_n p(n)\langle \Psi_n|\hat{O}|\Psi_n\rangle \tag{2}$$

4 The Fundamental Assumption

We focus on systems that have been left alone for a long time, meaning memory of initial conditions has been lost and the system has reached **equilibrium**. Operationally, this means $p(n)$ is time-independent.

The Fundamental Assumption of Statistical Mechanics: For an isolated system in equilibrium, all accessible microstates are equally likely.

For the microcanonical ensemble (fixed total E), the accessible microstates are all states with energy E. We define the **multiplicity**, $\Omega(E)$, as the number of states with energy E.

The probability of finding the system in state $|\Psi_n\rangle$ with energy E is:

$$p(n) = \frac{1}{\Omega(E)} \tag{3}$$

Notes:

- $\Omega(E)$ is ridiculously large (e.g., $2^{10^{23}}$ for a two-state system).
- While discussed in terms of Quantum Mechanics, this carries over to the classical case. $p(n)$ represents our ignorance of the system, not necessarily quantum indeterminacy.

5 Examples

5.1 Coin Toss System

Consider a system of 3 coins (Two-state system: Heads H or Tails T).

Coin 1	Coin 2	Coin 3	Microstate
H	H	H	HHH
H	H	T	HHT
H	T	H	HTH
T	H	H	THH
H	T	T	HTT
T	H	T	THT
T	T	H	TTH
T	T	T	TTT

Total microstates = 8.

Macrostates and Multiplicity:

- 3 Heads (3H): 1 microstate $\rightarrow \Omega(3H) = 1$.
- 2 Heads (2H): 3 microstates $\rightarrow \Omega(2H) = 3$.
- 1 Head (1H): 3 microstates $\rightarrow \Omega(1H) = 3$.
- 0 Heads (0H): 1 microstate $\rightarrow \Omega(0H) = 1$.

The probability of a macrostate is $p(m_i) = \frac{\Omega(m_i)}{\Omega_{\text{total}}}$.

- $p(3H) = 1/8$
- $p(2H) = 3/8$
- $p(1H) = 3/8$
- $p(0H) = 1/8$

In the microcanonical picture with the fundamental assumption of statistical mechanics, we say that for the macrostate 2H, the 3 corresponding microstates (HHT, HTH, THH) are all equally probable.

5.2 Large-ish N System (100 Coins)

For 100 coins, there are 2^{100} microstates, but only 101 macrostates (100H, 99H... 0H). Calculating multiplicity $\Omega(nH)$ (number of ways to get n Heads):

- For 0H: $\Omega(0H) = 1$.
- For 1H: $\Omega(1H) = 100$.
- For 2H: $\Omega(2H) = \frac{100\cdot 99}{2}$ (dividing by 2 to avoid double counting).
- For 3H: $\Omega(3H) = \frac{100\cdot 99\cdot 98}{2\cdot 3}$.

General Formula: For N coins and n heads, the multiplicity is given by the binomial coefficient (N choose n):

$$\Omega(N, n) = \binom{N}{n} = \frac{N!}{n!(N-n)!} \tag{4}$$

This represents the number of ways of choosing n objects out of N.

5.3 Non-Interacting Spins

Consider a physical system: N non-interacting spins. Each spin can take one of two values: Up or Down.

We set the energy levels as follows:

- Energy of down spin = 0.
- Energy of up spin = ϵ.

If the system has $N_\uparrow$ particles with spin up, the total energy is:

$$E = N_\uparrow \epsilon \tag{5}$$

The multiplicity of a state with energy E (the macrostate) corresponds to the number of ways to arrange the spins for that energy:

$$\Omega(E) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!} \tag{6}$$