Lecture 9 “Fundamentals of Statistical Thermodynamics: Microstates and Distributions”

Goal of the lecture: To understand the microscopic interpretation of thermodynamics using statistical principles, define the concept of microstates and macrostates, and explore how probability distributions describe the behavior of particles in a system.

Brief lecture notes: Statistical thermodynamics is a branch of physical chemistry that connects the microscopic properties of individual atoms and molecules to the macroscopic observables such as temperature, pressure, and entropy. It provides a molecular-level interpretation of classical thermodynamics by using the principles of **probability** and **statistics**.

Every thermodynamic system can be described in two ways:

1. **Microscopic view:** Describes the behavior of individual particles (molecules, atoms, ions).
2. **Macroscopic view:** Describes the overall properties of the system (e.g., pressure, volume, temperature).

The link between these two views is established through the concept of **microstates** and **macrostates**.

1. Microstates and Macrostates

A **microstate** is a specific arrangement of all particles in a system, defined by their positions and momenta at a given instant. Each microstate represents one possible way in which the system’s total energy can be distributed among the particles. A **macrostate**, on the other hand, is defined by macroscopic quantities such as temperature, pressure, and total energy. Many microstates can correspond to the same macrostate.

The number of possible microstates (W) associated with a given macrostate determines the **entropy (S)** of the system, according to **Boltzmann’s equation**:

$$S = klnW$$

where

- S = entropy,
- k = Boltzmann constant (1.3806×10^{-23} J/K),
- W = number of microstates.

This equation shows that entropy is a measure of the **disorder or randomness** of a system — the greater the number of microstates, the higher the entropy.

2. Probability and Distribution of Particles

In a system containing many identical particles (such as a gas), not all microstates are equally probable. Statistical thermodynamics determines the **most probable distribution** of particles among available energy levels, which corresponds to **thermal equilibrium**.

The **Boltzmann distribution law** gives the fraction of particles (N_i/N) having energy ε_i at temperature T:

$$\frac{N_i}{N} = \frac{e^{-\varepsilon_i/kT}}{\Sigma e^{-\varepsilon_i/kT}}$$

where

- N_i = number of particles in energy level iii,
- N = total number of particles,
- ε_i = energy of level iii,
- T = absolute temperature,
- $\Sigma e^{-\varepsilon_i/kT}$ = normalization factor (partition function).

This equation shows that particles occupy lower energy states more frequently, but as temperature increases, higher energy states become more populated.

3. The Partition Function

The **partition function (Q)** is a central quantity in statistical thermodynamics that connects microscopic properties to thermodynamic quantities. It is defined as:

$$Q = \Sigma e^{-\varepsilon_i/kT}$$

The partition function acts as a statistical "sum" over all possible energy states of a system and provides a bridge between molecular-level behavior and macroscopic observables.

For example:

- Internal energy U is related to Q by:

$$U = kT^2(\frac{\partial lnQ}{\partial T})$$

Entropy S can also be derived from Q, linking it to the number of accessible microstates.

4. Types of Distributions

Different types of statistical distributions describe how indistinguishable particles occupy energy states:

1. **Maxwell–Boltzmann distribution:**
   Applies to **classical particles** (atoms, molecules) that are distinguishable and do not obey quantum restrictions.
2. **Bose–Einstein distribution:**
   Applies to **bosons** (particles with integer spin, such as photons) that can occupy the same energy state simultaneously.
3. **Fermi–Dirac distribution:**
   Applies to **fermions** (particles with half-integer spin, such as electrons) that obey the **Pauli exclusion principle**, meaning no two can occupy the same quantum state.

These distributions are fundamental in describing the properties of gases, metals, semiconductors, and radiation.

5. Significance of Microstates and Distributions

The concept of microstates and distributions explains how macroscopic properties arise from molecular behavior.

- Temperature corresponds to the average kinetic energy of particles.
- Entropy measures the number of possible microstates.
- Equilibrium occurs when the probability distribution of energy among particles is most probable (maximum entropy).

Statistical thermodynamics thus provides a powerful molecular interpretation of classical thermodynamic laws, especially the **Second Law**, which states that systems tend to move toward states of maximum entropy.

Questions for self-control

1. Define microstate and macrostate. How are they related to entropy?
2. Write and explain Boltzmann's entropy equation.
3. What does the Boltzmann distribution law describe?
4. What is the partition function, and why is it important?
5. Explain the differences between Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distributions.

Literature:

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