Chapter 1

Introduction

1.1 Literature

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1.2 What is thermodynamics? What is statistical physics?

$\boxed{\text{Thermodynamics}}$ is the *phenomenological theory* of the macroscopic properties of systems with a large number of constituents (particles, degrees of freedom). This theory describes the many-body system in terms of a few experimentally measurable parameters like

- Volume V,
- Pressure P,
- Temperature T,
- Density ρ.

Phenomenological theory means that it does not provide the microscopic origin of a phenomenon.

A large number of constituents means that the fluctuation effects of the constituents are negligible at the scale at which we are studying the system. A macroscopic object (1 cm^3) has usually

$$N \simeq N_{Avogadro} = 1 \text{ mole} \simeq 6.022 \times 10^{23} \text{ particles.}$$

In such a system, the fluctuation effects of a macroscopic observable O are of the order:

$$\frac{\Delta O}{O} \sim \frac{1}{\sqrt{N}} \approx 10^{-12},$$

which is a negligible effect if we study the system at the meter scale but will gain in importance if we consider shorter scales as would be required, for instance, for present electronic devices, which have sizes of $1\,\text{nm}=10^{-9}\,\text{m}$.

$\boxed{\text{Statistical physics}}$ provides a description of the *macroscopic* properties of a many-body system in terms of the *microscopic* structure of the system.

Statistical physics considers the basic equations of Classical Mechanics (classical statistical physics) or Quantum Mechanics (quantum statistical physics) and describes the macroscopic quantities in terms of the microscopic behavior. Statistical physics is more general than thermodynamics and the laws of thermodynamics can be derived from statistical physics.

Classical statistical physics. As a reminder, the basic equations in classical mechanics for a system of N particles are given in the Hamilton formalism as

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \qquad i = 1, 2, \ldots, 3N, \tag{1.1}$$

with $H = H(q_1 \ldots q_{3N}, p_1 \ldots p_{3N}, t)$ being the Hamilton function and q_i and p_i the generalized position and momentum coordinates.

Our objective in this course will be to relate equations (1.1) to such concepts as "temperature", "pressure", "internal energy", i.e., to establish relations

$$\text{microscopic equations} \;\longleftrightarrow\; \text{macroscopic equations.}$$

Quantum statistical physics. In quantum mechanics, the basic equation for a system with N particles is the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t}(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N,\, t) \;=\; \left[\sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + V(\vec{r}_1, \ldots, \vec{r}_N,\, t) \right] \Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N,\, t),$$

where $\Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \ldots, \vec{r}_N\sigma_N,\, t)$ is the wave-function of the N-particle system. The individual particles are characterized here by their real-space positions $\vec{r}_j$ and their spins σ_j.

We have in quantum mechanics two types of particles:

> **Bosons**: particles with integer spin. Their wave-function is symmetric with respect to interchange of two particles:
>
> $$\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_i\sigma_i, \ldots, \vec{r}_j\sigma_j, \ldots, \vec{r}_N\sigma_N) \;=\; \Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_j\sigma_j, \ldots, \vec{r}_i\sigma_i, \ldots, \vec{r}_N\sigma_N);$$
>
> **Fermions**: particles with half-integer spin. Their wave-function is antisymmetric with respect to interchange of two particles:
>
> $$\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_i\sigma_i, \ldots, \vec{r}_j\sigma_j, \ldots, \vec{r}_N\sigma_N) = -\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_j\sigma_j, \ldots, \vec{r}_i\sigma_i, \ldots, \vec{r}_N\sigma_N).$$

As in the classical statistical physics, our aim in quantum statistical physics is to obtain, out of the *microscopic* equations, a description of the macroscopic properties, which can be related to experiment.

1.3 Historical development

Thermodynamics was born out of a few unresolved important questions like:

- what is heat?
- what is temperature?
- why do some reactions happen and others do not?
- is it possible to convert heat into useful energy?

1.3.1 Thermodynamics

1600's - *Concept of heat*: already in the seventeenth century some scientists thought that *heat* is associated with the *motion* of microscopic constituents of matter but the idea was too revolutionary at that time.

1700's - there was a general belief that heat is a separate fluid-like substance.

1840's - experiments of James Joule invalidating the theory of a separate fluid.

1850's - it became accepted that *heat* is a form of *energy*.

1824 - **Sadi Carnot** (French engineer and physicist) showed that the *work* produced by a steam engine is *proportional* to the *heat* transferred from the boiler to the condenser and that, in general, work could only be gained from heat by a transfer from a *warmer* to a *colder* body (Carnot's law).

1842 - **Julius Robert von Mayer** (German physicist) formulated the general law of conservation of energy and defined heat as a form of energy.

1843 - **James Joule** (British physicist) formulated the Joule's laws and determined the mechanical equivalent of heat.

- The heat Q generated by a current I flowing through a conductor is $Q = I^2Rt$, where R is the resistance and t time. IR is the voltage drop.
- The internal energy of an ideal gas depends only on its temperature.

1850 - **Rudolf Clausius** (German physicist) formulated the *second law of thermodynamics* and introduced the *entropy* concept (1865) (in the same year Maxwell postulated the Maxwell equations in electrodynamics).

The second law of thermodynamics reads:

> *"Heat cannot be transformed from a colder to a warmer body."*

1.3.2 Ideal Gas

In the nineteenth century, there were also a few advances concerning the behavior of the *gas phase*:

1807 - **Joseph Gay-Lussac** (French chemist and physicist) investigated the changes in volume of a gas at different temperatures and showed that at constant pressure

$$\frac{V}{T} = \frac{V_0}{T_0}, \tag{1.2}$$

where T is absolute temperature in K (remember $T = 273.15\ \mathrm{K} + t$ (in Celsius)). At constant temperature $VP = V_0P_0$.

1811 - **Amadeo Avogadro** (Italian physicist and chemist) postulated the Avogadro's law:

> *"The same volume of different gases under same conditions (T, P) contains the same number of particles."*

This postulate together with (1.2) can be summarized in the equation of state for an ideal gas, which we will analyze in detail in the coming chapters:

$$PV \;=\; Nk_BT \;, \tag{1.3}$$

where N is number of particles and k_B=1.381×10^{-23} Joule/K is the Boltzmann constant.

1.3.3 Statistical physics

1860 - **James Maxwell** (British physicist) laid the foundations of the modern electrodynamic theory of light. He was also involved in the development of the kinetic gas theory.

1870's - **Ludwig Boltzmann** (Austrian physicist). His contributions were fundamental. He was the first scientist to provide a *statistical interpretation* of the 2^{nd} law of thermodynamics:

$$S = k_B \ln \Gamma,$$

namely that the entropy is proportional to the logarithm of *the number of available states* given by Γ.

The fact that he used the concept of atoms in motion in order to explain the concept of heat provoked very strong criticisms at that time (Ernst Mach, Wilhelm Otswald).

1902 - **Josiah Willard Gibbs** (US American physicist and mathematician) formulated the "Gibbs phase rule" which allows to calculate thermodynamical properties out of microscopic quantities.

1.3.4 Twentieth Century

The twentieth century is the century of *quantum mechanics* and *quantum statistical mechanics.*

1900 - **Max Planck** (German physicist) postulated that the *energy exchange* of the radiation with the walls of a black body does not take place continuously but in *discrete* units of $\hbar\omega$,

$$\varepsilon_n = n\hbar\omega \quad \leftrightarrow \quad \text{quantization of the radiation energy},$$

so that the energy density of radiation of a black body is given by

$$u(\omega, T) = \frac{k_BT\omega^2}{\pi^2c^3}\frac{\hbar\omega/k_BT}{e^{\hbar\omega/k_BT}-1}.$$

For his derivation, Planck used concepts of electrodynamics, quantum mechanics (quantization of energy) and statistical physics, following Boltzmann.

1925 - **Satyendranath Bose** (Indian physicist) and **Albert Einstein** (German physicist)

- derived the statistics (Bose-Einstein statistics) for photons and, in general, for a system of bosons.
- predicted the phenomenon of "Bose-Einstein condensation" which was first corroborated experimentally 70 years later by W. Ketterle, E. Cornell and C. E. Wieman (Nobel Prize 2001).

1926 - **Enrico Fermi** (Italian physicist) and **Paul Dirac** (British physicist) derived the quantum statistics for fermions (Fermi-Dirac statistics).

1940: **Wolfgang Pauli** (Austrian physicist) stated the spin-statistics theorem which associates the value of the spin of a particle to the nature of the particle.

Bosons : integer spin
Fermions : half-integer spin

1.3.5 Further developments

Some selected examples for the wide range of further developments.

1 - treatment of phase transitions, both macroscopically and microscopically (Landau, Ginzburg, Bardeen, Cooper, Schrieffer, ...).
Important phase transitions are of type
"disordered" phase → "ordered" phase, which include
  - gas-liquid-solid,
  - paramagnetic-ferromagnetic (antiferromagnetic),
  - liquid-superfluid (He^4, He^3) transitions,
  - metal-superconductor.

2 - treatment of *interacting* many-particle systems, especially if the interactions are *strong*. Areas of application are
  - solid state theory: correlated systems (strong Coulomb repulsion),
  - high-energy physics: quantum chromodynamics (QCD).

3 - *systems in equilibrium ⟷ non-equilibrium systems.*

1.4 Effective vs. fundamental theories

We have defined thermodynamics as a phenomenological theory which was developed to describe phenomena at the scale of our naked-eye observations (length-scales $\approx$ 1cm, time-scales ≈ 1s). At these scales the knowledge of the atomic constituents is irrelevant. Thermodynamics is an *effective theory* and, in general, effective theories are useful for the understanding of observations at a given length- and time-scale.

Statistical physics is, on the other hand, a *fundamental theory* since it intends to describe macroscopic phenomena out of the laws governing the microscopic constituents (atoms, electrons) of the systems.