

Statistical Mechanics
from the context of the course
PHY 410: Statistical Mechanics

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0.1 The SI System

In physics it's often important to have precisely defined units for the purposes of making very accurate measurements or simply having a coherent unit system. It's possible to derive all necessary units from five measurements of **length, mass, time, current, and temperature**. The standard SI units for these properties are listed below:

Type	Unit	Definition
Length	Meter(m)	Length of distance light in a vacuum travels in $\frac{1}{299792458}$ seconds
Mass	Kilogram(kg)	Defined by fixing the Planck's constant $h = 6.62607015 \times 10^{-34} kg \cdot m^2 s^{-1}$
Time	Second(s)	Defined by fixing the ground-state hyperfine transition frequency of the caesium-133 atom, to be $9192631770 s^{-1}$
Current	Ampere(A)	Defined by fixing the charge of an electron as $1.602176634 \times 10^{-19} A \cdot s$
Temperature	Kelvin(K)	Defined by fixing the value of the Boltzmann constant k to $1.380649 \times 10^{-23} kg \cdot m^2 s^{-2} K^{-1}$

Common prefixes are listed below:

Prefix	Symbol	Definition
mega	M	10^6
kilo	k	10^3
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}

Additionally, the following are defined constants:

Symbol	Definition
\hbar	$\hbar = \frac{h}{2\pi} \approx 1.0546 \times 10^{-34} kg \cdot m^2 s^{-1}$

0.2 Introduction

Statistical mechanics is the probabilistic study of extremely complex systems. It seeks to describe the equilibrium or averages behaviors of such systems. Very often in nature we deal with systems containing so many possible states that it would be impossible to completely describe and calculate the expected behavior. By focusing on large measurable properties of such systems and the average behavior of the microstates we can derive there behavior. With a combination of statistical arguments and microscopic knowledge, statistical mechanics predicts the macro equilibrium properties, which can be used to derive the laws of thermodynamics.

Thermodynamics is fundamentally connected with statistical mechanics and we will derive the laws of thermodynamics in the book. For reference here are the laws of thermodynamics.

Law 0.2.1. The 0th Law of Thermodynamics - Thermal equilibrium is transitive. If system A and B are in equilibrium and systems B and C are also in equilibrium, then systems A and C are in equilibrium.

Law 0.2.2. The 1st Law of Thermodynamics - Heat is a form of energy. Let ΔE be the change in energy, W be the work done on the system, and Q the heat energy added to the system.

$$\Delta E = W + Q$$

Law 0.2.3. The 2nd Law of Thermodynamics - Total entropy always increases. Let ΔS be the change in entropy and S_f and S_i be the final and initial entropy.

$$\Delta S = S_f - S_i > 0$$

$$\Delta S = \int_i^f \frac{1}{T} \partial Q = S_f - S_i$$

Law 0.2.4. The 3rd Law of Thermodynamics - Absolute Zero. Let S be entropy and T be temperature.

$$\lim_{T \rightarrow 0} S(T) = 0$$

We will seek to derive each of these laws in this book. Additionally, the logarithm function is used very often in statistical mechanics, we will used \log to refer to the natural logarithm (aka \log_e).

Chapter 1

Microstates of a System

Throughout this book we will refer to microscope and macroscopic systems. This distinction is determined by the solvability of systems. Using Quantum mechanics one can predict the behavior of a small number of particles or similar small systems with high levels of symmetry. However, as the number of particles increases, Schrödinger's becomes impossible to solve without an impossible amount of computation. However the microscopic quantum states of a system determine many measurable macroscopic properties, such as temperature, energy, volume or pressure. Towards making predictions about these macroscopic properties is useful to count the number of possible microstates for a given macrostate.

Definition 1.0.1. A **Multiplicity function** is the number of microstates that produce a given macrostate denoted

$$g(N, T, U, V, P) = \# \text{ of microstates that fit the given macrostate}$$

Assumption 1.0.2. Boltzmann's Assumption - All accessible microstates are equally probable. Let $P(n)$ be the probability that a system is in microstate n .

$$P(n) = \frac{1}{g(N, T, U, V, P)}$$

1.1 Binary System

Definition 1.1.1. A **binary system** is a system of N particles where each particles has two possible states. Let N_{\uparrow} is the number of particle in the up state and N_{\downarrow} be the number of particles in the down state. The multiplicity function is

$$g(N, N_{\uparrow}) = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!}$$

Corollary 1.1.2. The binary system can be rewritten in terms of the **difference between up states and down states**.

$$2S = N_{\uparrow} - N_{\downarrow}$$
$$g(N, S) = \frac{N!}{(\frac{N}{2} + S)!(\frac{N}{2} - S)!}$$

Example. Consider a system of N spin 1/2 particles in an external magnetic field B . The total energy of the system is

$$U = \sum_{i=1}^N -\vec{m}_i \cdot \vec{B} = -(N_{\uparrow} - N_{\downarrow})mB = -2SmB$$

$$g(N, U) = \frac{N!}{(\frac{N}{2} - \frac{U}{2mB})!(\frac{N}{2} + \frac{U}{2mB})!}$$

Theorem 1.1.3. Stirling's Approximation - for very large N the factorial can be very accurately approximated with the following

$$N! = \sqrt{2\pi N} N^N e^{-N}$$

Proposition 1.1.4. Applying Stirling's approximation to the binary model, for large N we have

$$g(N, S) \approx g(N, 0) e^{-2s^2/N}$$

Proposition 1.1.5. The fractional uncertainty of S in the binary model is determined by

$$\frac{\Delta S}{N} = \frac{1}{\sqrt{N}}$$

Definition 1.1.6. An **einstein solid** is a system of N atoms where each atom is modeled as a harmonic oscillator the total energy of the system is determined by the number of atoms n oscillating at frequency ω .

$$U = n\hbar\omega$$

$$g(N, n) = \frac{(n + N - 1)!}{n!(N - 1)!}$$

1.2 Equilibrium State

Since the uncertainty of our system is extremely small for large N , the most probable state as determined by Boltzmann's assumption will determine the macrostate of the system.

Definition 1.2.1. The **equilibrium** state two systems is the most probable macrostate of the shared system.

Example. Consider two isolated binary systems

$$g_1(4, 2) \text{ and } g_2(6, 0)$$

The initial condition of the two states are $N_1 = 4, S_1 = 2$ and $N_2 = 6, S_2 = 0$. Now, allowing contact between the two systems the equilibrium state is the most probable state that conserves energy. To find this we need to maximize the total multiplicity function

$$g(N_1 + N_2, S'_1, S'_2) = g_1(N_1, S'_1)g_2(N_2, S'_2)$$

For this simple system the max is found when $S'_1 = 1$ and $S'_2 = 1$.

Definition 1.2.2. The **entropy** of a system is defined as the natural log of the multiplicity function.

$$\sigma(N, T, U, V, P) \equiv \log[g(N, T, U, V, P)]$$

Proposition 1.2.3. The equilibrium point is reached when the derivative of the total multiplicity function is zero.

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}$$