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

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Contents

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 bellow:

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 $h = 6.62607015 \times 10^{-34} kg\ m^2 s^{-1}$
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 bellow:

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
k_B	$k_B = 1.380649 \times 10^{-23} \mathrm{m^2\,s^{-2}\,K^{-1}}$
h	$h = 6.62607015 \times 10^{-34} \mathrm{kg\,m^2\,s^{-1}}$
$\hbar$	$\hbar = \frac{h}{2\pi} \approx 1.0546 \times 10^{-34} kg\ m^2 s^{-1}$

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 ΔD 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.

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

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 $\log_e$).

0.3   Reference

Multiplicity Function

$$g = \# \text{ of microstates}, \quad \mathcal{P}(n) = \frac{1}{g}$$

Partition Function

$$z = \sum_n e^{-\varepsilon_n/\tau}, \quad \mathcal{P}(\varepsilon_n) = \frac{1}{z} e^{-\varepsilon_n/\tau}$$

Helmholtz Free Energy

$$F = U - \sigma\tau = U - ST = -\tau \log z$$

Entropy

$$\sigma \equiv \log g = -\left(\frac{\partial F}{\partial \tau}\right)_V, \quad S = k_B \sigma$$

Temperature

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_{N,V}, \quad T = \frac{\tau}{k_B}$$

Pressure

$$P = -\left(\frac{\partial U}{\partial V}\right)_\sigma = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

Energy

$$U = \tau^2 \frac{\partial}{\partial \tau} \log z = -\tau^2 \frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right)$$

Equilibrium Conditions

Name	Equilibrium Condition
Thermal Equilibrium	$\left(\dfrac{\partial \sigma_1}{\partial U_1}\right)_{N_1,V_1} = \left(\dfrac{\partial \sigma_2}{\partial U_2}\right)_{N_2,V_2}$
Quasi-static Compression	$\left(\dfrac{\partial U_1}{\partial V_1}\right)_{\sigma_1} = \left(\dfrac{\partial U_2}{\partial V_2}\right)_{\sigma_2}$

Chapter 1

Microcanonical Ensemble

Throughout this book we will refer to microscope and macroscopic 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 practically impossible to solve. 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 is useful to count the number of possible microstates for a given macrostate.

Definition 1.0.1. The **microcanonical ensemble** is the system of calculations where the total energy, particle number, and volume are fixed.

1.1 Multiplicity Functions

Definition 1.1.1. 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 1.1.2. Boltzmann's Assumption - All accessible microstates are equally probable. Let $P(n)$ be the probability that a system is in microstate n.

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

Definition 1.1.3. The **expected value** of a property $\mathbb{X}$ of a system is determined by the average of that value across all possible microstates.

$$\langle \mathbb{X} \rangle = \sum_n \mathbb{X}(n)\mathcal{P}(n) = \frac{1}{g}\sum_n \mathbb{X}(n)$$

Definition 1.1.4. The **fractional uncertainty** of a property $\mathbb{X}$ is defined in terms of the expected value.

$$\frac{\Delta \mathbb{X}}{N} = \frac{\sqrt{\langle \mathbb{X}^2 \rangle - \langle \mathbb{X} \rangle^2}}{N}$$

1.2 Binary System

Definition 1.2.1. 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.

$$g(N, N_\uparrow) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}, \quad \sum_{N_\uparrow=0}^{N} g(N, N_\uparrow) = 2^N$$

Corollary 1.2.2. The binary system can be rewritten in terms of the **differnce between up states and down states**.

$$2S = N_\uparrow - N_\downarrow$$

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

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

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

Proposition 1.2.4. Applying Stirling's approximation to the binary model, for large N the multiplicity function and fractional uncertainty are

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

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

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

Definition 1.2.5. 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.

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

1.3   Thermal Equilibrium

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 1.3.1. The **equilibrum** state two systems is the most probable macrostate of the shared system.

$$g_{TOT}(N, V, U) = \sum_{U_1'} g_1(N_1, V_1, U_1')g_2(N_2, V_2, U - U_1')$$

$$\mathcal{P}(U_1') = \frac{g_1(N_1, V_1, U_1')g_2(N_2, V_2, U - U_1')}{g_{TOT}(N, V, U)}$$

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

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

Definition 1.3.3. Thermal equilibrium is reached when the energy derivative of the total multiplicity function is zero.

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1, V_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2, V_2}$$

Definition 1.3.4. The **temperature** of a system is defined with the derivative of entropy σ in terms of energy U. Kelvin temperature T is directly proportional to the fundamental temperature via the Boltzmann constant k_B.

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_{N, V}$$

$$\tau = k_B T$$

Chapter 2

The Canonical Ensemble

Up until this point we've been working with closed systems where to total amount of energy is fixed. If the real world it is often very difficult to thermally isolate a system. It is must easier to operate at a fixed temperature and a fixed number of particles. We separate each of these cases into ensembles.

Definition 2.0.1. The **canonical ensemble** is the system of calculations where the temperature and particle number are fixed.

2.1 Partition Function

Definition 2.1.1. The **partition function** of the canonical ensemble is the probability of a particular energy ε_n.

$$\mathcal{P}(\varepsilon_n) = \frac{1}{z} e^{-\varepsilon_n/\tau}$$

$$z = \sum_n e^{-\varepsilon_n/\tau}$$

Corollary 2.1.2. For systems with degeneracy $g(\varepsilon_\alpha)$ for each distinct energy level ε_α, the partition function can be rewritten.

$$z = \sum_\alpha g(\varepsilon_\alpha) e^{-\varepsilon_\alpha/\tau}$$

Definition 2.1.3. The **expected energy** in the canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z} \sum_n \varepsilon_n e^{-\varepsilon_n/\tau}$$

$$U = \langle \varepsilon \rangle = \tau^2 \frac{1}{z} \frac{\partial z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \log z$$

Example. One and many simple harmonic oscillators at temperature τ. Starting with a system of just one harmonic oscillator we find

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega$$

$$z = \sum_n e^{-\left(n+\frac{1}{2}\right)\frac{\hbar\omega}{\tau}} = \frac{e^{-\hbar\omega/2\tau}}{1 - e^{-\hbar\omega/\tau}}$$

$$U = \langle \varepsilon \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{-\hbar\omega/\tau} - 1}$$

Now, consider a system of N simple harmonic oscillators at temperature τ.

$$z_N = \sum_{n_1, n_2, \ldots, n_N} e^{-\frac{1}{\tau}(\varepsilon_{n_1} + \varepsilon_{n_2} + \cdots + \varepsilon_{n_N})} = z^N$$

$$U = \langle \epsilon \rangle = \tau^2 \frac{\partial}{\partial \tau} \log z_N = N\tau^2 \frac{\partial}{\partial \tau} \log z = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{-\hbar\omega/\tau} - 1}$$

2.2 Reversible Processes

Definition 2.2.1. A **quasi-static process** is an idealization where parameters are changed so slowly that the system is indefinitely close to thermal and mechanical equilibrium during the process.

Definition 2.2.2. A **reversible process** is a quasi-static process where the system retraces its steps if you reverse the changes in the parameters.

Definition 2.2.3. The **pressure** of a system is defined as the negative derivative of energy with respect to volume.

$$P_n = -\left(\frac{\partial \varepsilon_n}{\partial V}\right)_\sigma$$

$$P = \langle -\frac{\partial \varepsilon_n}{\partial V} \rangle = \sum_n -\frac{\partial \varepsilon_n}{\partial V} e^{-\varepsilon_n/\tau}$$

Proposition 2.2.4. For quasi-static compression the pressure is simply the derivative of energy with respect to volume.

$$P = -\frac{\partial}{\partial V}\frac{1}{z}\sum_n \varepsilon_n e^{-\varepsilon_n/\tau} = -\left(\frac{\partial U}{\partial V}\right)_\sigma$$

2.3 Helmholtz Free Energy

Definition 2.3.1. The **Helmholtz Free Energy** F of a system is defined in terms of the energy U the entropy σ, S and the temperature τ, T.

$$F = U - \sigma\tau = U - ST$$

Proposition 2.3.2. Equilibrium in the canonical ensemble is achieved when the Helmoltz free energy F is minimized

$$\partial F = 0, \quad \Delta F \leq 0$$

Proposition 2.3.3. The entropy, pressure, and expected energy of a system in the canonical ensemble can be written in terms of the Helmholtz free energy.

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_\tau, \quad U = -\tau^2 \frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right)$$

Proposition 2.3.4. The Helmholtz free energy is determined by the temperature τ and partition function z.

$$F = -\tau \log z$$

$$z = e^{-F/\tau}$$

Definition 2.3.5. Maxwell relations are relations that are derive from the following form

$$df = A dx + B dy$$

$$\frac{\partial}{\partial y}\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}\frac{\partial f}{\partial y}$$

Proposition 2.3.6. Using Maxwell relations we can derive the following

$$\left(\frac{\partial \sigma}{\partial V}\right)_\tau = \left(\frac{\partial P}{\partial \tau}\right)_V$$

$$\left(\frac{\partial P}{\partial \sigma}\right)_V = -\left(\frac{\partial \tau}{\partial V}\right)_\sigma$$

2.4 Ideal Gas

Definition 2.4.1. The **concentration** of a system is the inverse of the volume

$$n = \frac{1}{V}$$

Definition 2.4.2. The **quantum concentration** is the density of quantum state per particle. It is used to define when a system will behave classically (when $n << n_Q$) and when a system will be dominated by quantum effects (when $n >> n_Q$).

$$n_Q = \frac{1}{\lambda_T^3}$$

Definition 2.4.3. The **DeBroglie thermal wavelength** is the wavelength of the wave functions of matter at a given temperature.

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m\tau}}$$

Definition 2.4.4. Single particle ideal gas is a system in the canonical ensemble consisting of a single particle in a box of side lengths L. The energy levels, partition function and average energy are

$$E_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

$$z_1 = \sum_{n_x,n_y,n_z} e^{\frac{-E_{n_x,n_y,n_z}}{\tau}} = \left(L\sqrt{\frac{m\tau}{\hbar^2 2\pi}}\right)^3 = \frac{V}{\lambda_T^3} = \frac{n_Q}{n} = \frac{V}{\lambda_T^3}$$

$$U_1 = \frac{3}{2}\tau$$

$$\sigma_1 = \log\left(\frac{V}{\lambda_T^3}\right) + \frac{3}{2}$$

Proposition 2.4.5. Gibbs resolution states that for systems in the classical regime the partition function for an ideal gas with N particles is

$$z_N = \frac{1}{N!}(z_1)^N$$

$$U_N = \frac{3}{2}N\tau$$

$$\sigma_N = N\left[\log\left(\frac{V}{N\lambda_T^3} + \frac{5}{2}\right)\right]$$

Law 2.4.6. Ideal gas law states that the pressure and volume are related to temperature and particle number

$$PV = N\tau$$

$$PV = Nk_BT$$

2.5 Ideal Diatomic Gas

Definition 2.5.1. Single particle diatomic gas is a system in the canonical ensemble consisting of a a single particle in a box with vibration and rotational excitation.The energy levels, partition function and average energy are

$$E_{\vec{\rho},n,\ell} = \frac{\rho^2}{2m} + (n + \frac{1}{2})\hbar\omega_{vib} + \frac{\hbar^2}{2I}\ell(\ell+1)$$

$$z_1 = \sum_{\vec{\rho},n,\ell} (2\ell+1)e^{-[E_{KE}+E_{Vib}+R_{Rot}]/\tau} = \frac{V}{\lambda_T^3} + \sum_n e^{-(n+\frac{1}{2})\hbar\omega/\tau} + \sum_\ell (2\ell+1)e^{\frac{\hbar^2\ell(\ell+1)}{2I}/\tau}$$

$$U_1 = \frac{3}{2}N\tau + \delta U_{Vib} + \delta U_{Rot}$$

$$U_1 = -\tau\log\left(\frac{V}{\lambda_T^3}\right) + \delta F_{Vib} + \delta F_{Rot}$$