

Gibbs classical statistical mechanics I

Introductory remarks

- Since matter is built of atoms, a description of macroscopic systems should be derived from a mechanics of atoms.
- The number of atoms in a macroscopic system is of order of the Avogadro number $N_A \approx 6 \cdot 10^{23}$. It greatly complicates and simplifies the problem at the same time.
- A macroscopic description of a gas should be obtained through characteristics of individual atoms averaged over microscopically long interval of time τ .
- If $\mathbf{r}(t) \equiv \{\mathbf{r}_1(t), \mathbf{r}_2(t), \dots, \mathbf{r}_N(t)\}$ and $\mathbf{p}(t) \equiv \{\mathbf{p}_1(t), \mathbf{p}_2(t), \dots, \mathbf{p}_N(t)\}$ are positions and momenta of all atoms of a gas, the aim of statistical mechanics is to get

$$\langle A(t) \rangle \equiv \frac{1}{\tau} \int_t^{t+\tau} dt' A(\mathbf{r}(t'), \mathbf{p}(t')), \quad (1)$$

where $A(\mathbf{r}(t), \mathbf{p}(t))$ is a gas characteristics.

- The ergodic hypothesis: all accessible microstates of a given system are equiprobable over a long period of time. Consequently, the average of A over a long time equals the average over ensemble of microscopic states of a system

$$\frac{1}{\tau} \int_t^{t+\tau} dt' A(\mathbf{r}(t'), \mathbf{p}(t')) = \frac{\int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \rho(\mathbf{r}, \mathbf{p}) A(\mathbf{r}, \mathbf{p})}{\int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \rho(\mathbf{r}, \mathbf{p})}, \quad (2)$$

where $d^{3N}r \equiv d^3r_1 d^3r_2 \dots d^3r_N$, $\frac{d^{3N}p}{(2\pi\hbar)^{3N}} \equiv \frac{d^3p_1}{(2\pi\hbar)^3} \frac{d^3p_2}{(2\pi\hbar)^3} \dots \frac{d^3p_N}{(2\pi\hbar)^3}$; (\mathbf{r}, \mathbf{p}) is a microscopic state of the system of a given, say, energy and volume; $\rho(\mathbf{r}, \mathbf{p})$ is a density of states. The Planck constant $\hbar \equiv \frac{h}{2\pi}$ is introduced to keep the phase-space element $d^3r \frac{d^3p}{(2\pi\hbar)^3}$ dimensionless.

- The ergodic hypothesis is a pillar of the statistical mechanics formulated by Josiah Willard Gibbs (1839 - 1903) around 1875.

Microcanonical ensemble

- Microcanonical ensemble is a set of microscopic states of an isolated system. The states are uniformly distributed in a phase space that is $\rho(\mathbf{r}, \mathbf{p}) = \text{const.}$. The actual value is meaningless, see Eq. (2), so we choose $\rho(\mathbf{r}, \mathbf{p}) = 1$. This is the postulate of equal a priori probabilities.
- The term 'probability' is somewhat misleading as we deal here with classical deterministic system.
- The postulate of equal a priori probabilities should not be confused with the Liouville theorem.
- The phase-space (dimensionless) volume:

$$\Gamma_N(U, V) \equiv \int_{U \leq \mathcal{H} \leq U + \delta U} d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}}, \quad (3)$$

where $\mathcal{H}(\mathbf{r}, \mathbf{p})$ is the system Hamilton function.

- $\Gamma_N(U, V)$ can be written as

$$\Gamma_N(U, V) = \int \exp \left[-\frac{(U - \mathcal{H})^2}{2(\delta U)^2} \right] d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}}. \quad (4)$$

- Since

$$\frac{1}{\sqrt{2\pi} \delta U} \exp \left[-\frac{(U - \mathcal{H})^2}{2(\delta U)^2} \right] \xrightarrow{\delta U \rightarrow 0} \delta(U - \mathcal{H}), \quad (5)$$

we have

$$\Gamma_N(U, V) \equiv \delta U \int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \delta(U - \mathcal{H}(\mathbf{r}, \mathbf{p})). \quad (6)$$

The extra factor $1/\sqrt{2\pi}$ is ignored.

- The relation to thermodynamics is established through the relation

$$S(U, V) \equiv k_B \ln \Gamma_N(U, V), \quad (7)$$

where $k_B = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$ is the Boltzmann constant. $[S] = \frac{\text{J}}{\text{K}}$.

- Below I show that the entropy (7) is like the entropy in thermodynamics that it is extensive and consistent with the thermodynamical identity

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V, \quad (8)$$

which follows from $dS = dQ/T = (dU + pdV)/T$.

- To show that the entropy (7) is extensive I divide the system into two subsystems

$$N = N_a + N_b, \quad V = V_a + V_b, \quad \mathcal{H} = \mathcal{H}_a + \mathcal{H}_b. \quad (9)$$

Then,

$$\Gamma_N(U, V) = \frac{1}{\delta U} \int_0^U dU_a \Gamma_{N_a}(U_a, V_a) \Gamma_{N_b}(U - U_a, V_b). \quad (10)$$

Substituting $\Gamma_N(U, V)$ of the form (6) into Eq. (10), one gets Eq. (6) after taking the integral over U_a .

- Let $U_a = \bar{U}_a$ is the energy of the subsystem a when the integrand is maximal. Then, we easily find the upper and the lower estimates of the integral (10) as

$$\Gamma_{N_a}(\bar{U}_a, V_a) \Gamma_{N_b}(\bar{U}_b, V_b) \leq \Gamma_N(U, V) \leq \frac{U}{\delta U} \Gamma_{N_a}(\bar{U}_a, V_a) \Gamma_{N_b}(\bar{U}_b, V_b), \quad (11)$$

where $\bar{U}_b \equiv U - \bar{U}_a$. Taking the logarithm of the equalities (11), one finds

$$S_a(\bar{U}_a, V_a) + S_b(\bar{U}_b, V_b) \leq S(U, V) \leq S_a(\bar{U}_a, V_a) + S_b(\bar{U}_b, V_b) + k_B \ln \frac{U}{\delta U}. \quad (12)$$

One observes that $U/\delta U \sim N$ and consequently, the the difference of the upper and lower estimates is of the order $k_B \ln N$ while $S(U, V) \equiv k_B \ln \Gamma_N(U, V) \sim k_B N$ because it is $6N$ -dimensional volume (it will be explicitly shown in case of ideal gas). Since $N \gg \ln N$ for $N \gg 1$, we get the approximate equality

$$S(U, V) = S_a(\bar{U}_a, V_a) + S_b(\bar{U}_b, V_b), \quad (13)$$

which shows an extensive character of the entropy defined by Eq. (7).



Figure 1: Boltzmann's grave in the Zentralfriedhof, Vienna

- Once $U_a = \bar{U}_a$ is the energy of the subsystem a when the integrand (10) is maximal, we have

$$\left. \frac{\partial}{\partial U_a} \Gamma_{N_a}(U_a, V_a) \Gamma_{N_b}(U - U_a, V_b) \right|_{U_a = \bar{U}_a} = 0. \quad (14)$$

Computing the derivative, the condition (14) reads

$$\frac{1}{\Gamma_{N_a}(\bar{U}_a, V_a)} \frac{\partial \Gamma_{N_a}(\bar{U}_a, V_a)}{\partial \bar{U}_a} = \frac{1}{\Gamma_{N_b}(\bar{U}_b, V_b)} \frac{\partial \Gamma_{N_b}(\bar{U}_b, V_b)}{\partial \bar{U}_b}, \quad (15)$$

or

$$\frac{\partial S(\bar{U}_a, V_a)}{\partial \bar{U}_a} = \frac{\partial S(\bar{U}_b, V_b)}{\partial \bar{U}_b}, \quad (16)$$

which according to the identity (8) gives $T_a = T_b$. As expected, the two subsystems are in a mutual equilibrium if they have the same temperature.

Ideal gas

- Energy of ideal gas is by definition dominated by the kinetic energy and

$$\mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}. \quad (17)$$

- Substituting the Hamilton function (17) into the formula (6), one gets

$$\Gamma_N(U, V) = \delta U V^N \int \frac{d^3 p_1}{(2\pi\hbar)^3} \frac{d^3 p_2}{(2\pi\hbar)^3} \cdots \frac{d^3 p_N}{(2\pi\hbar)^3} \delta\left(U - \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}\right), \quad (18)$$

where the trivial integrations over particles' positions are performed. Each integration provides the factor V .

- To get rid of the Dirac's delta we perform the Laplace transform with respect of U

$$\Gamma_N(\beta, V) = \int_0^\infty dU e^{-\beta U} \Gamma_N(U, V), \quad (19)$$

which gives

$$\Gamma_N(\beta, V) = \delta U V^N \int \frac{d^3 p_1}{(2\pi\hbar)^3} \frac{d^3 p_2}{(2\pi\hbar)^3} \cdots \frac{d^3 p_N}{(2\pi\hbar)^3} \exp\left(-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}\right). \quad (20)$$

The momentum integrals factorize

$$\Gamma_N(\beta, V) = \delta U V^N \left[\int_{-\infty}^{\infty} \frac{dp_x}{2\pi\hbar} \exp\left(-\frac{\beta}{2m} p_x^2\right) \right]^{3N}, \quad (21)$$

and are easily computed as

$$\Gamma_N(\beta, V) = \delta U V^N \left[\frac{m}{2\pi\beta\hbar^2} \right]^{\frac{3N}{2}}, \quad (22)$$

using

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}. \quad (23)$$

- To perform the inverse Laplace transform I use the formula

$$\int_0^\infty dU e^{-\beta U} U^\nu = \frac{\Gamma(\nu + 1)}{\beta^{\nu+1}}, \quad (24)$$

where $0 \leq \nu \in \mathbb{R}$ and $\Gamma(x)$ is the Gamma function. For integer arguments $\Gamma(n) = (n-1)!$. Using the formula (24) with $\nu = \frac{3N}{2} - 1$, one gets

$$\Gamma_N(U, V) = \delta U V^N \left[\frac{m}{2\pi\hbar^2} \right]^{\frac{3N}{2}} \frac{U^{\frac{3N}{2}-1}}{\Gamma\left(\frac{3N}{2}\right)}. \quad (25)$$

- With the rough estimate $\Gamma(x) \approx x^x$ for $x \gg 1$, we find

$$\Gamma_N(U, V) = \frac{\delta U}{U} \left[V \left(\frac{m}{3\pi\hbar^2} \frac{U}{N} \right)^{3/2} \right]^N, \quad (26)$$

and

$$S(U, V) = Nk_B \ln \left[V \left(\frac{m}{3\pi\hbar^2} \frac{U}{N} \right)^{3/2} \right], \quad (27)$$

where I neglected the term $\ln \frac{\delta U}{U}$ which is of the order $k_B \ln N$. The argument of the logarithm function is dimensionless as it should.

- Using the relation (8), one finds

$$\frac{1}{T} = \frac{3Nk_B}{2U}, \quad (28)$$

which gives the famous formula

$$U = \frac{3}{2} Nk_B T. \quad (29)$$

- The ideal-gas pressure is found from the relation

$$p \equiv T \left(\frac{\partial S}{\partial V} \right)_U, \quad (30)$$

which follows from $dS = dQ/T = (dU + pdV)/T$. The relation provides the well-known equation of state

$$pV = Nk_B T. \quad (31)$$

Gibbs paradox

- Let us perform a thought experiment. We divide the gas system into two parts

$$N = N_1 + N_2, \quad V = V_1 + V_2, \quad U = U_1 + U_2, \quad (32)$$

such that

$$\frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}, \quad \frac{U}{N} = \frac{U_1}{N_1} = \frac{U_2}{N_2}. \quad (33)$$

- One expects that

$$S(U, V) = S_1(U_1, V_1) + S_2(U_2, V_2), \quad (34)$$

but using (27), the equality (34) does not hold because

$$N \ln V \neq N_1 \ln V_1 + N_2 \ln V_2. \quad (35)$$

(Check it choosing $N_1 = N_2 = N/2$ and $V_1 = V_2 = V/2$.)

- The problem we encountered is known as the Gibbs paradox – unexpected entropy growth due to a gas mixing.
- The solution is to divide the phase-space volume (3) or (6) by $N!$ to avoid taking into account repeatedly the microstates which merely differ by interchange of pairs of identical particles. Gibbs guessed the principle of indistinguishability of identical particles long before the quantum mechanics was born.
- With the extra factor $1/N!$ approximated as N^{-N} in Eq. (6), one gets instead of the formula (27) the expression

$$S(U, V) = Nk_B \ln \left[\frac{V}{N} \left(\frac{m}{3\pi\hbar^2} \frac{U}{N} \right)^{3/2} \right], \quad (36)$$

which satisfies the equality (34), if the conditions (32, 33) hold. The results on the energy and pressure remain unchanged.

- There is a subtle issue how to prove Eq. (13) with Γ_N divided by $N!$.

Canonical ensemble

The microcanonical ensemble is applicable to isolated systems. When a system is in a thermal contact with a thermostat and consequently its temperature but not energy is fixed, the canonical ensemble is more relevant.

- We derive the density of microstates in the canonical ensemble of considering a small subsystem (labeled with the index 1) of an isolated system. Then, the particle numbers and Hamilton function are

$$N = N_1 + N_2, \quad \mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2, \quad (37)$$

and

$$N_1 \ll N_2, \quad \mathcal{H}_1 \ll \mathcal{H}_2. \quad (38)$$

- The observation of crucial importance is

$$\rho(\mathbf{r}_1, \mathbf{p}_1) \sim \Gamma_{N_2}(U - U_1). \quad (39)$$

Since

$$S(U, V) \equiv k_B \ln \Gamma_N(U, V), \quad (40)$$

the relation (39) reads

$$\rho(\mathbf{r}_1, \mathbf{p}_1) \sim \exp \left[\frac{1}{k_B} S_2(U - U_1, V_2) \right]. \quad (41)$$

Because $U \gg U_1$, we expand $S_2(U - U_1, V_2)$ in the Taylor series

$$S_2(U - U_1, V_2) = S_2(U, V_2) - \frac{\partial S_2(U, V_2)}{\partial U} U_1, \quad (42)$$

which gives

$$\rho(\mathbf{r}_1, \mathbf{p}_1) \sim \exp \left[\frac{1}{k_B} S(U, V) \right] \exp \left[- \frac{U_1}{k_B T} \right], \quad (43)$$

due to the identity

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V. \quad (44)$$

- The density of microstates in the canonical ensemble is chosen as

$$\rho(\mathbf{r}, \mathbf{p}) = \exp \left[- \frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{k_B T} \right], \quad (45)$$

where the indices 1 and 2 are suppressed.

- The partition function is defined as

$$Q_N(T, V) \equiv \frac{1}{N!} \int d^3r \frac{d^3p}{(2\pi\hbar)^3} \exp \left[- \frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{k_B T} \right], \quad (46)$$

where $d^3r \equiv d^3r_1 d^3r_2 \dots d^3r_N$, $\frac{d^3p}{(2\pi\hbar)^3} \equiv \frac{d^3p_1}{(2\pi\hbar)^3} \frac{d^3p_2}{(2\pi\hbar)^3} \dots \frac{d^3p_N}{(2\pi\hbar)^3}$. The factor $\frac{1}{N!}$ is introduced following the Gibbs recipe. Up to the factor δU , the partition function is the Laplace transform of the phase-space volume $\Gamma_N(U, V)$.

- The relation with thermodynamics is established by means of the formulas

$$U(T, V) \equiv \langle \mathcal{H} \rangle \equiv \frac{1}{Q_N(V, T)} \frac{1}{N!} \int d^3r \frac{d^3p}{(2\pi\hbar)^3} \mathcal{H}(\mathbf{r}, \mathbf{p}) \exp \left[-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{k_B T} \right], \quad (47)$$

$$F(T, V) \equiv -k_B T \ln Q_N(T, V). \quad (48)$$

The first formula is evident. In case of the second one we show that (48) is consistent with the thermodynamical identity

$$F = U - TS. \quad (49)$$

Observing that Eq. (47) can be written as

$$U \equiv \langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln Q_N, \quad (50)$$

where $\beta \equiv \frac{1}{k_B T}$, we get

$$U = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right)_V = F - T \left(\frac{\partial F}{\partial T} \right)_V, \quad (51)$$

where Eq. (48) has been used. Due to the identity

$$S = -\left(\frac{\partial F}{\partial T} \right)_V, \quad (52)$$

the equality (51) becomes equivalent to the relation (49).

Ideal gas

- The partition function is easily computed as

$$Q_N(T, V) = \frac{V^N}{N!} \left[\int_{-\infty}^{\infty} \frac{dp_x}{2\pi\hbar} \exp \left(-\frac{p_x^2}{2mk_B T} \right) \right]^{3N} = \left(\frac{V}{N} \right)^N \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3N}{2}}, \quad (53)$$

where $N! \approx N^N$.

- According to Eq. (48), the free energy equals

$$F(T, V) = -Nk_B T \ln \left[\frac{V}{N} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right]. \quad (54)$$

- By means of the relation (51), one finds

$$U = \frac{3}{2} Nk_B T. \quad (55)$$

- The pressure is found via

$$p = -\left(\frac{\partial F}{\partial V} \right)_T, \quad (56)$$

and

$$pV = Nk_B T. \quad (57)$$

- The entropy provided by Eq. (52) is

$$S(T, V) = Nk_B \ln \left[\frac{V}{N} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} Nk_B. \quad (58)$$

Energy fluctuations

- While the system's energy is fixed in the microcanonical ensemble, the energy can fluctuate in the canonical ensemble but the temperature is fixed. How big are the energy fluctuations? When the two ensembles are equivalent?
- The energy fluctuation δU is defined as

$$(\delta U)^2 \equiv \langle (\mathcal{H} - \langle \mathcal{H} \rangle)^2 \rangle = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2. \quad (59)$$

- We already know that

$$\langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln Q_N = U, \quad (60)$$

where $\beta \equiv \frac{1}{k_B T}$, and one observes that

$$\langle \mathcal{H}^2 \rangle = \frac{1}{Q_N} \frac{\partial^2 Q_N}{\partial \beta^2}, \quad (61)$$

which gives

$$\langle \mathcal{H}^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln Q_N + \left(\frac{\partial}{\partial \beta} \ln Q_N \right)^2. \quad (62)$$

Since

$$\frac{\partial^2}{\partial \beta^2} \ln Q_N = -\frac{\partial U}{\partial \beta} = k_B T^2 \left(\frac{\partial U}{\partial T} \right)_V = k_B T^2 C_V, \quad (63)$$

where C_V is the heat capacity at fixed volume we finally get

$$\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = k_B T^2 C_V. \quad (64)$$

- Let us estimate the quantities which enter Eq. (64). One sees that $\langle \mathcal{H}^2 \rangle \sim N^2$ and $\langle \mathcal{H} \rangle^2 \sim N^2$ but $C_V \sim N$. Consequently $\delta U \sim \sqrt{N}$. Since $N^2 \gg N \gg \sqrt{N}$ for $N \gg 1$, the energy fluctuation is much smaller than the energy itself, as long as C_V is finite. The canonical ensemble is then equivalent to the microcanonical one.
- The heat capacity is sometimes infinite as in second order phase transitions. The two ensembles are then no longer equivalent to each other.