

Matteo Zandi

Theoretical Physics

On statistical mechanics:

ensemble and all that

October 21, 2023

Study notes taken during the master degree

Contents

	Page
Contents	ii
I Classical statistical mechanics	1
1 Classical mechanics	2
2 Microcanonical ensemble	3
2.1 Thermodynamics potentials	4
3 Canonical ensemble	7
3.1 Thermodynamics variable	10
3.2 Equipartition theorem	11
List of Theorems	13

Part I

Classical statistical mechanics

Chapter 1

Classical mechanics

$$\int_{\mathcal{M}^N} \rho = 1 \tag{1.1}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{1.2}$$

$$\frac{\partial F}{\partial T} = -S \tag{1.3}$$

Chapter 2

Microcanonical ensemble

A microcanonical ensemble is a system which is isolated from the environment, i.e. it cannot exchange neither energy nor matter, so E , N and V are fixed. Since energy is conserved and the hamiltonian is time-independent, the trajectory of motion is restricted on the surface S_E and not on all the phase space.

Assume an a-priory uniform probability

$$\rho_{mc}(q^i, p_i) = C\delta(\mathcal{H}(q^i, p_i) - E)$$

where C is a normalisation constant, which can be evaluated by (1.1)

$$1 = \int_{\mathcal{M}^N} d\Omega \rho_{mc} = \int_{\mathcal{M}^N} d\Omega C\delta(\mathcal{H} - E) = C \int_{\mathcal{M}^N} d\Omega \delta(\mathcal{H} - E) = C\omega(E)$$

Hence

$$\rho_{mc}(q^i, p_i) = \frac{1}{\omega(E)}\delta(\mathcal{H}(q^i, p_i) - E)$$

Consider a displacement on an infinitesimal displacement of energy $\Delta E \ll 1$, then

$$\Gamma(E) = \int_E^{E+\Delta E} dE' \omega(E') \simeq \omega(E)\Delta E$$

and the distribution is

$$\rho_{mc}(q^i, p_i) = \begin{cases} \frac{1}{\Gamma(E)} & \mathcal{H} \in [E, E + \Delta E] \\ 0 & otherwise \end{cases}$$

Let $f(q^i, p_i)$ be an observable, then its microcanonical average is

$$\langle f(q^i, p_i) \rangle_{mc} = \int_{\mathcal{M}} d\Omega \rho_{mc} f = \int_{\mathcal{M}} d\Omega \frac{1}{\omega(E)}\delta(\mathcal{H} - E)f = \frac{1}{\omega(E)} \int_{S_E} dS_E f = \langle f \rangle_E \quad (2.1)$$

2.1 Thermodynamics potentials

The microcanonical entropy S_{mc} is defined by

$$S_{mc}(E, V, N) = k_B \ln \omega(E)$$

The logarithm is justified by the fact that the volume of a N-particle phase space is $(W_1)^N$, where W_1 is the volume of a single particle phase space. According to the properties of the logarithm, entropy becomes extensive.

In the thermodynamic limit, the following equations hold

$$s_{mc} = \lim_{td} \frac{S_{mc}}{N} = k_B \lim_{td} \frac{\log \omega(E)}{N} = k_B \underbrace{\lim_{td} \frac{\log \Sigma(E)}{N}}_{\mathcal{H} \in [0, E]} = k_B \underbrace{\lim_{td} \frac{\log \Gamma(E)}{N}}_{\mathcal{H} \in [E, E + \Delta E]}$$

Entropy is additive, so given two systems 1 and 2

$$s_{mc}^{tot} = s_{mc}^{(1)} + s_{mc}^{(2)}$$

Proof. Consider two isolated systems in contact at equilibrium with the same temperature $T = T_1 = T_2$. The total energy is $E = E_1 + E_2 + E_{surface}$ but, in the thermodynamic limit, the energy exchanged by the surface is a subleading term (E_1 and E_2 go as L^3 whereas $E_{surface}$ goes as L^2) and can be neglected. The energy density is

$$\begin{aligned} \omega(E) &= \int_{\mathcal{M}^N} d\Gamma_1 d\Gamma_2 \delta(\mathcal{H} - E) \\ &= \int dE_1 \int dS_{E_1} \int dE_2 \int dS_{E_2} \delta(E - E_1 - E_2) \\ &= \int dE_1 \int dE_2 \omega_1(E_1) \omega_2(E_2) \delta(E - E_1 - E_2) \\ &= \int_0^E dE_1 \omega_1(E_1) \omega_2(E_2 = E - E_1) \end{aligned}$$

Since the integrand is a positive function with a maximum in $E_1 \in [0, E]$

$$\begin{aligned} \int_0^E dE_1 \omega_1(E_1) \omega_2(E_2 = E - E_1) &\leq \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) \int_0^E dE_1 \\ &= \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) E \end{aligned} \quad (2.2)$$

On the other hand, it is always possible to find a value for ΔE in order to have

$$\Delta E \omega_1(E_1^*) \omega_2(E_2^*) \leq \omega(E) \quad (2.3)$$

Putting together (2.2) and (2.3)

$$\Delta E \omega_1(E_1^*) \omega_2(E_2^*) \leq \omega(E) \leq \omega_1(E_1^*) \omega_2(E_2^*) E$$

$$\omega_1(E_1^*)\Delta E\omega_2(E_2^*)\Delta E \leq \omega(E)\Delta E \leq \frac{E}{\Delta E}\omega_1(E_1^*)\Delta E\omega_2(E_2^*)\Delta E$$

$$\Gamma_1(E_1^*)\Gamma(E_2^*) \leq \Gamma(E) \leq \frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)$$

Since the logarithm is a monotonic function

$$\log\left(\Gamma_1(E_1^*)\Gamma(E_2^*)\right) \leq \log \Gamma(E) \leq \log\left(\frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)\right)$$

$$k_B \log\left(\Gamma_1(E_1^*)\Gamma(E_2^*)\right) \leq k_B \log \Gamma(E) \leq k_B \log\left(\frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)\right)$$

$$k_B \log \Gamma_1(E_1^*) + k_B \log \Gamma(E_2^*) \leq k_B \log \Gamma(E) \leq k_B \log \frac{E}{\Delta E} + k_B \log \Gamma(E_1^*) + k_B \log \Gamma(E_2^*)$$

$$\frac{k_B \log \Gamma_1(E_1^*) + k_B \log \Gamma(E_2^*)}{N} \leq \frac{k_B \log \Gamma(E)}{N} \leq \frac{k_B \log \frac{E}{\Delta E} + k_B \log \Gamma(E_1^*) + k_B \log \Gamma(E_2^*)}{N}$$

In the thermodynamic limit, the last term vanishes, since $\lim_{td} \frac{1}{N} \log \frac{N}{\Delta N} = 0$. Hence

$$s_{mc}(E) = s_{mc}^{(1)} + s_{mc}^{(2)}$$

q.e.d.

The last result tells also that at equilibrium entropy is maximum.

In the thermodynamic limit, microcanonical entropy coincides with the thermodynamical one

$$s_{mc} = s_{td}$$

Proof. Since entropy is maximum at equilibrium, also $\Gamma_1(E_1)\Gamma_2(E_2)$ is so and

$$\begin{aligned} 0 &= \delta(\Gamma_1(E_1^*)\Gamma_2(E_2^* = E - E_1^*)) \\ &= \delta\Gamma_1(E_1^*)\Gamma_2(E_2^*) + \Gamma_1(E_1^*)\delta\Gamma_2(E_2^*) \\ &= \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \delta E_1 \Gamma_2(E_2^*) + \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \delta E_2 \end{aligned}$$

Since $E = \text{const}$, $0 = \delta E = \delta E_1 + \delta E_2$, $\delta E_2 = -\delta E_1$ and

$$\begin{aligned} 0 &= \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \delta E_1 \Gamma_2(E_2^*) - \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \delta E_1 \\ 0 &= \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \Gamma_2(E_2^*) - \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \\ \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} \Gamma_2(E_2^*) &= \Gamma_1(E_1^*) \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \\ \frac{1}{\Gamma_1(E_1^*)} \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} &= \frac{1}{\Gamma_2(E_2^*)} \frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*} \end{aligned}$$

$$\left. \frac{\partial \log \Gamma_1}{\partial E_1} \right|_{E_1^*} = \left. \frac{\partial \log \Gamma_2}{\partial E_2} \right|_{E_2^*}$$

Using the thermodynamical relation (1.2)

$$S_{mc}(E) = S_{td}(E) \times \text{const}$$

where the constant can be chosen in order to have k_B in the same unit. q.e.d.

The universal Boltzmann's formula is

$$s_{mc} = s_{td} = k_B \log \omega(E) = -k_B \langle \log \rho_{mc} \rangle_{mc}$$

Proof. Using (2.1),

$$\begin{aligned} \langle \log \rho_{mc} \rangle_{mc} &= \int d\Gamma \rho_{mc} \log \rho_{mc} \\ &= \int d\Gamma \frac{1}{\omega(E)} \delta(\mathcal{H} - E) \log \left(\frac{1}{\omega(E)} \delta(\mathcal{H} - E) \right) \\ &= \int dS_E \frac{1}{\omega(E)} \log \frac{1}{\omega(E)} \\ &= -\frac{1}{\omega(E)} \log \omega(E) \int dS_E \\ &= -\log \omega(E) \end{aligned}$$

q.e.d.

Chapter 3

Canonical ensemble

A canonical ensemble is a system which is immersed in a bigger environment or reservoir, which can exchange energy but not matter, so T , N and V are fixed. Globally, energy is conserved, since the universe composed by the union of the system and the environment can be considered as a microcanonical ensemble.

The canonical probability density distribution is

$$\rho_c(q^i, p_i) = \frac{1}{Z_N} \exp(-\beta \mathcal{H}(q^i, p_i))$$

where β is

$$\beta = \frac{1}{k_B T}$$

and Z_N is the partition function

$$Z_N[V, T] = \int_{\mathcal{M}^N} d\Omega \exp(-\beta \mathcal{H}(q^i, p_i)) \quad (3.1)$$

which depends on the temperature through β and volume and temperature due to the integration domain $\mathcal{M}^N = V \otimes \mathbb{R}^d$.

Notice that the probability is a function of the hamiltonian, like Liouville's theorem said.

Proof. Consider the universe as a microcanonical ensemble. Its probability density distribution is

$$\rho_{mc}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \frac{1}{\omega(E)} \delta(\mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) - E)$$

where the total hamiltonian is

$$\mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \mathcal{H}_1(q_i^{(1)}, p_i^{(1)}) + \mathcal{H}_2(q_i^{(2)}, p_i^{(2)})$$

Integrating it to all the possible state in the environment

$$\rho^{(1)} = \int d\Omega_2 \rho_{mc} = \int d\Omega_2 \frac{1}{\omega(E)} \delta(\mathcal{H} - E) = \frac{1}{\omega(E)} \int dS_{E_2} = \frac{1}{\omega(E)} \omega(E_2 = E - E_1)$$

and the corresponding entropy is

$$S_2(E_2) = k_B \ln \omega_2(E_2)$$

Applying small variation δE_1 to E_1 to preserve equilibrium, the entropy transforms, using (1.2)

$$k_B \ln \omega_2(E_2) = S_{mc}(E) - E_1 \left. \frac{\partial S_{mc}}{\partial E} \right|_{E_2} = S_{mc}(E) - E_1 \frac{1}{T}$$

$$\ln \omega_2(E_2) = \frac{S_{mc}(E)}{k_B} - E_1 \frac{1}{k_B T}$$

$$\omega_2(E_2) = \exp\left(\frac{S_{mc}(E)}{k_B} - E_1 \frac{1}{k_B T}\right) = \exp\left(\frac{S_{mc}(E)}{k_B}\right) \exp\left(-\frac{E_1}{k_B T}\right)$$

Putting together, dropping the indices

$$\rho_c = \frac{\omega(2)(E_2)}{\omega(E)} = \frac{1}{\omega(E)} \exp\left(\frac{S_{mc}(E)}{k_B}\right) \exp\left(-\frac{E_1}{k_B T}\right) = C \exp\left(-\frac{E_1}{k_B T}\right) \quad (3.2)$$

where C is a normalisation constant, which can be evaluated by (1.1)

$$1 = \int_{\mathcal{M}^N} d\Omega \rho = \int_{\mathcal{M}^N} d\Omega C \exp\left(-\frac{E_1}{k_B T}\right) = C \int_{\mathcal{M}^N} d\Omega \exp\left(-\frac{E_1}{k_B T}\right)$$

q.e.d.

The partition function can also be written as

$$Z_N[T, V] = \int_0^\infty dE \omega(E) \exp(-\beta E)$$

Proof. Foliating the phase space in energy hyper-surfaces

$$Z_N = \int_{\mathcal{M}^N} d\Omega \exp(-\beta \mathcal{H}) = \int_0^\infty dE \int dS_E \exp(-\beta \mathcal{H}) = \int_0^\infty dE \omega(E) \exp(-\beta E)$$

q.e.d.

Taking also in consideration indistinguishable particles, the partition function

$$Z_N = \int \frac{\prod_{i=1}^N d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \mathcal{H})$$

where ζ_N is

$$\zeta_N = \begin{cases} 1 & \text{distinguishable} \\ N! & \text{indistinguishable} \end{cases}$$

The partition function of two systems is the multiplication of the single system ones

$$Z_N = Z_{N_1} Z_{N_2} \quad (3.3)$$

Proof. Since $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$,

q.e.d.

If the hamiltonian is the sum of N identical ones, like N non-interacting particles

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i$$

the partition function becomes

$$Z_N = \frac{(Z_1)^N}{\zeta_N}$$

Proof. Denominating Z_1 the single-particle partition function

$$\begin{aligned} Z_N &= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \dots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \mathcal{H}) \\ &= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \dots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \sum_{i=1}^N \mathcal{H}_i) \\ &= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \dots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \prod_{i=1}^N \exp(-\beta \mathcal{H}_i) \\ &= \int_{\mathcal{M}^N = \mathcal{M}^{(1)} \otimes \dots \otimes \mathcal{M}^{(1)}} \prod_{i=1}^N \frac{d^d q^i d^d p^i}{h^{dN} \zeta_N} \exp(-\beta \mathcal{H}_i) \\ &= \frac{Z_1 Z_1 \dots Z_1}{\zeta_N} = \frac{(Z_1)^N}{\zeta_N} \end{aligned}$$

q.e.d.

Let $f(q^i, p_i)$ be an observable, then its canonical average is

$$\langle f(q^i, p_i) \rangle_c = \int_{\mathcal{M}} d\Omega \rho_c f = \int_{\mathcal{M}} d\Omega \frac{\exp(-\beta \mathcal{H})}{Z_N} f$$

3.1 Thermodynamics variable

The canonical Helmotz free energy F is defined by

$$Z[V, T] = \exp(-\beta F[N, V, T])$$

or, equivalently,

$$F[V, N, T] = -\frac{1}{\beta} \ln Z_N \quad (3.4)$$

Furthermore, the canonical internal energy is

$$E = \langle \mathcal{H} \rangle_c = \int d\Omega \frac{\exp(-\beta(\mathcal{H}))}{Z_N} \mathcal{H} \quad (3.5)$$

Proof. By normalisation condition

$$1 = \int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N} = \int d\Omega \frac{\exp(-\beta\mathcal{H})}{\exp(-\beta F)} = \int d\Omega \exp(-\beta(\mathcal{H} - F))$$

Since F depends on the temperature, it is possible to derive with respect to β

$$\begin{aligned} 0 &= \frac{\partial}{\partial \beta} \left(\int d\Omega \exp(-\beta(\mathcal{H} - F)) \right) \\ &= \int d\Omega \exp(-\beta(\mathcal{H} - F)) \left(-(\mathcal{H} - F) + \beta \frac{\partial F}{\partial \beta} \right) \\ &= - \underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N} \mathcal{H}}_E + F \underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}}_1 + \beta \frac{\partial F}{\partial \beta} \underbrace{\int d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N}}_1 \\ &= -E + F + \beta \frac{\partial F}{\partial \beta} \end{aligned}$$

Hence, using (1.3)

$$F = E + \beta \frac{\partial F}{\partial \beta} = E + T \frac{\partial F}{\partial T} = E - TS$$

showing that is indeed the Helmotz free energy.

q.e.d.

Notice that in the last result, the entropy can be also written as

$$S_c = \frac{E - F}{T} \quad (3.6)$$

The internal energy can also be written as

$$E = -\frac{\partial}{\partial \beta} \ln Z_N$$

Proof. Using (3.5),

$$-\frac{\partial}{\partial \beta} \ln Z_N = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\frac{1}{Z_N} \frac{\partial}{\partial \beta} \int d\Omega \exp(-\beta \mathcal{H}) = \int d\Omega \frac{\exp(-\beta \mathcal{H})}{Z_N} \mathcal{H} = \langle \mathcal{H} \rangle_c = E$$

q.e.d.

The universal Boltzmann's formula is still valid

$$S_c = -k_B \langle \ln \rho_c \rangle_c$$

Proof. Using (3.5) and (3.4)

$$\begin{aligned} -k_B \langle \ln \rho_c \rangle_c &= -k_B \int d\Omega \rho_c \ln \rho_c \\ &= -k_B \int d\Omega \rho_c \ln \frac{\exp(-\beta \mathcal{H})}{Z_N} \\ &= -k_B \int d\Omega \rho_c \ln \exp(-\beta \mathcal{H}) - k_B \int d\Omega \rho_c \ln Z_N \\ &= k_B \int d\Omega \beta \mathcal{H} - k_B \underbrace{\ln Z_N}_{\beta F} \underbrace{\int d\Omega \rho_c}_1 \\ &= \frac{E - F}{T} = S_c \end{aligned}$$

q.e.d.

3.2 Equipartition theorem

Theorem 3.1 (Generalised equipartition theorem)

Let $\xi \in [a, b]$ and ξ_j with $j \neq 1$ all the other coordinates or momenta. Suppose also

$$\int \prod_{j \neq 1} d\xi_j [\xi_1 \exp(-\beta \mathcal{H})]_a^b = 0 \quad (3.7)$$

Then

$$\langle \xi_1 \frac{\partial \mathcal{H}}{\partial \xi_1} \rangle_c = k_B T$$

Proof. By normalisation condition

$$1 = \int d\Omega \frac{\exp(-\beta \mathcal{H})}{Z_N} = \frac{1}{Z_N} \int \prod_{j \neq 1} d\xi_j \exp(-\beta \mathcal{H})$$

Using

$$d\xi_1(\xi_1 \exp(-\beta\mathcal{H})) = d\xi_1 \exp(-\beta\mathcal{H}) + \xi_1 \exp(-\beta\mathcal{H})(-\beta) \frac{\partial\mathcal{H}}{\partial\xi_1} d\xi_1$$

and integrating per parts

$$\begin{aligned} 1 &= \frac{1}{Z_N} \int \underbrace{\prod_{j \neq 1} d\xi_j [\xi_1 \exp(-\beta\mathcal{H})]_a^b}_0 + \frac{\beta}{Z_N} \int \prod_{j \neq 1} d\xi_j d\xi_1 \xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1} \exp(-\beta\mathcal{H}) \\ &= \beta \int d\Omega_{\xi_1} \frac{\partial\mathcal{H}}{\partial\xi_1} \frac{\exp(-\beta\mathcal{H})}{Z_N} \\ &= \beta \langle \xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1} \rangle_c \end{aligned}$$

Hence

$$\langle \xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1} \rangle_c = \frac{1}{\beta} = k_B T$$

q.e.d.

Examples of system that satisfies the condition (3.7) are hamiltonians which depend on the square of momentum or confining potentials which go to infinity on the extremes a and b .

List of Theorems

3.1 Theorem (Generalised equipartition theorem)	11
---	----