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On Statistical Mechanics:

Classical and Quantum

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Theoretical Physics

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Part I

Thermodynamics

Chapter 1

Laws of Thermodynamics

1.1 The laws of Thermodynamics

In this chapter, we will recall some notions of Thermodynamics.

In Thermodynamics, a state is defined by a set of macroscopic quantities, called thermodynamical variables. They can be divided into two groups, one conjugate to the other, according to their behaviour when the physical system is rescaled, i.e. when the volume and the number of particles change: extensive variables do scale with it whereas intensive ones do not. See Table 1.1. An equation of state is a functional relation among them.

Extensive	Intensive
Energy E	-
Entropy S	Temperature T
Volume V	Pression p
Number of particles E	Chemical potential μ
Polarization $\mathbf{P}$	Electric field $\mathbf{E}$
Magnetization $\mathbf{M}$	Magnetic field $\mathbf{B}$

Table 1.1: Extensive and intensive thermodynamical variables.

Thermodynamics is described by four laws.

Law 1.1 (0th)
Two systems in thermal contact have the same empirical temperature T at equilibrium

$$T_1 = T_2$$

.

Law 1.2 (1st)
The (generalised) principle of conservation of energy states that

$$dE = \delta Q - \delta L + \mu dN \tag{1.1}$$

where E is the internal energy, Q is the heat, L is the work, μ is the chemical potential (the necessary energy to add or remove a particle) and N is the number of particles.

Recall that E is a exact differential, i.e $\oint dE = 0$, whereas heat and word are not, i.e $\oint \delta Q \neq 0$ and $\oint \delta H \neq 0$.

Law 1.3 (2nd)
A system naturally evolves in order to maximize its entropy S. For reversible processes

$$dS = \frac{\delta Q}{T} \tag{1.2}$$

whereas for irreversible processes

$$dS \geq \frac{\delta Q}{T}$$

Law 1.4 (3rd)
For any reversible isothermal process

$$\Delta S \to 0 \text{ as } T \to 0$$

1.2   Thermodynamical potentials

For reversible processes, using (1.2) and $\delta L = pdV$, (1.1) can be expressed as

$$dE = TdS - pdV + \mu dN \tag{1.3}$$

Notice that the left variables are intensive and the right variables (those with the differential) are extensive.

E is a function of S, V, N, hence it must be extensive and a homogeneous function of degree one, satisfying the property

$$E(\lambda S, \ \lambda V, \ \lambda N) = \lambda E(S, \ V, \ N)$$

where $\lambda > 0$ is the scale factor. It can be proved that the only function is

$$E(S, \ V, \ N) = TS - pV + \mu N$$

Similar expression can be found for other thermodynamical quantities, simply exchanging the role of conjugate functions. See Table 1.2.

Potentials	Differential
Internal energy $E(S,\ V,\ N) = TS - pV + \mu N$	$dE = TdS - pdV + \mu dN$
Helmotz free energy $F(T,\ V,\ N) = E - TS = -pV + \mu N$	$dF = -SdT - pdV + \mu dN$
Entalpy $H(S,\ p,\ N) = E + pV = St + \mu N$	$dH = TdS + Vdp + \mu dN$
Gibbs free energy $G(T,\ p,\ N) = E - TS + pV = \mu N$	$dG = -SdT + Vdp + \mu dN$
Granpotential $\Omega(T,\ V,\ \mu) = E - TS - \mu N = -pV$	$d\Omega = -SdT - pdV - Nd\mu$

Table 1.2: Thermodynamical potentials.

Proof. Maybe in the future.   q.e.d.

Fixing three of the thermodynamical variables to be constant, a system evolves in order to minimises the corresponding thermodynamical potential until it reaches its minimum, i.e the equilibrium state. Mathematically, it means that the first derivative must be vaninshing and the hessian must be positive defined. See Table 1.3.

Inequality	Constant quantities
$dE \leq 0$	S, V, N
$dF \leq 0$	T, V, N
$dH \leq 0$	S, p, N
$dG \leq 0$	T, p, N
$d\Omega \leq 0$	T, V, μ

Table 1.3: Thermodynamical variation principles.

Proof. Maybe in the future.   q.e.d.

Part II

Classical statistical mechanics

Chapter 2

Classical mechanics

A state constitued by a system of N particles is described by a point in a $2N$-dimensional manifold $\mathcal{M}^N$, called the phase space, which is the Cartesian product of N single particle manifolds

$$\{(q^i,\ p_i)\} \in \mathcal{M}^N$$

where $i = 1, \ldots N$.

An observable is a smooth real function

$$f\ :\ \mathcal{M}^N \to \mathbb{R}$$

and its measurement in a fixed point $(\tilde{q}^i,\ \tilde{p}_i)$ is its value in it

$$f = f(\tilde{q}^i,\ \tilde{p}_i)$$

The time evolution is governed by a real function, called the hamiltonian $H(q^i,\ p_i,\ t)$, which is the solution of the equations of motion, called the Hamilton's equations

$$\dot{q}^i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q^i}$$

Theorem 2.1 (Conservation of energy)
If the hamiltonian does not depend explicitly on time, it can be intepreted physically as the energy of the system, which is constants

$$H(q^i(t),\ p_i(t)) = H(q^i(0),\ p_i(0)) = E = const$$

Since they are deterministic, once the initial conditions are given, the trajectory in phase space is completely determined

2.1 Probability density distribution

A macrostate is defined by setting the macroscopic thermodynamical quantities. A microstate is the knowledge of the phase space behaviour $(q^i, \ p_i)$.

In general, there are more microstates associated to the same macrostates, raising the concept of ensemble: fixing a macrostate, it is created a large number of copies of the same physical system but with different microstates. It can be studied with the introduction of a probability density distribution

$$\rho(q_i(t), \ p_i(t), \ t)$$

such that it satisfies the following properties

1. positivity, i.e.
$$\rho(q_i, \ p_i, \ t) \geq 0$$

2. normalisation, i.e.
$$\int_{\mathcal{M}^n} \underbrace{\prod_{i=1}^{N} d^d q^i d^d p^i}_{d\Gamma} \ \rho(q_i, \ p_i, \ t) = \int_{\mathcal{M}^n} d\Gamma \ \rho(q_i, \ p_i, \ t) = 1$$

To solve the dimensional problem of the volume element $d\Gamma$, which must be adimensional but it has the dimension of an action to the power of d, it can be introduced the adimensional volume element

$$d\Omega = \frac{d\Gamma}{h^d} = \frac{\prod_{i=1}^{N} d^d q^i d^d p^i}{h^d}$$

where the scale factor h has the dimension of an action.

The probability to find the system in a finite portion of the phase space $\mathcal{U} \subset \mathcal{M}^N$ is

$$\int_{\mathcal{U}} d\Gamma \ \rho(q_i, \ p_i, \ t)$$

2.2 Liouville's theorem

The flow of a system of particles keeps trasf of all their motions. See Figure.

Theorem 2.2 (Liouville)
The volume through the flow generated by the hamilton's equations is constant. See Figure. Mathematically

$$vol\Omega(t=0) = vol\Omega(t) \ \Rightarrow \ \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, \ H] = 0$$

Proof. Maybe in the future.   q.e.d.

The physical intepretation of this theorem is that particles do not appear nor disappear due to conservation of charge, mass, etc...

For stationary systemas, i.e. when $\frac{\partial \rho}{\partial t} = 0$, the necessary condition for equilibrium is $[\rho, \ H] = 0$, which is satisfied only if

$$\rho = const$$

like in the microcanonical ensemble, and

$$\rho = \rho(H)$$

like in the canonical or the grancanonical ensembles.

Proof. Maybe in the future.   q.e.d.

The average value of an observable is weighted by the probability density distribution

$$\langle f \rangle = \int_{\mathcal{M}^N} d\Gamma \ \rho(q^i, \ p_i) f(q^i, \ p_i)$$

and the standard deviation is

$$(\Delta f)^2 = \langle f^2 \rangle - \langle f \rangle^2$$

2.3   Time-independent Hamiltonian

Consider a time-independent hamiltonian. Since the energy is constant for the theorem 2.1.

$$\int_{\mathcal{M}^N} \rho = 1 \tag{2.1}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{2.2}$$

$$\frac{\partial F}{\partial T} = -S \tag{2.3}$$

$$\Omega = -pV = E - TS - \mu N \tag{2.4}$$

Chapter 3

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 (2.1)

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

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

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

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

$$\langle f(q^i,p_i)\rangle_{mc} = \int_{\mathcal{M}} d\Omega\ \rho_{mc} f = \int_{\mathcal{M}} d\Omega\ \frac{1}{\omega(E)}\delta(\mathcal{H} - E)f = \frac{1}{\omega(E)} \int_{S_E} dS_E\ f = \langle f\rangle_E \tag{3.1}$$

3.1   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

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

Entropy is additive, so given two sistems 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

$$\omega(E) = \int_{\mathcal{M}^N} d\Gamma_1 d\Gamma_2 \delta(\mathcal{H} - E)$$

$$= \int dE_1 \int dS_{E_1} \int dE_2 \int dS_{E_2} \delta(E - E_1 - E_2)$$

$$= \int dE_1 \int dE_2 \omega_1(E_1) \omega_2(E_2) \delta(E - E_1 - E_2)$$

$$= \int_0^E dE_1 \, \omega_1(E_1) \omega_2(E_2 = E - E_1)$$

Since the integrand is a positive function with a maximum in $_1 \in [0, E]$

$$\int_0^E dE_1 \, \omega_1(E_1) \omega_2(E_2 = E - E_1) \leq \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) \int_0^E dE_1$$

$$= \omega_1(E_1^*) \omega_2(E_2^* = E - E_1^*) E \tag{3.2}$$

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

$$\Delta E \omega_1(E_1^*) \omega_2(E_2^*) \leq \omega(E) \tag{3.3}$$

Putting together (3.2) and (3.3)

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

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

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

Since the logarithm is a monotomic 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 thermo-dynamical 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 $E = const$, $0 = \delta E = \delta E_1 + \delta E_2$, $\delta E_2 = \delta E_1$ and

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

$$0 = \frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*}\Gamma_2(E_2^*) - \Gamma_1(E_1^*)\frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*}$$

$$\frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*}\Gamma_2(E_2^*) = \Gamma_1(E_1^*)\frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*}$$

$$\frac{1}{\Gamma_1(E_1^*)}\frac{\partial\Gamma_1}{\partial E_1}\Big|_{E_1^*} = \frac{1}{\Gamma_2(E_2^*)}\frac{\partial\Gamma_2}{\partial E_2}\Big|_{E_2^*}$$

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

Using the thermodynamical relation (2.2)

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

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 (3.1),

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

q.e.d.

Chapter 4

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

$$Z_N[V, T] = \int_{\mathcal{M}^N} d\Omega \ \exp(-\beta \mathcal{H}(q^i, p_i)) \tag{4.1}$$

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 trasforms, using (2.2)

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

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

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

Putting together, dropping the indices

$$\rho_c = \frac{\omega(2)(E_2)}{\omega(E)} = \frac{1}{\omega(E)} \exp(\frac{S_{mc}(E)}{k_B}) \exp(-\frac{E_1}{k_B T}) = C \exp(-\frac{E_1}{k_B T}) \qquad (4.2)$$

where C is a normalisation constant, which can be evaluated by (2.1)

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

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

$$Z_N = Z_{N_1} Z_{N_2} \tag{4.3}$$

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

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

q.e.d.

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

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

4.1   Thermodynamics variable

The canonical Helmotz free energy F is defined by

$$Z_{[}V, T] = \exp(-\beta F[N, V, T]) \tag{4.4}$$

or, equivalently,

$$F[V, N, T] = -\frac{1}{\beta} \ln Z_N \tag{4.5}$$

Furthermore, the canonical internal energy is

$$E = \langle \mathcal{H} \rangle_c = \int d\Omega \frac{\exp(-\beta(\mathcal{H}))}{Z_N} \mathcal{H} \tag{4.6}$$

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 (2.3)

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

showing that is indeed the Helmotz free energy.   q.e.d.

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

$$S_c = \frac{E - F}{T} \tag{4.7}$$

The internal energy can also be written as

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

Proof. Using (4.6),

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

<div align="right">q.e.d.</div>

The universal Boltzmann's formula is still valid

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

Proof. Using (4.6) and (4.5)

$$
\begin{aligned}
-k_B \langle\ln\rho_c\rangle_c &= -k_B \int d\Omega \rho_c \ln\rho_c \\
&= -k_B \int d\Omega \rho_c \ln\frac{\exp(-\beta\mathcal{H})}{Z_N} \\
&= -k_B \int d\Omega \rho_c \ln\exp(-\beta\mathcal{H}) - k_B \int d\Omega \rho_c \ln Z_N \\
&= k_B \int d\Omega \beta\mathcal{H} - k_B \underbrace{\ln Z_N}_{\beta F} \underbrace{\int d\Omega \rho_c}_{1} \\
&= \frac{E-F}{T} = S_c
\end{aligned}
$$

<div align="right">q.e.d.</div>

4.2 Equipartition theorem

Theorem 4.1 (Generalised equipartition theorem)
Let $\xi \in [a,b]$ and ξ_j with $j \neq 1$ all the other coordinates or momenta. Suppose also

$$\int \prod_{j\neq 1} d\xi_j [\xi_1 \exp(-\beta\mathcal{H})]_a^b = 0 \tag{4.8}$$

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

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

and integrating per parts

$$1 = \frac{1}{Z_N}\int \underbrace{\prod_{j\neq 1} d\xi_j[\xi_1 \exp(-\beta\mathcal{H})]_a^b}_{0} + \frac{\beta}{Z_N}\int \prod_{j\neq 1} d\xi_j d\xi_1 \xi_1 \frac{\partial\mathcal{H}}{\partial\xi_1}\exp(-\beta\mathcal{H})$$

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

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

Hence

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

<div align="right">q.e.d.</div>

Examples of system that satisfies the condition (4.8) are hamiltonians which depend on the square of momentum or confining potentials which go to infinity on the extremes a and b.

Corollary 4.1 (Equipartition theorem)
If ξ_1 appears quadratically in $\mathcal{H}$, then its contribution to E is $\frac{1}{2}k_B T$

Proof. Consider $\mathcal{H} = A\xi_1^2 + B\xi_j^2$ with $j \neq 1$, then by the previous theorem

$$\langle\xi_1\frac{\partial\mathcal{H}}{\partial\xi_1}\rangle_c = \langle\xi 2A\xi_1\rangle_c = k_B T$$

and

$$\langle A\xi_1^2\rangle_c = \frac{1}{2}k_B T$$

<div align="right">q.e.d.</div>

Chapter 5

Grancanonical ensemble

A grancanonical ensemble is a system which is immersed in a bigger environment or reservoir, which can exchange both energy and matter, so T, and V are fixed. Globally, both energy and number of particles are conserved, since the universe composed by the union of the system and the environment can be considered as a microcanonical ensemble. First, with the same method used in the previous chapter, microcanonical can be transformed into canonical. Now, the universe is canonical and, globally, the number of particles is conserved.

The grancanonical probability density distribution is

$$\rho_{gc}(q^i, p_i) = \frac{\exp(-\beta \mathcal{H}_1)}{N_1! h^{dN_1}} \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]}$$

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

$$\rho_c(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \frac{\exp(-\beta \mathcal{H}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}))}{Z_N[T, V]}$$

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

$$\rho^{(1)} = \int d\Omega_2 \, \rho_c$$

$$= \int \prod_{i=1}^N \frac{d^d q_i^{(2)} d^d p_i^{(2)}}{N! h^{dN}} \frac{\exp(-\beta(\mathcal{H}_1 + \mathcal{H}_2))}{Z_N}$$

$$= \frac{\exp(-\beta \mathcal{H}_1)}{N_1! h^{dN_1}} \frac{1}{Z_N} \int \prod_{i=1}^N \frac{d^d q_i^{(2)} d^d p_i^{(2)}}{N_2! h^{dN_2}} \exp(-\beta \mathcal{H}_2)$$

$$= \frac{\exp(-\beta \mathcal{H}_1)}{N_1! h^{dN_1}} \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]}$$

q.e.d.

The normalisation condition becomes

$$\sum_{N_1=0}^{N} \int_{\mathcal{M}^{N_1}} d\Omega_1 \rho_{gc} = 1$$

Proof. Using the expression to evaluate the power of a sum

$$(a+b)^n = \sum_{i=1}^{n} \binom{n}{i} a^i b^{n-i}$$

and

$$
\begin{aligned}
\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \rho_{gc} &= \int_{\mathcal{M}^{N_1}} d\Omega_1 \frac{\exp(-\beta\mathcal{H}_1)}{N_1! h^{dN_1}} \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]} \\
&= \frac{N!}{N_1! N_2} \frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta\mathcal{H}_1) \int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta\mathcal{H}_2)}{\int_{\mathcal{M}^{N}} d\Omega \ \exp(-\beta\mathcal{H})} \\
&= \frac{N!}{N_1! N_2} \frac{\frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta\mathcal{H}_1)}{(V_1)^{N_1}} \frac{\int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta\mathcal{H}_2)}{(V_2)^{N_2}}}{\frac{\int_{\mathcal{M}^{N}} d\Omega \ \exp(-\beta\mathcal{H})}{V^N}} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N}
\end{aligned}
$$

which in the thermodynamical limit

$$\lim_{td} \frac{\frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta\mathcal{H}_1)}{(V_1)^{N_1}} \frac{\int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta\mathcal{H}_2)}{(V_2)^{N_2}}}{\frac{\int_{\mathcal{M}^{N}} d\Omega \ \exp(-\beta\mathcal{H})}{V^N}} = 1$$

Hence

$$\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \rho_{gc} = \frac{N!}{N_1! N_2} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N}$$

and the normalisation condition becomes, using $N = N_1 + N_2$,

$$\sum_{N_1=0}^{N} \int_{\mathcal{M}^{N_1}} d\Omega_1 \rho_{gc} = \sum_{N_1=0}^{N} \frac{N!}{N_1! N_2!} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N} = \sum_{N_1=0}^{N} \binom{N}{N_1} \left(\frac{V}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N-N_1} = \left(\frac{V_1+V_2}{V}\right)^N$$

which in the thermodynamical limit is

$$\lim_{td} \left(\frac{V_1+V_2}{V}\right)^N = 1$$

q.e.d.

5.1   Thermodynamical potentials

The grancanonical probability density distribution can be also written as

$$\rho_{gc}(q_i, p_i) = \frac{\exp(-\beta(\mathcal{H}(q_i, p_i) - \mu N))}{\mathcal{Z}}$$

where μ is the chemical potential and $\mathcal{Z}$ is the grancanonical partition function

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N = \exp(-\beta\Omega)$$

where $z = \exp(\beta\mu)$ is the fugacity and Ω is the granpotential.

Proof. Using (4.4) and Taylor expanding to first order in $N_1 \ll N$ and $V_1 \ll V$,

$$\begin{aligned}
\frac{Z_{N_2}[T, V]}{Z_N[T, V]} &= \frac{\exp(-\beta F(T, N_2, V_2))}{\exp(-\beta F(T, N, V))} \\
&= \exp(-\beta(F(T, N - N_1, V - V_1) - F(T, N, V))) \\
&\simeq \exp(-\beta(\underbrace{\left.\frac{\partial F}{\partial N}\right|_{T,V}}_{\mu}(-N_1) + \underbrace{\left.\frac{\partial F}{\partial V}\right|_{T,N}}_{-p}(-V_1))) \\
&= \exp(-\beta(-\mu N_1 + pV_1))
\end{aligned}$$

Hence, now all the degrees of freedom of the environment has been removed

$$\begin{aligned}
\rho_{gc} &= \frac{\exp(\beta\mathcal{H})}{N!h^{dN}}\exp(-\beta(-\mu N + pV)) \\
&= \frac{\exp(\beta\mathcal{H})}{N!h^{dN}}\underbrace{\exp(\beta\mu)^N}_{z^N}\exp(-\beta pV) \\
&= \frac{z^N \exp(\beta\mathcal{H})}{N!h^{dN}}\exp(-\beta pV)
\end{aligned}$$

where we introduced the fugacity.

Recall (2.4), the normalisation condition becomes

$$
\begin{aligned}
1 &= \sum_{N=0}^{\infty} \int_{\mathcal{M}^N} d\Omega \, \rho_{gc} \\
&= \sum_{N=0}^{\infty} \int_{\mathcal{M}^N} d\Omega \frac{z^N \exp(\beta\mathcal{H})}{N! h^{dN}} \exp(-\beta p V) \\
&= \exp(-\beta p V) \sum_{N=0}^{\infty} z^N \frac{\int_{\mathcal{M}^N} d\Omega}{h^{dN} N!} \\
&= \exp(-\beta p V) \underbrace{\sum_{N=0}^{\infty} z^N Z_N}_{\mathcal{Z}} \\
&= \exp(-\beta p V) \mathcal{Z}
\end{aligned}
$$

Hence

$$
\mathcal{Z} = sum_{N=0}^{\infty} z^N Z_N = \exp(\beta p V)
$$

and

$$
\rho_{gc}(q_i, p_i) = \frac{\exp(-\beta(\mathcal{H}(q_i, p_i) - \mu N))}{\mathcal{Z}} = \frac{\exp(-\beta \mathfrak{H}(q_i, p_i))}{\mathcal{Z}}
$$

where $\mathfrak{H} = \mathcal{H} - \mu N$ is the grancanonical hamiltonian.   q.e.d.

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

$$
\begin{aligned}
\langle f(q^i, p_i) \rangle_{gc} &= \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega \, \rho_{gc} f_N \\
&= \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega \, \frac{\exp(-\beta(\mathcal{H} - \mu N))}{\mathcal{Z}} f_N \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \int_{\mathcal{M}} d\Omega \frac{\exp(-\beta\mathcal{H})}{Z_N} f_N \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle f_N \rangle_c
\end{aligned}
$$

The grancanonical internal energy is

$$
E = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} \Big|_z
$$

Proof.

$$-\frac{\partial}{\partial\beta}\ln\mathcal{Z}\bigg|_z = -\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\beta}\mathcal{Z}\bigg|_z$$

$$= -\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\beta}\sum_{N=0}^{\infty} z^N Z_N\bigg|_z$$

$$= -\sum_{N=0}^{\infty}\frac{z^N}{\mathcal{Z}}\frac{\partial}{\partial\beta}\int d\Omega\exp(-\beta\mathcal{H})$$

$$= \sum_{N=0}^{\infty}\int d\Omega\,\frac{\exp(-\beta(\mathcal{H}+\mu N))}{\mathcal{Z}}\mathcal{H}$$

$$= \langle\mathcal{H}\rangle_{gc} = E$$

q.e.d.

The grancanonical number of particles is

$$\langle N\rangle_{gc} = z\frac{\partial}{\partial z}\ln\mathcal{Z}\bigg|_T$$

Proof.

$$z\frac{\partial}{\partial z}\ln\mathcal{Z}\bigg|_T = \frac{z}{\mathcal{Z}}\frac{\partial}{\partial z}\mathcal{Z}\bigg|_T$$

$$= \frac{z}{\mathcal{Z}}\frac{\partial}{\partial z}\sum_{N=0}^{\infty} z^N Z_N$$

$$= fracz\mathcal{Z}\sum_{N=0}^{\infty} N z^{N-1} Z_N$$

$$= \sum_{N=0}^{\infty} z^N Z_N N = \langle N\rangle_{gc}$$

q.e.d.

The grancanonical potential is

$$\Omega = -\frac{1}{\beta}\ln\mathcal{Z} \tag{5.1}$$

The universal Boltzmann's formula is still valid

$$S_{gc} = -k_B\langle\ln\rho_{gc}\rangle_{gc}$$

Proof. Using (5.1),

$$
\begin{aligned}
-k_B \langle \ln \rho_{gc} \rangle_{gc} &= -k_B \int d\Omega \; \rho_{gc} \ln \rho_{gc} \\
&= -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \; \exp(-\beta \mathcal{H}) \ln \rho_{gc} \\
&== -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \; \exp(-\beta \mathcal{H})(-\beta \mathcal{H} + \beta \mu N + \ln \mathcal{Z}) \\
&= k_B \beta \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \; \exp(-\beta \mathcal{H}) \mathcal{H}}_{E} - k_B \beta \mu \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \; \exp(-\beta \mathcal{H}) N}_{N} \\
&\quad + k_B \ln \mathcal{Z} \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega \; \exp(-\beta \mathcal{H})}_{1} \\
&= \frac{E - \mu N - \Omega}{T} = S
\end{aligned}
$$

q.e.d.

List of Theorems