F CANONICAL ENSEMBLE

The canonical ensemble is characterised by temperature T, volume V and particle number N, instead of energy E, volume V and particle number N (or any other series of extensive state variables), effectively, the temperature is controlled instead of the energy. Physically one can reach that by putting the system into thermal contact with a larger system acting as an energy reservoir: The zeroth law of thermo dynamics will then make sure that a common equilibrium temperature is reached. If the second system is very large compared to the first one, it will determine this temperature.

As there are two microcanonical systems in thermal contact with an exchange of thermal energy, one would write down a common Hamilton function with an interaction term $h(p_i, q_i, P_j, Q_j)$ that allows the coupling of the two systems,

$$\mathcal{H} = \mathcal{H}(p_i, q_i) + \mathcal{H}(P_j, Q_j) + h(p_i, q_i, P_j, Q_j) \qquad (F.235)$$

The first Hamilton-function describes a system with f degrees of freedom, the second Hamilton-function a system with F degrees of freedom, and usually $f \ll F$. If the interaction term $h(p_i, q_i, P_j, Q_j)$ is zero, the two systems are isolated. We will assume that the interaction $h(p_i, q_i, P_j, Q_j)$ is nonzero to allow coupling, but small compared to the two energies $\mathcal{H}(p_i, q_i)$ and $\mathcal{H}(P_i, Q_i)$, such that the thermodynamical properties follow from these two energies alone.

F.1 *Marginalisation procedure*

For a given phase space coordinate (p_i, q_i) of the smaller system with an associated energy $\mathcal{H}_1$, the larger system is left with all configurations that are compatible with the energy $E - \mathcal{H}_1 \leq \mathcal{H}_2 \leq E + \delta E - \mathcal{H}_1$ which is an immediate consequence of $E \leq \mathcal{H}_1 + \mathcal{H}_2 \leq E + \delta E$. The probability of finding the smaller system at (p_i, q_i) needs to take into account all states (P_j, Q_j), which are compatible with the energies $\mathcal{H}_1$ and $\mathcal{H}_2$. Therefore, this probability is given by

$$W(p_i, q_i) \prod_i d^3 p_i d^3 q_i \propto \prod_i d^3 p_i d^3 q_i \int_{E-\mathcal{H}_1 \leq \mathcal{H}_2 \leq E+\delta E - \mathcal{H}_1} \prod_j d^3 P_j d^3 Q_j \qquad (F.236)$$

with the identification

$$\omega_2(E) = \frac{d\phi_2(E)}{dE} = \int_{E-\mathcal{H}_1 \leq \mathcal{H}_2 \leq E+\delta E - \mathcal{H}_1} \prod_j d^3 P_j d^3 Q_j \qquad (F.237)$$

as the phase space volume of the second system. Mathematically, this is called a marginalisation: We are interested in the distribution of the smaller system *irrespective* of the particular distribution over (Q_j, P_j), so we are *integrating out* that part of the distribution.

By integrating of the phase space (p_i, q_i) with $E \leq \mathcal{H} \leq E + \delta E$ we get

$$W(E_1)\delta E_1 \propto \omega_1(E_1)\omega_2(E - E_1)\delta E_1 \qquad (F.238)$$

which should have a maximum at a certain value $\tilde{E}_1$ for the energy E_1. In fact, in thermodynamic equilibrium the energy should be distributed among the two parts of the system in a way that the temperatures become equal. In order to get a feeling

for this, let's look at a Bernoulli-probability as a model, as in the case of ideal gases. Then,

$$W(E_1) = E_1^{n_1}(E - E_1)^{n_2}, \qquad n_1, n_2 \sim 10^{23} \tag{F.239}$$

with the logarithm

$$\ln W(E_1) = n_1 \ln E_1 + n_2 \ln(E - E_1) \tag{F.240}$$

and a maximum at

$$\frac{d \ln W(E_1)}{dE_1} = 0 \quad \text{yields} \quad \tilde{E}_1 = E\frac{n_1}{n_1 + n_2}, \quad \tilde{E}_2 = E - \tilde{E}_1 = E\frac{n_2}{n_1 + n_2} \tag{F.241}$$

We expand this probability around the maximum $\tilde{E}_1$ and write $E_1 = \tilde{E}_1 + \epsilon$

$$\ln W(\tilde{E}_1 + \epsilon) = n_1 \ln \tilde{E}_1 + n_2 \ln \tilde{E}_2 + n_1 \ln\left(1 + \frac{\epsilon}{\tilde{E}_1}\right) + n_2 \ln\left(1 + \frac{\epsilon}{\tilde{E}_2}\right) \tag{F.242}$$

in a parabolic expansion. Then, the probability around $\tilde{E}_1$ becomes

$$\ln W(\tilde{E}_1 + \epsilon) = \text{const} - \frac{\epsilon^2}{2}\frac{n_1 + n_2}{\tilde{E}_1 \tilde{E}_2} \tag{F.243}$$

as the linear term is $= 0$ at the maximum. Consequently, there will be a Gaussian distribution

$$W(\tilde{E}_1 + \epsilon) = W(\tilde{E}_1) \exp\left(-\frac{\epsilon^2}{2}\frac{n_1 + n_2}{\tilde{E}_1 \tilde{E}_2}\right) \tag{F.244}$$

around $\tilde{E}_1$, with the variance approaching zero for large $n_1 + n_2$, such that the contribution to the phase space appears at a single, well-defined energy $\tilde{E}_1$, leaving $E - \tilde{E}_1$ to the second system.

Let's return to the probability $W(E_1)$, whose most probable value is defined by

$$\frac{\partial}{\partial E_1}(\omega_1(E_1)\omega_2(E - E_2)) = 0 \tag{F.245}$$

Because the logarithm is monotonic we can conclude

$$\frac{\partial}{\partial E_1} \ln \omega_1(E_1)\bigg|_{E_1 = \tilde{E}_1} = \frac{\partial}{\partial E_1} \ln \omega_2(E_2)\bigg|_{E_2 = \tilde{E}_2 = E - \tilde{E}_1} \tag{F.246}$$

which would suggest the identification

$$S = k_B \ln \omega \quad \text{and} \quad \frac{\partial \ln \omega}{\partial E} = \frac{1}{k_B T} \tag{F.247}$$

in contradiction with previous results where

$$S = k_B \ln \phi \quad \text{and} \quad \frac{\partial \ln \phi}{\partial E} = \frac{1}{k_B T} \tag{F.248}$$

 i.e. the actual phase space volume was replaced by the differential phase space volume. There is actually no issue because for a highly dimensional phase space most of the volume is contained in an incredibly thin layer just below the surface such that the two measures become approximately equal,

$$\lim_{N\to\infty} \frac{\ln \phi}{N} = \lim_{N\to\infty} \frac{\ln \omega}{N} \tag{F.249}$$

such that

$$\phi \sim \omega \delta E \tag{F.250}$$

 Specifically for an ideal gas one would write

$$\phi = CE^{\frac{3N}{2}} \quad \text{as well as} \quad \omega = \frac{3N}{2}CE^{\frac{3N}{2}-1} = \frac{3N}{2}\frac{\phi}{E} \tag{F.251}$$

such that the temperature in both definition coincides,

$$\frac{\partial}{\partial E} k_B \ln \phi = \frac{1}{T} = \frac{\frac{3}{2}Nk_B}{E} = \frac{1}{T} = \frac{\left(\frac{3}{2}N - 1\right)k_B}{E} = \frac{\partial}{\partial E} k_B \ln \omega \tag{F.252}$$

as the difference between N and $N - 1$ becomes irrelevant.

 We are missing now the actual shape of the phase space distribution for a canonical system, which is defined to be the distribution over the degrees of freedom of the smaller system by a temperature defined through the larger system, acting as a reservoir of thermal energy. The energy is shared among both systems, but effectively in a way that $\mathcal{H}_1(p_i, q_i) \ll E$ and from the argument in the previous example, such that the energy of both parts is well defined and fixed to $\tilde{E}_1$ and $E - \tilde{E}_1 \simeq E$, in particular if the thermostat is huge compared to the controlled system:

$$\ln \omega_2(E - \mathcal{H}_1) = \ln \omega_2(E_2)|_{E_2=E} - \frac{\partial}{\partial E_2} \ln \omega_2(E_2)|_{E_2=E}\mathcal{H}(p_i, q_i) \tag{F.253}$$

in the limit $E_1 = \mathcal{H}_1 \ll E_2 \simeq E$. But at the same time, $\frac{\partial}{\partial E} \ln \omega_2 = \frac{1}{k_B T}$, such that

$$W(p_i, q_i) \prod_i d^3 p_i d^3 q_i \propto \prod_i d^3 p_i d^3 q_i \omega_2(E - \mathcal{H}_1)dE \propto \prod_i d^3 p_i d^3 q_i \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_B T}\right) \tag{F.254}$$

and similarly

$$W(E_1)dE_1 \propto \omega_1(E_1) \exp\left(-\frac{E_1}{k_B T}\right)dE_1 \tag{F.255}$$

with the Boltzmann-factor appearing, with the effect of down-weighting states of high energy.

F.2 *Canonical ensemble*

For defining a new ensemble where temperature T is controlled instead of energy E we need to be aware of the fact that energy is not fixed anymore, clearly the system

can exchange energy with the thermostat through the interaction term of the common Hamilton-function. Recapitulating the argument about the maximisation of Shannon-entropy and the search for the "most random" distribution that is normalised and for which the expectation value of energy is fixed led to the Boltzmann-factor: For a given energy all states are equally probable, and states of higher energy are less probable according to $\exp(-E/(k_BT))$. Defining an ensemble average of a phase space function $A(p_i, q_i)$ this entire ensemble (not just the $(\mathcal{H} = E)$-surface!), leads to

$$\langle A(p_i, q_i) \rangle = \frac{\int \prod_i d^3 p_i d^3 q_i \, A(p_i, q_i) \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_B T}\right)}{\int \prod_i d^3 p_i d^3 q_i \, \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_B T}\right)} \tag{F.256}$$

i.e. with the weighting function is now being $\rho \sim \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_B T}\right)$ instead of a constant $\rho = 0, 1$; where in addition the normalising factor $N! h^{3N}$ has been dropped. Then, the expectation value of energy would be

$$\langle E \rangle = \frac{\int \prod_i d^3 p_i d^3 q_i \, \mathcal{H} \exp(-\beta \mathcal{H}(p_i, q_i))}{\int \prod_i d^3 p_i d^3 q_i \, \exp(-\beta \mathcal{H}(p_i, q_i))} \tag{F.257}$$

and of pressure

$$\langle p \rangle = \frac{\int \prod_i d^3 p_i d^3 q_i \, \left(-\frac{\partial \mathcal{H}}{\partial V}\right) \exp(-\beta \mathcal{H}(p_i, q_i))}{\int \prod_i d^3 p_i d^3 q_i \, \exp(-\beta \mathcal{H}(p_i, q_i))} \tag{F.258}$$

with $p = -\partial \mathcal{H}/\partial V$, and the inverse temperature $\beta = \frac{1}{k_B T}$.

F.3 *Equipartition theorem*

Remembering how difficult it was in the microcanonical ensemble to derive the equipartition theorem, we should try to rederive it in the canonical ensemble. Exploiting the virial law implies

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = 2 \langle \mathcal{H}_{\text{kin}} \rangle = k \langle \mathcal{H}_{\text{pot}} \rangle \tag{F.259}$$

if the Hamilton-function has the archetypical form $\mathcal{H} \sim p^2 + q^k$ with the potential being a homogeneous function of order k. Then,

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \frac{\int \prod_i d^3 p_i d^3 q_i p_i \frac{\partial \mathcal{H}}{\partial p_i} \exp(-\beta \mathcal{H}(p_i, q_i))}{\int \prod_i d^3 p_i d^3 q_i \, \exp(-\beta \mathcal{H}(p_i, q_i))} \tag{F.260}$$

Rewriting the term in the numerator involving the Boltzmann-factor as

$$\frac{\partial \mathcal{H}}{\partial p_i} \exp\left(-\frac{\mathcal{H}}{k_B T}\right) = -k_B T \frac{\partial}{\partial p_i} \exp\left(-\frac{\mathcal{H}}{k_B T}\right) \tag{F.261}$$

with the chain rule gives

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \frac{\int \prod\limits_i d^3 p_i d^3 q_i \; (-k_B T p_i) \frac{\partial}{\partial p_i} \exp(-\beta \mathcal{H}(p_i, q_i))}{\int \prod\limits_i d^3 p_i d^3 q_i \; \exp(-\beta \mathcal{H}(p_i, q_i))} = +k_B T \tag{F.262}$$

with a sign change due to an integration by parts to obtain $\partial p_i / \partial p_i = 1$. Therefore, we can conclude that on average the kinetic energy and the potential energy for every degree of freedom are similar and of order $k_B T$, essentially in a one-line calculation!

F.4 *Canonical partition function*

The idea of the canonical partition function Z is again that the weighting function in the numerator is the normalisation function in the denominator, such that for instance the state variable $E = \mathcal{H}$ can be generated by differentiation with respect to $\beta = 1/(k_B T)$. Just as in the discussion of characteristic functions one would proceed by interchanging differentiation and integration, and have the differentiation act on the partition function as a carried-out integral:

$$Z(T, V, N) = \int \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_B T}\right) \tag{F.263}$$

now with the normalising factor $N! h^{3N}$, yielding the expectation value for the energy as a logarithmic derivative: The logarithm makes sure that exactly the right shape of the canonical average is generated, with a normalisation from the differentiation of the logarithm, and the state variable to be averaged over as the internal derivative required by the chain rule:

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 \frac{1}{Z} \frac{\partial Z}{\partial T} \tag{F.264}$$

The expecation value for the pressure p follows in analogy through differentation with respect to its extensive partner V

$$\langle p \rangle = k_B T \frac{\partial \ln Z}{\partial V} = k_B T \frac{1}{Z} \frac{\partial Z}{\partial V} \tag{F.265}$$

Given the form of these expressions we should start looking for a suitable thermodynamic potential:

$$-\frac{F}{k_B T} = -\beta F \tag{F.266}$$

called the Helmholtz-free energy F.

F.5 *Helmholtz-free energy F*

The Helmholtz-free energy F is obtained through Legendre-transform of the energy E by replacing the dependence on volume V as an extensive quantity through pressure p. Therefore, we write

$$F = E - TS \quad \text{with the differential} \quad dF = dE - TdS - SdT \tag{F.267}$$

together with the Euler relation

$$dE = TdS - pdV \quad \rightarrow \quad dF = -SdT - pdV \tag{F.268}$$

Therefore, including $1/(k_B T)$ into the definition of F gives for the differential

$$d\left(-\frac{F}{k_B T}\right) = \frac{F}{k_B T^2}dT - \frac{1}{k_B T}dF = \frac{F + TS}{k_B T^2}dT + \frac{p}{k_B T}dV = \underbrace{\frac{E}{k_B T^2}}_{\frac{\partial \ln Z}{\partial T}}dT + \underbrace{\frac{p}{k_B T}}_{\frac{\partial \ln Z}{\partial p}}dV \tag{F.269}$$

And therefore

$$d\left(-\frac{F}{k_B T}\right) = \frac{\partial \ln Z}{\partial T}dT + \frac{\partial \ln Z}{\partial V}dV \tag{F.270}$$

which strongly suggests the definition $F(T, V) = -k_B T \ln Z$ for obtaining the Helmholtz-free energy F from the logarithmic canonical partition function, in analogy to $S = k_B \ln \phi$ in the microcanonical case. Alternatively, one can argue that

$$Z = \int \frac{\prod_i d^3 p_i d^3 q_i}{N! h^{3N}} \exp\left(\frac{-\mathcal{H}(p_i, q_i)}{k_B T}\right) = \int_0^\infty dE \underbrace{\int \frac{\prod_i d^3 p_i d^3 q_i}{N! h^{3N}} \exp\left(-\frac{\mathcal{H}}{k_B T}\right)}_{=\omega(E)} \tag{F.271}$$

or equivalently

$$Z = \int_0^\infty dE \frac{d}{dE} \underbrace{\underbrace{\int_0^E \frac{\prod_i d^3 p_i d^3 q_i}{N! h^{3N}} \exp\left(-\frac{\mathcal{H}}{k_B T}\right)}_{=\phi(E)}}_{=\omega(E)} \tag{F.272}$$

such that the canonical partition function originates directly from a reweighting of the microcanonical phase space density with the Boltzmann-factor: That is in fact an incredibly intuitive result, as extremisation of Shannon-entropy yields naturally a uniform distribution at fixed energy and an exponentially decreasing probability with increasing energy, in accordance with the fundamental postulate of statistical physics.

F.6 *Gibbs-enthalpy*

The Helmholtz free energy $F(T, V, N)$ has the temperature being controlled as an intensive state variable, while V and N are clearly extensive. Physically, this would mean that there is a larger thermal reservoir acting as a thermostat for the system. But often, the pressure p is fixed rather than the volume V, for instance in a chemical reaction at atmospheric pressure if one does not use a closed container for the chemical substances. A suitable thermodynamic potential with T, p and N controlled is the Gibbs enthalpy $G(T, p, N)$. Here, apart from being a thermostat the second system is in pressure equilibrium with the first system, such that $E = E_1 + E_2$ and $V = V_1 + V_2$.

In this case one can write

$$W(E_1, V_1)dE_1 dV_1 \sim \omega(E_1, V_1)\omega_2(E - E_1, V - V_1)dE_1 dV_1 \qquad (F.273)$$

extending the previous relation by volume. An expansion of the logarithm $\ln \omega_2$ in terms of energy and volume yields

$$\ln \omega_2(E - E_1, V - V_1) = \ln \omega_2(E, V) - \underbrace{\frac{\partial \ln \omega_2}{\partial E_1}}_{=\frac{1}{k_B T}} E_1 - \underbrace{\frac{\partial \ln \omega_2}{\partial V_1}}_{=\frac{p}{k_B T}} V_1 \qquad (F.274)$$

and because $S = k_B \ln \omega$,

$$\frac{\partial S}{\partial E} = \frac{1}{k_B T} \frac{\partial \ln \omega}{\partial E} = \frac{1}{k_B T}$$

$$\frac{\partial S}{\partial V} = \frac{1}{k_B} \frac{\partial \ln \omega}{\partial V} = \frac{p}{k_B T}$$

Looking a the Legendre-transform relation

$$dE = TdS - pdV \quad \rightarrow \quad dS = \frac{1}{T}(dE + pdV) \qquad (F.275)$$

such that

$$\ln \omega_2(E - E_1, V - V_2) = \ln \omega_2(E, V) - \frac{1}{k_B T}(E_1 - pV_1) \qquad (F.276)$$

and the Boltzmann-factor is extended to include pressure work. Using this extended Boltzmann-factor to compute expectation values in the canonical ensemble gives for instance for $\langle E + pV \rangle$,

$$\langle E + pV \rangle = \frac{\int dEdV \, (E + pV)\omega(E, V) \exp\left(-\frac{E+pV}{k_B T}\right)}{\int dEdV \, \omega(E, V) \exp\left(-\frac{E+pV}{k_B T}\right)} =$$

$$k_B T^2 \frac{\partial}{\partial T} \ln \int dEdV \, \omega(E, V) \exp\left(-\frac{E + pV}{k_B T}\right) \quad (F.277)$$

and for $\langle V \rangle$,

$$\langle V \rangle = \frac{\int dEdV \, V\omega(E, V) \exp\left(-\frac{E+pV}{k_B T}\right)}{\int dEdV \, \omega(E, V) \exp\left(-\frac{E+pV}{k_B T}\right)} = -k_B T \frac{\partial}{\partial p} \ln \int dEdV \, \omega(E, V) \exp\left(-\frac{E + pV}{k_B T}\right)$$

$$(F.278)$$

where again the variables $E + pV$ or V alone have been generated by suitable differentiation of the partition function, and interchanging differentiation and integration determines the expectation values as suitable derivatives of the logarithmic partitions functions. These relations lead naturally to the definition of the Gibbs-enthalpy

$G(T, p, N)$

$$G(T, p, N) = -k_B T \ln \int dE dV \omega(E, V) \quad \rightarrow$$

$$E + pV = k_B T^2 \frac{\partial}{\partial T} \left(-\frac{G}{k_B T} \right) \quad \text{and} \quad V = \frac{\partial G}{\partial p} \quad \text{(F.279)}$$

Linking this up to the Legendre-transform of F for the replacement of V with p

$$G = E - TS + pV \quad \rightarrow \quad dG = -SdT + Vdp + \mu dN \quad \text{(F.280)}$$

makes it possible to write

$$d\left(-\frac{G}{k_B T} \right) = \frac{G}{k_B T^2} dT - \frac{1}{k_B T} dG = \frac{E + pV}{k_B T^2} dT - \frac{V}{k_B T} dp - \frac{\mu}{k_B T} dN \quad \text{(F.281)}$$

Such that a differentiation in T will yield $E + pV$ and a differentiation in p the corresponding volume. Separating the combined Boltzmann-factor the allows to compute the partition function for the enthalpy G as following from the canonical partition function Z defining the Helmholtz free energy F

$$G(T, p, N) = -k_B T \ln \int dV \, Z(T, V, N) \exp \left(-\frac{pV}{k_B T} \right) \quad \text{(F.282)}$$

with an interesting picture emerging: Replacement of a state variable by Legendre-transform corresponds to a reweighting of the partition function with a modified Boltzmann-factor. Naturally we would ask now if a replacement of N with the chemical potential μ would be possible: This leads to the macrocanonical partition function. Please keep in mind that a thermodynamic potential can not depend on all intensive state variables as a consequence of the Gibbs-Duhem relation, so we are aiming at macrocanonical partitions and their corresponding potentials as functions of T, V and μ.