

Chapter 8

Canonical Ensemble (E, V, N)

6. Thermodynamic properties: Once the partition function Z_N and the free energy $F(T, V, N) = -k_B T \ln Z_N(T, V, N)$ are calculated, one obtains the pressure P , the entropy S and the chemical potential μ as usual via $dF = -SdT - PdV + \mu dN$. Using

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T, N}, \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V, N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T, V}$$

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{V, N} = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_{N, V}$$

Specific heat: The specific heat C_V is given in particular by

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T^2} = \frac{\partial^2}{\partial T^2} (k_B T \ln Z_N) \quad (12)$$

where we have used $F = -k_B T \ln Z_N$

Canonical vs. Microcanonical ensemble

We have seen that the calculations in the microcanonical and canonical ensembles reduce to a phase space integration and a calculation of a thermodynamic potential:

For one particle

	Microcanonical ensemble	Canonical ensemble
Phase-space integration	Density of states: $\Omega_N(E) = \int d^{3N}q d^{3N}p \delta(E-H)$	Partition function: $Z_N(T) = \int \frac{d^{3N}q d^{3N}p}{h^{3N}N!} e^{-\beta H(q,p)}$
Thermodynamic potential	$S(E, V, N) = k_B \ln \left(\frac{\Omega_N(E)\Delta}{h^{3N}N!} \right)$	$F(T, V, N) = -k_B \ln Z_N(T)$

For one particle

	Microcanonical ensemble	Canonical ensemble
Phase-space integration	Density of states: $\Omega_1(E) = \int d^3q d^3p \delta(E-H)$	Partition function: $Z_1(T) = \int \frac{d^3q d^3p}{h^3} e^{-\beta H(q,p)}$
Thermodynamic potential	$S(E, V, N) = k_B \ln \left(\frac{\Omega_1(E)\Delta}{h^3} \right)$	$F(T, V, N) = -k_B \ln Z_1(T)$

Where, For Indistinguishable $Z_N(T) = \frac{(Z_1)^N}{N!}$

For distinguishable $(Z_1)^N$

Laplace transform: The relation between the density of states $\Omega_N(E)$ and the partition function $Z_N(T)$ can be defined as a Laplace transformation in the following way. We use the definition of the density of states $\Omega(E)$,

$$\int dq dp \delta(E-H) = \Omega(E), \quad H = H(q, p)$$

in order to obtain

$$\int_0^\infty \frac{dE e^{-\beta E}}{h^{3N}N!} \Omega_N(E) = \int d^{3N}q d^{3N}p \int_0^\infty \frac{dE e^{-\beta E}}{h^{3N}N!} \delta(E-H)$$

$$= \int \frac{d^{3N} q d^{3N} p}{h^{3N} N!} e^{-\beta H(q,p)} = Z_N(T) \quad (13)$$

We have thus shown that $Z_N(T)$ is the Laplace transform of $\Omega_N(E)$.

Additive Hamilton functions. In both the microcanonical and in the canonical ensemble we have to perform an integration which is usually difficult. When the Hamilton function is additive, $H = \sum_i H_i$, the integration in the canonical ensemble can be factorized, which is not the case for the microcanonical ensemble. Therefore, it is usually easier to calculate in the canonical ensemble than in the microcanonical ensemble.

Additivity of $F(T, V, N)$

An important property of the free energy is that it has to be additive.

$$\begin{array}{|c|c|} \hline N_1 & N_2 \\ \hline V_1 & V_2 \\ \hline \end{array} T$$

Non-interacting systems. Let us consider two systems in thermal equilibrium. Neglecting the interaction among the systems, the total Hamilton function can be written as a sum of the Hamiltonians of the individual systems,

$$H = H_1 + H_2, \quad N = N_1 + N_2$$

Multiplication of partition functions. The partition function of the total system is

$$Z_N(T, V) = \frac{1}{h^{3N} N_1! N_2!} \int d^{3N} q d^{3N} p e^{-\beta(H_1+H_2)}$$

$$= Z_{N_1}(T, V_1) Z_{N_2}(T, V_2)$$

and that the free energy $F = -k_B T \ln Z_N$ is additive

$$F(T, V, N) = F_1(T, V_1, N_1) + F_2(T, V_2, N_2)$$

Convolution of densities of states. That the overall partition function factorizes follows also from the fact that the density of states $\Omega(E)$ of the combined system,

$$\Omega(E) = \int d^{3N} q d^{3N} p \delta(E - H_1 - H_2)$$

$$= \int d^{3N_1} q d^{3N_1} p d^{3N_2} q d^{3N_2} p \int dE_2 (E - H_1 - E_2) \delta(E_2 - H_2)$$

$$= \int dE_2 \Omega_1(E - E_2) \Omega_2(E_2)$$

is given by the (convolution) of the density of states $\Omega_i(E_i)$ of the individual systems.

Using the representation (13) for the partition function we obtain

$$\begin{aligned} Z_N &= \int \frac{dE e^{-\beta E}}{h^{3N} N_1! N_2!} \Omega(E) \\ &= \int \frac{dE e^{-\beta(E_1+E_2)}}{h^{3N} N_1! N_2!} \int dE_2 \underbrace{\Omega_1(E-E_2)}_{\Omega_1(E_1)} \Omega_2(E_2) \end{aligned}$$

A change of the integration variable from dE to dE_1 then leads again to

$$\boxed{Z_N(T, V) = Z_{N_1}(T, V_1) Z_{N_2}(T, V_2)} \quad (14)$$

Note that this relation is only valid if $H = H_1 + H_2$ and $H_{12} = 0$