# Chapter 10

Grand canonical ensemble

10.1 Grand canonical partition function

The grand canonical ensemble is a generalization of the canonical ensemble where the restriction to a definite number of particles is removed. This is a realistic representation when then the total number of particles in a macroscopic system cannot be fixed.

Heat and particle reservoir. Consider a system A_1 in a heat and particle reservoir A_2. The two systems are in equilibrium with the thermal equilibrium.

– Thermal equilibrium results form the exchange of heat. The two temperature are then equal: $T = T_1 = T_2$

– The equilibrium with respect to particle exchange leads to identical chemical potentials: $\mu = \mu_1 = \mu_2$.
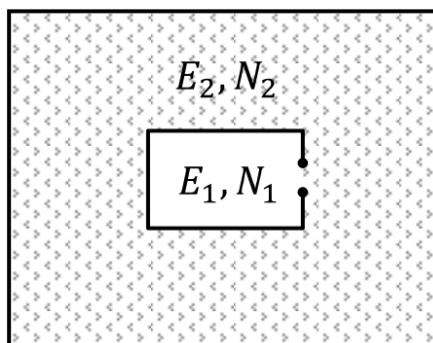
Energy and particle conservation. We assume that the system A_2 is much larger than the system A_1, i.e., that

$$E_2 \gg E_1, \qquad N_2 \gg N_1 ,$$

with

$$N_1 + N_2 = N = \text{const.} \qquad E_1 + E_2 = E = \text{const.}$$

where N and E are the particle number and the energy of the total system $A = A_1 + A_2$.

Hamilton function. The overall Hamilton function is defined as the sum of the Hamilton functions of A_1 and A_2:

$$H(q,p) = H_1(q(1), p(1), N_1) + H_2(q(2), p(2), N_2) .$$

For the above assumption to be valid, we neglect interactions among particles in A_1 and A_2:

$$H_{12} = 0 .$$

This is a valid assuming for most macroscopic systems.

Microcanonical ensemble. Since the total system A is isolated, its distribution function is given in the microcanonical ensemble as

$$\rho(q,p) \; = \; \frac{1}{\Omega(E,N)} \delta(E - H_1 - H_2) \,,$$

as in (9.1), with t

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

being the density of states.

Sub-macroscopic particle exchange. The total entropy of the combined system is given by the microcanonical expression

$$S \; = \; k_B \ln \left(\frac{\Omega(E,N)\Delta}{\Gamma_0(N)} \right) , \qquad \Gamma_0(N) \; = \; h^{3N} N_1! N_2! \,, \qquad (10.1)$$

where Δ is the width of the energy shell. Compare (9.4) and Sect. 9.4.

The reason that $\Gamma_0(N) \sim N_1! N_2!$ in (10.1), and not $\sim N!$, stems from the assumption that there is no particles exchange on the macroscopic level. This is in line with the observation made in Sect. 9.6 that energy fluctuations, i.e. the exchange of energy between a system and the heat reservoir, scale like $1/\sqrt{N}$ relatively to the internal energy. We come back to this issue in Sect. 10.3.2.

Integrating out the reservoir. We are now interested in the system A_1. As we did for the canonical ensemble, we integrate the total probability density $\rho(q,p)$ over the phase space of the reservoir A_2. We obtain

$$\begin{aligned}
\rho_1(q(1), p(1), N_1) & \equiv \int dq(2) \, dp(2) \, \rho(q,p) \\
& = \frac{\int dq(2) \, dp(2) \, \delta(E - H_1 - H_2, N)}{\Omega(E,N)} \\
& \equiv \frac{\Omega_2(E - H_1, N - N_1)}{\Omega(E,N)}
\end{aligned} \qquad (10.2)$$

in analogy to (9.2).

Expanding in E_1 and N_1. With $E_1 \ll E$ and $N_1 \ll N$, we can approximate the slowly varying logarithm of $\Omega_2(E_2, N_2)$ around $E_2 = E$ and $N_2 = N$ and thus obtain:

$$\begin{aligned}
S_2(E - E_1, N - N_1) & = k_B \ln \left(\frac{\Omega_2(E - E_1, N - N_1)\Delta}{\Gamma_0(N)} \right) \\
& = S_2(E,N) - E_1 \left(\frac{\partial S_2}{\partial E_2} \right)_{N_2} \Bigg|_{\substack{E_2 = E \\ N_2 = N}} - N_1 \left(\frac{\partial S_2}{\partial N_2} \right)_{E_2} \Bigg|_{\substack{E_2 = E \\ N_2 = N}} .
\end{aligned}$$

Using (5.14), $TdS = dU + PdV - \mu dN$, the derivatives may be substituted by

$$k_b \frac{\partial}{\partial E} \ln \left(\frac{\Omega_2(E,N)\Delta}{\Gamma_0(N)} \right) = \left(\frac{\partial S_2}{\partial E_2} \right)_{\substack{N_2 = N \\ E_2 = E}} = \frac{1}{T} \tag{10.3}$$

and

$$k_b \frac{\partial}{\partial N} \ln \left(\frac{\Omega_2(E,N)\Delta}{\Gamma_0(N)} \right) = \left(\frac{\partial S_2}{\partial N_2} \right)_{\substack{N_2 = N \\ E_2 = E}} = -\frac{\mu}{T} \, . \tag{10.4}$$

Expansion of the probability density. (10.3) and (10.4) allow to expand $\Omega_2(E - E_1, N - N_1)$ as

$$k_B \ln \left(\frac{\Omega_2(E - E_1, N - N_1)\Delta}{\Gamma_0(N)} \right) = k_B \ln \left(\frac{\Omega_2(E,N)\Delta}{\Gamma_0(N)} \right) - \frac{E_1}{T} + \frac{N_1\mu}{T} \, ,$$

which leads via $E_1 = H_1$ and (10.2) to a probability distribution of the form

$$\rho_1(q(1), p(1), N_1) \sim \exp \left(- \left[H_1(q(1), p(1)) - \mu N_1 \right]/(k_B T) \right) \, .$$

Grand canonical partition function. The constant of proportionality for the probability distribution is given by the *grand canonical partition function* $\mathcal{Z} = \mathcal{Z}(T, V, \mu)$,

$$\boxed{\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} \int \frac{d^{3N}q \, d^{3N}p}{h^{3N} N!} e^{-\beta[H(q,p,N) - \mu N]}} \, , \tag{10.5}$$

where we have dropped the index to the first system substituting ρ, N, q and p for ρ_1, N_1, $q(1)$ and $p(1)$. The partition function normalizes the distribution function

$$\boxed{\rho(q, p, N) = \frac{1}{h^{3N} N!} \frac{1}{\mathcal{Z}(T, V, \mu)} e^{-\beta[H(q,p,N) - \mu N]}} \tag{10.6}$$

to 1:

$$\sum_{N=0}^{\infty} \int d^{3N}q \, d^{3N}p \, \rho(q, p, N) = 1$$

Note that the normalization factor $h^{3N} N!$ in (10.5) and (10.6) cancel each other. It is in any can not possible to justify this factor within classical mechanics, as discussed previously in Sect. 8.2.

Internal Energy. From the definition (10.5) of the grand canonical potential function it follows that internal energy $U = \langle H \rangle$ is given by

$$\boxed{U - \mu N = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}(T, V, \mu)} \, . \tag{10.7}$$

10.2   Grand canonical potential

In Sect. 5.4 we defined the grand canonical potential* as

$$\boxed{\Omega(T,V,\mu) \;=\; F(T,V,N) - \mu N}\;, \qquad \Omega \;=\; -PV \;,$$

and showed with Eq. (5.21) that

$$U - \mu N \;=\; \frac{\partial}{\partial \beta}\big(\beta\Omega\big) \;=\; -\frac{\partial}{\partial \beta}\ln \mathcal{Z}(T,V,\mu) \;, \tag{10.8}$$

where we have used in the last step the representation (10.7) of $U - \mu N = \partial \ln \mathcal{Z}/\partial\beta$.

Grand canonical potential. From (10.8) we may determine (up-to a constant) the grand canonical potential with

$$\boxed{\Omega(T,V,\mu) \;=\; -k_B T \,\ln \mathcal{Z}(T,V,\mu)}\;, \qquad \mathcal{Z} \;=\; e^{-\beta\Omega} \tag{10.9}$$

as the logarithm of the grand canonical potential. Note the analog to the relation $F = -k_B T \ln Z_N$ valid within the canonical ensemble.

Calculating with the grand canonical ensemble. To summarize, in order to obtain the thermodynamic properties of our system in contact with a heat and particle reservoir, we do the following:

1 - calculate the grand canonical partition function:

$$\mathcal{Z} \;=\; \sum_{N=0}^{\infty}\int \frac{d^{3N}q\,d^{3N}p}{h^{3N}N!}\,e^{-\beta(H-\mu N)} \;;$$

2 - calculate the grand canonical potential:

$$\Omega \;=\; -k_B T \ln \mathcal{Z} \;=\; -PV, \qquad d\Omega \;=\; -SdT - PdV - Nd\mu \;;$$

3 - calculate the remaining thermodynamic properties through the equations:

$$S \;=\; -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}$$

$$P \;=\; -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} \;=\; -\frac{\Omega}{V}$$

$$N \;=\; -\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V}$$

and the remaining thermodynamic potentials through Legendre transformations.

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* Don't confuse the grand canonical potential $\Omega(T,V,\mu)$ with the density of microstates $\Omega(E)$!

10.3 Fugacity

By using the definition of the partition function in the canonical ensemble,

$$Z_N = \frac{1}{h^{3N} N!} \int d^{3N}q \, d^{3N}p \, e^{-\beta H},$$

we can rewrite the partition function in the grand canonical ensemble as

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} e^{\mu N \beta} Z_N(T) = \boxed{\sum_{N=0}^{\infty} z^N Z_N(T)}, \tag{10.10}$$

where $z = \exp(\mu/k_B T)$ is denoted as the *fugacity*. Equation (10.10) shows that $\mathcal{Z}(T, \mu)$ is the discrete Laplace transform of $Z_N(T)$.

10.3.1 Particle distribution function

In the canonical ensemble the particle number N was fixed, whereas it is a *variable* in the in the grand canonical ensemble. We define with

$$w_N = e^{\beta \mu N} \frac{Z_N(T)}{\mathcal{Z}(T, \mu)} \tag{10.11}$$

the probability that the system at temperature T and with chemical potential μ contains N particles. It is normalized:

$$\sum_{N=0}^{\infty} w_n = \sum_{N=0}^{\infty} \frac{e^{\beta \mu N} Z_N(T)}{\mathcal{Z}(T, \mu)} = 1 \ .$$

Average particle number. That mean particle number $\langle N \rangle$ is given by

$$\langle N \rangle = \sum_{N=0}^{\infty} N \, w_N(T, V) = \frac{\sum_{N=0}^{\infty} N \, z^N \, Z_N(T, V)}{\sum_{N=0}^{\infty} z^N \, Z_N(T, V)} \ , \tag{10.12}$$

which can be rewritten as

$$\boxed{\langle N \rangle = \frac{1}{\beta} \left[\frac{\partial}{\partial \mu} \ln \mathcal{Z}(T, V, \mu) \right]_{T,V}}, \tag{10.13}$$

or, alternatively, as

$$\boxed{\langle N \rangle = z \left(\frac{\partial}{\partial z} \ln \mathcal{Z}(T, V, \mu) \right)_{T,V}}, \tag{10.14}$$

when making use of the definition of fugacity z.

Chemical potential. Conversely, the chemical potential for a given average particle number $N = \langle N \rangle$,

$$\mu = \mu(T, V, N) \ ,$$

is obtained by by inverting (10.13).

10.3.2   Particle number fluctuations

We start by noting that from

$$\Omega = -PV, \qquad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$$

it follows that

$$\left(\frac{\partial P}{\partial \mu}\right)_{T,V} = \frac{-1}{V}\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = \frac{N}{V} \ . \tag{10.15}$$

Particle number fluctuations. From (10.12),

$$\langle N \rangle = \frac{\sum_N N\, e^{\beta \mu N}\, Z_N(T,V)}{\sum_N e^{\beta \mu N}\, Z_N(T,V)} \ ,$$

it follows that

$$\boxed{\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \beta\Big[\langle N^2 \rangle - \langle N \rangle^2\Big]} \ , \tag{10.16}$$

where the second term results from the derivative of the denumerator.

Two systems are in equilibrium with respect to the exchange in particle if their chemical potentials are identical, $\mu = \mu_1 = \mu_2$. It hence makes sense that the the dependence of the particle number on the chemical potential is proportional to the size of the particle number fluctuations $\langle N^2 \rangle - \langle N \rangle^2$, which mediate the equilibrium.

Scaling to the thermodynamic limit. Using (10.15) we can recast (10.16) into

$$\left(\frac{\partial^2 P}{\partial \mu^2}\right)_{T,V} = \frac{\beta}{V}\Big[\langle N^2 \rangle - \langle N \rangle^2\Big] \ . \tag{10.17}$$

The left-hand side of (10.17) is intensive, viz it scales like V^0, since both the pressure P and the chemical potential are intensive. For the right-hand side to scale like V^0 for large volume V we hence need that

$$\sqrt{\langle N^2 \rangle - \langle N \rangle^2} \sim \sqrt{V}, \qquad \frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{N} \sim \frac{1}{\sqrt{N}} \ , \tag{10.18}$$

where we have used that $V \sim N$ for fixed densities. The relative particle number fluctuations hence vanish in the thermodynamic limit; a precondition for the grand-canonical and the canonical ensemble to yield identical results.

10.3.3   Stability conditions

The mechanical stability condition for a system implies that its compressibility κ_T cannot take negative values, i.e.,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \geq 0 \ .$$

In fact, this can be proven within the grand canonical ensemble in the same way as it was proven in Sect. 9.6 that the energy fluctuations in the canonical ensemble fulfill the thermal stability criterion

$$C_V = k_B \beta^2 \left\langle \left(H - \langle H \rangle \right)^2 \right\rangle \geq 0 . \tag{10.19}$$

Intensive variables. We start be defining the free energy per particle, $a = F/N$, as

$$\boxed{a(T,v) \equiv \frac{F(T,V,N)}{N}} \qquad v = V/N , \tag{10.20}$$

where the v is the volume per particle (the specific volume).

  – $a = F/N$ is intensive and a function of the intensive variable T. It can therefore not be a independently a function of the volume V or the particle number N (which are extensive), only of V/N (which is intensive).

  – The circumstance that a is a function of V/N only allows to transform derivative with respect to V and to N into each other, the reason of using this representation.

Chemical potential. With (10.20) we find

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial \left(NF/N \right)}{\partial N} = a + N \frac{\partial a}{\partial N} = a + N \frac{\partial a}{\partial (V/N)} \underbrace{\frac{\partial (V/N)}{\partial N}}_{-V/N^2} ,$$

when using (5.12), namely that $dF = -SdT - PdV + \mu dN$. This relation yields

$$\mu = a - v \frac{\partial a}{\partial v}, \qquad \boxed{\frac{\partial \mu}{\partial v} = -v \frac{\partial^2 a}{\partial v^2}} . \tag{10.21}$$

Note, that μ is intensive.

Pressure. For the pressure P, an intensive variable, we find likewise that

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial \left(NF/N \right)}{\partial V} = -N \frac{\partial a}{\partial (V/N)} \underbrace{\frac{\partial (V/N)}{\partial V}}_{1/N} ,$$

which results in

$$P = -\frac{\partial a}{\partial v}, \qquad \frac{\partial P}{\partial v} = -\frac{\partial^2 a}{\partial v^2}, \qquad \boxed{\frac{\partial \mu}{\partial v} = v \frac{\partial P}{\partial v}} , \tag{10.22}$$

where we have used in the last step the comparison with (10.21).

Particle fluctuations in intensive variables. Using intensive variables for (10.17),

$$\frac{\beta}{V}\Big[\langle N^2\rangle - \langle N\rangle^2\Big] = \frac{\partial^2 P(T,v)}{\partial\mu^2} = \left(\frac{\partial}{\partial v}\frac{\partial P}{\partial\mu}\right)\frac{\partial v}{\partial\mu} , \qquad (10.23)$$

the last relation of (10.22) and (10.15), namely $\partial P/\partial\mu = 1/v$, we obtain

$$\frac{\partial^2 P(T,v)}{\partial\mu^2} = \underbrace{\left(\frac{\partial}{\partial v}\frac{1}{v}\right)}_{-1/v^2}\underbrace{\left(\frac{1}{v}\frac{\partial v}{\partial P}\right)}_{-\kappa_T}, \qquad \kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{v}\frac{\partial v}{\partial P} .$$

Compressibility. Taking the results together we obtain

$$\boxed{\;\kappa_T = \frac{\beta v^2}{V}\Big[\langle N^2\rangle - \langle N\rangle^2\Big] = \beta\frac{V}{N}\frac{\langle N^2\rangle - \langle N\rangle^2}{N}\;}. \qquad (10.24)$$

for the compressibility κ_T.

– The compressibility is strictly positive, $\kappa_T \geq 0$, which implies that the system constricts when the pressure increases. The basic stability condition.

– The compressibility is finite if the size of the fluctuations $\sqrt{\langle N^2\rangle - \langle N\rangle^2}$ vanishes in the thermodynamic limit relative to the number of particles N present in the system.

Response vs. fluctuations. The specific heat C_V and the compressibility κ_T are measure the *response* of the system to a change of variables.

– A temperature gradient ΔT to the heat reservoir leads to a transfer of heat,

$$\Delta Q = C_V\Delta T,$$

which is proportional to C_V. Compare Sect. 3.2.

– An increase in temperature by ΔP leads to relative decrease of the volume by

$$\frac{\Delta V}{V} = \kappa_T\Delta P,$$

which is proportional to κ_T.

It is not a coincidence, that both response functions, C_V and κ_T, as given respectively by (10.19) and (10.24), are proportional to the fluctuations of the involved variables.

A system in which a certain variable A is not fluctuating (and hence fixed) cannot respond to perturbations trying to change A. The response always involves the fluctuation

$$\Big\langle\big(A - \langle A\rangle\big)^2\Big\rangle = \langle A^2\rangle - \langle A\rangle^2 .$$