Generalized ensembles

The procedure we have been used to move from the microcanonical to the canonical ensemble and from the canonical to the grandcanonical ensemble can be made more general and extended to other ensembles. Let us consider an ensemble I whose natural potential W depends, among the others, on the variable A. The partition function of this enesemble has the form

$$Z_I(A) = e^{-\alpha W(A)},$$

where α is a constant. Let $\bar{A}$ be the conjugate variable of A

$$\bar{A} = \frac{\partial W}{\partial A} \Rightarrow A = f\left(\bar{A}\right),$$

we want to move to another ensemble II whose natural potential is

$$\bar{W}\left(\bar{A}\right) = W\left(f\left(\bar{A}\right)\right) - f\left(\bar{A}\right)\bar{A},$$

with

$$\frac{\partial \bar{W}\left(\bar{A}\right)}{\partial \bar{A}} = \frac{\partial W(A)}{\partial \bar{A}} - A - \bar{A}\frac{\partial A}{\partial \bar{A}} = -A + \frac{\partial W(A)}{\partial A}\frac{\partial A}{\partial \bar{A}} - \bar{A}\frac{\partial A}{\partial \bar{A}} = -A,$$

and

$$Z_{II}\left(\bar{A}\right) = e^{-\alpha \bar{W}\left(\bar{A}\right)}.$$

We shown that this can be done by integrating

$$\boxed{Z_{II}\left(\bar{A}\right) = \int dA\, e^{-\alpha\left[W(A) - A\bar{A}\right]}}.$$

To prove it, we remember that one of the two conjugate variables must be intensive and the other extensive and consider the two cases

Case A intensive and $\bar{A}$ extensive Defining $w = \frac{W}{N}$ and $\bar{a} = \frac{\bar{A}}{N}$ it is possibe to write the function $D = W(A) - A\bar{A}$ of the two independent variables A and $\bar{A}$ as

$$D = N\left[w(A) - A\bar{a}\right].$$

Expanding around $\langle A\rangle$ which is an extremal point for D

$$\begin{aligned} D &\simeq N\left[w\left(\langle A\rangle\right) - \langle A\rangle\,\bar{a}\right] + N\left[\frac{\partial w(A)}{\partial A} - \bar{a}\right]_{A=\langle A\rangle}\left(A - \langle A\rangle\right) + \frac{1}{2}N\left[\frac{\partial^2 w(A)}{\partial^2 A}\right]_{A=\langle A\rangle}\left(A - \langle A\rangle\right)^2 = \\ &= \bar{W}\left(\bar{A}\right) + \frac{1}{2}\frac{\left(A - \langle A\rangle\right)^2}{\sigma_A^2}, \end{aligned}$$

$$\sigma_A^2 = \frac{1}{N\left[\frac{\partial^2 w(A)}{\partial^2 A}\right]_{A=\langle A\rangle}},$$

one gets

$$Z_{II}\left(\bar{A}\right) = \int dA\, e^{-\alpha\left[W(A) - A\bar{A}\right]} \sim e^{-\alpha \bar{W}\left(\bar{A}\right)}\sqrt{2\pi\sigma_A^2},$$

$$\bar{W}\left(\bar{A}\right) = -\frac{1}{\alpha}Z_{II}\left(\bar{A}\right) + O\left(\ln N\right).$$

Case A extensive and $\bar{A}$ intensive Here we define $a = \frac{A}{N}$The function $D = W(A) - A\bar{A}$ of the two independent variables A and $\bar{A}$ as

$$D = N\left[w(a) - a\bar{A}\right].$$

Expanding around $\langle a\rangle$

$$\begin{aligned} D &\simeq N\left[w(\langle a\rangle) - \langle a\rangle \bar{A}\right] + N\left[\frac{\partial w(a)}{\partial a} - \bar{A}\right]_{a=\langle a\rangle}(a - \langle a\rangle) + \frac{1}{2}N\left[\frac{\partial^2 w(a)}{\partial^2 a}\right]_{a=\langle a\rangle}(a - \langle a\rangle)^2 = \\ &= \bar{W}\left(\bar{A}\right) + \frac{1}{2}\frac{(a - \langle a\rangle)^2}{\sigma_a^2}, \end{aligned}$$

$$\sigma_a^2 = \frac{1}{N\left[\frac{\partial^2 w(a)}{\partial^2 a}\right]_{a=\langle a\rangle}},$$

one gets

$$Z_{II}\left(\bar{A}\right) = \int dA\, e^{-\alpha\left[W(A) - A\bar{A}\right]} \sim e^{-\alpha\bar{W}\left(\bar{A}\right)} N\sqrt{2\pi\sigma_a^2},$$

$$\bar{W}\left(\bar{A}\right) = -\frac{1}{\alpha}Z_{II}\left(\bar{A}\right) + O(\ln N).$$

Example 0.0.1. From canonical to grandcanonical ensemble ($F(N) \to \Omega(\mu)$):

$$Z_{gc}(\mu) = \sum_N e^{-\beta[F(N) - \mu N]}.$$

From microcanonical to canonical ensemble ($S(E) \to Z_c(T)$):

$$Z_c(T) = \int dE\, e^{\frac{1}{k_B}\left(S(E) - \frac{E}{T}\right)}.$$

Example 0.0.2. Isobaric ensemble ($F \to G$)

$$Z_{isob}(p) = \int dV\, e^{-\beta(F(V) + pV)}$$

Classical fluids

We consider here a system of interacting particles with Hamiltonian

$$H = K(\mathbf{p}) + U(\mathbf{q}),$$

where $U(\mathbf{q})$ contains all the interactions. The partition function at fixed N is

$$Z_N = \frac{1}{N!}\int D\mathbf{x}\, e^{-\beta K(\mathbf{p})} e^{-\beta U(\mathbf{q})} = \frac{1}{N!\lambda^{3N}}\int_V d\mathbf{q}\, e^{-\beta U(\mathbf{q})} = \frac{Q(T, V, N)}{N!\lambda^{3N}},$$

and the grandcanonical one

$$Z_{gc} = \sum_{N=0}^{\infty} Z_N z^N = \sum_{N=0}^{\infty} Q(T, V, N)\frac{z^N}{N!\lambda^{3N}}.$$

We assume that the potential is bounded from below

$$U(\mathbf{q}) \geq -BN, \qquad B > 0,$$

which implies the inequalities

$$Z_N \leq \frac{V^N e^{\beta BN}}{N! \lambda^{3N}},$$

and

$$|Z_{gc}| \leq \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{V e^{\beta B} |z|}{\lambda^3} \right)^N = e^{\frac{V e^{\beta B_{|z|}}}{\lambda^3}},$$

meaning that $Z_{gc}(z)$ is analytical on $\mathbb{C}$ for any finite volume V. We also notice that Z_{gc} has no zeroes for $z \in \mathbb{R}^+$. It can be proved that (**Lee and Young theorems**)

- If the frontier of the spatial volume scales as $\partial(V) \sim V^{\frac{2}{3}}$, then the grand-potential Ω is continuous and monotonic for $z \in \mathbb{R}^+$.
- For regions not containing zeroes of Z_{gc}, and for $V \to \infty$, then Ω is analytic.

As a consequence:

- p is a continuous function of z
- There are no singularities in the thermodynamic functions for z in regions which do not contain zeroes of Z_{gc}. In these regions correspond to stable phases of the system.

Typically, the zeroes of Z_{gc} are finite for a finite V and increase increaesing V. This can be understood thinking about a sistem composed by **hard spheres**, meaning that two particles cannot stay closer that twice their "radius". In this example $Q = 0$ for N larger than a certain maximum amount N^* of particles, corresponding to the volume completely filled with particles. Then Z_{gc} becomes a polynomial of degree N^* of z with N^* complex zeroes.

Sending $V \to \infty$ it **may** happen that, at some temperatures, the zeroes of Z_{gc} accumulate around $z = z_c > 0$. Then, if z_c is an isolate point, it could be a critical point separating different phases. The pressure remains continuous in z_c but its derivate or its second derivative could be discontinuous in z_c. In the first case in z_c a first order phase transition appears while in the second case the transition is of the econd order.

Virial expansion

From the virial theorem

$$\frac{\beta p}{\rho} = 1 + \frac{\beta}{3N} \sum_j \left\langle \vec{q_j} \cdot \vec{F}_j^{int} \right\rangle,$$

and assuming that the virial tends to zero if the density goes to zero (diluite limit and short-range interactions) one can expand (**virial expansion**)

$$\frac{\beta p}{\rho} = \sum_{l=1}^{\infty} B_l \rho^{l-1}, \quad B_0 = 1.$$

In the diluite limit, the system approaches the perfect gas behavior where we shown in the grand-canonical ensemble that $z = \frac{\lambda^3 N}{V} = \lambda^3 \rho$. This means that the limit of $\rho \to 0$ at finite temperature corresponds also to the limit of $z \to 0$. So the expansion in ρ is equivalent to the expansion in z. To see it better, consider a system of interacting particles

$$H = H_0 + \sum_{j<l} v_{j,l},$$

with

$$H_0(\mathbf{x}) = T(\mathbf{p}) + V_{ext}(\mathbf{q}),$$

and interaction

$$v_{j,l} = v\left(|\vec{q}_j - \vec{q}_l|\right).$$

The first order expansion in the fugacity of the partition function gives the coefficients

$$Z_{gc} = \sum_{N=0}^{\infty} Z_N z^N, \qquad Z_0 = 1, \quad Z_1 = \int D\mathbf{x}\, e^{-\beta H_0(D\mathbf{x})} = \frac{G\left(V\right)}{\lambda^3}.$$

Expanding the particle number

$$N = z\frac{\partial \ln Z_{gc}}{\partial z} = z\frac{\partial \ln \sum_{n=0}^{\infty} Z_N z^n}{\partial z},$$

in z one obtains

$$\begin{aligned}
N &= z\frac{\partial}{\partial z}\ln\left(1 + Z_1 z + Z_2 z^2 + \ldots\right) = \\
&= z\frac{\partial}{\partial z}\left[\left(Z_1 z + Z_2 z^2 + \ldots\right) - \frac{1}{2}\left(Z_1 z + Z_2 z^2 + \ldots\right)^2 + \ldots\right] = \\
&= z\frac{\partial}{\partial z}\left[Z_1 z + \left(Z_2 - \frac{Z_1^2}{2}\right) z^2 + \ldots\right] = \\
&= Z_1 z + 2\left(Z_2 - \frac{Z_1^2}{2}\right) z^2 + O\left(z^3\right) = \\
&= Z_1 z + 2\epsilon z^2 + O\left(z^3\right),
\end{aligned}$$

with

$$\epsilon = \left(Z_2 - \frac{Z_1^2}{2}\right).$$

In the diluite limit the density is:

$$\rho = \frac{N}{V} \simeq \frac{Z_1 z}{V} = \frac{G\left(V\right)}{V\lambda^3} z.$$

where $\frac{G(V)}{V\lambda^3}$ is an intensive quantity so in this limit

$$\rho = O\left(z\right).$$

Expansion of the grandpotential:

$$\begin{aligned}
\Omega &= -\frac{1}{\beta}\ln\sum_{N=0}^{\infty} Z_N z^N = \\
&= -\frac{1}{\beta}\left[Z_1 z + \left(Z_2 - \frac{Z_1^2}{2}\right) z^2 + \ldots\right] \\
\frac{pV}{k_B T} &= Z_1 z + \epsilon z^2 + O\left(z^3\right).
\end{aligned}$$

$$\begin{aligned}
\frac{p}{\rho}\beta &\simeq \frac{Z_1 z + \epsilon z^2}{Z_1 z + 2\epsilon z^2} = \frac{1 + \frac{\epsilon}{Z_1} z}{1 + 2\frac{\epsilon}{Z_1} z} = \left(1 + \frac{\epsilon}{Z_1} z\right)\left(1 - 2\frac{\epsilon}{Z_1} z\right) + O\left(z^2\right) = \\
&= 1 - \frac{\epsilon}{Z_1} z + O\left(z^2\right).
\end{aligned}$$

$$\frac{p}{\rho}\beta = 1 - \frac{\epsilon V}{Z_1^2}\rho + O\left(\rho^2\right) = 1 + B_2\rho + O\left(\rho^2\right),$$

where B_2 is the second virial coefficient.

- Evaluation of B_2

$$Z_2 = \frac{1}{2\lambda^6}\int d\vec{q}_1 d\vec{q}_2\, e^{-\beta(V_{ext}(\vec{q}_1)+V_{ext}(\vec{q}_2)+v_{1,2})},$$

$$B_2 = -V\left(\frac{Z_2}{Z_1^2}-\frac{1}{2}\right) = -V\left(\frac{1}{2G^2(V)}\int d\vec{q}_1 d\vec{q}_2\, e^{-\beta(V_{ext}(\vec{q}_1)+V_{ext}(\vec{q}_2)+v_{1,2})}-\frac{1}{2}\right).$$

- Meyer (cluster) expansion. If $V_{ext}=0$

$$\begin{aligned} B_2 &= -V\left(\frac{Z_2}{Z_1^2}-\frac{1}{2}\right) = -\frac{1}{2}\left(\frac{1}{V}\int d\vec{q}_1 d\vec{q}_2\, e^{-\beta v_{1,2}} - V\right) = \\ &= -\frac{1}{2}\left(\frac{1}{V}\int d\left(\vec{q}_1-\vec{q}_2\right) e^{-\beta v_{1,2}} \int_V d\left(\frac{\vec{q}_1+\vec{q}_2}{2}\right) - \int d\vec{q}\right) = \\ &= -2\pi\int dr\, r^2\left(e^{-\beta v(r)}-1\right) = -2\pi\int dr\, r^2 M(r), \end{aligned}$$

  Meyer's function

$$M(r) = \left(e^{-\beta v(r)}-1\right).$$

  This is the first order of the so-called cluster expansion.

Van der Waals gas. The equation of state for the Van der Waals gas is

$$p = \frac{k_B T}{v-b} - \frac{a}{v^2} = \frac{1}{\beta v}\frac{1}{1-b\rho} - a\rho^2,$$

whose virial expansion gives

$$\frac{\beta p}{\rho} = \frac{1}{1-b\rho} - \beta a\rho \simeq (1+b\rho) - a\beta\rho = 1+(b-a\beta)\rho,$$

with second coefficient

$$B_2 = b - a\beta.$$

We can give an extimation of B_2 from a Lennard-Jones potential

$$v(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

$$B_2 = -2\pi\int_0^\infty dr\, r^2 M(r) = -2\pi\left(\int_0^\sigma dr\, r^2 M(r) + \int_\sigma^\infty dr\, r^2 M(r)\right).$$

To compute the integral we use the incompressible sphere approximation for $r<\sigma$ and the first order expansion of $M(r)$ for $z>\sigma$

$$M(r) \simeq \begin{cases} -1 & r<\sigma \\ -4\beta\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & r>\sigma \end{cases}$$

$$\begin{aligned} B_2 &\simeq 2\pi\left(\int_0^\sigma dr\, r^2 + 4\beta\varepsilon\sigma^6\int_\sigma^\infty dr\,\left[\sigma^6\left(\frac{1}{r}\right)^{10} - \left(\frac{1}{r}\right)^4\right]\right) = \\ &= \frac{2\pi}{3}\sigma^3 - \frac{8\pi\beta\varepsilon\sigma^3}{9} + \frac{8\pi\beta\varepsilon\sigma^3}{3} = \\ &= \frac{2\pi}{3}\sigma^3\left(1-\frac{8}{3}\beta\varepsilon\right). \end{aligned}$$

So the Van der Waals coefficients are

$$a = \frac{16}{9}\pi\beta\varepsilon\sigma^3, \quad b = \frac{2\pi}{3}\sigma^3.$$