

# Isobaric phase space distribution and partition function

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Assume two system coupled to a common thermal reservoir so that each system is described by a canonical distribution at temperature  $T$ . System 2 act as a barostat whose number of particles and volume is much larger than system 1, respectively.

If the volume of each system were fixed, the total canonical partition function would be

$$\begin{aligned} Q(N, V, T) &= C_N \int dx_1 dx_2 e^{-\beta \mathcal{H}_1(x_1) + \mathcal{H}_2(x_2)} \\ &= g(N, N_1, N_2) C_{N_1} \int dx_1 de^{-\beta \mathcal{H}_1(x_1)} C_{N_2} \int dx_2 de^{-\beta \mathcal{H}_2(x_2)} \end{aligned} \quad (1)$$

Where  $g(N, N_1, N_2)$  is an overall normalization constant.

The canonical phase space distribution function  $f(x)$  of combined system 1 and 2 is

$$f(x) = \frac{C_N e^{-\beta \mathcal{H}}}{Q(N, V, T)} \quad (2)$$

To determine the distribution function of system 1, we need to integrate over the phase space of system 2

$$\begin{aligned} f_1(x_1, V_1) &= \frac{g(N, N_1, N_2)}{Q(N, V, T)} C_{N_1} de^{-\beta \mathcal{H}_1(x_1)} C_{N_2} \int dx_2 de^{-\beta \mathcal{H}_2(x_2)} \\ &= \frac{Q_2(N - N_1, V - V_1, T)}{Q(N, V, T)} C_{N_1} de^{-\beta \mathcal{H}_1(x_1)} \end{aligned} \quad (3)$$

Express the partition function in terms of Helmholtz free energies according to  $Q(N, V, T) = e^{\beta A(N, V, T)}$ ,

$$\frac{Q_2(N_2, V - V_1, T)}{Q(N, V, T)} = e^{\beta [A(N - N_1, V - V_1, T) - A(N, V, T)]} \quad (4)$$

Expand  $A(N - N_1, V - V_1, T)$  to first order

$$\begin{aligned} A(N - N_1, V - V_1, T) &\approx A(N, V, T) - N_1 \left( \frac{\partial A}{\partial N} \right) \Big|_{N_1=0, V_1=0} - V_1 \left( \frac{\partial A}{\partial V} \right) \Big|_{N_1=0, V_1=0} \\ &= A(N, V, T) - \mu N_1 + P V_1 \end{aligned} \quad (5)$$

So

$$f_1(x_1, V_1) = g(N, N_1, N_2) e^{\beta \mu N_1} e^{-\beta P V_1} e^{-\beta \mathcal{H}_1} \quad (6)$$

which means the distribution can of the system can be obtained. If we focus on the system and drop the extraneous "1" subscript, the equation can be rearranged as

$$e^{-\beta \mu N} \int_0^\infty dV \int dx f(x, V) = I_N \int_0^\infty dV \int dx e^{-\beta[\mathcal{H} + pV]} \quad (7)$$

which defines the partition function of the isothermal-isobaric ensemble as

$$\Delta(N, P, T) == I_N \int_0^\infty dV \int dx e^{-\beta[\mathcal{H} + pV]} \quad (8)$$