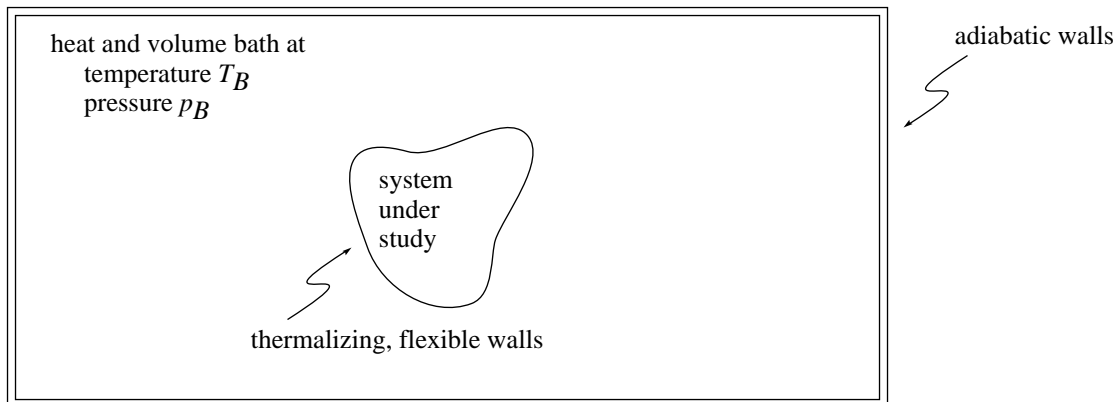


Derivation of Isobaric Ensemble

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Microstate x of system under study means, for example, positions and momenta of all atoms plus volume of balloon.

Macrostate of system under study specified by variables (T, p, N) .

What is the probability $\mathcal{P}(x)$ that system under study is in microstate x ?

Total energy is bath energy plus system energy; total volume is bath volume plus system volume

$$E_T = E_B + H(x); \quad V_T = V_B + V(x).$$

As with the canonical ensemble

$$\frac{\mathcal{P}(x_2)}{\mathcal{P}(x_1)} = e^{[S_B(2) - S_B(1)]/k_B}.$$

As system under study changes from state x_1 to x_2 , bath changes through

$$\begin{aligned} dS_B &= \frac{1}{T_B} (dE_B + p_B dV_B - \mu_B dN_B) \\ \Delta S_B &= \frac{1}{T_B} (\Delta E_B + p_B \Delta V_B) = -\frac{1}{T_B} (\Delta E + p_B \Delta V) \end{aligned}$$

so

$$\frac{\mathcal{P}(x_2)}{\mathcal{P}(x_1)} = e^{-\{H(x_2) + p_B V(x_2)\} - \{H(x_1) + p_B V(x_1)\} / k_B T_B}.$$

But $T_B = T$ of system under study, and $p_B = p$ of system under study. All references to the bath have vanished. Using separation of variables

$$\frac{\mathcal{P}(x_1)}{e^{-\{H(x_1) + pV(x_1)\} / k_B T}} = \frac{\mathcal{P}(x_2)}{e^{-\{H(x_2) + pV(x_2)\} / k_B T}} \equiv \frac{1}{\Upsilon(T, p, N)}$$

and

$$\mathcal{P}(x) = \frac{e^{-\{H(x) + pV(x)\} / k_B T}}{\Upsilon(T, p, N)}.$$

The isobaric partition function is the normalization factor

$$\Upsilon(T, p, N) = \sum_x e^{-\beta\{H(x) + pV(x)\}},$$

where now the sum over microstates includes a sum (actually integral) over microstates with different $V(x)$. Exactly what is meant by a “sum over all states” depends on the system under study. For classical atoms modeled as point particles

$$\Upsilon(T, p, N) = \frac{1}{N! h_0^{3N}} \int_0^\infty dV \int d\Gamma e^{-\{H(\Gamma) + pV\} / k_B T}$$

where the right-hand integral extends over all phase space.

What is the connection to thermodynamics?

Interpret the thermodynamic volume V as $\langle V(\mathbf{x}) \rangle$:

$$V = \langle V(\mathbf{x}) \rangle = \frac{\sum_{\mathbf{x}} V(\mathbf{x}) e^{-\beta\{H(\mathbf{x})+pV(\mathbf{x})\}}}{\sum_{\mathbf{x}} e^{-\beta\{H(\mathbf{x})+pV(\mathbf{x})\}}} = -\frac{1}{\beta} \frac{\partial}{\partial p} \ln \left\{ \sum_{\mathbf{x}} e^{-\beta\{H(\mathbf{x})+pV(\mathbf{x})\}} \right\}_{T,N}$$

Comparison of this equation to the corresponding thermodynamic equation,

$$V = -k_B T \left. \frac{\partial \ln \Upsilon}{\partial p} \right)_{T,N} \quad \text{to} \quad V = \left. \frac{\partial G}{\partial p} \right)_{T,N},$$

leads to the identification

$$G(T, p, N) = -k_B T \ln \Upsilon(T, p, N).$$

Additional reasoning results in (1) the interpretation of pressure as control parameter for volume and (2) a dispersion-susceptibility relation

$$\Delta V \sim \sqrt{\left. \frac{\partial V}{\partial p} \right)_{T,N}} \sim \sqrt{\kappa_T}.$$

This equation shows that in the thermodynamic limit the spread of volumes grows small in the sense that

$$\frac{\Delta V}{\langle V(\mathbf{x}) \rangle} \rightarrow 0.$$