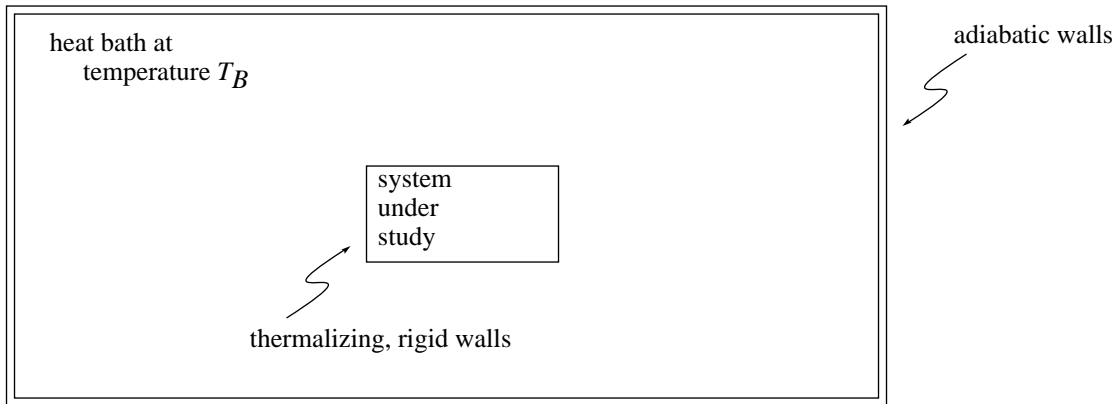# Derivation of Canonical Ensemble

Dan Styer, 17 March 2017, revised 20 March 2018

Microstate x of system under study means, for example, positions and momenta of all atoms, or direction of all spins.

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

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

Total energy is bath energy plus system energy,

$$E_T = E_B + H(\mathsf{x}).$$

Using $\Omega_B(1)$ for number of bath microstates when system under study is in microstate x_1, and $S_B(1)$ for entropy of bath when system under study is in microstate x_1,

$$
\begin{aligned}
\mathcal{P}(\mathsf{x}_1) &\propto \Omega_B(1) = e^{S_B(1)/k_B} \\
\mathcal{P}(\mathsf{x}_2) &\propto \Omega_B(2) = e^{S_B(2)/k_B} \\
\frac{\mathcal{P}(\mathsf{x}_2)}{\mathcal{P}(\mathsf{x}_1)} &= e^{[S_B(2) - S_B(1)]/k_B}
\end{aligned}
$$

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

$$
\begin{aligned}
dS_B &= \frac{1}{T_B}(dE_B + p_B\, dV_B - \mu_B\, dN_B) \\
\Delta S_B &= \frac{1}{T_B}\Delta E_B = -\frac{1}{T_B}[H(\mathsf{x}_2) - H(\mathsf{x}_1)]
\end{aligned}
$$

so

$$\frac{\mathcal{P}(\mathsf{x}_2)}{\mathcal{P}(\mathsf{x}_1)} = e^{-[H(\mathsf{x}_2) - H(\mathsf{x}_1)]/k_B T_B}.$$

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

$$\frac{\mathcal{P}(\mathsf{x}_1)}{e^{-H(\mathsf{x}_1)/k_B T}} = \frac{\mathcal{P}(\mathsf{x}_2)}{e^{-H(\mathsf{x}_2)/k_B T}} \equiv \frac{1}{Z(T, V, N)}$$

and

$$\mathcal{P}(\mathsf{x}) = \frac{e^{-H(\mathsf{x})/k_B T}}{Z(T, V, N)}.$$

The partition function (German "Zustandsumme") is the normalization factor

$$Z(T, V, N) = \sum_{\mathsf{x}} e^{-H(\mathsf{x})/k_B T} = \sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}.$$

Exactly what is meant by a "sum over all states" depends on the system under study. For classical atoms modeled as point particles

$$Z(T, V, N) = \frac{1}{N! \, h_0^{3N}} \int d\Gamma \, e^{-H(\Gamma)/k_B T}$$

where the integral extends over all phase space.

What is the connection to thermodynamics?

Interpret the thermodynamic energy E as $\langle H(\mathsf{x}) \rangle$:

$$E = \langle H(\mathsf{x}) \rangle = \frac{\displaystyle\sum_{\mathsf{x}} H(\mathsf{x}) e^{-\beta H(\mathsf{x})}}{\displaystyle\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}} = -\frac{\partial}{\partial \beta} \ln \left\{ \sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})} \right\},$$

where the derivative is taken with constant mechanical parameters (V, N, etc.).

Comparison of this equation to the Gibbs-Helmholtz equation,

$$E = -\left. \frac{\partial \ln Z}{\partial \beta} \right)_{V,N} \qquad \text{to} \qquad E = \left. \frac{\partial (\beta F)}{\partial \beta} \right)_{V,N},$$

leads to the identification

$$F(T, V, N) = -k_B T \ln Z(T, V, N).$$

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

$$\Delta E = T \sqrt{k_B C_V} = T \sqrt{k_B \left. \frac{\partial E}{\partial T} \right)_{V,N}}.$$

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

$$\frac{\Delta E}{\langle H(\mathsf{x}) \rangle} \to 0.$$