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 \( \mathcal{P}(x) \) that system under study is in microstate \( x \)?**

Total energy is bath energy plus system energy,

\[
E_T = E_B + H(x).
\]

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 \( x_1 \),

\[
\begin{align*}
\mathcal{P}(x_1) & \propto \Omega_B(1) = e^{S_B(1)/k_B} \\
\mathcal{P}(x_2) & \propto \Omega_B(2) = e^{S_B(2)/k_B} \\
\frac{\mathcal{P}(x_2)}{\mathcal{P}(x_1)} & = e^{[S_B(2) - S_B(1)]/k_B}
\end{align*}
\]

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

\[
\begin{align*}
dS_B &= \frac{1}{T_B} (dE_B + p_B \, dV_B - \mu_B \, dN_B) \\
\Delta S_B &= \frac{1}{T_B} \Delta E_B = -\frac{1}{T_B} [H(x_2) - H(x_1)]
\end{align*}
\]

so

\[
\frac{\mathcal{P}(x_2)}{\mathcal{P}(x_1)} = e^{-[H(x_2) - H(x_1)]/k_B T_B}.
\]

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

\[
\frac{\mathcal{P}(x_1)}{e^{-H(x_1)/k_B T}} = \frac{\mathcal{P}(x_2)}{e^{-H(x_2)/k_B T}} = \frac{1}{Z(T, V, N)}
\]

and

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

The partition function (German “Zustandsumme”) is the normalization factor

\[
Z(T, V, N) = \sum_x e^{-H(x)/k_B T} = \sum_x e^{-\beta H(x)}.
\]
Exactly what is meant by a “sum over all states” depends on the system under study. For classical atoms modeled as point particles

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

where the integral extends over all phase space.

**What is the connection to thermodynamics?**

Interpret the thermodynamic energy \( E \) as \( \langle H(x) \rangle \):

\[ E = \langle H(x) \rangle = \frac{\sum_x H(x) e^{-\beta H(x)}}{\sum_x e^{-\beta H(x)}} = -\frac{\partial}{\partial \beta} \ln \left\{ \sum_x e^{-\beta H(x)} \right\}, \]

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

Comparison of this equation to the Gibbs-Helmholtz equation,

\[ E = -\frac{\partial \ln Z}{\partial \beta}_{V, N} \quad \text{to} \quad E = \frac{\partial (\beta F)}{\partial \beta}_{V, N}, \]

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

\[ \Delta E = T \sqrt{k_B C_V} = T \sqrt{k_B \frac{\partial E}{\partial T}}_{V, N}. \]

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

\[ \frac{\Delta E}{\langle H(x) \rangle} \to 0. \]