Isobaric Ensemble

In the isobaric ensemble with temperature $T$ and pressure $P$, a macroscopic system has fluctuations in its energy $E$ and its volume $V$. The isobaric ensemble can be derived by considering a system that can exchange energy and volume with a much larger reservoir. The system and reservoir are described by the microcanonical ensemble with total energy $E_{\text{tot}}$ and total volume $V_{\text{tot}}$. The number of microstates for the system + reservoir in which the system has energy $E$ and volume $V$ is

$$\Omega_{\text{res}}(E_{\text{tot}} - E, V_{\text{tot}} - V) \times \Omega(E, V).$$

The logarithm of $\Omega_{\text{res}}$ can be expanded in powers of $E$ and $V$ and truncated after the first-order terms:

$$S_{\text{res}}(E_{\text{tot}} - E, V_{\text{tot}} - V) = S_{\text{res}}(E_{\text{tot}}, V_{\text{tot}}) - \frac{\partial S_{\text{res}}}{\partial E_{\text{res}}}(E_{\text{tot}}, V_{\text{tot}}) E - \frac{\partial S_{\text{res}}}{\partial V_{\text{res}}}(E_{\text{tot}}, V_{\text{tot}}) V.$$  

A. Use the fundamental thermodynamic relation to express the partial derivatives in terms of simpler thermodynamic properties of the reservoir.

$$dU = TdS - PdV \implies \left(\frac{\partial S_{\text{res}}}{\partial E_{\text{res}}}\right)_{V_{\text{res}}} = \frac{1}{T_{\text{res}}} \quad \left(\frac{\partial S_{\text{res}}}{\partial V_{\text{res}}}\right)_{E_{\text{res}}} = \frac{P_{\text{res}}}{T_{\text{res}}}$$

Upon inserting $\Omega_{\text{res}} = \exp(S_{\text{res}})$ back into the expression for the number of microstates, it has the form

$$\Omega_{\text{res}}(E_{\text{tot}}, V_{\text{tot}}) \Omega(E, V) \exp(-\beta E - \gamma V).$$

B. Identify $\beta$ and $\gamma$ with thermodynamic properties of the system.

$$\beta = \frac{1}{T}, \quad \gamma = \frac{P}{T}$$

C. Deduce an expression for the probability $P_r$ for a microstate $r$ of the system.

$$P_r = \frac{1}{Z} e^{-\beta E_r - \gamma V_r}, \quad Z = \sum_r e^{-\beta E_r - \gamma V_r}$$

D. Express the normalizing factor in the probability as a sum over microstates. Express it as an integral over the volume $V$ involving the canonical partition function $Z(E, V)$.

$$Z = \int_0^V dV \sum_r e^{-\beta E_r - \gamma V_r} = \int_0^V dV e^{-\gamma V} \sum_r e^{-\beta E_r} = \int_0^V dV e^{-\gamma V} Z(T, V)$$
The probability of a microstate \( r \) in the isobaric ensemble with temperature \( T = 1/\beta \) and pressure \( P = \gamma/\beta \) is

\[
P_r = \frac{1}{Z} \exp(-\beta E_r - \gamma V_r), \quad Z(\beta, \gamma) = \sum_r \exp(-\beta E_r - \gamma V_r).
\]

The average energy \( U \) of the system is defined by a weighted sum, and it can be expressed as a partial derivative of \( \log Z \):

\[
U \equiv \sum_r P_r E_r = \frac{1}{Z} \sum_r E_r e^{-\beta E_r - \gamma V_r} = \frac{1}{Z} \left( \frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r - \gamma V_r} \right) = -\frac{\partial}{\partial \beta} \log Z.
\]

E. Define the average volume \( \overline{V} \) of the system by a weighted sum. Use it to derive an expression for \( \overline{V} \) as a partial derivative of \( \log Z \).

\[
\overline{V} = \sum_r P_r V_r = \frac{1}{Z} \sum_r V_r e^{-\beta E_r - \gamma V_r}
\]

\[
= \frac{1}{Z} \left( -\frac{\partial}{\partial \gamma} \sum_r e^{-\beta E_r - \gamma V_r} \right) = -\frac{\partial}{\partial \gamma} \log Z
\]

The entropy is \( S = -\sum_r P_r \log P_r \).

F. By inserting the expression for \( P_r \) into the argument of the logarithm, express \( S \) as a linear combination of \( U \), \( \overline{V} \), and \( \log Z \).

\[
\begin{align*}
S &= -\sum_r P_r (\beta E_r - \gamma V_r - \log Z) \\
   &= \beta \sum_r P_r E_r + \gamma \sum_r P_r V_r + \log Z \sum_r P_r = \beta U + \gamma \overline{V} + \log Z
\end{align*}
\]

The Gibbs free energy is defined by \( G = U - T S + P V \).

G. Show that the expression for \( S \) in part F implies \( Z = \exp(-\beta G) \).

\[
\log Z = S - \beta U - \gamma \overline{V} = -\beta \left( U - \frac{1}{\beta} S + (\gamma/\beta) \overline{V} \right)
\]

\[
= -\beta (U - TS + PV) = -\beta G
\]

H. Determine the thermodynamic relation for the Gibbs free energy.

\[
\begin{align*}
dG &= dU - d(TS) + d(PV) \\
   &= (TdS - PV) - (Tds + sdt) + (\betaPV + Vdp) = -sdt + Vdp
\end{align*}
\]