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 $E_{\rm tot}$ and total volume $V_{\rm tot}$. The number of microstates for the system+reservoir in which the system has energy E and volume V is

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

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

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

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

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

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

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

B. Identify β and γ with thermodynamic properties of the system.

$$\beta = \frac{1}{T} \qquad \gamma = \frac{P}{T}$$

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

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

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 $Z(\underset{T}{\cancel{E}}, V)$.

$$\mathcal{Z} = \int_0^V dV \sum_{r:V_r=V} e^{-\beta E_r - \gamma V_r} = \int_0^V dV e^{-\gamma V} \sum_{r:V_r=V} e^{-\beta E_r}$$

$$= \int_0^V dV e^{-\gamma V} Z(T, V)$$

The probability of a microstate r in the isobaric ensemble with temperature $T = 1/\beta$ and pressure $P = \gamma/\beta$ is

$$P_r = \frac{1}{\mathcal{Z}} \exp(-\beta E_r - \gamma V_r), \qquad \mathcal{Z}(\beta, \gamma) = \sum_r \exp(-\beta E_r - \gamma V_r).$$

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

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

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

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

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

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, $\bar{V}$, and $\log \mathcal{Z}$.

$$S = -\sum_r P_r \left(-\beta E_r - \gamma V_r - \log Z \right)$$

$$= \beta \sum_r P_r E_r + \gamma \sum_r P_r V_r + \log Z \sum_r P_r = \beta U + \gamma \bar{V} + \log Z$$

The Gibbs free energy is defined by $G = U - TS + PV$.
G. Show that the expression for S in part F implies $\mathcal{Z} = \exp(-\beta G)$.

$$\log Z = S - \beta U - \gamma \bar{V} = -\beta \left(U - \tfrac{1}{\beta} S + (\gamma/\beta) \bar{V} \right)$$

$$= -\beta \left(U - TS + P\bar{V} \right) = -\beta G$$

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

$$dG = dU - d(TS) + d(PV)$$

$$= (T\cancel{dS} - \cancel{PdV}) - (\cancel{TdS} + SdT) + (\cancel{PdV} + VdP) = -SdT + VdP$$