

1. **The Helmholtz free energy and the canonical partition function** In lecture I argued that in a macroscopic system ($N \gg 1$), the Helmholtz free energy A can be equated with the logarithm of the canonical partition function Q : $\beta A(N, V, T) = -\ln Q(N, V, T)$. I'm not convinced that my presentation was very crisp, so here is a short problem to convince yourself that the function we've defined in macroscopic thermodynamics to be $A = E - TS$ should behave like $\ln Q$ when N is large.

(i) Start with the microscopic picture. Each microstate ν has energy $E(\nu)$, so the canonical partition function is

$$Q(N, V, T) = \sum_{\nu \text{ consistent with } N, V} e^{-E(\nu)/k_B T}.$$

Confirm that

$$\left(\frac{\partial \ln Q}{\partial \beta} \right)_{V, N} = -\langle E \rangle.$$

(This may be as simple as recognizing that $\ln Q$ has the structure of a cumulant generating function.)

(ii) Now let's think about the thermodynamic picture. Apply the chain rule to demonstrate that

$$\left(\frac{\partial(-\beta A)}{\partial \beta} \right)_{V, N} = -E.$$

(iii) In the thermodynamic limit ($N \rightarrow \infty$), we replace $\langle E \rangle$ by E , which we now take to be a deterministic quantity. Hence in that limit, the derivative of $\ln Q$ with respect to β is exactly the same as the derivative of $-\beta A$ with respect to β . Conclude that it must be the case that in the large system size limit $A = -k_B T \ln Q + C$, where C is some constant that does not depend on β . Why do you think we suppressed the constant in lecture?

2. **Practice connecting partition functions to thermodynamic potentials.** Consider an isothermal-isobaric ensemble of microstates in which both energy and volume are allowed to fluctuate but the number of particles N is fixed.

(i) Following our development of canonical ensemble in lecture, determine the probability distribution $P(\nu)$ and partition function $\zeta(\beta, \beta p, N)$ for this ensemble.

(ii) By grouping together microstates with the same volume, the isothermal-isobaric partition function can be written in the form

$$\zeta = \sum_V (\dots) \tag{1}$$

Identify the summand that belongs in this expression.

(iii) For a macroscopic system, the sum in Eq. 1 is overwhelmingly dominated by the contribution from a single value V^* of the volume. Exploiting this fact, determine a relationship between $\ln \zeta$ and basic thermodynamic quantities. Could your answer have been easily anticipated? Explain.

(iv) Compute the derivative $(\partial \ln \zeta / \partial(\beta p))_{\beta, N}$. Using this result, verify the relationship you determined in part (iii).

(v) Compute the derivative $(\partial^2 \ln \zeta / \partial(\beta p)^2)_{\beta, N}$. Using this result, derive a relationship between mean square volume fluctuations $\langle \delta V^2 \rangle$ (where $\delta V = V - \langle V \rangle$) and the isothermal compressibility $\kappa_T = -V^{-1}(\partial V / \partial p)_{T, N}$.