

1. Assuming that the probability of fluctuations in a small subvolume is

$$f = C e^{-\frac{1}{2k_B T}(\Delta T \Delta S - \Delta p \Delta V)},$$

calculate the fluctuation matrix g when independent variables are ΔS and ΔV , i.e. find g so that

$$f = C e^{-\frac{1}{2} x^T g x}, \quad x = (\Delta S, \Delta V)^T.$$

Use this g to calculate the variances $\langle(\Delta V)^2\rangle$, $\langle(\Delta S)^2\rangle$ and $\langle\Delta S \Delta V\rangle$, and verify that you get the results obtained at lectures.

2. Using the Einstein theory of fluctuations for SVT-systems discussed at lectures, show that the magnitude of the fluctuations of the internal energy of a small mass element (const. N) is

$$\langle(\Delta U)^2\rangle = k_B T^2 C_V + k_B V T \kappa_T \left[p - T \left(\frac{\partial p}{\partial T} \right)_V \right]^2$$

In the lectures it was shown that the canonical distribution implies that internal energy fluctuations are

$$\langle(\Delta U)^2\rangle = k_B T^2 C_V.$$

What is the reason that these results differ?

3. Gibbs potential $G(p, T)$ is a Legendre transform of the Helmholtz free energy $F(V, T)$, substituting the free variable $V \rightarrow p$. Show that this corresponds to a Laplace transform

$$e^{-\beta G(p, T)} = \int_0^\infty dV e^{\beta p V} e^{-\beta F(T, V)}$$

What is the physical interpretation?