*Comment.* We can show that the extremum is a minimum. The total energy is $U = U_{\mathcal{R}} + U_{\mathcal{S}}$. Then the total entropy is

$$\begin{aligned}\sigma = \sigma_{\mathcal{R}} + \sigma_{\mathcal{S}} &= \sigma_{\mathcal{R}}(U - U_{\mathcal{S}}) + \sigma_{\mathcal{S}}(U_{\mathcal{S}}) \\ &\simeq \sigma_{\mathcal{R}}(U) - U_{\mathcal{S}}(\partial\sigma_{\mathcal{R}}/\partial U_{\mathcal{R}})_{V,N} + \sigma_{\mathcal{S}}(U_{\mathcal{S}}). \end{aligned} \tag{38}$$

We know that

$$(\partial\sigma_{\mathcal{R}}/\partial U_{\mathcal{R}})_{V,N} \equiv 1/\tau \ , \tag{39}$$

so that (38) becomes

$$\boxed{\sigma = \sigma_{\mathcal{R}}(U) - F_{\mathcal{S}}/\tau \ ,} \tag{40}$$

where $F_{\mathcal{S}} = U_{\mathcal{S}} - \tau\sigma_{\mathcal{S}}$ is the free energy of the system. Now $\sigma_{\mathcal{R}}(U)$ is constant; and we recall that $\sigma = \sigma_{\mathcal{R}} + \sigma_{\mathcal{S}}$ in equilibrium is a maximum with respect to $U_{\mathcal{S}}$. It follows from (40) that $F_{\mathcal{S}}$ must be a minimum with respect to $U_{\mathcal{S}}$ when the system is in the most probable configuration. The free energy of the system at constant $\tau$, $V$ will increase for any departure from the equilibrium configuration.

***Example: Minimum property of the free energy of a paramagnetic system.*** Consider the model system of Chapter 1, with $N_\uparrow$ spins up and $N_\downarrow$ spins down. Let $N = N_\uparrow + N_\downarrow$; the spin excess is $2s = N_\uparrow - N_\downarrow$. The entropy in the Stirling approximation is found with the help of an approximate form of (1.31):

$$\sigma(s) \simeq -\left(\frac{1}{2}N + s\right)\log\left(\frac{1}{2} + \frac{s}{N}\right) - \left(\frac{1}{2}N - s\right)\log\left(\frac{1}{2} - \frac{s}{N}\right). \tag{41}$$

The energy in a magnetic field $B$ is $-2smB$, where $m$ is the magnetic moment of an elementary magnet. The free energy function (to be called the Landau function in Chapter 10) is $F_L(\tau,s,B) \equiv U(s,B) - \tau\sigma(s)$, or

$$F_L(\tau,s,B) = -2smB + \left(\frac{1}{2}N + s\right)\tau\log\left(\frac{1}{2} + \frac{s}{N}\right) + \left(\frac{1}{2}N - s\right)\tau\log\left(\frac{1}{2} - \frac{s}{N}\right). \tag{42}$$

At the minimum of $F_L(\tau,s,B)$ with respect to $s$, this function becomes equal to the equilibrium free energy $F(\tau,B)$. That is, $F_L(\tau,\langle s\rangle,B) = F(\tau,B)$, because $\langle s\rangle$ is a function of $\tau$ and $B$. The minimum of $F_L$ with respect to the spin excess occurs when

$$(\partial F_L/\partial s)_{\tau,B} = 0 = -2mB + \tau\log\frac{N + 2s}{N - 2s}. \tag{43}$$