Exercise 2.3

The key point here is to consider an inequality from near the top of page 31 in IMSM:

$$0 \leq (\delta E)_{S,V,n_i} = \left(T^{(1)} - T^{(2)}\right)\delta S^{(1)} - \left(p^{(1)} - p^{(2)}\right)\delta V^{(1)} + \sum_{i=1}^{r}\left(\mu_i^{(1)} - \mu_i^{(2)}\right)\delta n_i^{(1)} \tag{1}$$

The inequality comes from energy minimization as seen in chapter 1; however, we'll see here that at equilibrium the inequality becomes equality.

The conditions to which Chandler refers are that

$$T^{(1)} = T^{(2)} \tag{2}$$

$$p^{(1)} = p^{(2)} \tag{3}$$

$$\mu_i^{(1)} = \mu_i^{(2)} \qquad \forall i \tag{4}$$

It is trivial to see that these conditions are sufficient to satisfy Eq. (1). Plug them in, and you get the equality.

Showing that they are also necessary takes a little more subtlety. First, let's consider a case where all but two of these conditions (we'll choose temperature and pressure) are satisfied.[1] In that case, we have some given temperature difference $\Delta T = T^{(1)} - T^{(2)}$ and some given pressure difference $\Delta p = p^{(1)} - p^{(2)}$.

This means we have to satisfy the inequality:

$$0 \leq \Delta T\,\delta S^{(1)} - \Delta p\,\delta V^{(1)} \tag{5}$$

There certainly are situations where this can be satisfied, but they put a condition on one fluctuation in terms of the other. That is, since we have fixed $\kappa = \Delta T/\Delta p$, we obtain the condition

$$\pm\delta V^{(1)} \leq \pm\kappa\,\delta S^{(1)} \tag{6}$$

where we take the plus sign if Δp is positive, and the minus sign if it is negative. Therefore, the fluctuations are no longer uncoupled, violating one of out assumptions about equilibrium.

That argument can be generalized to more conditions; in the case that only one of our conditions isn't satisfied, the argument is even easier. Consider the case of a nonzero ΔT. Again, that is a *fixed* value, we have that ΔT is either positive or negative. This requires that $\delta S^{(1)}$ have the same sign, which, of course, violates the fact that Eq. (1) must hold for *all* small variations, positive or negative.

NB: I think there might be a more mathematically elegant proof of this based on the fact that the fluctuations have to add up to zero. However, I'm not in the mood to try that derivation right now (especially since I wasn't even assigned this problem!)

[1] Generalization to an arbitrary number of conditions is straightforward and follows the same reasoning.