Exercise 1.6

In this exercise we're asked to construct Legendre transforms of the entropy that are natural functions of various sets of variables. The first step is to isolate the entropy differential. We start with the energy differential for a one-component system, based on the equation at the bottom of page 17 in IMSM:

$$\mathrm{d}E = T\ \mathrm{d}S - p\ \mathrm{d}V + \mu\ \mathrm{d}n \tag{1}$$

Simple algebra isolates the entropy as a natural function of the extensive variables:

$$\mathrm{d}S = -\frac{1}{T}\mathrm{d}E + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}n \tag{2}$$

Now we can do some Legendre transforms!

First, we want to have the natural variables $(1/T, V, n)$. The differential above has the natural variables (E, V, n), so we only need to swap E and $1/T$:

$$\begin{aligned}
\mathrm{d}\left(S + \frac{1}{T}E\right) &= \mathrm{d}S + E\ \mathrm{d}\frac{1}{T} + \frac{1}{T}\mathrm{d}E && (3)\\
&= -\frac{1}{T}\mathrm{d}E + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}n + E\ \mathrm{d}\frac{1}{T} + \frac{1}{T}\mathrm{d}E && (4)\\
&= E\ \mathrm{d}\frac{1}{T} + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}n && (5)
\end{aligned}$$

So we'll call the first one

$$S'\left(\frac{1}{T}, V, n\right) = S + \frac{1}{T}E \tag{6}$$

The second transform we're asked to do takes the natural variables $(1/T, V, \mu/T)$. From S', that's only a matter of changing n to μ/T, so we'll use S' as our starting point:

$$\begin{aligned}
\mathrm{d}\left(S' + \frac{\mu}{T}n\right) &= \mathrm{d}S' + n\ \mathrm{d}\frac{\mu}{T} + \frac{\mu}{T}\mathrm{d}n && (7)\\
&= E\ \mathrm{d}\frac{1}{T} + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}n + n\ \mathrm{d}\frac{\mu}{T} + \frac{\mu}{T}\mathrm{d}n && (8)\\
&= E\ \mathrm{d}\frac{1}{T} + \frac{p}{T}\mathrm{d}V + n\ \mathrm{d}\frac{\mu}{T} && (9)
\end{aligned}$$

This gives us the second function:

$$S''\left(\frac{1}{T}, V, \frac{\mu}{T}\right) = S' + \frac{\mu}{T}n = S + \frac{1}{T}E + \frac{\mu}{T}n \tag{10}$$