

Exercise 2.1

Trivially, we can define a set of $\lambda_S^{(\alpha)}$ such that the equations from the bottom of page 30 can be rewritten

$$\sum_{\alpha=1}^{\nu} \delta S^{(\alpha)} = \delta S^{(1)} \sum_{\alpha=1}^{\nu} \lambda_S^{(\alpha)} = 0 \quad (1)$$

and similarly define $\lambda_V^{(\alpha)}$ and $\lambda_{n_i}^{(\alpha)}$. In order for this to hold nonzero $\delta S^{(1)}$ (which it must), we know that

$$\sum_{\alpha=1}^{\nu} \lambda_{\mathbf{x}}^{(\alpha)} = 0 \quad (2)$$

There's also a free scaling parameter in that definition, since the sum is equal to zero. In fact, taking a two-component system and choosing the free scaling parameter such that $\lambda_{\mathbf{x}}^{(1)} = 1$, we see at the top of page 31 that the unique choice for $\lambda_{\mathbf{x}}^{(2)}$ is -1 . However, there is not a unique solution when there are an arbitrary number of partitions.

Now, following Chandler's example in the 2-partition system, we write the variational displacement in terms of these coefficients. This gives us:

$$\delta E = \delta S^{(1)} \sum_{\alpha=1}^{\nu} T^{(\alpha)} \lambda_S^{(\alpha)} - \delta V^{(\alpha)} \sum_{\alpha=1}^{\nu} p^{(\alpha)} \lambda_V^{(\alpha)} + \sum_{i=1}^r n_i^{(1)} \sum_{\alpha=1}^{\nu} \mu_i^{(\alpha)} \lambda_{n_i}^{(\alpha)} \quad (3)$$

As with the 2-partition system, each of those sums over α has to equal zero, because the fluctuations in the extensive variables are independent. From here, we can make identical arguments for each of the intensive variables, but I'll just focus on the case of temperature.

We're left with the equation

$$\sum_{\alpha=1}^{\nu} \lambda_S^{(\alpha)} T^{(\alpha)} = 0 \quad (4)$$

It's easy to see that if it happened that $T^{(\alpha)} = T \neq 0 \forall \alpha$, we would regain Eq. (2). But the equation above can be rewritten as

$$T^{(1)} = -\frac{1}{\lambda_S^{(1)}} - \sum_{\alpha=2}^{\nu} \lambda_S^{(\alpha)} T^{(\alpha)} \quad (5)$$

This indicates that, in order to have a nontrivial solution, the intensive variable $T^{(1)}$ has to depend on the fluctuations in the extensive variable. This cannot be, so the trivial solution is the only solution.