Of Many, One

Dan Styer, 30 March 2017

The traditional motto of the United States is *e pluribus unum*, “out of many, one”. This document discusses what happens not when we make one nation out of many states, but when we make one single system out of many smaller subsystems.

A system consists of N subsystems — most frequently, a system is made up of N molecules. In classical mechanics

$$\text{microstate of system} = \text{microstate}_1 + \text{microstate}_2 + \cdots + \text{microstate}_N. \tag{1}$$

(This is *not* necessarily true in quantum mechanics, because of the phenomenon called “entanglement”.) If the subsystems (molecules) don’t interact, then

$$\mathcal{H}_{\text{system}} = \mathcal{H}_1 + \mathcal{H}_2 + \cdots + \mathcal{H}_N. \tag{2}$$

The partition function is

$$\begin{aligned} Z_{\text{system}} &= \sum_{\text{microstates of system}} e^{-\beta\mathcal{H}_{\text{system}}} \\ &= \sum_{\text{microstates}_1}\sum_{\text{microstates}_2}\cdots\sum_{\text{microstates}_N} e^{-\beta(\mathcal{H}_1+\mathcal{H}_2+\cdots+\mathcal{H}_N)} \\ &= \left(\sum_{\text{microstates}_1} e^{-\beta\mathcal{H}_1}\right)\left(\sum_{\text{microstates}_2} e^{-\beta\mathcal{H}_2}\right)\cdots\left(\sum_{\text{microstates}_N} e^{-\beta\mathcal{H}_N}\right) \\ &\equiv z_1 z_2 \cdots z_N. \end{aligned} \tag{3}$$

and the Helmholtz function is

$$\begin{aligned} F_{\text{system}} &= -k_B T \ln Z \\ &= -k_B T(\ln z_1 + \ln z_2 + \cdots + \ln z_N) \\ &\equiv f_1 + f_2 + \cdots + f_N. \end{aligned} \tag{4}$$

Whence all extensive thermodynamic quantities, such as the heat capacity, are additive:

$$C_{V,\text{system}} = c_{V,1} + c_{V,2} + \cdots + c_{V,N}. \tag{5}$$

If all N subsystems (molecules) are identical, then

$$C_{V,\text{system}} = N c_{V,1}. \tag{6}$$

The previous paragraph took the subsystems to be different molecules. But the result is more general. For example, if a single diatomic molecule is modeled as a rigid rotor, the Hamiltonian breaks up into a translational part plus a rotational part:

$$\mathcal{H} = \left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}\right) + \left(\frac{\ell_\theta^2}{2I} + \frac{\ell_\varphi^2}{2I}\right) \equiv \mathcal{H}^{\text{trans}} + \mathcal{H}^{\text{rot}}. \tag{7}$$

Our theorem shows that the heat capacity must break up in this way as well:

$$c_V = c_V^{\text{trans}} + c_V^{\text{rot}}. \tag{8}$$