

The Boltzmann Factor and Partition Functions

PROBLEMS AND SOLUTIONS

3-1. How would you describe an ensemble whose systems are one-liter containers of water at 25°C?

An unlimited number of one-liter containers of water in an essentially infinite heat bath at 298 K.

3-2. Show that Equation 3.8 is equivalent to $f(x+y) = f(x)f(y)$. In this problem, we will prove that $f(x) \propto e^{\alpha x}$. First, take the logarithm of the above equation to obtain

$$\ln f(x+y) = \ln f(x) + \ln f(y)$$

Differentiate both sides with respect to x (keeping y fixed) to get

$$\begin{aligned} \left[\frac{\partial \ln f(x+y)}{\partial x} \right]_y &= \frac{d \ln f(x+y)}{d(x+y)} \left[\frac{\partial(x+y)}{\partial x} \right]_y = \frac{d \ln f(x+y)}{d(x+y)} \\ &= \frac{d \ln f(x)}{dx} \end{aligned}$$

Now differentiate with respect to y (keeping x fixed) and show that

$$\frac{d \ln f(x)}{dx} = \frac{d \ln f(y)}{dy}$$

For this relation to be true for all x and y , each side must equal a constant, say α . Show that

$$f(x) \propto e^{\alpha x} \quad \text{and} \quad f(y) \propto e^{\alpha y}$$

Let $x = E_1 - E_2$ and $y = E_2 - E_3$. Then $x+y = E_1 - E_3$, and we can write Equation 3.8 as $f(x+y) = f(x)f(y)$. Taking the logarithm of this equation gives

$$\begin{aligned} \ln f(x+y) &= \ln [f(x)f(y)] \\ &= \ln f(x) + \ln f(y) \end{aligned}$$

We then differentiate with respect to x and find

$$\begin{aligned} \left[\frac{\partial \ln f(x+y)}{\partial x} \right]_y &= \left[\frac{\partial \ln f(x)}{\partial x} \right]_y + 0 \\ \frac{d \ln f(x+y)}{d(x+y)} \left[\frac{\partial(x+y)}{\partial x} \right]_y &= \frac{d \ln f(x)}{dx} \\ \frac{d \ln f(x+y)}{d(x+y)} &= \frac{d \ln f(x)}{dx} \end{aligned} \tag{1}$$

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Jianzhong Wu, John M. Prausnitz



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