

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 $f(x) \propto e^{ax}$. 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

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

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

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

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

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

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

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

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web reservations are required and you have to provide a credit card to book the reservation you are not charged until the day of you can cancel with 48 hours notice project oceanology is actually inside the uconn groton campus the gps address works fine to get you to the campus and then just look for the signs pointing to project oceanology