

# 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?

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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  $\alpha$ . Show that

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

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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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