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) \u221d e^{xx}. 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

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

Now differentiate with respect to y (keeping a 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 a. Show that

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

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

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

We then differentiate with respect to x and find

$$\left[\frac{\partial \ln f(x+y)}{\partial x}\right]_{f} = \left[\frac{\partial \ln f(x)}{\partial x}\right]_{f} + 0$$

$$\frac{d \ln f(x+y)}{d(x+y)} \left[\frac{\partial (x+y)}{\partial x}\right]_{f} = \frac{d \ln f(x)}{dx}$$

$$\frac{d \ln f(x+y)}{d(x+y)} = \frac{d \ln f(x)}{dx}$$
(1)

Mcquarrie Solution Manual

Jianzhong Wu, John M. Prausnitz

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