Supplemental material for Hanson, R. M., “Playing Card Equilibrium”

Mathematical Derivation of the Relationship:

$$W_f / W_{max} \approx e^{-2n(f-0.5)^2}$$

where:

f = the fraction of HD molecules in a system containing n H atoms and n D atoms, ignoring differences in energy between H_2, D_2, and HD.

W_f = the number of ways of finding the system with $f \times 100\%$ HD molecules.

W_{max} = the number of ways of finding the system in its most probable distribution, namely with $n/4$ H_2, $n/4$ D_2, and $n/2$ HD molecules.

First we define the variable $x = f - 0.5$. Then we have:

$$n_{H_2} = \frac{n}{4}(1-2x)$$
$$n_{D_2} = \frac{n}{4}(1-2x)$$
$$n_{HD} = \frac{n}{2}(1+2x)$$

Starting with the definition of W:

$$W = \frac{n!}{n_{H_2}!\ n_{D_2}!\ n_{HD}!}2^{n_{HD}}$$

we then have:

$$W_f / W_{max} = \frac{(n/4)!(n/4)!(n/2)!}{[(n/4)(1-2x)]![(n/4)(1-2x)]![(n/2)(1+2x)]!}2^{nx}$$

Approximating the natural logarithm of this quantity using

(a) Stirling’s approximation: $\ln(x!) \approx x \ln x - x$, and
(b) a two-term Taylor expansion of $\ln(1 +/- x) \approx +/-x - (x^2)/2$

virtually all of the terms cancel, and we arrive at:

$$
\begin{aligned}
\ln\left(W_f / W_{max}\right) &\approx -\frac{n}{2}(1-2x)\ln(1-2x) - \frac{n}{2}(1+2x)\ln(1+2x) \\
&\approx -\frac{n}{2}(1-2x)(-2x-2x^2) - \frac{n}{2}(1+2x)(2x-2x^2) \\
&= -2nx^2
\end{aligned}
$$

Replacing x by $(f - 0.5)$ and exponentiating leads to the result to be derived:

$$W_f / W_{max} \approx e^{-2n(f-0.5)^2}$$