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Course 565/665 Lecture Number ______ Date 2/18/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

"S" can be computed for any distribution function

E.g., Color of socks in our class. $N = 16$ (# of people in the class).

$$p_{bla} = \frac{n_{bla}}{N} = \frac{4}{16} = \frac{1}{4} = 0.25$$

$$p_w = \frac{8}{16} = 0.5$$

$$p_{blu} = \frac{1}{16} = 0.0625$$

$$p_y = \quad ''$$

$$p_g = \quad ''$$

$$p_{bro} = \quad ''$$

$$\frac{S}{N k_B} = -\sum_{i=1}^{t} p_i \ln p_i = -\left[\frac{1}{4}\ln\frac{1}{4} + \frac{1}{2}\ln\frac{1}{2} + 4\cdot\frac{1}{16}\ln\frac{1}{16}\right]$$

$$\boxed{\frac{S}{N k_B} = 1.39}$$

Properties of Entropy

Entropy is an extensive quantity, this meaning that it is a quantity that is equal to the sum of its parts. The entropy of the system is equal to the sum of the entropies of all of the subsystems.

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Multiplicities, however, must be multiplied.

$$W = W_A W_B \qquad \text{while} \qquad S = S_A + S_B$$

$$S = S_A + S_B = k \ln W_A + k \ln W_B = k \ln (W_A W_B)$$

$$S = k \ln W$$

Thus, the entropy equalling the log of the multiplicity is a very convenient form being that it satisfies that entropy is extensive and that the multiplicities must be multiplied. See the optional chapter 6 supplement for more information about this topic.

<u>Going From Coin Flips and Die Rolls to Real Molecules</u>

Let "t" be the number of possible outcomes.

① Coin Flips, Die Rolls } t is small → Easy to deal with.

Real Life Molecule } t is very large → More complicated to deal with accurately, but conclusions are similar.

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(2) In real life situations, you typically cannot follow individual molecules in a macroscopic sample, but can typically measure averages.

Using the Maximum Entropy Principle

A) Systems with no constraints:

$S_{MAX} \longrightarrow$ tends toward flat distribution functions.

t-sided die.

$N \rightarrow$ large

We need $\sum_{i=1}^{t} p_i = 1$, implying that $\sum_{i=1}^{t} dp_i = 0$.

We would like to find the set $\{p_1^*, p_2^*, \cdots, p_t^*\}$ that maximizes entropy S.

S is an increasing function of W_i

$$\left(\frac{\partial S}{\partial p_i}\right)_{p_{j \neq i}} = 0$$ Maximum (or more correctly, an extremum)

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$$S_N = -k_B \sum_{i=1}^{t} p_i \ln p_i$$

To solve for these p_i's, we must use our old friend, the Method of Lagrange Undetermined Multipliers.

We know that $\sum_{i=1}^{t} dp_i = 0$. This is our constraint equation, and we can easily add this to anything since it is equal to zero. Thus,

$$\sum_{i=1}^{t} \left[\left(\frac{\partial S_N}{\partial p_i} \right)_{p_j \neq i} - \alpha \right] dp_i = 0$$

For each i, we have

$$\left(\frac{\partial S_N}{\partial p_i} \right)_{p_j \neq i} - \alpha = 0$$

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Also, from

$$S = -k \sum_i p_i \ln p_i$$

$$\left(\frac{\partial S}{\partial p_i}\right)_{i \neq j} = -k_B \ln p_i - k_B$$

$$= -1 - \ln p_i$$

Thus, going back

$$\left(\frac{\partial S}{\partial p_i}\right) - \alpha = 0$$

$$= -1 - \ln p_i - \alpha = 0$$

$$+ \ln p_i = -1 - \alpha$$

$$\boxed{p_i^* = e^{-1-\alpha}}$$

So, $\dfrac{p_i}{\sum_{i=1}^{t} p_i^*} = \dfrac{e^{-1-\alpha}}{t\, e^{-1-\alpha}} = \dfrac{1}{t}$

$\boxed{\text{Flat Distribution}}$