The Seinfeld Syndrome* & Entropy:
Why Doing Nothing at All is Better than Doing Anything

How much energy goes into growing a human being, or any other animal, or a tree? How much energy gets wasted in the process, harming sentient beings along the way? What is the entropy differential among our choices? All choices includes all the laws we support and oppose by how we vote, whom/what/how much we consume, how much we reproduce. While I have contemplated such questions since the early 1980s and have worked on the problem intermittently, intense work had not begun on actually computing the utility values of these choices until I was asked to give a talk on behalf of Bioenergia America, LLC for a course in renewable energy at Burlington County College in Pemberton, New Jersey.

We will begin the long complicated process of answering these questions and computing these values. We will start with a completely mindless model – one which counts the number of distinct arrangements of atoms in chemical bonds and makes use of only the following physical laws: the existence of common chemical bonds and their energies of formation, which are used to compute the probabilities of certain bond formations. The computation of entropy at this level of modeling involves a great deal of combinatorial algebra. Involving the Schrodinger wave equation in the computation demands differential algebra.

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What is entropy?

Definition. A system Λ is any defined volume in space or set of atoms that you want it to be (engineering courses super-emphasize the need to well-define any system)

Definition. Kinetic Energy (K.E.) Just as the definition of the velocity of a particle makes sense only relative to an arbitrarily fixed point in space or relative to another particle or system, so, too, does the kinetic energy of a particle.

i.e. If in a system all particles moved with parallel constant velocity vectors, in violation of electrostatic laws of repulsion or attraction, the kinetic energy could be defined to be 0 at any point in time. The kinetic energy would then remain 0 forever.

Definition. Potential Energy (P.E.) Just as in the definition of kinetic energy, potential energy of a system is defined only relative to another fixed point in space or relative to another particle or system. This P.E. comes from both gravitational and electromagnetic force from *outside* the system. We may *arbitrarily choose* this P.E. to be zero. But, you must always ask: what *would* the system do if these gravitational and electromagnetic forces did not exist. (See definition of **pressure** below.)

P.E. also includes the energy *within the system* relative to free atoms that gets released when chemical bonds are formed between atoms: i.e. to the state the system *would* have been in with the same set of atoms but if the atoms were "free" of each other. It is due to both gravitational and electromagnetic (carrier particle: the photon) forces between subatomic particles (electrons, neutrons, protons).

Definition. Internal energy. Let U denote the *internal energy* of a system Λ, which is the sum total of the kinetic energy of all the particles in the system, plus the chemical bond energy (potential energy *within* the system).

Pressure. What is pressure? If it is *not* the case that the velocity vector of all particles in the system are parallel and constant, then either the volume of the system would have to be defined to expand without limit, or, for a bounded volume over time, particles would fly out of the system, unless they are all chemically bonded together, as in, say, a single living organism.

But, since we know that arbitrarily defined volumes of air do not suddenly become vacuums, for instance, that implies there are forces – electromagnetic repulsive forces – from particles *outside* the system that force the particles, which had already been defined to be part of the system, back *into* the system. This potential energy force from the outside is defined to be the pressure *on* the system.

Example. If we define our system to *not* have fixed volume, but to encapsulate always the same set of atoms, then that volume would expand forever, in order to avoid having any atoms inside "cross" the boundary.

Example. If we define our system to have a fixed volume, but have the atoms *not* cross the boundary, then that means we must have a *potential force from atoms outside the system* keeping the original atoms inside the system. This potential force *is part of the pressure on the boundary (surface) of the volume.*

Example. If we try to define our system to have a fixed volume but include part of the "outside wall", which keeps the gaseous/liquid/chemically unbonded atoms from "flying out of the system", as part of the system itself, then the potential forces (and hence potential energy) of that wall acting on those unbonded (and otherwise "unbounded") atoms would be counted towards the *internal energy* of the system.

Macroscopic definition: the Inequality of Clausius Noggle (3.7) page 128:

$$dU = T \cdot dS - P \cdot dV$$

for any type of process *for which no particles enter or leave the system: however, the temperature, pressure, and volume of this system may change* (obviously – that's what a differential means!)

Let t denote time. Then we may rewrite this differential balance in the form of a differential equation with respect to time:

$$\frac{dU}{dt} = T \cdot \frac{dS}{dt} - P \cdot \frac{dV}{dt}$$

Equation of State An equation of state, of which the ideal gas law is the simplest example, relates pressure, temperature, volume, and the numbers of and types of molecules.

$$E(P,T,V) = 0$$

I prefer to work with the differential equation form that relates U, S, P, T, V, rather than the discrete form: $U(t_2) - U(t_1) = \int_{t_1}^{t_2} T \cdot dS - \int_{t_1}^{t_2} P \cdot dV$ because in the discrete form, one has more variables to deal with, namely, the initial conditions on the integrals, which are not explicitly seen in the integrals, and $U(t_1)$.

Whereas, in the differential form, we have the 2 equations above, and 6 variables: t, U, S, P, T, V. Hence, we must specify 4 variables in order to fix the other 2. Or, equivalently, we must specify 3 of the variables as functions of time, t, which then specifies the remaining 2 variables as functions of time.

In particular, this means that we should be able to construct two systems with the same pressure, temperature and volume, yet different entropies (and internal energies), due to the arrangements of the atoms inside. In practice, however, in a comparison of any two systems one cares to measure, at least one of P, T, V will be different, and the entropy difference is due to the difference in P, T, or V.

Definition of General Laws of Conserved Quantities. From Sandler (3.1-1) page 112:

$$\frac{d\theta}{dt} \equiv \text{ rate of change of } \theta \text{ inside a system}$$

General balance equation for conserved quantities θ:

$\frac{d\theta}{dt} =$ rate of flux of θ into the system minus the rate of flux of θ out of the system plus the rate that θ is generated in the system

Wikipedia macroscopic definition http://en.wikipedia.org/wiki/Entropy

Entropy is a thermodynamic property that is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.

Boltzmann's constant $k_B = 1.38062 \cdot 10^{-23}$ J/K (joules per Kelvin)
Fundamental dimensions of entropy Energy per temperature = $\mathrm{M} \cdot \mathrm{L}^2 \cdot \mathrm{T}^{-2} \cdot \theta^{-1}$
M = mass L = length T = time θ = temperature

Typical units of entropy would be joules per degree Kelvin.

Wikipedia microscopic definition

$$S = -k_B \cdot \sum_k p_k \ln p_k = k_B \cdot \sum_k p_k \ln \frac{1}{p_k}$$

where the sum is over the probabilities, $0 \le p_k \le 1$, over the k-th microstate. This implies we sum over states that our system *could* have been in, not just the one it *is* in. Hence, $\sum_k p_k = 1$.

Ludwig Boltzmann's definition of entropy Noggle (5.1) page 203
$k_B \cdot \ln p$ where p is the probability that the current state *is* in. Observe that for a *finite* number Ω of microstates, if *all* probabilities are equal, i.e. $\forall k \Rightarrow p_k = \frac{1}{\Omega}$, then the above equation reduces to $k_B \cdot \ln \Omega$. This situation is called the *fundamental postulate in statistical mechanics for an isolated system in equilibrium: in such a system the number of particles, volume, and internal energy is fixed. This is the maximum possible entropy the isolate system can be in.*

The universe tends towards maximum fairness.

Note that either definition of entropy requires the concept of probability: i.e. of *not* knowing precisely which state the system is in. If we *knew* (with impossible accuracy) which state the system was in, say, state 1, then p_1 would equal 1 for that state, all other probabilities would equal 0, and the entropy would be 0.

Leonid Zhigilei Entropy is the measure of the number of microstates possible for a given macrostate

Definition of conditional probability Bean page 66

If events *E* and *F* are events in a sample space, then the *conditional probability of E given F*, denoted by $\Pr(E|F)$ is defined by

$$\Pr(E|F) \equiv \frac{\Pr(E \cap F)}{\Pr(F)}$$

Bayes' Theorem Bean page 73

$$\Pr(E|F) = \frac{\Pr(F|E)\cdot\Pr(E)}{\Pr(F)}$$

Hence, using Zhigilei's definition of entropy, we see that

$$\Pr(k\text{-th microstate}|\text{macrostate}) = \frac{\Pr(\text{macrostate}|k\text{-th microstate})\cdot\Pr(k\text{-th microstate})}{\Pr(\text{macrostate})}$$

What we can *estimate* from thermodynamic data is the probability of a particular free atom, say, C(1), combining with one of the atoms {C(2),H,N,O}:

C(1) -> C(1)-C(2), C(1)-H, C(1)-N, C(1)-O

Definition. The energy released going from atom(1) and atom(2) to atom(1)-bonded-to-atom(2), whether a single, double or triple bond, is called the *energy of formation* of that pair of atoms with that particular bond. They are given as *negative* values, because the potential energy of atom(1)-atom(2) is (usually) *less* than the potential energy of the unbonded atoms. Therefore, the more negative bond energy a bond has, the more likely it is to occur.

Fact. Except for the occasional addition of material by asteroids, the total number of hydrogen, carbon, nitrogen, oxygen and sulfur atoms – in fact, of each element – on earth has stayed exactly the same for 4.5 billion years. That means, the only thing that has changed over this time period has been the arrangment of chemical bonds (electron distributions) among these atoms. These changes have been powered only by internal heat from the earth or by the sun.

Example. From www.science.waterloo.ca and www.cem.msu.edu/~reusch/OrgPage/bndenrgy.htm we have the energies of formation of diatomic bonds

C=O -741 kJ/mole
C-H -413 kJ/mole
O-H -366 kJ/mole
C-O -360 kJ/mole
C-C -348 kJ/mole
O-O –146 kJ/mole

Due to constraints given by the orbital filling rules, *none* of these diatomic "molecules" would exist in reality (except for O_2). Carbon has valence 4, nitrogen has valence 3, oxygen has valence 2, hydrogen has valence 1. Hence, *any combination* of molecules put together by this collection of diatomic bonds which does *not* satisfy these valence rules has *observed* probability 0.

Therefore, if we were given this set of atoms: {C(1), C(2), O, H} whose potential energy we can set at 0 kJ/mole, the following are the *approximate* potential energies of combinations of bonded atoms. True energies are *not* simply additive, but we have nothing else to go by at this time. Each line is a *distinct* macrostate. Each set on the same line (just 2 sets at most, in this case) are distinct *microstates* (with the same macrostate).

{C(1)=O, C(2), H} , {C(2)=O, C(1), H}		-741 kJ/mole
{C(1)-H, C(2), O}, {C(2)-H, C(1), O}		-413 kJ/mole
{C(1), C(2), O-H}		-366 kJ/mole
{C(1)-O, C(2), H} , {C(2)-O, C(1), H}		-360 kJ/mole
{C(1)-C(2), O, H}		-348 kJ/mole
{C(1)=O, C(2)-H}, {C(1)-H, C(2)=O}	(-741-413) kJ/mole =	-1154 kJ/mole
{C(1)-O, C(2)-H}, {C(1)-H, C(2)-O}	(-360-413) kJ/mole =	-773 kJ/mole
{C(1)-C(2), O-H}	(-348-366) kJ/mole =	- 714 kJ/mole

We have 13 distinct microstates, 8 distinct macrostates.
Assumption. The probability of a given microstate existing approximately equals the weighted average of its energy of formation over all microstates.

Example. The probability of {C(1)=O, C(2), H} occurring is approximately

$$\frac{741}{741\cdot(2)+413\cdot(2)+366+360\cdot(2)+348+1154\cdot(2)+773\cdot(2)+714}=\frac{741}{8310}\approx 0.08917$$

The probabilities of each of these microstates.

{C=O, C, H}	0.17834 (= 2*0.8917)
{C-H, C, O}	0.09940 (= 2*0.04970)
{C, C, O-H}	0.04404
{C-O, C, H}	0.08664 (= 2*0.04332)
{C-C, O, H}	0.04188
{C=O, C-H}	0.27774 (= 2*0.13887)
{C-H, C-O}	0.18604 (= 2*0.09302)
{C-C, O-H}	0.08592

Check: these probabilities sum to 1.

However, the bond formation energies and defining the sample space of microstates to be all the possible ways *labeled* atoms can combine to form a given macrostate yields the *maximal* entropy for *any* given combination of molecules.

Example. Suppose our macrostate is {2 CO2 molecules}.
There exist 6 microstates which yield this same macrostate, if we label the atoms as

{C(1), C(2), O(1), O(2), O(3), O(4)}

Namely,

{O(1)=C(1)=O(2), O(3)=C(2)=O(4)}
{O(1)=C(1)=O(3), O(2)=C(2)=O(4)}
{O(1)=C(1)=O(4), O(2)=C(2)=O(3)}

{O(2)=C(1)=O(3), O(1)=C(2)=O(4)}
{O(2)=C(1)=O(4), O(1)=C(2)=O(3)}
{O(3)=C(1)=O(4), O(1)=C(2)=O(2)}

each with equal probability (1/6). Hence, counting microstates this way, the entropy would simply be its maximum possible value, $k_B \cdot \ln 6$.

Question: What is the *sample space* over which we count the number of possible "states"? What is a "state"? Could not the positions and momenta of all particles take on *uncountably* many possible values? Hence, would not the sum in the definition above have to be replaced by an *integral* of some kind? In fact, that IS the proper *physical* definition of entropy. See equation (1) in Bochvar, et al.

$$S = -\int \psi^* \psi \cdot \ln(\psi^* \psi) \cdot dV$$

where ψ is the normalized solution of Schrodinger's wave equation, ψ^* is its complex conjugate, and the integral is over all space. The connection of this paper to *differential* algebra comes because Schrodinger's wave equation is a partial differential equation. More accurately, entropy should be computed from the Schrodinger wave equations.

Page 28 chapter 2 of the book by Ditman, et al explains that a single wavefunction ψ, which is a function of 3N coordinates, is used, rather than separate wavefunctions for each particle. The absolute value of the wavefunction squared is the probability distribution function for finding a particle of a given charge at coordinates (x_n, y_n, z_n) for N particles. The webpage http://en.wikipedia.org/wiki/Schr%C3%B6dinger_equation explains that $\frac{\hbar^2}{2}\sum_{n=1}^{N}\frac{1}{m_n}\left(\frac{\partial^2\psi}{\partial x_n^2}+\frac{\partial^2\psi}{\partial y_n^2}+\frac{\partial^2\psi}{\partial z_n^2}\right)+V(\vec{r}_1,\ldots,\vec{r}_N)\cdot\psi = E\cdot\psi$ is the proper general time-independent non-relativistic equation for given potential energy

$V(\vec{r}_1,\ldots,\vec{r}_N)$ among interacting particles with coordinate vector $\vec{r}_n = (x_n, y_n, z_n)$, mass m_n, and reduced Planck constant $\hbar = 1.054571726 \cdot 10^{-34}$ J*s.

Let us assume our particles are atomic nuclei and atomic electron clouds. For our purposes of modeling proteins, we will therefore have 10 types of particles: C+,H+,O+,N+, S+, C-,H-,O-,N-,S-. All particles of a given type have the same charge and mass. From Halliday & Resnick:

Electron rest mass = $m_e = 9.11 \cdot 10^{-31}$ kg

Proton rest mass = $m_p = 1.67 \cdot 10^{-27}$ kg

Elementary charge of an electron or a proton = $1.60 \cdot 10^{-19}$ C (coulombs)

Coulomb's Law (23-3) page 423: the electrostatic force between two particles of charges q_1 and q_2 a distance r apart equals $F = \frac{1}{4\pi\varepsilon_0} \cdot \frac{q_1 q_2}{r^2}$ where $\varepsilon_0 = 8.854 \cdot 10^{-12} \mathrm{C}^2 / (\mathrm{Nt} \cdot \mathrm{m}^2)$ is the permittivity constant. So $F = (8.99 \cdot 10^9 \frac{\mathrm{Nt} \cdot \mathrm{m}^2}{\mathrm{C}^2}) \cdot \frac{q_1 q_2}{r^2}$. For particles with the same charge, $q_1 q_2 > 0$ and this force is positive and repulsive. This force is technically a vector, but in this case a scalar, since we deal only with 1 space dimension: radial distance. Since force is done to bring repelling charges together from infinite distance, their potential energy at any finite distance will be positive. Hence, integrating the negative of this force with respect to the distance *r* between the particles starting from infinity, where the force is zero and the potential energy is arbitrarily defined to be 0, yields a positive potential energy

$$V = -\int_{r=\infty}^{r} F \cdot dr = (8.99 \cdot 10^9 \frac{\mathrm{Nt} \cdot \mathrm{m}^2}{\mathrm{C}^2}) \cdot \frac{q_1 q_2}{r}$$

See http://en.wikipedia.org/wiki/Electric_potential_energy to check that I got the sign correct!

We list the standard atomic weights, which we round to the nearest integer, to compute the masses of the electrons (denoted with a postfix minus sign) and the masses of the protons (denoted with a postfix plus sign) of the 5 most common elements comprising amino acids

H 1.00794	H-	$9.11 \cdot 10^{-31}$ kg	H+	$1.67 \cdot 10^{-27}$ kg
C 12.011	C-	$1.0932 \cdot 10^{-29}$ kg	C+	$2.004 \cdot 10^{-26}$ kg
N 14.0067	N-	$1.2754 \cdot 10^{-29}$ kg	N+	$2.338 \cdot 10^{-26}$ kg
O 15.9994	O-	$1.4576 \cdot 10^{-29}$ kg	O+	$2.672 \cdot 10^{-26}$ kg
S 32.065	S-	$2.9152 \cdot 10^{-29}$ kg	S+	$5.344 \cdot 10^{-26}$ kg

Their electric charges are $\pm 1.60 \cdot 10^{-19}, \pm 9.60 \cdot 10^{-19}, \pm 1.12 \cdot 10^{-18}, \pm 1.28 \cdot 10^{-18}, \pm 2.56 \cdot 10^{-18}$ coulombs, respectively.

The electrostatic potential among such hypothetical point charges would equal

$$V(\vec{r}_1,\ldots,\vec{r}_N) = (8.99\cdot 10^9\ \frac{\text{Nt}\cdot\text{m}^2}{\text{C}^2})\times$$

$$\left\{\begin{array}{l} \displaystyle\sum_{\substack{X\in\\ \{H,C,O,N,S\}}} q_{X-}q_{X-}\sum_{i<j}\frac{1}{\left|\vec{r}_{X-,i}-\vec{r}_{X-,j}\right|} + \sum_{\substack{X\in\\ \{H,C,O,N,S\}}} q_{X+}q_{X+}\sum_{i<j}\frac{1}{\left|\vec{r}_{X+,i}-\vec{r}_{X+,j}\right|} \\ \displaystyle + \sum_{\substack{X<Y,X,Y\in\\ \{H,C,O,N,S\}}} q_{X-}q_{Y-}\sum_{i,j}\frac{1}{\left|\vec{r}_{X-,i}-\vec{r}_{Y-,j}\right|} + \sum_{\substack{X<Y,X,Y\in\\ \{H,C,O,N,S\}}} q_{X+}q_{Y+}\sum_{i,j}\frac{1}{\left|\vec{r}_{X+,i}-\vec{r}_{Y+,j}\right|} \\ \displaystyle - \sum_{\substack{X,Y\in\\ \{H,C,O,N,S\}}} q_{X-}q_{Y+}\sum_{i,j}\frac{1}{\left|\vec{r}_{X-,i}-\vec{r}_{Y+,j}\right|} \end{array}\right\}$$

where $X,Y\in\{H,C,O,N,S\}$ and in the middle two summations we are careful not to double count the same charge of the same atom. The outer summations partition the inner summations into a total of 5+5+10+10+25 = 55 distinct electric charge products.

Ansatz We expect the form of the wave function to be symmetrical with respect to all pairs of particles with the same charge, including sign. This means ψ should be symmetrical with respect to all the carbon atomic nuclei:

$$\vec{r}_{C+,1}-\vec{r}_{C+,2},\vec{r}_{C+,1}-\vec{r}_{C+,3},\vec{r}_{C+,2}-\vec{r}_{C+,3}$$

or all the hydrogen electron clouds:

$$\vec{r}_{H-,1}-\vec{r}_{H-,2},\vec{r}_{H-,1}-\vec{r}_{H-,3},\vec{r}_{H-,2}-\vec{r}_{H-,3}$$

If we have N particles, then we have 3N independent variables. This implies for this PDE we require (3N-1)-dimensional boundary conditions. But the wave function needs to be 0 on *any* hypersurface of dimension less than 3N, since such surfaces have measure 0 inside the larger 3N-dimensional space. We can take the (3N-1)-dimensional boundary condition to be that the wave function equals 0 whenever any one of the 3N coordinates equals infinity. Since the wave equation is a 2nd order equation, we need a second (3N-1)-dimensional boundary condition.

Example. Consider the wave equation for 2 carbon nuclei

$$\frac{(1.054571726\cdot 10^{-34}\,\text{J}\cdot\text{s})^2}{2}\frac{1}{2.004\cdot 10^{-26}\ \text{kg}}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)$$

$$=(E-(8.99\cdot 10^9\ \frac{\text{Nt}\cdot\text{m}^2}{\text{C}^2})\cdot\frac{(9.60\cdot 10^{-19}\ \text{C})^2}{r})\cdot\psi$$

or $(2.774754304589\cdot 10^{-43}\text{kg}\cdot\text{m}^4\cdot\text{s}^{-2})\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=(E-\frac{8.285184\cdot 10^{-27}\ \text{Nt}\cdot\text{m}^2}{r})\cdot\psi$

So $\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=(E\cdot 3.60392269\cdot 10^{42}\cdot\text{kg}^{-1}\cdot\text{m}^{-4}\cdot\text{s}^2-\frac{2.985916262\cdot 10^{16}\cdot\text{m}^{-1}}{r})\cdot\psi$.

Example. Observe that for N particles, there exist 3N coordinates but $\frac{N\cdot(N-1)}{2}$ possible distances. Since $N>7\Rightarrow\frac{N\cdot(N-1)}{2}>3N$ one cannot choose this many distances arbitrarily. To get around this problem, we make use of the physical observation that not all particles are "bonded" with all other particles. When we show a familiar molecular skeleton diagram, we are *already assuming certain restrictions on the boundary conditions of the wave function*. N atoms with B bonds implies 3N coordinates with B constraints on their distances. Thus 3N-B of the coordinates can be chosen arbitrarily. Therefore, among the N*(N-1)/2 pairs of atoms/distances between pairs, there exist N*(N-1)/2 – (3N-B) geometric constraints: i.e. only 3N-B of the distances among the N*(N-1)/2 pairs can be chosen freely. If B of the distances between pairs of atoms are already given (constrained), then there really are only (N*(N-1)/2-B)-(3N-B) = N*(N-1)-3N constraints remaining among the remaining N(N-1)/2 – B unbonded pairs of atoms.

Example. Let

$$x_{n+1}=x_n+b_{n\to n+1}\cos\theta_{n\to n+1}\cos\tau_{n\to n+1}$$
$$y_{n+1}=y_n+b_{n\to n+1}\cos\theta_{n\to n+1}\sin\tau_{n\to n+1}$$
$$z_{n+1}=z_n+b_{n\to n+1}\sin\theta_{n\to n+1}$$

I use an arrow rather than a comma so as to visually keep the 2 indices better separated. In general for bonded atomic nuclei we have

$$x_n=x_m+b_{m\to n}\cos\theta_{m\to n}\cos\tau_{m\to n}$$
$$y_n=y_m+b_{n\to m}\cos\theta_{m\to n}\sin\tau_{m\to n}$$
$$z_n=z_m+b_{n\to m}\sin\theta_{m\to n}$$

Example. 2 particles with a fixed bond length b between them. Uniform distribution Pr($\theta'\le\theta_{m\to n}\le\theta''\wedge\tau'\le\tau\le\tau''$)=$\frac{\theta''-\theta'}{2\pi}\frac{\tau''-\tau'}{\pi}$. The p.d.f. (probability density function) is $\frac{1}{2\pi}\cdot\frac{1}{\pi}$. The entropy equals $-k_B\cdot\int_{\theta=0}^{2\pi}\int_{\tau=0}^{\pi}\frac{1}{2\pi}\cdot\frac{1}{\pi}\ln\left(\frac{1}{2\pi}\cdot\frac{1}{\pi}\right)\cdot d\tau\cdot d\theta=k_B\cdot\ln(2\pi^2)$.

Example. 3 particles P(1) connected to P(2) connected to P(3) with fixed bond lengths $b_{1\to 2}$ and $b_{2\to 3}$ between them, respectively. The probability density function $|\psi|^2=|\psi|^2(\theta_{1\to 2},\tau_{1\to 2},\theta_{2\to 3},\tau_{2\to 3})$. We want this to vary proportionately with

$$\begin{aligned}r_{1\to 3}^2&=(x_3-x_1)^2+(y_3-y_1)^2+(z_3-z_1)^2=(b_{1\to 2}\cos\theta_{1\to 2}\cos\tau_{1\to 2}+b_{1\to 3}\cos\theta_{1\to 3}\cos\tau_{1\to 3})^2\\&+(b_{1\to 2}\cos\theta_{1\to 2}\sin\tau_{1\to 2}+b_{1\to 3}\cos\theta_{1\to 3}\sin\tau_{1\to 3})^2+(b_{1\to 2}\sin\theta_{1\to 2}+b_{1\to 3}\sin\theta_{1\to 3})^2\\&=b_{1\to 2}^2+b_{1\to 3}^2+\\&2b_{1\to 2}b_{1\to 3}\{\cos\theta_{1\to 2}\cos\tau_{1\to 2}\cos\theta_{1\to 3}\cos\tau_{1\to 3}\\&+\cos\theta_{1\to 2}\sin\tau_{1\to 2}\cos\theta_{1\to 3}\sin\tau_{1\to 3}+\sin\theta_{1\to 2}\sin\theta_{1\to 3}\}\end{aligned}.$$

The simplest function of $r_{1\to 3}^2$ that varies proportionately with $r_{1\to 3}^2$ is $r_{1\to 3}^2$!

We know that $r_{1\to3}^2$ varies from a low of $(b_{1\to2}-b_{1\to3})^2$, which could be 0, to a maximum of $(b_{1\to2}+b_{1\to3})^2$. Therefore, define

$$|\psi|^2(\theta_{1\to2},\tau_{1\to2},\theta_{2\to3},\tau_{2\to3})=\frac{\begin{array}{l}b_{1\to2}^2+b_{1\to3}^2+\\ 2b_{1\to2}b_{1\to3}\{\cos\theta_{1\to2}\cos\tau_{1\to2}\cos\theta_{1\to3}\cos\tau_{1\to3}\\ +\cos\theta_{1\to2}\sin\tau_{1\to2}\cos\theta_{1\to3}\sin\tau_{1\to3}+\sin\theta_{1\to2}\sin\theta_{1\to3}\}\end{array}}{\int\begin{array}{l}b_{1\to2}^2+b_{1\to3}^2+\\ 2b_{1\to2}b_{1\to3}\{\cos\theta_{1\to2}\cos\tau_{1\to2}\cos\theta_{1\to3}\cos\tau_{1\to3}\\ +\cos\theta_{1\to2}\sin\tau_{1\to2}\cos\theta_{1\to3}\sin\tau_{1\to3}+\sin\theta_{1\to2}\sin\theta_{1\to3}\}\\ d\theta_{1\to2}\cdot d\tau_{1\to2}\cdot d\theta_{2\to3}\cdot d\tau_{2\to3}\end{array}}$$

Let us compute the simpler integral

$$\int_0^{2\pi}\{b_{1\to2}^2+b_{1\to3}^2+2b_{1\to2}b_{1\to3}\{\cos\theta_{1\to2}\cos\tau_{1\to2}\cos\theta_{1\to3}\cos\tau_{1\to3}+\cos\theta_{1\to2}\sin\tau_{1\to2}\cos\theta_{1\to3}\sin\tau_{1\to3}+\sin\theta_{1\to2}\sin\theta_{1\to3}\}\}d\theta_{1\to2}$$
$$=2\pi\cdot(b_{1\to2}^2+b_{1\to3}^2)+2b_{1\to2}b_{1\to3}\cdot0=2\pi\cdot(b_{1\to2}^2+b_{1\to3}^2)$$

We must integrate with respect to the remaining 3 variables:

$$\int_{\tau_{2\to3}=0}^{\pi}\int_{\theta_{2\to3}=0}^{2\pi}\int_{\tau_{1\to2}=0}^{\pi}2\pi\cdot(b_{1\to2}^2+b_{1\to3}^2)\cdot d\tau_{1\to2}\cdot d\theta_{2\to3}\cdot d\tau_{2\to3}=4\pi^4\cdot(b_{1\to2}^2+b_{1\to3}^2)$$

The infinitely harder integral to compute is

$$\frac{1}{4\pi^4\cdot(b_{1\to2}^2+b_{1\to3}^2)}\int_{\theta_{1\to2}=0}^{2\pi}\begin{array}{l}\{b_{1\to2}^2+b_{1\to3}^2+\\ 2b_{1\to2}b_{1\to3}\{\cos\theta_{1\to2}\cos\tau_{1\to2}\cos\theta_{1\to3}\cos\tau_{1\to3}\\ +\cos\theta_{1\to2}\sin\tau_{1\to2}\cos\theta_{1\to3}\sin\tau_{1\to3}+\sin\theta_{1\to2}\sin\theta_{1\to3}\}\}\cdot\\ \ln\{\frac{1}{4\pi^4}+\frac{b_{1\to2}b_{1\to3}}{2\pi^4\cdot(b_{1\to2}^2+b_{1\to3}^2)}\{\cos\theta_{1\to2}\cos\tau_{1\to2}\cos\theta_{1\to3}\cos\tau_{1\to3}\\ +\cos\theta_{1\to2}\sin\tau_{1\to2}\cos\theta_{1\to3}\sin\tau_{1\to3}+\sin\theta_{1\to2}\sin\theta_{1\to3}\}\}\cdot d\theta_{1\to2}\end{array}$$

What is $\int_{x=0}^{2\pi}(A+B\cos x+C\sin x)\cdot\ln(A+B\cos x+C\sin x)\cdot dx$?

Here $A=\frac{1}{4\pi^4}$

$$B=\frac{b_{1\to2}b_{1\to3}}{2\pi^4\cdot(b_{1\to2}^2+b_{1\to3}^2)}\{\cos\tau_{1\to2}\cos\tau_{1\to3}+\sin\tau_{1\to2}\sin\tau_{1\to3}\}\cos\theta_{1\to3}$$
$$=\frac{b_{1\to2}b_{1\to3}}{2\pi^4\cdot(b_{1\to2}^2+b_{1\to3}^2)}\cos(\tau_{1\to2}-\tau_{1\to3})\cdot\cos\theta_{1\to3}$$
$$C=\frac{b_{1\to2}b_{1\to3}}{2\pi^4\cdot(b_{1\to2}^2+b_{1\to3}^2)}\sin\theta_{1\to3}$$

Since $0<u<v\Rightarrow0<\frac{(u-v)^2}{u^2+v^2}=1-\frac{2uv}{u^2+v^2}\Rightarrow0<\frac{2uv}{u^2+v^2}<1$, replace $u\to b_{1\to2},v\to b_{1\to3}$

We have

$$\int_{x=0}^{2\pi} \cos x \cdot \ln(A + B\cos x + C\sin x)\cdot dx = \int_{t=0,x=0}^{t=1,x=\pi/2} \ln(A + B\cdot\sqrt{1-t^2} + C\cdot t)\cdot dt$$

$$+ \int_{t=1,x=\pi/2}^{t=-1,x=3\pi/2} \ln(A - B\cdot\sqrt{1-t^2} + C\cdot t)\cdot dt + \int_{t=-1,x=3\pi/2}^{t=0,x=2\pi} \ln(A + B\cdot\sqrt{1-t^2} + C\cdot t)\cdot dt$$

$$= \int_{t=-1}^{t=1} \ln(A + B\cdot\sqrt{1-t^2} + C\cdot t)\cdot dt - \int_{t=-1}^{t=1} \ln(A - B\cdot\sqrt{1-t^2} + C\cdot t)\cdot dt$$

Since

$$\ln(A + B\cdot\sqrt{1-t^2} + C\cdot t) - \ln(A - B\cdot\sqrt{1-t^2} + C\cdot t) =$$

$$\ln A + \ln\left(1 + \frac{C\cdot t + B\cdot\sqrt{1-t^2}}{A}\right) - \ln A - \ln\left(1 + \frac{C\cdot t - B\cdot\sqrt{1-t^2}}{A}\right) =$$

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n}\{\left(\frac{C\cdot t - B\cdot\sqrt{1-t^2}}{A}\right)^n - \left(\frac{C\cdot t + B\cdot\sqrt{1-t^2}}{A}\right)^n\} =$$

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n}\{\sum_{k=0}^{n}\binom{n}{k}\left(\frac{C\cdot t}{A}\right)^{n-k}\{\left(\frac{-B\cdot\sqrt{1-t^2}}{A}\right)^k - \left(\frac{B\cdot\sqrt{1-t^2}}{A}\right)^k\}\} =$$

$$2\sum_{n=1}^{\infty} \frac{(-1)^n}{n}\{\sum_{\substack{k=1 \\ k\equiv 1 \bmod 2}}^{n}\binom{n}{k}\left(\frac{C\cdot t}{A}\right)^{n-k}\left(\frac{B\cdot\sqrt{1-t^2}}{A}\right)^k\}$$

Let m and n be positive integers. Define $I_{m,n} \equiv \int_{t=-1}^{t=1} t^m (\sqrt{1-t^2})^n\, dt$,

$J_{m,n} \equiv \int_{t=0}^{t=1} t^m (\sqrt{1-t^2})^n\, dt$, and $u \equiv t^{m-1}$ and $dv = t\cdot(1-t^2)^{n/2}\cdot dt \Rightarrow v = -\frac{1}{n+2}(1-t^2)^{(n+2)/2}$.

So

$$I_{m,n} = \int_{t=-1}^{t=1} u\cdot dv = u\cdot v\Big|_{t=-1}^{t=1} - \int_{t=-1}^{t=1} v\cdot du = -\frac{t^{m-1}}{n+2}(1-t^2)^{(n+2)/2}\Bigg|_{t=-1}^{t=1} + \frac{m-1}{n+2}\int_{t=-1}^{t=1}(1-t^2)^{(n+2)/2}\cdot t^{m-2}dt$$

$$= 0 + \frac{m-1}{n+2}\int_{t=-1}^{t=1} t^{m-2}\cdot(\sqrt{1-t^2})^n\, dt - \frac{m-1}{n+2}\int_{t=-1}^{t=1} t^m\cdot(\sqrt{1-t^2})^n\, dt$$

$$= \frac{m-1}{n+2}\int_{t=-1}^{t=1} t^{m-2}\cdot(\sqrt{1-t^2})^n\, dt - \frac{m-1}{n+2} I_{m,n}$$

$$\Rightarrow \left(1 + \frac{m-1}{n+2}\right)\cdot I_{m,n} = \frac{m-1}{n+2}\int_{t=-1}^{t=1} t^{m-2}\cdot(\sqrt{1-t^2})^n\, dt \Rightarrow I_{m,n} = \frac{m-1}{n+m+1} I_{m-2,n}$$

Also

$$J_{m,n} = -\frac{t^{m-1}}{n+2}(1-t^2)^{(n+2)/2}\Bigg|_{t=0}^{t=1} + \frac{m-1}{n+2}\int_{t=0}^{t=1}(1-t^2)^{(n+2)/2}\cdot t^{m-2}dt$$

$$= \frac{\delta_{m,1}}{n+2} + \frac{m-1}{n+2}\int_{t=0}^{t=1} t^{m-2}\cdot(\sqrt{1-t^2})^n\,dt - \frac{m-1}{n+2}\int_{t=0}^{t=1} t^m\cdot(\sqrt{1-t^2})^n\,dt$$

$$= \frac{\delta_{m,1}}{n+2} + \frac{m-1}{n+2}\int_{t=0}^{t=1} t^{m-2}\cdot(\sqrt{1-t^2})^n\,dt - \frac{m-1}{n+2}J_{m,n}$$

$$\Rightarrow\left(1+\frac{m-1}{n+2}\right)\cdot J_{m,n} = \frac{\delta_{m,1}}{n+2} + \frac{m-1}{n+2}\int_{t=0}^{t=1} t^{m-2}\cdot(\sqrt{1-t^2})^n\,dt \Rightarrow J_{m,n} = \frac{(m-1)\cdot J_{m-2,n}+\delta_{m,1}}{n+m+1}$$

Since $I_{1,n} = \int_{t=-1}^{t=1} t\cdot(\sqrt{1-t^2})^n\,dt = -\frac{1}{n+2}(\sqrt{1-t^2})^n\Big|_{t=-1}^{t=1} = 0$ it follows that $I_{m,n} = 0$ for all odd positive m. If m is even, then

$$I = \frac{m-1}{m+2}\cdot\frac{m-3}{m}\cdot\frac{m-5}{m-2}\cdot\cdots\cdot\frac{1}{4}\cdot\int_{t=-1}^{t=1} t^0\cdot\sqrt{1-t^2}\,dt$$

$$= \frac{m!}{(m+2)((m/2)!)^2\cdot 2^{m-1}}\cdot\frac{1}{2}(t\cdot\sqrt{1-t^2}+\arcsin t)\Big|_{t=-1}^{t=1} = \frac{m!}{(m+2)((m/2)!)^2\cdot 2^m}\cdot\pi$$ if m is even and if m is odd.

And $J_{m,n} = \frac{\prod_{i=0}^{(m/2)-1}(m-2i-1)}{\prod_{i=0}^{(m/2)-1}(n+1+m-2i)}\cdot J_{0,n} = \frac{m!}{(m/2)!2^{m/2}}\cdot\frac{\prod_{i=0}^{(m/2)-1}(n+m-2i)}{\prod_{i=n+2}^{n+m+1} i}J_{0,n}$ if m is even

So, in the summation above where k must be odd, we must also have n-k be even for a nonzero definite integral over [-1,1]. So, n must be odd for a nonzero definite integral. But we don't even have to perform the integration with respect to t over [-1,1] at this point. The power on B, which is a constant with respect to $\theta_{1\to3}$ times $\cos\theta_{1\to3}$, is k, which is odd and positive. Integrating a positive odd power of $\cos\theta_{1\to3}$ with respect to $\theta_{1\to3}$ over $[0,2\pi]$ equals 0.

By the same argument $\int_{\theta_{1\to3}=0}^{2\pi}\int_{\theta_{1\to2}=0}^{2\pi}\sin x\cdot\ln(A+B\cos x+C\sin x)\cdot d\theta_{1\to2}\cdot d\theta_{1\to3} = 0$ by switching the roles of B and C, since C is a constant with respect to $\theta_{1\to3}$ times $\sin\theta_{1\to3}$.

If m is even and n is even, then the only thing that does not vanish is

$$\frac{n-1}{m+n}\cdot\frac{n-3}{m+n-2}\cdots\frac{1}{m+2}\cdot\int_{x=0}^{2\pi}\cos^m(x)\cdot dx$$

$$=\frac{n-1}{m+n}\cdot\frac{n-3}{m+n-2}\cdots\frac{1}{m+2}\cdot\frac{m-1}{m}\cdot\frac{m-3}{m-2}\cdots\frac{1}{2}\cdot\int_{x=0}^{2\pi}\cos^0(x)\cdot dx$$

$$=2\pi\frac{\left\{\prod_{i=1}^{m/2}(m+1-2i)\right\}\left\{\prod_{i=1}^{n/2}(n+1-2i)\right\}}{\prod_{i=1}^{(m+n)/2}(2i)}=\pi 2^{-\left(\frac{m+n-2}{2}\right)}\frac{n!m!}{\left(\frac{m+n}{2}!\right)\left(\prod_{i=1}^{n/2}(2i)\right)\left(\prod_{i=1}^{m/2}(2i)\right)}$$

$$=\pi 2^{-\left(\frac{m+n-2}{2}\right)}\frac{n!m!}{\left(\frac{m+n}{2}!\right)2^{n/2}2^{m/2}\left(\frac{n}{2}!\right)\left(\frac{m}{2}!\right)}=\frac{2^{1-m-n}\pi\cdot\Gamma(m+1)\cdot\Gamma(n+1)}{\Gamma\left(\frac{m}{2}+1\right)\Gamma\left(\frac{n}{2}+1\right)\Gamma\left(\frac{m+n}{2}+1\right)}$$

$$\ln(A+B\cos x+C\sin x)=\ln A+\ln(1+\frac{B}{A}\cos x+\frac{C}{A}\sin x)$$

$$=\ln A-\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\left(\frac{B}{A}\cos x+\frac{C}{A}\sin x\right)^n$$

$$=\ln A-\sum_{n=1}^{\infty}\frac{(-A)^{-n}}{n}\sum_{k=0}^{n}\binom{n}{k}B^kC^{n-k}\cos^k x\cdot\sin^{n-k}x$$

If n is odd and k is even, then n-k is odd, and the integral over the period $[0,2\pi]$ vanishes. If n is odd and k is odd, then the integral again vanishes. So, we may ignore all odd n and include only even k.

$$\int_0^{2\pi}\ln(A+B\cos\theta_{1\to2}+C\sin\theta_{1\to2})\cdot d\theta_{1\to2}=2\pi\ln A$$

$$-\sum_{n=1}^{\infty}\frac{(-A)^{-2n}}{2n}\sum_{k=0}^{n}\binom{2n}{2k}B^{2k}C^{2n-2k}\int_0^{2\pi}\cos^{2k}\theta_{1\to2}\cdot\sin^{2n-2k}\theta_{1\to2}\cdot d\theta_{1\to2}=$$

$$2\pi\ln A-\sum_{n=1}^{\infty}\frac{(-A)^{-2n}}{2n}\sum_{k=0}^{n}\binom{2n}{2k}B^{2k}C^{2n-2k}\frac{2^{1-2k-(2n-2k)}\pi\cdot\Gamma(2k+1)\cdot\Gamma(2n-2k+1)}{\Gamma(k+1)\Gamma(n-k+1)\Gamma(n+1)}=$$

$$2\pi\ln A-\pi\cdot\sum_{n=1}^{\infty}\frac{(-A)^{-2n}}{n}\sum_{k=0}^{n}B^{2k}C^{2n-2k}2^{1-2n}\frac{\Gamma(2n+1)}{\Gamma(2k+1)\cdot\Gamma(2n-2k+1)}\frac{\Gamma(2k+1)\cdot\Gamma(2n-2k+1)}{\Gamma(k+1)\Gamma(n-k+1)\Gamma(n+1)}$$

$$=2\pi\ln A-2\pi\cdot\sum_{n=1}^{\infty}\frac{(2A)^{-2n}}{n}\sum_{k=0}^{n}B^{2k}C^{2n-2k}\frac{\Gamma(2n+1)}{\Gamma(k+1)\Gamma(n-k+1)\Gamma(n+1)}$$

$$= 2\pi \ln \frac{1}{4\pi^4}$$

$$-2\pi \cdot \sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{1}{2} \frac{4\pi^4 b_{1\to2} b_{1\to3}}{2\pi^4 \cdot (b_{1\to2}^2 + b_{1\to3}^2)} \right)^{2n} \sum_{k=0}^{n} \cos^{2k}(\tau_{1\to2} - \tau_{1\to3}) \cos^{2k}\theta_{1\to3} \sin^{2n-2k}\theta_{1\to3} \frac{\Gamma(2n+1)}{\Gamma(k+1)\Gamma(n-k+1)\Gamma(n+1)}$$

Integrating with respect to $\theta_{1\to3}$ over the interval $[0, 2\pi]$ yields

$$= -4\pi^2 \ln(4\pi^4)$$

$$-4\pi^2 \cdot \sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{b_{1\to2} b_{1\to3}}{b_{1\to2}^2 + b_{1\to3}^2} \right)^{2n} 2^{-(2n-2k)-2k} \sum_{k=0}^{n} \cos^{2k}(\tau_{1\to2} - \tau_{1\to3}) \frac{\Gamma(2k+1)\cdot\Gamma(2n-2k+1)}{\Gamma(k+1)\Gamma(n-k+1)\Gamma(n+1)} \frac{\Gamma(2n+1)}{\Gamma(k+1)\Gamma(n-k+1)\Gamma(n+1)}$$

Integrating with respect to $\tau_{1\to2}$

$$\int_{\tau_{1\to2}=0}^{\pi} \cos^{2k}(\tau_{1\to2} - \tau_{1\to3}) \cdot d\tau_{1\to2} = -\left. \frac{\cos^{2k-1}(\tau_{1\to2} - \tau_{1\to3}) \cdot \sin(\tau_{1\to2} - \tau_{1\to3})}{2k} \right|_{\tau_{1\to2}=0}^{\pi}$$

$$+ \frac{2k-1}{2k} \cdot \int_{\tau_{1\to2}=0}^{\pi} \cos^{2k-2}(\tau_{1\to2} - \tau_{1\to3}) \cdot d\tau_{1\to2}$$

Repeating this integration we get

$$\int_{\tau_{1\to2}=0}^{\pi} \cos^{2k}(\tau_{1\to2} - \tau_{1\to3}) \cdot d\tau_{1\to2} = \frac{\prod_{i=1}^{k-1}(2\cdot(k-i)+1)}{\prod_{i=0}^{k-1} 2\cdot(k-i)} \int_{\tau_{1\to2}=0}^{\pi} \cos^{0}(\tau_{1\to2} - \tau_{1\to3}) \cdot d\tau_{1\to2}$$

$$-\sum_{j=1}^{k} \frac{\prod_{i=1}^{j-1}(2\cdot(k-i)+1)}{\prod_{i=0}^{j-1} 2\cdot(k-i)} \cos^{2(k-j)+1}(\tau_{1\to2} - \tau_{1\to3}) \cdot \sin(\tau_{1\to2} - \tau_{1\to3}) \Big|_{\tau_{1\to2}=0}^{\pi}$$

$$= 2^{-k} \frac{\prod_{i=1}^{k-1}(2\cdot(k-i)+1)}{k!} \cdot \pi - \sum_{j=1}^{k} \frac{\prod_{i=1}^{j-1}(2\cdot(k-i)+1)}{\prod_{i=0}^{j-1} 2\cdot(k-i)} \{\cos^{2(k-j)+1}(\pi - \tau_{1\to3}) \cdot \sin(\pi - \tau_{1\to3}) - \cos^{2(k-j)+1}(-\tau_{1\to3}) \cdot \sin(-\tau_{1\to3})\}$$

$$2^{-k}\frac{\prod_{i=1}^{k-1}(2\cdot(k-i)+1)}{k!}\cdot\pi-\sum_{j=1}^{k}\frac{\prod_{i=1}^{j-1}(2\cdot(k-i)+1)}{\prod_{i=0}^{j-1}2\cdot(k-i)}\{-\cos^{2(k-j)+1}(\tau_{1\to3}-\pi)\cdot\sin(\tau_{1\to3}-\pi)$$

$$+\cos^{2(k-j)+1}(\tau_{1\to3})\cdot\sin(\tau_{1\to3})\}$$

$$=2^{-k}\frac{\prod_{i=1}^{k-1}(2\cdot(k-i)+1)}{k!}\cdot\pi-\sum_{j=1}^{k}\frac{\prod_{i=1}^{j-1}(2\cdot(k-i)+1)}{\prod_{i=0}^{j-1}2\cdot(k-i)}\{-\cos^{2(k-j)+1}(\tau_{1\to3})\cdot\sin(\tau_{1\to3})$$

$$+\cos^{2(k-j)+1}(\tau_{1\to3})\cdot\sin(\tau_{1\to3})\}$$

$$=2^{-k}\frac{\prod_{i=1}^{k-1}(2\cdot(k-i)+1)}{k!}\cdot\pi$$

$$\frac{S}{-k_B}=-4\pi^2\ln(4\pi^4)\int_{\tau_{1\to3}=0}^{\pi}d\tau_{1\to3}$$

$$-4\pi^2\cdot\sum_{n=1}^{\infty}\frac{\frac{1}{n}\left(\frac{1}{2}\frac{b_{1\to2}b_{1\to3}}{b_{1\to2}^2+b_{1\to3}^2}\right)^{2n}}{\sum_{k=0}^{n}2^{-k}\frac{\prod_{i=1}^{k-1}(2\cdot(k-i)+1)}{k!}\cdot\pi\frac{\Gamma(2k+1)\cdot\Gamma(2n-2k+1)\cdot\Gamma(2n+1)}{(\Gamma(k+1))^2(\Gamma(n-k+1))^2(\Gamma(n+1))^2}\int_{\tau_{1\to3}=0}^{\pi}d\tau_{1\to3}}$$

$$\frac{S}{-k_B}=-4\pi^3\ln(4\pi^4)-4\pi^4\cdot\sum_{n=1}^{\infty}\frac{\frac{1}{n}\left(\frac{1}{2}\frac{b_{1\to2}b_{1\to3}}{b_{1\to2}^2+b_{1\to3}^2}\right)^{2n}}{\sum_{k=1}^{n}2^{-k}\frac{\prod_{j=1}^{2k}j}{\prod_{i=1}^{k}(2i)}\cdot\frac{\Gamma(2k+1)\cdot\Gamma(2n-2k+1)\cdot\Gamma(2n+1)}{(\Gamma(k+1))^3(\Gamma(n-k+1))^2(\Gamma(n+1))^2}\}}\{\frac{(\Gamma(2n+1))^2}{(\Gamma(n+1))^4}+$$

$$\frac{S}{-k_B}=-4\pi^3\ln(4\pi^4)$$

$$-4\pi^4\cdot\sum_{n=1}^{\infty}\frac{1}{n}\left(\frac{1}{2}\frac{b_{1\to2}b_{1\to3}}{b_{1\to2}^2+b_{1\to3}^2}\right)^{2n}\{\binom{2n}{n}^2+\binom{2n}{n}\sum_{k=1}^{n}2^{-2k}\binom{2k}{k}^2\binom{2n-2k}{n-k}\}$$

An extension of Stirling's approximation is given by Robbins as the double inequality

$$\sqrt{2\pi}\cdot n^{n+\frac{1}{2}}e^{-n+\frac{1}{12n+1}}<n!<\sqrt{2\pi}\cdot n^{n+\frac{1}{2}}e^{-n+\frac{1}{12n}}$$

So $\frac{1}{\sqrt{2\pi}}2^{2n}n^{-1/2}e^{-\frac{3}{24n+1}-\frac{1}{(6n)(24n+1)}} < \binom{2n}{n} < \frac{1}{\sqrt{2\pi}}2^{2n}n^{-1/2}e^{-\frac{3}{2}\cdot\frac{1}{(12n+1)}+\frac{1}{(24n)(12n+1)}}$

So

$$\frac{2^{2n}}{(2\pi)^{3/2}}\sum_{k=1}^{n-1}\frac{e^{-\frac{6}{24k+1}-\frac{1}{(3k)(24k+1)}-\frac{3}{24(n-k)+1}-\frac{1}{(6n-6k)(24n-24k+1)}}}{k\sqrt{(n-k)}}$$

$$\sum_{k=1}^{n-1}2^{-2k}\left\{\frac{1}{\sqrt{2\pi}}2^{2k}k^{-1/2}e^{-\frac{3}{24k+1}-\frac{1}{(6k)(24k+1)}}\right\}^2\left\{\frac{1}{\sqrt{2\pi}}2^{2n-2k}(n-k)^{-1/2}e^{-\frac{3}{24(n-k)+1}-\frac{1}{(6n-6k)(24n-24k+1)}}\right\}$$

$$<\sum_{k=1}^{n-1}2^{-2k}\binom{2k}{k}^2\binom{2n-2k}{n-k}<$$

$$\sum_{k=1}^{n-1}2^{-2k}\left\{\frac{1}{\sqrt{2\pi}}2^{2k}k^{-1/2}e^{-\frac{3}{2}\cdot\frac{1}{(12k+1)}+\frac{1}{(24k)(12k+1)}}\right\}^2\left\{\frac{1}{\sqrt{2\pi}}2^{2n-2k}(n-k)^{-1/2}e^{-\frac{3}{2}\cdot\frac{1}{(12(n-k)+1)}+\frac{1}{(24(n-k))(12(n-k)+1)}}\right\}$$

$$<\frac{2^{2n}}{(2\pi)^{3/2}}\sum_{k=1}^{n-1}\frac{e^{-\frac{3}{(12k+1)}-\frac{3}{2}\cdot\frac{1}{(12(n-k)+1)}+\frac{1}{(12k)(12k+1)}+\frac{1}{(24(n-k))(12(n-k)+1)}}}{k\sqrt{(n-k)}}<\frac{2^{2n}}{(2\pi)^{3/2}}\sum_{k=1}^{n-1}\frac{1}{k\sqrt{n-k}}$$

$$\frac{1}{n-2}+\int_1^{n-1}\frac{dx}{x\cdot\sqrt{n-x}}<\sum_{k=1}^{n-1}\frac{1}{k\sqrt{n-k}}<\frac{1}{\sqrt{n-1}}+\int_1^{n-1}\frac{dx}{x\cdot\sqrt{n-x}}$$

From 182 page 25 in Peirce,

$$\int_1^{n-1}\frac{dx}{x\cdot\sqrt{n-x}}=-\frac{1}{\sqrt{n}}\ln\left(\frac{\sqrt{n-x}+\sqrt{n}}{x}-\frac{1}{2\sqrt{n}}\right)\Bigg|_{x=1}^{x=n-1}=$$

$$\frac{1}{\sqrt{n}}\ln\left(\frac{\sqrt{n-1}+1-\frac{1}{2\sqrt{n}}}{\frac{1+\sqrt{n-1}}{n-1}-\frac{1}{2\sqrt{n}}}\right)=\frac{1}{\sqrt{n}}\ln\left(\frac{2\sqrt{n}\sqrt{n-1}+2\sqrt{n}-1}{2\sqrt{n}\sqrt{n-1}-n+1}\right)$$

From

$$-\frac{6}{24k+1}-\frac{1}{(3k)(24k+1)}-\frac{3}{24(n-k)+1}-\frac{1}{(6n-6k)(24n-24k+1)}>$$

$$-\frac{1}{4k}-\frac{1}{72k^2}-\frac{1}{8(n-k)}-\frac{1}{6\cdot 24\cdot(n-k)^2}>-\frac{1}{4}-\frac{1}{72}-\frac{1}{8}-\frac{1}{144}=-0.3958\overline{3}$$

$$e^{-0.3958\overline{3}}\approx 0.673118873$$

So $<\sum_{k=1}^{n-1}2^{-2k}\binom{2k}{k}^2\binom{2n-2k}{n-k}<\frac{2^{2n}}{(2\pi)^{3/2}}\frac{(0.673118873)}{\sqrt{n}}\ln\left(\frac{2\sqrt{n}\sqrt{n-1}+2\sqrt{n}-1}{2\sqrt{n}\sqrt{n-1}-n+1}\right)$

So

$$\binom{2n}{n}^2 + \binom{2n}{n}\sum_{k=1}^{n} 2^{-2k}\binom{2k}{k}^2\binom{2n-2k}{n-k} <$$

$$\binom{2n}{n}^2 + \frac{2^{2n}}{(2\pi)^{3/2}}\frac{(0.673118873)}{\sqrt{n}}\ln\left(\frac{2\sqrt{n}\sqrt{n-1}+2\sqrt{n}-1}{2\sqrt{n}\sqrt{n-1}-n+1}\right)\binom{2n}{n} <$$

$$\frac{1}{2\pi n}2^{4n}e^{-\frac{3}{(12n+1)}+\frac{1}{(12n)(12n+1)}} + \frac{(0.673118873)}{4\pi^2 n}2^{4n}e^{-\frac{3}{2(12n+1)}+\frac{1}{(24n)(12n+1)}}\ln\left(\frac{2\sqrt{n}\sqrt{n-1}+2\sqrt{n}-1}{2\sqrt{n}\sqrt{n-1}-n+1}\right)$$

In general For a straight chain of atomic nuclei, we want the probability density function $|\psi|^2$ to vary with the distance squared between *all* pairs of unbonded nuclei. 5 atoms always lie in 3-dimensional space, hence, the 4-dimensional volume of the 4-simplex whose vertices are these atoms equals 0. The Cayley-Menger matrix therefore has $\det\begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & r_{i_1i_2}^2 & r_{i_1i_3}^2 & r_{i_1i_4}^2 & r_{i_1i_5}^2 \\ 1 & r_{i_1i_2}^2 & 0 & r_{i_2i_3}^2 & r_{i_2i_4}^2 & r_{i_2i_5}^2 \\ 1 & r_{i_1i_3}^2 & r_{i_2i_3}^2 & 0 & r_{i_3i_4}^2 & r_{i_3i_5}^2 \\ 1 & r_{i_1i_4}^2 & r_{i_2i_4}^2 & r_{i_3i_4}^2 & 0 & r_{i_4i_5}^2 \\ 1 & r_{i_1i_5}^2 & r_{i_2i_5}^2 & r_{i_3i_5}^2 & r_{i_4i_5}^2 & 0 \end{bmatrix} = 0$ for all quintuplets of distinct indices $1 \le i_1 < i_2 < i_3 < i_4 < i_5 \le N$, forcing a condition on the 10 distances. Now, among the $\binom{6}{5} = 6$ equations relating the $\frac{6\cdot 5}{2} = 15$ distances $s_{i_1i_2}$ through $s_{i_5i_6}$ one of them does not involve any of the 5 variables $s_{i_1i_6}, s_{i_2i_6}, s_{i_3i_6}, s_{i_4i_6}, s_{i_5i_6}$, while the other 5 equations each do. Hence, fixing any of the 10 remaining distances $s_{i_1i_2}$ through $s_{i_4i_5}$ ought to fix these 5 distances.

Solving the many systems of equations given by setting to zero the determinants of the Cayley-Menger matrices is a long-standing problem in computational chemistry.

See "Cayley-Menger coordinates". Sippl, Manfred J. and Harold A. Scheraga. *Proc. Natl. Acad. Sci.* Vol. 83, pp 2283-2287, April 1986. Applied Physical and Mathematical Sciences.

Example. In the amino acid glycine $\mathrm{H_2N-CH_2-COOH}$ there are N=10 atoms and B=9 bonds. 45 pairs of distances,

$$\binom{9}{5} = 126$$

equations on these 45 pairs. How many of these equations are independent?

Inclusion-exclusion principle $\left|\bigcup_{i=1}^{n} A_i\right| = \sum_{k=1}^{n} (-1)^{k+1} \sum_{1 \le i_1 < \cdots < i_k \le n} \left|\bigcap_{j=1}^{k} A_{i_j}\right|$

So, for which collections of countably many probabilities can we get entropies *between* these two extremes: zero or the (finite) maximum value of $k_B \cdot \ln \Omega$ when $\Omega < \infty$?

Note: go to http://en.wikipedia.org/wiki/Lagrange_multiplier for the standard proof that indeed $k_B \cdot \ln \Omega$ *is* the maximum value for entropy for a *finite* number Ω of microstates. Or Noggle pages 217-218.

Variation or perturbation from maximal entropy for a finite number of microstates

Let the number of possible states, Ω, the system could be in (whatever that means) be even. Let half of these states have an equal probability slightly less than 0.5 by an amount ε, and the other half have states slightly more than 0.5 by an amount ε.
Consider $\forall i \in [\frac{\Omega}{2}] \Rightarrow p_i = \frac{1}{\Omega} - \varepsilon, \forall i \in [\Omega] - [\frac{\Omega}{2}] \Rightarrow p_i = \frac{1}{\Omega} + \varepsilon$ where $0 < \varepsilon < \frac{1}{\Omega}$.
So entropy in this case depends upon 2 free variables: Ω and ε. Define $x \equiv \Omega\varepsilon$.
Then $0 < x < 1$ and

Then $$\frac{S}{k_B} = \sum_{i=1}^{\Omega} p_i \ln\left(\frac{1}{p_i}\right) = \sum_{i=1}^{\Omega/2} (\frac{1}{\Omega} + \varepsilon) \ln\left(\frac{1}{\frac{1}{\Omega} + \varepsilon}\right) + \sum_{i=1}^{\Omega/2} (\frac{1}{\Omega} - \varepsilon) \ln\left(\frac{1}{\frac{1}{\Omega} - \varepsilon}\right)$$

$$= \ln\left(\frac{\Omega}{(1-x)^{(1-x)/2}(1+x)^{(1+x)/2}} \cdot\right)$$

So $S(0) = k_B \cdot \ln(\Omega)$ and $S(1) = k_B \cdot \ln(\Omega / 2)$. If Ω is enormous, say, $\Omega \approx 10^{27}!$, then the relative difference between $\ln(\Omega) = \ln(2) + \ln(\Omega/2)$, the *maximum* possible value, and ln(M), the *minimal* possible value for this particular model, is miniscule.

Example. When counting molecular arrangements, we will almost ubiquitously be forced to deal with counting observably indistinguishable arrangements. Thus, summations involving multinomial functions will arise. Let us consider the simplest such example. To avoid writing $\Omega - 1$ everywhere instead of Ω, let the total number of microstates be $\Omega + 1$ instead of Ω, with probabilities given by
$\forall k \in [\Omega]_0 \Rightarrow p_k = p^k (1-p)^{\Omega - k} \binom{\Omega}{k}$. Hence, as in the previous example, the entropy will depend upon 2 free parameters: Ω and p. Define $\lambda \equiv \frac{p}{1-p}$ and $\bar{\lambda} \equiv \frac{1-p}{p}$ and $q \equiv 1 - p$. Let us compute $\frac{S_\Omega(p)}{-k_B} = \sum_{k=0}^{\Omega} p^k q^{\Omega-k} \binom{\Omega}{k} \ln\left\{ p^k q^{\Omega-k} \binom{\Omega}{k} \right\}$.

This quantity equals

$$(\ln p)\cdot\sum_{k=0}^{\Omega} k\cdot p^k q^{\Omega-k}\binom{\Omega}{k}+(\ln q)\cdot\sum_{k=0}^{\Omega}(\Omega-k)\cdot p^k q^{\Omega-k}\binom{\Omega}{k}$$

$$+\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}\cdot\ln\binom{\Omega}{k}=$$

$$((\ln p)-(\ln q))\cdot\sum_{k=0}^{\Omega} k\cdot p^k q^{\Omega-k}\binom{\Omega}{k}+\Omega\cdot(\ln q)\cdot\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}$$

$$+\ln((\Omega+1)!)\cdot\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}-\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}\cdot\ln(k!)-\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}\cdot\ln((\Omega-k)!)$$

The first of these five summations equals $\sum_{k=0}^{\Omega} k\cdot p^k q^{\Omega-k}\binom{\Omega}{k}=\Omega\cdot p$.

The second and third summations equal $\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}=1$.

So $\frac{S_\Omega(p)}{-k_B}=(p\cdot\ln p+q\cdot\ln q)\cdot\Omega+\ln((\Omega+1)!)-R(p)-R(q)$ where

$$R(p)\equiv\sum_{k=0}^{\Omega} p^k q^{\Omega-k}\binom{\Omega}{k}\cdot\ln(k!)$$

By a change of variables in the index, we see that the fifth summation equals the fourth summation obtained by replacing p with $1-p$. For $k\in\mathbb{N}$ we have

$$\sqrt{2\pi}\cdot k^{k+\frac{1}{2}}e^{-k+\frac{1}{12k+1}}<k!<\sqrt{2\pi}\cdot k^{k+\frac{1}{2}}e^{-k+\frac{1}{12k}}$$

$$\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k+1}<\ln(k!)<\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k}$$

Let $0\le p\le q\le 1$. Define $(\Omega)_k=\prod_{i=0}^{k-1}(\Omega-i)$.

If $1\le k\le[\![\Omega\cdot p]\!]$ then for each $i\in[k-1]_0$ we have $\Omega\cdot q\le\Omega-[\![\Omega\cdot p]\!]\le\Omega-k<\Omega-i\le\Omega$. Thus $(\Omega)_k$ is a product of k integers strictly larger than $\Omega\cdot q$ but less than or equal to Ω . Hence $\Omega^k\cdot q^k<(\Omega)_k\le\Omega^k$.

Now, keep in mind that $\Omega\cdot p$ and $\Omega\cdot q$ need not be integers, so we cannot replace the strict inequalities on the right with nonstrict inequalities: $\Omega\cdot q\le\Omega-[\![\Omega\cdot p]\!]<\Omega\cdot q+1$ and $\Omega\cdot p\le\Omega-[\![\Omega\cdot q]\!]<\Omega\cdot p+1$.

If $[\![\Omega\cdot p]\!]+1\le k\le[\![\Omega\cdot q]\!]$ then for each $i\in[[\![\Omega\cdot p]\!]-1]_0$ we still have $\Omega\cdot q<\Omega-i\le\Omega$ but for each $i\in[k-1]_0\ni i\ge[\![\Omega\cdot p]\!]$ we have $\Omega\cdot p\le\Omega-[\![\Omega\cdot q]\!]\le\Omega-k<\Omega-i\le\Omega-[\![\Omega\cdot p]\!]<\Omega\cdot q+1$, Thus, $(\Omega)_k$ is a product of $[\![\Omega\cdot p]\!]$ numbers strictly larger than $\Omega\cdot q$ but less than or equal to Ω times a product of

$k-[\![\Omega\cdot p]\!]$ numbers strictly larger than $\Omega\cdot p$ but strictly less than $\Omega\cdot q+1$. Hence $\Omega^k\cdot q^{[\![\Omega\cdot p]\!]}p^{k-[\![\Omega\cdot p]\!]}<(\Omega)_k<\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{k-[\![\Omega\cdot p]\!]}$.

If $[\![\Omega\cdot q]\!]+1\le k\le\Omega$ then for each $i\in[k-1]_0\ni i\ge[\![\Omega\cdot q]\!]$ we have $\Omega-k<\Omega-i\le\Omega-[\![\Omega\cdot q]\!]<\Omega\cdot p+1$. So $(\Omega)_k$ is a product of $[\![\Omega\cdot p]\!]$ numbers strictly larger than $\Omega\cdot q$ but less than or equal to Ω, times a product of $[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]$ numbers strictly larger than $\Omega\cdot p$ but strictly less than $\Omega\cdot q+1$, times a product of $k-[\![\Omega\cdot q]\!]$ numbers greater than or equal to 1 but strictly less than $\Omega\cdot p+1$. Hence
$\Omega^{[\![\Omega\cdot q]\!]}\cdot q^{[\![\Omega\cdot p]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}<(\Omega)_k<\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot p+1)^{k-[\![\Omega\cdot q]\!]}$
From these inequalities and the product formula for $(\Omega)_k$ we summarize

When $1\le k\le[\![\Omega\cdot p]\!]$ then $\Omega^k\cdot q^k<(\Omega)_k\le\Omega^k$ so $\dfrac{\Omega^k q^k}{k!}<\dbinom{\Omega}{k}\le\dfrac{\Omega^k}{k!}$.

When $[\![\Omega\cdot p]\!]+1\le k\le[\![\Omega\cdot q]\!]$ then $\Omega^k\cdot q^{[\![\Omega\cdot p]\!]}p^{k-[\![\Omega\cdot p]\!]}<(\Omega)_k<\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{k-[\![\Omega\cdot p]\!]}$ so

$$\frac{\Omega^k\cdot q^{[\![\Omega\cdot p]\!]}p^{k-[\![\Omega\cdot p]\!]}}{k!}<\binom{\Omega}{k}<\frac{\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{k-[\![\Omega\cdot p]\!]}}{k!}$$

When $[\![\Omega\cdot q]\!]+1\le k\le\Omega$ then
$\Omega^{[\![\Omega\cdot q]\!]}\cdot q^{[\![\Omega\cdot p]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}<(\Omega)_k<\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot p+1)^{k-[\![\Omega\cdot q]\!]}$ so

$$\frac{\Omega^{[\![\Omega\cdot q]\!]}\cdot q^{[\![\Omega\cdot p]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}}{k!}<\binom{\Omega}{k}<\frac{\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot p+1)^{k-[\![\Omega\cdot q]\!]}}{k!}$$

So for $1\le k\le[\![\Omega\cdot p]\!]$ we have

$$q^{\Omega}\frac{\Omega^k p^k}{k!}\left\{\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k+1}\right\}\le p^k q^{\Omega-k}\binom{\Omega}{k}\ln(k!)$$
$$\le\frac{\Omega^k}{k!}p^k q^{\Omega-k}\left\{\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k}\right\}$$

So for $[\![\Omega\cdot p]\!]+1\le k\le[\![\Omega\cdot q]\!]$ we have

$$p^k q^{\Omega-k}\frac{\Omega^k\cdot q^{[\![\Omega\cdot p]\!]}p^{k-[\![\Omega\cdot p]\!]}}{k!}\left\{\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k+1}\right\}<p^k q^{\Omega-k}\binom{\Omega}{k}\ln(k!)$$
$$<p^k q^{\Omega-k}\frac{\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{k-[\![\Omega\cdot p]\!]}}{k!}\left\{\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k}\right\}$$

So for $[\![\Omega\cdot q]\!]+1\le k\le\Omega$ we have

$$p^k q^{\Omega-k}\frac{\Omega^{[\![\Omega\cdot q]\!]}\cdot q^{[\![\Omega\cdot p]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}}{k!}\cdot\left\{\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k+1}\right\}$$

$$<p^k q^{\Omega-k}\binom{\Omega}{k}\ln(k!)<$$

$$p^k q^{\Omega-k}\frac{\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot p+1)^{k-[\![\Omega\cdot q]\!]}}{k!}\cdot\left\{\ln\sqrt{2\pi}+\left(k+\frac{1}{2}\right)\ln k-k+\frac{1}{12k}\right\}$$

We need to get rid of the ln k term.
For $1\le k\le[\![\Omega\cdot p]\!]$ we have

$$q^{\Omega}\frac{(\Omega\cdot p)^k}{k!}\left\{\ln\sqrt{2\pi}-k+\frac{1}{12(k+1)}\right\}\le p^k q^{\Omega-k}\binom{\Omega}{k}\ln(k!)$$

$$\le q^{\Omega}\frac{\left(\frac{\Omega\cdot p}{q}\right)^k}{k!}\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln[\![\Omega\cdot p]\!]}{2}+\frac{1}{12}\right\}+\left(\ln[\![\Omega\cdot p]\!]-1\right)\cdot k\right\}$$

For $[\![\Omega\cdot p]\!]+1\le k\le[\![\Omega\cdot q]\!]$ we have

$$q^{\Omega+[\![\Omega\cdot p]\!]}p^{-[\![\Omega\cdot p]\!]}\frac{\left(\frac{\Omega p^2}{q}\right)^k}{k!}\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln([\![\Omega\cdot p]\!]+1)}{2}\right\}+\left(\ln([\![\Omega\cdot p]\!]+1)-1\right)\cdot k+\frac{1}{12(k+1)}\right\}<p^k q^{\Omega-k}\binom{\Omega}{k}\ln(k!)$$

$$<q^{\Omega}\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{-[\![\Omega\cdot p]\!]}\frac{\left((\Omega\cdot q+1)\frac{p}{q}\right)^k}{k!}\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln[\![\Omega\cdot q]\!]}{2}+\frac{1}{12([\![\Omega\cdot p]\!]+1)}\right\}+\left(\ln[\![\Omega\cdot q]\!]-1\right)\cdot k\right\}$$

For $[\![\Omega\cdot q]\!]+1\le k\le\Omega$ we have

$$\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}\cdot\frac{\left(\frac{p}{q}\right)^k}{k!}\cdot\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln([\![\Omega\cdot q]\!]+1)}{2}\right\}+\left(\ln([\![\Omega\cdot q]\!]+1)-1\right)\cdot k+\frac{1}{12(k+1)}\right\}$$

$$<p^k q^{\Omega-k}\binom{\Omega}{k}\ln(k!)<$$

$$\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}(\Omega\cdot p+1)^{-[\![\Omega\cdot q]\!]}\cdot q^{\Omega}\frac{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)^k}{k!}\cdot\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln\Omega}{2}+\frac{1}{12([\![\Omega\cdot q]\!]+1)}\right\}+\left(\ln\Omega-1\right)\cdot k\right.$$

Now we sum over k over the indicated domains. The remainder in Taylor's series: $\left|e^x - \sum_{k=0}^{N} \frac{x^k}{k!}\right| \le \frac{e^x |x|^{N+1}}{(N+1)!}$ implies

$$x > 0 \Rightarrow \max(0, e^x \cdot \left(1 - \frac{x^{N+1}}{(N+1)!}\right)) \le \sum_{k=0}^{N} \frac{x^k}{k!} \le e^x \cdot \left(1 + \frac{x^{N+1}}{(N+1)!}\right).$$

We can get a better lower bound by recognizing that the function $g(k) = \frac{x^k}{k!}$ for fixed real x reaches at most 1 maximum on any interval $k \in [A, B]$, so is monotonic on either side. Hence, $\sum_{k=A+1}^{B} \frac{x^k}{k!} \ge (B-A) \cdot \min\left\{\frac{x^{A+1}}{(A+1)!}, \frac{x^B}{B!}\right\}$. In particular, $\sum_{k=0}^{B} \frac{x^k}{k!} \ge 1 + \min\left\{x, \frac{x^B}{(B-1)!}\right\}$.

This implies

$$x > 0 \Rightarrow (B-A) \cdot \min\left\{\frac{x^{A+1}}{(A+1)!}, \frac{x^B}{B!}\right\} \le \sum_{k=A+1}^{B} \frac{x^k}{k!} \le e^x \cdot \left(1 + \frac{x^{B+1}}{(B+1)!}\right) - 1 - \min\left\{x, \frac{x^A}{(A-1)!}\right\}$$

From $\sum_{k=A+1}^{B} \frac{x^k}{k!} \cdot k = \sum_{k=A+1}^{B} \frac{x^k}{(k-1)!} = x \cdot \sum_{k=A+1}^{B} \frac{x^{k-1}}{(k-1)!} = x \cdot \sum_{j=A}^{B-1} \frac{x^j}{j!}$ we get

$$x > 0 \Rightarrow (B-A) \cdot \min\left\{\frac{x^{A+1}}{A!}, \frac{x^B}{(B-1)!}\right\} \le \sum_{k=A+1}^{B} \frac{x^k}{k!} \cdot k \le e^x \cdot \left(x + \frac{x^{B+1}}{B!}\right) - x - \min\left\{x^2, \frac{x^A}{(A-2)!}\right\}$$

From $\sum_{k=A+1}^{B} \frac{x^k}{k!} \cdot \frac{1}{k+1} = \sum_{k=A+1}^{B} \frac{x^k}{(k+1)!} = x^{-1} \sum_{k=A+1}^{B} \frac{x^{k+1}}{(k+1)!} = x^{-1} \cdot \sum_{j=A+2}^{B+1} \frac{x^j}{j!}$ we get

$$(B-A) \cdot \min\left\{\frac{x^{A+1}}{(A+2)!}, \frac{x^B}{(B+1)!}\right\} \le \sum_{k=A+1}^{B} \frac{x^k}{k!} \frac{1}{k+1} \le e^x \cdot \left(x^{-1} + \frac{x^{B+1}}{(B+2)!}\right) - x^{-1} - \min\left\{1, \frac{x^A}{A!}\right\}$$

One can easily check that the k=0 term of R(p) is zero. So, we drop that term from the left and right sides.

Adding up the lower bounds first

$$\sum_{k=1}^{[\![\Omega \cdot p]\!]} q^{\Omega} \frac{(\Omega \cdot p)^k}{k!} \left\{\ln\sqrt{2\pi} - k + \frac{1}{12(k+1)}\right\} +$$

$$\sum_{k=[\![\Omega \cdot p]\!]+1}^{[\![\Omega \cdot q]\!]} q^{\Omega + [\![\Omega \cdot p]\!]} p^{-[\![\Omega \cdot p]\!]} \frac{\left(\frac{\Omega p^2}{q}\right)^k}{k!} \left\{\left\{\ln\sqrt{2\pi} + \frac{\ln([\![\Omega \cdot p]\!]+1)}{2}\right\} + \left(\ln([\![\Omega \cdot p]\!]+1) - 1\right) \cdot k + \frac{1}{12(k+1)}\right\} +$$

$$\sum_{k=[\![\Omega \cdot q]\!]+1}^{\Omega} \Omega^{[\![\Omega \cdot q]\!]} p^{[\![\Omega \cdot q]\!] - [\![\Omega \cdot p]\!]} q^{\Omega + [\![\Omega \cdot p]\!]} \cdot \frac{\left(\frac{p}{q}\right)^k}{k!} \cdot \left\{\left\{\ln\sqrt{2\pi} + \frac{\ln([\![\Omega \cdot q]\!]+1)}{2}\right\} + \left(\ln([\![\Omega \cdot q]\!]+1) - 1\right) \cdot k + \frac{1}{12(k+1)}\right\}$$

$$> \Omega\cdot p - e^{\Omega\cdot p}\cdot\left(\Omega\cdot p + \frac{(\Omega\cdot p)^{[\![\Omega\cdot p]\!]+1}}{[\![\Omega\cdot p]\!]!}\right)$$

$$+q^{\Omega}\ln\sqrt{2\pi}\,[\![\Omega\cdot p]\!]\cdot\min\left\{(\Omega\cdot p), \frac{(\Omega\cdot p)^{[\![\Omega\cdot p]\!]}}{[\![\Omega\cdot p]\!]!}\right\} + \frac{q^{\Omega}}{12}[\![\Omega\cdot p]\!]\cdot\min\left\{\frac{(\Omega\cdot p)}{2}, \frac{(\Omega\cdot p)^{[\![\Omega\cdot p]\!]}}{([\![\Omega\cdot p]\!]+1)!}\right\}$$

$$+q^{\Omega+[\![\Omega\cdot p]\!]}p^{-[\![\Omega\cdot p]\!]}\left\{\ln\sqrt{2\pi} + \frac{\ln([\![\Omega\cdot p]\!]+1)}{2}\right\}\cdot([\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!])\cdot\min\left\{\frac{\left(\frac{\Omega p^2}{q}\right)^{[\![\Omega\cdot p]\!]+1}}{([\![\Omega\cdot p]\!]+1)!}, \frac{\left(\frac{\Omega p^2}{q}\right)^{[\![\Omega\cdot q]\!]}}{[\![\Omega\cdot q]\!]!}\right\}$$

$$+q^{\Omega+[\![\Omega\cdot p]\!]}p^{-[\![\Omega\cdot p]\!]}\left(\ln([\![\Omega\cdot p]\!]+1)-1\right)\cdot([\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!])\cdot\min\left\{\frac{\left(\frac{\Omega p^2}{q}\right)^{[\![\Omega\cdot p]\!]+1}}{[\![\Omega\cdot p]\!]!}, \frac{\left(\frac{\Omega p^2}{q}\right)^{[\![\Omega\cdot q]\!]}}{([\![\Omega\cdot q]\!]-1)!}\right\}$$

$$+\frac{q^{\Omega+[\![\Omega\cdot p]\!]}p^{-[\![\Omega\cdot p]\!]}}{12}([\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!])\cdot\min\left\{\frac{\left(\frac{\Omega p^2}{q}\right)^{[\![\Omega\cdot p]\!]+1}}{([\![\Omega\cdot p]\!]+2)!}, \frac{\left(\frac{\Omega p^2}{q}\right)^{[\![\Omega\cdot q]\!]}}{([\![\Omega\cdot q]\!]+1)!}\right\}$$

$$+\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}\left\{\ln\sqrt{2\pi} + \frac{\ln([\![\Omega\cdot q]\!]+1)}{2}\right\}(\Omega-[\![\Omega\cdot q]\!])\cdot\min\left\{\frac{\left(\frac{p}{q}\right)^{[\![\Omega\cdot q]\!]+1}}{([\![\Omega\cdot q]\!]+1)!}, \frac{\left(\frac{p}{q}\right)^{\Omega}}{\Omega!}\right\}$$

$$+\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}\left(\ln([\![\Omega\cdot q]\!]+1)-1\right)\cdot(\Omega-[\![\Omega\cdot q]\!])\cdot\min\left\{\frac{\left(\frac{p}{q}\right)^{[\![\Omega\cdot q]\!]+1}}{[\![\Omega\cdot q]\!]!}, \frac{\left(\frac{p}{q}\right)^{\Omega}}{(\Omega-1)!}\right\}$$

$$+\frac{\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}}{12}(\Omega-[\![\Omega\cdot q]\!])\cdot\min\left\{\frac{\left(\frac{p}{q}\right)^{[\![\Omega\cdot q]\!]+1}}{([\![\Omega\cdot q]\!]+2)!}, \frac{\left(\frac{p}{q}\right)^{\Omega}}{(\Omega+1)!}\right\}$$

Adding up the upper bounds

$$\sum_{k=1}^{[\![\Omega\cdot p]\!]} q^{\Omega}\frac{\left(\dfrac{\Omega\cdot p}{q}\right)^{k}}{k!}\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln[\![\Omega\cdot p]\!]}{2}+\frac{1}{12}\right\}+\left(\ln[\![\Omega\cdot p]\!]-1\right)\cdot k\right\}+$$

$$\sum_{k=[\![\Omega\cdot p]\!]+1}^{[\![\Omega\cdot q]\!]} q^{\Omega}\Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{-[\![\Omega\cdot p]\!]}\frac{\left((\Omega\cdot q+1)\dfrac{p}{q}\right)^{k}}{k!}\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln[\![\Omega\cdot q]\!]}{2}+\frac{1}{12([\![\Omega\cdot p]\!]+1)}\right\}+\left(\ln[\![\Omega\cdot q]\!]-1\right)\cdot k\right\}$$

$$\sum_{k=[\![\Omega\cdot q]\!]+1}^{\Omega} \Omega^{[\![\Omega\cdot p]\!]}\cdot(\Omega\cdot q+1)^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}(\Omega\cdot p+1)^{-[\![\Omega\cdot q]\!]}\cdot q^{\Omega}\frac{\left(\dfrac{(\Omega\cdot p+1)\cdot p}{q}\right)^{k}}{k!}\cdot\left\{\left\{\ln\sqrt{2\pi}+\frac{\ln\Omega}{2}+\frac{1}{12([\![\Omega\cdot q]\!]+1)}\right\}+\left(\ln\Omega\right.\right.$$

$$< \left\{ \ln\sqrt{2\pi} + \frac{\ln\llbracket \Omega\cdot p\rrbracket}{2} + \frac{1}{12} \right\} q^{\Omega} \{ e^{\left(\frac{\Omega\cdot p}{q}\right)} \cdot \left(1 + \frac{\left(\frac{\Omega\cdot p}{q}\right)^{\llbracket \Omega\cdot p\rrbracket+1}}{(\llbracket \Omega\cdot p\rrbracket+1)!} \right) - 1 \}$$

$$+ q^{\Omega} \left(\ln\llbracket \Omega\cdot p\rrbracket - 1 \right) \{ e^{\left(\frac{\Omega\cdot p}{q}\right)} \cdot \left(\left(\frac{\Omega\cdot p}{q}\right) + \frac{\left(\frac{\Omega\cdot p}{q}\right)^{\llbracket \Omega\cdot p\rrbracket+1}}{\llbracket \Omega\cdot p\rrbracket!} \right) - \left(\frac{\Omega\cdot p}{q}\right) \}$$

$$+ q^{\Omega}\Omega^{\llbracket \Omega\cdot p\rrbracket} \cdot (\Omega\cdot q+1)^{-\llbracket \Omega\cdot p\rrbracket} \left\{ \ln\sqrt{2\pi} + \frac{\ln\llbracket \Omega\cdot q\rrbracket}{2} + \frac{1}{12(\llbracket \Omega\cdot p\rrbracket+1)} \right\}$$

$$\cdot \{ e^{\left((\Omega\cdot q+1)\frac{p}{q}\right)} \cdot \left(1 + \frac{\left((\Omega\cdot q+1)\frac{p}{q}\right)^{\llbracket \Omega\cdot q\rrbracket+1}}{(\llbracket \Omega\cdot q\rrbracket+1)!} \right) - 1 - \min\left\{ \left((\Omega\cdot q+1)\frac{p}{q}\right), \frac{\left((\Omega\cdot q+1)\frac{p}{q}\right)^{\llbracket \Omega\cdot p\rrbracket}}{(\llbracket \Omega\cdot p\rrbracket-1)!} \right\} \}$$

$$+ q^{\Omega}\Omega^{\llbracket \Omega\cdot p\rrbracket} \cdot (\Omega\cdot q+1)^{-\llbracket \Omega\cdot p\rrbracket} \left(\ln\llbracket \Omega\cdot q\rrbracket - 1 \right) \cdot$$

$$\{ e^{\left((\Omega\cdot q+1)\frac{p}{q}\right)} \cdot \left(\left((\Omega\cdot q+1)\frac{p}{q}\right) + \frac{\left((\Omega\cdot q+1)\frac{p}{q}\right)^{\llbracket \Omega\cdot q\rrbracket+1}}{\llbracket \Omega\cdot q\rrbracket!} \right) - \left((\Omega\cdot q+1)\frac{p}{q}\right) - \min\left\{ \left((\Omega\cdot q+1)\frac{p}{q}\right)^{2}, \frac{\left((\Omega\cdot q+1)\frac{p}{q}\right)^{\llbracket \Omega\cdot p\rrbracket}}{(\llbracket \Omega\cdot p\rrbracket-2)!} \right.$$

$$+ q^{\Omega}\Omega^{\llbracket \Omega\cdot p\rrbracket} \cdot (\Omega\cdot q+1)^{\llbracket \Omega\cdot q\rrbracket-\llbracket \Omega\cdot p\rrbracket} (\Omega\cdot p+1)^{-\llbracket \Omega\cdot q\rrbracket} \left\{ \ln\sqrt{2\pi} + \frac{\ln\Omega}{2} + \frac{1}{12(\llbracket \Omega\cdot q\rrbracket+1)} \right\}$$

$$\cdot \{ e^{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)} \cdot \left(1 + \frac{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)^{\Omega+1}}{(\Omega+1)!} \right) - 1 - \min\left\{ \left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right), \frac{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)^{\llbracket \Omega\cdot q\rrbracket}}{(\llbracket \Omega\cdot q\rrbracket-1)!} \right\} \}$$

$$+ q^{\Omega}\Omega^{\llbracket \Omega\cdot p\rrbracket} \cdot (\Omega\cdot q+1)^{\llbracket \Omega\cdot q\rrbracket-\llbracket \Omega\cdot p\rrbracket} (\Omega\cdot p+1)^{-\llbracket \Omega\cdot q\rrbracket} \left(\ln\Omega - 1 \right) \cdot$$

$$\cdot \{ e^{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)} \cdot \left(\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right) + \frac{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)^{\Omega+1}}{\Omega!} \right) - \left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right) - \min\left\{ \left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)^{2}, \frac{\left(\frac{(\Omega\cdot p+1)\cdot p}{q}\right)}{(\llbracket \Omega\cdot q\rrbracket-2)} \right.$$

We have computed lower and upper bounds for R(p) only. Switching p and q yields lower and upper bounds for R(q). We must now get bounds for the total entropy. Since the negative of R(p)+R(q) appears in the entropy, the lower bounds of R(p)+R(q) become upper bounds of entropy and the upper bounds of R(p)+R(q) become lower bounds.

$$\frac{S_\Omega(p)}{-k_B} < (p\cdot\ln p + q\cdot\ln q)\cdot\Omega + \ln((\Omega+1)!)$$

$$+e^{\Omega\cdot p}\cdot\left(\Omega\cdot p + \frac{(\Omega\cdot p)^{[\![\Omega\cdot p]\!]+1}}{[\![\Omega\cdot p]\!]!}\right) + e^{\Omega\cdot q}\cdot\left(\Omega\cdot q + \frac{(\Omega\cdot q)^{[\![\Omega\cdot q]\!]+1}}{[\![\Omega\cdot q]\!]!}\right) - \Omega$$

$$-q^\Omega \ln\sqrt{2\pi}\,[\![\Omega\cdot p]\!]\cdot\min\left\{(\Omega\cdot p), \frac{(\Omega\cdot p)^{[\![\Omega\cdot p]\!]}}{[\![\Omega\cdot p]\!]!}\right\} + \frac{q^\Omega}{12}[\![\Omega\cdot p]\!]\cdot\min\left\{\frac{(\Omega\cdot p)}{2}, \frac{(\Omega\cdot p)^{[\![\Omega\cdot p]\!]}}{([\![\Omega\cdot p]\!]+1)!}\right\}$$

$$-p^\Omega \ln\sqrt{2\pi}\,[\![\Omega\cdot q]\!]\cdot\min\left\{(\Omega\cdot q), \frac{(\Omega\cdot q)^{[\![\Omega\cdot q]\!]}}{[\![\Omega\cdot q]\!]!}\right\} + \frac{p^\Omega}{12}[\![\Omega\cdot q]\!]\cdot\min\left\{\frac{(\Omega\cdot q)}{2}, \frac{(\Omega\cdot q)^{[\![\Omega\cdot q]\!]}}{([\![\Omega\cdot q]\!]+1)!}\right\}$$

$$-q^{\Omega+\llbracket\Omega\cdot p\rrbracket}p^{-\llbracket\Omega\cdot p\rrbracket}\left\{\ln\sqrt{2\pi}+\frac{\ln(\llbracket\Omega\cdot p\rrbracket+1)}{2}\right\}\cdot(\llbracket\Omega\cdot q\rrbracket-\llbracket\Omega\cdot p\rrbracket)\cdot\min\left\{\frac{\left(\frac{\Omega p^2}{q}\right)^{\llbracket\Omega\cdot p\rrbracket+1}}{(\llbracket\Omega\cdot p\rrbracket+1)!},\frac{\left(\frac{\Omega p^2}{q}\right)^{\llbracket\Omega\cdot q\rrbracket}}{\llbracket\Omega\cdot q\rrbracket!}\right\}$$

$$-p^{\Omega+\llbracket\Omega\cdot q\rrbracket}q^{-\llbracket\Omega\cdot q\rrbracket}\left\{\ln\sqrt{2\pi}+\frac{\ln(\llbracket\Omega\cdot q\rrbracket+1)}{2}\right\}\cdot(\llbracket\Omega\cdot p\rrbracket-\llbracket\Omega\cdot q\rrbracket)\cdot\min\left\{\frac{\left(\frac{\Omega q^2}{p}\right)^{\llbracket\Omega\cdot q\rrbracket+1}}{(\llbracket\Omega\cdot q\rrbracket+1)!},\frac{\left(\frac{\Omega q^2}{p}\right)^{\llbracket\Omega\cdot p\rrbracket}}{\llbracket\Omega\cdot p\rrbracket!}\right\}$$

$$-q^{\Omega+\llbracket\Omega\cdot p\rrbracket}p^{-\llbracket\Omega\cdot p\rrbracket}\left(\ln(\llbracket\Omega\cdot p\rrbracket+1)-1\right)\cdot(\llbracket\Omega\cdot q\rrbracket-\llbracket\Omega\cdot p\rrbracket)\cdot\min\left\{\frac{\left(\frac{\Omega p^2}{q}\right)^{\llbracket\Omega\cdot p\rrbracket+1}}{\llbracket\Omega\cdot p\rrbracket!},\frac{\left(\frac{\Omega p^2}{q}\right)^{\llbracket\Omega\cdot q\rrbracket}}{(\llbracket\Omega\cdot q\rrbracket-1)!}\right\}$$

$$-p^{\Omega+\llbracket\Omega\cdot q\rrbracket}q^{-\llbracket\Omega\cdot q\rrbracket}\left(\ln(\llbracket\Omega\cdot q\rrbracket+1)-1\right)\cdot(\llbracket\Omega\cdot p\rrbracket-\llbracket\Omega\cdot q\rrbracket)\cdot\min\left\{\frac{\left(\frac{\Omega q^2}{p}\right)^{\llbracket\Omega\cdot q\rrbracket+1}}{\llbracket\Omega\cdot q\rrbracket!},\frac{\left(\frac{\Omega q^2}{p}\right)^{\llbracket\Omega\cdot p\rrbracket}}{(\llbracket\Omega\cdot p\rrbracket-1)!}\right\}$$

$$-\frac{q^{\Omega+\llbracket\Omega\cdot p\rrbracket}p^{-\llbracket\Omega\cdot p\rrbracket}}{12}(\llbracket\Omega\cdot q\rrbracket-\llbracket\Omega\cdot p\rrbracket)\cdot\min\left\{\frac{\left(\frac{\Omega p^2}{q}\right)^{\llbracket\Omega\cdot p\rrbracket+1}}{(\llbracket\Omega\cdot p\rrbracket+2)!},\frac{\left(\frac{\Omega p^2}{q}\right)^{\llbracket\Omega\cdot q\rrbracket}}{(\llbracket\Omega\cdot q\rrbracket+1)!}\right\}$$

$$-\frac{p^{\Omega+\llbracket\Omega\cdot q\rrbracket}q^{-\llbracket\Omega\cdot q\rrbracket}}{12}(\llbracket\Omega\cdot p\rrbracket-\llbracket\Omega\cdot q\rrbracket)\cdot\min\left\{\frac{\left(\frac{\Omega q^2}{p}\right)^{\llbracket\Omega\cdot q\rrbracket+1}}{(\llbracket\Omega\cdot q\rrbracket+2)!},\frac{\left(\frac{\Omega q^2}{p}\right)^{\llbracket\Omega\cdot p\rrbracket}}{(\llbracket\Omega\cdot p\rrbracket+1)!}\right\}$$

$$-\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}\left\{\ln\sqrt{2\pi}+\frac{\ln([\![\Omega\cdot q]\!]+1)}{2}\right\}(\Omega-[\![\Omega\cdot q]\!])\cdot\min\left\{\frac{\left(\frac{p}{q}\right)^{[\![\Omega\cdot q]\!]+1}}{([\![\Omega\cdot q]\!]+1)!},\frac{\left(\frac{p}{q}\right)^{\Omega}}{\Omega!}\right\}$$

$$-\Omega^{[\![\Omega\cdot p]\!]}q^{[\![\Omega\cdot p]\!]-[\![\Omega\cdot q]\!]}p^{\Omega+[\![\Omega\cdot q]\!]}\left\{\ln\sqrt{2\pi}+\frac{\ln([\![\Omega\cdot p]\!]+1)}{2}\right\}(\Omega-[\![\Omega\cdot p]\!])\cdot\min\left\{\frac{\left(\frac{q}{p}\right)^{[\![\Omega\cdot p]\!]+1}}{([\![\Omega\cdot p]\!]+1)!},\frac{\left(\frac{q}{p}\right)^{\Omega}}{\Omega!}\right\}$$

$$-\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}\left(\ln([\![\Omega\cdot q]\!]+1)-1\right)\cdot(\Omega-[\![\Omega\cdot q]\!])\cdot\min\left\{\frac{\left(\frac{p}{q}\right)^{[\![\Omega\cdot q]\!]+1}}{[\![\Omega\cdot q]\!]!},\frac{\left(\frac{p}{q}\right)^{\Omega}}{(\Omega-1)!}\right\}$$

$$-\Omega^{[\![\Omega\cdot p]\!]}q^{[\![\Omega\cdot p]\!]-[\![\Omega\cdot q]\!]}p^{\Omega+[\![\Omega\cdot q]\!]}\left(\ln([\![\Omega\cdot p]\!]+1)-1\right)\cdot(\Omega-[\![\Omega\cdot p]\!])\cdot\min\left\{\frac{\left(\frac{q}{p}\right)^{[\![\Omega\cdot p]\!]+1}}{[\![\Omega\cdot p]\!]!},\frac{\left(\frac{q}{p}\right)^{\Omega}}{(\Omega-1)!}\right\}$$

$$-\frac{\Omega^{[\![\Omega\cdot q]\!]}p^{[\![\Omega\cdot q]\!]-[\![\Omega\cdot p]\!]}q^{\Omega+[\![\Omega\cdot p]\!]}}{12}(\Omega-[\![\Omega\cdot q]\!])\cdot\min\left\{\frac{\left(\frac{p}{q}\right)^{[\![\Omega\cdot q]\!]+1}}{([\![\Omega\cdot q]\!]+2)!},\frac{\left(\frac{p}{q}\right)^{\Omega}}{(\Omega+1)!}\right\}$$

$$-\frac{\Omega^{[\![\Omega\cdot p]\!]}q^{[\![\Omega\cdot p]\!]-[\![\Omega\cdot q]\!]}p^{\Omega+[\![\Omega\cdot q]\!]}}{12}(\Omega-[\![\Omega\cdot p]\!])\cdot\min\left\{\frac{\left(\frac{q}{p}\right)^{[\![\Omega\cdot p]\!]+1}}{([\![\Omega\cdot p]\!]+2)!},\frac{\left(\frac{q}{p}\right)^{\Omega}}{(\Omega+1)!}\right\}$$

And we get the lower bounds on entropy

Tests on Maple by graphing show that the function $f(\Omega\cdot p)=\dfrac{\left((\Omega\cdot p)\frac{p}{q}\right)^{[\![\Omega\cdot p]\!]+1}}{([\![\Omega\cdot p]\!]+1)!}$ goes asymptotically towards 0 if $p\le\frac{1}{4}+\frac{1}{53}$ but shoots off to infinity if $p\ge\frac{1}{4}+\frac{1}{52}$ when plotted on a domain of [5,1000]. At $p=\frac{1}{4}+\frac{1}{53}$ $f(\Omega\cdot p)$ has a global maximum of around 0.068255 at $\Omega\cdot p\approx 1.29 \Leftrightarrow \Omega\approx 4.80$. At $p=\frac{1}{4}+\frac{1}{52}$ the graph shows a local maximum of around 0.068545 at $\Omega\cdot p\approx 1.3 \Leftrightarrow \Omega\approx 4.83$.

The maximum value of $S_\Omega(p)$ for any given Ω always occurs at $p=\frac{1}{2}$, increases indefinitely with Ω, and equals $S_\Omega(\frac{1}{2})=k_B\cdot\{\Omega\ln 2-2^{-\Omega}\sum_{k=0}^{\Omega}\binom{\Omega}{k}\ln\binom{\Omega}{k}\}$.

Computations on Maple show that

$$S_{20}(\frac{1}{2})\approx 2.2\cdot k_B$$
$$S_{120}(\frac{1}{2})\approx 3.11\cdot k_B\ .$$
$$S_{200}(\frac{1}{2})\approx 3.35\cdot k_B$$

Since $\forall\Omega\Rightarrow S_\Omega(0)=0=S_\Omega(1)$, the plot of $S_\Omega(p)$ versus p looks like an inverted bell that gets flatter and flatter at the top.

Example. Let $\Omega=\infty$. Can we create an infinite sequence of (nonzero) probabilities whose entropy limit is infinite? Let us choose 3 (mostly free) parameters, constrained only by $p,q,r\in(0,1)\ni pqr=(1-p)(1-q)(1-r)$. Let us index our infinitely many microstates by a triplet of positive integers (i,j,k), except for the last one. Let $p^i q^j r^k$ be the probabilities for $i,j,k\in\mathbb{N}$. So $\sum_{k=1}^{\infty}\sum_{j=1}^{\infty}\sum_{i=1}^{\infty}p^i q^j r^k=\frac{p}{1-p}\frac{q}{1-q}\frac{r}{1-r}=1$. The normalized entropy equals

$$\frac{S}{k_B}=\sum_{k=1}^{\infty}\sum_{j=1}^{\infty}\sum_{i=1}^{\infty}p^i q^j r^k\cdot\ln(p^i q^j r^k)=$$
$$-(\ln p)\frac{1}{(1-p)^2}\frac{q}{1-q}\frac{r}{1-r}-(\ln q)\frac{1}{(1-q)^2}\frac{p}{1-p}\frac{r}{1-r}-(\ln r)\frac{1}{(1-r)^2}\frac{p}{1-p}\frac{q}{1-q}$$
$$=-\left(\frac{1}{p}\frac{\ln p}{1-p}+\frac{1}{q}\frac{\ln q}{1-q}+\frac{1}{r}\frac{\ln r}{1-r}\right)\frac{p}{1-p}\frac{q}{1-q}\frac{r}{1-r}=-\left(\frac{1}{p}\frac{\ln p}{1-p}+\frac{1}{q}\frac{\ln q}{1-q}+\frac{1}{r}\frac{\ln r}{1-r}\right)$$

Example. Let $p=\frac{2}{3},q=\frac{5}{7},r=\frac{1}{6}$, which corresponds to $n=3$ in the next example. Then $\frac{S}{k_B}=-\left(\frac{9}{2}\ln\frac{2}{3}+\frac{49}{10}\ln\frac{5}{7}+\frac{36}{5}\ln\frac{1}{6}\right)\approx 16.373975$. We chose these particular values for *p, q,* and *r* by substituting *n*=3 into the following generalization.

Generalize the previous idea from n=3 to arbitrary n numbers, $\{p_{k,n}\}_{k=1}^{n}$, between 0 and 1, such that $\sum_i \prod_{k=1}^{n} p_{k,n}^{i_k} = \prod_{k=1}^{n} \frac{p_{k,n}}{1-p_{k,n}} = 1$ always holds, then as in the previous example: $\frac{S}{k_B} = -\sum_{k=1}^{n} \frac{\ln p_{k,n}}{p_{k,n}(1-p_{k,n})}$.

Now we want to choose the $\{p_{k,n}\}_{k=1}^{n}$ such that $\lim_{n\to\infty} \frac{S}{k_B}$ equals infinity. We obtain this sequence by choosing all but the n-th subsequence to satisfy

$$\forall k \in [n-1] \Rightarrow \frac{p_{k,n}}{1-p_{k,n}} = \frac{k^2+1}{k^2+k+1} \Leftrightarrow p_{k,n} = \frac{\frac{k^2+1}{k^2+k+1}}{1+\frac{k^2+1}{k^2+k+1}} = \frac{k^2+1}{2k^2+k+2}$$

And then choose the n-th subsequence so that the sum of all infinitely many probabilities equals 1.

$$\frac{p_{n,n}}{1-p_{n,n}} = \prod_{k=1}^{n-1} \frac{k^2+k+1}{k^2+1} \Rightarrow p_{n,n} = \frac{\prod_{k=1}^{n-1} \frac{k^2+k+1}{k^2+1}}{1+\prod_{k=1}^{n-1} \frac{k^2+k+1}{k^2+1}}$$

Then we get

$$\frac{S}{k_B} = -\sum_{k=1}^{n-1} \frac{\ln\left(\frac{k^2+1}{2k^2+k+2}\right)}{\frac{k^2+1}{2k^2+k+2}(1-\frac{k^2+1}{2k^2+k+2})} - \frac{\ln(p_{n,n})}{p_{n,n}(1-p_{n,n})}$$

$$= -\sum_{k=1}^{n-1} \frac{(2k^2+k+2)^2}{(k^2+1)} \frac{\ln\left(\frac{k^2+1}{2k^2+k+2}\right)}{(k^2+k+1)} - \frac{\ln(p_{n,n})}{p_{n,n}(1-p_{n,n})}$$

Lemma. The reduced entropy is asymptotic to $n \cdot 4\ln 2$, i.e.

$$\frac{S}{k_B} \sim n \cdot 4\ln 2 \text{ as } n \to \infty.$$

Proof. Experiments on Java suggest this lemma is true.

Lemma. $\lim_{n\to\infty} p_{n,n} = 1$. More specifically, $p_{n,n} \to 1^-$

Proof. Define $x_n \equiv \prod_{k=1}^{n} \frac{k^2+k+1}{k^2+1}$. Then $x_n = \prod_{k=1}^{n}\left(1+\frac{k}{k^2+1}\right) = 1+\sum_{k=1}^{n} \frac{k}{k^2+1} + \cdots$ where $\cdots$ stands for a sum of positive numbers. For all $k \ge 1$ implies $k^2+1 \le 2k^2$. Hence

$\sum_{k=1}^{n}\frac{k}{k^2+1} > \sum_{k=1}^{n}\frac{k}{2k^2} = \frac{1}{2}\sum_{k=1}^{n}\frac{1}{k}$, which is half the harmonic series, which diverges. Hence $\lim_{n\to\infty} x_n = \infty$. Therefore $\lim_{n\to\infty} p_{n,n} = \lim_{n\to\infty}\frac{x_{n-1}}{1+x_{n-1}} = \lim_{x\to\infty}\frac{x}{1+x} = 1$.

Q.E.D.

Lemma. $\lim_{n\to\infty}\frac{\ln(p_{n,n})}{p_{n,n}(1-p_{n,n})} = \frac{1}{1}\lim_{n\to\infty}\frac{\ln(p_{n,n})}{(1-p_{n,n})} = \lim_{x\to 1^-}\frac{\ln(x)}{(1-x)} = \lim_{x\to 1^-}\frac{x^{-1}}{-1} = -1$

Q.E.D.

Corollary. $\lim_{n\to\infty}\frac{1}{n}\frac{\ln(p_{n,n})}{p_{n,n}(1-p_{n,n})} = 0$.

So, the last term contributes nothing to our conjectured asymptotic formula.

Examine the formula for the first n-1 terms in the summation for the reduced entropy.

$$-\sum_{k=1}^{n-1}\frac{\ln\left(\frac{k^2+1}{2k^2+k+2}\right)}{\frac{k^2+1}{2k^2+k+2}(1-\frac{k^2+1}{2k^2+k+2})} = -\sum_{k=1}^{n-1}\frac{(2k^2+k+2)^2\ln\left(\frac{k^2+1}{2k^2+k+2}\right)}{(k^2+1)((2k^2+k+2)-(k^2+1))}$$

$$= \sum_{k=1}^{n-1}\frac{(2k^2+k+2)^2\ln\left(\frac{2k^2+k+2}{k^2+1}\right)}{(k^2+1)(k^2+k+1)} = \ln\prod_{k=1}^{n-1}\left(\frac{2k^2+k+2}{k^2+1}\right)^{\frac{(2k^2+k+2)^2}{(k^2+1)(k^2+k+1)}}$$

$$= \ln\prod_{k=1}^{n-1}\left(2\cdot\frac{k^2+k/2+1}{k^2+1}\right)^{4\cdot\frac{(k^2+k/2+1)^2}{(k^2+1)(k^2+k+1)}} = \ln\{2^{4\cdot\sum_{k=1}^{n-1}\frac{(k^2+k/2+1)^2}{(k^2+1)(k^2+k+1)}}\left\{\prod_{k=1}^{n-1}\left(\frac{k^2+k/2+1}{k^2+1}\right)^{\frac{(k^2+k/2+1)^2}{(k^2+1)(k^2+k+1)}}\right\}^4\}$$

Compute

$$\lim_{n\to\infty}\frac{1}{n}\sum_{k=1}^{n-1}\frac{(k^2+k/2+1)^2}{(k^2+1)\cdot(k^2+k+1)} = \lim_{n\to\infty}\frac{1}{n}\sum_{k=1}^{n-1}\frac{k^4+k^3+(9/4)k^2+k+1}{k^4+k^3+2k^2+k+1}$$

$$= \lim_{n\to\infty}\frac{1}{n}\sum_{k=1}^{n-1}\{1+\frac{1}{4}\frac{k^2}{k^4+k^3+2k^2+k+1}\} \le \lim_{n\to\infty}\frac{1}{n}\{n-1+\frac{1}{4}\sum_{k=1}^{n-1}\frac{k^2}{k^4}\} \le \lim_{n\to\infty}\{1-\frac{1}{n}+\frac{1}{4n}\sum_{k=1}^{\infty}\frac{1}{k^2}\}$$

$$= 1-\lim_{n\to\infty}\frac{1}{n}\frac{\pi^2}{24} = 1$$

We need to bound this summation from below for large *n*.

Definition. For any real-valued constant *p*, let $O(n^p)$ denote any function $f(n)$ of n such that there exists a positive constants $M, N > 0$ such that $\forall n > N \Rightarrow |f(n)| \le M\cdot n^p$.

Then

$$\frac{1}{n}\sum_{k=1}^{n-1}\frac{k^4+k^3+(9/4)k^2+k+1}{k^4+k^3+2k^2+k+1}=\frac{1}{n}\sum_{k=1}^{n-1}\{1+\frac{1}{4}\frac{k^2}{k^4+k^3+2k^2+k+1}\}$$

$$=1-\frac{1}{n}+\frac{1}{4n}\sum_{k=1}^{n-1}\frac{k^2}{k^4+k^3+2k^2+k+1}$$

$$>1-\frac{1}{n}+\frac{1}{4n}\sum_{k=1}^{n-1}\frac{k^2}{(n-1)^4+(n-1)^3+2(n-1)^2+(n-1)+1}$$

$$=1-\frac{1}{n}+\frac{1}{4n}\cdot\frac{\sum_{k=1}^{n-1}k^2}{n^4+O(n^3)}=1-\frac{1}{n}+\frac{O(n^3)}{4n^5+O(n^4)}$$

Therefore $\lim_{n\to\infty}\frac{1}{n}\sum_{k=1}^{n-1}\frac{k^4+k^3+(9/4)k^2+k+1}{k^4+k^3+2k^2+k+1}\geq\lim_{n\to\infty}\{1-\frac{1}{n}+\frac{O(n^3)}{4n^5+O(n^4)}\}=1$.

Combined with the preceding bound from above we conclude

$$\lim_{n\to\infty}\frac{1}{n}\sum_{k=1}^{n-1}\frac{k^4+k^3+(9/4)k^2+k+1}{k^4+k^3+2k^2+k+1}=1$$

So $\ln 2^{4\cdot\sum_{k=1}^{n-1}\frac{(k^2+k/2+1)^2}{(k^2+1)(k^2+k+1)}}$ is asymptotic to $\ln 2^{4n}=n\cdot 4\ln 2$ as $n\to\infty$.

Now examine the other term in the logarithm above

$$\ln\prod_{k=1}^{n-1}\left(\frac{k^2+k/2+1}{k^2+1}\right)^{\frac{(k^2+k/2+1)^2}{(k^2+1)(k^2+k+1)}}=\sum_{k=1}^{n-1}\left(1+\frac{1}{4}\frac{k^2}{k^4+k^3+2k^2+k+1}\right)\cdot\ln\left(1+\frac{1}{2}\frac{k}{k^2+1}\right)$$

Now, we want to see if this summation is asymptotic to a constant times *n*. So we divide by *n*. As long as we can prove that an upper bound of (1/*n*) times this summation has a limit equal to 0, since the product is clearly bounded below by zero, since it is the logarithm of a product of terms all greater than 1, we will not have to find a separate bound from below.

Let *y* denote $\frac{1}{2}\frac{k}{k^2+1}$. So $\forall k\in\mathbb{N}\Rightarrow 0<y\leq\frac{1}{4}$. By comparing termwise the Taylor series expansion of the natural logarithm with that of the geometric series, it is easy to see that $|y|<1\Rightarrow\ln(1+y)\leq\frac{y}{1-y}=\frac{k}{2k^2-k+2}<\frac{k}{2k^2-k}=\frac{1}{2k-1}$.

Hence

$$\sum_{k=1}^{n-1}\left(1+\frac{1}{4}\frac{k^2}{k^4+k^3+2k^2+k+1}\right)\cdot\ln\left(1+\frac{1}{2}\frac{k}{k^2+1}\right)$$

$$<\sum_{k=1}^{n-1}\left(1+\frac{1}{4}\frac{k^2}{k^4+k^3+2k^2+k+1}\right)\cdot\frac{1}{2k-1}<\sum_{k=1}^{n-1}\left(1+\frac{1}{4}\frac{k^2}{k^4}\right)\cdot\frac{1}{2k-1}=\sum_{k=1}^{n-1}\left(\frac{1}{2k-1}+\frac{1}{4}\frac{1}{k^2}\frac{1}{2k-1}\right)$$

Dividing by *n* and taking the limit as $n \to \infty$, we easily see we get 0, as the first summation is the sum of the odd terms in the harmonic series and the second term is a sum of $O(k^{-3})$ terms from *k* to *n*-1, hence the summation is $O(n^{-2})$.
Q.E.D.

So, yes: the system with these countably infinitely many probabilities will be unbounded

$$\left\{\prod_{k=1}^{n} p_{k,n}^{i_k}\right\}_{(i_1,\ldots,i_n)\in\mathbb{N}^n} = \left\{\left(\frac{\prod_{k=1}^{n-1}\frac{k^2+k+1}{k^2+1}}{1+\prod_{k=1}^{n-1}\frac{k^2+k+1}{k^2+1}}\right)^{i_n}\cdot\prod_{k=1}^{n-1}\left(\frac{k^2+1}{2k^2+k+2}\right)^{i_k}\right\}_{(i_1,\ldots,i_n)\in\mathbb{N}^n}$$

Example. Energy to ride my Omega Stores electric-assist tricycle.

Nt = Newton J = joule KW= kilowatt

The mass of myself and my tricycle has been measured at the Columbus Recovery Complex in Columbus, NJ many times. About 325 pounds = 1445 Nt = 1445 J/m
Coefficient of rolling for "production bicycle tires" is about 0.0022 to 0.005 from http://en.wikipedia.org/wiki/Rolling_resistance. Multiply by 3 tires to account for a tricycle. The energy to push myself and the tricycle 1 meter equals

(1445 J/m)*(0.0022)*3 = 9.537 J
to (1445 J/m)*(0.005)*3 = 21.675 J

So the energy to go 10,000 miles ranges from
(9.537 J/m)*(10^3 m/km)*(10^4 miles)*(1.601 km/mile) = 1.5268737*10^8 J
to (21.675 J/m)*(10^3 m/km)*(10^4 miles)*(1.601 km/mile) = 3.4701675*10^8 J

My electricity from Veridian all-green energy costs about 12.3956 cents per KW*hr, or

$3.4425 \cdot 10^{-6}$ cents/J

So electric cost for me to trike 10,000 miles *if my trike were 100% efficient, which we know is thermodynamically impossible*, equals

($3.4425 \cdot 10^{-6}$ cents/J) * 1.5268737*10^8 J = 5.256262712*10^2 cents
= \$5.26 to \$11.95

How much electricity *do* I spend on the trike? Unfortunately, there is not a separate coulombmeter or joule-ometer on the charger for my trike, for counting total accumulated energy. However, I can estimate how many joules the trike consumed: take the amount of electricity I consumed in the annual period 2011 August 2 to 2012 November 2 from my utility bill: 4954 kW*hr. This is roughly the period from when I first got the trike until now. We'll say this was 15 months. Scale this value down to a year: 3963.2 kW*hr

Now, add up the electricity I consumed *before* I bought the trike. For the period 2011 February 3 to 2011 August 2 this value was 2317 kW*hr. We'll say this was 6 months. Scale up to a year: 4634 kW*hr.

Unfortunately, if we compare these two values: 3963.2 kW*hr < 4634 kW*hr they show that I used less per annum *after* I bought the trike than before it. Obviously, my trike does *not* generate "negative entropy": I had simply overcompensated by reducing electricity consumption during my triking days in various ways.

Nonetheless, the entropy difference per annum *can* be calculated :

$$S = \frac{(4634 - 3963.2)\text{kW}\cdot\text{hr}}{T \approx 290\text{K}} \cdot \frac{3.6\cdot 10^6\,\text{J}}{\text{kW}\cdot\text{hr}} = \frac{8.33\cdot 10^6\,\text{J}}{\text{K}}$$

From this we can back calculate what the sum of the discrete probabilities and their logarithms must be

$$\frac{S}{k_B} = \frac{8.33\cdot 10^6\,\text{J/K}}{1.38062\cdot 10^{-23}\ \text{J/K}} \approx 6.03\cdot 10^{29}$$

Therefore, if everything in my house that consumes electricity, including the trike, are taken as a system comprised of countably many *discrete* thermal microstates, each of probability p_k, then $6.03\cdot 10^{29} \approx -\sum_k \ln(p_k^{p_k})$. From this we get a lower bound on the number of such microstates. As explained above, since the *maximum* value any such probability/log-probability sum can have is $\ln\Omega$ for Ω microstates, this implies

$$6.03\cdot 10^{29} \approx -\sum_{k=1}^{\Omega} \ln(p_k^{p_k}) \le \ln\Omega \Leftrightarrow \Omega \ge e^{6.03\cdot 10^{29}}$$

For a continuum of microstates we have

$$\frac{1}{V}\int \psi^*\psi \cdot \ln(\psi^*\psi)\cdot dV \approx 6.03\cdot 10^{29}$$

where V is the volume of the system containing everything in my house that consumes electricity.

Example. Susan Schindler, a vegan trucker for FeatherSuTransport, drives a class A truck for many trips along the east coast, between Virginia and Maine. Her truck weighs 30,000 lbs. The legal maximum limit on gross weight (truck + load) is 80,000 lbs. She typically hauls up to 50,000 lbs, usually shingles or metal pipe, for a combined weight of 80,000 lbs. The coefficient of friction for a truck tire is 0.0045 to 0.0080. So for an 18-wheel truck that's a coefficient of 0.081 to 0.144. That's a horizontal force ranging from

(80,000 lbs)*(0.081) = 6480 lbs = 28824 Nt = 28824 J/m
to
(80,000 lbs)*(0.144) = 11520 lbs = 51243 Nt = 51243 J/m

Susan drives an average of 2500 miles/week = 130,000 miles/year = 208,127 km/year
So Susan expends from (28,824,000 J/km)*(208,127 km/year) = 5,999,052,648,000 J/year to (51,243,000 J/km)*(208,127 km/year) = 10,665,051,861,000 J/year. Or $6.0\cdot 10^{12}$ to $11\cdot 10^{12}$ J/yr.

Susan's "rocket", as she calls her truck, gets about 7 miles per gallon of diesel. Hence, she consumes (130,000 miles/year)/(7 miles/gal) = 18571 gal/year. At $4.15/gal, this costs her $77,071/year in fuel alone.

Petrodiesel has carbon chains between 8 and 21 carbon atoms per molecule. The general formula for a fully saturated hydrocarbon is C_nH_{2n+2}. So we may assume petrodiesel varies between the extremes of being all C_8H_{18} and $C_{21}H_{44}$. From the stoichiometric equation:

$$2 \cdot C_nH_{2n+2} + (3n+1) \cdot O_2 \rightarrow 2n \cdot CO_2 + 2(n+1) \cdot H_2O$$

we calculate the change in the numbers of each type of bond

{2n-2 C-C, 4n+4 C-H, 3n+1 O-O bonds} $\rightarrow$ {4n C-O, 4n+4 O-H bonds}

and the change in potential energy of bond formation
{4n*(-360kJ/mol)+(4n+4)*(-366kJ/mol)} –
{(3n+1)*(-146 kJ/mol) + (4n+4)*(-413 kJ/mol) + (2n-2)*(-348 kJ/mol)}
= (-118*n –362) kJ/mol
which ranges from –1306 kJ/mol when n=8 to –2840 kJ/mol when n=21.

Remember: a mole here means a mole of $2 \cdot C_nH_{2n+2}$ which weighs 2n*(12.011)+2*(2n+2)*(1.00794) grams = 28.05376*n+4.03176 grams, which ranges from 228 grams when n=8 to 593 grams when n=21. So the energy density of petrodiesel ranges from 1306 kJ/228 g = 5728 J/g to 2840 kJ/593g = 4789 J/g.

The density of petrodiesel is 832 g/liter. So Susan burns between
(832 g/liter)(4789 J/g)(18571 gal/yr)(3.785 liter/gal) = $2.8 \cdot 10^{11}$ J/yr
and (832 g/liter)(5728 J/g)(18571 gal/yr)(3.785 liter/gal) = $3.4 \cdot 10^{11}$ J/yr

The wikipedia link for petrodiesel says petrodiesel has an energy density of 35.86 megajoules/liter = 43101 J/g. Using the wikipedia value for the energy density of petrodiesel, rather than computing the energy density from fundamental quantities,

$3.586 \cdot 10^7$

Susan burns
($3.586 \cdot 10^7$ J/liter)*(18571 gal/yr)*(3.785 liter/gal) = $2.52 \cdot 10^{12}$ J/yr

$2.52 \cdot 10^{12}$

J/yr This value is closer to, but still less than by at least a factor of 3, the value obtained above from the coefficient of friction of truck tires.

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