The 2nd Law of Thermodynamics – a paradox-free reformulation

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Abstract:

Entropy has been misunderstood because it is a redundant concept that lacks explanatory power and is based on a partly inadequate theory.

The 2nd Law of thermodynamics should simply be "energy disperses". This Law is not fundamental. Instead it is a corollary of the 1st Law and the definition of energy as that which "puts in motion".

The directionality of the 2nd Law (arrow of time) is not due to the statistical availability of certain states more than others. Rather, fluctuations out of equilibrium are self-limiting (negative feedback).

Contrary to the previous consensus, reversibility and retrace-ability are not possible in our quantum universe due both to quantum uncertainty and the wave-function materialization (collapse).

Introduction:

1. **The 2nd Law of thermodynamics has been poorly understood.** The most common interpretation of the phenomenon is Boltzmann's that defines entropy as the measure of the number of possible microscopic arrangements or states of individual atoms and molecules of a system that comply with the macroscopic condition of the system. The main issues of this definition are:
    a. Macrostate is poorly defined. Bulk measures such as PVTN are not exhaustive and are simply **ASSUMED** uniform. This excludes dynamic systems and is impossible to confirm. Polarity, magnetism, gravity are just a few characteristics that complicate the model making it unusable.
    b. The number of microstates conforming to a macrostate should be infinite in classical mechanics. Recognizing this problem, Boltzmann used an **AD-HOC** quantization method.
    c. All microstates IN EQUILIBRIUM are simply **POSTULATED** equally probable.
    d. When the 1st Law is about energy conservation and the 3rd Law about the lowest possible [kinetic] energy, the 2nd Law should also be about energy. Not entropy. There is no reason to extend this Law of thermodynamics to arrangements of coins, cards, dice, marbles, etc.
    e. Boltzmann's formula ($S = k_B \log W (\ln \Omega)$) is not intuitive and must be approximated as calculations are impossible.
    f. Loschmidt's paradox – the idea that microscopic reversibility is incompatible with macroscopic irreversibility - has never been resolved.
    g. Zermelo's recurrence paradox (using Poincare Recurrence Theorem) shows that the 2nd Law must be absolute, not statistical.
    h. In this model, the arrow of time is just a probabilistic outcome of a system. However, there is an offsetting infinite number of instances, making the arrow of time universally uncertain ($\infty * (1/\infty)$) opening the door to speculations like the Boltzmann Brain.
    i. The problem of low-entropy origin
    j. Entropy itself is probably not fundamental to the 2nd Law and thermodynamics in general.
2. **Other definitions are also inadequate.**
    a. *Clausius' formula* for change in entropy, $\Delta S = \Delta Q / T$, applies to heat transfer only, therefore it does not fully describe the phenomenon.
    b. Definition: *"Entropy is a measure of disorder".* If cream and coffee are initially separated, that is supposed to be *low entropy and higher order* than after mixing. Yet oil floating on water is *high entropy and higher order* while thoroughly mixed oil and water is *low entropy and lower order*. This is the opposite of cream and coffee. The supporting argument is that oil forces water molecules into a highly ordered configuration when oil and water are thoroughly mixed and therefore separate oil and water make a more disordered configuration. Yet order and disorder are elusive concepts. One can use a

different criteria, for instance the count of adjacent dissimilar particles. And by this criteria, separate oil and water is the more ordered state.

  c. Definition: *"Entropy is the energy of a closed system that is unavailable to do work".* This definition might work but it is unnecessarily complicated because it must count all energy types. Furthermore, most often we care about the energy *available (not unavailable)* to do work. Note, the "not available to do work" definition equates entropy with energy. This is important and will be addressed later. The link between Boltzmann's formula and 'energy available to do work' is at best tenuous.

3. **"Information entropy" was erroneously introduced by Claude Shannon** at Von Neumann's suggestion: "[because] *nobody knows what entropy really is, so in a debate you will always have the advantage*". Shannon incorrectly conflated data transmission (his actual research target) with information. Although there is a perpetual "information entropy" increase, meaning information can only degrade over time, there is no corresponding conservation of information (as quantum mechanics shows), no zero Kelvin for information and no multiple forms of information like the multiple forms of energy. For these reasons, information theory should play no role in any aspect of the 2nd Law of thermodynamics.

Methods of research:

The following proposed model simplifies and reformulates the 2nd Law eliminating the troubled concept of entropy. The proposed 2nd Law is applicable to all forms of energy in all settings.

4. **To understand the 2nd Law of thermodynamics we must** show and prove the flaws of the entropy concept. We then must follow by reanalyzing the 2nd Law fundamentals at the particle level and reformulate this law. 'Energy' is a human concept that may or may not align perfectly with reality since nature does not provide that label and definition. As such, the concept was hotly debated when first adopted and it remains tentative like everything else in science. For the purpose of this analysis we will assume 'energy' is a fundamental concept and that the 1st Law of thermodynamics (conservation of energy) is true. We will first focus on kinetic energy transfers in thermodynamic systems since the laws under consideration are specific to thermodynamics and the 1st Law is about energy. **The essence of the 2nd Law is directionality towards equilibrium**, so we will consider an isolated system in equilibrium and analyze if and how it can or cannot fluctuate out of that state. This paper explains and provides proof for why this 2nd Law is necessarily unidirectional despite the underlying assumptions not being directional.

Research itself, discussion:

5. **How micro-level improbabilities cause macro-level impossibilities**. To understand the 2nd law, we must first build a simplified thermodynamic model *(Fig 1)* in which energy is only transferred through conduction. We will ignore for now radiation, convection, chemical reactions, nuclear decay, and all other energy transfers besides kinetic energy transfers from one particle to another through elastic collisions.

   Assumptions:

   a. Isolated system composed of Identical Molecules of gas (first approximation)
   b. Consider only kinetic energy (ignore other energy transfers)
   c. Elastic collisions only (excludes particles breakdowns at extreme temperatures and intermolecular forces like van der Waals)
   d. Linear motion (external forces too small or balance out)
   e. Constant speed between collisions
   f. Spherical particle (second approximation)
   g. Chose coordinates so that the higher energy (HiE) particle (P 1) has only an x-axis component with speed Vx which is the x-axis relative velocity of particle HiE to particle LoE (P 2)
   h. Thus V1 = V1x; V1y = V1z = 0; V2x = 0. This can be done because the common speed of the system (V2x) is irrelevant to energy transfers between its component particles (P1 and P2).
   i. Rotate the system around the x-axis so that V2z = 0 and V2 = V2y. Thus, V1 (=V1x) and V2 (=V2y)

j. Therefore, before the collision, V1 and V2 are perpendicular and |V1x| ≥ |V2y| (by convention)

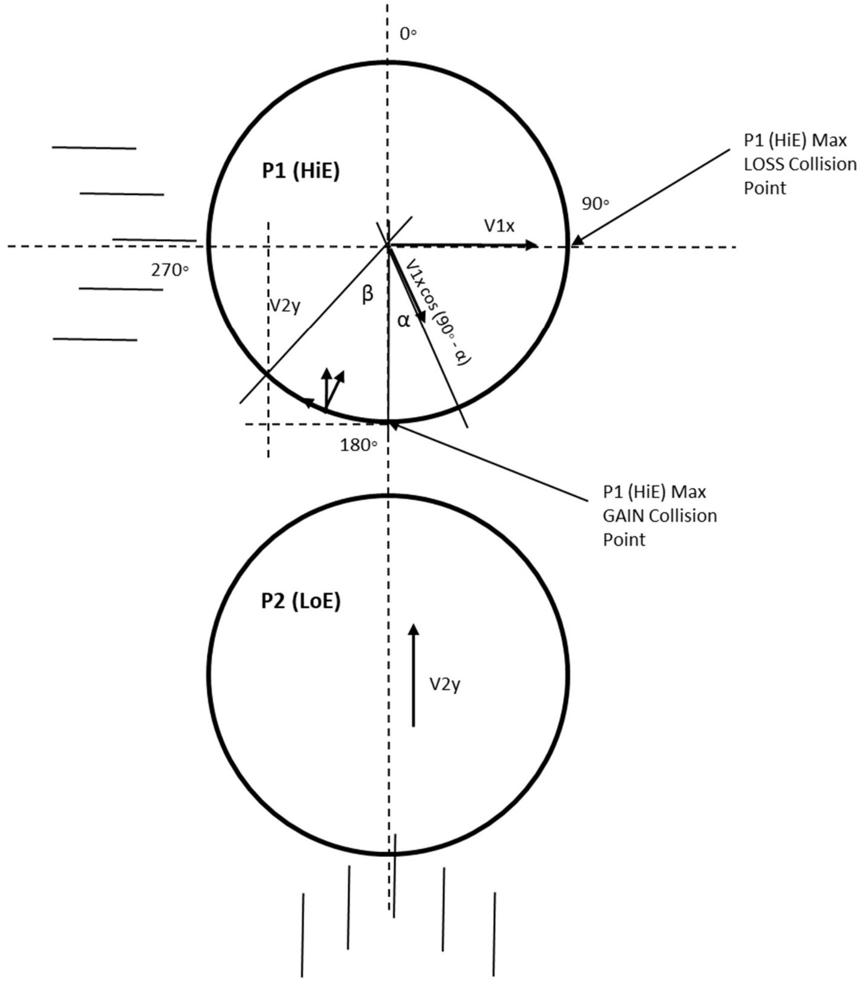

Figure 1

Results (Elastic Collision Model):

a. Considering *(Fig 1)*, no collision is possible between 270⁰ and 0⁰
b. P1 loses energy on any collision between 0⁰ and 90⁰
c. When colliding, the particles have a tangential momentum which is conserved and a perpendicular momentum which simply transfers from one particle to the other given identical particles.
d. Between 90⁰ and 180⁰ , the perpendicular component of V1x is V1x cos(90⁰ - α) and that of the V2y is V2y sin(90⁰ - α)
e. In this range, P1 loses energy if V1x/V2y > tan (90⁰ - α)
f. At the boundaries, if V1x >> V2y, then α -> 0⁰ and if V2y -> V1x (cannot be higher as assumed), then α -> 45⁰
g. Between 180⁰ and 270⁰, P1 always gains energy from the collision provided the two particles meet. This is only possible if V2y is above a minimum
h. Therefore, the collision is possible from 180⁰ to 180⁰ + β only if:
i. Sin β = V1x t / R
j. Cos β = (R – V2y t) / R
k. V2y > V1x (1-cos β) / sin β
l. Thus, if V1x >> V2y, then β -> 0⁰ and if V2y -> V1x, then β -> 90⁰

Conclusions (Elastic Collision Model):

a. Kinetic energy transfers in isolated gas systems are limited by negative feedback – the higher the energy of P1 vs P2, the lower the probability it will gain even more and the higher the probability it will lose energy *(Fig 2)*. This is consistent with the Maxwell-Boltzmann distribution of kinetic energies in a gas.

Particle-level probabilities translate into macro-level certainties including the **impossibility of out of equilibrium energy-carrying fluctuations**.

b. **Numerical table**:

V1x/V2y	atan(90° - α) (rad)	(90° - α) (°)	α at no energy exchanged	β max (goalseek V1x/V2y) (°)	β max (rad)	(1-cos β) / sin β	V1x/V2y = sin β / (1-cos β)	α + β (°) = P(P1 gains from P2)	180 - α (°) = P(P2 gains from P1)	P(P1 gains) from collision	% Avg Energy gain (P1 from P2)
1	0.79	45	45	90	1.6	1.00	1	135	135	50%	25%
2	1.11	63	27	53	0.9	0.50	2	80	153	34%	6%
3	1.25	72	18	37	0.6	0.33	3	55	162	26%	3%
4	1.33	76	14	28	0.5	0.25	4	42	166	20%	2%
5	1.37	79	11	23	0.4	0.20	5	34	169	17%	1%
6	1.41	81	9	19	0.3	0.17	6	28	171	14%	1%
7	1.43	82	8	16	0.3	0.14	7	24	172	12%	1%
8	1.45	83	7	14	0.2	0.13	8	21	173	11%	0%
9	1.46	84	6	13	0.2	0.11	9	19	174	10%	0%
10	1.47	84	6	11	0.2	0.10	10	17	174	9%	0%
100	1.56	89	0.6	1	0.0	0.01	100	2	179	1%	0%

Figure 2

c. Therefore, if V1x = V2y, P1 will gain energy from P2 in the interval α + β = 135° and will lose energy in the equal size interval (180° - α)

d. The higher V1x / V2y, the lower the probability P1 further gains energy from P2 (down to 10% if V1x = 10 x V2y, and to 1% if V1x = 100 x V2y)

e. Energy transferred from P2 to P1 is zero at 180° - α and at 180° + β with a peak equal to $mV2y^2$ at 180°. Therefore, with a linear approximation, the expected energy transferred in that interval is $mV2y^2/4$

    I. Thus, P1 can gain 25% of its energy with a 50% probability when V1x = V2y and only 6% with a 34% probability when V1x = 2 * V2y

    II. To gain the same 25% as above, more than four favorable collisions are required instead of one, each with at most 34% probability for a combined 1% probability (34%^4). Therefore, gaining more energy becomes extremely unlikely as V1x / V2y increases

    III. The Maxwell-Boltzmann distribution in an isolated system at equilibrium is necessarily a direct outcome of the elastic collision model *(Fig 3)*

        i. The probability of a particle exceeding twice the average speed is very low as calculated above. An order of magnitude or higher than the average speed is statistically impossible.

        ii. Asymmetrical distribution: N times the average speed is much less probable than 1/N the average speed. As calculated, speed gain is incremental with lower and lower probabilities while speed loss can occur in a single collision

        iii. Probability of close to zero speed is almost nil as only a collision near the 180° point can reduce the speed of particle P2 to almost zero.

        iv. There's a central peak of speed probabilities with particles both slower and faster being less and less probable the further they are from this peak.

        v. With the right assumptions, the elastic collision model should yield the Maxwell-Boltzmann distribution.

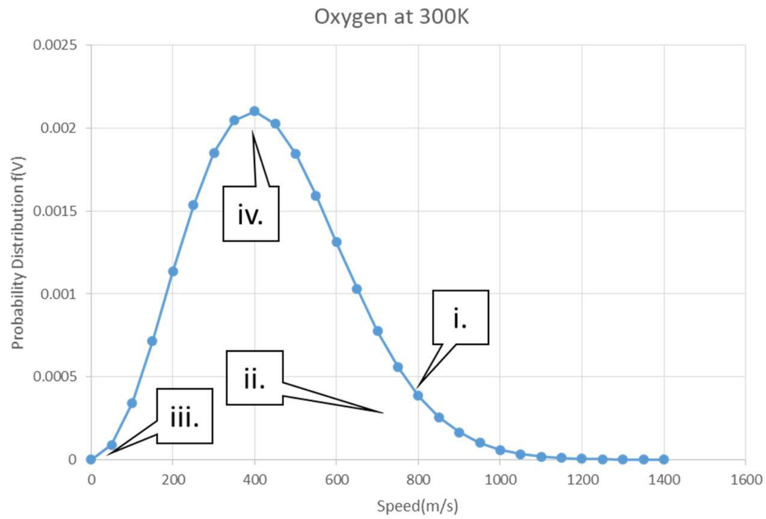

Figure 3

f. A mix of different size particles still interact via point collisions. It does not matter if the energy ratio $E_{(P\ 1)}$ / $E_{(P\ 2)}$ is due to higher velocity or equivalent higher mass. Therefore, the first approximation above is valid *(Fig 4A)*.
g. Gas molecules are generally not spherical. However, removing that assumption does not change the results as collisions are still at a single contact point *(Fig 4B)*. Because we assumed perfectly elastic collisions, there is no friction to transfer angular momentum to angular momentum. Therefore, at the contact point, maximum energy transfer is achieved when the angular momentum of the energy-losing particle fully adds up to its translational momentum. For the energy-gaining particle it is irrelevant if that gained energy is split between translational and angular energy. In addition, compound collisions can be analyzed as a sequence of independent events – the scenario discussed above. Therefore, the second approximation above is valid.
h. Molecular speeds match the Maxwell-Boltzmann distribution at equilibrium, but this distribution is not necessarily indicative of the equilibrium having been reached *(Fig 4C)*. **The key is that the momenta sum is zero on any arbitrary axis.** If they are all in the same direction or at least the combined momentum is nonzero, a pressure is present in that direction and it may be harnessed to do work. For instance, a set of homogeneous particles with the molecular speeds matching the Maxwell-Boltzmann distribution moving in the same direction can generate work.

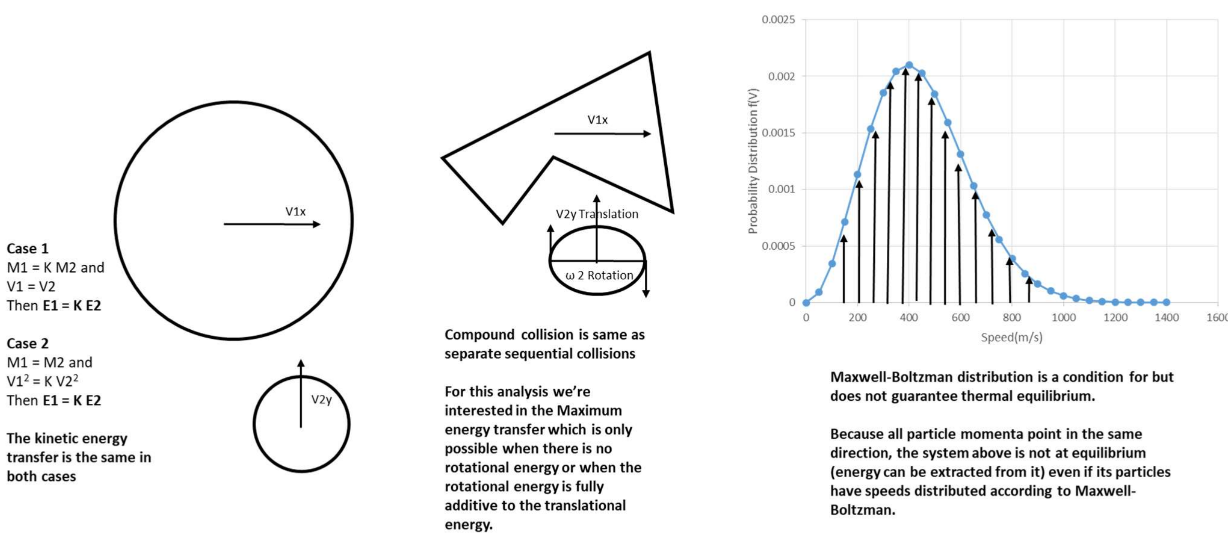

Figure 4 - A. Particle size does not change the results. B. Angular momentum and molecules shape does not change the results. C. Maxwell-Boltzmann distribution is necessary but not sufficient to indicate equilibrium.

i. The model can be extended (further research) to liquids, solids, and various external forces including gravity and electromagnetism. In those cases, collisions are sometimes still elastic while other times particles combine, dissociate, or emit/absorb radiations when colliding.

6. **Let's apply this model to two classic macro examples.** Consider a pool (billiard) table with the cue ball breaking the rack *(Fig 5A)*. Balls spontaneously coming back together to the initial position is an impossible occurrence even if these balls were molecule-size and all collisions were elastic. This can be proven with the thermodynamic model discussed. Unlike billiard balls, the particles do not rest, so to simplify, we assume that the cue ball has a speed 100 times that of the resting balls (10 m/s vs 1 m/s for the moving player and 0.1 m/s or another order of magnitude slower for the "resting" balls). Once the rack is broken, all balls including the cue ball reach a new average "resting" speed calculated from the conservation of energy. $10^2 + 15 \times 0.1^2 = 16 \times new\_rest\_speed^2$ So new_rest_speed ~ 2.5 m/s which, unlike in real life, is considerably higher than "zero" because we assumed perfect elastic collisions of just a handful of particles and no losses to the environment. From a 16-ball average of 2.5 m/s, with the collision model discussed, there is an effectively zero probability of the system spontaneously returning to the initial condition (per Fig 2). The arrow of time cannot be reversed.

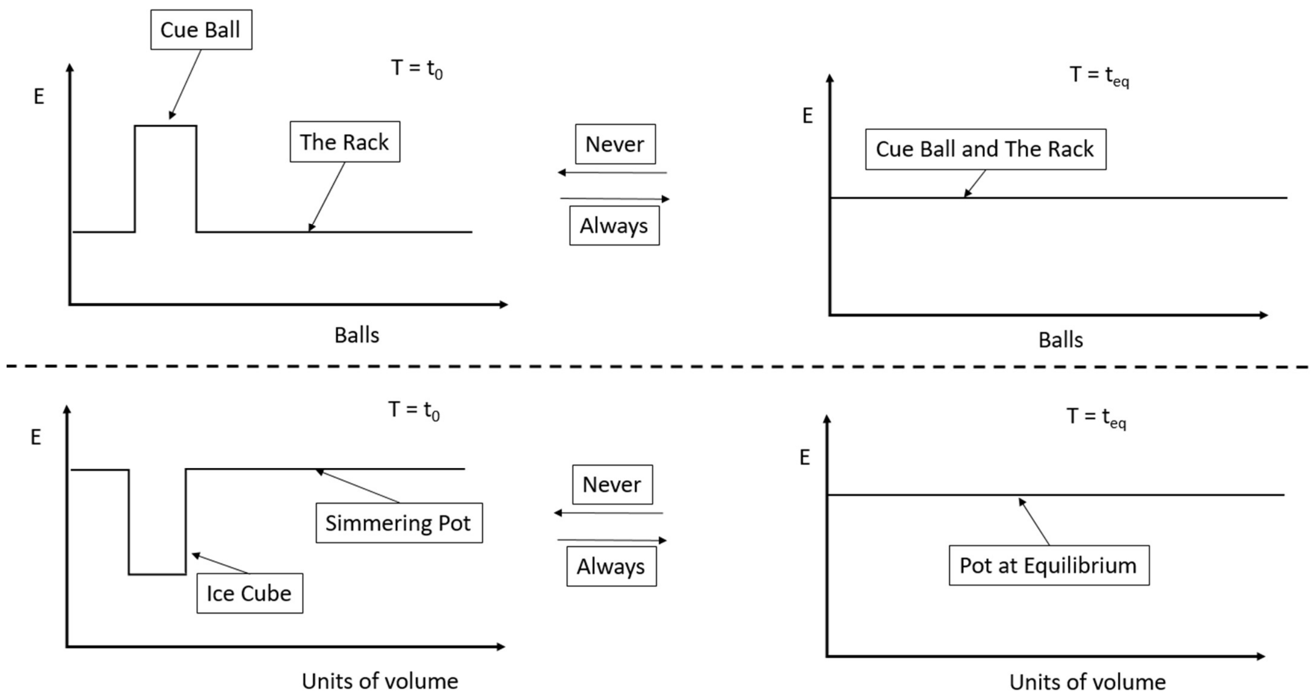

Figure 5 A. Break the rack in a pool game B. Cube of ice into a boiling pot

The cube of ice into a boiling pot case *(Fig 5B)* is a bit more complex as one particle can lose all kinetic energy in a single elastic collision and therefore reach "zero" speed - hence 0 K not just 0^0 C - albeit with an almost zero probability. We will instead consider a forming ice crystal in the boiling pot at equilibrium that either grows into an ice cube or melts back into the pot. To avoid phase transition complications, we will consider a gas (instead of water) at 100^0 C and ask how big of a 0^0 C "crystal" can form and for how long. Mean thermal velocity is proportional with sqrt(T_abs), therefore $V(100^0 C) / V(0^0 C) \sim 1.17$. Given the elastic collision model above, this translates in a probability of ~47% for the slower particle to lose energy to the faster one (ice crystal grows). This is one-particle-one-collision. For a crystal to grow, we will only consider the collisions between particles within a thin skin around the crystal. This is because the crystal can only grow if it loses more kinetic energy through this interface with the environment. If it gains energy, it melts in the environment and if the energy transfer is balanced, it neither grows nor melts. The mean free path for water vapor at 100^0 C is 281 nm. This is the average distance a water molecule travels between collisions with other molecules in the vapor. We will therefore consider a skin of 280 nm within which an energy transfer is likely to occur between the crystal and its environment. The molecule collision frequency at 100^0 C is Z ~ 2.5 x 10exp10/s. There will be ~2.5 * 10 exp (35) collisions per m^3 **per second**. Given the immense number of collisions, there is no way the $1mm^3$ ice crystal can survive, let alone grow *(Fig 6 and Fig 7)*. To improve the odds, we need to reduce the survival time from 1 sec to something extremely short like 1 psec, the crystal size from 1mm^3 to 100 nm^3, as anything smaller can hardly be called a crystal, and the temperature differential to 10° C or smaller. The results are presented in the table below. Only a 100 nm^3 at 99° C "crystal" can survive for 1 psec with an 86% probability. At 90° C the "crystal" can survive for 1 psec with a 6% probability and at 0° C, the 100 nm^3 "crystal" has no chance of lasting even 1 psec. The bottom line is that ice crystals cannot emerge out of boiling pots.

Crystal size	**1mm3**	**100nm3**
Mean path of water vapor (nm)	281	281
Collisions/**sec** in 1m3	2E+35	2.46E+35
Collisions/**sec** in crystal	2E+26	2.46E+14
The volume of the skin vs 1mm3	3E-04	1
Collisions/**sec** in the skin volume	**7E+22**	**2.46E+14**
Collisions/**psec** in the skin volume	**7E+10**	**246**

Figure 6

														one collision	1mm3, 1 s	100nm3, 1 psec
T2 (°C)	T1(°C)	T1(°K) / T2(°K)	**V1x/V2y**	atan(90° - α) (rad)	(90° - α) (°)	α at no energy exchanged	β max (goalseek V1x/V2y) (°)	β max (rad)	(1-cos β) / sin β	V1x/V2y = sin β / (1-cos β)	α + β (°) = P(P1 gains from P2)	180 - α (°) = P(P2 gains from P1)	P(P1 gains) from collision	Crystal grows if (P(P1 gains) /P(P1 loss)) ^collisions > 0		
0	100	1.37	**1.17**	0.86	49	**41**	**81**	1.4	0.86	**1.169**	122	139	**47%**	0.87	-	0.00
50	100	1.15	**1.07**	0.82	47	**43**	**86**	1.5	0.93	**1.075**	129	137	**48%**	0.94	-	0.00
90	100	1.03	**1.01**	0.79	45	**45**	**89**	1.6	0.99	**1.014**	134	135	**49.71%**	0.99	-	0.06
99	100	1.00	**1.00**	0.79	45	**45**	**90**	1.6	1.00	**1.000**	135	135	**49.98%**	1.00	-	0.86

Figure 7

7. **<u>The 2nd Law should simply be reformulated as 'Energy Disperses'.</u>**
   I. Energy is that which puts in motion (definition).
   II. To be in motion is to have kinetic energy (definition).
   III. To put in motion is therefore (from I and II) to transfer [kinetic] energy.
   IV. Energy is conserved (axiom).
   V. Therefore (from III and IV), the transferring entity must lose energy in favor of the entity put in motion.
   VI. Energy can flow in both directions, from Low to High and High to Low energy.
   VII. We **<u>proved</u>** in a simple thermodynamic system that, statistically, Low to High energy transfer is lower probability and %-wise magnitude limited **hence statistically self-limiting**.
   VIII. Therefore, **<u>Energy Disperses. This is the 2nd Law of thermodynamics</u>**. The elastic collision model quantifies dispersal in a simple thermodynamic system.
   IX. Corollary of (II), kinetic energy is special. It puts in motion while the other energies are potential – they have the capacity to do work.
   X. Corollary of (V), transfer efficiency is always less than 100% if (and this is always true) energy transfers to more than one entity.

'Energy disperses' is spontaneous energy transfer bidirectional yet statistically predominant from High Energy to Low Energy entities in a closed system until a steady state (equilibrium) is reached. A **System** is any entity that can be described and analyzed independently. While systems are never isolated, we must consider them quasi-isolated temporary and in large part to analyze them. To analyze a system without including the whole universe, we must consider just the approximate net force a field exercises on the system. **Closed System** is an ideal system that exchanges no energy with the environment. In practice we label systems closed if they exchange less than a minimum of energy in a unit of time with the environment. **Equilibrium** in a closed system is when spontaneous energy transfers within the system can no longer be measured with a passive sensor. Such a sensor is necessary because active sensors inject energy altering the system. Individual particles within the system continue to both lose and gain energy, just that this process is strongly self-limiting enough for no fluctuation to be measurable with a passive detector. Because there are no perfectly closed systems, **an equilibrium is reached when the system's energy distribution remains confined to a satisfactory range.** External trigger can take the system to a different equilibrium. For instance fuel is stable without a trigger that would take it to an entirely different equilibrium. System balanced on a gravitational peak. Constant temperature if perfect isolation from the environment. Even when considering only the energy available for transfer (generally not all energy), the **Energy Transfer Efficiency** is necessarily less than 100% because energy dispersal does not discriminate between the preferred transfer and other transfers to the surrounding (aka losses). One certain way to reduce losses is to lower the probability of interaction with the environment, often by reducing the number of particles in the environment (aka by creating a vacuum).

8. **Entropy is at best a redundant concept** (*Clausius' formula)* **and at worst a flawed concept** (**micro-macro** *state interpretation)*. This is because:
   a. **Boltzmann's formula is limited in scope.** We need a theory that includes all forms of energy.
   b. **Macrostate is meaningless beyond a few specific cases** like [purely theoretical] isolated homogeneous gases that can be described by PVTN. Even then, the PVT profile changes when the gas is locally compressed or heated which makes that macrostate different than that of the homogeneously distributed gas. Furthermore, those extreme states are unstable (and the more extreme the more unstable). This means that those are not different microstates of the same macrostate as commonly interpreted. Conversely, if one insists that different PVT profiles represent the same macrostate, one must observe that its microstates do NOT have the same probability of occurrence. Compressed to homogenously distributed gas transition is spontaneous and violent while homogenous to compressed is never spontaneous and requires more and more external intervention as the gas is further compressed. Yet in the micro-macro model IN EQUILIBRIUM all microstates are simply **POSTULATED** equally probable.
   c. **It is claimed that in the compressed state, the gas has fewer microstates** than in the expanded (homogeneously distributed) state and therefore the probability of finding the system in the compressed state is much smaller. This cannot possibly be the case as in both instances there are the same number of particles so the same number of combinations are possible. The only difference is that the unit volume statistically allocated to a particle is smaller when the gas is compressed than when the gas is expanded. Yet this volume is not a factor anywhere in the **micro-macro** model.
   d. The number of microstates conforming to a macrostate should be infinite in classical mechanics. Recognizing this problem, Boltzmann used an **AD-HOC** quantization method.
   e. **System is arbitrary.** The enclosure is ignored (not part of the system). However, it interacts with the content to keep it confined. And through the enclosure, the whole external universe affects the system.
   f. **When the 1st Law is about energy conservation** and the 3rd Law about the lowest possible [kinetic] energy, the 2nd Law should also be about energy.
   g. **Boltzmann's formula (S = kB log W (ln Ω))** is not intuitive and must be approximated as calculations are impossible.
   h. The low-entropy origin is problematic. How low is the original entropy? Why not zero? How did the lowest entropy universe look like? This is an extra complication to the conservation of energy picture. If energy dispersal fully explains the 2nd Law of thermodynamics, this redundant problem goes away.
   i. **Loschmidt's paradox** – the idea that microscopic reversibility is incompatible with macroscopic irreversibility - has never been resolved until now. Yet, as shown, the 2nd Law is demonstrably irreversible statistically due to the very strong negative feedback loop in energy dispersal in conjunction with the impossibility of preventing energy dispersal to the environment. This is in agreement with all observations - no measurable fluctuation has ever been observed in a system in equilibrium.
   j. **Zermelo's recurrence paradox** (using Poincare Recurrence Theorem) shows that the 2nd Law must be absolute, not statistical. To evaluate this with the elastic collision model, let's again consider the rack breaking example. We said "effectively zero" probability of return to the initial state, but let us be even more specific. Consider the last collision that restores the initial speeds to all balls. For that to happen, fifteen balls are already at the 0.1 m/s speed, the cue ball (P1) is close to 10 m/s and the sixteenth ball (P2) is close to 0.1 m/s but not quite, ready to strike the cue ball so that this sixteenth ball loses the bit of extra energy to end up at 0.1 m/s while the cue ball gains this difference to reach 10 m/s. P2 will necessarily hit P1 just past 180^{o} precisely in one point. The probability of that hit is thus exactly 0%, therefore Zermelo's paradox does not apply.

Of course, nothing prevents us (Clausius) from defining entropy as $\Delta S = \Delta Q / T$, and this formula may even be useful in certain applications with the clear understanding that entropy is not fundamental and not related to the 2nd Law of thermodynamics that, as shown, is not itself fundamental either. Or, like caloric, phlogiston and ether, entropy can be abandoned without a major scientific loss.

9. **If there is no energy dispersal, the 2nd Law does not apply.** Often used erroneous examples of 2nd Law (entropy) changes include: arrangements of marbles, cards, pebbles on the Go board, pollen grains, etc. Because there is no energy interaction between these macro objects, shuffling them does not change the system's energy dispersal and thus the 2nd Law does not apply to these systems. One such arrangement does not spontaneously transition into another. Is there an equivalent microscopic phenomenon? Yes, photons (bosons) do not transfer energy from one another. Shine a beam of light and measure the energy received. Then shine a counter beam to cross the original beam. The energy received from the original beam is not affected. On the other hand, electron colliders (fermions) do disperse energy and illustrate the 2nd Law of thermodynamics. No interaction, no energy dispersal, no "entropy" change. 'Energy Disperses' fully explains the phenomenon with no need of "entropy".
10. **Kinetic energy is special.** We define kinetic energy as the energy of movement, meaning anything that has a momentum also has kinetic energy. Yes, this includes massless particles radiation. Energy is defined only relative to kinetic energy because (1) it is the only active type of energy while all other energy types are potential; (2) it is the measure of all energies meaning no potential energy can be measured directly without first being converted to kinetic energy; and (3) conversions from one energy type to another is impossible without kinetic energy intermediation. Even transfers of the same energy type from one entity to another are less than 100% efficient with most of the difference being transferred to kinetic energy. We define Zero Kelvin as the state in which kinetic energy is zero. At that point, all energy transfers cease since that kinetic energy intermediates all of them. Conversely, it is not that 0 K makes kinetic energy zero; instead, 0 K is not attainable for as long as any energy is transferred, i.e. if any particle vibration, translation, radiation, decay, etc. occurs.
11. **Can any work at all be obtained from an isolated system in equilibrium?** Let's see what would happen if the smallest fluctuation energy could be extracted from the system. Consider the case of compressed vs expanded gas initially at the environmental temperature. Compressed gas expands doing work which is captured externally. Fluctuations then recompress the gas which then expands again releasing more energy. With every cycle, more energy is lost. But other than the work done externally, the system is isolated, so its internal energy keeps decreasing given the 1st Law of energy conservation. Over and over again until its particles lose all kinetic energy (See also Brownian ratchet). However this scenario is prevented by three factors. **First**, as proved, fluctuations in isolated systems are self-limiting much closer to equilibrium than the previous **micro-macro** model allowed. **Second**, an efficient enough ratchet cannot be built at the atomic scale and at the macro scale all fluctuations average away. **Third**, perfect isolation from the environment is impossible. And the more the system's internal temperature drops, the higher the leaks from the environment (less and less effective isolation). For these reasons, the final answer appears to be "NO" as to date, no work has ever been obtained from spontaneous fluctuation out of equilibrium. **Finally**, fluctuations would make perpetual motion of the 2nd kind(?) possible consider System 1 (Sy1) and System 2 (Sy2) fully enclosing Sy1. If work could be obtained from Sy1 fluctuations out of equilibrium, this work would be transferred to Sy2. Sy1 temperature would drop and then Sy1 would again reach equilibrium and again fluctuate transferring energy to Sy2 and so on until Sy1 temperature drops to 0K. Then if the barrier Sy1-Sy2 is open, the two systems would evolve back to the initial condition and restart the perpetual motion machine.

12. **The 2nd Law and the 'energy available to do work'.** The link between the **micro-macro** model and the energy available to do work is at best tenuous. Also, the **micro-macro** model assumes equilibrium (or else no macro-state measures are defined), so it is not suitable for dynamic systems. Assuming the elastic collision model with no energy transitions, we can consider unavailable all other energies other than kinetic and therefore zero with regards to the energy available to do work. The **'energy available to do work' (E_{wk}) is also** statistically zero at equilibrium. Yet the **micro-macro** model allows for fluctuations out of equilibrium – however improbable – that create E_{wk} in violation of the 2nd Law of thermodynamics. In contrast, the **elastic collision** model proposed shows self-limiting fluctuations from equilibrium. Thus fluctuations cannot be measured with a passive detector which means that no work can be obtained from a system in equilibrium. The particles speeds of the system in equilibrium are described by the Maxwell-Boltzmann distribution. We can employ the **elastic collision** model in a dynamic system to estimate the actual speed distribution of particles at any time and compare that to the equilibrium distribution to determine E_{wk} at that moment. For instance, mixing one mole of oxygen at 300 K with one mole at 400 K results, at equilibrium, in two moles at 350 K *(Fig 8)*. This is the ice cube into the simmering pot example from above. The initial E_{wk} in this closed system is simply (½) * Mass (1mole) * ($Vrms_{400K}^2$ –

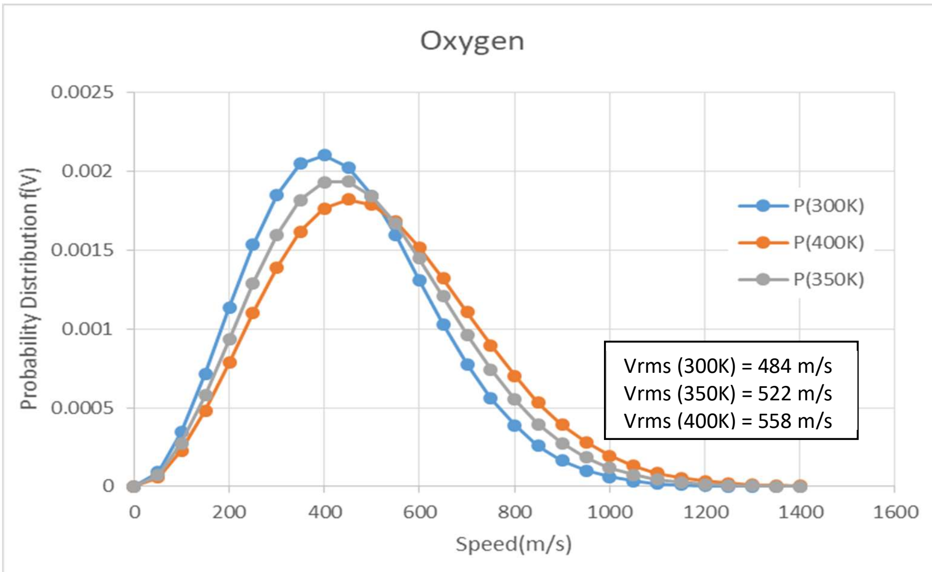

Figure 8

$Vrms_{350K}^2$) = (½) * Mass (1mole) * ($Vrms_{350K}^2$ – $Vrms_{300K}^2$) meaning the extra energy of the mole at higher temperature is equal to the energy deficit of the mole at lower temperature. Let us assume a transitional step in the spontaneous mixing process is described as a set of 0.5 mole each at 400 K, 375 K, 325 K and 300 K. In that case, the instantaneous E_{wk} is (½) * Mass (0.5 mole) * ($Vrms_{400K}^2$ – $Vrms_{350K}^2$) + (½) * Mass (0.5 mole) * ($Vrms_{375K}^2$ – $Vrms_{350K}^2$). As it must be, this energy is more than zero (at equilibrium) yet less than the initial E_{wk}. Once equilibrium is reached, E_{wk} in this idealized isolated system is zero and the system can no longer fluctuate out of this state. Note 1 - the concept of entropy is not needed for this analysis. The **elastic collision** model could be used to estimate non-uniformities in the dynamic system and thus the instantaneous E_{wk}. Note 2 – this scenario started the thermodynamic revolution: one hot and one cold reservoir, each contributing the matter to be mixed, a thermodynamic cycle (Carnot) that siphons E_{wk} from the spontaneous mixing process to the target application, and the inevitable environment that leaks part of E_{wk}. More energy can be obtained if the temperature differential is higher, if the reservoirs are bigger, and if the leaks to the environment are minimized. For the rack break model introduced above, t_2 is just an average "equilibrium state", as in the ideal model collisions never stop. E_{wk} is thus only statistically defined *(Fig 9)*. Assuming 0.1 kg balls, the initial speed of 10 m/s for the cue ball, and 0.1 m/s for all other balls "at rest", the initial E_{wk} is 9.4 J which is the difference between the cue ball initial energy (0.1 kg * $(10\ m/s)^2$) and the average equilibrium energy of 0.6 J per ball. At t_1, **in this particular example**, E_{wk} drops to 4.5 J which is the sum of extra energy of balls 3, 5, 7, 10, 13, and 15. At t_2 ("equilibrium"), E_{wk} is only statistically zero, the speeds of individual balls at equilibrium being described by the Maxwell-Boltzmann distribution. The E_{wk} decay curve is different from trial to trial although it starts with the same energy, is always decreasing, and ends with the statistical zero value. In addition, this model allows for fluctuations out of “equilibrium”. In reality, macro objects like pool balls collisions are not perfectly elastic while the particles that do collide elastically, are always analyzed statistically in much larger groups (than the 16 in this

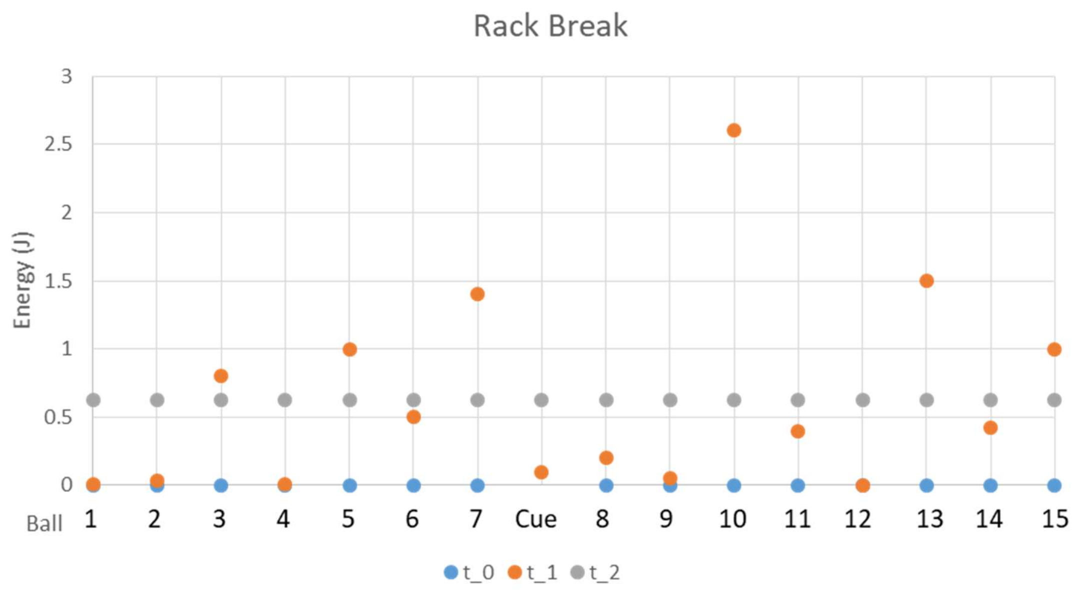

Figure 9

example). Although not real, this example validates the elastic collision model at the macro level for short durations as long as frictions can be minimized and isolation from the environment can be maximized.

Conclusions:

a. The 2nd Law of thermodynamics must be reformulated as previously it has been poorly understood, incomplete, and largely incorrect.
b. As shown, energy concentration is not absolutely impossible, but it is self-limiting improbable at the particle level and therefore statistically impossible at the macro level. Self-limiting means the more a system deviates from equilibrium, the less likely it is to deviate further and the more likely it is to return to equilibrium. Self-limiting is very fast acting becoming certainty over just a few particles interactions. This resolves the problem previous models have, where very low probabilities may be offset by very high number of iterations (Zermelo’s recurrence paradox).
c. The 2nd Law is not fundamental. It is a corollary of the 1st Law and is fully described as "Energy Disperses"
d. Thermodynamic evolution is not symmetrical in time hence the arrow of time
e. The asymmetry of the 2nd Law in a simple thermodynamic system is embedded in geometry
f. We can continue to use entropy where beneficial. While $\Delta S = \Delta Q / T$ is not fundamental, there is nothing wrong with using this compound metric whenever it is useful.

References: