Non-equilibrium systems and growth of complexity

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James Clerk Maxwell

1 Historical introduction

1.1 The founding fathers of thermodynamics

The history of thermodynamics reaches back to the 1600s when first rudimentary thermoscopes (the ancestor of the thermometer) started to be constructed and a scientists, like Francis Bacon began to formulate the right ideas about the nature of heat.

It took however until 1850s, after the experiments of James Joule, for the wide scientific community to finally accept heat as a form of energy. The relation between heat and energy was important for the development of steam engines and led to the description of idealized heat engines and their theoretical efficiency in 1824 by Sadi Carnot.

After that, around 1850 Rudolf Clausius and William Thomson (Lord Kelvin) stated both the First Law (the conservation of total energy) as well as the Second Law (heat does not spontaneously flow from colder to hotter objects). Other formulations followed quickly and the general implications of the laws were understood.

More important developments came after the recognition by Rudolf Clausius and James Clerk Maxwell in 1850s (first noticed by Daniel Bernoulli in 1738) that gases consist of molecules at motion. This simple idea allowed Maxwell to derive and calculate many macroscopic properties of gases at equilibrium.

Shortly after that, Rudolf Clausius introduced the notion of entropy, defined as the ratio of heat and temperature and redefined the Second Law stating that for isolated systems this quantity can only increase in time.

In 1872 Ludwig Boltzmann constructed an equation that he thought could describe the detailed time development of any gas and used it to derive the so-called H-theorem. The theorem stated that a quantity equal to entropy must always increase in time. Therefore it seemed that Boltzmann had successfully proved the Second Law. During his times however, a famous objection was poised known as the Loschmidt paradox which stated basically, that due to time-reversal property of Newton laws the evolution could be run in reverse leading to decrease in entropy.

The resolution of this paradox was noted much later and should probably classified as hard to grasp or at least hard to get accustomed to, because even today one can find discussions and erroneous statements about the "arrow of time" in the literature. Indeed, those difficulties were noted by Gibbs as well[1]: "Any method involving the notion of entropy, the very existence of which depends on the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension." We will intentionally postpone the discussion to the later part of this

paragraph in order to go through it thoroughly and to highlight the more recent paths of developments in non-equilibrium thermodynamics and statistical physics.

In responding to some of the other objections Boltzmann realized around 1876 that in a gas there are many more states that seem chaotic and random than seem orderly. This realization led him to argue that entropy must be proportional to the logarithm of the number of possible states of a system and the nature of the Second Law - probabilistic.

Around 1900, Williard Gibbs formulated statistical mechanics in more general context and introduced the notion of ensemble - a collection a collection of many macroscopically similar copies of the system upon which the notion of ergodicity was built. It was argued that if a single particle visits every possible piece of the phase space, then when averaged over a sufficiently long time then a property in question would have the same value if one would instead think of ensembles.

Gibbs also introduced another definition of entropy, which, as noted by him [?] would only increase in a closed system if it were measured in a "coarse-grained" way in which nearby states were not distinguished. In literature one can sometimes find statements [2] that this property of Gibbs entropy is problematic, but in fact the resolution of this paradox in very similar to the resolution of the Loschmidt paradox.

During the beginning of the XX century, the development of thermodynamics was largely overshadowed by quantum theory and little fundamental work was done on it. Nevertheless, the Second Law had become to be regarded as a fundamental principal, whose foundations should be questioned only as a curiosity. Ergodic theory on the other hand has became an active area of pure mathematics, and between 1920-1960 many properties of simple systems related to ergodicity were established [3].

1.2 The information era and Schrödingers influence on physics

In the 1940s Claude Shannon introduced the notion of information quantity [?] and during the 1950s, it was recognized that entropy is simply the negative of Shannon's quantity. This way a fundamental link between information theory and thermodynamics was established. This coincided with the discovery of the structure of DNA by James Watson and Francis Crick and together with written a little earlier, influential book titled "What is life?" by Erwin Schrödinger sparked enthusiasm and inspired generations of physicists to answer the alluring (though not easy) question of the role of physics in biological processes.

In any event it probably wouldn't be an exaggeration to say that Schrödinger himself (as he admits), was inspired by the work of German-American physicists Max Delbrück; who helped launch the molecular biology research program in the late 1930s and explained (in main part) the mechanism of heredity and mutation. Regardless, Schrödinger makes some very essential observations on the nature of living organisms.

First, their operation (living organisms) as a macroscopic system resembles approximately, a purely mechanical system rather than a thermodynamical system. Even though

their size is far from what is considered a thermodynamic limit, they tend stay unaffected (in special environments) by random molecular motion known as heat and; at the same time, evade the decay towards equilibrium for an unusually long time. This is essentially the definition of a living system.

Secondly, he notices that the way an organism accomplishes the above is through the exchange of energy and matter with it's environment, that leaves it's own internal state in low entropy. He withdraws from considerations of free energy, although he acknowledges that the exact physical understanding should be accomplished through it rather than through entropy. Worth mentioning is his hypothesis of "life intensity" the term which ought to parallel with the rate at which the system produces entropy or dissipates heat.

Thirdly, each cell depends on very small group of atoms, the genetic code, which determine it's evolution, something unprecedented, beyond the description of ordinary statistical physics. He proposes, that perhaps, a partial explanation for this dynamical behaviour (rather than statistical) can be traced to rigidity and tightness of chemical bonds. However the very vital point Schrödinger tries to make is the hypothesis, that there must exist a yet unknown, new law of physics that would explain fully how order can be produced out of order.

Lastly, even though Schrödinger introduces some quantum mechanics principles, like the uniqueness of Heitler-London bond in order to defend the theory laid down by Delbrück, he assures that quantum indeterminacy should play only marginal role in the future laws of dynamics of living systems. The possibility that remains is that the origins of life, not their evolution could be quantum mechanical.

As mentioned earlier, Schrödinger influence driven many researchers to focus on the topic of non-equilibrium phenomena, however their individual approaches diverged widely, due to, as we will see the resolution of the Loschmidt paradox.

1.3 The resolution of the Loschmidt paradox

The Loschmidt paradox confronts the fact that the fundamental equations of motion are time-reversible. How therefore the irreversibility enters the picture?

The answer lies in the time-asymmetric probabilistic way in which we make predictions about the world. Besides the pure probabilistic description we need the common sense, axiom of causality in order to obtain the time-asymmetric description. We use it so frequently implicitly, that we often forget about it [2].

Indeed, Boltzmann himself didn't noticed that the way in which he derived the H-Theorem from his equation, implicitly assumed that the particles are uncorrelated before the collisions (through Stosszahlansatz), but become correlated after the collision[4][3], thus causing the time-reversal asymmetry.

One can also see this most clearly in a generic example, reviewing the procedure in which we compute some future macroscopic state from an initial state macrostate. The final state is obtained by taking the *sum* of the probabilities over the indistinguishable microstates, however the initial state is obtained by taking the *avarage* over the initial microstates.

However, if we would consider a scenerio where we either know the initial configuration exactly or are able to study all degrees of freedom at the final state, the arrow of time would indeed disappear as is the case with microscopic or structureless objects.

1.4 Different approaches towards irreversibility and non-equilibrium

As one might tell from the large amount of literature on the subject [5] [6] [3] [7] [8] that this explanation of irreversibility noticed long time ago by Clausius, Boltzmann, Kelvin, Maxwell [3] and also Einstein (in the polemic with Walter Ritz over time-reversal symmetry of Maxwell equations) still leaves dissatisfaction in many.

Different alternatives for explanations of irreversible processes have been proposed over the years, including retarded potentials of electromagnetism, randomness of the radiative process, quantum mechanics, CP violation, fluctuations, cellular automata and even gravity. We now will shortly discuss each of those approaches, starting our discussion from the most direct one, given Ilya Prigogine.

The motivation for such development was clearly articulated by Prigogine: "I have always found it difficult to accept this conclusion [macroscopic irreversibility emerging from initial conditions] ... especially because of the constructive role of irreversible processes. Can dissipative structures be the result of mistakes?" [9].

His personal dissatisfaction with lack of irreversibility and unitary evolution at the microscopic level led him to postulate the existence of microscopic representation of entropy in the equations of motion. In essence, the idea was to change the fundamental laws of physics as to make them irreversible at the microscopic level. The details of this approach, known in literature as Misra-Prigogine-Courbage theory[8], will not be presented here, as in so far no evidence for its validity has been found[10].

Somewhat related is the Ritz argument about the irreversibility of Maxwell's laws of electromagnetism. In the polemic with Einstein he states that the retarded and advanced potentials should not be treated on equal footing, to which Einstein disagrees. According to John Fox, who was a later commentator of the debate, based on the long lifetimes of fast muons (which are taken as evidence for time dilation) and the speed-of-light gamma rays from rapidly moving sources, Fox gave a decision in favor of Einstein [11].

Now to see why irreversibility cannot be driven by quantum mechanics one just needs to notice that all quantum phenomena are controlled by Planck's constant, while the manifestations of the irreversibility - such as friction - are clearly macroscopically large.

A different school of thought [?][?], claims that gravity is the source of irreversibility. However, it is a well known fact that in the absence of gravitational fields friction and irreversibility occurs as well. Beside that, similarly to the quantum case the Newton's

constant is to small to have such an effect. It is demonstrable that the magnitude of friction is controlled by atomic physics and electromagnetism and therefore is a *local* effect.

One of often cited local causes of irreversibility is CP violation. The weak nuclear interactions violate the CP symmetry which is equivalent to saying that they violate the T symmetry, because to our best knowledge the CPT symmetry is strictly conserved. However the case here, is again similar to the discussion of gravitational and quantum mechanical effects, namely the effect is again to small to explain the friction force. Friction would have to be proportional to the small angle from the Cabibbo-Kobayashi-Matrix matrix. Once again, this is clearly not the case because the friction force is much stronger and it is controlled by electromagnetic collisions - collisions caused by a force whose microscopic description is time-reversal-symmetric.

To summarise, one can see that the Second Law and irreversibility are intimately connected with statistics, inference methods and our lack of full information about systems.

1.5 Jaynes formulation of statistical mechanics (MaxEnt)

In 1957 Edwin Jaynes published an illuminating article on the information theoretical basis of statistical mechanics which, with agreement to our earlier discussion, equated entropy to our lack of knowledge about the system. From this approach it follows that the maximum entropy state i.e. equilibrium state of statistical physics can be viewed through information theory as the least biased state given the available information (e.g. energy constraints). Statistical mechanics then becomes, in a strict sense, a form of statistical inference rather than a physical theory.

The essence of MaxEnt method can be summarized in the formula for maximization of relative entropy (negative Kullback-Leibler divergence)

$$H(p \lor q) = -\sum_{i} \ln p_{i} \frac{p_{i}}{q_{i}}$$

with respect to p_i (new aposteriori distribution). H(p||q) can be interpreted as the information gained by using p_i instead of q_i .

1.6 Physics of computation

After Shannon and Jaynes established the links between information theory, statistical mechanics and thermodynamics, there was a growing need to include the concept of computation as well. Following some preliminary statements by John von Neumann, it was thought that any computational process must necessarily increase entropy. However in 1970s, Charles Bennett pointed out that it is not the case[?], laying some early groundwork for relating computational and thermodynamic ideas.

2 Treatment of entropy in standard contexts

2.1 Gibbs entropy

The Gibbs Entropy defined with the use of the N particle distribution function ρ and the Boltzmann constant k_B :

 $S_G = k_B \int \rho \log \rho, \tag{1}$

is a generalization of Boltzmann entropy $S_B = k_B \log W$ where W represents the number of possible microscopic configuration of a macrostate (phase volume). From this fact we see that $\log k_B^{-1} S_G$ is a measure of the phase volume of microstates or measure of our degree of ignorance as to the true unknown microstate.

Gibbs entropy is also the correct generalization of Boltzmann H useful only for description of systems of non-interacting molecules [12].

Moreover can also be demonstrated [12] that the change of Gibbs entropy over a reversible path is equal to Clausius entropy:

$$\Delta S_G = \int_1^2 \frac{d\langle K + B \rangle + \langle P \rangle d\Omega}{T} = \frac{dQ}{T}.$$
 (2)

Here K is the total kinetic energy, V is the interparticle potential and P, T are pressure and temperature. We may therefore drop the G, and from now on speak of entropy S.

In closed Hamiltonian systems Gibbs entropy stays constant. This feature of entropy was first noted by Gibbs himself and was solved by a coarse-graining procedure[1]. This alleged arbitrariness of this procedure was subject to critique [13].

However, even without coarse-graining one can use Gibbs entropy for closed systems subject to adiabatic change. If we knew that on the beginning, at time t_0 the system is in *complete* thermodynamic equilibrium having entropy S_G , then we know that at the later time; after the external adiabatic ceased the new "test" or experimental distribution function will have entropy $S_e \geq S_G$. By saying that we demand *complete* thermodynamic equilibrium at the beginning, we say that the systems history has to be followed by the experimenter to become confident of the obtained equilibrium, as some otherwise unexplainable exceptions exist, such as the Hahn experiment.

It is perhaps worth underlying, that the increase of entropy is linked to our knowledge about the system, rather than it is doing internally. This should not come up as particularly surprising as our division between work and heat is somewhat arbitrary.

One can propose a thought experiment, leading to paradox to see the case more clearly. Consider a case of an simple gas closed in an isolated box container of size L which molecules are localized in an imaginary box-like area of size L/2 at time t_0 (Figure 1a). It is obvious that the gas will expand, but according to the constancy of Gibbs entropy for an isolated system the entropy will not change. Of course the answer to this apparent paradox is very simple - if we had the ability to wait the time necessary for particles

to localize in the volume L/2, we would probably not need the Second Law. In every imaginable case, we would need to place the particles in the initial state by hand, that is close them in an actual box of size L/2 and then release. In this scenerio, the final phase space is of course larger than the initial one and Gibbs entropy increases, as expected.

Classical entropy is by construction, an additive property. The Second Law of course holds for isolated systems as a whole and one can therefore imagine that out of equilibrium some subsystems may maintain lower entropy. We'll demonstrate this in the next paragraph.

2.1.1 Decrease of entropy in a simple model

Let's consider a model consisting of three elements: the cooler C, the heater H and the system under consideration S, staying out of equilibrium. We assume, that the temperatures of the cooler and the heater stay constant, and that heat Q_H flows into the system S and heat Q_C flows out. The situation is illustrated by the picture 1.

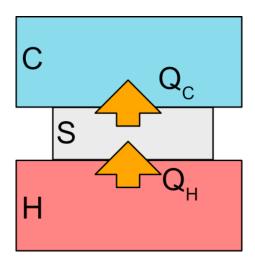


Figure 1: System (S) model

Treating the heater and the cooler as the environment, we can think of our system S as an open system. Further on we'll analyze the system S from the perspective of internal (i) entropy production and external (e) entropy flux, flowing to the system S. Of course the change in entropy will be the sum of those two contributions:

$$dS_S = dS_i + dS_e. (3)$$

In the current analysis let's consider a situation in which the same amount of heat flows in as flows out, that is $dQ_C = -dQ_H$. Using this relation we get the following term for the change of entropy:

$$dS_e = \frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = dQ_H \left(\frac{1}{T_H} - \frac{1}{T_C}\right) = dQ_H \left(\frac{T_C - T_H}{T_H T_C}\right) < 0.$$
 (4)

From which it follows, that the heat flow takes the entropy out of our system. For the purpose of further discussion we introduce the concept of rate of entropy change connected with the heat flow:

$$j_e \equiv \frac{dS_e}{dt}.\tag{5}$$

In the considered scenerio, the j_e is held constant (steady-state) and we suspect a continuous fall in system's entropy

Yet, moving away from the equilibrium state we suspect, that the a major role will be played by dS_i moving the system back to equilibrium state. Similarly, as before we define the rate of internal entropy production:

$$j_i \equiv \frac{dS_i}{dt}. (6)$$

When $T_H = T_C$, i.e. the system is in equilibrium with constant entropy S_{EQ} then it follows that $j_i = 0$. Therefore the rate of internal entropy production j_i should be a function of system's entropy S_S , i.e. $j_i = j_i(S_S)$ with the boundary condition $j_i(S_S = S_{EQ}) = 0$.

Near the equilibrium state $S_S = S_{EQ}$, we can Taylor expand the function $j_i(S_S)$ to it's linear term

$$j_i(S_S) = j_i(S_{EQ}) + (S_S - S_{EQ}) C_1 + \mathcal{O}(S_S^2),$$
 (7)

fulfilling $j_i(S_{EQ}) = 0$.

The dimensional and stability analysis tells us that C_1 has the dimension of inverse time and in the case of $j_e = 0$ should simply be equal to S_{EQ} , therefore we set $C_1 = -\frac{1}{\tau}$, where τ is a positive defined relaxation constant.

Using the equation (3) we get

$$\frac{dS_S}{dt} = j_i(S_S) = (S_S - S_{EQ})C_1, \tag{8}$$

The solution of the equation (8) is then

$$S_S(t) = S_{EQ} + (S_0 - S_{EQ})e^{-t/\tau}, (9)$$

where the initial condition was set $S_S(0) = S_0$.

Now we include the term j_e into our considerations. In this case the equation (3) results in the following

$$\frac{dS_S}{dt} = j_e + j_i(S_S) = j_e + \frac{S_{EQ} - S_S}{\tau}.$$
 (10)

Given a boundary condition $S_S(0) = S_{EQ}$ it has a solution

$$S_S(t) = S_{EQ} + j_e \tau \left(1 - e^{-t/\tau}\right),$$
 (11)

where j_e is a negative constant (graph of this function is presented on 2). In the limit $t \to \infty$ the entropy of the system falls to the minimal value

$$S_{min} = S(t \to \infty) = S_{EQ} + j_e \tau < S_{EQ}. \tag{12}$$

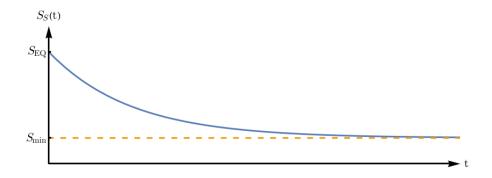


Figure 2: Inducing lower entropy with heat flow.

This is of course consistent with the second law of thermodynamics as we're describing an open system. It's easy to notice that the total entropy change is equal to $dS = dS_i \ge 0$ (for simplicity it was assumed that the heater and cooler don't act as producers of entropy).

2.2 von Neumann entropy

Although this work is meant to stay within the classical limit, it might be worth while to clear out the notion of entropy in quantum context.

The von Neumann entropy is defined as

$$S_{vN} = -\operatorname{Tr}(\hat{\rho}\log\hat{\rho}). \tag{13}$$

For which the general form of the density matrix operator is

$$\hat{\rho} = \sum_{k} p_k |\psi_k\rangle \langle \psi_k| \tag{14}$$

in case of pure state $|\psi\rangle$ the density matrix is simply

$$\hat{\rho} = |\psi\rangle\langle\psi|\tag{15}$$

and it is easy to verify that the entropy of a pure state is equal to zero. The entropy of mixed state is always greater than zero. If the system is in a pure state, it will continue to be in a pure state as long as it stays isolated. For a mixed state, the degree of mixedness measured by the entropy will stay constant as long as it is isolated. This follows from the fact that the time evolution is unitary and the eigenvalues of the density operator therefore do not change with time.

An interesting question one might ask (and not really discussed in textbooks) is how the entropy changes after a measurement of a particle in many-body system which, initially, was in pure state.

Without loss of generalization let's consider an isolated system of two identical particles described solely by their momentum states. In the scenario of two particles of identical

momentum we can write the initial pure state as

$$|2,0,0,\ldots\rangle \tag{16}$$

which entropy is of course zero. In second quantization formalism the measurement of a particle is realized by the field operator $\hat{\Psi}(x) = \sum_k \phi_k(x) \hat{a}_n$ which annihilates a single particle at position x. Therefore after the measurement of particle at some position x, one particle is "virtually" removed from the system under consideration, but the system stays in pure state

$$\hat{\Psi}(x) |2, 0, 0, \dots\rangle = \phi_1(x) |1, 0, 0, \dots\rangle, \qquad (17)$$

which entropy is zero. It's important to notice though that our system lost a particle and therefore the systems before and after measurement are not equivalent! Of course, in reality the particle doesn't disappear. After determination of it's position by experiment $(\Delta x \to 0)$, the uncertainty of it's momentum approaches infinity $(\Delta p \to \infty)$, which means that we can reconstruct the state using a linear combination of states with *any* value of momentum:

$$c_1 |2, 0, ...\rangle + c_2 |1, 1, 0, ...\rangle + c_3 |1, 0, 1, ...\rangle + ...$$
 (18)

where the squared modulus of the coefficients has to sum up to one $(\sum_{i} |c_{i}|^{2} = 1)$.

Now depending on the precision of the measurement we can recalculate entropy of course getting a value greater than zero. If we would perform the same analysis for a pure state of two particles in different states i.e. ket1, 1, ... then we would obtain an increase of entropy even without accounting for the lost particle. This crude example gives a clear illustration of the fact that after **any** measurement the von Neumann entropy has to increase. However it's change is ultimately related to lost information about the system in the act of the measurement.

Correct also for correlated systems?

There's another interesting feature of quantum entropy, namely inequalities that it fullfills. If we bipartite the system into subsystems A and B each containing it's own set of commuting observables, then in order to calculate the entropy S_A of a subsystem A we need to calculate the entropy with respect to density matrix traced over the other subsystem, namely

$$\hat{\rho}^A = \text{Tr}_B \,\hat{\rho} \tag{19}$$

then in general the following identities are satisfied

$$S(\rho) \le S_A + S_B$$

$$S(\rho) \ge |S_A - S_B|$$
(20)

The interpretation of the first inequality is that the full information about the states of the subsystems A and B will in general not be sufficient to give full information about the state of the total system A + B. Or in other words, when there are correlations between the two subsystems, these are not seen in the description of A and B separately.

3 Near-equilibrium thermodynamics

3.1 Concepts

3.2 Theory of fluctuations

3.3 Onsager relations

[IN PROGRESS] a term for entropy for open systems, an extension of Clausius entropy for isolated systems:

$$dS = d_i S + d_e S$$

Where d_iS is connected with entropy produced within the system and d_eS is the entropy transferred across the boundaries of the system. The second law states that $d_iS \geq 0$, so if a system is to stay in law entropy state it's production must be compensated by an inflow of negative entropy.

He then develops an explicit expression for entropy production, assuming that even outside equilibrium (but near) entropy depends only on the same variables as at equilibrium ("local" equilibrium)

$$P = \frac{d_i S}{dt} = \sum_{\rho} J_{\rho} X_{\rho} \ge 0$$

where J_{ρ} are the rates of the various irreversible processes involved (chemical reactions, heat flow, diffusion...) and X_{ρ} are the corresponding, generalized forces (affinities, gradients of temperature, of chemical potentials...). The flows are described using different empirical laws (Fourier's law, Fick's law, etc.)

$$J_{\rho} = \sum_{\rho} L_{\rho\rho'} X_{\rho'}$$

Onsager relations $L_{\rho\rho'} = L_{\rho'\rho}$ [IN PROGRESS END]

3.4 MinEP

The most well known contribution of Ilya Prigogine to statistical physics, often called the Minimum Entropy Production (MinEP) principle, sprouts from the analysis of second order excess entropy around a steady state $(\delta^2 S)_{ss}$.

If we perturb the system around it's equilibrium state we obtain

$$S = S_0 + \delta S + \frac{1}{2}\delta^2 S \tag{21}$$

This quantity is than used as a Lyuponov function and has benefits over other (not necessarily all) Lyupanov functions one could define. Its macroscopic meaning is conserved

independently of microscopic details of the system under consideration and is also independent of the nature of particular (possibly inhomogeneous) fluctuations. It is important however, that this result holds only for steady states near-equilibrium. It is only near-equilibrium that the quantity $(\delta^2 S)_{ss}$ generates probability of fluctuations, as Prigogine insisted in response to criticism [14].

The term "dissipative structures" was also coined by Prigogine. In Prigogine's view the fluctuations are the trigger for the instabilities (or rather bifurcations in the equations of motion), which in turn give rise to spacetime structures, called poetically "dissipative structures". An often given example of instabilities leading to formation of structures are the Rayleigh-Bénard convection cells. In further part of this it will be demonstrated that this non-equilibrium system indeed lowers it's entropy.

3.5 Green-Kubo relations

4 General Irreversibility

P(H/E) = P(E/H)P(H)/P(E) "P(E)" is the so-called marginal probability of evidence "E" in all contradicting hypotheses, equal to the sum of $P(E/H_i)P(H_i)$ over "i". The main point of this discussion is to emphasize that the conditional probabilities "(E/H) and P(H/E) are two very different animals. There is no symmetry between assumptions and assertions in conditional probability calculus. The additional factor of "P(H) / P(E)" that distinguishes them is a more general version of the "1/N" factor in the averaging over the initial states that we discussed previously, in the comments about particle physics.

References

- [1] J. W. Gibbs, "The collected works of J. Willard Gibbs," 1928.
- [2] D. J. Evans, Fundamentals of Classical Statistical Thermodynamics. Apr. 2016.
- [3] S. Wolfram, A new kind of science. Urbana-Champaign, IL: Wolfram Media, 2002.
- [4] J. R. Dorfman, "An Introduction to Chaos in Nonequilibrium Statistical Mechanics, 1999."
- [5] R. O. Doyle, "The Origin of Irreversibility," Information Philosopher.
- [6] D. Layzer, "Cosmic evolution and thermodynamic irreversibility," *Pure and Applied Chemistry*, vol. 22, no. 3-4, 1970.
- [7] C. Rovelli, "Is Time's Arrow Perspectival?," arXiv.org, May 2015.

- [8] M. Courbage and I. Prigogine, "Intrinsic randomness and intrinsic irreversibility in classical dynamical systems," *Proceedings of the National Academy of Sciences*, vol. 80, pp. 2412–2416, Apr. 1983.
- [9] I. Prigogine, "Time, structure and fluctuations," Nobel Lectures in Chemistry 1971-1980, 1993.
- [10] J. Bricmont, "SCIENCE OF CHAOS OR CHAOS IN SCIENCE?," Annals of the New York Academy of Sciences, vol. 775, pp. 131–175, June 1995.
- [11] J. G. Fox, "Evidence Against Emmision Theories," American Journal of Physics, vol. 33, pp. 1–17, Jan. 1965.
- [12] E. T. Jaynes, "Gibbs vs Boltzmann Entropies," American Journal of Physics, vol. 33, no. 5, pp. 391–398, 1965.
- [13] D. J. Evans, D. J. Searles, and S. R. Williams, Fundamentals of classical statistical thermodynamics: dissipation, relaxation, and fluctuation theorems. Berlin: John Wiley & Sons, 2016.
- [14] G. Nicolis and I. Prigogine, "Irreversible processes at nonequilibrium steady states and Lyapounov functions," *Proceedings of the National Academy of Sciences*, vol. 76, no. 12, pp. 6060–6061, 1979.