ENTROPY THEN
AND
ENTROPY NOW

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HAPPY NEW YEAR

Plan of the Talk

- Entropy then
  - Clausius invents entropy;
  - Δq is not a perfect differential
  - $dS = \Delta q/T$ is a perfect differential
  - Carnot's principle
  - Clausius' explanation
  - Boltzmann statistical entropy
- entropy now:
  - Shanon and information theory
  - Renyi and fractal measures
  - nonlinear dynamical entropy: Kolmogrov and Sinai
  - Tsallis non extensive entropy

entropy then : Clausius

- Entropy is one of the most influential of the terms coined so far in human history
- Formally, entropy was invented in the year 1865 by Rudolf Julius Emmanuel Clausius (1822 - 1888)
- Clausius(1851, 1862, 1865, 1867): *The kind of motion we call Heat*
- "Entropy" in Greek means "transformation"
- Clausius: *I have intentionally formed the word entropy to be as similar as possible to the word energy; for, the two magnitudes to be denoted by these words are so nearly allied in their physical meanings that a certain similarity in designation appears to be desirable*
- Entropy was understood as the penalty incurred when we convert *heat* to *work* : more on it later.

Clausius: Heat is not a perfect differential

$$
\begin{aligned}
dU &= \Delta q + \Delta W \quad \text{(Energy is conserved)} \\
\Delta q &= dU - \Delta W \\
&= C_V\, dT + P\, dV \\
&= (C_V + nR)dT - nR\frac{T}{P}dP \\
&= F_1(T,P)dT + F_2(T,P)dP
\end{aligned}
$$

It is readily seen that

$$
\left(\frac{\partial F_1}{\partial P}\right)_T \neq \left(\frac{\partial F_2}{\partial T}\right)_P
$$

which implies that Δq is **NOT A PERFECT DIFFERENTIAL.**

heat divided by temperature is a perfect differential

- Consider the quantity: heat exchanged divided by temperature

$$\begin{aligned}
\frac{\Delta q}{T} &= \frac{dU}{T} - \frac{\Delta W}{T} \\
&= C_V \frac{dT}{T} + \frac{P}{T}\, dV \\
&= \frac{C_V + nR}{T} dT - nR\, PdP \\
&= \phi_1(T,P)dT + \phi_2(T,P)dP
\end{aligned}$$

It is readily seen that

$$\left(\frac{\partial \phi_1}{\partial P}\right)_T = \left(\frac{\partial \phi_2}{\partial T}\right)_P$$

- Thus the quantity

$$\frac{\Delta q}{T}$$

is a **PERFECT DIFFERENTIAL.**

- Clausius called it entropy and denoted it by the symbol S, after Sadi Carnot

$$dS = \frac{\Delta q}{T}$$

- Heat is energy in transit. Entropy looks very much like heat *i.e.* like energy except that it is divided by temperature

- Having invented a new thermodynamic variable Entropy, Clausius asserted
  - Energy of the universe remains constant
    - This assertion is about energy conservation; called the first law of thermodynamics
  - Entropy of the universe tends to a maximum
- Why was this ’strange’ assertion made ?
- What were his compulsions to make this assertion ?
- to answer this question we have to go back by a few decades, to the year 1824

Carnot and his engine

- Nicolas Leonard Sadi Carnot (1796 - 1832)
- Sadi Carnot was working on the basic principle of heat engines
- Sadi Carnot (1824), Reflexions on the motive power of fire and on the machine to develop that power
- Carnot reasoned that *mere production of heat is not sufficient to give birth to impelling power. It is necessary there should be cold - without it heat is useless.*
- In other words we need both heat source and a heat sink to get work from heat.
- Carnot found that the amount of energy you get out as useful work from a machine is always less than the heat you put in.

- Carnot reasoned:
  - when q_1 Calories of heat fall from temperature T_1 to 0 then, the whole of heat will be converted to work: $W = q_1$.
  - However since the calory falls to temperature $T_2 > 0$, only the corresponding proportion $(T_1 - T_2)/(T_1 - 0)$ of q_1 shall yield work;
  - the remaining q_2 is rejected to the heat sink at temperature T_2.
  - $W = q_1 \times \eta; \quad \eta = \frac{T_1 - T_2}{T_1} < 1, \text{when } T_2 > 0$
- Thus heat can not be completely converted into work
- Work, however, can be completely converted into heat
- this is called thermodynamics irreversibility

Entropy is penalty paid for extracting work from heat

- whenever we extract work from heat we have to pay a penalty
- Forty years later Clausius is going to term this penalty as entropy - a name that rhymes with energy !!
- For a few decades scientists did not recognize the fundamental import of Carnot's finding
- nor did they recognize that entropy is fundamentally quite different from energy
- Entropy was invented for purpose of explaining why the efficiency of a Carnot engine is less than unity

Clausius explains Carnot's principle

- Entropy lost by the heat source is q_1/T_1
- Entropy gained by the heat sink is q_2/T_2
- change in entropy of the machine is zero since it comes back to its original state after one cycle: Entropy is a state function of the state variables.
- for an ideal engine

$$dS = \frac{q_2}{T_2} - \frac{q_1}{T_1} = 0$$

- From the first law we have: $q_1 - q_2 = W$
- Therefore $\eta = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1} \qquad \text{QED}$

Entropy then: Thermodynamic entropy

- Thus thermodynamic entropy is simple:
  - It is a measure of that part of energy extracted from a heat source by an irreversible process which can not be converted into work
- The statement $dS \geq 0$ is an assertion .... an AXIOM.
- we call it the Second Law of Thermodynamics
- you can not derive it;
  - of course, for that matter, you can not derive any law of nature
  - the best you can do is to show that one law of nature is based on another
- Ludwig Eduard Boltzmann (1844 - 1906) made one such bold attempt

Boltzmann and his bold attempts

- Boltzmann tried to derive the law of increasing entropy from Newton's laws of motion.
- What are the issues ?
  - Newton's laws are time reversal invariant
  - Thermodynamic or macroscopic behaviour has an arrow of time - the direction of increasing entropy
  - in the synthesis of a macroscopic object from its microscopic constituents, when and why the time symmetry gets broken ?
- Boltzmann did not quite succeed in his attempt to derive time asymmetric macroscopic behaviour from time symmetric microscopic laws.
- But then, his bold, though 'failed' attempts gave rise to a new subject called statistical mechanics and a new definition of entropy ... the STATISTICAL ENTROPY

Boltzmann entropy

$$S = k_B \log \widehat{\Omega}$$

- $\widehat{\Omega}$ denotes the number of microstates of a macroscopic system and $k_B = 1.381$ Joules per Kelvin
- for an isolated system of N non-interacting particles (ideal gas) with energy E confined to a volume V,

$$\widehat{\Omega} = \frac{1}{h^{3N}} \frac{V^N}{N!} \frac{(2\pi m E)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}$$

- Boltzmann liberated entropy from its thermal confines:
  we can define entropy of coin tossing: $S = k_B \log(2)$ (there are two outcomes);
  entropy for the throw of a die: $S = k_B \log(6)$ (there are six outcomes)
- *etc*

microstate and macrostate

- The basic idea behind statistical entropy is as follows:
  - A macroscopic system starts from an arbitrary initial microstate;
  - it goes from one microstate to another dictated by well defined dynamics
  - Given enough time the system visits all possible microstates: ERGODICITY
  - Consider a macroscopic property;
  - to each microstate there corresponds a value of the macroscopic property under consideration;
  - in this sense we can consider the macroscopic property as a random variable
  - let us follow the time evolution of the random variable as the system evolves from an initial microstate

it is natural to seek maximum entropy state

- The macroscopic value changes initially with time
- eventually the system settles down to a unique equilibrium state whence the macroscopic property does not change with time .... except for fluctuations which are inversely proportional to the size of the system. Why ?
- There are overwhelmingly large number of microstates, all of which correspond to the same macroscopic property. Stated simply: Equilibrium corresponds to maximum entropy state.
- Invariably the equilibrium value of the macroscopic property corresponds to to the average value: average of the random variable over the microstates of the equilibrium ensemble

very old notions of entropy

- this picture of the equilibrium state of a macroscopic system is intuitive and appealing.
- Such a notion existed some two thousand years before Boltzmann
- Diogenes Laertius (200 AD): Everything existing in the Universe is the fruit of chance and necessity
- Chance : Entropy and Necessity : Energy
- Look at the following lines from the book de Rerum Natura written by Titus Lucreitus Carus (94 - 55 BC) summarizing the prevailing thoughts besides those of his masters Leucippus (440 BC), Democritus (370 BC) and Epicurus (341 -271 BC).

Leucritus (94 - 55 BC), de Rerum Natura

....

It was certainly not by design that the particles fell into order.
They did not work out what they were going to do,
but because many of them by many chances
struck one another in the course of infinite time
and encountered every possible form and movement,
that they found at last the disposition they have,
and that is how the universe was created.
Particles, kept together for so many years,
when by a chance they had found harmonious movements,
brought it about that rivers flow into the sea
to keep it going, while earth by the heat of the sun
renews its products, and living creatures breed on
and the gliding lights in the sky are never put out.

....

old notions die

- There was no role for God in the scheme of things.
- The view of nature based on chance, necessity and atomism of the very early times was inherently and fiercely atheistic.
- Perhaps this explains why it lost favour and languished into oblivion for over two thousand years.
- Let us get back to the statistical entropy of Boltzmann proposed in the year 1877 in his paper on the relation between the second law of thermodynamics and probability theory with respect to the law of thermal equilibrium Weiner Berischte vol. 76, page 373 (1877)

Boltzmann-Gibbs entropy

- For an isolated system, all microstates are equally probable;
- for a system which is not isolated, the microstates are not equally probable
- Let $\{p_i \; : \; i = 1, \widehat{\Omega}\}$ denote the probabilities of the microstates
- We have the so-called Boltzmann-Gibbs entropy

$$S = -k_B \sum_{i=1}^{\widehat{\Omega}} p_i \log(p_i)$$

- Claude Elwood Shanon (1916 - 2001) was investigating the transmission of information through noisy channels;
- He showed, in the year 1948, that the amount of information contained in a series of events with probabilities $\{p_i\}$ is given by

$$S(p_1, p_2, \cdots, p_N) = -K \sum_i p_i \log p_i$$

  where K is a constant.
- This heralded a new subject called Information Theory
- We call this the Boltzmann-Gibbs-Shanon entropy

Rényi Entropy

- Alfréd Rényi (1921 - 1970) generalized the notion of entropy and defined what we call now as the Renyi entropy given by

$$S = \frac{k}{1-q} \log \sum_i p_i^q$$

  In the above k is constant and q is a real number between $-\infty$ and $+\infty$.

- It is readily seen that Rényi entropy reduces to Boltzmann-Gibbs-Shanon entropy in the limit of $q \to 1$
- Let $Z(q) = \sum_i p_i^q(\epsilon)$ be sum over intervals indexed by i for which the measure $p_i \neq 0$.

- $Z(q)$ is like partition function and q is like inverse temperature.
- we make an ansatz $Z(q) \sim \epsilon^{\tau(q)}$ where $\tau(q)$ is like free energy

$$\begin{aligned} Z(q) &= \sum_i p_i^q(\epsilon) \\ &= \sum_p \rho(p) p^q \\ &= \exp\left[\log \rho(p) \; + q \log(p)\right] \\ &= \rho(p^\star)(p^\star)^q \end{aligned}$$

where $p^\star$ is the value of p for which $\log \rho(p) \; + q \log(p)$ is maximum: Called saddle point method of evaluating integrals

scaling of p and of $\rho(p)$

For convenience let us denote $p^\star$ by p.

$$\begin{aligned} p &\sim \epsilon^{\alpha} \\ \rho(p) &\sim \epsilon^{-f(\alpha)} \end{aligned}$$

Then we get

$$Z(q) \sim \epsilon^{-f(\alpha)+q\alpha} = \epsilon^{\tau(q)}$$

Thus $\tau(q) = -\left[f(q) - q\alpha(q)\right]$ which is negative Legendre transformation. We have

$$\alpha(q) = \frac{d}{dq}\tau(q)$$

- Thus α is like energy and
- $f(\alpha)$ is like entropy.
- This completes the thermodynamics description of multifractals.
- We have what are known as multifractal or Renyi dimension given by

$$D(q) = \frac{\tau(q)}{q-1}$$

origin of statistics in macroscopic evolution

- What is the origin of the stochasticity in description of macroscopic system ?
- What is the origin for statistics in the description of the thermodynamic variable entropy ?
- Is statistics a convenient tool for describing the macroscopic object ?
- Or is there an element of truth in the statistical description ?
- Remember what Einstein said in a different context: Does God play dice ?
- At the root of statistical behaviour lies the element of unpredictability

- We have systems which obey deterministic equations of motion;
- but the time evolution they produce become unpredictable at least at long times.
- Such systems are called chaotic system.
- All systems for which thermodynamic description holds good are chaotic.
- Thus chaos provides the *raison d'etre* for statistical description of deterministic evolution
- this leads to Kolmogrov-Sinai entropy

- Two phase space trajectories of a chaotic system starting off from arbitrarily close phase space points diverge exponentially and become completely uncorrelated asymptotically.
- This means that you can not have any hope of making long term predictions of several properties of the system from deterministic equations if they also happen to be chaotic.
- In other words *determinism does not necessarily imply predictability*.
- Possibility of dynamical instability due to sensitive dependence on initial conditions was known to Poincaré in 1890

Lyapunov exponents

- But the full import of Poincaré's findings was lost on the physicists for over half a century.
- They did not think much of it until computers arrived on their desktops and helped them see on graphic terminals, the strange attractors traced by low dimensional, nonlinear, dissipative chaotic systems
- A standard way of determining whether or not a nonlinear dynamical system is chaotic is to calculate the Lyapunov exponents
- There are as many . Lyapunov exponents as the dimensions of the phase space in which the dynamics takes place.

- Let us concentrate on a dynamical system in an n-dimensional phase space.
- Consider an n - dimensional sphere of initial conditions.
- You can visualize them as a dust of phase space points occupying an n-dimensional sphere.
- With the passage of time each phase space point (*i.e.* each dust particle) moves deterministically.
- The sphere of phase space points shall sweep the phase space and occupy a different region in the phase space at a later time.
- In other words, the cloud sweeps through and moves to another region changing, in general, its volume and shape during the process

folding and divergence of dynamical trajectories

- For an Hamiltonian system the volume - *i.e* the volume occupied by the phase space points of initial conditions - remains constant.
- This is due to Liouville theorem.
- If the system is dissipative, the volume decreases with time and eventually becomes zero.
- However, in general, the shape changes, for both Hamiltonian and dissipative dynamics
- For chaotic systems the shape change can be rather weird. The cloud sort of thins out and begins to cover regions rather sparsely.

spectrum of Lyapunov exponents

- Let us consider dynamical evolution over a duration of time τ.
- In general the n - dimensional sphere would evolve into an n - dimensional ellipsoid.
- Let the diameter of the initial sphere be d.
- Let $\{d_i(\tau)\ : i = 1, n\}$ denote the major axes of the ellipsoid at time τ.
- We arrange them in a descending order:

$$d_n \le d_{n-1} \le \cdots \le d_2 \le d_1.$$

- The Lyapunov exponents are defined as,

$$\lambda_i = \frac{1}{\tau} \log \left(\frac{d_i(\tau)}{d} \right), \tag{1}$$

  in the limit $d \to 0$ and $\tau \to \infty$.
- The above equation defines local Lyapunov exponents. Figure depicts a circle of initial conditions evolving into an ellipse over an interval of time τ.

sphere morphs into an ellipsoid

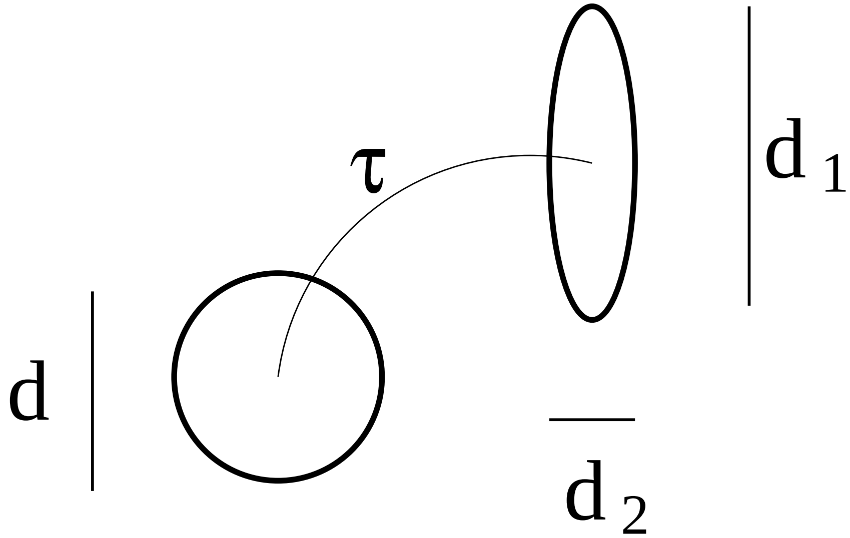

Figure 1: Illustration for understanding Lyapunov exponents

- A way to calculate the Lyapunov exponents consists of linearizing the evolution equations at a point on a trajectory and determine the $n \times n$ stability matrix which describes the local exponential separation rates along the eigenvectors.
- Lyapunov exponents can be calculated from the corresponding eigenvalues.
- The Lyapunov exponents can be in general positive or negative or zero: some of them can be positive and some, negative and at least one zero.
- The eigenvectors corresponding to positive Lyapunov exponents indicate directions of expansion while the eigenvectors corresponding to the negative ones indicate directions of contraction.

- The dynamical system will be highly unstable along expanding directions in the phase space and highly stable along directions of contraction.
- If $\delta V_n(0)$ is the volume of the sphere of initial conditions at a phase space point $\vec{x_0}$, then due to dynamical evolution over time τ it becomes

$$\delta V_n(\tau) = \delta V_n(0)\exp[(\lambda_1 + \lambda_2 + \cdots \lambda_n)\tau]. \qquad (2)$$

- We can average the local Lyapunov exponents over the strange attractor and calculate global Lyapunov exponents.
- When we talk of a single Lyapunov exponent we always mean the largest one, denoted by λ_1.

- The dynamical system is chaotic if the largest Lyapunov exponent is positive.
- Lyapunov exponents help quantify the predictive capabilities of deterministic (nonlinear and chaotic) equations.
- Let us suppose that we can specify the initial conditions with a precision $\epsilon_{\mathbf{I}}$.
- Also suppose we are required to predict the phase space variables with a precision say $\epsilon_{\mathbf{F}}$.
- We can make such predictions only up to time $t < t_{\mathbf{L}}$, given by,

$$t_{\mathbf{L}} \sim \frac{1}{\lambda_1} \log\left(\frac{\epsilon_{\mathbf{F}}}{\epsilon_{\mathbf{I}}}\right). \tag{3}$$

determinism does not imply predictability

- The predictions become imprecise beyond $t_{\mathbf{L}}$.
- If we want to make precise predictions beyond $t_{\mathbf{L}}$, then we have to specify more precisely the initial conditions.
- For systems with many degrees of freedom this difficulty of prediction becomes all the more acute because of the dimensionality of the phase space.
- Initial error is amplified in each unstable phase space direction (eigenvector) at rates given by the corresponding (positive) Lyapunov exponent (eigenvalue).
- Therefore precision required on the initial conditions should be increased at a rate proportional to the sum of positive Lyapunov exponents

Kolmogrov - Sinai entropy

- the sum of positive Lyapunov exponents is usually called as Kolmogrov Sinai entropy
- We can say asymptotically the system becomes unpredictable.
- In other words, the system becomes amenable to a statistical description.
- We recognize thus, that at least in principle, Chaos provides *raison d'etre* for statistics in statistical mechanics.
- All systems that obey the laws of . thermodynamics are chaotic.
- Nonlinear dynamics and chaos provide the link between deterministic micro and stochastic macro

Tsallis Entropy

- Constantino Tsallis proposed in the year 1988, proposed an entropy given by

$$S = k\frac{1 - \sum_i p_i^q}{q - 1}$$

where the microstates are indexed by i and their corresponding probabilities are given by p_i.

- in the limit $q \longrightarrow 1$, we recover the Boltzmann - Gibbs - Shannon entropy
- Tsallis entropy is not extensive.
- Like Gaussian is natural to Boltzmann-Gibbs-Shannon entropy, Levy distributions are natural to Tsallis entropy

- There are several entropies I have not discussed here
- these include
  - Brillouin - Schrödinger Negentropy
  - Fisher entropy
  - von Neumann entropy
  - Algorithmic entropy
  - Ruelle - Bowen- Sinai (RBS) entropy
  - Kaniadakis entropy
  - and many more ......

and

THANKS