Abstract

Ludwig Boltzmann had a hunch that irreversibility exhibited by a macroscopic system arises from the reversible dynamics of its microscopic constituents. He derived a nonlinear integro-differential equation - now called the Boltzmann equation - for the phase space density of the molecules of a dilute fluid. He showed that the Second law of thermodynamics emerges from Newton’s equations of motion. However Boltzmann realized that stosszahlansatz, employed in the derivation, smuggles in an element of stochasticity into the transport equation. He then proposed a fully stochastic description of entropy which laid the foundation for statistical mechanics. Recent developments, embodied in different fluctuation theorems, have shown that Boltzmann’s hunch was, in essence, correct.
Everything existing in the Universe is the fruit of chance and necessity

Diogenes Laertius IX
1 Prologue

The Boltzmann transport equation has played an important role in basic and applied sciences. It is a nonlinear integro-differential equation for the phase space density of the molecules of a dilute gas. It remains today, an important theoretical technique for investigating non-equilibrium systems. It was derived by Ludwig Eduard Boltzmann (1844 - 1906) in his further studies on thermal equilibrium between gas molecules [1], published in the year 1872. Boltzmann did this work solely for purpose of addressing the conflict between time-reversal-invariant Newtonian mechanics and time-arrowed thermodynamics. Linear version of this equation [2] provides an exact description of neutron transport in nuclear reactor core and shields. Linear transport equation constitutes the backbone of nuclear industry. It is indeed appropriate that the Indian Society for Radiation Physics (ISRP) has chosen Boltzmann transport equation as focal theme for the sixteenth National Symposium on Radiation Physics (NSRP-16), in Meenakshi College for Women, Chennai during January 18 - 21, 2006. The year 2006 marks the hundredth anniversary of Boltzmann’s death.

There are going to be several talks [3] in this symposium, covering various aspects of linear transport equation. However, in this opening talk, I shall deal with nonlinear transport equation. I shall tell you of Boltzmann’s life-long struggle for comprehending the mysterious emergence of time asymmetric behaviour of a macroscopic object from the time symmetric behaviour of its microscopic constituents. In the synthesis of a macro from its micro, why and when does time reversal invariance break down? This is a question that haunted the scientists then, haunts us now and most assuredly shall haunt us in the future, near and far.

The Second law is about macroscopic phenomena being invariably time asymmetric; it is about
macroscopic behaviour being almost always irreversible \(^1\). Physicists think the Second law can not be derived from Newton’s equations of motion. According to them, the Second law must be a consequence of our inability to keep track of a large number, typically of the order of \(10^{23}\) or more, of molecules. In other words, the origin of the Second law is statistical. It is one thing if statistics is used merely as a convenient descriptor of a macroscopic phenomenon. It is quite another thing if we want to attribute an element of truth to such a description. Is it conceivable that nature is deterministic at micro level and stochastic at macro level? Can (microscopic) determinism give rise to (macroscopic) unpredictability? Boltzmann thought so.

Boltzmann believed that the Second law is of dynamical origin. He proved it through his transport equation and H-theorem. At least he thought he did. Several of his fellow men thought otherwise. It is this fascinating story of the Second law that I am going to narrate to you in this talk. I am going to tell you of the insights that Boltzmann provided through his early work on transport equation and his later work that laid the foundation for Statistical Mechanics - a subject that aims to derive the macroscopic properties of matter from the properties of its microscopic constituents and their interactions. I am also going to tell you of nonlinear dynamics and chaos, subjects that have completely changed our views about determinism, dynamics and predictability. Now we know that determinism does not necessarily imply predictability. There are a large number of systems that exhibit chaotic behavior. Chaos and hence unpredictability is a characteristic of dynamics. Thus, Boltzmann’s hunch was, in essence, right. It was just that he was ahead of his time.

Boltzmann staunchly defended the atomistic view. He trusted atoms [4]. He was of the opinion that atomistic view helps at least comprehend thermal behaviour of dilute fluids. But the most

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\(^1\)Deterioration, dissipation, decay and death characterize macroscopic objects and macroscopic phenomena. A piece of iron rusts; the reverse happens never. A tomato rots, inevitably, invariably and irreversibly. An omelet is easily made from an egg; never an egg from an omelet.

The physicists are puzzled at the Second law. How does it arise? An atom - the constituent of a macroscopic object, obeys Newton’s laws. Newtonian dynamics is time reversal invariant. You can not tell the past from the future; there is the determinism - the present holding both, the entire past and the entire future. The atoms, individually obey the time reversal invariant Newtonian dynamics; however their collective behaviour breaks the time symmetry.

The philosophers are aghast at the implications of the Second law. Does it hold good for the Creator? They are upset at the Second law since it spoils the optimism and determinism implicit in for example in the verse below from Bhagavat Gita, an ancient text from the Hindu Philosophy:

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Whatever happened, it happened
for good.
Whatever is happening, is
happening for good.
Whatever that will happen, it will
be for good.
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Omar Khayyam surrenders to the irreversibility of life when he writes,

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The Moving Finger writes; and, having writ,
Moves on: nor all your Piety nor Wit
Shall lure it back to cancel half a Line,
Nor all your Tears wash out a Word of it.
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Bernard Shaw, frustrated with the Second law, exclaims *youth is wasted on the young*. Mark Twain hopes fondly for Second law violation when he wonders *life would be infinitely happier if only we could be born at eighty and gradually approach eighteen.*
influential and vociferous of the German-speaking physics community - the so-called energeticists, led by Ernst Mach (1838 - 1916) and Wilhelm Ostwald (1853 - 1932) did not approve of this. For them, energy was the only fundamental physical entity. They dismissed with contempt any attempt to describe energy or transformation of energy in more fundamental atomistic terms or mechanical pictures. This lack of recognition from the members of his own community allegedly led Boltzmann to commit suicide \(^2\). Ironically, Boltzmann died at the dawn of the victory of the atomistic view. For, in the year 1905, Albert Einstein (1879 - 1955) established unambiguously the reality of atoms and molecules in his work [5] on Brownian motion.

2 On the nature of things

It all started with our efforts to understand the nature of matter, in general and of heat, in particular. Ancient man must have definitely speculated on the possibility of tiny, invisible and indivisible particles assembling in very large numbers into a visible continuum of solids and liquids and an invisible continuum of air that surround us. The Greeks had a name for the tiny particle: *atom* - the uncuttable. According to Leucippus (440 B.C.) and his student Democritus (370 B.C.) atom moves in void, unceasingly and changing course upon collision with another atom. Titus Lucretius Carus (99 B.C. - 55 B.C.) mused on the nature of things \(^3\). According to him all the phenomena we see around are caused by invisible atoms moving hither and thither \(^4\). There was no role for God in his scheme of things. Atomism of the very early times was inherently and fiercely atheistic. Perhaps this explains why it lost favour and languished into oblivion for several centuries.

3 Revival of Atomistic view

The revival came with the arrival of Galileo Galilei (1564-1642) who wrote in the year 1638, of the air surrounding the earth and of its ability to stand thirty four feet of water in a vertical tube closed at the top with the open bottom end immersed in a vessel of water. He also knew of air expanding upon heating and invented a water-thermo-graph (thermometer). A few years later, his student

\[^2\]Boltzmann enjoyed the respect of all his colleagues. Rejection of his ideas by the energeticists does not seem to be the only reason or even one of the reasons that drove him to his tragic end. Men like myths. Men like heroes. Scientists are no exception. Scientists need heroes - tragic or otherwise. Boltzmann is one such.

\[^3\]Lucretius wrote a six books long poem called *De Rerum Natura* (On the Nature of Things) on atomism. He writes of

\[\begin{align*}
&\text{clothes hung above a surf-swept shore} \\
&\text{grow damp; spread in the sun they dry again.} \\
&\text{Yet it is not apparent to us how} \\
&\text{the moisture clings to the cloth, or flees the heat.} \\
&\text{Water, then, is dispersed in particles,} \\
&\text{atoms too small to be observable.....}
\end{align*}\]

\[^4\]The atoms are

\[\begin{align*}
&\text{... shuffled and jumbled in many ways, in the course} \\
&\text{of endless time they are buffeted, driven along} \\
&\text{chancing upon all motions, combinations.} \\
&\text{At last they fall into such an arrangement} \\
&\text{as would create this universe....}
\end{align*}\]
Evangelista Torricelli (1608-1647) correctly concluded of air pressure and surmised that mercury, fourteen times heavier, would rise in the tube only up to thirty inches. He showed it experimentally. Blaise Pascal (1623 -1662) was quick to point out that Torricelli’s reasoning would imply that the pressure of air on top of a mountain should be less, which was also verified through experiments in 1648. Daniel Gabriel Fahrenheit (1686 - 1736) invented the mercury thermometer and the Fahrenheit scale of temperature in the year 1714. Andres Celsius (1701-1744) invented the centigrade or Celsius scale of temperature in the year 1742. Robert Boyle (1627 - 1691) carried out numerous experiments on the static and kinetic nature of air pressure and showed that the product of pressure and volume of a given amount of air remains constant if the temperature is also kept constant. This is called Boyle’s law. Boyle modeled air as a collection of springs that resist compression (which explains air - pressure) and expands into available space. Guillaume Amontons (1663 - 1705) experimented on expansion of gases with increase of temperature under constant pressure. He proposed an absolute zero of temperature at which, volume of a gas becomes zero at constant pressure or the pressure becomes zero under constant volume. The absolute zero temperature calculated from Amontons’ experiments turned out to be \(-248^\circ \text{C}\). But nobody took notice of the Amontons’ suggestion of an absolute temperature scale and absolute zero of temperature. Another important work carried out in the early eighteenth century was that of Daniel Bernoulli (1700 - 1782), who gave a derivation of Boyle’s law from his billiard ball atomic model. Bernoulli’s billiard ball atom moves freely in space, colliding with other billiard ball atoms and with the walls of the container. Bernoulli interpreted gas pressure as arising due to numerous impacts the billiard ball atoms make with the walls of the container.

4 Caloric Theory

Despite these remarkably insightful work, both experimental and theoretical, carried out in the seventeenth and early eighteenth century, kinetic theory did not take off. Scientists could not simply comprehend heat as arising out of atomic motion: be it undulating motion around fixed position, like Boyle imagined or free motion in the available space of the container, like Bernoulli modeled. This difficulty is perfectly understandable since it was known that heat could be transmitted through vacuum, like for example, the heat from the sun. Hence, heat can not be a property of a substance; it has to be a substance by itself. Antoine Lavoisier (1743 - 1794) gave the name Calorique (or in English Caloric) to this fluid substance. In fact the French chemists included Calorique as one of the elements in the list prepared in the late eighteenth century. Caloric fluid always flowed from higher to lower temperatures. Heat engines that produced locomotion from burning of coal started dotting the European country side.

\[5^5\text{Boyle got the idea from the paper of Richard Townley (1638 - 1707) describing the work Townley carried out with Henry Power, see S. G. Brush [8] Book 1; p.12.}\]

\[6^6\text{A century later, Jacques Alexandre César Charles (1746 - 1823) and Joseph Louis Gay-Lussac (1778 - 1850) established the law of thermal expansion of gases as we know of it today: The pressure (at constant volume) or the volume (at constant pressure) is proportional to } T + \alpha, \text{ where } T \text{ is the temperature measured in some scale say Fahrenheit or Celsius; } \alpha \text{ is a constant that depends on the scale chosen for } T. \text{ We can define } T + \alpha \text{ as absolute temperature whose zero will be lowest attainable temperature; in the scale chosen for measuring } T \text{ the lowest attainable temperature is thus } -\alpha. \text{ In fact the notion of absolute scale and absolute zero of temperature got the acceptance of the scientific community only after William Thomson (Kelvin) proposed it [20] in the year 1848 based on Carnot engine i.e. the Second law: the partial derivative of entropy with respect to energy gives the inverse of absolute temperature.}\]
5 Carnot’s Engine and Caloric heat

Nicolas Leonard Sadi Carnot (1796 - 1832) was investigating why a French heat engine delivered invariably less work than its British counterpart. Carnot was intrigued by the very idea of a heat engine which manages to do what even the almighty Nature could not: A heat engine converts heat into movement. In nature you find that it is the movement which due to friction generates heat and never the other way. There is no phenomenon like un-friction or anti-friction which would spontaneously re-assemble the heat back into a movement. Thinking along these lines Carnot came to the conclusion [10] that mere production of heat is not sufficient to give birth to the impelling power; it is necessary there should be cold; without it, heat is useless. Thus the work produced should depend on the temperature difference between the boiler (heat source) and the radiator (the heat sink). This is a remarkable finding. The heat engine is like a mill wheel. A mill wheel simply extracts work from falling water. Larger the quantity of water and higher the fall, more is the work produced in the mill wheel. Analogously, larger the heat source and higher the temperature fall, more is the work produced in the heat engine. If a certain quantity $q$ of caloric falls from absolute temperature $T_1$ to zero, then the work produced will be $W = q$; since it falls only to a finite temperature $T_2$ ($0 < T_2 < T_1$), only the proportional fraction of $q$ should equal the work produced.

In the year 1824, Carnot announced in his historic treatise [10] entitled, Reflexions on the motive power of fire and on machines to develop that power, that the ratio of work (W) delivered by a heat engine to the heat (q) generated in the boiler at temperature $T_1$, is given by

$$\eta = \frac{W}{q} = \frac{T_1 - T_2}{T_1} < 1 \text{ for } 0 < T_2 < T_1 < \infty,$$

where $T_2$ is the temperature of the heat sink (the radiator). Even ideally, a heat engine can not have unit efficiency. The best you can get is Carnot’s efficiency given by Eq. (1). When Carnot measured the actual work delivered by a heat engine it was much less than what his formula suggested. Real-life heat engines have moving parts that rubbed against each other and against other parts; the resulting friction - which produces heat from work - is thus completely antagonistic to the heat engine which is trying to produce work from heat. Not surprisingly a practical engine is less efficient than Carnot’s ideal engine. In fact Carnot’s engine is a double idealization: its efficiency is less that unity since it is not realistic to set $T_2$ to zero; it should also work without friction which is not practical either.

Carnot’s picture of a heat engine is completely consistent with the Caloric theory of heat. In fact it constitutes a triumph of the Caloric theory. Water that rotates the mill wheel is never consumed. Likewise the Caloric fluid that powers the heat engine is never destroyed. In the radiator the Caloric fluid is reabsorbed in the water and returned to the boiler for conversion to steam again.

It looked like the Caloric theory had come to stay for good. It was becoming immensely and increasingly difficult for the kinetic heat to dethrone the Caloric heat and regain its lost and forgotten glory. A sense of complacency started prevailing amongst the scientists at that time. There arose a certain reluctance to accept new ideas. It often happens in science: when a scientific theory is confirmed and firmly established, it loses its character and becomes a dogma; the practitioners of the theory become dogmatic.
6 The tragedy of Herpath and Waterston

Consider the manuscript of John Herpath (1790-1868) submitted in the year 1820, containing new ideas on kinetic theory of heat. Herpath, unaware of Bernoulli’s work, proposed an atomic model for the gas; he said heat is proportional to total momentum of the molecules of gas and absolute temperature corresponds to momentum per gas molecule. Herpath’s work was found to be too speculative. The Royal Society did not find it fit to publish it in their Philosophical Transactions. Obviously the reviewers were also unaware of the work of Bernoulli.

The same fate awaited the brilliant work scripted by John James Waterston (1811 - 1883), then at Bombay (now called Mumbai) and submitted in the year 1845, to the Royal Society. Waterston’s model of gas contained molecules moving incessantly and colliding with each other and with the walls of the container. Waterston correctly identified the temperature as measuring the energy of motion of the molecules. One of the two reviewers considered Waterston’s work as ‘nothing but nonsense’. The other reviewer was less harsh. He wrote that Waterston’s suggestion that the pressure is due to molecular impacts on the walls of the container was ‘extremely hypothetical and difficult to admit’. The manuscript was rejected and buried in the archives of the Royal Society. Much later, in the year 1891, John William Strutt (Lord) Rayleigh (1842 - 1919) stumbled on the 1845-manuscript of Waterston; to his astonishment he found it contained essentially the same ideas proposed by August Karl Krönig (1822 - 1879) in 1856 [12] and by Rudolf Julius Emmanuel Clausius (1822 - 1888) in the year 1857 and in the later years. He got Waterston’s manuscript published [13] in the Philosophical Transactions of the Royal Society, in the year 1893.

7 Experimental evidence against Caloric heat

But then there were significant developments in experimental thermal physics that started knocking at the very foundations of the Caloric theory.

In the year 1798, Benjamin Thompson Rumford (1753 - 1814) noticed [14] that a canon became hot while boring. The heat it generated was sufficient to melt the canon. This means that the Caloric fluid produced is more than what was originally contained in the canon. This is not possible under Caloric theory. Julius Robert von Mayer (1814 - 1878), in the year 1840, came to the same conclusion [15] that heat is like mechanical energy. The paddle wheel experiment of James Prescott Joule (1818 - 1889) [16] carried out in the year 1845 established the mechanical equivalence of heat\(^7\). These experiments of Rumford, Mayer and Joule, thus established unambiguously that the Caloric theory of heat was wrong and heat, like work, is actually energy or more precisely energy in transit, see section 15.1. Once we identify heat with energy, Carnot’s finding becomes intriguing. Why?

The first law of thermodynamics\(^8\) tells us, energy can neither be created nor destroyed. However energy can be converted from one form to the other. Carnot’s finding amounts to saying that heat energy can not be converted completely into mechanical energy whereas mechanical energy

\(^7\)1 Calorie = 4.184 Joules where Joule is the SI unit of energy denoted by the symbol J and given by, 1 J=1Kg. M^2/sec^2.

\(^8\)This principle of conservation of energy, called the first law of thermodynamics, was proposed independently by several scientists in the middle of the nineteenth century, notable amongst them are Mayer [15], Joule [16, 17] and Helmholtz [18].
can be completely converted into heat. There is a kind of thermodynamic irreversibility. In the (first-) law abiding democratic society of energies, heat occupies a special place. Perhaps it is like what Bernard Shaw said: *In a democracy, all men are equal but some are more equal than others.* There is an apparent injustice in nature’s scheme.

Nobody took notice of Carnot’s work for over two decades. Benoit Paul Emilie Clapeyron (1799 - 1864) felt that Carnot had discovered something profound. He provided the required physical and mathematical scaffolding which caught the attention of William Thomson (Kelvin) (1824 - 1907) and Clausius. Kelvin proposed an absolute temperature scale based on Carnot’s engine.

## 8 Clausius invents Entropy

Clausius was intrigued by Carnot’s finding. He felt that Carnot’s basic conclusion is correct and also considered it as of great fundamental importance. He called it the Second law of thermodynamics. But then he rejected Carnot’s reasoning based on Caloric theory of heat. From the experiments of Rumford, Mayer and Joule, he understood that heat and work are simply two different forms of energy transfer, see section 15.1. He had known by then that heat was a kind of motion. To explain Carnot’s finding in the context of this emerging picture, Clausius invented a new thermodynamic variable. His reasoning was simple.

Consider a thermodynamic process described by a path in an appropriate phase space of thermodynamic variables like internal energy \((E)\), volume \((V)\), pressure \((P)\), temperature \((T)\), number of molecules \((N)\), chemical potential \((\mu)\) etc. During the process, the system absorbs or liberates energy in the form of heat \((Q)\) and/or work \((W)\). Both \(dQ\) and \(dW\) are path-dependent. Hence they are not state variables. In other words \(dQ\) and \(dW\) are not perfect differentials. However \(dW = PdV\). Inverse of pressure provides integrating factor for work. Clausius discovered that inverse of temperature provides integrating factor for heat. The quantity \(dQ/T\) turned out to be a perfect differential. Clausius denoted this perfect differential by the symbol \(dS\). There was no known thermodynamic state variable, whose perfect differential corresponded \(dS\). Clausius, in his 1865 paper, named the state variable \(S\) in \(dS = dQ/T\) as entropy. Let me quickly illustrate this on a simple example.

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9Ginsberg’s restatement of the three laws of thermodynamics:

First law : You can’t win;
Second law : You can’t even break even;
Third law : You can’t even quit.

10The isotherms and the adiabats in the pressure - volume phase diagram (describing Carnot’s engine) that you find in text books on thermodynamics were actually drawn by Clapeyron.

11The cross on \(d\) denotes they are not perfect differentials.

12in the words of Clausius ... *We now seek an appropriate name for \(S\). .... We would call \(S\) the transformation content of the body. However I have felt it more suitable to take names of important scientific quantities from the ancient languages in order that they may appear unchanged in all contemporary languages. Hence I propose that we call \(S\) the entropy of the body after Greek word ‘\(\eta\)τροπη’, meaning ”transformation”. I have intentionally formed word entropy to be as similar as possible to the word energy, since the two quantities that are given these names are so closely related in their physical significance that a certain likeness in their names has seemed appropriate.*
Start with the first law of thermodynamics,

\[ dU = dQ + d\bar{W} \]  

(2)

Consider an ideal gas to which energy in the form heat is supplied at constant volume; its internal energy increases by \( dU = C_V dT \), where \( C_V \) is the specific heat at constant volume. The ideal gas law is given by \( PV = \Theta T \), where \( \Theta \) is a constant. From this we get

\[ dV = \Theta \left[ \frac{1}{P} dT - \frac{T}{P^2} dP \right] = 0. \]  

(3)

The work done \((-P dV = 0\) is given by

\[ dW = \Theta \left[ \frac{T}{P} dP - dT \right] = 0. \]  

(4)

Therefore we have,

\[ dQ = (C_V + \Theta) dT - \Theta \frac{T}{P} dP. \]  

(5)

Let us investigate if \( dQ \) is a perfect differential. From the above, we have

\[ \frac{\partial Q}{\partial T} = C_V + \Theta, \]  

(6)

\[ \frac{\partial Q}{\partial P} = -\Theta \frac{T}{P}. \]  

(7)

Differentiating once more we get,

\[ \frac{\partial^2 Q}{\partial P \partial T} = 0 \]  

(8)

\[ \frac{\partial^2 Q}{\partial T \partial P} = -\frac{\Theta}{P}. \]  

(9)

Therefore,

\[ \frac{\partial^2 Q}{\partial P \partial T} \neq \frac{\partial^2 Q}{\partial T \partial P}, \]  

(10)

showing that \( dQ \) is not a perfect differential and \( Q \) is not a state function of \( P \) and \( T \). We shall cross the ‘\( d \)’ to denote this.

Consider now, the quantity \( dS = dQ/T \), obtained by dividing all the terms in Eq. (5) by \( T \). We have,

\[ \frac{\partial S}{\partial T} = \frac{C_V + \Theta}{T}, \]  

(12)

\[ \frac{\partial S}{\partial P} = -\frac{\Theta}{P}. \]  

(13)
It is easily seen that
\[
\frac{\partial^2 S}{\partial P \partial T} = \frac{\partial^2 S}{\partial T \partial P} = 0,
\]  
(14)
demonstrating that \( S \) is a state function. Clausius gave the name entropy to this state function. Thus for the very definition of entropy, we need a thermodynamic process that can be represented by a path in the space of state variables. We call this a quasi-static process, described below.

8.1 Quasi-static processes

Consider a macroscopic system in equilibrium e.g. a gas in a cylinder fitted with a piston. Let \( \Lambda \) be a degree of freedom which can be manipulated from outside. For example \( \Lambda \) can be taken as volume of the gas which can be changed by moving the piston. Consider a thermodynamic process in which we switch the value of \( \Lambda \) from say \( \Lambda_0 \) to \( \Lambda_\tau \) over a duration of time \( \tau \). This switching can be carried out with some pre-determined protocol. For example we can change \( \Lambda \) uniformly. We say the process becomes quasi-static when the switching takes place extremely slowly. Strictly for a quasi-static process \( \tau \) equals infinity. It is a process of slow stepping through equilibrium states. At each step the state variables assume the relationship given by equation of states; the system is sort of dragged through a set of dense succession of equilibrium states. A quasi-static process can not be realized in practice. At best we can approximate it by an extremely slow process. A quasi-static process is reversible if it takes place at constant total entropy. In other words during a quasi-static process the change in entropy of the system plus the change in the entropy of the surroundings equals zero.

8.2 The Second law: \( dS \geq 0 \)

For defining entropy, Clausius considers a quasi-static reversible process. During the process the system absorbs a quantity \( dQ_{\text{rev}} \) of reversible heat, from a heat source at temperature \( T \). The entropy of the system increases by an amount given by,
\[
dS = \frac{dQ_{\text{rev}}}{T}. 
\]  
(15)
Since the process is quasi-static and reversible, the entropy of the heat source decreases by precisely the same amount so that the total change in entropy is zero.\(^{13}\)

Consider an isolated system and let \( dS \) denote the change in entropy of the system during a process. If the system is not isolated, then \( ds \) denotes the change in entropy of the system plus the change in entropy of its surroundings. Clausius states the Second law as,
\[
dS \geq 0,
\]  
(16)
in any thermodynamic process. In the above, equality obtains when the process is quasi-static and reversible. With this Second law assertion, Clausius was able to show that the efficiency of any heat engine is less than or equal to that of Carnot’s engine, see below.

\(^{13}\)For the definition of entropy the reversibility of the quasi-static process is only a sufficient condition but not necessary; the necessary condition is that the process should be quasi-static.
9 Kinetic heat replaces Caloric heat in Carnot’s engine

Consider an engine, M, which, operating in a cycle, draws a quantity \( q_1 \) of energy in the form of heat quasi-statically and reversibly from a heat reservoir (R) at temperature \( T_1 \). Let us say the engine converts the entire heat \( q_1 \) into work \( W \) and returns to its initial state. Such an engine is called a perfect engine, shown in Fig. (1). Under the first law of thermodynamics it is possible, in principle, to construct a perfect engine. Let us investigate what happens when we impose the Second law. The change in entropy of the heat source is \( -\frac{q_1}{T_1} \). Since the engine returns to its initial thermodynamic state there is no change in its entropy. We just saw that entropy is a state function. Thus, the total change in the entropy is \( dS = -\frac{q_1}{T_1} \). The Second law demands that \( dS \geq 0 \). The machine can not deliver work. Second law forbids perfect engines. However, the engine can convert mechanical energy \( W \) completely into heat, since during such a process \( dS > 0 \).

Consider now an ideal engine M, shown in Fig. (2). It draws a quantity \( q_1 \) of energy in the form of heat, quasi-statically and reversibly from a source, R, kept at temperature \( T_1 \); it converts a part of it into work; it junks the remaining part \( q_2 < q_1 \) into a sink (S), kept at temperature \( T_2 < T_1 \); then it returns to the state it started with.

![Fig 1: Perfect Engine](image)

From the first law we have \( q_1 - q_2 = W \). The efficiency of the engine is given by, \( \eta = \frac{W}{q_1} = 1 - \frac{q_2}{q_1} \). The change in entropy of the heat source is \( -\frac{q_1}{T_1} \) and that of the sink is \( \frac{q_2}{T_2} \). Since the machine returns to its initial state its entropy does not change. Therefore we have,

\[
dS = \frac{q_2}{T_2} - \frac{q_1}{T_1}.
\] (17)

The Second law demands that \( dS \geq 0 \). For an ideal engine \( dS = 0 \). Therefore, for an ideal engine \( \frac{q_2}{q_1} = \frac{T_2}{T_1} \), from which we get \( \eta = 1 - \frac{T_2}{T_1} \), a result identical to what Carnot obtained for his Caloric fluid, see Eq. (1).
This is precisely how the Caloric heat became kinetic heat in Carnot’s engine. If heat is kinetic \textit{i.e.} motion, then what kind of motion is it? It must be the irregular motions of the gas molecules; for, the regular motion is already described by work given in terms of pressure and change of volume. Entropy, which is heat divided by temperature must be a measure of this irregularity of molecular motions; a measure of disorder; a measure of randomness. James Clerk Maxwell (1831 - 1879) asserted that the very Second law that talks of increasing entropy, must be statistical in character; hence it should be possible to contravene the Second law with non zero probability. He even proposed a demon - now called Maxwell’s demon - that violates the Second law \textsuperscript{14}. For Maxwell, stochasticity was intrinsic to macroscopic behaviour \textsuperscript{15}.

\textsuperscript{14} For an interesting account of Maxwell’s demon and other demons, see [24].

\textsuperscript{15} Maxwell was amongst the first to recognize the need for statistical approach to kinetic theory. In fact his derivation of the distribution of speed of the molecules of an ideal gas is ingenious and elegant, see [25]. He assumes that the three components \((v_1, v_2, v_3)\), of the velocity \(\vec{v}\) of an ideal gas molecule are independent and identically distributed: \(f(v_1, v_2, v_3) = f(v_1)f(v_2)f(v_3)\), where \(f\) is the density of molecules in the velocity space. He argues that since there is no preferred direction of motion the function \(f\) must depend only on \(v_1^2 + v_2^2 + v_3^2\); this leads to functional equation: \(f(v_1)f(v_2)f(v_3) = \phi(v_1^2 + v_2^2 + v_3^2)\) whose solution is the famous Maxwell-Boltzmann distribution of molecular speed,

\[
f(v) = 4\pi \left( \frac{2\pi k_B T}{m} \right)^{-3/2} v^2 \exp \left[ -\frac{mv^2}{2k_B T} \right]
\]

that we are all familiar with. In the same paper [25], Maxwell correctly recognizes that the Maxwell-Boltzmann distribution is a simple consequence of Central Limit Theorem concerned with additive random variables, see footnote (30).
10 Boltzmann Transport Equation

However Boltzmann, at least in his early years, felt there was no need to invoke statistics to comprehend the Second law. At the age of twenty two, Boltzmann wrote on the mechanical meaning of the Second law of the theory of heat [23]. Of interest to us is Boltzmann’s paper [1] published in the year 1872 in which he derived his transport equation and in which he also announced the $H$ theorem to prove the Second law. Boltzmann considers the density $f(\vec{r}, \vec{p}, t)$ of molecules, each of mass $m$, at the six-dimensional phase space point $(\vec{r}, \vec{p})$, and at time $t$. Aim is to find an equation (of motion) for this function. The density changes with time since molecules enter and leave a given six dimensional phase space volume element $d^3r d^3p$ at the phase space point $(\vec{r}, \vec{p})$.

Let $\vec{F}$ denote an external force (e.g. due to gravitation) acting on the molecules. Suppose there are no collisions. A molecule at $(\vec{r}, \vec{p})$ at time $t$ will be found at $(\vec{r} + \vec{p} \Delta t/m, \vec{p} + \vec{F} \Delta t, t + \Delta t)$ at time $t + \Delta t$. Hamiltonian evolution preserves volume element $d^3r d^3p$ along a trajectory, called Liouville theorem 17. Therefore,

$$f(\vec{r} + \frac{\Delta t}{m}, \vec{p} + \vec{F} \Delta t, t + \Delta t) = f(\vec{r}, \vec{p}, t).$$  \hspace{1cm} (18)

When there are collisions, we must add the contribution from collisions and write 18,

$$f(\vec{r} + \frac{\Delta t}{m}, \vec{p} + \vec{F} \Delta t, t + \Delta t) = f(\vec{r}, \vec{p}, t) + \left( \frac{\partial f}{\partial t} \right)_{\text{Col.}} \Delta t. \hspace{1cm} (19)$$

Taylor-expanding to first order in $\Delta t$ and taking the limit $\Delta t \rightarrow 0$ we get,

$$\frac{\partial f}{\partial t} = -\frac{1}{m} \vec{p}. \nabla_r f - \vec{F}. \nabla_p f + \left( \frac{\partial f}{\partial t} \right)_{\text{Col.}},$$  \hspace{1cm} (20)

where $\nabla_r$ and $\nabla_p$ are the gradient operators with respect to position and momentum, respectively. Boltzmann proposes a simple model for the collision term, see below.

Consider only binary collisions, true for a dilute gas, where a pair of molecules with momenta $\vec{p}_1$ and $\vec{p}_2$ bounce off, after a collision, with momenta $\vec{p}'_1$ and $\vec{p}'_2$, respectively. Let $f(\vec{r}, \vec{p}_1, \vec{p}_2, t)$ denote the density of pairs of particles with momenta $\vec{p}_1$ and $\vec{p}_2$ at position $\vec{r}$ and at time $t$.

10.1 Stosszahlansatz

Boltzmann invokes stosszahlansatz - collision number assumption - of Maxwell, which states,

$$f(\vec{r}, \vec{p}_1, \vec{p}_2, t) = f(\vec{r}, \vec{p}_1, t) f(\vec{r}, \vec{p}_2, t).$$  \hspace{1cm} (21)

The above is also called the assumption of molecular chaos. The momenta of two particles are uncorrelated. The stosszahlansatz is time symmetric. For both Maxwell and Boltzmann, this assumption looked innocuous and self evident. From this, Boltzmann derives an expression for the collision term, as described below.

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16Classically a particle is specified by three position and three momentum coordinates. It is represented by a point in the six-dimensional phase space, called the $\mu$ space. A system of $N$ particles is represented by a point in a $6N$ dimensional phase space called $\Gamma$ space.

17discovered by Joseph Liouville (1809-1882).

18Eq. (19) can be taken as definition of the collision term.
Let $d^3 p_1, d^3 p_2, d^3 p_1'$ and $d^3 p_2'$ be the momentum volume elements at $\vec{p}_1, \vec{p}_2, \vec{p}_1'$, and $\vec{p}_2'$ respectively. Let us consider binary collisions that knock a molecule from $d^3 p_1$ into $d^3 p_1'$, while its collision partner gets knocked from $d^3 p_2'$ into $d^3 p_2$. Since we are interested only in the collision term, we shall omit, for notational convenience, reference to the dependence on position $\vec{r}$ and time $t$. The rate at which these collisions take place is given by,

$$f(\vec{p}_1)d^3 p_1 f(\vec{p}_2)d^3 p_2 \Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2')d^3 p_1'd^3 p_2'.$$

In the above, $\Sigma$ denotes the rate of transition from $(\vec{p}_1, \vec{p}_2)$ to $(\vec{p}_1', \vec{p}_2')$. The total rate of binary collisions that result in molecules getting knocked out of volume element $d^3 p_1$ is given by,

$$R(\text{OUT}) = d^3 p_1 f(\vec{p}_1) \int d^3 p_2 \int d^3 p_1' \int d^3 p_2' f(\vec{p}_2') \Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2').$$

(22)

While carrying out the integrals in the above, we must ensure that momentum and energy are conserved. Let $R(\text{IN})$ denote the rate of binary collisions that knock molecules into the volume element $d^3 p_1$. This can be obtained exactly the same way described above except that we interchange the labels of momenta before and after collision: $\vec{p}_1 \leftrightarrow \vec{p}_1'$ and $\vec{p}_2 \leftrightarrow \vec{p}_2'$. In other words we consider binary collisions that knock molecules from $d^3 p_1'$ into $d^3 p_1$ and from $d^3 p_2'$ into $d^3 p_2$. We get,

$$R(\text{IN}) = d^3 p_1 \int d^3 p_2 \int d^3 p_1' \int d^3 p_2' f(\vec{p}_1') f(\vec{p}_2') \Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2').$$

(23)

We consider molecule - molecule interaction potential to be spherically symmetric. We first note that a binary collision is time symmetric. In other words, the process seen in reverse is also an acceptable collision process. Hence,

$$\Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2') = \Sigma(-\vec{p}_1', -\vec{p}_2', -\vec{p}_1, -\vec{p}_2).$$

(24)

Also $\Sigma$ is unchanged under simultaneous reflection of all momenta:

$$\Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2') = \Sigma(-\vec{p}_1, -\vec{p}_2, -\vec{p}_1', -\vec{p}_2').$$

(25)

Combining the above two we get,

$$\Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2') = \Sigma(\vec{p}_1', \vec{p}_2', \vec{p}_1, \vec{p}_2).$$

(26)

Thus we can write the collision term as,

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col.}} = \int d^3 p_2 \int d^3 p_1' \int d^3 p_2' \Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2') \left[f(\vec{p}_1') f(\vec{p}_2') - f(\vec{p}_1) f(\vec{p}_2)\right].$$

(27)

$\Sigma$ depends on the geometry of collision, the relative velocity of the two particles entering collision and the nature of the colliding particles. The full nonlinear Boltzmann transport equation reads as,

$$\frac{\partial f}{\partial t} = -\frac{1}{m} \vec{p}_1 \cdot \nabla f - \vec{F} \cdot \nabla_p f + \int d^3 p_2 \int d^3 p_1' \int d^3 p_2' \Sigma(\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2') \left[f(\vec{p}_1') f(\vec{p}_2') - f(\vec{p}_1) f(\vec{p}_2)\right].$$

(28)
11 Boltzmann H function

Boltzmann defines his famous $H$ function,

$$H(t) = \int d^3 p \ f(\vec{p}, t) \log [f(\vec{p}, t)],$$  \hspace{1cm} (29)

and then shows that a density $f(\vec{p}, t)$ that solves the transport equation obeys,

$$\frac{dH}{dt} \leq 0.$$  \hspace{1cm} (30)

The above is clearly time asymmetric. In contrast to Newtonian dynamics which does not distinguish the future from the past, the $H$-function has a well defined direction of time, which is what the Second law is all about. To prove the $H$ theorem, we write from Eq. (29),

$$\frac{dH}{dt} = \int d^3 p \ [1 + \log(f)] \frac{\partial f}{\partial t}.$$  \hspace{1cm} (31)

Therefore,

$$\frac{\partial f}{\partial t} = 0 \text{ implies } \frac{dH}{dt} = 0.$$  \hspace{1cm} (32)

The $H$ function does not change with time when the system is in equilibrium. Eq. (31) in conjunction with the transport equation, see Eq. (28) yields after a few simple steps, the following expression for the time evolution of the $H$ function.

$$\frac{dH}{dt} = -\frac{1}{4} \int d^3 p_1 \int d^2 p_2 \int d^3 p'_1 \int d^3 p'_2 \ \Sigma(\vec{p}_1, \vec{p}_2, \vec{p}'_1, \vec{p}'_2) \left[ f(\vec{p}_1)f(\vec{p}_2) - f(\vec{p}'_1)f(\vec{p}'_2) \right] \times \left[ \log[f(\vec{p}_1)f(\vec{p}_2)] - \log[f(\vec{p}'_1)f(\vec{p}'_2)] \right]$$  \hspace{1cm} (33)

We recognize that due to the concavity of the logarithm function,

$$(y - x)(\log y - \log x) \geq 0 \ \forall \ x, y > 0$$  \hspace{1cm} (34)

$H$ decreases with time monotonically giving rise to an arrow of time for macroscopic evolution. Thus Boltzmann, like a magician, produced a time asymmetric rabbit from a time symmetric hat!

The crucial point overlooked was in the usage of the stosszahlansatz before and after collision. Momentum conservation, $\vec{p}_1 + \vec{p}_2 = \vec{p}'_1 + \vec{p}'_2$, tells us that writing,

$$f(\vec{p}'_1, \vec{p}'_2) = f(\vec{p}'_1) \times f(\vec{p}'_2),$$  \hspace{1cm} (35)

is not correct, since a pair of uncorrelated particles gets correlated after collision. The reversibility paradox [26] of Josef Loschmidt (1821 - 1895) and the recurrence paradox [27] of Ernst Zermelo (1871 - 1956) showed Boltzmann’s claim was untenable. Let me quickly tell what these two paradoxes are.
11.1 Loschmidt and reversibility paradox

Loschmidt’s argument was based on microscopic reversibility. Consider an isolated system that evolves from time $t = 0$ to time $t = \tau$. Let there be a spontaneous increase of entropy during this evolution. At time $t = \tau$ reverse the momenta of all the molecules. Allow the system to evolve from time $t = \tau$ to time $t = 2\tau$. At time $t = 2\tau$ reverse once again the momenta of all the molecules. Since the system obeys time-reversal invariant Newtonian dynamics, it will end up at the same phase space point it started from. There would be a decrease in entropy during the evolution from time $t = \tau$ to time $t = 2\tau$, contrary to the claim made by Boltzmann. This is called Loschmidt’s reversibility paradox.

11.2 Zermelo and Recurrence paradox

Zermelo argued that an isolated system, under Hamiltonian dynamics will return arbitrarily close to its initial point in the phase space and infinitely often. This is called recurrence theorem, discovered by Poincaré [28, 29]. According to Poincaré recurrence theorem, every dynamical system is at least quasi-periodic if not exactly periodic. This follows from Liouville theorem: a phase space volume of initial conditions evolve without change of its volume. Hence it is described by a tube shaped region of ever-increasing length. As the total region of phase space available to the dynamical system is finite, the tube must somewhere intersect itself. This means that the initial and final states eventually come close to each other. The dynamical system returns arbitrarily close to its initial state and it does so infinitely often. If there is a spontaneous increase of entropy during an interval of time, there will be a spontaneous decrease of entropy during the interval of Poincaré recurrence; this contradicts Boltzmann’s claim.

12 Statistical Entropy of Boltzmann

Boltzmann conceded that perhaps, the use of stosszahlansatz has smuggled in an element of stochasticity (albeit in a very subtle way) into his otherwise purely dynamical derivation of the transport equation. He contended correctly that his H theorem is violated only when the system starts off from some special microstates which are very small in number. For an overwhelmingly large number of initial conditions, the dynamical evolution does obey the $H$ theorem. In other words, the typical behaviour of a macroscopic system is invariably consistent with the H theorem.

Nevertheless, in the year 1877, Boltzmann changed tack completely and proposed a fully stochastic approach to the problem of macroscopic irreversibility. He presented his ideas in a paper [30] on the relation between the Second law of thermodynamics and probability theory with

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19 Time reversal as discussed in the text can be implemented in a computer employing molecular dynamics simulation techniques. We find that even small errors in the calculations of positions and momenta of the molecules are sufficient to reduce and eventually eliminate this effect. The phase space trajectory of the macroscopic system is extremely unstable with respect to initial conditions. Two arbitrarily close trajectories move arbitrarily far apart asymptotically. This is called chaos. This was known to Julius Henry Poincaré (1854 - 1912) [28, 29], a contemporary of Ludwig Boltzmann. Chaos contains the seed for modern developments in non-equilibrium statistical mechanics. We shall see more on these issues later.

20 Poincaré recurrence is easily observed in systems with a very few degrees of freedom. But the recurrence time increases exponentially with the system size i.e. with the number of molecules. Hence Poincaré recurrence is seldom observed in the thermodynamic limit.
respect to the law of thermal equilibrium. Of course Boltzmann interprets probability in a dynamical way: The probability of finding a system in a region of its phase space is the fraction of the observation time the dynamical trajectory spends in that region.

Consider an isolated macroscopic system of $N$ particles. It is represented by a point in a $6N$ dimensional phase space ($\Gamma$ space), moving incessantly along a trajectory dictated by its dynamics. Let us coarse-grain the phase space in terms of hyper cubes each of volume $h^{3N}$. It is like a graph sheet that coarse-grains a plane in terms of tiny squares. Here $h$ represents a constant having the dimension of action $^{21}$ A phase space hyper cube is called a microstate. Let $\vec{x}$ be the $6N$ dimensional vector denoting the phase space point of the system and let $\rho(\vec{x}, t) d^{6N}x$ be the probability of finding the system in an infinitesimal volume $d^{6N}x$ at $\vec{x}$ at time $t$. Let the system be in equilibrium. In other words the density $\rho$ is independent of time. Let $\{\rho_i\}$ denote the discrete representation of the phase space density $\rho(\vec{x})$.

Boltzmann’s $H$ function, see Eq. (29), is then given by,

$$H = \sum_{i=1}^{\hat{\Omega}} \rho_i \log(\rho_i)$$

where $\hat{\Omega}$ is the total number of microstates accessible to the system under macroscopic constraints of energy $U$, volume $V$ and number of molecules $N$. Boltzmann defines entropy as,

$$S(U, V, N) = -k_B \sum_{i=1}^{\hat{\Omega}} \rho_i \log(\rho_i) ,$$

where $k_B$ is now called the Boltzmann constant $^{22}$. If we assume that all the microstates are equally probable, then $\rho_i = 1/\hat{\Omega} \ \forall \ i$, and we get the famous formula for Boltzmann entropy,

$$S = k_B \log(\hat{\Omega}),$$

engraved on his tomb in Zentralfriedhof, Vienna $^{23}$. Notice Boltzmann defines absolute entropy. In thermodynamics only change in entropy is defined.

12.1 Is Boltzmann entropy consistent with thermodynamic entropy?

Let $V$ be the number of coarse-grained volume cells occupied by $N$ non interacting molecules. For simplicity we ignore the momentum coordinates. Number of ways of configuring $N$ molecules in $V$ cells is given by $\hat{\Omega} = V^N$, from which it follows $^{24} S = k_B N \log(V)$. Pressure is temperature times the partial derivative of entropy with respect to volume. We have,

$$\frac{\partial S}{\partial V} = \frac{NK_B}{V} = \frac{P}{T},$$

$^{21}$Now we identify $h$ with Planck’s constant; $h = 6.626 \times 10^{-34}$ Joules-second.

$^{22}k_B = 1.381 \times 10^{-23}$ Joules per degree kelvin.

$^{23}$Strangely, Boltzmann never wrote down this formula in any of his papers, though he implied it. It was Max Planck who wrote it down explicitly from the $H$ function.

$^{24}$This expression for entropy is not extensive - called Gibbs’ paradox. Boltzmann resolved the paradox by introducing the notion of indistinguishable particles and corrected for over counting of microstates by dividing $\hat{\Omega}$ by $N!$. 

from which we get the ideal gas law: $PV = Nk_B T$. This leads to

$$dS = \frac{\partial S}{\partial V} dV = \frac{1}{T} P dV. \quad (40)$$

Consider a quasi-static process in which the system draws a quantity $dQ$ of reversible heat and produces work equal to $P dV$. Thus $dQ = P dV$, from which it follows that $dQ = T dS$. Thus Boltzmann entropy is consistent with the thermodynamic entropy \(^{25}\). But Boltzmann liberated entropy from its thermal confines. We can now define entropy for a coin toss, $S = k_B \log 2$ or throw of a dice, $S = k_B \log 6$, etc. In general if an experiment has $\Omega$ outcomes and they are all equally probable, then we can associate an entropy, $k_B \log \Omega$, with the experiment.

### 13 Boltzmann Entropy and Gibbs Entropy

Consider an experiment of tossing $N$ identical and fair coins. An outcome $\omega$ of this experiment is a string of Heads and Tails. We call $\omega$ a microstate. The set of all possible microstates of the experiment is denoted by by $\Omega(N)$ called the sample space. The number of elements of the sample space is given by $\hat{\Omega}(N) = 2^N$. Let us count the number of Heads in a string $\omega$ and call it $n(\omega)$. The random variable $n$ can take any value between 0 and $N$. We call $n$ a macro state. Let $\Omega(n; N) = \{\omega : n(\omega) = n\}$ be the set of all strings having $n$ Heads. In other words it is a set of all microstates belonging to the macro state $n$. The number of elements of the set $\Omega(n; N)$ or equivalently the number of microstates associated with the the macro state $n$, is given by

$$\hat{\Omega}(n; N) = \frac{N!}{n!(N-n)!} \quad (41)$$

We have

$$\hat{\Omega}(N) = \sum_{n=0}^{N} \hat{\Omega}(n; N) = 2^N. \quad (42)$$

\(^{25}\)The full expression for $\hat{\Omega}(E,V,N)$ obtained taking into account the momentum coordinates of the ideal gas molecules is given by the Sackur-Tetrode Equation, see below.

#### Sackur-Tetrode Equation

$$\hat{\Omega}(E,V,N) = \frac{1}{h^{3N}} \frac{V^{N}}{N!} \left( \frac{2\pi m E}{\hbar^2} \right)^{3N/2} \frac{1}{\Gamma\left(\frac{3N}{2} + 1\right)},$$

where $E$ is the total energy of the isolated system, $m$ is the mass of a molecule, $h$ is Planck constant employed for coarse-graining the phase space ($h^{3N}$ is the volume of a $6N$ dimensional cube in units of which the phase space volume is measured) and $\Gamma(\cdot)$ is the usual Gamma function,

$$\Gamma(n) = \int_{0}^{\infty} dt \ t^{n-1} e^{-t}.$$ 

The entropy of an ideal gas is thus given by,

$$S(E,V,N) = Nk_B \log \left( \frac{E^{3/2} V}{N^{5/2}} \right) + \frac{5Nk_B}{2} + \frac{3Nk_B}{2} \log \left( \frac{4\pi m}{3\hbar^2} \right).$$

The above is known as Sackur-Tetrode equation.
Boltzmann associates an entropy $S$ with each macro state $n$:

$$S(n) = \log \left[ \hat{\Omega}(n; N) \right]. \quad (43)$$

Note we have set the Boltzmann constant $k_B$ to unity. Boltzmann postulates that the system, switching all the time from one microstate to another microstate, would evolve in an entropy increasing way and eventually reach an equilibrium state characterized by an unchanging value of $n$ for which entropy is maximum. We immediately see that $\hat{\Omega}(n; N)$ is maximum when $n = N/2$. Therefore Boltzmann entropy for the equilibrium system is given by

$$S_B = \log \left[ \hat{\Omega}(n = N/2; N) \right] = \log \left[ \frac{N!}{\left( \frac{N}{2} \right)! \left( \frac{N}{2} \right)!} \right]. \quad (44)$$

Josiah Gibbs (1839 - 1903), proposed that equilibrium value of the macroscopic property $n$ should be calculated by averaging over an appropriate ensemble of microstates. In the coin-tossing example considered here the ensemble consists of microstates from a Binomial distribution. Thus in Gibbs picture of statistical mechanics,

$$n_{eq} = \langle n \rangle = \sum_{n=0}^{N} n \hat{\Omega}(n; N) \frac{1}{2^N} = \frac{N}{2}, \quad (45)$$

which is the same as that given by Boltzmann. Gibbs’ entropy, given by

$$S_G = N \log(2), \quad (46)$$

is different from Boltzmann’s entropy, see Eq. (44). However, in the thermodynamic limit, Gibbs entropy and Boltzmann entropy coincide. We have, in the limit of $N \rightarrow \infty$,

$$S_G = S_B + \mathcal{O}(\log N). \quad (47)$$

## 14 Gibbs Ensembles

Gibbs developed statistical mechanics into a fine tool for calculating equilibrium properties of macroscopic systems as averages over what we now call Gibbs’ ensembles [31].

### 14.1 Microcanonical Ensemble

The properties of an isolated system can be obtained by averaging over a microcanonical ensemble in which all microstates are of the same energy and occur with the same probability. For example footnote (25 ) expresses the number of microstates, $\hat{\Omega}$ of $N$ ideal gas molecules confined to a volume $V$ and with energy $E$.

### 14.2 Canonical Ensemble

A closed system is one which exchanges only energy with the outside world and not material or volume. It is described by a canonical ensemble. The probability that a closed system will be
found in a microstate $C$, is given by

$$P(C) = \frac{1}{Z(T,V,N)} \exp \left[ -\beta E(C) \right], \quad (48)$$

where $\beta = 1/(k_B T)$ and $Z(T,V,N)$ is called the canonical partition function given by

$$Z(T,V,N) = \sum_C \exp \left[ -\beta E(C) \right]. \quad (49)$$

Let $\tilde{\Omega}(E,V,N)dE$ be the number of microstates of the closed system having energy between $E$ and $E + dE$. We call $\tilde{\Omega}(E,V,N)$ the density of states. We can express the canonical partition function as,

$$Z(T,V,N) = \int dE \tilde{\Omega}(E,V,N) \exp(-\beta E) \quad (50)$$

The density of states is a rapidly increasing function of energy: understandably so, since more the energy more is the number of ways of distributing it and hence more is the entropy. The exponential function decreases with increase of energy. The product of these two will be a sharply peaked function energy, peaking at the thermodynamic energy $U = \langle E \rangle$. A saddle point estimate of the integral can be made and we get,

$$Z(T,V,N) = \exp \left[ \frac{S}{k_B} - \beta U \right] \quad (51)$$

from which we get

$$F(T,V,N) = -k_B T \log Z(T,V,N) = U(S,V,N) - TS(U,V,N) \quad (52)$$

where $F(T,V,N)$ is the Helmholtz free energy, proposed by Hermann von Helmholtz (1821-1894).

### 14.3 Grand canonical ensemble

An open system is one which exchanges both energy and material with the outside world. It is described by a grand canonical ensemble and the partition function is given by,

$$Q(T,V,\mu) = \sum_C \exp \left[ -\beta E(C) + \mu \beta N(C) \right], \quad (53)$$

where $N(C)$ is the number of molecules in the microstate $C$ of the open system and $\mu$ is the chemical potential.

We can construct different Gibbs ensembles depending on the system we are investigating. Gibbs provided a general framework of statistical mechanics based on static Gibbs ensembles and averages over them. This is in contrast to the ensemble of Boltzmann which is dynamical. It is the typical behaviour that forms the basis of Boltzmann’s picture of statistical mechanics.
The expression for entropy given by Eq. (37) was also derived by Claude Elwood Shannon (1916 - 2001), in the context of information theory [32]. We say Eq. (37) defines Boltzmann-Gibbs-Shannon entropy 26.

Boltzmann entropy, laid the foundation for statistical mechanics - a subject that helps us calculate macroscopic properties of an equilibrium system from those of its microscopic constituents and their interactions. This subject has since grown to a very high degree of sophistication. More importantly the predictions of statistical mechanics have been borne out by experiments. Statistical mechanics has become such a successful enterprise that physicists do not anymore question the use of statistics for describing macroscopic phenomena 27. But the nagging doubt remains: What is the origin for the observed stochasticity?

### 15 Dynamical Entropy from Chaos

Then came a meteorologist and mathematician named Edward Norton Lorenz with his three coupled first-order nonlinear differential equations. He had obtained them by truncating Navier-Stokes equations 28. The three equations of Lorenz were intended to provide a simple and approximate description of atmospheric behaviour. Lorenz was solving them on a computer. He discovered [40] that he had two very different numerical solutions for the same problem with almost identical initial conditions. This chance observation heralded a new field called chaotic dynamics [41, 42]. 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 any long term predictions from deterministic equations if they 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 [28, 29]. I have already mentioned of this while discussing Loschmidt’s reversibility paradox [26] and Zermelo’s recurrence paradox [27]. 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 trajectories traced by chaotic dynamical systems.

A standard way of determining whether or not a dynamical system is chaotic is to calculate the Lyapunov exponent. There are as many Lyapunov exponents as the dimensions of the phase space. Consider dynamics in an $n$ dimensional phase space. Consider an $n$ - dimensional sphere of initial conditions. At a later time all the trajectories emanating from the sphere will form an $n$-dimensional ellipsoid. We can calculate a Lyapunov exponent for each dimension. When talking of a single Lyapunov exponent we normally refer to the largest and denote it by $\lambda$. Thus if $\lambda > 0$, we

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26Ever since, there have been several ‘entropies’ proposed in different contexts. These include for example, Fisher information [33], von Neumann entropy [34] Renyi entropy [35], Kolmogrov-Sinai entropy [36], Algorithmic entropy [37], Tsallis entropy [38] and Kaniadakis entropy [39].

27Physicists were in for a greater embarrassment with the advent of quantum mechanics. Statistics enters into microscopic laws. Stochasticity is intrinsic to quantum mechanics. The notion of ensemble of Maxwell, Boltzmann and Gibbs came in handy in describing the results of measurements in quantum mechanics.

28The Navier-Stokes equation of Claude Louis Marie Navier (1785-1836) and Sir George Gabriel Stokes (1819-1903), is the primary equation of computational fluid dynamics, relating pressure and external forces acting on a fluid to the response of the fluid flow. Forms of this equation are used in computations for aircraft and ship design, weather prediction, and climate modeling.
say the dynamics is chaotic. The system becomes unpredictable for times greater than of the order of \(1/\lambda\). On these asymptotic time scales the system becomes amenable to 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 the stochastic macro - a link that Boltzmann was struggling to figure out.

In fact Boltzmann’s interpretation of probability was entirely based on dynamics. The dynamical trajectory of an isolated equilibrium system is confined to a constant energy surface in a \(6N\) dimensional phase space. Boltzmann first shows that the phase space density \(\rho\) remains constant along a trajectory; this is now called the Liouville theorem. He then assumes that all the points on the energy surface lie on a single trajectory. This is called ergodicity. Then \(\rho(\vec{x}) = \delta(\mathcal{H}(\vec{x}) - E)\) is the stationary density, where \(\mathcal{H}\) is the Hamiltonian, \(E\) is energy and \(\delta\) is the usual Dirac delta function.

Boltzmann’s ergodicity has been generalized by Sinai \[43\], Ruelle \[44\] and Bowen \[45\] to describe dissipative systems in a steady state. The strange attractor of the dissipative dynamics is the non-equilibrium analogue of the equilibrium constant energy surface considered by Boltzmann. The SRB measure \[44, 46\] on the attractor expressed in terms of phase space volume contraction is analogous to the Liouville measure on the energy surface of an equilibrium isolated system. Such a generalization permits assignment of dynamical weights to non-equilibrium states. These weights, let me repeat, are based on the dynamical properties of the microscopic constituents of a macroscopic system. To appreciate the import of this statement, we must recognize that words like equilibrium, heat, entropy, temperature etc., belong to the vocabulary of the macroscopic world of thermodynamics. They do not have any meaning in the microscopic world. Paraphrasing Maxwell, at microscopic level you cannot tell heat from work, since both are essentially energy, see below.

### 15.1 Microscopic description of work and heat

Let \(U\) denote the thermodynamic energy of a closed system obtained by averaging the statistical mechanical energy \(E_i\), over a canonical ensemble of microstates. Let the microstates accessible to the system be indexed by natural numbers \(i\). Let \(p_i\) denote the probability for the system to be in microstate \(i\) whose energy is \(E_i\). The thermodynamic energy \(U\) is then given by,

\[
U = \sum_i p_i E_i.
\]

We have formally,

\[
dU = \sum_i \frac{\partial U}{\partial E_i} dE_i + \sum_i \frac{\partial U}{\partial p_i} dp_i
\]

\[
= \sum_i p_i dE_i + \sum_i E_i dp_i .
\]

Thus we can change the energy of a system by an amount \(dU\), through work \(d\bar{W}\), given by the first term on the right and/or heat \(dq_{\text{rev}}\), given by the second term on the right in the above equation. Thus work and heat are simply two modes of energy transfer.
Work

To identify the first term as work we proceed as follows. We have,

\[ \sum_i p_i dE_i = \sum_i p_i \frac{\partial E_i}{\partial V} dV \]

\[ = \left( \frac{\partial}{\partial V} \sum_i p_i E_i \right) dV \]

\[ = \frac{\partial U}{\partial V} dV \]

\[ = -P dV \]

\[ = dW \]  \hspace{1cm} (55)

where \( P \) denotes pressure. Work corresponds to change in energy of the macroscopic system brought about by changing the energies of its microstates without altering in any way their probabilities \( \{ p_i \} \).

Heat

To identify the second term as heat, we start with the definition of Boltzmann-Gibbs-Shanon entropy

\[ S = -k_B \sum_i p_i \log p_i , \]

and proceed as follows.

\[ dq_{rev} = T dS \]

\[ = -k_B T \sum_i dp_i - k_B T \sum \log p_i dp_i \]

\[ = -k_B T \sum_i dp_i - k_B T \sum \log p_i dp_i \]

\[ = -k_B T \sum_i dp_i \log p_i \]

\[ = k_B T \sum_i dp_i \left[ \beta E_i + \log Z \right] \]

\[ = \sum_i E_i dp_i \]  \hspace{1cm} (56)

where \( Z \) denotes the canonical partition function, see Eq. (49). In the above derivation we have made use of the fact that in a canonical ensemble describing a closed system, \( p_i = Z^{-1} \exp(-\beta E_i) \). Thus heat is change of energy of a closed system brought about by changing the probabilities \( \{ p_i \} \).
without altering in any way the energies $\{E_i\}$ of the microstates. It is in fact because of this identification we relate heat and hence entropy to randomness.

In the phase space of the thermodynamic variables only an equilibrium system can be represented by a point; only a quasi-static process can be represented by a curve. However in the $6N$ dimensional phase space of statistical mechanics, a macroscopic system in equilibrium or not, can be represented by a point; any process can be represented by a trajectory, to which we can attach a suitably defined dynamical weight.

Thus dynamical measures of recent times, have liberated the notion of entropy from its equilibrium and quasi-static confines, into non-equilibrium realms. We have, indeed, come a long way: from the thermal entropy of Clausius to the statistical entropy of Boltzmann (both applicable to equilibrium systems and quasi-static processes), and now to the SRB measures (defined for non-equilibrium systems and processes). Recently SRB measure has been shown to provide a correct description [47] of a far from equilibrium system in a computer simulation [48].

### 16 Entropy Fluctuation Theorems

These new developments are embodied in what we call fluctuation theorems [48, 49]. The general idea behind a fluctuation theorem can be stated as follows. Let $S_\tau$ denote entropy production rate calculated by averaging over segments of a long trajectory of duration $\tau$. Note that $S_\tau$ is a dynamical entropy obtained from observing the phase space expansion/contraction. Let $\Pi(S_\tau)$ be the probability of $S_\tau$. This can be calculated by considering an ensemble of long trajectories each of duration $\tau$. Fluctuation theorem states,

$$\frac{\Pi(S_\tau)}{\Pi(-S_\tau)} = \exp[\tau S_\tau].$$

(57)

Fluctuation theorem helps us calculate the probability for the entropy to change in a way opposite to that dictated by the Second law; this probability of Second law violation is exponentially small for large systems and for long observation times. By the same token fluctuation theorems predict and more importantly quantify Second law violation in small systems and on small time scales of observation. The predictions of fluctuation theorems have since been verified experimentally [50, 51]. See also [52] for an interesting examination of the experimental tools of fluctuation theorems.

### 17 Jarzynski Identity

In the year 1997, C. Jarzynski [53] discovered a remarkable identity relating non-equilibrium work fluctuation to equilibrium free energies. Consider a switching process, discussed earlier, carried out over a time $\tau$, with the system thermostatted $^{29}$ at temperature $T = 1/(k_B\beta)$. Let $W$ denote the work done during the switching process. We carry out the switching several times and collect an ensemble $\{W_i\}$, formally represented by the probability density $\rho(W; \tau)$. All the switching experiments are carried out with the same protocol. If $\tau = \infty$, the process is quasi-static. We have $W_i = W_R \forall i$. The work done is called reversible work, $W_R$. For a general switching experiment

$^{29}$A thermostat exchanges energy with the system without changing its temperature or performing any work.
where $\tau < \infty$, the Second law says that

$$\Delta F \leq \langle W \rangle,$$

where $\Delta F$ is the change in the Helmholtz free energy.

Jarzynski’s identity is given by,

$$\langle \exp(-\beta W) \rangle = \exp (-\beta \Delta F),$$

(59)

where $\langle \cdot \rangle$ denote averaging over the distribution of $W$.

17.1 Jarzynski identity and the Second law

It may be noticed that since the exponential function is convex, we have,

$$\langle \exp(-\beta W) \rangle \geq \exp \left[ -\beta \langle W \rangle \right],$$

(60)

which in conjunction with Jarzynski’s identity implies that,

$$\exp(-\beta \Delta F) \geq \exp \left[ -\beta \langle W \rangle \right],$$

$$-\beta \Delta F \geq -\beta \langle W \rangle,$$

$$\Delta F \leq \langle W \rangle,$$

(61)

which is a statement of the Second law. In this sense, proof of Jarzynski’s identity is a proof of the Second law.

17.2 Jarzynski identity: cumulant expansion

Let us express Jarzynski’s equality as a cumulant expansion [54],

$$\langle \exp(-\beta W) \rangle \equiv \exp \left[ \sum_{n=1}^{\infty} \frac{(-\beta)^n \zeta_n}{n!} \right] = \exp(-\beta \Delta F),$$

(62)

where $\zeta_n$ denotes the $n-$th cumulant of $W$. The cumulants and the moments are related to each other. The $n$-th cumulant can be expressed in terms of the moments of order $n$ and less. The first cumulant, $\zeta_1$, is the same as the first moment $\langle W \rangle$; the second cumulant, $\zeta_2$ is the variance $\sigma^2 = \langle W^2 \rangle - \langle W \rangle^2$; etc. From the cumulant expansion given by Eq. (62), we get,

$$\Delta F = \langle W \rangle - \frac{1}{2} \beta \sigma_w^2 + \sum_{n=3}^{\infty} \frac{(-\beta)^{n-1} \zeta_n}{n!}.$$

(63)
17.2.1 Reversible work and free energy

Consider a quasi-static switching process for which,

$$\rho(W; \tau = \infty) = \delta(W - W_R),$$  \hspace{1cm} (64)

by definition. Then, in Eq. (63), only the first term (of the cumulant expansion) is non-zero. We get,

$$\langle W \rangle = W_R = \Delta F,$$  \hspace{1cm} (65)

consistent with thermodynamics.

17.2.2 Fluctuation and dissipation

Now consider a switching process, during which the system remains very close to equilibrium; it is reasonable to expect the statistics of $W$ to obey the Central Limit Theorem $^{30}$. Hence $\rho(W; \tau >> 0)$ shall be a Gaussian; for a Gaussian, all the cumulants from the third up-wards are identically zero; hence, in Eq. (63), only the first two terms survive and we get

$$\Delta F = \langle W \rangle - \frac{1}{2} \beta \sigma_W^2.$$  \hspace{1cm} (66)

Dissipation given by,

$$\langle W_d \rangle = \langle W \rangle - \Delta F = \frac{1}{2} \beta \sigma_W^2,$$  \hspace{1cm} (67)

$^{30}$According to the Central Limit Theorem, the sum of $N$ independent and identically distributed, finite variance random variables, has an asymptotic ($N \to \infty$) Gaussian distribution with both mean and variance diverging linearly with $N$. This means that the relative fluctuation is inversely proportional to $\sqrt{N}$ and hence is small for large $N$. See e.g. [55]. This is easily seen as follows.

The Central Limit Theorem

Let

$$Y = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} X_i,$$

where $\{X_i : i = 1, N\}$ are identically distributed independent random variables with zero mean and finite variance $\sigma^2$. Let $\Phi_X(k)$ denote the characteristic function of the random variable $X$. Then

$$\Phi_Y(k) = \left[ \Phi_X(k \to \frac{k}{\sqrt{N}}) \right]^N = \exp \left[ -\frac{1}{2} k^2 \sigma^2 + \sum_{n=3}^{\infty} \frac{(ik)^n}{n!} N^{-(n-2)/2} \zeta_n \right]$$

$$\sim N \to \infty \exp \left[ -\frac{1}{2} k^2 \sigma^2 + O(1/\sqrt{N}) \right]$$

where $\zeta_n$ denotes the $n$-th cumulant of $X$. The Fourier inverse of the asymptotic ($N \to \infty$) expression for $\Phi_Y(k)$ is Gaussian with mean zero and variance $\sigma^2$. 
is proportional to fluctuation, $\sigma^2_{W_f}$. This result is identical to the fluctuation dissipation relation of Callen and Welton [56]. See [57] for an interesting discussion on Gaussian Work fluctuation, Jarzynski identity and fluctuation dissipation theorem. However, if the switching process drives the system far from equilibrium, the work distribution would no longer be Gaussian and we need to include contributions from higher order cumulants to calculate the dissipation $\langle W_d \rangle$ and hence free energy: $\Delta F = \langle W \rangle - \langle W_d \rangle$. Jarzynski’s equality has been shown to hold good for Hamiltonian evolution [53] as well as stochastic evolution [58]; its validity has been established in computer simulation [58] and in experiments [59].

18 Microscopic Reversibility and Crooks identity

In another parallel, independent and interesting development, Gavin E. Crooks [60] discovered a fluctuation theorem for a thermostatted, Markovian dynamical process. During the process, the degree of freedom $\Lambda$ switches from an initial value of $\Lambda_0$ to a final value $\Lambda_N$ in $N$ time steps. The switching process is not necessarily quasi-static.

18.1 Heat Step, Work step and Markov Chain

The system is initially in a microstate $C_0(\Lambda_0) \in \Omega(\Lambda_0)$, where $\Omega(\Lambda_0)$ denote the set of all microstates of the system with $\Lambda = \Lambda_0$. Each step is considered as made up of a heat sub-step: $C_0(\Lambda_0) \to C_1(\Lambda_0)$ and a work sub-step: $C_1(\Lambda_0) \to C_1(\Lambda_1)$. Thus we get a Markov chain\(^{31}\) of microstates given by,

$\mathcal{F}|C_0(\Lambda_0) = C_0(\Lambda_0) \to C_1(\Lambda_0) \to C_1(\Lambda_1) \to \cdots \to C_k(\Lambda_k) \to C_{k+1}(\Lambda_{k+1}) \to \cdots \to C_{N-1}(\Lambda_{N-1}) \to C_N(\Lambda_{N-1}) \to C_N(\Lambda_N)$

Let us consider a heat sub-step $C_k(\Lambda_k) \to C_{k+1}(\Lambda_{k+1})$, described by a Markov transition matrix $M(k)$ whose elements are given by

$$M_{i,j}(k) = P(C_{k+1} = C_i|C_k = C_j),$$

where $C_i \in \Omega(\Lambda_k)$. We have used script symbol $C$ to denote microstates of the system and roman symbol $C_k$ to denote those on the Markov chain with $k$ serving as the time index. The matrix $M(k)$ has the following properties:

- The elements of $M(k)$ are all non-negative:

$$M_{i,j}(k) \geq 0 \quad \forall \; i, j.$$

Note $M_{i,j}$ denotes (transition) probability.

- $M(k)$ is column stochastic:

$$\sum_i M_{i,j}(k) = 1 \quad \forall \; j.$$

This follows from the normalization. After a step the system must be found in any one of its microstates with unit probability.

\(^{31}\)A Markov chain describes the time evolution of a system with a finite or countable number of microstates. We also specialize to Markov chain in discrete time. In general for a Markov process, the past has no influence over the future once the present is specified.
• $M(k)$ is regular: There exists an integer $n > 0$, such that

$$
\left( [M(k)]^n \right)_{i,j} > 0 \ \forall \ i, j.
$$

This ensures ergodicity.

• $M(k)$ is balanced: There exists a unique invariant probability vector $\pi(k)$ such that

$$
M(k)\pi(k) = \pi(k).
$$

• $\pi(k)$ describes the equilibrium distribution of the closed system at $\beta$ and with $\Lambda = \Lambda_k$. The components of $\pi$ are given by,

$$
\pi_i(k) = \frac{\exp\left[ -\beta E(C_i, \Lambda_k) \right]}{Z(\beta, \Lambda_k)}, \quad (69)
$$

where $E(C_i, \Lambda_k)$ is the energy of the microstate $C_i$ belonging to the system with $\lambda = \Lambda_k$. The canonical partition function is denoted by $Z(\beta, \Lambda_k)$.

### 18.2 Metropolis and Heat-bath algorithms

We need a model for $M(k)$. For example Metropolis algorithm [62] prescribes,

$$
M_{i,j}(k) = \alpha \times \min\left(1, \frac{\pi_i(k)}{\pi_j(k)}\right) \ \forall \ i, j \text{ and } i \neq j, \quad (70)
$$

$$
M_{i,i}(k) = 1 - \sum_{j \neq i} M_{j,i} \ \forall \ i, \quad (71)
$$

where the constant $\alpha$ has been introduced to ensure that no diagonal element is negative or exceeds unity.

The heat-bath algorithm [63] also known as Glauber algorithm [65] or Gibbs’ sampler [64] is given by

$$
M_{i,j} = \frac{\pi_i}{\pi_i + \pi_j} \ \forall \ i, j. \quad (72)
$$

Once a model for $M$ is defined, we can calculate the probability for the Markov chain $\mathcal{F}|C_0(\Lambda_0)$, where we take each work sub-step with unit probability.
18.3 Time-Reversal of Markov Chain

Let us now run the Markov chain back-wards and call it the time - reversal. Let $\mathcal{R}|C_N(\Lambda_N)$ denote the time reversal of $\mathcal{F}|C_0(\Lambda_0)$. It is given by,

$$
\mathcal{R}|C_N(\Lambda_N) = C_N(\Lambda_N) \rightarrow C_N(\Lambda_{N-1}) \rightarrow C_{N-1}(\Lambda_{N-1}) \rightarrow \cdots \rightarrow C_{k+1}(\Lambda_{k+1}) \rightarrow C_{k+1}(\Lambda_k) \rightarrow C_k(\Lambda_k) \cdots \rightarrow C_1(\Lambda_1) \rightarrow C_1(\Lambda_0) \rightarrow C_0(\Lambda_0)
$$

Note that in the time-reversed Markov chain, the work sub-step comes first followed by the heat sub-step in every time step. We need to calculate the probability for the time reversed Markov chain. Reversing the work sub-step is easily visualized. We switch the parameter $\Lambda$ back-wards with unit probability. Let the time reversed heat step $C_{k+1}(\Lambda_k) \rightarrow C_k(\Lambda_k)$ be described by $\widehat{M}(k)$, called the reversal of $M(k)$. To construct $\widehat{M}(k)$ we proceed as follows.

Consider the heat sub-step $C_{k+1}(\Lambda_k) \rightarrow C_k(\Lambda_k)$ in the forward Markov chain. Define a two-step joint probability matrix $W$ whose elements are given by,

$$
W_{i,j}(k) = P(C_{k+1}(\Lambda_k) = C_i, C_k(\Lambda_k) = C_j) = M_{i,j}(k)\pi_j(k)
$$

(73)

In the above the second step follows from the definition of conditional probability. Thus, given $M(k)$ we can get the corresponding $W(k)$ and vice versa. To this end we define a diagonal matrix $D(k)$ with elements,

$$
D_{i,j}(k) = \pi_i(\Lambda_k)\delta_{i,j}.
$$

(74)

Then,

$$
W(k) = M(k)D(k)
$$

(75)

and

$$
M(k) = W(k)D^{-1}(k)
$$

(76)

Also it is easily checked that $W(k)$ is matrix-stochastic:

$$
\sum_i \sum_j W_{i,j}(k) = 1.
$$

(77)

Let $\widehat{W}(k)$ denote the time reversal of $W(k)$. A little thought will convince you that a good choice of $\widehat{W}(k)$ is $W^\dagger(k)$, where the superscript $^\dagger$ denotes transpose operation. The corresponding $\widehat{M}(k)$ can be obtained as follows.

$$
\widehat{M}(k) = \widehat{W}(k)D^{-1}(k) = W^\dagger(k)D^{-1}(k) = D(k)M^\dagger(k)D^{-1}(k).
$$

(78)
We say a Markov chain is time symmetric if $W$ is symmetric. In other words,

$$\hat{W}(k) = W^+(k) = W(k),$$

(79)

for time symmetry. Also for a time symmetric Markov chain, we have

$$\hat{M}(k) = \hat{W}(k)D^{-1}(k) = W^+(k)D^{-1}(k) = W(k)D^{-1}(k) = M(k).$$

(80)

This implies that $\pi_j(k)M_{i,j}(k) = \pi_i(k)M_{j,i}(k)$, called detailed balance 33. A sequence of microstates visited by an equilibrium system constitutes a time-symmetric Markov chain.

### 18.4 Crooks Identity

The probability of $R|C_N(\Lambda_N)$ can be calculated from the matrices $\{\hat{M}(k)\}$. Let $\Pi_F$ denote the probability of $F|C_0(\Lambda_0)$ and $\Pi_R$ that of its reverse. The ratio of these two probabilities can be calculated and is given by,

$$\frac{\Pi_F}{\Pi_R} = \exp \left[ -\beta Q(F) \right],$$

(81)

where $Q$ is the energy absorbed by the system, in the form of heat, from the thermostat during forward Markov chain evolution. The above is called Crooks identity. The import of Crooks’ finding can be understood if we consider switching from an equilibrium ensemble at $\beta$ and with $\Lambda = \Lambda_0$ to another equilibrium ensemble at the same $\beta$ but with $\Lambda = \Lambda_N$ through a process which is not necessarily quasi-static. Thus $C_0(\Lambda_0)$ and $C_N(\Lambda_N)$ belong to equilibrium ensembles at the

33 The Metropolis [62] and the heat-bath algorithms [63–65] obey detailed balance. There are algorithms that do not obey detailed balance. It is often said that a simple balance condition, $M|\pi\rangle = |\pi\rangle$ is adequate to drive the system to equilibrium in a computer simulation, see e.g. [66,67]. We see that it is detailed balance that ensures time symmetry in a sequence of microstates visited by the system after equilibration. If the computer algorithm obeys only balance and not detailed balance then time asymmetry in the Markov chain of microstates sampled, would be present even during equilibrium runs.
same temperature. Then,

\[
\frac{\Pi\left(C_0(\Lambda_0)\right)}{\Pi\left(C_N(\Lambda_N)\right)} \times \frac{\Pi_F}{\Pi_R} = \frac{\exp\left(-\beta E\left(C_0(\Lambda_0)\right)\right)}{Z(\beta, \Lambda_0)} \times \frac{Z(\beta, \Lambda_N)}{\exp\left(-\beta E\left(C_N(\Lambda_N)\right)\right)} \times \exp(-\beta Q)
\]

\[
= \exp\left[\beta \left\{ \Delta E - \Delta F - Q \right\}\right]
\]

\[
= \exp\left[\beta \left\{ \langle W \rangle - \Delta F \right\}\right]
\]

\[
= \exp\left[\beta \langle W_d \rangle\right]. \tag{82}
\]

In the above we have used the definition of free energy, \( F(T, V, N) = -k_B T \log Z(T, V, N) \) for going from the first line to the second line. In going to the third line from the second, we have made use of the first law: \( \langle W \rangle = \Delta E - Q \). Physically Eq. (82) means that the probability of finding a dissipating segment of a Markov chain evolution is exponentially large compared to that of finding its reverse. Starting from Crooks identity we can derive fluctuation theorems and Jarzynski’s equality, see e.g. [68]. Very recently Cleuren, Van den Broeck and Kawai [69] have derived equivalent of Crooks identity in microcanonical ensemble description and have obtained analytical expressions for the work fluctuations in an idealized experiment consisting of a convex body moving at constant speed through an ideal gas. Crooks identity has since been verified experimentally [70].

19 Epilogue

Thus, recent developments have helped improve our understanding of the issues that link time asymmetric macroscopic world to the time symmetric microscopic world. These developments are not inconsistent with the hunch Boltzmann had. Let me conclude à la Cohen [71], quoting from Boltzmann. In his 1899 lecture at Munich, Germany, on recent developments of methods of theoretical physics [72], Boltzmann talks of the conflict between dynamics and statistics in describing macroscopic phenomena. He asks if statistics would continue to dominate in the future, or would it give way to dynamics. He concludes saying ‘ · · · interesting questions! One almost regrets to have to die long before they are settled. Oh! immodest mortal ! Your destiny is the joy of watching the ever-shifting battle’.

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