

Josiah Willard Gibbs and his Ensembles

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Prologue

Josiah Willard Gibbs was amongst the last of the intellectual giants of the classical era of physical sciences. He was born in New Haven, Connecticut, USA, where his father was a professor at Yale University's Divinity school.

Gibbs studied at Yale and obtained his doctoral degree in the year 1863. His thesis was *On the Form of the Teeth of Wheels in Spur Gearing*. It is indeed remarkable that though Gibbs kicked off his career with a practical problem in engineering, in later years he pursued and contributed to some of the most abstract ideas in the history of science. His was the first to receive a doctorate in engineering and the second in science, awarded in the United States of America. He then joined Yale College and taught Latin for two years and natural philosophy for one year. In the year 1866, Gibbs went to Europe for studies where he came under the influence of Gustav Robert Kirchhoff and Hermann Ludwig Ferdinand von Helmholtz. The three years he spent in Europe were almost the only time he ever spent away from his hometown. On return he was appointed a professor of mathematical physics; this post was without salary partly because Gibbs had never published!

Gibbs remained in Yale until his death in the year 1903. He led an uneventful life. He never married and lived with his sister and brother-in-law; his brother-in-law was a librarian in Yale. He never tried to socialize. He published sparsely. This was chiefly because Gibbs was a perfectionist and strove hard for a very high degree of rigour, economy of words and clarity in presentation.

Keywords

Gibbs, thermodynamics, statistical mechanics, Gibbs ensembles, vector algebra.



Also he took great care to tie up, as much as possible, all the loose ends before even thinking of writing up his work for publication.

Early Work on Thermodynamics

The early work of Gibbs was on thermodynamics. As the name suggests, thermodynamics deals with heat and work. This subject was chiefly motivated by man's desire to extract work from heat. More generally thermodynamics explains the behaviour of macroscopic systems on the basis of empirical laws. Thermodynamic laws are directly deduced from experiments. A simple example is the ideal gas law, also known as Charles' law or Boyle's law. According to it, the product of pressure and volume of a given quantity of an ideal gas (any dilute gas, say air, can be considered as an ideal gas) is a constant at constant temperature. (See article by V Kumaran in this issue.)

Gibbs' early work [1] was on geometrical representation of thermodynamic quantities such as energy, volume and entropy. The change of thermodynamic state of the system is given by a surface in these three dimensions. The tangent at any point on the surface will indicate the temperature and pressure of the macroscopic system when it is in the particular thermodynamic state represented by the point. From the shape of the surface Gibbs deduced geometrically the conditions for equilibrium and criteria for stability. James Clerk Maxwell was so fascinated by the simplicity and elegance of the geometrical method that he constructed a model for the thermodynamic surface for water, a plaster cast of which he presented to Gibbs. This plaster cast is on permanent exhibition at the Sloane Physics Laboratory in New Haven.

The papers that Gibbs published during 1876–1878, on *equilibrium of heterogeneous substances* [2] laid the foundation for chemical thermodynamics. This work is one



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of the greatest achievements in the physical sciences of the nineteenth century. In these papers Gibbs announced his invention of the concept of chemical potential. Physicists were then familiar with the role of temperature in establishing thermal equilibrium and of pressure in establishing mechanical equilibrium. Gibbs showed that equality of chemical potential establishes diffusional equilibrium. He also wrote of what we now call ‘Gibbs’ phase rule’ for describing equilibria amongst different phases of matter.

Vector Algebra, Optics, and Fourier Series

In the years 1880–1884 Gibbs worked on vector analysis. The dot and cross products that we are familiar with were invented by Gibbs. He combined the ideas of William Rowan Hamilton on quaternions and those of Hermann Günther Grassman on the theory of extension, to produce the mathematical field of vector analysis. He rightly held the modern view that a vector is an entity by itself and should never be confused for its components. Gibbs’ *Elements of vector analysis* was printed privately in New Haven in 1881 and 1884.

Early in his career Gibbs recognized and asserted that phase transition occurs truly in infinite systems. Another interesting piece of mathematical work that Gibbs did relate the convergence of a Fourier series for a piecewise continuous and differentiable function. The Fourier series approximation displays an overshoot in the left-sided interval and a symmetric undershoot in the right-sided interval. The height of the overshoot or the depth of the undershoot does not decrease with increase of the number of terms in the summation, a counter-intuitive result. This behaviour, now known as Gibbs phenomenon, is described in the two brief letters that Gibbs submitted to the editor of *Nature* in December 1898 and April 1899. Between 1882 and 1889, Gibbs published five papers [3] comparing electromagnetic theory



with elastic theories and showed unambiguously that the empirical phenomena in optics can be explained on the basis of electromagnetic theory of Maxwell and not by the elastic theories.

As pointed out earlier Gibbs was extremely careful when it came to publication. He insisted on rigour and completion so much so that his monumental work on *Elementary principles in statistical mechanics* [4] was published just one year before his death. It contains the results of his research carried over a period of nearly thirty years.

Gibbs – The Founder of Statistical Mechanics

We can say that Gibbs along with Boltzmann, Maxwell and Einstein founded the subject of *Statistical Mechanics*.

Stated in simple terms, Statistical Mechanics helps us calculate the macroscopic properties of an object from those of its microscopic constituents – atoms and molecules – and their interactions. To the students of statistical mechanics *Gibbs* is a house-hold name. They come to know of him through Gibbs' ensembles upon which is based the entire edifice of statistical mechanics. To appreciate Gibbs' contribution toward founding of statistical mechanics we have to start with mankind's early efforts to understand the nature of matter and of heat.

Atomism of Early Times

Ancient man, irrespective of which civilization he belonged to – the Indian or the Greek, the Mohist or the Mayan – 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 Indians had a name for it: Anu¹. The Greeks called it atom – that which cannot be cut. Titus

¹ The Indian school of atomism, dating back to 600 BC, talks of attribute-less particles combining in pairs to form dyads. A dyad is also imperceptible, though it has acquired an attribute of *two-ness*. It requires three dyads to combine and form a triad. The triad is perceptible; it has attributes that can be observed and measured.



Lucretius Carus (94–55 BC) mused on the nature of things and wrote a six-book long poem called *De Rerum Natura*. In it, he writes of matter, made of atoms that one cannot see. According to his verses all the natural phenomena we see around are caused by invisible atoms moving around randomly hither and thither, trying out all possible forms and movement in the course of infinite time and eventually settling down into a disposition that we see now. There was no role for God in the 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 over two thousand years.

Revival of Kinetic Theory

The revival came perhaps in the seventeenth century with the work of Galileo, Torricelli, Pascal, Boyle, Daniel Bernoulli, Charles, Gay-Lussac, Joseph Black, James Watt, and John Dalton and several others. Robert Boyle modeled air as a collection of springs in fixed positions; the springs resist compression (which explains air pressure) and expand into available space. Daniel Bernoulli went a step further and proposed a billiard ball atom model. Bernoulli's billiard ball atom moves freely in space and when it bounces off the wall of the container it exerts a tiny force. Bernoulli rightly concluded that pressure is the force exerted (per unit area) by a very large number of randomly moving molecules bouncing off the wall. It is not difficult to understand such a kinetic theory in the context of atomic motions giving rise to pressure. But physicists had difficulty in comprehending kinetic theory of heat: atomic motions giving rise to heat – be it undulating motion about fixed positions 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 the heat from the sun. Hence heat cannot be a property of a

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substance; it has to be a substance by itself. Antoine-Laurent de Lavoisier called the substance ‘Caloric’. It was found that Caloric fluid always flowed from higher to lower temperatures. Heat engines that produced locomotion from burning of coal started dotting the European countryside in the late eighteenth century.

Carnot and His Heat Engine

Sadi Carnot was intrigued by the very idea of a heat engine that managed to do something that even the almighty nature could not do. A heat engine converts heat into movement. In nature we find that it is the movement which due to friction generates heat and not the other way. There is no phenomenon like *un-friction* or *anti-friction* which would spontaneously re-assemble heat back into a movement. Carnot came to the brilliant conclusion that *mere production of heat is not sufficient to give birth to the impelling power; it is necessary that there should be cold; without it, heat is useless*. Carnot argued that if a certain quantity q of caloric substance falls from absolute temperature T_1 to zero then the work produced would be $W = q$. Since the caloric fluid falls only to a finite temperature T_2 ($0 < T_2 < T_1$), only the proportional fraction, $(T_1 - T_2)/(T_1 - 0)$, of q should equal the work produced. Hence the efficiency of a heat engine cannot exceed $1 - (T_2/T_1)$, where T_1 is the temperature of the heat source (the boiler) and T_2 that of the heat sink (the radiator). Thus even an ideal heat engine has an efficiency less than unity.

The Kind of Motion We Call Heat

Very soon it was realized through the meticulous experiments of Rumford, Mayer and Joule that heat is not a substance. Heat is actually energy or more precisely energy in transit. It is like work which is also energy in transit. Once we identify heat with energy, Carnot’s finding becomes intriguing. It amounts to saying that

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heat cannot be completely converted into work whereas work can be converted completely into heat – an imbalance in nature’s scheme. This thermodynamic irreversibility – the one-way nature of energy conversion – is what we now call the Second Law of Thermodynamics.

Rudolf Clausius came to know of Carnot’s work a decade later. He felt that Carnot’s basic conclusion about extracting work from heat was correct and considered it as of great fundamental importance. He called it Carnot’s principle or the Second law of thermodynamics. But then Clausius rejected Carnot’s ‘caloric’ reasoning. By then he knew that heat was a kind of motion – ceaseless and random – of the invisible atoms and molecules. To explain Carnot’s principle in the context of the emerging picture of heat as energy in transit, Clausius invented a new thermodynamic variable called entropy, denoted by the symbol S . He rephrased Carnot’s principle as $dS \geq 0$ in any thermodynamic process. In the above relation, equality obtains when the process is quasi-static² and also reversible³. Thus the Second law of thermodynamics captures an essential truth about macroscopic behaviour – namely it is not time reversal invariant. There is a definite direction of time – the direction of increasing entropy.

² Extremely slow; the process looks almost static.

³ A reversible process is one in which infinitesimal change in the external condition will cause a reversal of the process.

Physicists are puzzled by 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 cannot 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 seems to break the time symmetry.

Thus the two pillars of theoretical physics – Newtonian mechanics and thermodynamics seem to stand in contradiction. The former is time reversal invariant while



the latter is not. How do we comprehend this micro-macro dichotomy? In the synthesis of a macroscopic object from its microscopic constituents when and why does the 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.

Boltzmann and His Transport Equation

Boltzmann had an extraordinary courage to suggest that the time asymmetric macroscopic phenomena can be exactly derived from the time-symmetric microscopic laws. Indeed he derived a nonlinear transport equation starting from Newton's equations of motion. The solution of the Boltzmann transport equation – the so called H -function – is time asymmetric. The negative of H can be identified with entropy. H always decreases with time until it reaches a minimum when the system equilibrates. The statement that the derivative of H with respect to time is always less than or equal to zero is called 'Boltzmann H -theorem'. But very soon Boltzmann realized that the *stosszahlansatz* – collision number assumption – of Maxwell, which he employed, stole in an element of stochasticity into his otherwise purely dynamical derivation of the transport equation. But then he contended correctly that his H -theorem is violated only when the macroscopic system starts off from some special initial condition which are extremely 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.

Subsequently, Boltzmann formulated the entire problem in statistical terms and gave a definition of entropy as proportional to the logarithm of the number of microstates of a macroscopic system. Let us digress a little

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bit and try to understand what one means by an ensemble, a microstate and a macrostate.

Gibbs Ensembles

Consider a simple experiment of tossing of a coin. Let the probability of *Heads* be p and of *Tails* be $q = 1 - p$. The sample space Ω_S for this experiment consists of two outcomes $\{H, T\}$. Let us toss a coin M times and collect the results in a set denoted by Ω . Thus M is the number of elements of Ω . Let m_H denote the number of times *Heads* appears in Ω . We say that the set Ω is an ensemble if $p = m_H/M$. In other words an outcome of the sample space appears in the ensemble as often as to reflect correctly its probability. The size M of the ensemble is taken to be sufficiently large so that each outcome of the experiment appears in the ensemble a certain number of times proportional to its probability. If $p = 0.75$ then an example of an ensemble of size four is $\Omega = \{H, T, H, H\}$, where the outcome *Heads* occurs three times and the outcome *Tails* occurs once consistent with their probabilities. $\Omega = \{H, T, H, H, T, H, H, H\}$ is also an ensemble but of size eight. We find that three-fourth of Ω is *Heads* and one-fourth is *tails*. Notice we do not really need to make any assumption about how to construct an ensemble. We can construct it by a deterministic algorithm, a stochastic algorithm or by actually carrying out the experiment a very large number times.

Let us now consider an experiment of tossing N identical coins. An outcome of the experiment consists of a string of *Heads* and *Tails*. The length of the string is N . Let us call each outcome a microstate and denote it by the symbol ω . Let $n(\omega)$ be the number of *Heads* in microstate ω . The value of n differs in general from one microstate to another. In the example considered $\langle n \rangle = Np$. If we consider the case of $p = 1/2$, then all the 2^N microstates are equally probable and $\langle n \rangle = N/2$. Thus in the machinery of statistical mechanics developed by



Gibbs, corresponding to each thermodynamic variable, we identify a statistical mechanical random variable. We then construct a Gibbs ensemble of realizations of the random variable. The average of the random variable calculated over the ensemble gives the value of the corresponding thermodynamic variable.

The above has to be contrasted with Boltzmann's formulation. To each value of the macroscopic variable we attach an entropy defined as proportional to the logarithm of the number of microstates associated with that value. For example, in the coin tossing problem if the macroscopic variable denoting the number of *Heads* in a toss of N coins takes a value n then the number of microstates associated with it is given by

$$\Omega(n; N) = \frac{N!}{n! (N - n)!} \quad , \quad (1)$$

where we have taken $p = 1/2$. In Boltzmann's formulation the system takes that value of the macroscopic variable n for which entropy is maximum. $\Omega(n; N)$ is maximum for $n = N/2$. Hence in Boltzmann's formulation also, $N/2$ is the value of the corresponding thermodynamic variable. We can define Boltzmann entropy as

$$S_B = k_B \log \left[\frac{N!}{n! (N - n)!} \right] \quad (2)$$

which is different from Gibbs entropy $S_G = N \log(2)$. A quick calculation will show that the probability of n differing from $N/2$ by more than an arbitrarily small fraction of $N/2$ goes to zero when N is large. For example, the probability for n to lie outside the interval $N/2 - \epsilon, N/2 + \epsilon$ is 0.002 when ϵ is one percent of $N/2$ for $N = 10^5$. In the study of macroscopic systems we shall be dealing with N of the order 10^{25} . Thus for large N , Boltzmann entropy and Gibbs entropy have for practical purposes the same value.

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Gibbs' approach to statistical mechanics was to generalize Newtonian mechanics to arbitrary, though strictly finite, number of degrees of freedom.

Gibbs' approach to statistical mechanics was to generalize Newtonian mechanics to arbitrary, though strictly finite, number of degrees of freedom. To this end he knit position and momentum into a single fabric called 'phase space'. Let me explain this by considering an isolated system of N molecules confined to a volume V with a total energy E . Each molecule is specified by three coordinates of position and three coordinates of momentum. The system is thus specified by a point in a $6N$ dimensional phase space. Since the molecules in the system are constantly in motion colliding with each other and with the walls of the container, the phase space point representing the system is incessantly in motion. Consider a collection of a large number of mental copies of the system, all identical macroscopically – having the same value of E , V and N – but may differ in their microscopic details. This collection of systems is called a Gibbs ensemble. The members of this ensemble are represented by a distribution of points in the phase space. Each phase space point evolves as per Newtonian dynamics. Then a simple calculation of the number systems lying within infinitesimal limits of phase space yields the basic equation – the Liouville's equation – of classical statistical mechanics.

The energy of the system is a fluctuating quantity which when averaged over a Gibbs ensemble of microstates yields the corresponding thermodynamic energy.

Depending on the nature of the constraints, we get different Gibbs ensembles. We saw above an example of a Gibbs ensemble describing an isolated system. This is called microcanonical ensemble, determined by E , V and N . On the other hand if we fix the temperature, volume and the number of particles we get a canonical ensemble, which describes a closed system. It is in thermal contact with the surroundings – called the heat bath. It gives energy to the heat bath or takes energy from it. Thus the energy of the system is a fluctuating quantity which when averaged over a Gibbs ensemble of microstates yields the corresponding thermodynamic energy. The fractional number of entries in the Gibbs'



canonical ensemble that are in a microstate ω is proportional to $\exp[-E(\omega)/k_{\text{B}}T]$ where $E(\omega)$ is the energy of ω , T is the temperature and k_{B} is a constant named after Boltzmann. This is called ‘canonical distribution’. We can calculate the average of energy denoted by $\langle E \rangle$ over a Gibbs ensemble. Then $\langle E \rangle$ of statistical mechanics gives the thermodynamic energy, often denoted by U , *i.e.* $U \equiv \langle E \rangle$. Other thermodynamic properties can also be calculated by a similar averaging of their statistical mechanical counterparts over a Gibbs’ canonical ensemble.

If we allow both energy and number of molecules of the system to fluctuate (the surroundings constitute a heat bath as well as particle bath) we get a grand canonical ensemble for which the volume, temperature and chemical potential are the relevant variables.

Statistical Mechanics of Maxwell, Boltzmann, Gibbs and Einstein

A natural question that arises relates to the origin of probability in Gibbs statistical mechanics. It is precisely in this context that Gibbs formulation differs from that of Maxwell, Boltzmann and Einstein. Maxwell was perhaps the first to recognize the need for a statistical approach to kinetic theory. His derivation of the probability distribution of the speed of monoatomic non-interacting gas molecules is an exercise in ingenuity and elegance. The probability is proportional to exponential of kinetic energy. This was later generalized by Boltzmann who included potential energy arising due to external forces and due to internal interactions amongst the molecules and showed the probability of a microstate is proportional to $\exp[-E/k_{\text{B}}T]$, where E is the total energy of the microstate, T is the temperature and k_{B} is the Boltzmann constant. The probability distribution is now known as Maxwell–Boltzmann distribution. Maxwell categorically stated that the Second

Gibbs formulation differs from that of Maxwell, Boltzmann, and Einstein in the context of probability in statistical mechanics.



⁴ For an interesting account of Maxwell's demon and other demons see [6].

law of thermodynamics is statistical in nature and hence there is a non-zero probability of it being contravened. In fact he constructed a demon – now called Maxwell's demon – that violates the Second law⁴. Thus for Maxwell, probability arises as an extra assumption in statistical mechanics, for describing macroscopic behaviour.

For Boltzmann the probability is of dynamical origin. A single dynamical trajectory of an equilibrium isolated system visits all the phase space points lying on a constant energy surface. The probability of finding the system in a region of its phase space is the fraction of observation time the dynamical trajectory spends in that region.

Einstein's formulation follows the methods of kinetic theory of gases. In Einstein's statistical mechanics, the system must necessarily be formed by a very large number of molecules. The result of a measurement must be identified with time average. Therefore he constructs a time-ensemble. The average over the time ensemble is equated to phase average.

⁵ Boltzmann was perhaps the lone champion of molecular kinetic theory of heat. He had to contend with the criticism and ridicule from the most influential and vociferous of the German speaking community – the so called energeticists led by Ernst Mach and Wilhelm Ostwald. The energeticists did not approve of molecular composition of matter and the kinetic theory. For them energy was the only fundamental entity. They dismissed with contempt any attempts to describe energy or energy transformation in more fundamental atomistic terms or kinetic picture. Only in the year 1905, the reality of atoms and molecules was established unambiguously by Einstein in his work on Brownian motion.

In Gibbs formulation, probability enters not as an additional hypothesis nor as a consequence of the formulation but as a part of the data on initial conditions of an ensemble of mechanical systems. When applied to a system of a large number of molecules, Gibbs formulation reduces to those based on kinetic theory. Strictly his formulation does not require any assumption on the molecular composition of matter. We should realize that in the times of Gibbs, kinetic theory did not receive general acceptance⁵. Gibbs formulation hinges on combining the configuration and momentum into a single phase and integrating over a phase-space density describing equilibrium Gibbs ensemble. The phase space density is uniform on a constant energy surface for a microcanonical ensemble and is an exponential function of energy for a canonical ensemble, as we have seen earlier.



Epilogue

The rigour, economy, generality and elegance of Gibbs formulation of statistical mechanics is borne out by the fact that the entropy fluctuation theorem⁶ derived by Gallavotti and Cohen [7] has been shown as a Gibbs property.

For Gibbs, scientific recognition was slow in coming. This was mainly because Gibbs was not a propagandist for his own work; nor, for that matter, was he one, for science. But eventually his work spoke for him and his fame grew slowly and steadily. He was elected a member of several important scientific academies of the world like the American Philosophical Society, the Dutch Society of Sciences in Haarlem, the Royal Society of Sciences in Göttingen, the Royal Institution of Great Britain, the Cambridge Philosophical Society and the Royal Society of London, to name only a few. The American Academy of Boston awarded him the Rumford medal in 1901 and the Royal Society gave him the Copley medal in 1901, ‘the highest honour English Science has to bestow’. When Einstein was asked whom he considered to be the most powerful thinkers he had known, he replied, “.....Lorenz...but I never met Willard Gibbs; perhaps, had I done so, I might have placed him beside Lorenz”. Let me end by quoting Max Planck: “... Gibbs will ever be reckoned among the most renowned theoretical physicists of all times” .

⁶ The fluctuation theorem of Cohen and Gallavotti arises in the context of nonequilibrium steady systems. The entropy refers to phase space contraction rate.

Suggested Reading

- [1] Gibbs first two papers were entitled ‘Graphical methods in thermodynamics of fluids’ and ‘A method of Geometrical Representation of the Thermodynamic Properties of Substances by means of Surfaces’, in *The Scientific papers of J. Willard Gibbs*, (2 vols); edited by H A Bumstead and R Gibbs Van Name, Longmans, Green and Co., New York, 1906; Dover Reprint, New York, 1961.



- [2] J W Gibbs, *Trans. Conn. Acad.*, Vol.III, p.108, Oct. 1875–May 1876; p.343, May 1877–July 1878.
- [3] J W Gibbs, Note on the Electromagnetic Theory of Light, *Am. J. Sci.*, Vol.23, p.262, p.460, 1882; Vol.25, p.107, 1883; Vol.35, p.467, 1888; Vol.37, p.129, 1889.
- [4] J W Gibbs, *Elementary principles in statistical mechanics*, Yale University Press, 1902.
- [5] M Guillen, An unprofitable experience: Rudolf Clausius and the Second law of thermodynamics in *Five Equations that changed the world: the power and poetry of Mathematics*, Hyperion, New York, p.165, 1995.
- [6] H S Leff and A F Rex (Eds), *Maxwell's Demon: Entropy, Information and Computing*, Adam Higler, Bristol, 1990.
H S Leff and A F Rex (Eds.), *Maxwell's Demon*, Princeton Univ. Press, Princeton, 1990.
H S Leff and A F Rex (Eds.), *Maxwell's Demon 2: Entropy, Classical and Quantum Information, Computing*, Institute of Physics, 2003.
J D Collier, Two faces of Maxwell's demon reveal the nature of irreversibility, *Studies in History and Philosophy of Science*, p.257, June 1990.
D L Hogenboon, Maxwell's Demon: Entropy, Information, Computing, *American Journal of Physics*, p.282, March 1992.
H S Leff, Maxwell's Demon, Power and Time, *American Journal of Physics*, pp.135–142, Feb. 1990.
- [7] G Gallavotti and E G D Cohen, Dynamical ensembles in non-equilibrium statistical mechanics, *Phys. Rev. Lett.*, Vol.74, p.2694, 1995.
G Gallavotti and E G D Cohen, Dynamical ensembles in stationary states, *J. Stat. Phys.*, Vol.80, p.931, 1995.
D Ruelle, Smooth dynamics and new theoretical ideas in non-equilibrium statistical mechanics, *J. Stat. Phys.*, Vol.95, p.393, 1999.
- [8] <http://www.mlahanas.de/Physics/Bios/WillardJGibbs.html>
- [9] H A Bumstead, 'Josiah Willard Gibbs', *American Journal of Science*, XVI(4), 1903.
- [10] R C Cantelo, 'J Willard Gibbs, a brief biography and a summary of his contributions to chemistry', *Can. Chem. Metallurgy*, Vol.8, p.215, 1924.
- [11] L P Wheeler, *Josiah Willard Gibbs, The History of a Great Mind*, Yale University Press, 1952.
- [12] R J Seeger, *J Willard Gibbs, American mathematical physicist par excellence*, Pergamon Press, 1974.
- [13] Jagdish Mehra, *Josiah Willard Gibbs and the Foundations of Statistical Mechanics*, Foundations of Physics, Vol.28, p.1785, 1998.

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