11 Statistical Physics: Maxwell and Boltzmann

11.0 Texts

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11.1 Maxwell the man

From the Britannica, some extracts:

Maxwell, James Clerk (1831-1879)
Scottish physicist best known for his formulation of electromagnetic theory. He is regarded by most modern physicists as the scientist of the 19th century who had the greatest influence on 20th-century physics, and he is ranked with Sir Isaac Newton and Albert Einstein for the fundamental nature of his contributions. In 1931, on the 100th anniversary of Maxwell's birth, Einstein described the change in the conception of reality in physics that resulted from Maxwell's work as "the most profound and the most fruitful that physics has experienced since the time of Newton."

The concept of electromagnetic radiation originated with Maxwell, and his field equations, based on Michael Faraday's observations of the electric and magnetic lines of force, paved the way for Einstein's special theory of relativity, which established the equivalence of mass and energy. Maxwell's ideas also ushered in the other major innovation of 20th-century physics, the quantum theory. His description of electromagnetic radiation led to the development (according to classical theory) of the ultimately unsatisfactory law of heat radiation, which prompted Max Planck's formulation of the quantum hypothesis--i.e., the theory that radiant-heat energy is emitted only in finite amounts, or quanta. The interaction between electromagnetic radiation and matter, integral to Planck's hypothesis, in turn has played a central role in the development of the theory of the structure of atoms and molecules.

....His first scientific paper, published when he was only 14 years old, described a generalized series of oval curves that could be traced with pins and thread by analogy with an ellipse. This fascination with geometry and with mechanical models continued throughout his career and was of great help in his subsequent research.

At the age of 16 he entered the University of Edinburgh, where he read voraciously on all subjects and published two more scientific papers. In 1850 he went to the University of Cambridge, where his exceptional powers began to be recognized. His mathematics teacher, William Hopkins, was a well-known "wrangler maker" (a wrangler is one who takes first class honours in the mathematics examinations at Cambridge) whose students included Tait, George Gabriel (later Sir George) Stokes, William Thomson (later Lord Kelvin), Arthur Cayley, and Edward John Routh. Of Maxwell, Hopkins is reported to have said that he was the most extraordinary man he had met with in the whole course of his experience, that it seemed impossible for him to think wrongly on any physical subject, but that in analysis he was far more deficient. (Other contemporaries also testified to Maxwell's preference for geometrical over analytical methods.) This shrewd assessment was later borne out by several important formulas advanced by Maxwell that obtained correct results from faulty mathematical arguments.

....In 1856 he was appointed to the professorship of natural philosophy at Marischal College, Aberdeen. In 1860 the University of Aberdeen was formed by a merger between King's College and Marischal College, and Maxwell was declared redundant. He applied for a vacancy at the University of Edinburgh, but he was turned down in favour of his school friend Tait. He then was appointed to the professorship of natural philosophy at King's College, London.

The next five years were undoubtedly the most fruitful of his career. During this period his two classic papers on the electromagnetic field were published, and his demonstration of colour photography took place. He was elected to the Royal Society in 1861. His theoretical and experimental work on the viscosity of gases also was undertaken during these years and culminated in a lecture to the Royal Society in 1866. He supervised the experimental determination of electrical units for the British Association for the Advancement of Science, and this work in measurement and standardization led to the establishment of the National Physical Laboratory. He also measured the ratio of electromagnetic and electrostatic units of electricity and confirmed that it was in satisfactory agreement with the velocity of light as predicted by his theory.

Later life

In 1865 he resigned his professorship at King's College and retired to the family estate in Glenlair. He continued to visit London every spring and served as external examiner for the Mathematical Tripos (exams) at Cambridge. In the spring and early summer of 1867 he toured Italy. But most of his energy during this period was devoted to writing his famous treatise on electricity and magnetism.

It was Maxwell's research on electromagnetism that established him among the great scientists of history. In the preface to his Treatise on Electricity and Magnetism (1873), the best exposition of his theory, Maxwell stated that his major task was to convert Faraday's physical ideas into mathematical form. In attempting to illustrate Faraday's law of induction (that a changing magnetic field gives rise to an induced electromagnetic field), Maxwell constructed a mechanical model. He found that the model gave rise to a corresponding "displacement current" in the dielectric medium, which could then be the seat of transverse waves. On calculating the velocity of these waves, he found that they were very close to the velocity of light. Maxwell concluded that he could "scarcely avoid the inference that light consists in the transverse undulations of the same medium which is the cause of electric and magnetic phenomena."

Maxwell's theory suggested that electromagnetic waves could be generated in a laboratory, a possibility first demonstrated by Heinrich Hertz in 1887, eight years after Maxwell's death. The resulting radio industry with its many applications thus has its origin in Maxwell's publications.

In addition to his electromagnetic theory, Maxwell made major contributions to other areas of physics. While still in his 20s, Maxwell demonstrated his mastery of classical physics by writing a prizewinning essay on Saturn's rings, in which he concluded that the rings must consist of masses of matter not mutually coherent--a conclusion that was corroborated more than 100 years later by the first Voyager space probe to reach Saturn.

The Maxwell relations of equality between different partial derivatives of thermodynamic functions are included in every standard textbook on thermodynamics (see thermodynamics). Though Maxwell did not originate the modern kinetic theory of gases, he was the first to apply the methods of probability and statistics in describing the properties of an assembly of molecules. Thus he was able to demonstrate that the velocities of molecules in a gas, previously assumed to be equal, must follow a statistical distribution (known subsequently as the Maxwell-Boltzmann distribution law). In later papers Maxwell investigated the transport properties of gases--i.e. the effect of changes in temperature and pressure on viscosity, thermal conductivity, and diffusion.

In addition to these well-known contributions, a number of ideas that Maxwell put forward quite casually have since led to developments of great significance. The hypothetical intelligent being known as Maxwell's demon was a factor in the development of information theory. Maxwell's analytic treatment of speed governors is generally regarded as the founding paper on cybernetics, and his "equal areas" construction provided an essential constituent of the theory of fluids developed by Johannes Diederik van der Waals. His work in geometrical optics led to the discovery of the fish-eye lens. From the start of his career to its finish his papers are filled with novelty and interest. He also was a contributor to the ninth edition of Encyclopædia Britannica.

In 1871 Maxwell was elected to the new Cavendish professorship at Cambridge. He set about designing the Cavendish Laboratory and supervised its construction. Maxwell had few students, but they were of the highest calibre and included William D. Niven, Ambrose (later Sir Ambrose) Fleming, Richard Tetley Glazebrook, John Henry Poynting, and Arthur Schuster.

During the Easter term of 1879 Maxwell took ill on several occasions; he returned to Glenlair in June but his condition did not improve. He died on November 5, after a short illness. Maxwell received no public honours and was buried quietly in a small churchyard in the village of Parton, in Scotland.

11.2 Thermodynamics

Maxwell(1860) applied the theory of errors to finding " *the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of particles".*

To Laplace, mechanics provided an exact deterministic description of the motion of bodies. Given the field and initial positions and velocities of all particles, the motion is specified. However, since we make errors in measuring these quantities, are ignorant of the exact values, we can give only probabilistic descriptions of the results, reflecting our incomplete knowledge.

Maxwell, influenced by Quetelet, introduced probabilities into the science of mechanics itself; probabilities were necessary to provide an objective description of systems in motion. These probabilities can not be mere probabilities based on lack of knowledge, since the systems behave according to Maxwell's predictions, and the systems know not and care not about our lack of knowledge.

The mechanical theory of ideal gases attempts to derive the standard empirically determined gas law pV=RT from Newton's mechanics. Kroenig in 1856 considered a cubical container in which molecules moved with equal velocity, one third along each axes, and derived the gas law thereby. (The number of molecules striking per unit time is proportional to the velocity, and the change in velocity for each molecule is proportional to the velocity, so the change in velocity per unit time for all molecules is proportional to the velocity squared; pressure is force per unit area, proportional to the acceleration exerted by the wall on the molecules, the change in velocity per unit time , proportional to the square of the velocity. The temperature is proportional to the kinetic energy of the molecules, also the velocity squared.) Kroenig remarks " *the path of each molecule must be so irregular that it will defy all calculations. However, according to the laws of probability theory, we can assume a completely regular motion in place of this completely irregular motion."*

Kroenig is appealing to the law of large numbers, in which the average velocity of the particles is all that will matter, and that should be the same in all three directions. And yet, isn't it the square of the velocity that is important?

Maxwell(1860): He determines what the distribution of velocity is *"after a great number of collisions among a great number of equal particles":*

Let N be the whole number of the particles. Let x,y,z be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which x lies between x and x + dx be Nf(x)dx, where f(x) is a function of x to be determined.
The number of particles for which y lies between y and y + dy will be Nf(y)dy; and the number for which z lies between z and z + dz will be Nf(z)dz, where f always stands for the same function.
Now, the existence of the velocity x does not in any way affect that of the velocities y or z, because these are all at right angles to each other and independent, so that the number of particles whose velocity lies between x and x+ dx, between y and y + dy, and between z and z + dz is Nf(x)f(y)f(z)dxdydz.
If we suppose the N particles to start from the origin at the same instance, then this number will be the number in the element of volume (dxdydz) after a unit of time, and the number referred to as the unit of volume will be Nf(x)f(y)f(z).
But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is,

$$f(x)f(y)f(z) = F(x^2 + y^2 + z^2).$$

Solving this functional equation, we find

$$f(x) = Ce^{Ax^2}, F(r) = C^3 e^{Ar^2} \ .$$

If we make A positive, the number of particles will increase with the velocity, and we should find the whole number of particles infinite. We therefore make A negative and equal to $-\alpha^2$*, so that the number between x and x+ dx is* $NCe^{-\alpha^2 x^2} dx$
Integrating from plus to minus infinity, we find the whole number of particles,
$NC\sqrt{\pi}$ *=N so that C=*$1/\alpha\sqrt{\pi}$ *and f(x) is therefore* $(\alpha/\sqrt{\pi})e^{-x^2\alpha^2}$.

(I have corrected some obvious algebraic misprints in Maxwell's work.)
From this Maxwell concluded that the mean squared velocity is $3\alpha^2$.
The *Maxwell-Boltzmann* distribution is the density of the three velocities

$$f(x,y,z) = C\exp(-\tfrac{m}{2kT}(x^2 + y^2 + z^2)).$$

where m = mass, T= temperature, k= Boltzmann's constant.

11.3 Reversibility

Maxwell was concerned about the independence assumption for the velocities in three directions; after all, if you saw x to be rather high, would you not conclude that y and z are also high? In Maxwell(1867), he took another tack: From Guttman(1999)(p16, but almost all the equations have misprints):
Maxwell observed that the collisions between molecules must be the mechanism by which uniform pressure is maintained on the different walls of the vessel. Collisions between molecules will change the distributions of positions and velocities of the molecules in such a way as to preserve an equilibrium distribution. (The equilibrium distribution is the same as the stationary distribution in a Markov chain, which must bear a certain relationship to the transition probabilities of the chain.) Maxwell made the following two assumptions:

1. The velocities of the colliding molecules are uncorrelated. Hence, if $p(v_1, v_2)$ is the probability that a pair of colliding molecules will have, respectively, the velocities v_1, v_2 then $p(v_1, v_2) = p(v_1)p(v_2)$ where $p(v_1), p(v_2)$ are the probabilities of choosing at random a molecule with the respective velocities. (I would translate this into population terms as saying that the proportions of colliding molecules in time $(t, t+dt)$ having velocities in the ranges $v_1 + dv_1, v_2 + dv_2$ $p(v_1, v_2)dv_1 dv_2 dt^2 = p(v_1)dv_1 dt \times p(v_2)dv_2 dt$)

2. Let V_1, V_2 be the velocities of a pair of colliding molecules before the collision and v_1, v_2 their velocities after the collision. Maxwell's second assumption was that the probability that a colliding pair will undergo the velocity change $V_1, V_2 \to v_1, v_2$ because of the collision will be the same as the probability of the velocity change $v_1, v_2 \to V_1, V_2$. That is, the "reverse" change is as probable as the original change.

(In physical terms, there is no direction of time in the way the molecules interact. In Markov chain terms, the transition matrix is symmetric. For a symmetric transition matrix with positive entries, the stationary probabilities are uniform)
From the two assumptions it follows that the stationary distribution of v_1, v_2 is uniform over those states that can be reached from V_1, V_2. Thus $p(V_1)p(V_2) = p(v_1)p(v_2)$ for those states v_1, v_2 can be reached from V_1, V_2. Also conservation of energy requires that $|v_1|^2 + |v_2|^2 = |V_1|^2 + |V_2|^2$ from which it follows that $p(V) = \frac{\alpha}{\sqrt{\pi}} e^{-|V|^2 \alpha^2}$ as before. Here $|V|^2$ is the sum of squares of the component velocities.

11.4 Boltzmann the man

From the Britannica,

Boltzmann, Ludwig Eduard (1844-1906) physicist whose greatest achievement was in the development of statistical mechanics, which explains and predicts how the properties of atoms (such as mass, charge, and structure) determine the visible properties of matter (such as viscosity, thermal conductivity, and diffusion).

After receiving his doctorate from the University of Vienna in 1866, Boltzmann held professorships in mathematics and physics at Vienna, Graz, Munich, and Leipzig.

In the 1870s Boltzmann published a series of papers in which he showed that the second law of thermodynamics, which concerns energy exchange, could be explained by applying the laws of mechanics and the theory of probability to the motions of the atoms. In so doing, he made clear that the second law is essentially statistical and that a system approaches a state of thermodynamic equilibrium (uniform energy distribution throughout) because equilibrium is overwhelmingly the most probable state of a material system. During these investigations Boltzmann worked out the general law for the distribution of energy among the various parts of a system at a specific temperature and derived the theorem of equipartition of energy (Maxwell-Boltzmann distribution law). This law states that the average amount of energy involved in each different direction of motion of an atom is the same. He derived an equation for the change of the distribution of energy among atoms due to atomic collisions and laid the foundations of statistical mechanics.

Boltzmann was also one of the first continental scientists to recognize the importance of the electromagnetic theory proposed by James Clerk Maxwell of England. Though his work on statistical mechanics was strongly attacked and long-misunderstood, his conclusions were finally supported by the discoveries in atomic physics that began shortly before 1900 and by recognition that fluctuation phenomena, such as Brownian motion (random movement of microscopic particles suspended in a fluid), could be explained only by statistical mechanics.

11.5 The second law of thermodynamics

Boltzmann carried on the Maxwellian program of explaining thermodynamics by the statistical behaviour of populations of molecules. He introduced the notion of probability as time averaging.. the probability that the state (position and velocity) of a molecule is in set A is the proportion of time it lies in A over an infinitely long period of time. However, he also asserts that this is the same proportion as the relative number of molecules with states in the set A at any given period of time.

In Boltzmann(1872) the time evolution of states of a large number of molecules is considered; Boltzmann introduced a notion of entropy which increased over time until in the limit the distribution of states reaches a stationary distribution, the Maxwell distribution.

Let p(x|t) be the proportion of molecules with velocity x at time t. Due to collisions with other molecules, there is a distribution say p(x|t+dt) at a slightly later time. Boltzmann's equation gives $\frac{\partial p(x,t)}{\partial t}$; when this expression is zero, the system is in equilibrium, and the solution for p(x,t) is Maxwell's normal distribution of velocities. Boltzmann's entropy is $-\int p(x\mid t)\log(p(x\mid t)dx$ which increases over time unless $\frac{\partial p(x,t)}{\partial t}$=0 and Maxwell's normal distribution is attained for the velocities.

The increase in entropy may be connected to the fact that the distribution with fixed variance and mean zero maximizing the entropy is the normal. Jaynes advocates maximizing the entropy to specify families of distributions for which only some moments are specified.