

Statistical Mechanics—a lightning course

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What is statistical mechanics?

- Statistical mechanics is the study of the bulk properties of matter under the assumption that matter is composed of a very large number of particles (atoms, molecules etc.).
- Each particle is assumed to obey the laws of mechanics, and this may be classical, quantum, relativistic or whatever, the application of statistical methods means that we are considering the collective behaviour of the assembly of particles, and not the behaviour of individual particles.
- The development of the kinetic theory of gases can be considered a precursor to statistical mechanics, or even the first manifestation of it.
- Our story will begin with a study of the kinetic theory of gases.
- One must understand the zeitgeist to appreciate the development of statistical mechanics.

Kinetic theory background.

- Since the publication of Newton's *Principia Mathematica* in 1687, and subsequent developments, mechanics was considered the exemplar of a scientific theory, and one to which all other physical theories should aspire.
- Laplace cemented the centrality of mechanics by developing the idea that if one were supplied with complete information about the position and momenta of all individual atoms, one could, in principle, determine their subsequent positions and motions at all subsequent times.
- This deterministic view really only met its death in the 1920s with the development of quantum mechanics.
- Early in the 18th century, the presence of an ether was widely accepted.

Kinetic theory background.

- This mysterious fluid was held to be essential to the transmission of energy between bodies in the form of heat or light.
- Gas pressure was attributed to the *motion* of particles (rather than as a result of interactions), notably vibrational motion while suspended in the ether, or rotational motion caused by ether vortices.
- Other theories held that the fact that systems tend to thermal equilibrium—and not dis-equilibrium—must be due to some kind of interaction between molecules and the ether (Culverwell 1890).

Thermodynamics.

- Before discussing statistical mechanics, a brief mention of thermodynamics is necessary.
- Thermodynamics preceded statistical mechanics.
- In 1842, the German physician Julius Mayer (1814-78) first stated explicitly that heat is a form of energy.
- This was tacitly recognised earlier by Nicolas Sadi Carnot (1796-1824), who worked on heat engines, and was responsible for the second law of thermodynamics, in his *Réflexions sur la puissance motrice du feu*, published in the year of his death.
- Interestingly, Carnot's great achievements were ignored by the French (apart from one paper by his classmate Clapeyron in 1836), though in Germany and England his achievements were widely recognised and acknowledged.

Thermodynamics—the first law.

- The first law of thermodynamics says that heat is a form of energy, and that energy is conserved.
- More precisely, it says that the change in energy is given by the heat absorbed by a system minus the amount of work done by the system,

$$dU = dQ - dW.$$

- Here, dU is an exact differential, thus $\int dU$ is path independent, which is not true for $\int dW$ or $\int dQ$.
- Two special cases occur. Firstly, when $dQ = 0$, an *adiabatic* process, where there is no heat flow into or out of the system, and secondly when there is no work done $dW = 0$.

Thermodynamics—the second law.

- Consideration of naturally occurring processes points us to the second law.
- Experience tells us it is possible to convert work entirely into heat, but the converse is not so obvious.
- If a motor car heats up in the sun, it is unlikely to start moving of its own accord—fortunately—though this is allowed by energy conservation.
- The second law provides the answer to the question as to what extent heat can be converted into work by introducing a somewhat mysterious concept called entropy.
- This is a state variable like temperature, but is not something that can be directly measured. If a system at temperature T reversibly absorbs or releases an infinitesimal amount of heat, dQ , then the change of entropy $dS = \frac{dQ}{T}$.

Thermodynamics—the second law, continued.

- Here dS is a total differential.
- The second part, the irreversible part, states that the entropy of an isolated (adiabatic) system can never decrease.
- Digression C P Snow (The Two Cultures 1956)—criticised scientific illiteracy. Everyone knows a play by Shakespeare, but almost nobody knows what the second law of thermodynamics is about!
- There are two equivalent statements, one due to Lord Kelvin (1824-1907) in 1851, and the other to Rudolf Clausius (1822-88) in 1850.

Thermodynamics—the second law, continued.

- Clausius's version is that there is no thermodynamic process whose *sole* effect is to extract heat from a colder reservoir and deliver it to a hotter one.
- The Kelvin statement is that there is no thermodynamic process whose *sole* effect is to extract heat from a reservoir and convert it entirely into work.
- Another statement is that in a *closed* system, the entropy cannot decrease.
- Thus the second law states that, for an *isolated* system, undergoing an *adiabatic* process,

$$dS = \frac{dQ}{T}, \quad \frac{dS}{dt} \geq 0.$$

- Heuristically, it is a statement about approach to equilibrium.

Thermodynamics—the second law, continued.

- The Wikipedia statement is that *The entropy of an isolated system not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium.*
- It is a subtle and complex law, with many implications that required its refinement.
- Gibbs showed that a paradox occurs if one considers the entropy of mixing.
- Initial calculations gave a result that implied that the entropy of mixing two quantities of the same ideal gas depends on their history, and thus cannot be merely a function of state.
- Gibbs resolved the paradox by empirically including a factor $\frac{1}{N!}$, which removed the paradox.

Thermodynamics—the second law, continued.

- It was only years later, with the advent of quantum mechanics, that this assumption was justified.
- The state of a gas is quantum mechanically described by an N -particle wave function which is symmetric or anti-symmetric w.r.t. particle interchange.
- This only changes the sign, but doesn't produce a new state.
- Thus we justify the indistinguishability of the particles, which justifies the correction factor.

Thermodynamics—the second law, continued.

- In the 1860s and 1870s, there were attempts to “mechanise” the second law.
- It was realised that the first law was a special case of conservation of energy, and correspondingly the underlying mechanical principle yielding the second law was sought.
- The most popular candidate was Hamilton’s Principle of Least Action.
- What was sought was the mechanical identity of the integrating factor for the heat transferred in a reversible change.
- This would give a mechanical analogue of entropy. But the irreversible increase of entropy with time would still be unexplained.

The second law—statistical concepts appear.

- Both Boltzmann and Maxwell realised around 1870 that this reduction of the second law must revolve around statistical considerations.
- Boltzmann took a big step with his *H-theorem* for low-density gases,
- This asserts that a quantity $H(t) = \int d^3v f(\mathbf{p}, t) \log f(\mathbf{p}, t)$ dependent on the velocity distribution $f(\mathbf{p}, t)$ always decreases in time unless the gas is in thermal equilibrium.
- The mathematical statement is $\frac{dH}{dt} \leq 0$.
- H was then identified (up to a multiplicative constant) with the negative of the entropy.

The second law—entropy clarified.

- Later, Boltzmann proposed a simple, elegant interpretation: That the entropy of a system is proportional to its probability,

$$S = k \log W,$$

where W is the number of configurations (or microstates), corresponding to the macrostate of the system.

- This formula is engraved on Boltzmann's tombstone, under which he lies after committing suicide in 1906.
- If one samples at random from the microstates the probability of finding a given macrostate is proportional to the number of such microstates, or its W .

More on entropy.

- However given a macrostate, one doesn't know what microstate it is in, out of a possible W such microstates.
- If W is large, one thinks of the system as “disordered.” Boltzmann thus claimed that the statement “entropy tends to increase” can be interpreted to mean “a system tends to become more disordered.”
- Entropy also enters information theory through this same relation.
- The third law, developed by Walther Nernst in the period 1906-12, states that there is a minimum temperature, and as that temperature is approached, the entropy tends to zero. That is, $T \rightarrow 0$ implies $S \rightarrow 0$. This is a quantum-mechanical result.
- Before leaving thermodynamics, we'll recall (or introduce) some basic formulae:

Thermodynamic relations.

- In an isolated system, in a volume V we call its energy the *internal energy*, and write $U(S, V)$.
- Then the absolute temperature

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

the pressure

$$P = - \left(\frac{\partial U}{\partial V} \right)_S = - \left(\frac{\partial A}{\partial V} \right)_T$$

the Helmholtz free energy

$$A = U - TS$$

the Gibbs free energy

$$G = U + PV - TS = A + PV$$

Thermodynamic relations.

- the specific heat (at constant volume)

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

and also the entropy

$$S = - \left(\frac{\partial A}{\partial T} \right)_V.$$

Other thermodynamic relationships can be easily found by taking different independent variables than S and V .

Statistical Mechanics.

- Statistical mechanics is based on the application of probability theory to the field of mechanics.
- The most famous names associated with the historical development of statistical mechanics are Clausius, Maxwell, Boltzmann and Gibbs.
- However Stephen Brush persuasively argues that the real founding father is the forgotten Scottish scientist John J. Waterson (1811-83).
- In 1845, while living in Bombay, he submitted a paper entitled “On the Physics of Media that are composed of free and perfectly elastic molecules in a State of Motion” to the Royal Society
- He was seeking a consistent theory based on a few plausible assumptions, rather than the more comprehensive theories of his successors.

J. J. Waterson's contribution.

- He first assumed that heat is some kind of motion of the smallest parts of bodies (what we would consider molecules).
- His second assumption was that the molecules move rapidly, in various directions, with frequent “fortuitous encounters.”
- He then assumed that the properties could be obtained by averaging over all possible molecular states. This was the precursor to the later “ergodic hypothesis.”
- His third assumption was that, in equilibrium, a mixture of particles of different mass would have the same average kinetic energy. This assumption is now known as the “equipartition theorem.”

J. J. Waterson's contribution.

- Waterson then developed his theory, in an axiomatic style that we would now welcome, but that was not familiar 150 years ago, to explain some experimentally known facts, such as the ratio of specific heats, and the observed decrease of temperature with height in the atmosphere.
- He also identified the temperature of a gas with the square of the velocity of the molecules.
- He made other calculations too which were sound. Two referees however called the paper "nonsense," so the Royal Society declined to publish it.
- Even worse, they refused to give it back to him, so he was unable to publish it elsewhere, as he didn't have a copy.
- Some 50 years later, Lord Rayleigh discovered the paper and arranged for its publication (1893).

- He commented at the time: *The history of this paper suggests that highly speculative investigations, especially by an unknown author, are best brought before the world through some other channel than a scientific society, which naturally hesitates to admit into its printed records matter of uncertain value. Perhaps one may go further and say that a young author who believes himself capable of great things would usually do well to secure the favourable recognition of the scientific world by work whose scope is limited, and whose value is easily judged, before embarking on greater flights.*