

Statistical Mechanics—a lightning course

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Clausius's contribution

- After Waterson, Clausius, Maxwell and Boltzmann developed the kinetic theory of gases.
- The famous paper of Clausius *Über die Art der Bewegung welche wir Wärme nennen* (On the kind of motion which we call heat), was published in 1857.
- This was a consequence of several theoretical and experimental developments.
- Thermodynamics was one, in particular energy conservation as expressed by the first law.
- Experiments by Joule and Thompson showed that the pressure of a gas is not caused by repulsive intermolecular forces (these were associated with the *caloric* theory of fluids that prevailed at the time), and indeed that long range forces are attractive, rather than repulsive.

Clausius's contribution

- The wave theory of light was being accepted at that time, and that, together with the view that heat and light were similar phenomena, also led to the view that heat was a form of motion, and so the laws of mechanics could apply.
- Historically, there was an opposing view, led by Mayer and Ernst Mach (1838-1916), who felt that heat was a separate form of energy.
- This school was known as the “energetics” movement. It was becoming increasingly rejected by the end of the 19th century.
- Clausius had been thinking of molecular motion as the basis of heat as far back as 1850, and in 1857 developed a theory of gases based on including translational and rotational molecular motion.

Clausius's assumptions

- His theory contained a number of simplifying assumptions—the molecules must be very small, the interactions must be negligible, and he then calculated the specific heat as a consequence of the kinetic energy of the molecules.
- He also made the simplifying assumption that the molecules all had the same velocity.
- Clausius also proposed a qualitative description of other states of matter—liquid and solid, and was even able to develop a theory of changes of state, a precursor to our contemporary study of phase transitions.
- In the liquid state, the molecules were assumed to have no fixed positions, but to remain in close proximity to one another.
- In the solid state, they were assumed to be in fixed positions, vibrating about these positions.

Clausius's calculations

- Clausius was also able to calculate the average speeds of molecules of the gases making up the atmosphere, and got numbers in the range 460–1850 m/sec.
- A Dutch meteorologist, C H D Buys-Ballot realised an overlooked consequence of these values.
- If correct, the mixing of gases by diffusion should occur much more rapidly than is observed experimentally.
- A smell produced in one corner of a room should be noticed instantly in the opposite corner, and it isn't. (BB thought that this killed C's theory).
- Clausius then modified his theory in 1858 in an important way. He gave his molecules a non-zero diameter, and postulated an effective “sphere of action” so that a molecule will collide with another fairly rapidly. He quantified this with the notion of a *mean-free path* L , which is the average distance a molecule travels between collisions.

Clausius's calculations

- If N denotes the number of molecules of effective diameter d in a volume V , we have $L = \frac{kV}{Nd^2}$, where the constant k is of order-of-magnitude 1.
- While an *ad hoc* assumption, Maxwell (1831-79), in the first of three great papers on the subject, showed that it was a logical mechanism to explain viscosity, and incorporated it naturally into his theory.
- Clausius did realise that not all molecules travelled at the same speed, but used the average velocity in his calculations.
- Maxwell first pointed out in 1859 that the concepts of probability and statistics are appropriate to a model of collisions, as even if the molecules initially (whatever that means) had the same velocity, energy transfer by collisions would soon give a distribution of velocities.

Maxwell's contribution

- He obtained by heuristic, but non-rigorous arguments the famous distribution, now called the Maxwell-Boltzmann distribution function for a dilute gas of particle density $n = N/V$, each particle of mass m and average momentum \mathbf{p}_0 , at temperature T ,

$$f(\mathbf{p}) = \frac{n}{(2\pi mkT)^{3/2}} e^{-(\mathbf{p}-\mathbf{p}_0)^2/2mkT},$$

which gives the probability of finding a molecule with momentum \mathbf{p} in the gas.

Statistical mechanics—contemporary theory

- Statistical mechanics provides a framework for relating the microscopic properties of individual atoms and molecules to the macroscopic or bulk properties of materials that can be observed in everyday life, therefore explaining thermodynamics as a natural result of statistics and mechanics (classical and quantum) at the microscopic level.
- In particular, it can be used to calculate the thermodynamic properties of bulk materials from the spectroscopic data of individual molecules.
- This ability to make macroscopic predictions based on microscopic properties is the main asset of statistical mechanics over thermodynamics.
- Both theories are governed by the second law of thermodynamics through the medium of entropy.

Statistical mechanics—contemporary theory

- However, entropy in thermodynamics can only be known empirically, whereas in statistical mechanics, it is a function of the distribution of the system on its micro-states, as we will define and explain.
- It should be noted that statistical mechanics gives an explanation for the second law by postulating that a material is composed of atoms and molecules which are in constant motion.
- A particular set of positions and velocities for each particle in the system is called a *microstate* of the system and because of the constant motion, the system is constantly changing its microstate.
- Statistical mechanics postulates that, in equilibrium, each possible microstate is equally likely to occur.
- When this assumption is made, it leads to the conclusion that the second law must hold in a statistical sense.

Statistical mechanics—the 2nd law

- That is, the second law will hold on average, with a statistical variation on the order of $1/\sqrt{N}$ where N is the number of particles in the system.
- For everyday (macroscopic) situations, the probability that the second law will be violated is practically nil.
- However, for systems with a small number of particles, thermodynamic parameters, including the entropy, may show significant statistical deviations from that predicted by the second law.
- Classical thermodynamic theory does not deal with these statistical variations.

- In discussing the kinetic theory of gases, we found that a key result, the Maxwell-Boltzmann distribution, was elegantly simple, but the route to its discovery was quite complicated.
- In hindsight the result can be derived straightforwardly, without recourse to details of the molecular interactions, by making use of the method of most probable distribution.
- This suggests that a similar treatment might enable us to treat more general systems. This is indeed true, and gives rise to classical statistical mechanics.

Ensemble theory

- Statistical mechanics usually involves three different ensembles:
 - (i) The *microcanonical ensemble*, in which the number of particles and the energy are constant. Thus we are dealing with an isolated system.
 - (ii) More commonly, if we allow energy exchange, so that energy is not a constant, the appropriate ensemble is the *canonical ensemble*,
 - (iii) and if we permit the number of particles to vary, we then need to consider the *grand canonical ensemble*.
- In practice, the canonical ensemble is the most commonly used.
- In the following description of ensembles I have largely reproduced the treatment of K. Huang, *Statistical Mechanics*, 2nd edition, John Wiley & Sons 1987 and M. Plischke and B. Bergersen, *Equilibrium Statistical Mechanics*, 2nd edition, World Scientific 1994.

J W Gibbs 1839-1903

- Josiah Willard Gibbs (1839-1903) is considered the father of modern stat. mech. He is undoubtedly one of the greatest, and many would argue, the greatest American scientist.
- He was the 7th in a line of academics stretching from the 17th century.
- He obtained the first US PhD in engineering from Yale in 1863, and in 1866 went to Europe and worked in Paris, Berlin and Heidelberg, returning to Yale in 1869 where he was appointed to the first chair of mathematical physics (unpaid), which he held until his death.
- Between 1876 and 1878 he put physical chemistry on a thermodynamic footing.
- He developed the ensembles of statistical mechanics, defined the Gibbs free energy, introduced the concept of chemical potential and a number of other fundamental concepts.

Ensemble theory

- From 1880 he moved to mathematics, developing the subject of vector analysis, based on the quaternions of Hamilton and exterior algebra of Grassmann.
- He then applied this to the theory of optics, and electromagnetism, and subsequently to planetary and comet orbits.
- He never married, and received little recognition in his life-time.
- He wasn't elected to any of the US academies, and only when his papers were translated into German in 1892, and into French by Le Chatelier in 1899, did they receive widespread recognition in Europe.
- He was nevertheless quietly confident as to the value of his contribution. In 1901 he received the Copley Medal of the Royal society, the highest honour of the international community.

- Some quotations of Gibbs:
Mathematics is a language (at a Yale Faculty Board meeting), and
A mathematician may say anything he pleases, but a physicist must be at least partially sane.
- In 1945 Yale created the J. Willard Gibbs Chair of Theoretical Chemistry, held until 1973 by Lars Onsager, a worthy successor, who applied mathematical ideas to problems in physical chemistry and statistical mechanics. Onsager solved the 2d Ising model in 1944

Microcanonical ensemble

- We assume we are dealing with a large number of particles N , typically 10^{23} , in an appropriate volume V with the density N/V fixed.
- It is frequently the case that we consider the infinite limit of both N and V , while keeping the density fixed.
- Applying classical mechanics, we have Hamilton's equations of motion

$$\frac{\partial \mathcal{H}(p, q)}{\partial p_i} = \dot{q}_i$$

$$\frac{\partial \mathcal{H}(p, q)}{\partial q_i} = -\dot{p}_i,$$

$$i = 1 \dots 3N.$$

- We now introduce a $6N$ -dimensional phase space, often called Γ -space, in which each point represents a micro-state of the system.

Microcanonical ensemble—continued

- The energy surface is given by $H(p, q) = E$, and as time evolves, according to the above equations, a path is traced in Γ -space.
- The ensemble concept comes from the idea that we don't care about the state of the system at a particular time, but rather we want to know some macroscopic features of the system.
- Rather than trace the time evolution of the system, we take an infinite number of mental copies of the system, which can be in any state satisfying the conditions on N , V and E .
- The ensemble is represented by a density function $\rho(p, q, t)$ where

$\rho(p, q, t) d^{3N} p d^{3N} q$ = the number of points in the volume element centred around (p, q) at time t .

Microcanonical ensemble—continued

- Next we recall Liouville's theorem,

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) = 0,$$

which states that the distribution of points behaves like an incompressible fluid.

- Next we restrict our attention to ensembles which depend on (p, q) only through the Hamiltonian. Then $\frac{\partial \rho}{\partial t} = 0$, so the ensemble is time invariant.
- The fundamental postulate, which we need to continue, is the *Postulate of equal a priori probability*, which says that a macroscopic system is equally likely to be in any allowed state.
- This is logically not very satisfactory, as we should not require an independent postulate. The justification is usually *a posteriori*.

Microcanonical ensemble—continued

- Then the ensemble average of any quantity $f(p, q)$ is given by

$$\langle f \rangle \equiv \frac{\int d^{3N}p d^{3N}q f(p, q) \rho(p, q)}{\int d^{3N}p d^{3N}q \rho(p, q)}.$$

- In the usual formulation of this ensemble, we actually allow the energy to lie between E and $E + \delta E$.
- This is to take into account that in quantum mechanics, energy levels are discrete, but closely spaced.
- In classical statistical mechanics, this tolerance must play no role in the so called *thermodynamic limit* when $N \rightarrow \infty$, $V \rightarrow \infty$, n/V fixed.
- Define

$$\Gamma(E) \equiv \int_{E < \mathcal{H}(p, q) < E + \delta E} d^{3N}p d^{3N}q \rho(p, q),$$

then it is just the volume in Γ -space occupied by the microcanonical ensemble.

Microcanonical ensemble—continued

- Equivalently, it is often more convenient to consider the volume in Γ -space occupied by the energy surface of energy E , viz:

$$\Sigma(E) = \int_{\mathcal{H}(p,q) < E} d^{3N}p d^{3N}q,$$

- Then

$$\Gamma(E) = \Sigma(E + \delta E) - \Sigma(E).$$

This precludes us having to calculate ρ directly.

- The next step is to write the entropy $S(E, V)$ as

$$S(E, V) \equiv k \log \Gamma(E).$$

(This is defined up to an arbitrary additive constant).

- Here k is a constant, known as Boltzmann's constant, and the justification is by analogy with the formula derived above, and more particularly that it satisfies all the properties of the entropy function in thermodynamics.

Microcanonical ensemble—continued

- These are:
 - (i) it is extensive, which we prove below, and
 - (ii) it satisfies the properties of entropy as dictated by the second law.
- An equivalent definition (up to an additive constant of order $\log N$ or smaller) is

$$S(E, V) \equiv k \log \Sigma(E),$$

which is usually easier to use in calculations.

- The recipe for using the microcanonical ensemble is therefore
 - (i) to calculate the volume in Γ -space occupied by the microcanonical ensemble, and then
 - (ii) to calculate the entropy up to an additive constant by taking the logarithm, and then
 - (iii) solve for the energy E in terms of S and V .

Microcanonical ensemble—continued

- This gives the internal energy $U(S, V)$, and the rules of thermodynamics, given above, prevail
- Example: Consider an ideal gas of N particles of mass m in a volume V .
- The Hamiltonian is

$$\mathcal{H} = \frac{1}{2m} \sum_{i=1}^N p_i^2.$$

- We next calculate the entropy:

$$\Sigma(E) = \frac{1}{h^{3N}} \int_{\mathcal{H} < E} d^{3N}p \, d^{3N}q,$$

where h is a constant of dimension momentum \times distance, introduced to make $\Sigma(E)$ dimensionless.

- The integration over q immediately yields V^N .

Microcanonical ensemble—continued

- if $\Omega_n(R)$ denotes the volume of an n -dimensional sphere of radius R :

$$\Omega_n(R) = \int_{x_1^2 + x_2^2 + \dots + x_n^2 < R^2} dx_1 dx_2 \dots dx_n$$

then a little work establishes

$$\Omega_n(R) = \frac{2\pi^{n/2} R^n}{\Gamma(n/2 + 1)},$$

and

$$\Sigma(E) = \left(\frac{V}{h^3}\right)^N \Omega_{3N}(\sqrt{2mE}).$$

- Recall that $S(E, V) \equiv k \log \Sigma(E)$, and using Stirling's formula for the Gamma function, we obtain

$$S(E, V) = NK \log \left[V \left(\frac{4\pi mE}{3h^2 N} \right)^{3/2} \right] + \frac{3}{2} Nk.$$

Microcanonical ensemble—continued

- Solving for E , which is the internal energy $U(S, V)$, we find

$$U(S, V) = \frac{3h^2}{4\pi m} \frac{N}{V^{2/3}} \exp\left(\frac{2S}{3Nk} - 1\right).$$

- Applying the rules of thermodynamics above, we immediately obtain:

$$T = \frac{2U}{3Nk},$$

$$C_V = \frac{3}{2}Nk$$

and finally

$$P = \frac{2U}{3V} = \frac{NkT}{V},$$

or, in more familiar form, the ideal gas equation of state,

$$PV = NkT.$$