History of Statistical Physics

A short introduction
A good review on the history: [Darrigol and Renn(2000)]
Boltzmann's biography: [Cercignani(2000)].

March 20, 2022

What is Statistical Physics/Statistical Mechanics?

Statistical mechanics is the name given by the American physicist Josiah Willard Gibbs to the study of the statistical properties of **a large number of copies of the same mechanical system, with varying initial conditions**.

- In the beginning, people want to explore thermal properties of macroscopic matters.
- After quite a long time (centuries), people finally come to the conclusion that thermal properties comes from statistical properties of systems that have a very large number of identical constituents. This is what we call **statistical physics**.
- Then what is **statistical mechanics**? Statistical mechanics means trying to explain thermal phenomena on the basis of mechanics.

Early days of statistical mechanics

Early days of statistical mechanics focus on the model of **heat**, as people are figuring out the laws of thermodynamics. Some of those models are by no means correct (in today's point of view). (Since heat is energy!)

- Heat as a matter (Caloric theory): Heat, just like electricity, is a fluid that has no shape, can be stored in appropriate 'containers' like electricity, can flow from one body to another like electricity, can spread out and fill their containers as much as possible like electricity, and have no appreciable weight like electricity. This can be used to explain thermal expansion of matter including gases and chemical reactions. And this view is adopted by Sadi Carnot to discuss thermal machines. Laplace has some very sophisticated development of this model.
- But this is wrong! (Note that an infinite amount of heat can be produced from matter by mechanical work.)

Early days of statistical mechanics

- Heat as a motion:
  - The success of theory of light affected the understanding of heat.
  - By 1850 the model of heat as a motion was associated with the principle of energy conservation, whose most influential proponents were William Thomson and Hermann Helmholtz.
  - What kind of motion? Ampere's suggestion: a vibratory motion of molecules transmitted by the ether. (Nowadays we know that there is no ether.)
  - What kind of motion? William Rankine, William Thomson, and James Clerk Maxwell, imagined a vortex motion of gas molecules. In this picture, heat corresponded to the rotation of the molecules, and elasticity to their centrifugal force.
  - What kind of motion? Kinetic theory! Finally, a somewhat *correct* picture in today's point of view.

Kinetic theory

- Kinetic theory: a theory to explain the motion of gas.
- The molecules of a gas are assumed to occupy only a small fraction of its volume and to have a rectilinear, uniform motion, occasionally interrupted by mutual collisions or by collisions with the walls of the container.
- Kinetic theory has a very rich history dating back much earlier than 19th century.
- Daniel Bernoulli, 1738, assumed that the gas consists of a very large number of small particles in rapid motion, identified heat with kinetic energy, then derived Boyle-Mariotte's law (PV is constant) and the pressure is proportional to the square of the velocities of the gas-particles. (This is the starting point for most textbooks on thermodyanmics.)
- Bernoulli was about a century ahead of his time with his kinetic theory of gases. (Other people at that time believes in caloric theory.)

Kinetic theory

- Early pioneers: John Herapath (1820), James Joule (1847) (based on his experiments on energy conservation)
- Krönig (1856): Contrary to the widespread belief that gas molecules merely oscillate around positions of equilibrium he assumed that they move with constant velocity in straight lines until they strike against other molecules, or surface of container.
- Clausius (1850,1857,1858): already invented second law of thermodynamics, begin developing kinetic theory.
- Two attacks on kinetic theory:
  - How can heat traverse a vacuum if it is just irregular motion of matter particles?There is no matter in the vacuum which could propagate heat. However, caloric theory can explain this.
  - Some argued that since gas particles in the kinetic theory move with velocities of a few hundred meters per second, gases diffuse and mix much more rapidly than observed.
- Clausius introduces mean free path to resolve the second attack.

Kinetic theory

- Maxwell (1860): Maxwell distribution

$$f_0(\vec{v}) = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\frac{-m\vec{v}^2}{2kT} \tag{1}$$

  Maxwell derived that the viscosity of a dilute gas is independent of density (but depends on temperature). This is quite unexpected and was verified by experiments later.
- Boltzmann (1872):
  - Single particle distribution function $f = f(\vec{x}, \vec{v}, t)$.
  - Boltzmann's equation:

$$\frac{\partial f}{\partial t} = -\vec{v}\cdot\frac{\partial f}{\partial \vec{x}} + \text{ binary collision term} \tag{2}$$

  - In Boltzmann equation, one only consider collision of two particles, which is a good approximation for a dilute gas.
  - The assumption of ”molecular chaos”: the velocities of the colliding molecules must be uncorrelated.

Kinetic theory

More about Boltzmann:

- Boltzmann introduced the H function:

$$H[f] = \int d^3x \int d^3v f(\vec{x},\vec{v},t) \log f(\vec{x},\vec{v},t) \tag{3}$$

- He can show (for general interactions between molecules)

$$\frac{dH[f]}{dt} \leq 0 \tag{4}$$

  This is Boltzmann's famous H-theorem.

- Two attacks on Boltzmann's theory: reversibility paradox and recurrence paradox.
- His theory, was not widely accepted for a long time.

Equilibrium Statistcal Physics

More about Boltzmann, doing statistical physics:

- Reversibility paradox: consider time reversal of all the particles' movement in the system. Isn't that violating the H theorem?
- The procedure of time reversal violates the hypothesis of "molecular chaos".
- This motivates Boltzmann to work out his statistical interpretation of the second law.
- Boltzmann, 1877

$$S \propto \log \Omega \tag{5}$$

  Or by Max Planck $S = k \log W$. This relation has been called Boltzmann's Principle by Albert Einstein in 1905 since it can be used as the **foundation of statistical mechanics**.

Equilibrium Statistcal Physics

- In Boltzmann's statistical interpretation, the second law is thus not absolute but only probabilistic. The appearance of statistical fluctuations in small subsystems was predicted by Boltzmann and he recognized Brownian motion as such a phenomenon.
- The theory of Brownian motion has been worked out by Albert Einstein in 1905 and by others. The experimental verification of these theoretical results by Jean Baptiste Perrin was important evidence for the existence of molecules.
- Gibbs (1902): investigating three ensembles: microcanonical ensemble, canonical ensemble and grad canonical ensemble. Introducing chemical potential as a Lagrange multiplier.
- Quantum mechanical version of statistical physics: density $\hat{\rho}$ is an operator(matrix), and the entropy is defined by

$$S = -k\,\mathrm{Tr}(\hat{\rho}\log\hat{\rho}) \tag{6}$$

according to Von-Neumann.

C. Cercignani.
Ludwig boltzmann: the man who trusted atoms, 2000.

O. Darrigol and J. Renn.
The emergence of statistical mechanics.
In *The Oxford handbook of the history of physics*. 2000.