

The second law of thermodynamics and statistical mechanics

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Thermodynamics

First law:

The energy of the world is constant

Second law:

The entropy of the world increases

Clausius 1850

Mechanical explanation

- Assumptions about the mechanical structure. The system consists of very large numbers of equal particles. The motion is described by classical mechanics.
- Probabilistic assumptions: Regularities are observed in the relative frequencies of various configurations and velocities.

Leads to early versions of kinetic theory

Clausius 1857 about a gas in equilibrium

- The density is everywhere the same
- The velocity distribution is everywhere the same
- All directions of the velocity are equally probable
- Stosszahlansatz

Maxwell gives his distribution in 1859

$$f(u, v, w)du dv dw = A \exp(-B(u^2 + v^2 + w^2))du dv dw$$

These properties make it possible to give a kinetic interpretation of the equation of state, diffusion, heat conduction and viscosity

Boltzmann gives Maxwell-Boltzmann distribution in 1868

$$f(x, y, z, u, v, w)dx dy dz du dv dw = \alpha \exp\left\{-\beta\left[\frac{1}{2}m(u^2 + v^2 + w^2) + V(x, y, z)\right]\right\}dx dy dz du dv dw$$

Boltzmann proves the H - theorem in 1872 using the properties given by Clausius and Maxwell

- In a gas the H - function is always decreasing
- This is a kinetic derivation of the second law

$$H(t) = \int f(r, v, t) \ln f(r, v, t) dr dv = -\frac{S(t)}{k_B}$$

Where r and v are 3-dimensional vectors

On a constant energy surface a constant value $f = 1/W$ gives the smallest value of H . This gives Boltzmann's famous formula:

$$S = k_B \ln W$$

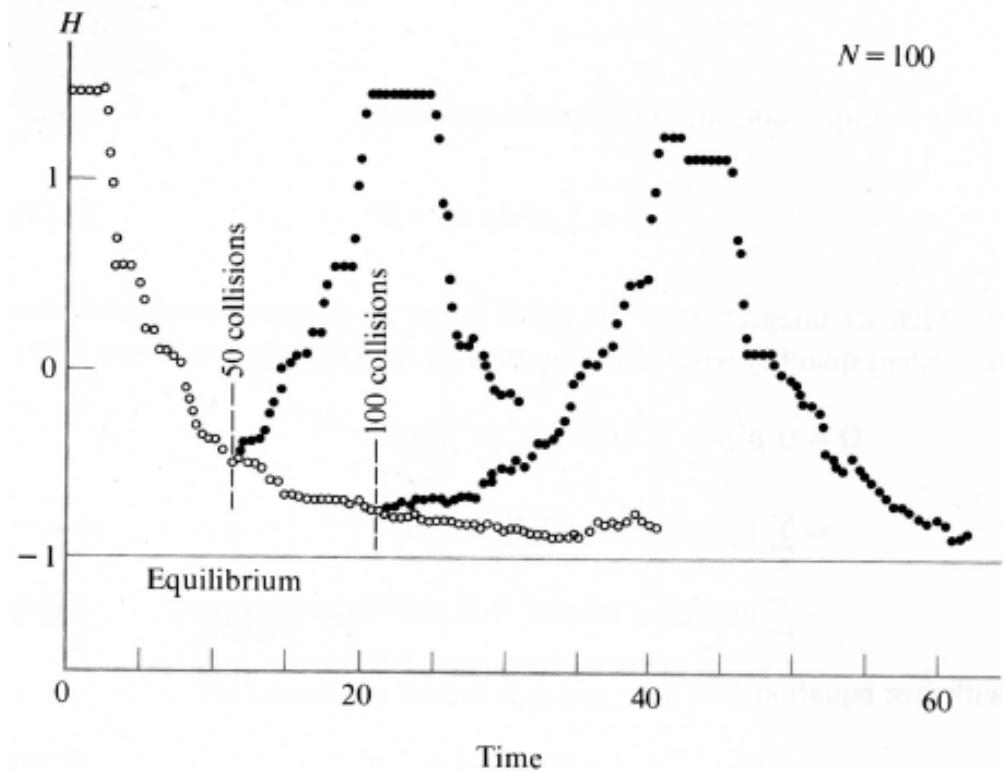
Boltzmann shows that H monotonically decreases until f becomes equal to the Maxwell-Boltzmann distribution when the system is in contact with a heat bath.

What about microscopic reversibility?

- Umkehrwand-Reversibility paradox, Loschmidt 1876: For every motion in phase space one can at any moment reverse the velocities and obtain an alternative solution. If H decreases before reversing the velocities H will increase after reversing the velocities.
- Wiederkehrwand-Reurrence paradox, Zermelo 1896: Poincaré 1890 had shown that the motion in phase space is quasi-periodic.

What is wrong in Boltzmann's derivation?

A. Bellemans and J. Orban,
Phys. Letters 24A (1967) 620



- H contains only the one particle distribution function. Contributions due to correlations are neglected.
- The Stosszahlansatz also assumes that there are no correlations between the particles when they collide. It even assumes that such correlations do not build up. This gives the Boltzmann equation

$$\frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial r} + F \cdot \frac{\partial f}{\partial v} = C(f)$$

The left hand side is antisymmetric for time reversal and the collision term on the right hand side is symmetric for time reversal.

We note that a statistical description is crucial to define the entropy

After much discussion and many years Boltzmann reformulated his H - theorem in the following way:

- H almost always decreases
- This holds both in the forward and in the backward direction
- H is quasi-periodic

This formulation solves the problem!

Can it be proven?

Statistical Mechanics

In order to verify the laws of thermodynamics on a molecular level, it is not necessary to follow a single trajectory in phase space. One imagines a great number of systems of the same nature and follows the behavior of the distribution $f_N(r_1, \dots, r_N, p_1, \dots, p_N, t)$ in phase space. The time dependence of such a distribution is given by the Liouville equation:

$$\frac{\partial f_N}{\partial t} = - \sum_{j=1}^N \left[\frac{\partial f_N}{\partial r_j} \cdot \frac{\partial r}{\partial t_j} + \frac{\partial f_N}{\partial v_j} \cdot \frac{\partial v_j}{\partial t} \right] = -[H, f_N]$$

This is an equation for incompressible flow of a $6N$ -dimensional fluid. It follows that the probability is conserved (Liouville's theorem).

We can therefore normalize the distribution in phase space and this normalization is conserved in time.

J. Williard Gibbs, Elementary principles in statistical mechanics, Yale Univ. Press, 1902; Dover, 1960.

N-particle H-function

$$H_N(t) = \int f_N(r_1, \dots, v_N, t) \ln f_N(r_1, \dots, v_N, t) dr_1 \dots dv_N = -\frac{S_N(t)}{k_B}$$

The Liouville equation gives:
$$\frac{dH_N(t)}{dt} = 0$$

H_N contains the contributions due to all correlations. Only when these correlations are neglected $H_N(t) = NH_1(t)$. This is N times Boltzmann's H-function.

A thermodynamic state of a system gives no precise definition of the state in phase space. A whole distribution in phase space corresponds to this state. According to Boltzmann the elements of this distribution which violate the second law have a measure zero.

Equilibrium statistical mechanics

Distributions which only depend on conserved quantities, like the Hamiltonian, are equilibrium distributions.

One has e.g. the micro-canonical, the canonical and the grand-canonical ensembles.

These ensembles make it possible to calculate the equilibrium thermodynamic properties of a system.

This method has been very successful

Non-equilibrium statistical mechanics

How do we show that a distribution $f_N(r_1, \dots, v_N; t)$ in phase space will approach the equilibrium distribution?

It is clear that H_N does not help!

A coarse grained description is needed.

Gibbs divided phase space in elements V_1, \dots, V_j, \dots and defined using f_N the probabilities P_j to be in different elements.

Gibbs was then able to show that any distribution $f_N(t=0)$ will as a function of the time redistribute itself and as a result $P_j(t)$ will for long enough times go to equilibrium.

In 1931 Birkhoff gives this result a more precise formulation and derives it.

Birkhoff's theorem 1931:

Consider a phase function $f(P)$ on an invariant part V of phase space then

$$\lim_{C \rightarrow \infty} \frac{1}{C} \int_0^C f(P, t) dt \quad \text{exists for almost all } P \text{ in } V$$

If V is metrically indecomposable it follows that

$$\lim_{C \rightarrow \infty} \frac{1}{C} \int_0^C f(P, t) dt = \frac{\int_V f(P) dV}{\int_V dV}$$

As energy surfaces are clearly invariant parts of phase space, the ergodic hypothesis is proven by Birkhoff's theorem if the energy surface is indecomposable.

Unsatisfactory is that the theorem does not give a clue how long it takes to reach the limit. If this is a Poincaré time it is too long!

The important clue to the resolution of this problem was the concept of the instability of trajectories in phase space, which goes back to the work of Poincaré in 1890

To characterise the instability of trajectories one introduces Liapunov exponents, who describe how adjacent points in phase space move relative to one another. For positive exponents the trajectories separate quickly. The Kolmogorov entropy is the sum of the positive exponents. When the Kolmogorov entropy is positive the trajectories are unstable.

Around 1970 Sinai was able to show that 2-dimensional systems with 2 or more hard disks have a positive Kolmogorov entropy and that they are therefore ergodic.

This was a great breakthrough!

Progress on the microscopic understanding of non-equilibrium problems

Einstein (1905) explained Brownian motion

Langevin formulated the Langevin equation for Brownian motion

$$m \frac{dv(t)}{dt} = K(t) - \xi v(t) + F_R(t)$$

The random force satisfies the fluctuation dissipation theorem:

$$\langle K_R(t) K_R(t') \rangle = 2k_B T \xi \delta(t - t')$$

Further developments gave the Fokker-Planck equation and the master equation to describe fluctuations in macroscopic systems.

In the 1960th and 70th al these descriptions were put on a solid footing using the Liouville equation and projection operator techniques developped by Zwanzig and Mori.

In all these approaches one follows Boltzmann in making a random phase like approximation. This then yields irreversible behaviour

What has happened further?

- Lebowitz (1970) pointed out that single trajectories in phase space will return to come close to their original position according to Poincaré, but that this was not the case for the distribution function in phase space used by Boltzmann. Zermelo's recurrence paradox is therefore not justified.

This argument seems very simple and correct. One wonders why nobody came up with it for more than 70 years. Prigogine quotes it with approval.

- Gaspard (2007) claims that dynamic system theory using concepts like the Kolmogorov-Sinai entropy per unit of time and Pollicott-Ruelle resonances proves the time asymmetry of mechanical systems

Rondoni and Cohen criticize this work. The information entropy is not the thermodynamic entropy and a property like local thermodynamic equilibrium is not fulfilled in the models considered.

Irreversibility on the microscopic level

- Prigogine (1980) in "From Being to Becoming" forwards the view that the microscopic equations of motion contain an irreversible contribution. He does not give an explicit equation of motion.
- Hatsopoulos, Gyftopoulos (1976) give an expression for the entropy of an isolated quantum mechanical system and together with Beretta (1985) give an extension of the Liouville-von Neumann equation with an irreversible contribution. For a single isolated two level system they give:

$$\frac{d\rho}{dt} + \frac{i}{\hbar} [H, \rho] = \begin{cases} -\frac{1}{\tau} \frac{\begin{vmatrix} \rho \ln \rho & \rho & \frac{1}{2}\{\rho, H\} \\ \text{Tr } \rho \ln \rho & 1 & \text{Tr } \rho H \\ \text{Tr } \rho H \ln \rho & \text{Tr } \rho H & \text{Tr } \rho H^2 \end{vmatrix}}{\text{Tr } \rho H^2 - (\text{Tr } \rho H)^2}, & \text{if } \rho^2 \neq \rho \\ 0, & \text{if } \rho^2 = \rho \end{cases}$$

It will go to far to discuss this proposal in more detail. The authors are right here organising the conference and can clarify their ideas themselves.

Conclusions

- In non-equilibrium statistical mechanics there is as yet no fully satisfactory derivation of the second law.
- Dynamic system theory should give a proof for a simple mechanical example (like hard disks between reflecting walls) in order to be convincing.
- Introducing irreversibility on the microscopic level gives entropy production already on this level. This solves the problem. Whether this is the way nature solves the problem only experiments can tell us.