What is the Minus First Law?

Introduction to the A. Szczepanek course

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A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overthrown.

Albert Einstein, Autobiographical Notes (in Albert Einstein: Philosopher–Scientist, edited by Paul Arthur Schilpp, 1949).

First Law. $\Delta U = Q - W$.

Energy cannot be created or destroyed, only transformed from one form to another.

The total energy of an isolated system remains constant, though it may change form (e.g., from heat to mechanical work).

Second Law. $\Delta S \geq 0$.

In any natural (spontaneous) process, the total entropy of an isolated system always increases or, in ideal reversible cases, remains constant.

Heat naturally flows from hot to cold bodies. No engine can convert all heat into work (some energy is always lost as waste heat). The second law defines the direction of processes and gives rise to the concept of irreversibility in nature.

Zeroth Law. *If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.*

This law establishes the concept of temperature. It allows us to define a consistent temperature scale — if system A and system B have the same temperature as system C, then A and B have the same temperature too.

Formulated and named by Ralph H. Fowler in 1931.

The First and Second Laws were by then already well known. The First Law was formulated by Mayer, Joule, and von Helmholtz in 1850's. The Second Law was formulated by Clausius and Lord Kelvin around the same time.

However, it was realized by Fowler and others that there was a fundamental principle — the concept of thermal equilibrium — that should logically come before the First Law, since it defines the basis for temperature and thermal measurement.

That is not how I have learned what is the Zeroth Law.

The Zeroth Law deals with the observed fact that large systems seems to normally have ”states” described by a few macroscopic parameters like temperature and that density, and that any system not in one of these states, left alone, rapidly approaches one of these states. When Boltzmann and Gibbs tried to find a microscopic basis for thermodynamics, they realized that approach to equilibrium was the deepest problem in such formalism.

B. Simon, Statistical Mechanics of Lattice Gases, Appendix to Section I.1.

How can one ”explain” the irreversible behaviour of macroscopic systems from the strictly reversible mechanical model? This question, which I call the problem of Boltzmann, has dominated the whole initial development of statistical mechanics and it is still being discussed. In its simplest form, one must ”explain” in which sense an isolated (that is a conservative) mechanical system consisting of a very large number of molecules approaches thermal equilibrium, in which all ”macroscopic” variables have reached steady values. This is sometimes called the **zeroth law of thermodynamics** *and it expresses the most typical irreversible behaviour of macroscopic systems familiar from common observation.*

Uhlenbeck and Ford, Lectures in Statistical Mechanics, page 6.

Between the two formulations, it is obviously the second one that is more fundamental.

An isolated system must reach the stable equilibrium before we even talk about temperature, energy conservation, or entropy changes.

To differentiate between the two formulations, a new name was invented/suggested (Brown and Uffink 2001?) for the second one, namely

The Minus First Law

In summary

(-1)-st Law. Equilibrium. An isolated system, left to itself, will evolve toward a state of thermodynamic equilibrium.

0-th Law. Temperature. Equilibrium allows the definition of temperature.

1-st Law. Conservation of energy.

2-nd law. Increase of entropy. Describes (and quantifies) the direction of spontaneous process that moves the system toward equilibrium.

The first attempts at validation of the Minus First Law.

Maxwell (1860's). The concept of probability distribution of molecular velocities. Recognition of importance of elastic collisions. Collisions are what allow the gas to reach a statistical equilibrium distribution of velocities. Symmetry considerations lead to the Maxwell-Boltzmann distribution.

Boltzmann (1860/s-1870's). Maxwell ideas inspired Boltzmann, and he formalized them using the H-theorem.

$$H(t) = \int f(\mathbf{v}, t) \ln f(\mathbf{v}, t) d^3\mathbf{v}$$

where $f(\mathbf{v}, t)$ is the velocity distribution function. For an ideal gas undergoing elastic collisions $\frac{\mathrm{d}H}{\mathrm{d}t} \leq 0$. $\frac{\mathrm{d}H}{\mathrm{d}t} = 0$ corresponds to the equilibrium and MB distribution

$$f(\mathbf{v}) = 4\pi \left(\frac{m}{2\pi k_B T} |\mathbf{v}|^2 \right) \mathrm{e}^{-\frac{m|\mathbf{v}|^2}{2k_B T}}.$$

Molecular collisions lead to decreasing of H and approach to equilibrium, or in other words, collisions are the microscopic mechanism behind the thermodynamic tendency toward maximum entropy.

Low density and the molecular chaos assumption (the velocity of two particles that are about to collide are uncorrelated).

History goes on ....

... and we turn to a Modern Mathematical Physics perspective.

Although the problem is often informally discussed in the modern literarure, there are very few contributions.

I will comment on those that have influenced us.

Radin, JMP, 1970, Approach to Equilibrium in a Simple Model

Abstract: The time evolution of a class of generalized quantum Ising models (with various long-range interactions, including Dyson's $1/r^2$) has been studied from the C*-algebraic point of view. We establish that: (1) All $\langle A\rangle_t$, are weakly almost periodic in time; (2) there exists a unique averaging procedure over time; (3) the time evolution in the thermodynamical limit can be locally implemented by effective Hamiltonians in the algebra of quasi-local observables; (4) there exists a specific connection between the spectral properties of the time evolution of the initial state and the approach to equilibrium; (5) there are examples in which the time evolution is not G-Abelian.

Lanford-Robinson, CMP, 1972. Approach to Equilibrium of Free Quantum Systems.

Abstract. It is proved for fermi systems that each translationally invariant state ω with square integrable correlation functions approaches a limit under the free time evolution. The limit state is the gauge invariant quasi-free state with the same two-point function as ω and it is characterized by a maximum entropy principle. Various properties of the limit are discussed, and the extension of the results to bose systems is also given.

The mechanism in both examples is diffusion, not scattering.

Dobrushin-Sukhov, 1979, Time evolution for some degenerate models of evolution of systems with an infinite number of particles.
Itogi Nauki i Tekhniki, Seriya Sovremennye Problemy Matematiki.

Abstract: The paper is devoted to the problem of convergence to the equilibrium state in the motion of infinite systems of classical particles. Two models of the motion are considered: free motion of point particles in Euclidean space $\mathbb{R}^d$, $d \geq 1$, and motion of solid rods on the line $\mathbb{R}$. The paper contains new results obtained by the authors and also a survey of previous results in this direction.

Again, the mechanism here is diffusion, not scattering.

Hugenholtz, JSP, 1983, Derivation of the Boltzmann equation for a Fermi gas.

Abstract: We consider the time evolution of a (lattice) Fermi gas with two-body interaction. For an initial state ρ which is translation invariant and sufficiently clustering we put $H = H_0 + \lambda V$, we take the limit $\lambda \to 0$, $t \to \infty$, such that $\lambda^2 t = \tau$ and show that (a) the limiting state ρ_τ does not depend on the p-point correlations of ρ for $p > 2$, (b) ρ has vanishing p-point correlations for $p > 2$, and (c) the two-point function that determines ρ_τ satisfies the Boltzmann equation.

Incomplete proofs. Follow up papers of Erdos, Yau, and Salmhofer. Research programs of Salmhofer and Phan Thanh Nam.

Scattering mechanism.

Lanford, LNP 38, 1975. Time evolution of classical large systems.

Section 6 deals with the derivation of Boltzmann equation (for (very) short times) in the Boltzmann-Grad limit. This work has generated a large literature that culminated in recent (spectacular) preprint:

Long time derivation of the Boltzmann equation from hard sphere dynamics by Yu Deng, Zaher Hani, Xiao Ma.

Abstract. We provide a rigorous derivation of Boltzmann's kinetic equation from the hard sphere system for rarefied gas, which is valid for arbitrarily long times, as long as the solution to the Boltzmann equation exists. This extends Lanford's landmark theorem, which justifies this derivation for a sufficiently short time.

Anna's course

Research program: Approach to equilibrium (attempt at justification of the Minus First Law) in the dynamical system (classical or quantum) setting.

Quantum setting. Infinitely extended translationally invariant quantum spin/fermionic systems.

The first step: developing structural theory of dynamical approach to equilibrium that parallels (and uses as input) the kinematical theory developed in 70's in the foundational works of Ruelle, Lanford, Robinson, Araki, and many others. This kinematical theory concerns thermodynamic formalism, Gibbs variational principle, structure of the phases (equilibrium states), KMS condition and all that, Araki-Gibbs condition......

The program was introduced in

0. J, Pillet, Tauber, AHP, 2024, Approach to equilibrium in translation-invariant quantum systems: some structural results.

Abstract. We formulate the problem of approach to equilibrium in algebraic quantum statistical mechanics and study some of its structural aspects, focusing on the relation between the zeroth law of thermodynamics (approach to equilibrium) and the second law (increase of entropy). Our main result is that approach to equilibrium is necessarily accompanied by a strict increase of the specific (mean) energy and entropy. In the course of our analysis, we introduce the concept of quantum weak Gibbs state which is of independent interest

Anna will talk about three papers that were worked out while she was a visitor/postdoc here at Politecnico.

1. J, Pillet, Szczepanek, Tauber: Approach to equilibrium in translation-invariant quantum systems: some structural results. Part II.

2. ——-: Dynamical conservation laws in quantum spin systems

3.———: On the nature of constants of motion in quantum spin systems

In the Epilogue lecture following Anna's course, I will discuss the paper 4 that concerns study of specific models and comment further on the the program.

Preliminary remarks prior to the Epilogue.

This a broad program that will take a decade to fully develop. It will be our central scientific focus for years to come.

Classical statistical mechanics part of the program.

0. Pozzoli, Raquepas: Conservation of specific quantities in infinite anharmonic systems. In preparation.

Continuation team: J, Pillet, Pozzoli, Raquepas, Shirikyan, Szczepanek

Classical program parallels the quantum one (with some fundamental changes).

Eigenstate Thermalization Hypothesis (ETH) direction: under construction, Benoist, J., Moscolari, Pillet, Szczepanek

Related to the quantum program by an exchange of limits (large time time limit versus thermodynamic (size of the system) limit).

Possible workshop on the subject during the long term visit of Teufel in May-June.

Talk by J at Rutgers math phys webinar, January 28.

8 hours course by J at Les Houches School: Quantum Theory on All Scales, Aug 3-26, 2026. Lecture notes in preparation.