Moving out of equilibrium

and fixing some old issues on the way

Michal Mandrysz

Faculty of Physics, Astronomy and Applied Computer Science
Jagiellonian University

Outline

- Old problems
  - The Loschmidt paradax
  - Less known fact
  - More troubles...
  - Even more troubles...
- New solutions
  - Can we go arbitrary far from equilibrium ?
  - Dissipation function - intuition
  - Dissipation function
  - Fluctuation Theorem
  - Fluctuation Theorem - second law and conditions
- Closing words

The Loschmidt paradax

An old objection to Boltzmann entropy

All equations of motion (both classical and quantum) are time-reversal symmetric. Therefore if we pick a set of trajectories and let the particles evolve, reaching a state of maximum entropy, then we can easily imagine a reverse trajectory (momentum $p \to -p$) which should lower the entropy...

Even though the mentioned paradox was understood it waited until 1993 for a full resolution.

Less known fact...

Clausius inequality

Clausius entropy is ill-defined for non-equilibrium paths and so is temperature.

$$\int \frac{dQ_{th}}{T} \tag{1}$$

Clausius only defined the temperature for quasi-static or equilibrium process.

In this scenerio the Clausius inequality

$$\oint \frac{dQ_{th}}{T} \geq 0 \tag{2}$$

is without meaning. This was noticed by Bertrand (1887), Orr (1904), Planck (1905)

More troubles...

Gibbs entropy

Gibbs showed that the thermodynamic entropy

$$S_G(t) \equiv -k_B \int d\Gamma f(\Gamma; t) ln[f(\Gamma; t)] \tag{3}$$

where $f(\Gamma; t)$ is the N-particle phase space distribution function at time t, is in fact a constant of the motion for autonomous Hamiltonian dynamics !

Seminar treatise "Elementary Principles in Statistical Mechanics" Gibbs 1902

Pointed out by Ehrenfests' Working solution : coarse graining, but then it's not an objective property of the system

Even more troubles...

Boltzmann H-theorem

Boltzmann proved that the Boltzmann equation for the time evolution of the single particle probability density implies, for uniform ideal gases, a monotonic decrease of the H-function in time (Boltzmann, 1872)

Essential problem : The Boltzmann equation (unlike Netwton's) is not time-reversal symmetric. It is therefore completely unsurprising that the Boltzmann equation predicts a time-irreversible result - the Boltzmann H-theorem.

Can we go arbitrary far from equilibrium ?

Can we go below the thermodynamic limit ?
Would that solution also solve the problems mentioned in the beginning ?

The answer to all those questions is yes.

How ? Using Fluctuation Theorem proposed in 1993 by Evans, Cohen and Morriss.

Prerequisite : Dissipation function

Dissipation function - intuition

Dissipation is not entirely new concept, it was implicit in some of the Lord Kelvin's XIX century papers.

Has a nice property of turning into spontaneous entropy production in linear irreversible thermodynamics and is complementary to entropy

For systems that are driven by an applied dissipative field (e.g., an electrically conducting system being driven by an electric field) the average dissipation is equal to the average power dissipated in the system divided by the thermodynamic temperature of the surrounding thermal reservoir.

Dissipation function

It's a functional of both the dynamical equations of motion that determine $S^t\mathbf{\Gamma} = exp[iL(\mathbf{\Gamma})t]\mathbf{\Gamma}$ from the initial phase $\mathbf{\Gamma}$ and also the initial distribution $f(\mathbf{\Gamma};0)$.

$$\int_0^t ds\Omega(S^s\mathbf{\Omega}) \equiv ln\frac{f(\mathbf{\Gamma};0)}{f(\mathbf{\Gamma}^*;0)} - \int_0^t \Lambda(S^s\mathbf{\Gamma})ds \equiv \overline{\Omega_t(\mathbf{\Gamma})}t \qquad (4)$$

Λ denotes the phase space expansion factor.
By losing a certain quantity of heat from an otherwise Hamiltonian system, the system also gives up a certain amount of phase space.

One way to think about the dissipation function is as a measure of the temporal asymmetry inherent in the sets of trajectories originating from an initial distribution of states.

Fluctuation Theorem

Gives a relation between probabilities of time integrals of the dissipation function.

$$\frac{p(\overline{\Omega_t} = A)}{p(\overline{\Omega_t} = -A)} = e^{At} \tag{5}$$

where $\overline{\Omega_t}$ is the time averaged dissipation function and p's are the probabilities at time zero of observing sets of phase space trajectories originating inside infinitesimal volumes of phase space

Confirmed both by molecular dynamics computer simulations and in actual laboratory experiments. The first unambiguous laboratory demonstration of a fluctuation.

Fluctuation Theorem - second law and conditions

Follows from fluctuation theorem by simple integration

$$\langle \Omega_t \rangle = \int_{-\infty}^{\infty} dBp(\Omega_t = B)B = \int_{0}^{\infty} dBp(\Omega_t = B)B(1 - exp[-B]) \geq 0$$

Conditions for fluctuation theorem to hold :

- Initial distribution should be even function of the momenta
- The system is ergodically consistent
- The dynamics must be time-reversal-symmetric
- The dynamics should be smooth
- Any time-dependent external fields must have a definite parity under time reversal, over the given time interval.

Closing words

Thank you for your attention !

Literature

- "Non-equilibrium thermodynamics" - S. Groot, P. Mazur ; S. Degroot
- "Fundamentals of Classical Statistical Thermodynamics" - D. Evans, D. Searles, S. Williams