The second law of thermodynamics in small systems, the Evans-Searles fluctuation theorem

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Science

science is humanity's endeavor to know and understand the world

the seven hundred-year-old linden from Szőkedencs

Mathematics

„ ... "Mathematics is the language with which God has written the universe."

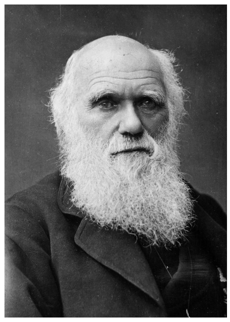
Advantages of applying math:

- accurate predictions (comparison with more sophisticated measurements)
- strict derivations
- abstract thinking

Galileo Galilei (1564 – 1642)

The role of mathematics

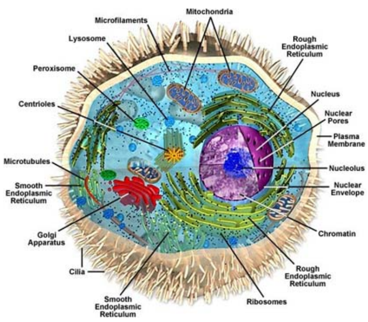
„… in after years I have deeply regretted that I did not proceed far enough at least to understand something of the great leading principles of mathematics, for men thus endowed seem to have an extra sense."



Charles Darwin (1809 –1882)

The role of mathematics

cell biology achieved great success without the use of mathematics



The role of mathematics

accumulated large amounts of observations of stars and planets

Tycho Brahe (1546 – 1601)

The role of mathematics

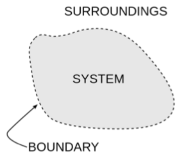
He recognized the laws of planetary motion - he created a mathematical model.

Johannes Kepler (1571 – 1630)

Thermodynamics

thermodynamics: the branch of physics that deals with heat and temperature, and their relation to energy, work, radiation, and properties of matter

thermodynamic system: a well-defined macroscopic part of the universe



environment: the part of the universe outside the thermodynamic system that surrounds the thermodynamic system

The thermodynamic system and its environment are bounded by a real or imaginary wall. Walls allow only certain types of interaction with the environment (e.g. metabolism, work, heat exchange).

Thermodynamic transformations

quasi-static process: a thermodynamic process that happens slowly enough for the system to remain in internal equilibrium

reversible process: the thermodynamic system moved from the initial state through some intermediate states to the final state returns from the final state to the initial state through the same intermediate equilibrium states

All reversible transformations are quasi-static.

Thermodynamic variables

state functions describe the equilibrium state of a system

extensive property is a physical quantity whose value is proportional to the size of the system it describes (volume, mass, internal energy, entropy …)

intensive property is a physical quantity whose value does not depend on the amount of the substance for which it is measured (pressure, temperature, concentration …)

state equations establish a relationship between the state functions of an equilibrium system

The second law of thermodynamics

direction of spontaneous processes

- Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

- It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

- The total entropy of an isolated system can never decrease over time.

Non-equilibrium systems

- if energy is exchanged with the environment, the system is out of equilibrium

- living systems are out of equilibrium

- classical thermodynamics is not applicable to out of equilibrium systems

Fluctuations in small systems

N atoms of an ideal gas

The kinetic energy of the atoms follows Maxwell-Boltzmann distribution.

$$<E_{\text{sum}}> = \frac{3}{2} N k_B T$$

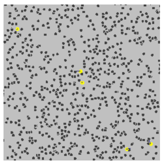
$$\text{Var}(E_{\text{sum}}) = \frac{3}{2} N (k_B T)^2$$

$$\text{Szórás}(E_{sum}) = \sqrt{\frac{3}{2}} N(k_B T)$$

The fluctuation is in the order of $\sqrt{N}$

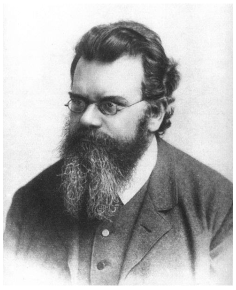
Brownian motion

Matter is not continuous but consists of particles.



Statistical mechanics

Statistical mechanics interprets the thermodynamic properties of macroscopic systems using probability theory and the laws of mechanics for the micro world (atoms, molecules).

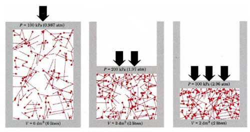


Ludwig Eduard Boltzmann
(1844 – 1906)

Pressure

Molecules that collide with the container wall, exert force on the wall.

The collision is elastic: the component of the particle velocity parallel to the wall remains unchanged, the component perpendicular to the wall changes in the opposite direction, while its magnitude remains the same.



Loschmidt paradox

Johann Josef Loschmidt (1876)

The equations of mechanics are symmetrical in time, thus they cannot lead to irreversible processes.

The second law of thermodynamics is clearly asymmetric in time.

Paradox: Both mechanics and thermodynamics have strong theoretical and experimental foundations, but the two seem to contradict each other.

Boltzmann H-theorem

$$H = \int \rho\,(q,p,t) \ln \rho(q,p,t) d^n q d^n p$$

Ludvig Boltzmann (1872)

H decreases continuously over time t or remains constant at most when H has reached a minimum.

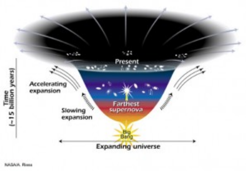
implicit assumption (molecular chaos hypothesis): the momenta of each molecule are uncorrelated and location-independent before the collision

$$S = -n \cdot k_B \cdot H$$

Initial conditions of the Universe

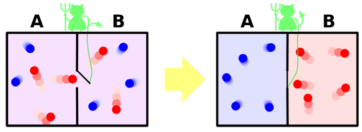
The equal a priori probability postulate:

In an isolated system, all micro-states are equally likely.



Maxwell demon

James Clerk Maxwell (1871)



Leó Szilárd (1929): the Maxwell demon uses energy to make measurements. The entropy of the demon-gas system increases.

Rolf Landauer (1960): It is not the measurement but the deletion of the collected information that results in an entropy increase:
for every deleted bit: $\Delta S = k_B \cdot \ln 2$

John Earman és John Norton (1998): Both explanations assume that the Maxwell demon obeys the second law of thermodynamics and uses this to derive the law of thermodynamics.

Landauer principle

There is a close relationship between information and entropy.

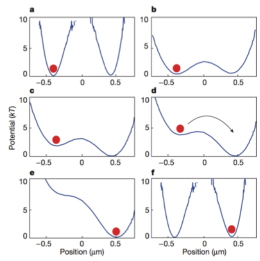
informare /latin/ - to shape (the thoughts of the other)

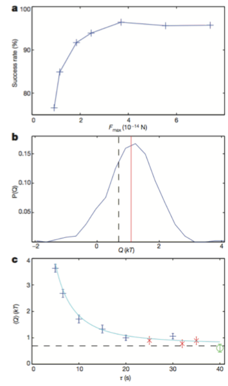
The heat generated by deleting one bit of information:

$$\langle Q\rangle = -T\Delta S = k_B T \ln 2 = Q_{Landauer}$$

$$Q_{Landauer} = 3 \cdot 10^{-21} J \quad \text{, if } T = 300\ K$$

Experimental demonstration of the Landauer principle





$$Q = -\int \dot{x}(t) \cdot \partial V(x,t)/\partial x \cdot dt$$

$$\langle Q\rangle = -T\Delta S = k_B T \ln 2 = Q_{Landauer}$$

Bérut et al. (2012) Nature 483: 187

Evans-Searles fluctuation theorem

Denis J Evans, Ezechiel DG Cohen, Gary P Morriss (1993)
Denis J Evans, Debra J Searles (1994)

$$\frac{P(\Omega_t = A)}{P(\Omega_t = -A)} = e^{At}$$

where Ω_t the average for time t of the entropy production

Evans and Searles (2002) Advances in Physics, 51: 1529

Different forms of the Evans-Searles fluctuation theorem

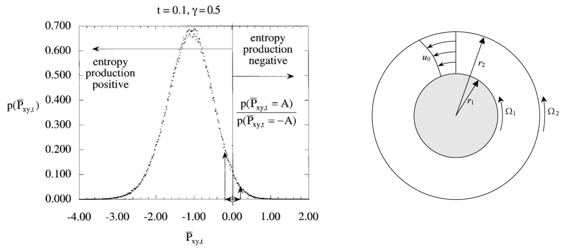
Evans and Searles (2002) Advances in Physics, 51: 1529

Isokinetic dynamics	$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -AtF_e\beta V$
Isothermal-isobaric[c]	$\ln \frac{p(\overline{JV}_t = A)}{p(\overline{JV}_t = -A)} = -AtF_e\beta$
Isoenergetic	$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -AtF_e\beta V$ or $\ln \frac{p(\bar{\Lambda}_t = A)}{p(\bar{\Lambda}_t = -A)} = -At$
Isoenergetic boundary driven flow	$\ln \frac{p(\bar{\Lambda}_t = A)}{p(\bar{\Lambda}_t = -A)} = -At$
Nosé-Hoover (canonical) dynamics	$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -AtF_e\beta V$
Wall ergostatted field driven flow[c]	$\ln \frac{p(\overline{J\beta_{wall}}_t = A)}{p(\overline{J\beta_{wall}}_t = -A)} = -AtF_e V$ or $\ln \frac{p(\bar{\Lambda}_t = A)}{p(\bar{\Lambda}_t = -A)} = -At$
Wall thermostatted field driven flow[c]	$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t - A)} = -AtF_e\beta V - \ln(\langle \exp[\bar{\Lambda}_t t(1 - \beta_{system}/\beta_{wall})]\rangle_{\bar{J}_t = A})$
Relaxation of a system with a non-homogeneous density profile imposed using a potential $\Phi_g(\mathbf{q})$; initial canonical distribution	$\ln \frac{p\left(\int_0^t ds\Phi_g(s) = A\right)}{p\left(\int_0^t ds\Phi_g(s) = -A\right)} = -A\beta$
Adiabatic response to a colour field	$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -AtF_e\beta V$
Isoenergetic dynamics with a stochastic force[d]	$\ln \frac{p(\bar{J}_t = A)}{p(\bar{J}_t = -A)} = -AtF_e\beta V$ or $\ln \frac{p(\bar{\Lambda}_t = A)}{p(\bar{\Lambda}_t = -A)} = -At$
Steady state isoenergetic dynamics:[e] $\overline{\beta J}_t = \frac{1}{t}\int_{t_0}^{t_0+t} \beta(s)J(s)\,ds$ where $t_0 \gg \tau_M$	$\ln \frac{p(\overline{J\beta}_t = A)}{p(\overline{J\beta}_t = -A)} = -AtF_e V - \ln\left(\left\langle \exp\left[F_e V\left(\int_0^{t_0} J(s)\beta(s)\,ds + \int_{t_0+t}^{2t_0+t} J(s)\beta(s)\,ds\right)\right]\right\rangle_{\overline{J\beta}_t = A}\right)$

The significance of Evans-Searles fluctuation theorem

- extension of the second law
- gives an analytical expression for the probability of the phenomena
- valid in the non-linear range
- valid for small systems (no thermodynamic limit)
- it is very general, with many version developed for a wide variety of systems and dissipations
- nano-systems are not reduced versions of their macroscopic counterpart, they behave fundamentally differently

Illustration of the FT – Couette flow



Non-equilibrium systems

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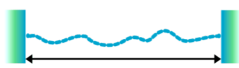
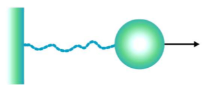
The state of the small system

The state of the small system is described by the control parameter.

Control parameter: length



Control parameter: force



Evans-Searles FT

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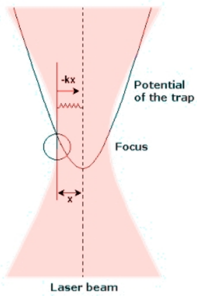
where Ω_t is the average for time t of the entropy production.

Evans-Searles FT (IFT) – violations of the second law

$$\frac{P(\Sigma_t = A)}{P(\Sigma_t = -A)} = e^{At}$$

$$\Sigma_t = (k_B T)^{-1} \cdot \int v_{opt} \cdot F_{opt}(x) \cdot dx$$

$$\frac{P(\Sigma_t < 0)}{P(\Sigma_t > 0)} = \langle e^{-\Sigma_t} \rangle_{\Sigma_t > 0}$$



Wang G.M. et al. (2002) Phys. Rev. Lett. 89: 050601

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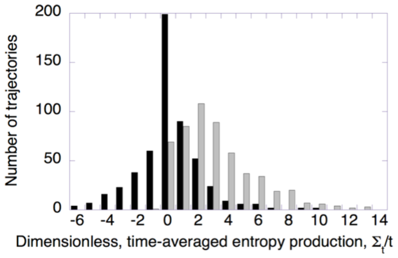

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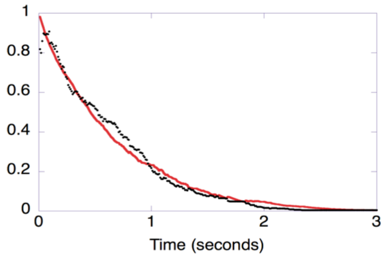

$$\frac{Pr(\Sigma_t < 0)}{Pr(\Sigma_t > 0)} = \langle \exp\{-\Sigma_t\} \rangle_{\Sigma_t > 0}$$

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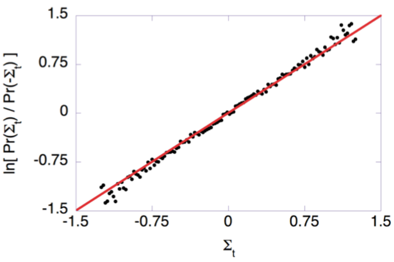

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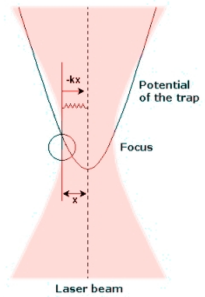
Evans-Searles FT (DFT) – violations of the second law

$$\Omega_t(\mathbf{r}_0, \mathbf{r}_t) = \ln\left[\frac{P(\{\mathbf{r}_0, \mathbf{r}_t\})}{P(\{\mathbf{r}_t, \mathbf{r}_0\})}\right]$$

$$\Omega_t = \frac{1}{2k_B T}(k_0 - k_1)(\mathbf{r}_t^2 - \mathbf{r}_0^2)$$



Carberry D.M. et al. (2004) Phys. Rev. Lett. 92: 140601

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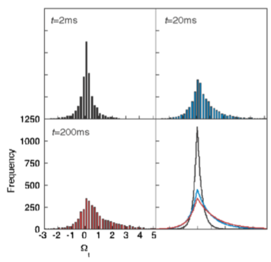

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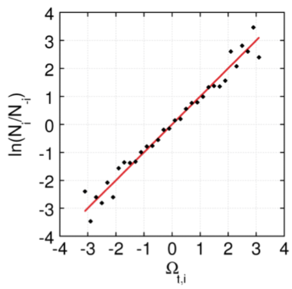

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