DAVIDE CHIUCHIÙ – NIPS SUMMER SCHOOL

ENERGY TRANSFORMATIONS AT THE MICRO SCALES

OUTLINE

- From microscopic to macroscopic.
- Microscopic interpretation of entropy.
- Fluctuations and dissipation

INTRODUCTION

- Lucretius, 50 BCE: bodies are made of atoms.
- Atoms rarely considered by other philosophers.
- Atoms accepted by physicists in the 20th century.
- The microscopic theory of thermodynamics built upon the belief that matter is made of atoms.
- Idea confirmed later with Brownian particles

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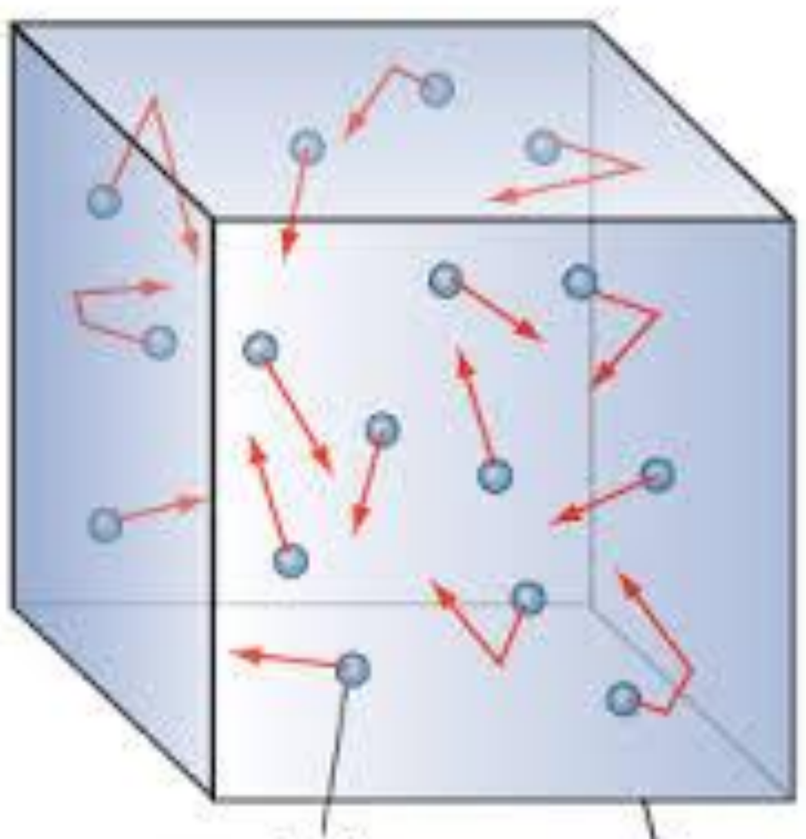
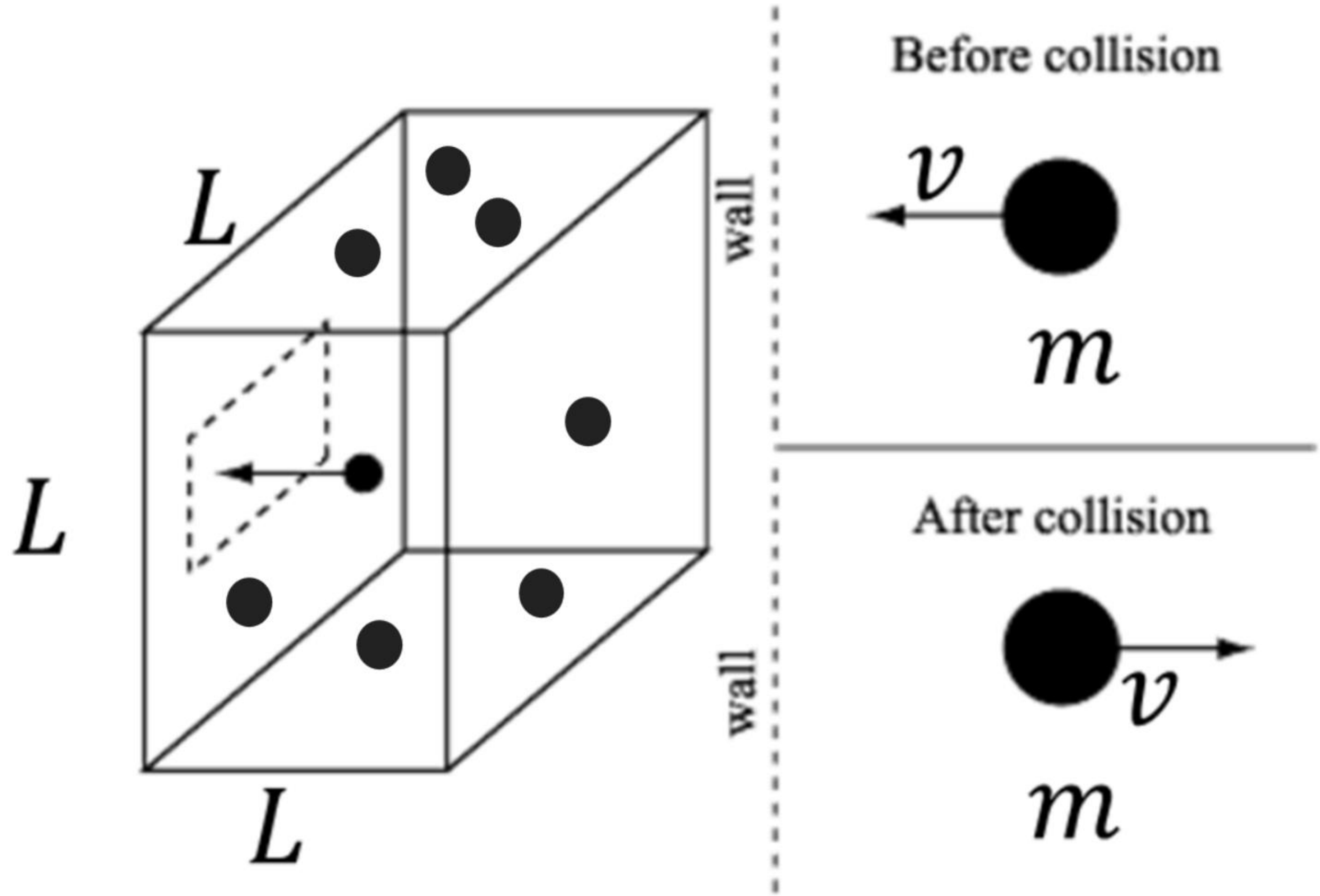
THE KINETIC THEORY

- Gas made of small particles with same mass.
- Average inter-particle distance larger than the particle size.
- Statistical treatment apply.
- Particles in constant motion.
- Elastic collisions between particles and the gas-container.



PRESSURE - 1

- Feynman Lectures on Physics, Volume 1, Lecture 39



PRESSURE - 2

- Momentum change by particle-wall collisions $\Delta p = 2mv$
- Force ofparticle-wall collision $F = \frac{\Delta p}{\Delta t} = \frac{mv^2}{L}$
- Δt = 2L/v time between two collisions.
- Total average force on wall $F_{tot} = N\frac{m\bar{v}^2}{3L}$
- Pressure of the gas $P = \frac{F_{tot}}{L^2} = N\frac{m\bar{v}^2}{3L^3}$

TEMPERATURE (EQUIPARTITION THEOREM)

- From before

$$PV = N\frac{m\bar{v}^2}{3}$$

- Perfect gas law

$$PV = Nk_bT$$

- Upon comparison

$$\frac{3}{2}k_bT = \frac{m\bar{v}^2}{2}$$

- **Equipartition theorem:** links the average kinetic energy of a particle with the temperature.

MAXWELL RELATIONS

- Formal derivation of P and T with the Maxwell relations

$$P = -\frac{\partial E}{\partial V}, \qquad \frac{1}{T} = \frac{\partial S}{\partial E}$$

- Entropy S needed.
- Clausius: S defines the minimum energy cost to perform a thermodynamic transformation.

K. Huang, Statistical Mechanics, 2nd Edition

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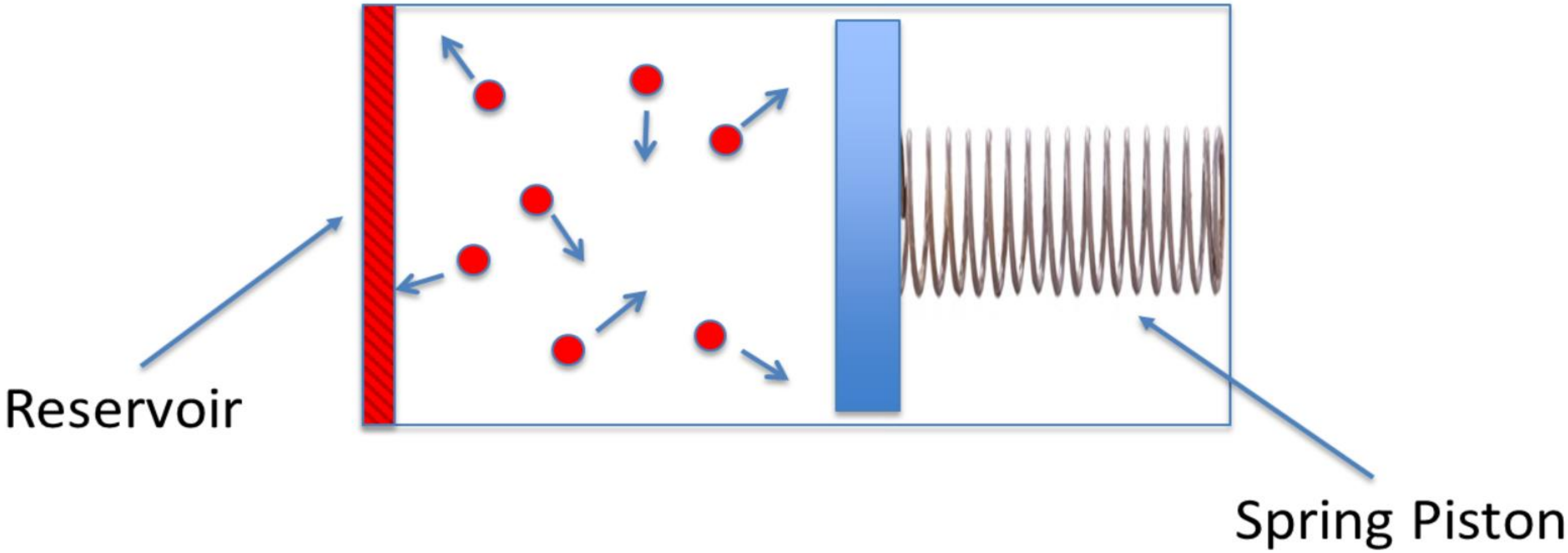
ENTROPY – A STUDY CASE

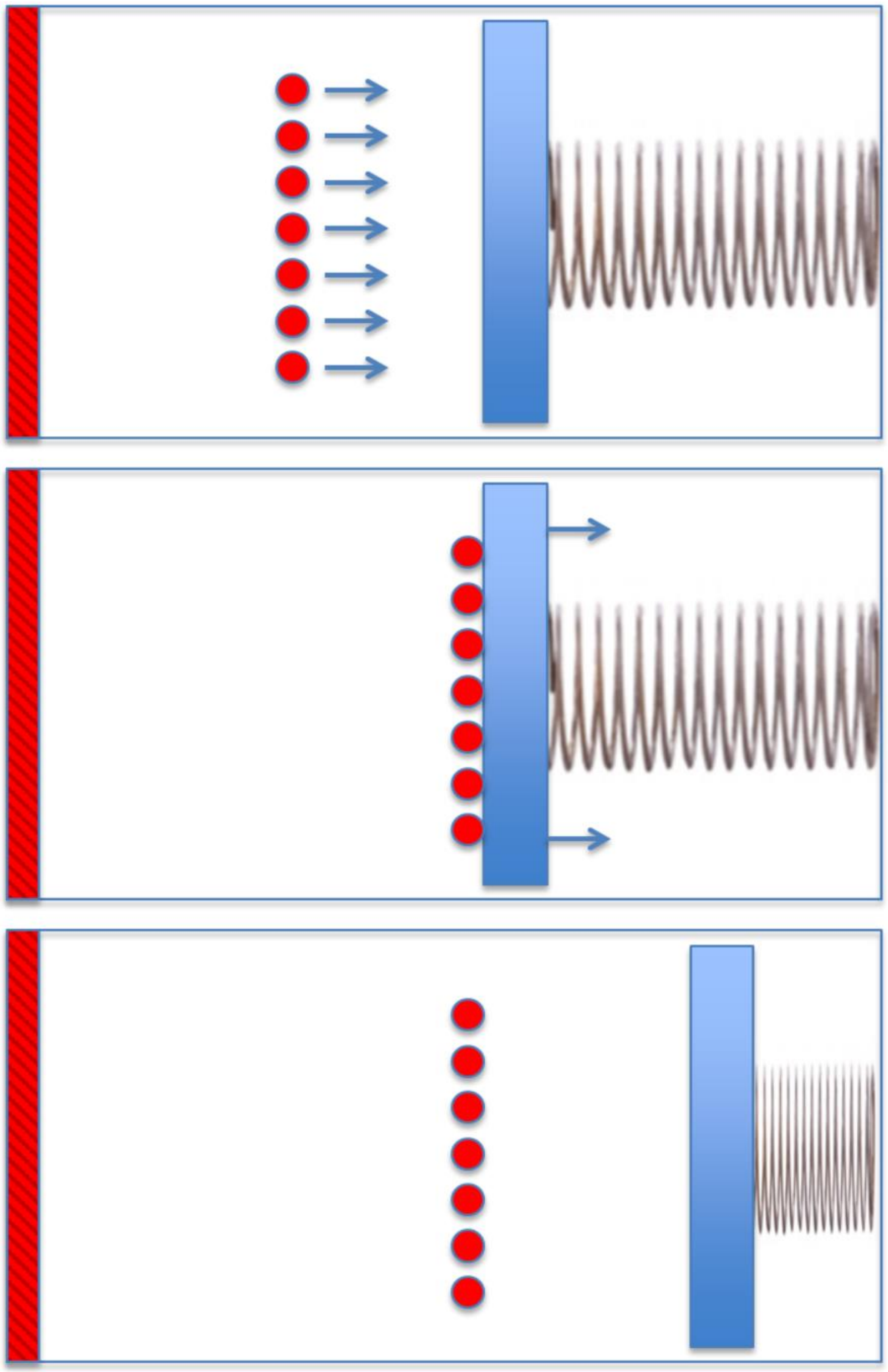
- Entropy associated with Disorder?



- Particle with same mass *m* and velocity *v*.
- Piston mass $M = Nm$

TRAVELING "WAVE"

- Piston at rest
- Particles aligned
- Particles-piston collisions at the same time.



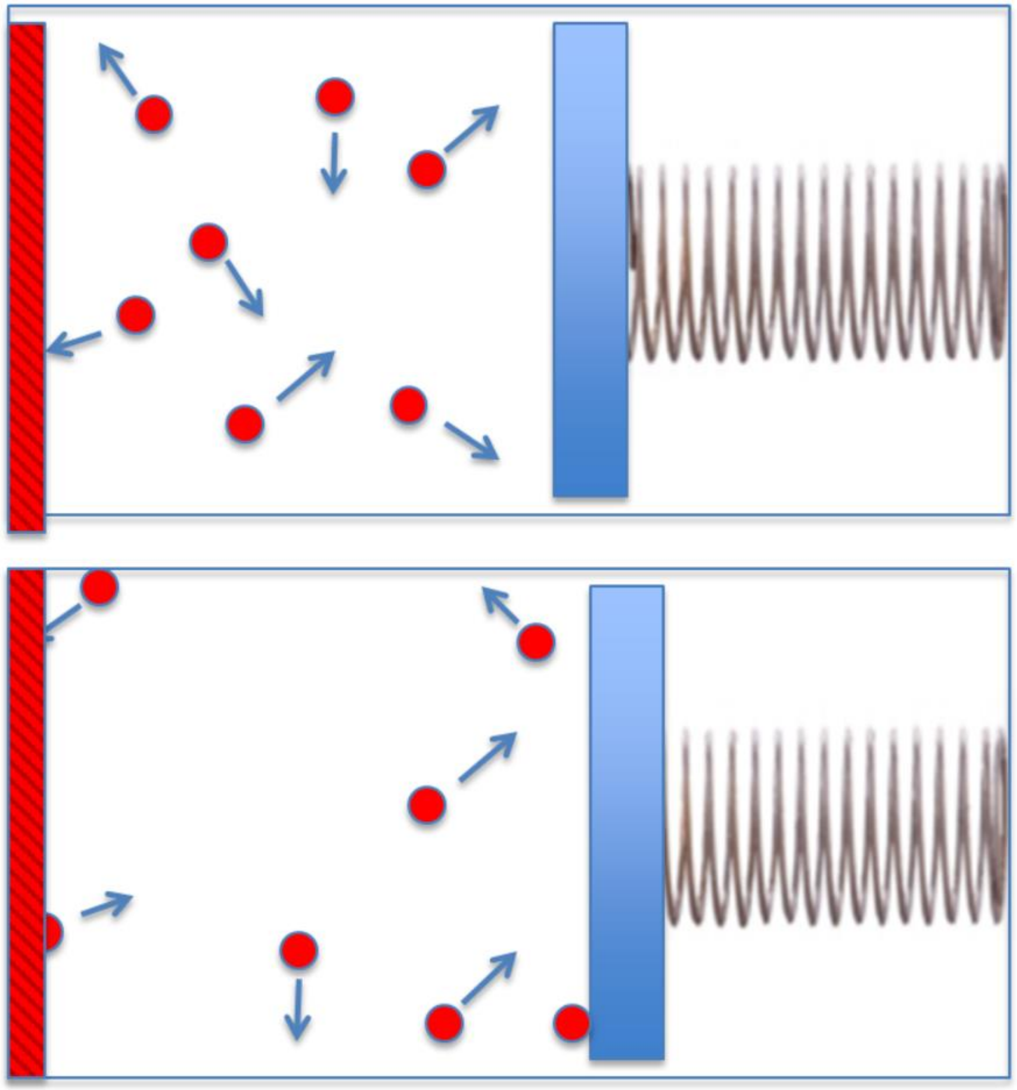
Spring compress by Δx

$$\frac{1}{2} N\, m\, v^2 = \frac{1}{2} k\, \Delta x$$

- **Large displacements (big amount of work)**

UNIFORM GAS MEDIUM

- Piston at rest.
- Particles randomly oriented.
- Particles-piston collisions at different times.



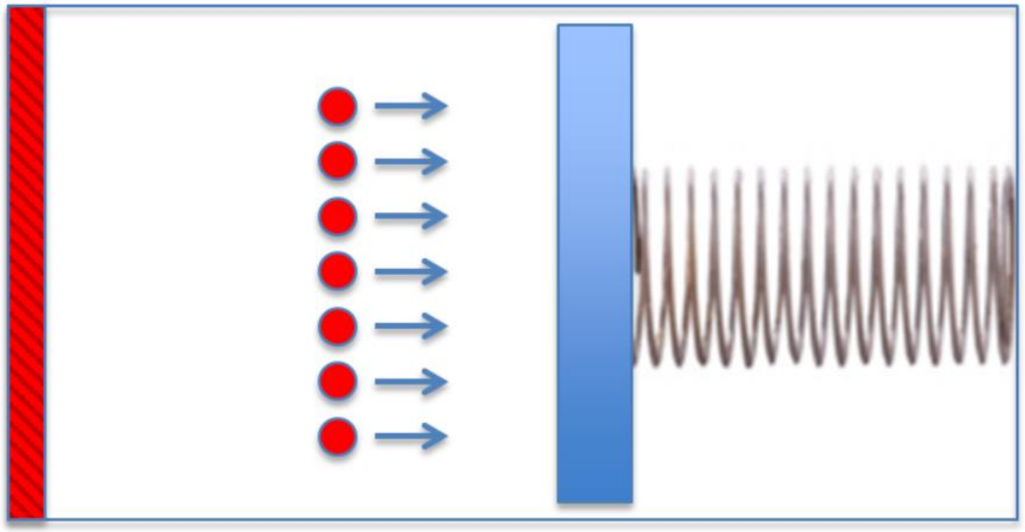
Spring compress by Δx

$$\frac{1}{2}\, m\, v^2 = \frac{1}{2} k\, \Delta x$$

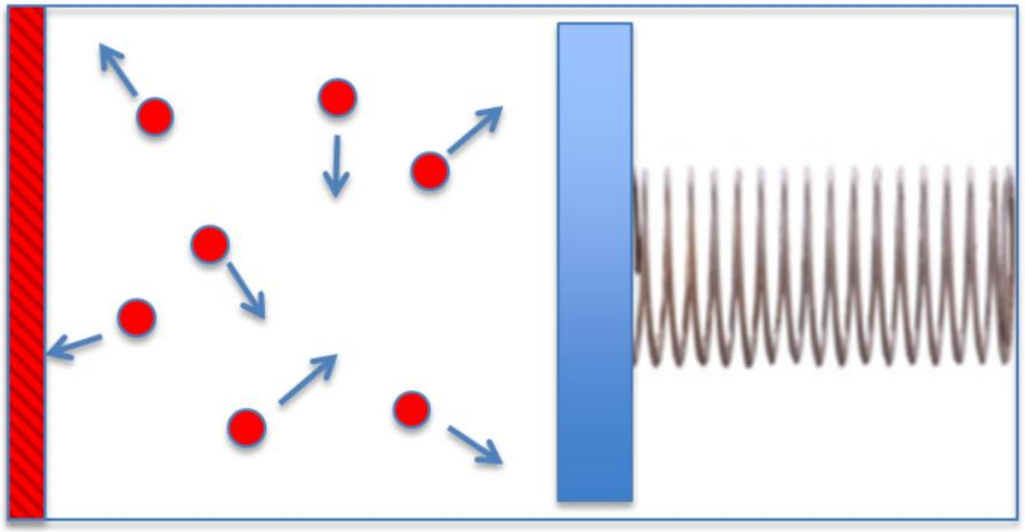
- **Small displacements (small amount of work).**

ENTROPY AS DISORDER

- Disorder limits the work.
- Entropy measures disorder.
- Entropy links disorder and the minimum energetic cost of transformation.



low entropy



high entropy

AN ENTROPIC PRANK

BOLTZMANN DEFINITION OF ENTROPY

Boltzmann (Isolated systems)

$$S_B = k_b \ln W$$

$$W = \int_E d^{3N}p \; d^{3N}q$$

W: number of arrangements with the same energy E.

S_B measures the number of particle arrangements.

GIBBS DEFINITION OF ENTROPY

Gibbs (Thermostatted systems)

$$S_G = -k_b \int P(p,q) \ln P(p,q)\, d^{3N}p \; d^{3N}q$$

$P(p,q)$:probability density to have a given arrangement of particle positions and velocities.

S_G measures of the shape of $P(p,q)$.

DIFFERENT ENTROPIES, SAME MEANING

- Funcionals like S_G have values that do not change if we consider different subsets with the same cumulated probability.
- Different entropies, same meaning

C. Shannon, The mathematical theory of computation, 1948
E. Jaynes, AJP, 33 (5) 391-398, 1965.

SECOND LAW OF THERMODYNAMICS

Clausius theorem:

For transformations between states A and B,

$$\int_A^B \frac{dQ}{T} \geq -\Delta S$$

- Minimum energetic cost given by the changes in disorder.
- Bad boy: you loose more in friction.

Microscopic interpretation of dissipation?

OUTLINE

- From microscopic to macroscopic.
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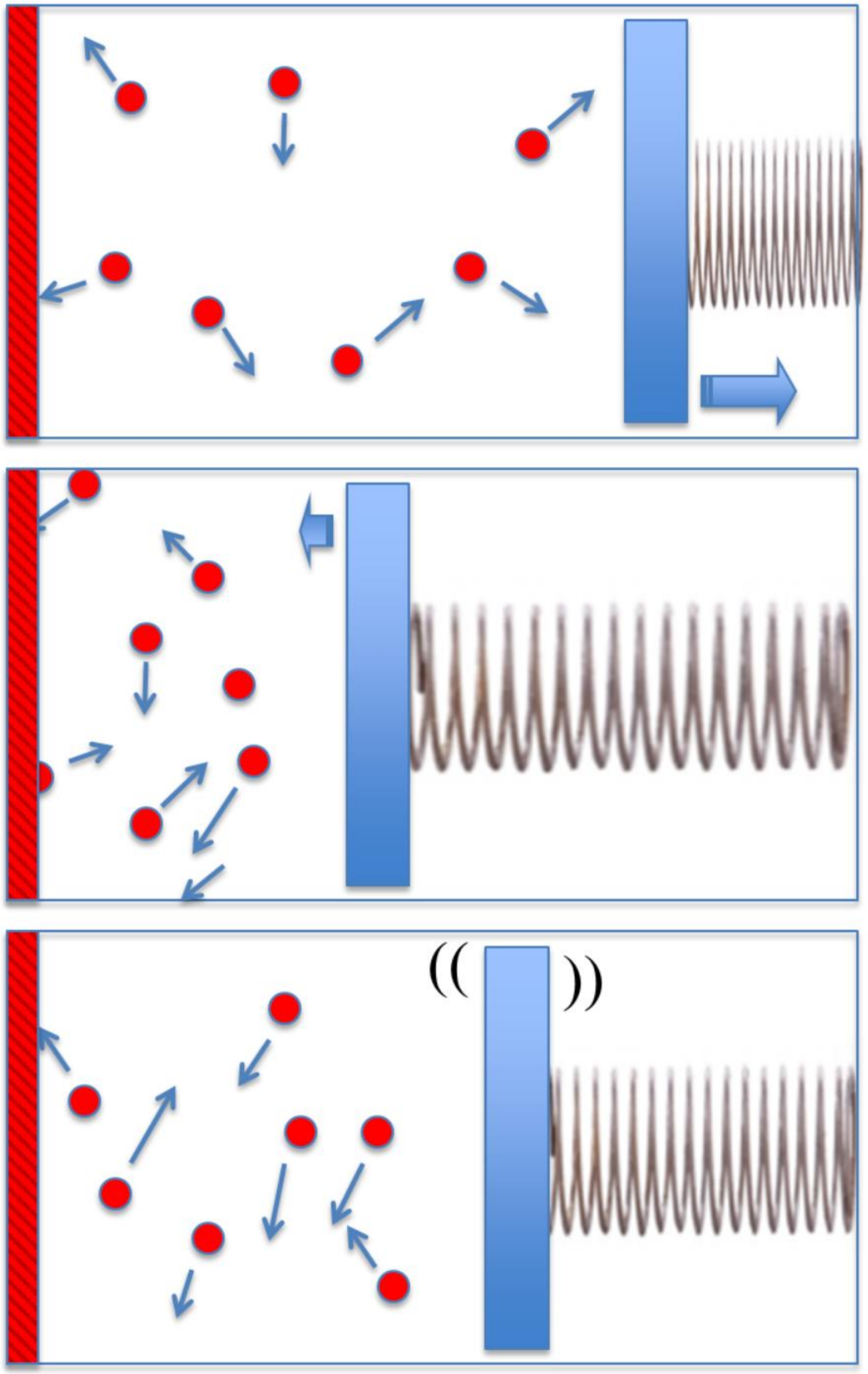
- **Fluctuations and dissipation.**

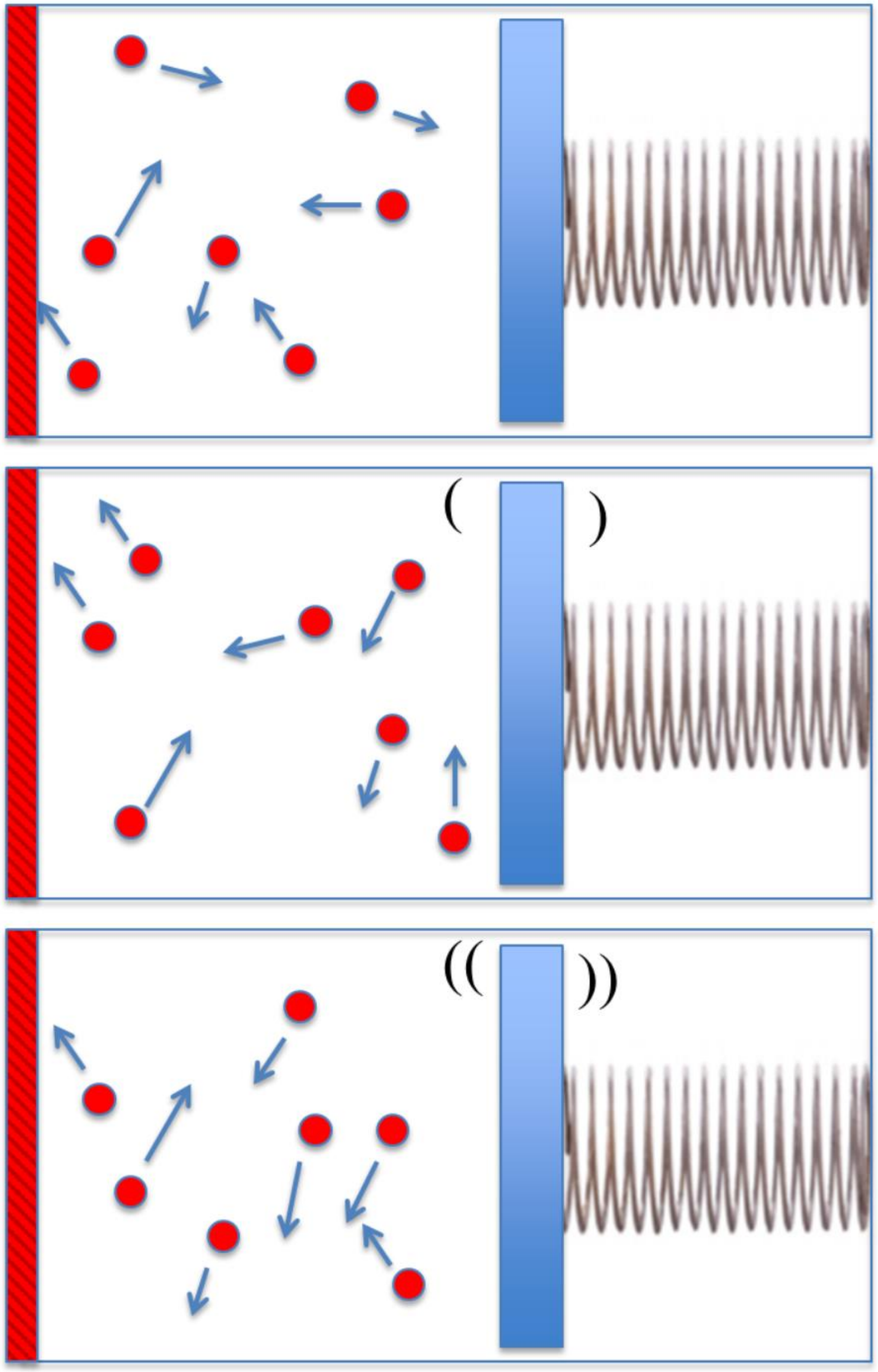
DISSIPATION

- Compress the spring by Δx.
- Leave the piston oscillate.
  - Amplitude decreases due to the gas
  - Amplitude reaches an equilibrium value.
  - Energy lost in the particles and the reservoir.



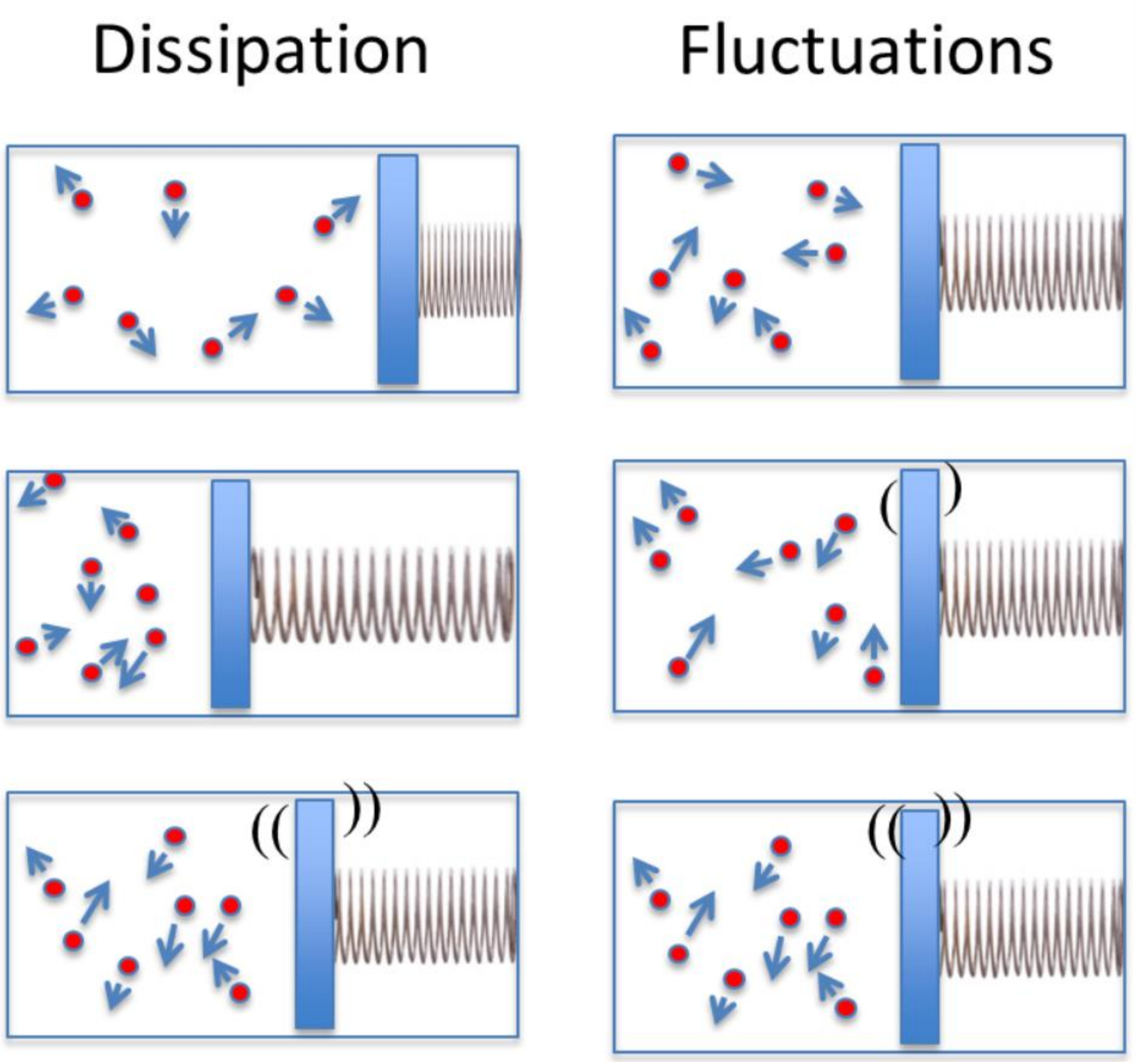
FLUCTUATION

- Piston at res.
- Piston starts oscillate.
  - Amplitude reaches an equilibrium value.
  - Energy put in the piston from the particle and the reservoir.

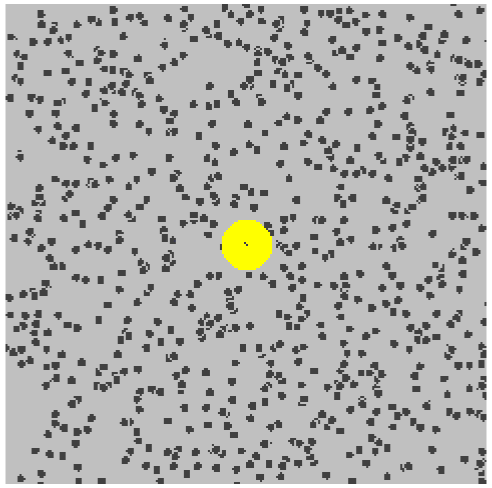


OSCILLATIONS AND DISSIPATION

- Same equilibrium amplitude for both cases.
- Gas as damping-force and push-force.
- Connection between dissipation and the equilibrium fluctuations.



EINISTEIN RELATION



- Brownian colloidal particle.

$$m\ddot{x} = -\gamma \dot{x} + \sqrt[2]{2d}\beta(t)$$

m: particle mass

γ: Stokes coefficient

$\sqrt[2]{2d}\beta(t)$: random Gaussian force, amplitude $\sqrt[2]{2d}$.

- Maxwellian at thermal equilibrium implies

$$d = \frac{k_B T}{\gamma}$$

- Einstein Relation: Links fluctuations and dissipation.

FLUCTUATION DISSIPATION THEOREM

- Linear response of the system
- The dissipation γ at frequency ω relates with the correlation G between two fluctuations at ω via

$$\gamma(\omega) = -\frac{\omega}{k_B T} G(\omega)$$

- Bridges the equilibrium properties of a thermodynamic system with its the non-equilibrium behaviors.

H. Callen, Phys. Rev. 83 34, 1951
R. Balescu, Equilibrium and nonequilibrium statistical mechanics 1977

BEYOND THE LINEAR RESPONSE - 1

Jarzynski equality

The work W to go from the equilibrium state A to the nonequilibrium state B relates to the Free energy change ΔF calculated as if B were at equilibrium via

$$\left\langle e^{-\frac{W}{k_B T}} \right\rangle = e^{-\frac{\Delta F}{k_B T}}$$

Insight on nonequilibrium transformations with equilibrium transformations.

C. Jarzynski, Phys. Rev. Lett. 78, 2690, 1997

BEYOND THE LINEAR RESPONSE - 2

Crooks fluctuation theorem

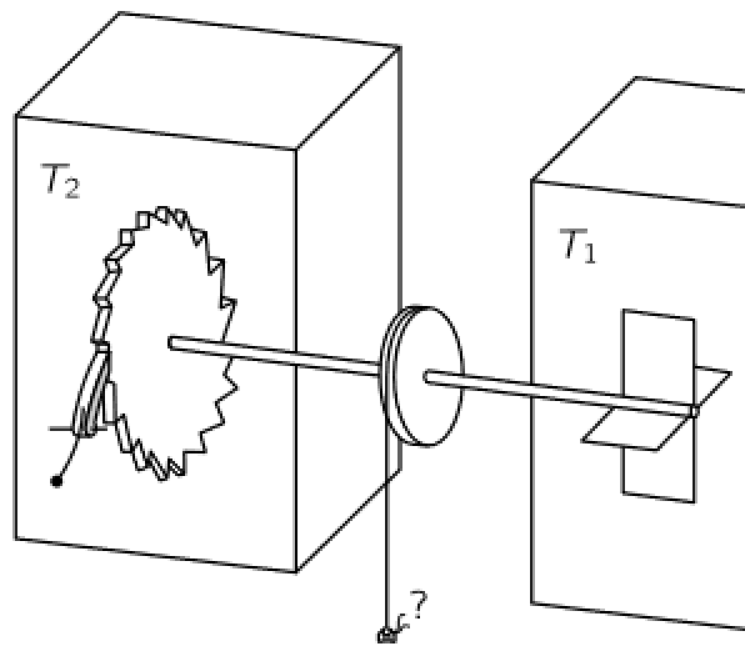
The probability of an entropy change ΔS in a forward process relates to the probability to observe the opposite entropy change $-\Delta S$ in the reversed trasformation via

$$\frac{P_F(\Delta S)}{P_R(-\Delta S)} = e^{\Delta S}$$

- Statistical behaviour of nonequilibrium processes.
- Fundamental for nonequilibrium thermodynamics today.

Gavin E. Crooks, Phys. Rev. E 60, 2721, 1999

RATCHET AND PAWL



Employ thermal fluctuations to do work

Possible only if we keep the system far from equilibrium.

The second law of thermodynamics is a harsh mistress.

Feynman lectures on physics, Volume 1, Lecture 46

CONCLUSIONS

- Matter is made by particles
- Entropy is the randomness of the particles of a system
- Entropy and the second principle of thermodynamics
- Fluctuations and dissipation.

FURTHER READINGS

- L. Gammaitoni, ICT - Energy - Concepts Towards Zero - Power Information and Communication Technology, Chapter 2
- S. de Groot, Non-equilibrium thermodynamics.
- U. Seifert, Rep. Prog. Phys., 75:126001, 2012.
- C. Gardiner, Stochastic methods
- A. Vulpiani, Meccanica statistica elementare