FLUCTUATION-DISSIPATION RELATIONS: A MACROSCOPIC WINDOW ON THE MICROSCOPIC REALM

The passage of an electric current under the action of a potential difference between the ends of a metallic wire is a familiar phenomenon of our daily life. Such an electric current is the response to the potential difference of electrons in the metal and, according to Ohm's law, is proportional to the potential difference, with a proportionality constant given by the inverse of the resistance of the wire. An interesting question, which is the central issue of this paper, is: can we compute the resistance without applying an electric potential? In other words: can we measure the response of the electrons in the wire by simply knowing their behavior in the absence of electric fields? *More generally, can we understand the nonequilibrium behavior of a many particle system just by observing its equilibrium properties or, viceversa, can we infer its equilibrium properties from nonequilibrium experiments?* (see Box 1 and Fig. 1).

This is the basic question of the Fluctuation-Dissipation (or Fluctuation-Response) problem, which plays a fundamental role, both from the conceptual and applied point of view, in statistical physics, the discipline which aims at deriving the macroscopic behavior of a system from its microscopic properties. The Fluctuation-Dissipation Relations (FDR) originated more than a century ago from Einstein's investigation of the Brownian Motion, and then have been investigated by Onsager, during the 30's of the last century, and by Kubo, in the 50's, with a renewed interest in the last decades (Morriss, Evans, Cohen, Gallavotti, Jarzynski and others, in the 90's). In the following we will touch these recent progresses, with a discussion on some interesting modern applications, e.g. for the physics of the proteins (studied by Bustamante and coworkers in 2005).

Einstein showed the possibility of obtaining the number of molecules contained in a mole of fluid, known as Avogadro's number N_A, by observing with a microscope the motion of small grains suspended in water (see Box 2). The experimental test of the theory was realized with success in 1909 by Perrin and led to the conclusion that molecules exist and cause the diffusive motion of grains. S. Arrhenius summarizing the work of Einstein and Perrin wrote: *after this, it does not seem possible to doubt that the molecular theory entertained by the philosophers of antiquity, Leucippus and Democritos, has attained the truth at least in essentials.*

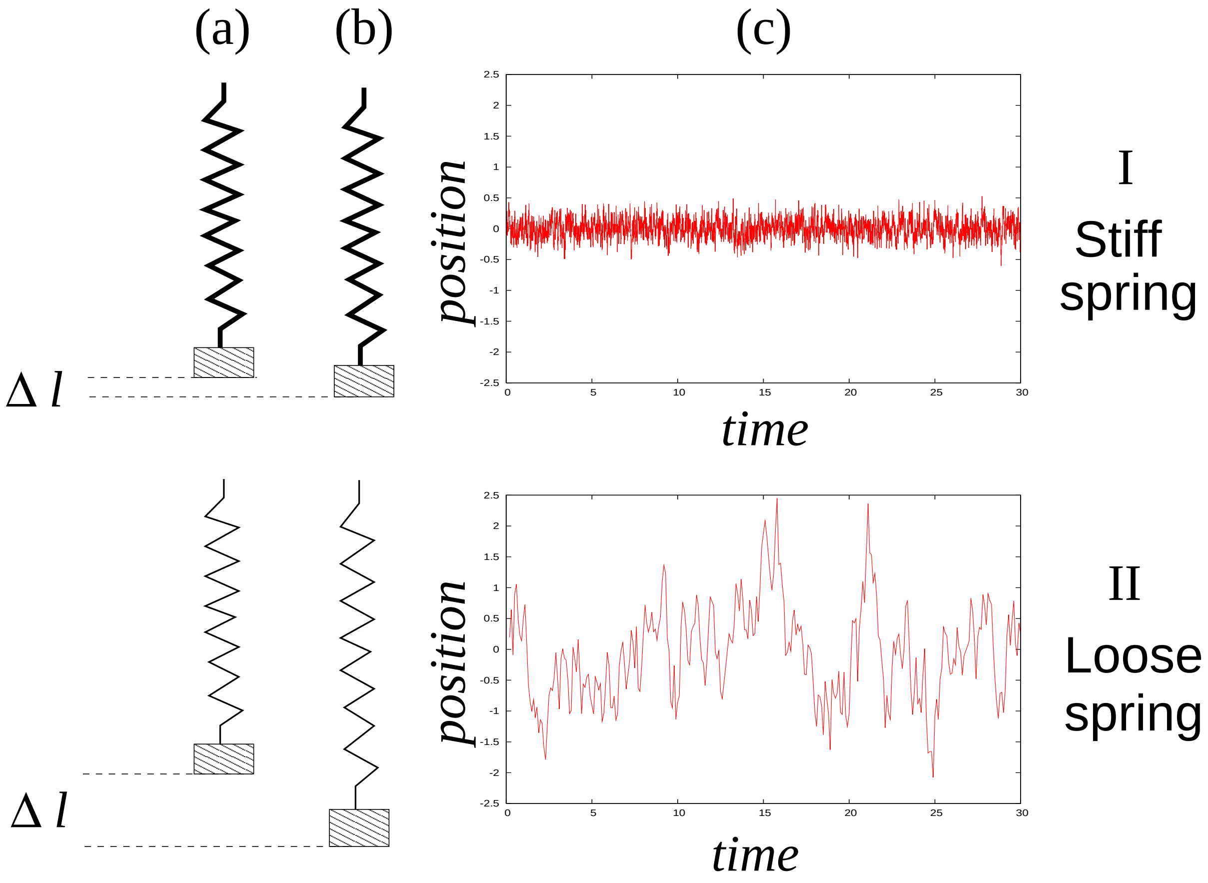

FIG. 1: An ideal experiment shows the essence of the Fluctuation-Dissipation relation: a stiff spring (case I) at rest (a), under the action of a small force F responds with an elongation Δl (b). Spontaneous fluctuations of the position as function of time are shown in (c). In II the same with a loose spring. Since $\Delta\ell$ is larger the spontaneous fluctuations are bigger. In a laboratory it is possible to perform a real experiment which shows the features above illustrated: using a laser beam one amplifies the rotational oscillations of a small mirror mounted on a torque pendulum which experiences thermal fluctuations due to interaction with the air molecules.

To obtain this crucial result, Einstein considered the two effects produced by fluid's molecules on a small but macroscopic (i.e. much larger than the molecules) object:

1. **fluctuation**: because of the continuous kicking of fluid's molecules, the velocity of the suspended object irregularly grows and decreases, displaying unpredictable fluctuations;
2. **relaxation**, also called dissipation or response: if an external force is applied to the object for a very small time, its velocity suddenly changes and then decays ("relaxes")

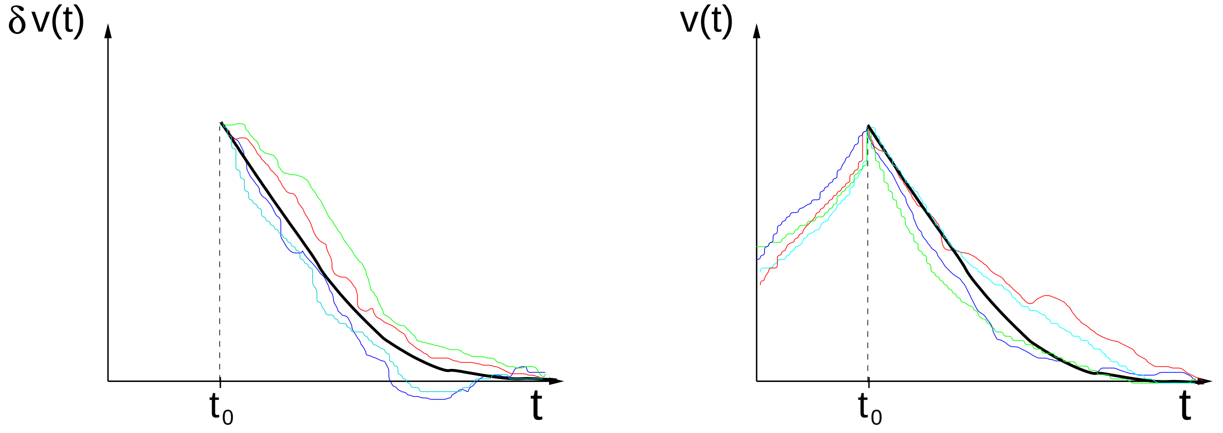

FIG. 2: Schematic behavior of the relaxation of perturbations (left) and of spontaneous fluctuations (right) of the velocity of the grain in the BM. Different colors indicates different realizations of the same experiment. The black curves are averages over many of these realizations: in the Gaussian limit, the mean relaxation coincides with the correlation function (equivalent to the average of the fluctuations starting from a given level).

toward zero (or to the mean fluid's velocity).

The fluctations of the (very small) instantaneous velocity of the suspended object may be depicted as in the right frame of Fig. 2, where it is assumed that the velocity rises up to a fixed threshold, in a time t_0. A quantitative description of the fluctuation and relaxation processes is given by the so-called "autocorrelation" functions.[1] The typical behavior following a spontaneous fluctuation is its decay, represented by the descending relaxation processes in Fig. 2. The chosen threshold may also be artificially produced, by initially perturbing the state of the system, in such a way that the initial velocity corresponds to the threshold value. Each relaxation process differs from case to case, as in the left frame of Fig. 2. However, the fundamental meaning of FDR is that the relaxation towards equilibrium of an external perturbation is on average the same as the decay of a spontaneous fluctuation.

More in general, the FDR expresses the relation between the fluctuations of an unperturbed system and an appropriate response function. This is a formal answer to the question about the electric current at the beginning of the article: it is possible to compute the resistance of the wire, which is a response to the applied potential difference, from the properties of the wire in absence of the potential. In Box 3 another classical example is discussed.

During the period following Einstein's work, the FDR was verified in a number of experiments and models leading to the conclusion that the erratic motion of small constituents of matter (atoms, molecules, electrons, etc.) results in a systematic dissipative effect and a much smaller fluctuating force. In 1931 L.Onsager proposed the universality of this relation, extending it to all systems near equilibrium (see Box 1). In particular, Onsager supposed that the averages of the physical quantities "respond" to external perturbations decaying from near-equilibrium states following correlation functions of the unperturbed system. In other words, the FDR states that the behaviour of a system out of, but close to, equilibrium may be understood in terms of averages of physical quantities computed in equilibrium states. Twenty years later, R. Kubo demonstrated the general validity of the FDR for systems near equilibrium, obtaining also very useful formula to compute transport coefficients. These coefficients express the response of more complicate quantities to external perturbations: for instance, thermal conductivity is the response to a temperature difference, shear viscosity is the response to an applied shear force. The process of unveiling the universality of the FDR took more or less 50 years and the resulting "linear response theory" is, even today, one of the most effective tools in non-equilibrium statistical physics. The relevance of FDT is due to its twofold nature: it is a fundamental result on a very general and abstract level, and is also a handy practical tool to make predictions.

Nowadays, the advancement of computational power and experimental techniques opens the possibility of investigating matter at scales smaller than micron, close to the nanometer. New classes of systems whose fluctuations play major roles have been met, and have stimulated the researchers to generalize the original FDT to far from equilibrium states (see box 1). This has led to the vast territory of the so-called Fluctuation Relations first discovered in 1993 by Evans, Cohen and Morris and two years later formalized by Gallavotti and Cohen.

The Fluctuation Relations concern a quantity called "entropy production" (representing the dissipation), and for perturbations which do not need to be small and states not necessarily close to equilibrium. Later, Fluctuation Relations for different quantities have been found, most of them concerning the fluctuations of heat exchanged by the system of interest with some external device. These relations have been tested and verified in experiments concerning "small systems", i.e. systems containing few thousand particles, such as macromolecules of biological interest. At such small scales the statistical nature of the second principle of thermodynamics, i.e. for short times a decrease of entropy seems to be realized. While further tests are necessary and under way, the Fluctuation Relations have widened

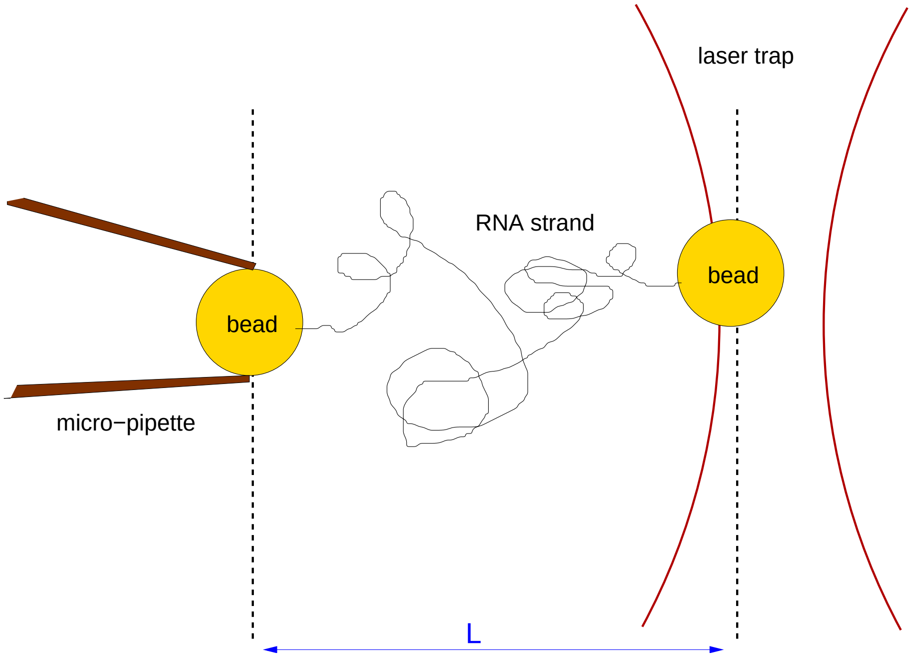

FIG. 3: A single biomolecule is stretched, by means of a moving laser trap pulling one end of the chain, while the other end is kept fixed by a micropipette; the increase of the distance L brings the molecule from a folded state A to an unfolded state B. The experiment is repeated a large number of times and the work done in each realization by the tweezer is recorded and analyzed through the Jarzynski's equality: this allows to obtain a precise estimate of the free energy difference ΔF_{AB}.

our understanding of the physics of matter.

For instance, the relation obtained in 1997 by C. Jarzynski, known as Jarzynski's equality (JE), has proved useful in experiments on biomolecules. It allows to infer the free energy difference ΔF_{AB}, between two equilibrium states A and B of a given system, from the collection of different values of the works done on the system, when the transformation from A to B is repeatedly imposed. The values of the free energy characterize the equilibrium states of a given system; in particular, lower values of F imply more stable states. As the free energy is a property of equilibrium thermodynamic states, the JE obtains information about equilibrium states from nonequilibrium experiments, in contrast with the FDT, which obtains information on nonequilibrium phenomena from equilibrium experiments.

For this reason, the JE has found applications in the study of protein folding (see Fig. 3). The structure of a protein, which determines its biological function (i.e. whether the protein "works" or not) may change when the environment changes. The stability of the "good" structure depends on the difference of free energies with other competing structures. Scientists have used extremely small "tweezers", obtained by interweaving laser rays, in order to manipulate an end of the protein (which is similar to a very long and entangled chain), while the other end is fixed to a substrate. The tweezers pull the protein from its original ("native") structure, stretching it out to a different non-native one. The same experiment is repeated a large number of times, and each time the different energy (the so-called "non-equilibrium works") required by the tweezers is recorded. A simple analysis of the histogram of these works, through the JE, is sufficient to determine ΔF_{AB}, an important result for biology and for non-equilibrium statistical physics.

The far from equilibrium generalizations of the FDT are valid either in a non-equilibrium stationary state (for example turbulent fluids, or a strongly shaken box containing sand), or in slowly relaxing systems (gels, pastes, colloidal melts, glassy materials, even real glasses), which are not fully understood states of matter. In these situations, there is no universally accepted microscopic definition of temperature. The efforts to generalize the FDT to these systems has led to the definition of "dynamical temperatures", whose meaning is matter of debate. It has been recently understood that *correlations* between velocities of molecules, which are negligible in equilibrium systems, may become significant far from equilibrium and may lead to a breakdown of the usual FDT. This may be be exploited to produce a new kind of thermometer, one based on a fluctuation-response measurement.

Assuming that the FDT holds beyond its original framework, i.e. the physics of Hamiltonian systems (i.e. evolving according to the Newton laws of the dynamics) with many degrees of freedom (for instance, a gas or a liquid appear to have many degrees of freedom from the microscopic point of view, because of their large number of molecules), one can conclude that the behavior of the response to external perturbations provides the same type of information contained in the spontaneous (internal) fluctuations. At present, there is no rigorous extension of FDT to generic chaotic systems (e.g. the celebrated Lorenz model which is a simplified but non trivial description of atmospheric convection). But in practice such a problem can be neglected in the vast majority of cases of physical interest, in which some noise is always present. Leith and Kraichnan, about 35 years ago, suggested that the FDT could be used to understand the climate, and the effects produced on it by abrupt changes of parameters, like the concentration of CO_2 in the atmosphere which could result, for instance, from anthropic or volcanic activity. This would require an analysis of the data concerning the past. However, the climate system has features which make this use of the FDT far from trivial:

- a) many different characteristic times (from few seconds to 10^3 years) are involved in climatic systems;
- b) the laws ruling the time evolution of the system are not well known;

The above issues do not imply conceptual limitations, since appropriate generalizations of FDT to finite size perturbations have been derived, but pose technical challenges due to the extremely complex dynamics of the systems. For instance, the characteristic decay time of a certain variable depends on the amplitude of the initial perturbation acting on it. Small perturbations may decay rapidly, while large perturbations may decay much more slowly. Such a behavior is brought about by the presence of many degrees of freedom with very different characteristic times, for instance the typical times of small scale turbulence and the deep oceanic currents are of the order of seconds and of millennia respectively. However, the main idea underlying the FDT, that external perturbations are equivalent to spontaneous fluctuations, leads to a severe difficulty in the case of climate: the understanding of the effects of large perturbations requires knowledge of rare fluctuations, whose statistics are necessarily affected by large uncertainties.

BOX 1 NON EQUILIBRIUM SYSTEMS

A macroscopic system is in mechanical equilibrium when there is a balance among the forces acting on it. Chemical reactions, and transport of matter may alter the state of a system in mechanical equilibrium. If this is not the case, the system is also in chemical equilibrium. Furthermore, the system is in thermal equilibrium if its state does not change when it is removed from the environment and is surrounded by adiabatic walls. The system is said to be in thermodynamic equilibrium when it is in mechanical, chemical and thermal equilibrium. Under these conditions, all parts of the system have the same temperature, which is also the temperature of the environment. Therefore, the state can be characterized by a few global quantities, which are constant in time.

Lack of mechanical equilibrium leads to acceleration, turbulence, waves etc. Lack of chemical equilibrium leads to variations in the chemical composition of the system or transport of matter. Lack of thermal equilibrium leads to heat flows.

If the system is not in thermodynamic equilibrium and it does not interact with the external environment, its state evolves till equilibrium is estabilished. However, the coupling of the system with the outer environment may prevent this relaxation to equilibrium; then energy is dissipated and nonequilibrium steady states may be realized.

A flask of hot coffee for few hours can be considered an equilibrium system, while the electric current in a metallic wire is a non-equilibrium system: in fact it is possible only in presence of a potential difference between the ends of the wire.

The coupling between a body and its environment often allows the formation of patterns and of ordered structures. This is the most common situation in nature. In particular, living organisms exist precisely because of the continuous flow of energy between them and their environment. Needless to say, life is the most striking nonequilibrium phenomenon.

BOX 2 BROWNIAN MOTION

In 1827 the botanist R. Brown, observing small (but macroscopic) grains suspended in water, through a microscope, noticed that each grain was performing a jiggling motion, now known as Brownian motion (BM). For decades the importance of BM was not appreciated until it was independently understood by Einstein and Smoluchowski, at the beginnning of the 20th century.

A few years later, Langevin proposed a description in terms of a stochastic differential equation, describing the total force acting on the pollen grains as the sum of a deterministic friction, due to the liquid seen as a continuum, and a random force resulting from the interactions with the liquid molecules. Both Einstein and Langevin assumed that a) the frictional force acting on such a small object is given by the Stokes law describing the friction force on a macroscopic body through a liquid and b) the equipartition of kinetic energy holds, i.e. the average kinetic energy of the grain coincides with the average kinetic energy of a molecule of the fluid. Using these two simple hypotheses they predicted that a Brownian particle diffuses, i.e. its displacement $\mathbf{x}(t)$ behaves in such an irregular way, that at long times is expressed by

$$\langle|\mathbf{x}(t)|^2\rangle \simeq 6Dt. \tag{1}$$

The diffusion coefficient D, which is a property of the system in the absence of any perturbation, was related to the mobility μ, which measures how the velocity of the particle responds to a small dragging force:

$$\mu = \frac{D}{k_B T} \tag{2}$$

where k_B, is Boltzmann's constant. Such a formula represents the first example of a FDT relation and illustrates the central role of fluctuations in statistical physics. Finally, expressing k_B in terms of the universal gas constant, R, and Avogadro's number $N_A = R/k_B$, and employing Stokes' relation, between the mobility, the viscosity (η) of the liquid and the radius of the Brownian particle (a), one finally obtains a prediction for the diffusion coefficient

$$D = \frac{RT}{6\pi N_A \eta a}. \tag{3}$$

Although the analytical aspects of Einstein's and Langevin's works are quite simple, one cannot overstate the profound subtlety of the assumption on which the theory is based, i.e. that Stokes' law (which has a macroscopic nature) holds together with the statistical equilibrium of the Brownian particle with the molecules of the liquid, notwithstanding the enormous mass difference between them. The importance of Eq. (3) lies in the fact that it provides a recipe for the determination of Avogadro's number, a microscopic quantity, from experimentally accessible macroscopic quantities (D, T, R and so on), thus providing a unambiguous link between the microscopic and macroscopic levels of description. Indeed, the Brownian particle, which is large enough to be visible at the microscope (it has a diameter around $1\mu m$), is thus turned into a kind of "magnifying glass" which unveils the atomic structure of matter.

BOX 3 FLUCTUATION-DISSIPATION RELATIONS AND ATOMS

The energy fluctuations in an N particle system are connected to the specific heat c_v, i.e. the heat quantity (per particle) necessary to increase the temperature of one centigrade degree:

$$\langle (E - \langle E \rangle)^2 \rangle = k_B T^2 N c_v, \tag{4}$$

since $c_v = \frac{1}{N}\frac{\partial}{\partial T}\langle E \rangle$, the specific heat, is a particular response function, i.e. it specifies how the mean energy changes when the temperature varies. In formula (4), $\langle\ \rangle$ indicates the statistical average and T is the absolute temperature. Einstein highlighted the conceptual relevance of Eq. (4) noting that it "*would yield an exact determination of the universal constant (the Avogadro number N_A), if it were possible to determine the square of the energy fluctuations of the system*". An important feature of the FDR, manifested by eq. (4), is its role as a "magnifying glass" for fluctuations. Indeed, in spite of their very small values in standard macroscopic systems, fluctuations can be indirectly measured, via FDR, by applying a perturbation to the systems of interest.

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[1] The autocorrelation of a given quantity X is the average of the product $X(t)X(0)$, the value of the quantity at the initial time by its value at any other time t. The average is computed over all possible initial states. The irreversible evolution of a given system towards a steady state, independent of the initial state, is characterized by the convergence to $\langle X \rangle^2$ of the autocorrelation functions.