Physics Reports 709–710 (2017) 1–60

Contents lists available at ScienceDirect

Physics Reports

journal homepage: www.elsevier.com/locate/physrep

Temperature in and out of equilibrium: A review of concepts, tools and attempts

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ARTICLE INFO

Article history:
Accepted 19 September 2017
Available online 5 October 2017
Editor: I. Procaccia

Keywords:
Temperature
Non-equilibrium
Fluctuations
Response
Large deviations

ABSTRACT

We review the general aspects of the concept of temperature in equilibrium and non-equilibrium statistical mechanics. Although temperature is an old and well-established notion, it still presents controversial facets. After a short historical survey of the key role of temperature in thermodynamics and statistical mechanics, we tackle a series of issues which have been recently reconsidered. In particular, we discuss different definitions and their relevance for energy fluctuations. The interest in such a topic has been triggered by the recent observation of negative temperatures in condensed matter experiments. Moreover, the ability to manipulate systems at the micro and nano-scale urges to understand and clarify some aspects related to the statistical properties of small systems (as the issue of temperature's "fluctuations"). We also discuss the notion of temperature in a dynamical context, within the theory of linear response for Hamiltonian systems at equilibrium and stochastic models with detailed balance, and the generalized fluctuation–response relations, which provide a hint for an extension of the definition of temperature in far-from-equilibrium systems. To conclude we consider non-Hamiltonian systems, such as granular materials, turbulence and active matter, where a general theoretical framework is still lacking.

Contents

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https://doi.org/10.1016/j.physrep.2017.09.001

> The meaning of the world is the separation of wish and fact.
>
> Kurt Gödel

1. Introduction

1.1. Introductory remarks and plan of the paper

Temperature is surely one of the central concepts in thermodynamics and statistical mechanics. Since we study such a topic in elementary courses, at first glance, a review on this argument can appear of mere scholarly interest, without particular relevance for the present research.

The recent developments in statistical mechanics of small systems, as well as for non-equilibrium and/or non-Hamiltonian systems, are becoming more and more important due to the theoretical and technological challenges of micro, and nano

Fig. 1. An example of Galileo's thermometer: the room temperature has an uncertainty of 1 °C.
Source: Courtesy of Andrea Baldassarri.

physics. In the treatment of situations far from the "traditional ones", i.e. equilibrium Hamiltonian systems with many degrees of freedom, the need to reconsider in a careful way the basic aspects of the notion of temperature appears in a natural way. Such a renewed interest in the foundations of statistical mechanics has shown that temperature is a rather difficult and subtle issue, and a clear understanding of its role in thermodynamics and statistical mechanics goes beyond the mere academic level.

The paper is organized as follows. In this Section we give a brief historical overview on the birth of the concept of temperature, focusing in particular on its connection with the fluctuations theory. Section 2 is devoted to some general aspects of temperature. In particular we review the role of temperature for the energy fluctuations and its connection with the ergodic hypothesis in the building of consistent statistical mechanics theory. In addition we discuss the link between entropy and large deviations, and how temperature can be computed as time average of a suitable observable. Such an approach allows one to determine the temperature for any Hamiltonian system. In Section 3 we treat several subtle points, namely the (non existing) temperature fluctuations and systems with negative temperature. Moreover we discuss some statistical features of small systems. In Section 4 we review the role of the temperature in the context of the Response Theory. The link between relaxation and fluctuations allows for a bridge from equilibrium to non equilibrium statistical mechanics, and in addition it suggests a possible path for the introduction of temperature out of equilibrium. The statistical mechanics approach, and the possibility to introduce a concept of temperature for non Hamiltonian systems is discusses in Section 5. We shortly review such a challenge in topics as granular media, chaotic systems, fluids and active matter. In Section 6 we present some general considerations and final remarks.

1.2. Historical overview

Let us start this review with a brief, non systematic, historical outlook. We believe to have an intuitive idea of temperature because of our physiological sense of hot and cold. Actually our sense of temperature depends also upon the heat flux across the skin. For instance, if we touch a piece of metal and a piece of wood at the same temperature we have different perceptions: the metal feels colder than the wood. Although one can find some ideas about the concept of temperature in the ancient Greek and Islamic science, the first attempts to give a coherent definition started in the 16th century [1,2]. Galileo had a crucial role in the development of the concept of temperature, starting several studies which led to the construction of the first thermometer, named after him: a closed glass cylinder containing a clear liquid and several glass vessels of varying densities, see Fig. 1. Actually such an instrument, which now is used as a decorative object, has been invented by a group of academics and technicians who included E. Torricelli and V. Viviani [3].

Using Galileo's thermometer, G. Sagredo had been able to understand the distinction between our physiological senses and physical properties. On February 7th, 1615, in a letter to Galileo he wrote

> *… Con questi istrumenti ho chiaramente veduto, essere molto piú freda l' aqua de' nostri pozzi il verno che l'estate. …, ancorché il senso nostro giudichi diversamente.* [… With these instruments I have clearly seen that water of our wells is colder in winter than in summer …, although our senses tell differently.] [1]

The introduction of the temperature at quantitative level needs a thermometric scale. For instance one can divide the interval between the values of two suitable temperatures into a given number of subdivisions. In the Celsius scale, 0 °C corresponds to the equilibrium between liquid water and ice, while 100 °C is the temperature at the equilibrium between liquid water and vapor, both at pressure of 1 atmosphere. For the Fahrenheit scale one has a rather similar procedure. A very important step has been the observation that in all the gases, if the pressure p is sufficiently low (ideal gases), the so-called Boyle–Charles–Gay-Lussac law holds:

$$pV = nR(t + 273.15\ ^{\circ}\mathrm{C}), \tag{1}$$

where V is the volume, n the number of moles, R a universal constant and t the temperature in Celsius degrees.

1.2.1. The zero law implies that temperature is a consistent concept

Before going on in the attempt to define temperature in a systematic way, even in systems different from ideal gases, it is necessary to be sure that the temperature "really exists", i.e. one has to show that it is possible to introduce such a concept in a non ambiguous way.

The key physical point for such an aim is the zero law of thermodynamics. If two systems A and B are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other; in other words thermal equilibrium between two systems is a transitive relation. Such an empirical (and intuitive) law is the physical basis which allows us to establish the concept of temperature, as shown by the following simple and elegant argument, see [4,5]. Consider two systems A and B whose volumes and pressures are (V_A, P_A) and (V_B, P_B) respectively. We can say that there exists a function of the variables of state such that, when the two systems are in equilibrium, one has:

$$F_1(P_A, V_A, P_B, V_B) = 0. \tag{2}$$

Of course the form of the function depends on the considered system. In the following we show that, assuming the zero law, one has

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B), \tag{3}$$

from which one can derive the existence of a quantity (the temperature) common to the two systems.

Let us consider three systems A, B and C; if A and C are in equilibrium we have:

$$F_2(P_A, V_A, P_C, V_C) = 0, \tag{4}$$

from which one can obtain P_C:

$$P_C = f_1(P_A, V_A, V_C). \tag{5}$$

If B and C are in equilibrium we can repeat the previous reasoning:

$$F_3(P_B, V_B, P_C, V_C) = 0, \tag{6}$$

and

$$P_C = f_2(P_B, V_B, V_C), \tag{7}$$

and therefore

$$f_2(P_B, V_B, V_C) = f_1(P_A, V_A, V_C). \tag{8}$$

Due to the zero law A is in equilibrium with B, and therefore (2) holds: however V_C appears in (8) but not in (2), therefore f_1 and f_2 must depend on V_C in a proper way. For instance the form

$$f_1(P_A, V_A, V_C) = \phi_1(P_A, V_A)\zeta(V_C) + \eta(V_C) \tag{9}$$

satisfies (8) and implies (3); in addition, see [4], it is possible to show that not only (9) is sufficient to have (3), but it is also necessary.

From the above reasoning one has that, for systems in equilibrium, there exists a quantity (empirical temperature θ) depending on P and V

$$\theta = \phi(P, V),$$

which defines the equation of state. For the ideal gases we have the equation

$$PV = f(\theta),$$

and the form of $f(\theta)$ is determined by the empirical scale. Being t the temperature in degrees Celsius, the experimental result (1) suggests a linear shape: $f(\theta) = nR\theta$ with $\theta = 273.15 + t$.

1.2.2. Absolute temperature in thermodynamics

Using Carnot's theorem on the efficiency of reversible engines working between two heat reservoirs, it is possible to go beyond the empirical temperature and introduce the absolute temperature. Let us recall Kelvin's idea [5]: denote Q_1 the heat absorbed by the engine from the hotter reservoir (with empirical temperature θ_1), and Q_2 the heat delivered by the engine to the colder reservoir (with empirical temperature θ_2), in one cycle; from Carnot's theorems one has that Q_2/Q_1 only depends on the empirical temperatures θ_1 and θ_2:

$$\frac{Q_2}{Q_1} = G(\theta_1, \theta_2).$$

It is easy to show that[1] the function $G(\theta_1, \theta_2)$ must be independent of the details of the reservoirs and the engine, one can write

$$\frac{Q_2}{Q_1} = \frac{g(\theta_2)}{g(\theta_1)}, \tag{10}$$

being $g(\theta)$ a universal function. Therefore, using the result (1) for the ideal gases, $g(\theta)$ can be identified, apart from a multiplicative constant, with the absolute temperature.

1.3. Temperature in statistical mechanics

Due to its intrinsic phenomenological character it is difficult to associate the thermodynamic temperature with any specific dynamical property of the considered system. However once it was clear that macroscopic systems are made of particles (atoms, molecules) ruled by the mechanical laws, it was mandatory an attempt to find a link between the mechanical world, on the one hand, and thermodynamics on the other.

The first approach, dating back to Daniel Bernoulli, has been for ideal gases considered to be point-like particles of mass m that collide with the walls of the container [6]. Later Clausius had been able to show that in such a model of matter, Eq. (1) holds, and the temperature T is proportional to the mean kinetic energy:

$$m\langle v^2\rangle = k_B T,$$

being v one component of the velocity, and k_B the Boltzmann's constant.

Such a first step toward the kinetic theory of gases has been the starting point for the building of a consistent bridge, both theoretical and concrete, between mechanics and thermodynamics. The most relevant contribution in such a great project is due to Boltzmann; we can summarize his grand vision in two points:

1. the introduction of probabilistic ideas and their use for the interpretation of physical observables;
2. the relationship linking the macroscopic world (thermodynamics) to the microscopic one (dynamics).

Point 1 is rather subtle and it is the object of intense study still today. Boltzmann's idea was to replace time averages with averages coming from a suitable probability density, which is nothing but the ergodic hypothesis. The relation connecting thermodynamics to the microscopic world (point 2) is given by the celebrated equation (engraved on Boltzmann's tombstone, see Fig. 2):

$$S = k \log W, \tag{11}$$

where S denotes the entropy of the macroscopic body (a thermodynamical quantity) and W is the number of microscopic states (a mechanical-like quantity) realizing the macroscopic configuration. Actually, Eq. (11), usually called Boltzmann's law, has been written by Planck [7].

If we are able to express W as a function of the energy E, from the thermodynamic relation we have

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

and therefore we obtain a mechanical definition of temperature.

In the canonical ensemble the temperature appears in the probability distribution in the phase space:

$$P(\mathbf{X}) = const.\, e^{-\beta H(\mathbf{X})}, \quad \beta = \frac{1}{k_B T}, \tag{12}$$

---

[1] Considering the cycles between θ_1 and θ_3, θ_2 and θ_3 and θ_1 and θ_2, we have

$$\frac{Q_1}{Q_3} = G(\theta_1, \theta_3), \qquad \frac{Q_2}{Q_3} = G(\theta_2, \theta_3), \qquad \frac{Q_1}{Q_2} = G(\theta_1, \theta_2),$$

therefore we have

$$G(\theta_2, \theta_3) = \frac{Q_2}{Q_1}\frac{Q_1}{Q_3} = \frac{G(\theta_1, \theta_3)}{G(\theta_1, \theta_2)} = \frac{g(\theta_2)}{g(\theta_3)},$$

proving Eq. (10).

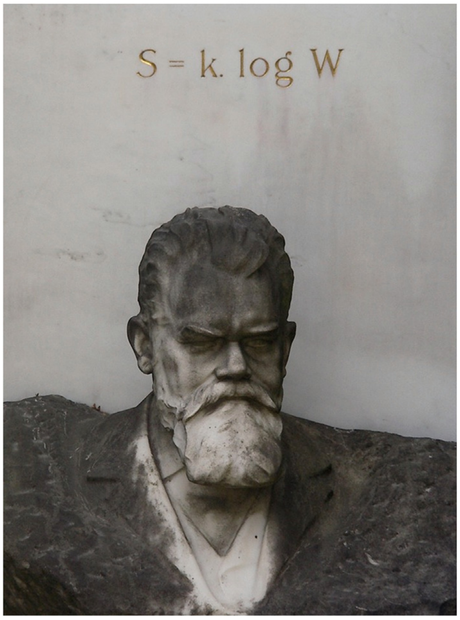

Fig. 2. The celebrated Boltzmann's relation engraved on his tomb.

being **X** the vector describing the microscopic state of the system, i.e. the coordinates and momenta of all the particles. In the case of systems with short range interactions, the canonical distribution describes the statistical features of a (small) part of the system interacting with the remaining (large) part. Therefore T can be seen as a property of the heat bath with which the system is in contact.

1.4. *Temperature and fluctuations*

The bridge law (11) has important consequences supported by empirical evidence, including, in particular, those derived by Einstein, see for instance [8]. Denote with $\alpha_1, \ldots, \alpha_m$ some macroscopic functions of the microscopic state $\mathbf{X}$: $\alpha_j = g_j(\mathbf{X})$, $j = 1, \ldots, m$. Einstein's idea was to use Eq. (11) with the constraints $\{\alpha_k\}$. Since $W(\{\alpha_k\})$ is proportional to the probability density of the variables $\{\alpha_k\}$, one can invert the formula and obtain

$$P(\alpha_1, \ldots, \alpha_m) \sim e^{[S(\{\alpha_k\})-S_e]/k_B}, \tag{13}$$

where $S_e = S(\{\alpha_k^*\})$ is the equilibrium entropy computed at the equilibrium values $\{\alpha_k^*\}$, and $S(\{\alpha_k\})$ is the entropy of a spontaneous fluctuation of the collective variables $\{\alpha_k\}$.

Formula (13) is meant to represent the probability of fluctuations around equilibrium states of macroscopic mechanical quantities. Since in the limit of large N the fluctuations are small, we can expand $S(\{\alpha_k\}) - S_e$ around the equilibrium values $\{\alpha_k^*\}$:

$$S(\{\alpha_k\}) - S_e \simeq \frac{1}{2}\sum_{i,j} \frac{\partial^2 S}{\partial\alpha_i \partial\alpha_j}\Big|_{\{\alpha_k^*\}} \delta\alpha_i \delta\alpha_j, \tag{14}$$

where $\delta\alpha_i = \alpha_i - \alpha_i^*$. With such an approximation, $P(\alpha_1, \ldots, \alpha_m)$ is nothing but a multivariate Gaussian distribution

$$P(\alpha_1, \ldots, \alpha_m) \sim e^{-\frac{1}{2k_B}\sum A_{ij}\delta\alpha_i\delta\alpha_j}, \tag{15}$$

where

$$A_{ij} = -\frac{\partial S}{\partial\alpha_i \partial\alpha_j}\Big|_{\{\alpha_k^*\}},$$

and therefore one has:

$$\langle \delta\alpha_i \delta\alpha_j \rangle = k_B \Big[\mathbf{A}^{-1}\Big]_{ij}. \tag{16}$$

Let us comment on the relevance of the above formula: the fluctuations of observable quantities can be described in terms of macroscopic equilibrium thermodynamic functions. For instance, if α is the energy, one identifies the average $\langle E\rangle$ of the energy with the internal energy U of the system, and one has the well known formula:

$$\langle E^2\rangle - \langle E\rangle^2 = k_B T^2 C_v, \tag{17}$$

which gives us information on the size of the energy fluctuations, being C_v the heat capacity at constant volume. Since C_v is extensive, i.e. proportional to the number N of particles in the system, the relative size of the energy fluctuations is negligible in large systems. Apparently this should lead one to relegate fluctuations to the set of only marginally interesting phenomena. For instance Boltzmann wrote

> *In the molecular theory we assume that the laws of the phenomena found in nature do not essentially deviate from the limits that they would approach in the case of an infinite number of infinitely small molecules.* [7]

Gibbs had rather similar opinions:

> *[the fluctuations] would be in general vanishing quantities, since such experience would not be wide enough to embrace the more considerable divergences from the mean values.* [7]

On the contrary the fluctuations have a key role in statistical mechanics. More than one century ago Einstein, in his search of an ultimate proof of the existence of atoms [9,10], realized that Eq. (17)

> *would yield an exact derivation of the universal constant* [k_B or, equivalently, Avogadro's number N_A] *if it were possible to determine the average of the square of the energy fluctuations of the system.*

Einstein's intuition was correct, and later he was able to understand how to relate Avogadro's number to a macroscopic quantity, namely the diffusion coefficient of Brownian particles; the theoretical work by Einstein and the experiments by Perrin gave a conclusive evidence of atomism [11]. In addition, Einstein's seminal paper on the Brownian motion contains another very important result, namely the first example of Fluctuation–Dissipation Theorem (FDT), see Section 4: a relation between the fluctuations (given by correlation functions) of an unperturbed system and the mean response to a perturbation [12–14]. In the specific case of Brownian motion, FDT appears as a link between the diffusion coefficient (a property of the unperturbed system) and the mobility, which measures how the system reacts to a small perturbation: a fundamental observation is that the temperature of the system appears in the proportionality factor between these two variables.

Beyond their conceptual relevance and the link with response functions, fluctuations in macroscopic systems are quantitatively extremely small and hard to detect (but for the case of second order phase transitions in equilibrium systems). On the other hand, in recent years statistical mechanics of small systems, where fluctuations are observable and cannot be neglected, is becoming more and more important due to the theoretical and technological challenges of micro and nano physics. For instance in [15] the energy fluctuations of a finite free-electron Fermi gas have been studied; one has quite a non-Gaussian effect at low temperature. Such a topic will be treated more in detail in Section 4.

2. General aspects of temperature and entropy

2.1. Different equilibrium definitions of temperature and entropy

Surely it is not possible to underestimate the conceptual difficulties around the notion of entropy (and therefore temperature), even in equilibrium conditions:

> *Entropy, like force, is an undefined object, and if you try to define it, you will suffer the same fate as the force definers of the seventeenth and eighteenth centuries. Either you will get something too special or you will run around in a circle.* [16]

Let us start noting that there are, at least, two natural definitions of entropy (and therefore temperature) in equilibrium statistical mechanics. In the most common cases (i.e. system described by a Hamiltonian with a kinetic contribution and a potential term) the two definitions are equivalent in the limit of large systems. However it is interesting to discuss in some details such a topic which, after the publication of experimental measurements of a negative absolute temperature [17], has been in the last years the subject of an intense debate. In Section 3 we discuss the issue in more details.

As already mentioned in the Introduction the starting point for a microscopic foundation of temperature is the definition of entropy in terms of mechanical quantities. Even if not historically precise [7], we adopt the current convention and call "Boltzmann entropy" of a system containing N particles, with Hamiltonian $H(\mathbf{Q}, \mathbf{P})$, where $\mathbf{Q}$ and $\mathbf{P}$ are vectors in $\mathbb{R}^{dN}$, being d the dimension of the system, the quantity

$$S_B(E, N) = k_B \ln \omega(E, N), \tag{18}$$

where

$$\omega(E, N) = \int \delta(H(\mathbf{Q}, \mathbf{P}) - E)d^{dN}Q\, d^{dN}P = \frac{\partial \Sigma(E, N)}{\partial E},$$

and

$$\Sigma(E,N)=\int_{H(\mathbf{Q},\mathbf{P})<E} d^{dN}Q\, d^{dN}P.$$

Assuming Eq. (18), one can define the "Boltzmann temperature" through

$$k_B\beta_B=\frac{1}{T_B}=\frac{\partial S_B(E,N)}{\partial E}.$$

On the other hand, one can adopt a different definition of microcanonical entropy, proposed by Gibbs [18]. The Gibbs entropy, which is always monotonically increasing, reads

$$S_G(E,N)=k_B\ln\Sigma(E,N),$$

and leads to the Gibbs temperature definition, which is always positive:

$$k_B\beta_G=\frac{1}{T_G}=\frac{\partial S_G(E,N)}{\partial E}\geq 0.$$

In the rest of this Section we consider systems made of a finite but large number $N\gg 1$ of particles with local interactions, i.e. we exclude long-range potentials or mean-field models [19].

2.1.1. Canonical ensemble and energy fluctuations

Let us consider a vector $\mathbf{X}$ in $\mathbb{R}^{2dN_1}$, with $N_1<N$, that is a subsystem of the full phase space $(\mathbf{Q},\mathbf{P})$ and let us indicate with $\widetilde{\mathbf{X}}$ in $\mathbb{R}^{2d(N-N_1)}$ the remaining variables. For the Hamiltonian we have

$$H=H_1(\mathbf{X})+H_2(\widetilde{\mathbf{X}})+H_I(\mathbf{X},\widetilde{\mathbf{X}}),$$

with an obvious meaning of symbols. Let us consider the case $N\gg 1$ and $N_1\ll N$. In the microcanonical ensemble with energy E, the probability density function for the full phase space is

$$P(\mathbf{Q},\mathbf{P})=\frac{1}{\omega(E,N)}\delta(H(\mathbf{Q},\mathbf{P})-E). \tag{19}$$

The probability distribution function (PdF) of $\mathbf{X}$ can be obtained from the latter with a marginalization procedure, i.e. integrating over $\widetilde{\mathbf{X}}$. Since the Hamiltonian $H_I(\mathbf{X},\widetilde{\mathbf{X}})$ is negligible (a consequence of our assumption of the absence of long-range interactions), we have

$$P(\mathbf{X})\simeq\frac{\omega(E-H_1(\mathbf{X}),N-N_1)}{\omega(E,N)}. \tag{20}$$

Now writing ω in terms of S_B:

$$\omega(E,N)=e^{S_B(E,N)/k_B}, \tag{21}$$

$$\omega(E-H_1(\mathbf{X}),N-N_1)=e^{S_B(E-H_1(\mathbf{X}),N-N_1)/k_B}, \tag{22}$$

and reminding that $N_1\ll N$ we can assume $H_1\ll E$, obtaining

$$S_B(E-H_1(\mathbf{X}),N-N_1)\simeq S_B(E)-\frac{\partial S_B(E,N)}{\partial E}H_1(\mathbf{X})+const. \tag{23}$$

Therefore, using Eqs. (20)–(23) one obtains the PdF in the canonical ensemble:

$$P(\mathbf{X})=\frac{1}{Z}e^{-\beta_B H_1(\mathbf{X})}.$$

The above derivation is quite standard, and it is presented in many textbooks. We repeated the reasoning with the aim to clarify that, once one assumes the microcanonical distribution, T_B is the "correct" temperature ruling the statistics of fluctuations of physical observables in a subsystem. For instance, the PdF of energy E_1 in the subsystem, is

$$P(E_1,N_1)\propto\omega(E_1,N_1)e^{-\beta_B E_1}. \tag{24}$$

2.2. Large deviation theory and convexity property of entropies

Let us discuss the following relevant property: $S_B(E,N)$ is always convex, i.e. $d^2S_B(E,N)/dE^2\leq 0$. This result is a consequence of the second law of thermodynamics, and, in addition, it can be proved in a rigorous way in the limit of vanishing interaction, and in short-range interacting systems, for large N [20,21]. Actually S_B is strictly related to the large deviation function associated with the density of states.

2.2.1. *Convexity of S_B and the second law of thermodynamics*

Let us consider a system $\mathcal{A}$ of $N_\mathcal{A}$ particles described by the variables $\{\mathbf{Q}_\mathcal{A}, \mathbf{P}_\mathcal{A}\}$ and Hamiltonian $H_\mathcal{A}(\mathbf{Q}_\mathcal{A}, \mathbf{P}_\mathcal{A})$, a system $\mathcal{B}$ of $N_\mathcal{B}$ particles described by the variables $\{\mathbf{Q}_\mathcal{B}, \mathbf{P}_\mathcal{B}\}$ and Hamiltonian $H_\mathcal{B}(\mathbf{Q}_\mathcal{B}, \mathbf{P}_\mathcal{B})$, and a small coupling among the two, so that the global Hamiltonian is

$$H = H_\mathcal{A}(\mathbf{Q}_\mathcal{A}, \mathbf{P}_\mathcal{A}) + H_\mathcal{B}(\mathbf{Q}_\mathcal{B}, \mathbf{P}_\mathcal{B}) + H_I(\mathbf{Q}_\mathcal{A}, \mathbf{Q}_\mathcal{B}).$$

If the two Hamiltonians have the same functional dependencies on the canonical variables (i.e. they correspond to systems with same microscopic dynamics, with possibly different sizes $N_\mathcal{A}$ and $N_\mathcal{B}$) for large N, we can introduce the (Boltzmann) entropy per particle $s(e)$

$$s(e) = \frac{S_B(E, N)}{N}, \quad e = \frac{E}{N},$$

with $s(e)$ a function which is identical for the two systems.

Let us now suppose that systems $\mathcal{A}$ and $\mathcal{B}$ have, respectively, energy $E_\mathcal{A} = N_\mathcal{A} e_\mathcal{A}$ and $E_\mathcal{B} = N_\mathcal{B} e_\mathcal{B}$ and the corresponding inverse Boltzmann temperatures are $\beta_B^{(\mathcal{A})}$ and $\beta_B^{(\mathcal{B})}$. When the two systems are put in contact, a new system is realized with $N = N_\mathcal{A} + N_\mathcal{B}$ particles. Indicate with $a = N_\mathcal{A}/N$ the fraction of particles from the system $\mathcal{A}$, the final energy is $E_f = E_\mathcal{A} + E_\mathcal{B} = Ne_f$, where $e_f = ae_\mathcal{A} + (1-a)e_\mathcal{B}$. From the second law of the thermodynamics we have that the final entropy cannot be smaller than the in initial one:

$$S_B(E_F, N) = Ns(e_f) \geq N_\mathcal{A} s(e_\mathcal{A}) + N_\mathcal{B} s(e_\mathcal{B}) = N[as(e_\mathcal{A}) + (1-a)s(e_\mathcal{B})].$$

The previous inequality is nothing but a way to express the convexity of $s(e)$, i.e.

$$s[ae_\mathcal{A} + (1-a)e_\mathcal{B}] \geq as(e_\mathcal{A}) + (1-a)s(e_\mathcal{B}).$$

The final inverse temperature $\beta_B^{(f)}$ is intermediate between $\beta_B^{(\mathcal{A})}$ and $\beta_B^{(\mathcal{B})}$, i.e. if $e_\mathcal{B} > e_\mathcal{A}$ - that is $\beta_B^{(\mathcal{A})} > \beta_B^{(\mathcal{B})}$ - then

$$\beta_B^{(\mathcal{B})} < \beta_B^{(f)} < \beta_B^{(\mathcal{A})}.$$

The energy flux obviously goes from smaller β_B (hotter) to larger β_B (colder). The consequence of convexity is that $\beta_B(E)$ is always decreasing and a negative value does not lead to any ambiguity.

In the next Section we will discuss a particularly interesting case with different Hamiltonians where in the system $\mathcal{A}$ negative temperatures can be present, whereas system $\mathcal{B}$ has only positive temperatures.

2.2.2. *Entropy and large deviations*

If we consider the energy per particle $e = E/N$, Eq. (24), dropping the subscript 1, can be written in the form

$$P(e) = \frac{1}{Z} \exp\{-N\beta_B[e - T_B s(e)]\},$$

where

$$Z \sim \exp\{-N\beta_B f(T_B)\},$$

being $f(T_B)$ the free energy per particle

$$f(T_B) = \min_e\{e - T_B s(e)\}.$$

The value $\bar{e}$ for which $e - T_B s(e)$ reaches its minimum is given by the condition

$$\frac{1}{T_B} = \left.\frac{\partial s(e)}{\partial e}\right|_{\bar{e}},$$

i.e. it is the value such that the corresponding microcanonical ensemble has temperature T_B. Therefore we can write

$$P(e) \sim \exp\{-N\mathcal{C}(e)\},$$

with

$$\mathcal{C}(e) = \beta_B[e - T_B s(e) - f(T_B)].$$

Of course the value of e such that $\mathcal{C}(e)$ is minimum (zero) is the mean energy: $\bar{e} = \langle e \rangle$. With the Gaussian approximation around $\bar{e}$ one can compute the variance of energy fluctuations obtaining the (exact) formula (17).

The above simple computations are nothing but an example of large deviations theory (LDT). For the sake of self-consistence let us briefly remind the basic aspects of this approach [21,22]. The general mathematical formulation of LDT has been introduced in the 1930s mainly by Cramér for independent identical distributed random variables $x_1, x_2, \ldots, x_N$ with mean value $\langle x \rangle$, and standard deviation σ. The main aim of the LDT is to go beyond the central limit theorem, which is able to describe only the typical fluctuations of the "empirical mean" $y = (x_1 + \cdots + x_N)/N$, i.e. for $|y - \langle y \rangle| < O(\sigma/\sqrt{N})$.

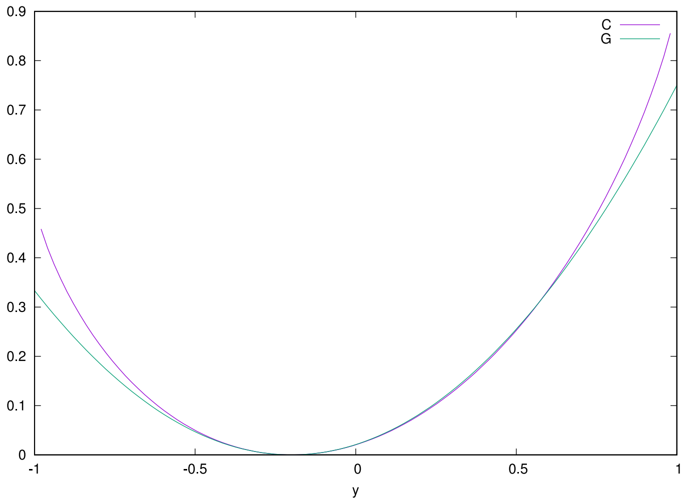

Fig. 3. An example of Cramér function as in Eq. (25) for $p = 0.4$. For comparison we show its parabolic approximation ("G" curve).

Under the rather general assumption of existence of the moment generating function $\langle e^{qx}\rangle$ in some neighborhood of $q = 0$, it is possible to prove that for $N \gg 1$ one has

$$P(y) \sim e^{-N\mathcal{C}(y)}.$$

The Cramér function $\mathcal{C}(y)$ depends on the probability distribution of x, it is positive everywhere but for $y = \langle x\rangle$ where it vanishes.

From an historical point of view it is interesting that the first LDT calculation has been carried out by Boltzmann [20]. He was able to express the asymptotic behavior of the multinomial probabilities in terms of relative entropy. In the case x_i takes the value $+1$ with probability p and -1 with probability $1 - p$, using the Stirling approximation it is possible to obtain the explicit expression for the Cramér function:

$$\mathcal{C}(y) = \frac{1+y}{2} \ln \frac{1+y}{2p} + \frac{1-y}{2} \ln \frac{1-y}{2(1-p)}. \tag{25}$$

(See Fig. 3.)

Let us stress that the Cramér function for independent variables must obey the following constraints:

(i) $\mathcal{C}(y) > 0$ for $y \neq \langle y\rangle = \langle x\rangle$;
(ii) $\mathcal{C}(y) = 0$ for $y = \langle y\rangle$;
(iii) $\mathcal{C}(y) \simeq (y - \langle y\rangle)^2/(2\sigma^2)$, where $\sigma^2 = \langle (y - \langle y\rangle)^2\rangle$, if y is close to $\langle y\rangle$;
(iv) $d^2\mathcal{C}/dy^2 > 0$.

Properties (i) and (ii) are consequences of the law of large numbers, and (iii) is nothing but the central limit theorem; property (iv) has not a simple justification, and in statistical physics it corresponds to a "mathematical translation" of the second law of thermodynamics. Moreover, the Cramér function is linked, via a Legendre transform, to the cumulant generating function of the variable x

$$\mathcal{C}(y) = \sup_q \{qy - L(q)\},$$

where

$$L(q) = \ln\langle e^{qx}\rangle.$$

The properties (i)–(iv) are valid under rather general hypothesis, in particular it is not necessary that the variables $\{x_n\}$ are independent, provided that the correlation function $c(k) = \langle (x_{n+k} - \langle x\rangle)(x_n - \langle x\rangle)\rangle$ goes to zero faster than $1/k$ as $k \to \infty$ [21–23].

2.3. *Entropy in the Γ-space and in the μ-space*

Let us now briefly discuss some aspects related to entropy, which, although simple from a technical point of view, are rather subtle and can induce confusion.

A popular way to formulate the second law of thermodynamics is to say that the entropy increases in time; such a statement deserves careful considerations, in particular on how to associate an entropy-like quantity to the state of a physical system [24–26]. Considering a Hamiltonian system with N weakly interacting particles, its microscopic state, in the so called Γ-space, is given by the vector $\mathbf{X} = (\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)$, where $\mathbf{q}_n$ and $\mathbf{p}_n$, are the position and the momentum of the nth particle respectively. From the probability distribution in the Γ- space $\rho(\mathbf{X}, t)$ at time t, following Gibbs, we can introduce an entropy

$$S_\Gamma(t) = -k_B \int \rho(\mathbf{X}, t) \ln \rho(\mathbf{X}, t) d\mathbf{X}. \tag{26}$$

If ρ is the stationary canonical distribution $e^{-\beta H(\mathbf{X})}/Z$, the quantity S_Γ is the usual entropy. More interesting is its dynamical aspect: using the Liouville theorem it is easy to show that $S_\Gamma(t)$ must be constant.

In order to observe an increase over time for $S_\Gamma(t)$-like quantities, one can introduce a coarse-graining of the Γ-space. Consider a partition of the phase space in cells $\{\Lambda_i(\epsilon)\}$ of size ϵ, and consider the probability to stay, at time t, in the ith cell:

$$P_i(\epsilon, t) = \int_{\Lambda_i(\epsilon)} \rho(\mathbf{X}, t) d\mathbf{X},$$

the ϵ coarse-grained Gibbs entropy is

$$S_\Gamma^{(\epsilon)}(t) = -k_B \sum_i P_i(\epsilon, t) \ln P_i(\epsilon, t). \tag{27}$$

Now $S_\Gamma^{(\epsilon)}(t)$, for any small $\epsilon \neq 0$ is, typically, an increasing function of time: for instance in a suitable time interval one has

$$S_\Gamma^{(\epsilon)}(t) - S_\Gamma^{(\epsilon)}(0) \simeq h_{KS} t + const., \tag{28}$$

where h_{KS} is the Kolmogorov–Sinai entropy. The above behavior is surely interesting in a dynamical systems context. Numerical results show that even such a coarse-grained Gibbs entropy remains constant up to a crossover time $t^*(\epsilon) \sim \ln(1/\epsilon)$. Only after $t^*(\epsilon)$, $S_\Gamma^{(\epsilon)}(t)$ increases, showing the linear growth (28) [27]. This ϵ-dependence indicates that the increasing of $S_\Gamma^{(\epsilon)}(t)$ has no genuine thermodynamic meaning and it is merely originated by the coarse-graining procedure; therefore (28) cannot be viewed as the second law of thermodynamics [27].

We discuss now another way, due to Boltzmann, to introduce the concept of entropy in weakly interacting systems. Instead of dealing with the probability distribution in the Γ-space, let us define the one particle distribution function in the μ-space:

$$f(\mathbf{r}, t) = \frac{1}{N} \sum_{n=1}^{N} \delta(\mathbf{r} - \mathbf{r}_n(t)), \tag{29}$$

where $\mathbf{r}_n = (\mathbf{q}_n, \mathbf{p}_n)$, and introduce the quantity

$$S_\mu(t) = -k_B \int f(\mathbf{r}, t) \ln f(\mathbf{r}, t) d\mathbf{r}. \tag{30}$$

It is easy to realize that at equilibrium the two entropies are equivalent: $S_\Gamma \simeq N S_\mu$.

At a first glance the two definitions of entropy, (26) and (30), appear rather similar, but a close analysis shows that their dynamical behaviors are rather different. We remind that from the celebrated H-theorem there follows that, under suitable conditions, S_μ increases in time [28,29]. It is remarkable the fact that a coarse-grained procedure for S_μ, at variance with the result for S_Γ, does not change the qualitative behavior of $S_\mu(t)$ vs t [27].

Let us note that the two definitions (26) and (30), somehow, reflect two different approaches to the foundations of the statistical mechanics and conceptual differences on how to consider probability. For the computation of the entropy S_Γ, one needs $\rho(\mathbf{X}, t)$, namely an ensemble. It is easy to realize that $\rho(\mathbf{X}, t)$, and therefore $S_\Gamma(t)$, is accessible only in numerical experiments with systems composed by few degrees of freedom [30]. On the contrary, if $N \gg 1$, the one particle distribution function $f(\mathbf{r}, t)$, and therefore $S_\mu(t)$, can be seen as an empirical distribution, it is a well defined macroscopic observable and can be, in principle, measured in a single system; actually this is the standard procedure in numerical simulations [24–26]. One may object that the introduction of $f(\mathbf{r}, t)$ is a form of coarse-graining, although different from $P_i(\epsilon, t)$. However, as briefly discussed above, we know that this is the "correct coarse-graining", which is consistent with thermodynamics and in addition it is quite natural in a numerical approach [31,32].

2.4. Helmholtz's monocycle and some Boltzmann's ideas about ergodicity

As already discussed, usually Boltzmann's journey toward a consistent formulation of statistical mechanics starting from mechanics, is summarized with two (apparently independent) items:

- the ergodic hypothesis;

- the law relating entropy to mechanics: the celebrated $S = k_B \ln W$. On the other hand there is an interesting way to introduce ergodicity using the second law of thermodynamics and the formula (11). Such a link between ergodicity and entropy, had an important role for the development of Boltzmann's ideas, and it is based on a result of Helmholtz for one-dimensional Hamiltonian systems. Apparently this topic seems to be almost unknown even to scholars interested in the history of physics. Luckily it was recently exhumed by Gallavotti [33] and discussed in a very clear way by Campisi and Kobe [34].

Consider a one dimensional system with Hamiltonian

$$H(q, p, V) = \frac{p^2}{2m} + \phi(q, V),$$

where V is a control parameter, for instance in a pendulum V is the length which can be varied. Assume that for each V, $\phi(q, V)$ has a unique minimum and in addition diverges as $|q| \to \infty$. In such a system, for any value of E, the motion is surely periodic; denote with $\tau(E, V)$ the period, $q_-(E, V)$ and $q_+(E, V)$ the minimum and maximal value of q respectively. Of course the motion is ergodic, i.e. the time averages coincide with the averages computed with the microcanonical distribution:

$$d\mu(p, q) = \frac{\delta(H(q, p, V) - E)dqdp}{\int\int \delta(H(q, p, V) - E)dqdp}. \qquad (31)$$

Let us mention Helmholtz's theorem:
Define the temperature T and the pressure P in terms of time averages $\langle(\ldots.)\rangle_t$ computed on the period $\tau(E, V)$:

$$T = \frac{2}{k_B}\left\langle \frac{p^2}{2m} \right\rangle_t, \quad P = -\frac{1}{k_B}\left\langle \frac{\partial \phi(q, V)}{\partial V} \right\rangle_t. \qquad (32)$$

Then, the function

$$S(E, V) = k_B \ln 2 \int_{q_-(E,V)}^{q_+(E,V)} \sqrt{2m[E - \phi(q, V)]}dq \qquad (33)$$

satisfies the following relations

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{P}{T}. \qquad (34)$$

To prove the above formulae it is enough to use

$$\delta(f(p)) = \sum_i \frac{\delta(p - p_i)}{|f'(p_i)|},$$

where $\{p_i\}$ are determined by $f(p_i) = 0$, and therefore one has

$$\langle f \rangle_t = \frac{2m}{\tau(E, V)} \int_{q_-(E,V)}^{q_+(E,V)} \frac{f(q, p(q))}{p(q)} dq$$

with $p(q) = \sqrt{2m[E - \phi(q, V)]}$, see [34] for the details. Let us note that $S(E, V)$ can be written in the usual form

$$S(E, V) = k_B \ln \int_{H(q,p,V)<E} dpdq.$$

The above results imply a rather interesting consequence, namely the *existence of a mechanical analogue for the entropy*: indeed, the following quantity

$$\frac{dE + PdV}{T},$$

where T and P are expressed via time averages of mechanical observable, is an exact differential.

Boltzmann's idea was to generalize the above result, which is surely valid for $1d$ Hamiltonian, to systems with many particles, in other words to find a function $S(E, V)$ such that the relations (32) and (34) are still valid. In a Hamiltonian system with N particles, assuming ergodicity it is possible to show a *generalized Helmholtz's theorem* for the function

$$S(E, V) = k_B \ln \int_{H(\mathbf{q},\mathbf{p},V)<E} d\mathbf{q}d\mathbf{p}.$$

The proof is quite similar to that one for the $1d$ case, see [34].

We can summarize Boltzmann's reasoning as follows: in systems with many particles the periodic trajectory of the $1d$ case is replaced by the hypothesis that the trajectory will sweep the whole surface $H = E$ (this is a way to say that the time averages can be replaced with the microcanonical averages). Then from the generalized Helmholtz's theorem one has the second law of thermodynamics, i.e. the existence of a function (the entropy S) which can be expressed in mechanical terms, and, in addition, dS/T is an exact differential.

In view of the discussion about the different possible definitions of entropy and temperature (see Section 3.3) we note that all the above arguments hold for systems with the typical Hamiltonian including a quadratic kinetic term.

2.5. *Temperature as a time average*

We now focus on a dynamical approach to temperature, which allows one to measure it as a time average. This result is due to Rugh [35,36], who has been able to show that the (microcanonical) temperature can be written as an average of a suitable observable, namely:

$$\frac{1}{k_B T} = \frac{\partial \ln \omega(E)}{\partial E} = \frac{1}{\omega(E)}\frac{\partial \omega(E)}{\partial E} = \left\langle \nabla \cdot \left(\frac{\nabla H}{\|\nabla H\|^2} \right) \right\rangle_E . \tag{35}$$

Here the average is computed with the microcanonical distribution on the energy constant hypersurface $\Sigma_E = \{\mathbf{X} : H(\mathbf{X}) = E\}$.

The physical relevance of the above result is that the temperature can be written in terms of an average of a mechanical observable [37], and therefore, assuming ergodicity, one can obtain the temperature with a time average along a trajectory:

$$\frac{1}{k_B T} = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} \Phi(\mathbf{X}(t))\, dt ,$$

where

$$\Phi = \nabla \cdot \left(\frac{\nabla H}{\|\nabla H\|^2} \right). \tag{36}$$

If the system is very large, one can write

$$\frac{1}{k_B T} = \left\langle \frac{\nabla^2 H}{\|\nabla H\|^2} \right\rangle_E \left(1 + O\left(\frac{1}{N}\right)\right) = \frac{\langle \nabla^2 H \rangle_E}{\langle \|\nabla H\|^2 \rangle_E} \left(1 + O\left(\frac{1}{N}\right)\right).$$

For ideal gases, as well as for harmonic systems, it is easy to see that, for $N \gg 1$, the above result coincides with the usual one, i.e. the temperature is proportional to mean kinetic energy.

Rugh's approach is much more interesting if the Hamiltonian is different from the standard, i.e. containing a kinetic term and a potential part:

$$H = \sum_{n=1}^{N} \frac{\mathbf{p}_N^2}{2m} + V(\mathbf{q_1}, \ldots, \mathbf{q}_N). \tag{37}$$

We discuss such a class of systems in Section 3.3.

2.5.1. *Generalization of Rugh's result*

The result (35) has been generalized, see e.g. [36,38,39], and it is possible to show that

$$\frac{1}{k_B T} = \left\langle \nabla \cdot \left(\frac{\mathbf{B}}{\mathbf{B} \cdot \nabla H} \right) \right\rangle_E , \tag{38}$$

where $\mathbf{B}$ is an arbitrary continuous and differentiable vector in phase-space. The original Rugh's result corresponds to the case $\mathbf{B} = \nabla H$.

For an Hamiltonian with the form (37), with the choice $\mathbf{B} = (0, \ldots, 0, \mathbf{p}_1, \ldots \mathbf{p}_N)$, Eq. (38) leads to

$$\frac{1}{k_B T} = \left\langle \frac{m\, d\, N}{\sum_n \mathbf{p}_n^2} \right\rangle_E , \tag{39}$$

where d is the spatial dimension, and in the limit $N \gg 1$ one has the usual relation

$$k_B T = \frac{1}{m\, d\, N} \left\langle \sum_n \mathbf{p}_n^2 \right\rangle_E .$$

With the choice $\mathbf{B} = (\mathbf{q}_1, \ldots \mathbf{q}_N, 0, \ldots, 0)$, in the limit $N \gg 1$ one obtains

$$k_B T = \frac{1}{d\, N} \left\langle \sum_n \mathbf{q}_n \cdot \frac{\partial}{\partial \mathbf{q}_n} V \right\rangle_E ,$$

which is nothing but the Clausius virial theorem.

Let us now consider the choice $\mathbf{B} = \nabla V$, for $N \gg 1$, which yields

$$\frac{1}{k_B T} = \left\langle \nabla \cdot \left(\frac{\nabla V}{\|\nabla V\|^2} \right) \right\rangle_E \simeq \frac{\langle \nabla^2 V \rangle_E}{\langle \|\nabla V\|^2 \rangle_E} . \tag{40}$$

The above formula provides a definition of the temperature only in terms of the coordinates and not of the momenta.

The generalization of Rugh's formula, in particular the configurational temperature, has been successfully used in numerical simulations, for instance for checking the algorithmic correctness of Monte Carlo computer programs, and (following the Nosé-Hoover approach) to design new thermostats [40,38].

2.5.2. *A brief mathematical parenthesis: derivation of Rugh's result*

For the sake of completeness and selfconsistency, we report the derivation of Eq. (35), which is a special case of the following result: for any function $F(\mathbf{X})$ one has

$$\frac{d}{dE}\int_{H=E} F(\mathbf{X})\, d\sigma(\mathbf{X}) = \int_{H=E} \nabla \cdot \left(F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\right)\frac{1}{\|\nabla H\|}\, d\sigma(\mathbf{X}), \tag{41}$$

where $d\sigma(\mathbf{X})$ is the infinitesimal "area" on Σ_E. Let us introduce the quantity

$$G_F(E, \Delta E) = \frac{1}{\Delta E}\Big(\int_{H=E+\Delta E} F(\mathbf{X})\, d\sigma(\mathbf{X}) - \int_{H=E} F(\mathbf{X})\, d\sigma(\mathbf{X})\Big),$$

and the unitary inner vector normal to Σ_E in $\mathbf{X}$ is $\mathbf{n}(\mathbf{X}) = \nabla H/\|\nabla H\|$. Using the identity $1 = \nabla H \cdot \nabla H/\|\nabla H\|^2$, we can write:

$$G_F(E, \Delta E) = \frac{1}{\Delta E}\Big(\int_{H=E+\Delta E} F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\cdot \mathbf{n}\, d\sigma(\mathbf{X}) - \int_{H=E} F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\cdot \mathbf{n}\, d\sigma(\mathbf{X})\Big) =$$

$$\frac{1}{\Delta E}\Big(\int_{H=E+\Delta E} F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\cdot \mathbf{n}_e\, d\sigma(\mathbf{X}) + \int_{H=E} F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\cdot \mathbf{n}_e\, d\sigma(\mathbf{X})\Big),$$

where $\mathbf{n}_e$ is the unitary normal pointing toward the exterior of the region $\{\mathbf{X} : E < H(\mathbf{X}) < E + \Delta E\}$. Now, applying the divergence theorem, we obtain

$$G_F(E, \Delta E) = \frac{1}{\Delta E}\int_{E<H<E+\Delta E} \nabla \cdot \left(F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\right) d\mathbf{X}.$$

Since we can write

$$d\mathbf{X} = dE\,\frac{d\sigma(\mathbf{X})}{\|\nabla H\|}, \tag{42}$$

one has

$$G_F(E, \Delta E) = \frac{1}{\Delta E}\int_E^{E+\Delta E} dE \int_{H=E} \nabla \cdot \left(F(\mathbf{X})\frac{\nabla H}{\|\nabla H\|}\right)\frac{1}{\|\nabla H\|} d\sigma(\mathbf{X}),$$

and, in the limit $\Delta E \to 0$, one obtains Eq. (41).

For our aim the interesting case is

$$F(\mathbf{X}) = \frac{1}{\|\nabla H\|}.$$

Reminding that

$$\omega(E) = \lim_{\Delta E\to 0}\frac{1}{\Delta E}\int_{E<H<E+\Delta E} d\mathbf{X},$$

using (42) and (41), one has

$$\omega(E) = \int_{H=E}\frac{1}{\|\nabla H\|}\, d\sigma(\mathbf{X}),\quad \frac{\partial\omega(E)}{\partial E} = \int_{H=E}\nabla\cdot\left(\frac{\nabla H}{\|\nabla H\|^2}\right)\frac{1}{\|\nabla H\|}\, d\sigma(\mathbf{X}).$$

Eventually, using the relation

$$\langle\!\langle \cdot \rangle\!\rangle_E = \frac{1}{\omega(E)}\int_{H=E}(\cdot)\frac{d\sigma(\mathbf{X})}{\|\nabla H\|},$$

one has a proof of Eq. (35).

3. Temperature beyond the mean kinetic energy

3.1. *Temperature cannot fluctuate*

The energy of a finite system interacting with a thermal reservoir may fluctuate, while the temperature is a constant representing a thermodynamic property of the reservoir. However, as discussed in Section 1.4, Einstein showed that the statistical properties of macroscopic variables can be determined in terms of quantities computed in thermodynamic equilibrium [41,8].

Some authors have suggested that Einstein's fluctuation theory can be extended to give expressions for $\langle(\delta T)^2\rangle$, leading to apparent relations of complementarity between temperature and energy, similar to position and momentum in quantum mechanics [42–45]. Discussion and measurements of temperature fluctuations have been given also in [46,47]. In contrast, others have stressed the contradictory nature of the concept of temperature fluctuations [48]: in the canonical ensemble, which describes systems in contact with a thermal reservoir, the temperature is a parameter, so it cannot fluctuate. Mandelbrot has shown that this problem can receive a satisfactory answer within the framework of estimation theory [49]. We summarize here the main points of this discussion, referring to [50] for more details.

As seen in Section 1.4, in statistical mechanics the fluctuations of n macroscopic variables $\{\alpha_1...\alpha_n\}$ close to their equilibrium values $\{\alpha_1^*...\alpha_n^*\}$ obey a multivariate Gaussian distribution with covariance matrix

$$\langle\delta\alpha_i\delta\alpha_j\rangle = k_B\Big[\mathbf{A}^{-1}\Big]_{ij},\quad A_{ij} = -\frac{\partial S}{\partial\alpha_i\partial\alpha_j}\Big|_{\{\alpha_k^*\}}, \tag{43}$$

where S is the entropy.

The A_{ij} are functions of quantities evaluated at thermodynamic equilibrium, so that we can write $\delta S = S(\{\alpha_k\}) - S(\{\alpha_k^*\})$ as a function of different variables. If we can express S as function of T and V [41], then

$$\delta S = -\frac{C_V}{2T^2}(\delta T)^2 + \frac{1}{2T}\frac{\partial P}{\partial V}\Big|_T(\delta V)^2, \tag{44}$$

where we assume $\delta T = \delta(\partial E/\partial S)$. This manipulation of variables is misleading if used inside Eq. (43), as it gives

$$\langle(\delta T)^2\rangle = \frac{k_B T^2}{C_V}, \tag{45}$$

whose meaning is not clear, although it appears in many textbooks. Let us note that the fluctuation of kinetic energy per particle is a well defined quantity, but it is conceptually very different from (45), although apparently rather similar (just a different numerical constant) [51].

If we insist in considering Eq. (45) valid, using also Eq. (17), we get

$$\langle(\delta T)^2\rangle\langle(\delta E)^2\rangle = k_B^2 T^4, \tag{46}$$

or

$$\langle(\delta\beta)^2\rangle\langle(\delta E)^2\rangle = 1. \tag{47}$$

Eq. (46) and (47) can be interpreted as "thermodynamic uncertainty relations" formally similar to the Heisenberg principle. Some authors discuss a "thermodynamic complementarity" where energy and β play the role of conjugate variables [42]. Let us briefly explain the origin of the trouble. Eq. (43) holds if S is function of the macroscopic variables $\{\alpha_k\}$, which are functions of the microscopic variables. On the contrary, Eq. (44) gives just δS as a function of δV and δT, and it is not related to a probability distribution.

Other authors, such as Kittel [52,48], claim that the concept of temperature fluctuations is misleading. The argument is simple: temperature is just a parameter of the canonical ensemble, which describes the statistics of the system, and therefore it is fixed by definition. In particular, when a system is in equilibrium with a thermal reservoir, we can have two situations: either we know the temperature of the reservoir and can describe the energy distribution of the system; or we do not know the temperature of the reservoir, and can determine it from the energy distribution of the system. The latter situation is called the inverse problem. For such a problem we can use the tools of estimation theory, which makes it possible to use the available data (in this case a series of energy values) to evaluate an unknown parameter (in this case T). We will see that Eq. (45) can be somehow considered valid, but now $\sqrt{\langle(\delta T)^2\rangle}$ must be interpreted as a measure of the uncertainty on the temperature.

In order to clarify the discussion, let us recall here a few basic concepts from estimation theory [53,54]. Consider a probability density function $f(x,\beta)$ of the variable x, which depends on the parameter β, together with a sample of n independent events $(x_1,\ldots,x_n)$, governed by the probability density f, so that the probability density of the sample is

$$L(x_1,\ldots,x_n,\beta) = \prod_{i=1}^{n} f(x_i,\beta). \tag{48}$$

We would like to estimate the unknown parameter β from the values $\{x_i\}$. For this purpose we have to define a suitable function of n variables, $\widehat{\beta}(x_1,\ldots,x_n)$, to obtain the estimate of β from the available information. The quantity $\widehat{\beta}$ is, by construction, a random variable. We call $F(\widehat{\beta},\beta)$ its probability density, which of course depends upon the parameter β. We can calculate, for instance, its expected value and its variance. When $\langle\widehat{\beta}\rangle = \beta$, one says that $\widehat{\beta}$ is an unbiased estimate of β. It is clear that the usefulness of an estimating function is tightly linked to its variance.

Given certain general conditions of regularity, the Cramér–Rao inequality [53] for unbiased estimators can be established:

$$\int\Big(\widehat{\beta}-\beta\Big)^2 F(\widehat{\beta})d\widehat{\beta} \geq \left\{n\int\Big(\frac{\partial}{\partial\beta}\ln f(x,\beta)\Big)^2 f(x,\beta)dx\right\}^{-1}, \tag{49}$$

where the quantity in the braces on the right hand side of Eq. (49) is known as the Fisher information [53]: it gives a measure of the maximum amount of information we can extract from the data about the parameter to be estimated. This inequality puts a limit on the ability of making estimates, and also suggests that the estimator should be chosen by minimizing the inequality. When the variance of $\widehat{\beta}$ is the theoretical minimum, the result $\widehat{\beta}$ is said to be an "efficient estimate" [53]. Here we follow the convention of distinguishing between an efficient estimate, which has minimum variance for finite n, and an asymptotically efficient estimate, which has minimum variance in the limit $n \to \infty$.

It is now useful to relate fluctuations of measurements of energy and fluctuations of estimates of temperature. For this purpose, let us consider a gas of N classical particles. For simplicity, we begin by measuring the energy u of a single particle, whose probability distribution we write as

$$P(u,\beta)=\frac{g(u)\exp(-\beta u)}{Z(\beta)}, \tag{50}$$

where the parameter β is $1/k_BT$ and the density of single particle states $g(u)$ is assumed to be known. Suppose that we have measured n independent values of particle energy $(u_1,\dots,u_n)$. We can write

$$P(u_1,\dots,u_n,\beta)=\frac{g(u_1)\exp(-\beta u_1)}{Z(\beta)}\cdots\frac{g(u_n)\exp(-\beta u_n)}{Z(\beta)}, \tag{51}$$

or

$$\begin{aligned}P(u_1,\dots,u_n,\beta)&=\frac{g(u_1)\cdots g(u_n)}{G_0(U)}\frac{G_0(U)\exp(-\beta U)}{Z^n(\beta)} &(52)\\ &\equiv h(u_1,\dots,u_{n-1}|U)P(U,\beta), &(53)\end{aligned}$$

where $U=\sum_{i=1}^n u_i$ and $G_0(U)$ is given by

$$G_0(U)=\int g(u_1)\cdots g(u_n)\delta\left(\sum_{i=1}^n u_i-U\right)du_1\cdots du_n. \tag{54}$$

Because $P(U,\beta)$ is the probability density of measuring a total energy U in n independent single particle energy measurements, we see that $h(u_1,\dots,u_{n-1}|U)$, which is the conditional distribution of the energy in the sample given the total measured energy, does not depend on β. We conclude that good estimators of β can be constructed as a function of the sum of the measured energies.

A possible choice of temperature estimator is the maximum likelihood estimator determined by the condition

$$-\frac{\partial}{\partial\beta}\ln Z^n(\beta)\Big|_{\widehat{\beta}_{\rm MLE}}=\sum_{i=1}^n u_i, \tag{55}$$

which – for the case of density of states $g(u)\propto u^\eta$ – reads

$$\widehat{\beta}_{\rm MLE}=\frac{n(\eta+1)}{U}, \tag{56}$$

which can be demonstrated not to be an unbiased estimate. In general, for large n, the values of $\widehat{\beta}$ extracted from Eq. (55) are normally distributed around the true value β, with variance $1/(n\sigma_u^2)$ where σ_u^2 is the variance of the single-particle energy calculated with the true β. Therefore $\widehat{\beta}$ is asymptotically efficient.

Another estimator for β is given by

$$\widehat{\beta}_G=\frac{\partial}{\partial U}\ln G_0(U). \tag{57}$$

Unlike the maximum likelihood estimator, $\widehat{\beta}_G$ is an unbiased estimator of β for any n, but like the maximum likelihood estimator, it is not an efficient estimator for finite n. It becomes asymptotically efficient when the density of states $g(u)\propto u^\eta$ is considered [55,56].

An important point of the preceding discussion is that, due to the exponential form of the canonical ensemble probability density, all the information about β is contained in the total energy of an isolated sample. We gain nothing by knowing the distribution of this energy among the n elements of the sample. We say that $U=\sum_{i=1}^n u_i$ is sufficient for estimating β. Therefore we may also argue as follows. Instead of n measurements of the molecular energy, we make one measurement of the energy E on the macroscopic system with density $P(E,\beta)=G(E)\exp(-\beta E)/Z_N(\beta)$, $G(E)$ being the density of states of the entire system, which reduces to $G_0(E)$ for systems made of non-interacting components. The Cramér–Rao inequality becomes

$$\int\left(\widehat{\beta}-\beta\right)^2F(\widehat{\beta})d\widehat{\beta}\geq\frac{1}{\sigma_E^2}, \tag{58}$$

where σ_E^2 is the variance of the canonical energy of the macroscopic body. For an ideal gas of N identical particles, $\sigma_E^2=N\sigma_u^2$, and Eq. (58) becomes $\sigma_{\widehat{\beta}}^2\geq 1/N\sigma_u^2$. With regard to the determination of β, a single value of the macroscopic energy contains the same information as N microscopic measurements.

We know that a non-ideal gas of N identical particles with short-range interparticle interactions behaves (if not at a phase transition) as if it were composed of a large number, $N_{\rm eff}\propto N$, of (almost) independent components, and $\sigma_E^2\approx N_{\rm eff}\,\sigma_c^2$,

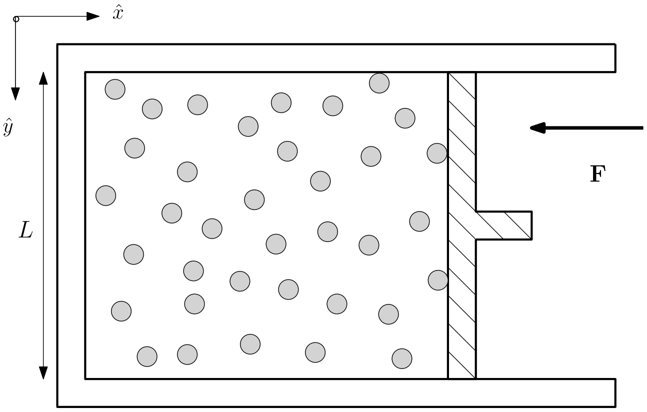

Fig. 4. Sketch of the mechanical model for a thermometer, see Eq. (60).

where σ_c^2 is the variance of one component. For instance, consider a system of N particles in a volume V with a correlation length $\ell = (cV/N)^{1/3}$, where $c \gg 1$ indicates strong correlations. We have $N_{\rm eff} \sim V/\ell^3 = c^{-1}N$. Thus, even if $n = 1$ in Eq. (58), that is, we perform a single measurement of energy, the variance of E, which is the energy of a macroscopic system, is extensive and the variance of $\widehat{\beta}$ may be small. We have $\sigma_{\widehat{\beta}}^2 \geq 1/N_{\rm eff}\,\sigma_c^2$, with $N_{\rm eff} \propto N \gg 1$. By looking at E as the result of $N_{\rm eff}$ elementary energy observations, our preceding considerations can be applied here with $N_{\rm eff}$ playing the role of n. In particular, the asymptotic properties for large $N_{\rm eff}$ of the two estimators are preserved, and the estimates of β obtained by the two expressions

$$-\frac{\partial}{\partial \beta}\ln Z_N(\beta)\Big|_{\widehat{\beta}_{\rm MLE}} = E, \tag{59a}$$

and

$$\widehat{\beta}_G = \frac{\partial}{\partial E}\ln G(E) \tag{59b}$$

approach the same value for $N_{\rm eff} \gg 1$, a condition that is verified for macroscopic bodies. Therefore, for a macroscopic system, we can obtain a good estimate of β even with a single measurement of its energy.

In conclusion we have given a justification, in terms of estimation theory, of the definition of temperature in statistical mechanics either in the canonical or microcanonical ensemble by means of Eq. (59). From our discussion we see that the fluctuations of the random variables $\widehat{\beta}_{\rm MLE}$ and $\widehat{\beta}_G$ when $n \gg 1$ are approximately Gaussian with a variance $1/(n\sigma_u^2)$. The fluctuations of the total energy of the sample $U = \sum_{i=1}^n u_i$ also become Gaussian (by the central limit theorem) with variance $n\sigma_u^2$. Therefore, in this limit, we have $\sigma_{\widehat{\beta}}^2\,\sigma_U^2 = 1$.

Let us notice that, although the Rao–Cramér inequality, Eq. (58), is formally similar to Eq. (46), which was obtained by an incorrect use of Einstein's fluctuation formula, the analogy is inexact and misleading. In mathematical statistics the quantity $\sigma_{\widehat{\beta}}^2$ measures the uncertainty in the determination of the value of β and not the fluctuations of its values.

3.1.1. *About temperature uncertainty in small systems*

It is useful to illustrate the above ideas by means of a mechanical model for a thermometer [50]. A box is filled with N non-interacting particles of mass m. On the top of the box there is a piston of mass M which can move without friction in the $\hat{x}$ direction, see Fig. 4. Although the box is three-dimensional, only the motion in the $\hat{x}$ direction is relevant because we assume that the particles interact only with the piston. The other directions are decoupled from $\hat{x}$, independently of their boundary conditions. The one-dimensional Hamiltonian of the system is

$$\mathcal{H} = \sum_{i=1}^{N}\frac{p_i^2}{2m} + \frac{P_M^2}{2M} + FX, \tag{60}$$

where X is the position along the $\hat{x}$ axis of the piston, and the positions of the particles x_i along the same axis are constrained to be between 0 and X. A force F acts on the piston, and in addition there are elastic collisions of the gas particles with the piston. The particles exchange energy with a thermostat at temperature T placed on the one side of the box at $x = 0$ (see [50] for details of its computational implementation). In the following we set $k_B = 1$, which is equivalent to measuring the temperature in units of $1/k_B$.

It is straightforward to compute the mean value of the piston position

$$\langle X\rangle = \frac{(N+1)T}{F}. \tag{61}$$

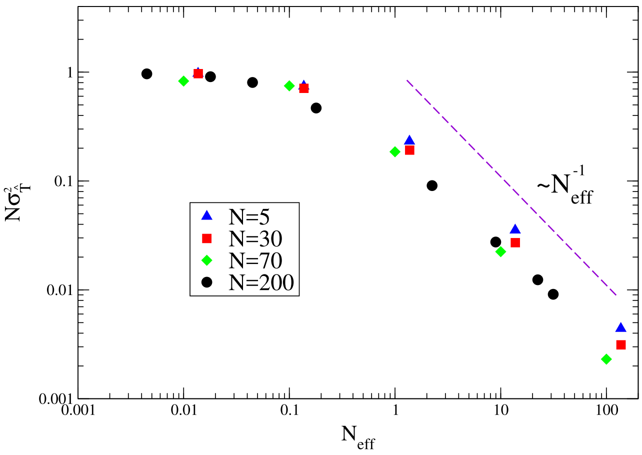

Fig. 5. The quantity $N\sigma^2_{\hat{T}}$ for different values of N is numerically calculated and plotted as a function of $\mathcal{N}_{\text{eff}} = \mathcal{N}\delta t/\tau$. For large times, the uncertainty goes to zero as $1/\mathcal{N}_{\text{eff}}$. The parameters are $\delta t = 0.01, M = 10, m = 1, F = 10, T = 1, N = 5, 30, 70$, and 200. It is clear that for the uncertainty of T, the relevant quantity is $\mathcal{N}_{\text{eff}}$ which depends both on N and τ.

As a consequence of this formula, an unbiased estimator for the temperature of the thermostat is

$$\hat{T} = \frac{F\hat{X}}{N+1}, \tag{62}$$

where $\hat{X}$ is an estimate of the average piston position. We use for it

$$\hat{X}_{\mathcal{N}} = (X^{(1)} + \cdots + X^{(\mathcal{N})})/\mathcal{N} \tag{63}$$

where $X^{(1)}, \ldots, X^{(\mathcal{N})}$ are $\mathcal{N}$ independent measurements of the piston position. The probability distribution function of the piston position is

$$P(X) = \frac{1}{N!}(\beta F)^{N+1} X^N e^{-\beta F X}, \tag{64}$$

which is an infinitely divisible distribution [57], so that the variable $\hat{X}_{\mathcal{N}}$ has a probability distribution function of the same shape, with N replaced by $N\mathcal{N}$. The variance of $\hat{X}_{\mathcal{N}}$ is $\sigma^2_{\hat{X}}/\mathcal{N}$, because the values of X are independent. From Eq. (64) we have also that $\sigma^2_{\hat{X}} = (N+1)/\beta^2 F^2$, and therefore

$$\sigma^2_{\hat{X}_{\mathcal{N}}} = \frac{1}{\mathcal{N}} \frac{N+1}{\beta^2 F^2}. \tag{65}$$

This gives the following variance for the temperature estimator $\hat{T}$ obtained by using $\hat{X}_{\mathcal{N}}$ as estimator of $\hat{X}$:

$$\sigma^2_{\hat{T}} = \frac{T^2}{\mathcal{N}(N+1)}, \tag{66}$$

which is exactly the Cramér–Rao lower bound, i.e. $\hat{T}$ is an unbiased and efficient estimator for every $\mathcal{N}$ [50]. In particular, Eq. (65) shows that the variance of the estimator is of order $\sim 1/N$, which can be non-negligible for single measurements on small systems, but it can be arbitrarily reduced by increasing the number $\mathcal{N}$ of measurements.

In a real experiment one cannot be sure that the $\mathcal{N}$ measurements are independent. In general, the data are correlated, and a correlation time τ must be estimated numerically. A simple and natural way is to look at the shape of the correlation functions of the observables of interest. If the distance in time δt between two successive measurements is smaller than τ, the effective number of independent measurements is approximately $\mathcal{N}_{\text{eff}} = \mathcal{N}\delta t/\tau$. By plotting $N\sigma^2_{\hat{T}}$ versus $\mathcal{N}_{\text{eff}}$ we expect that the dependence on N disappears, resulting in a collapse of the curves: this is exactly what happens in Fig. 5, where we have used for τ the minimum time such that the autocorrelation of piston's position $|C_X(t)| < 0.05$, where

$$C_X(t) = \frac{\langle \delta X(t)\delta X(0)\rangle}{\langle \delta X^2(0)\rangle}. \tag{67}$$

3.2. Small systems: models and stochastic thermodynamics

In recent years, the development of experimental techniques allowing us to observe and even manipulate objects on mesoscopic (nano and micro) scales, paved the way to the investigation of physical systems composed by a small number of elementary constituents [58]. This "middle world" includes several interesting topics, such as macromolecules (DNA, proteins and molecular motors) [59], colloidal suspensions [60], granular media [61] and active matter [62], just to name a few. Several results obtained in the last decades proved that the tools and the concepts introduced in statistical mechanics can predict with success the behavior of small systems.

This new range of applicability exceeds the original intent of statistical physics, i.e. the justification of thermodynamics from the microscopic level, and introduces new perspectives. However, extending statistical mechanics to small systems is a very delicate issue, that can generate misleading conclusions, when treated without the required care. From a theoretical perspective, a central issue is the possibility to use the ergodic hypothesis for these systems. Here, we identify three classes of small systems for which a statistical approach seems to be still meaningful. In the following, we restrict our attention, for the sake of consistency and simplicity, to classical systems: in fact, the description of quantum small systems, even with some similarities, must be developed independently, since it presents a very different phenomenology and a huge number of technical and conceptual subtleties [63].

Single (or very few) particle systems. A Hamiltonian system composed of a single particle in one dimension that moves in an external potential is trivially ergodic. In fact, in the phase space of such a system (which is two-dimensional) the "constant energy surface", where the system evolves, coincides with the trajectory of the system. This is not necessarily true when we increase the number of particles, since it is possible to exhibit systems composed of two constituents which are no longer ergodic (e.g. two coupled harmonic oscillators). Nevertheless there are many examples of few-dimensional ergodic systems and several authors claim that a notion of thermodynamics is possible also for this class of systems [18,64]. It is very interesting to note that one of the first historical efforts to derive thermodynamics from mechanics focused on isolated single particle systems, for which Helmholtz [65] derived a theorem (on the monocycle) later used by Boltzmann to introduce the ergodic hypothesis: in Section 2.4 this topic has been discussed in detail.

Small systems with stochastic dynamics. This class includes systems with a non-deterministic dynamics, such as Markov chains or systems ruled by stochastic differential equations, like the following Langevin equation

$$\ddot{x} = -\frac{dV(x)}{dx} - \gamma\dot{x} + \sqrt{2D}\eta, \tag{68}$$

where η represents white noise, $\langle\eta(t)\eta(t')\rangle = \delta(t-t')$, $V(x)$ is an external potential and γ and D are constants. The proof of the validity of ergodicity for Markov stochastic systems is far more accessible than its counterpart for deterministic systems: in particular it can be proven that every irreducible and non-periodic Markov process is ergodic [66,67] and that, in addition, it also satisfies the so-called *mixing* condition, i.e. the fact that any (non-pathological) initial probability distribution $\rho_0(\mathbf{X})$ of the system converges toward an asymptotic stationary state:

$$\rho(\mathbf{X}, t) \overset{t\to\infty}{\longrightarrow} \rho(\mathbf{X}). \tag{69}$$

Moreover, for these systems, the typical relaxation times are usually small, and analytical approaches are possible. These are some of the reasons why single particle stochastic systems have been extensively used in the most recent developments on stochastic thermodynamics [68].

Another conceptual advantage of small stochastic systems over deterministic ones is the fact that the aleatory dynamics can be interpreted as the effect of the interaction of the system of interest with a large environment. Consider a subsystem of a larger isolated system, its state is a many-to-one function: $(\mathbf{X}, \mathbf{Y}) \in \mathbb{R}^{2d(N_1+N_2)} \to \mathbf{Y} \in \mathbb{R}^{2dN_1}$, with $N_1 \ll N_2$, where $\mathbf{Y}$ is the variable representing the system of interest, N_1 and N_2 are, respectively, the number of particles of the system and of the environment, and d is the spatial dimension. This means that many different configurations of the environment correspond to the same $\mathbf{Y}$, allowing, at least heuristically, to interpret the state of the small subsystem as a "thermodynamical observable". Of course, in order to obtain a stochastic description for the subsystem, one has to assume that fluctuations induced by the environment are not too large: this condition can be realized, for instance, when the mass of the system particles is larger than that of the particles of the environment.

Many-Particle Small Systems (MPSS). By this term we mean systems composed of $\mathcal{O}(10-10^2)$ particles, where the interesting collective typical behaviors of large systems can be observed and that, at the same time, are far enough from the infinite-N limit, to exhibit several features of small systems (large fluctuations, non-standard equilibrium states, etc…). The question regarding the ergodicity of these systems may appear more difficult to answer with respect to single-particle or stochastic systems. However, from a physical and practical point of view, it is important to stress that the Khinchin argument for the validity of the ergodicity in systems with $N \gg 1$ for a class of collective observables applies to MPSS. In fact, even if N is not infinite, many large-N approximations (e.g. Laplace approximation for the computation of integrals) can be carried on safely, and discrepancies with the asymptotic behavior are small, and do not affect the overall phenomenology [69]. Regardless, since N is finite, the fluctuations are visible and non-negligible, and indeed their study is the main focus of stochastic thermodynamics.

Let us note that MPSS includes the class of systems usually studied in numerical simulations: in fact, typical computer simulations involve systems with a number of particles spanning from the few hundreds up to some tens of thousands. These numbers are clearly much smaller than the typical size of macroscopic systems $\mathcal{O}(10^{20})$, nevertheless they are commonly considered large enough for the study of the properties of macroscopic real systems.

3.2.1. Stochastic thermodynamics

As already stressed, the distinguishing feature of small systems is the relevance of fluctuations, which are negligible only when the number of constituents is very large, as for macroscopic bodies. The study of fluctuations of thermodynamics functions, such as energy or entropy, goes back to Einstein, Onsager and Kubo, but it has recently raised a renewed interest with the establishing of important results in response theory [14] and in the so-called stochastic thermodynamics [68,70–75]. The main aim of this theory concerns the statistical properties of fluctuations in systems which are *far* from thermodynamic equilibrium. Here we briefly give some definitions and describe the principal conceptual aspects, referring the interested reader to the review [68] and references therein, for an exhaustive presentation of the subject.

The first issue consists in the proper microscopic definition of work and heat for small systems. In particular, as we will show in the rest of this Section, the naive definition of infinitesimal work as $dW = pdV$ (being p the pressure and V the volume), is not appropriate in a large variety of situations, e.g. when the external varied parameter is not the volume. In fact this definition comes from a basic application of the classical definition of work ($dW = \boldsymbol{F} \cdot \boldsymbol{dx}$) and pressure ($\mathbf{F} \cdot \hat{\mathbf{n}} = pS$, where S is the surface): in systems beyond the usual applications of thermodynamics the definition must be reconsidered. We will first discuss the definition in the context of Hamiltonian systems.

Consider a time-dependent Hamiltonian $\mathcal{H}(\mathbf{X}, t)$ and let $\{\widetilde{\mathbf{X}}(t)\}_{t=0}^{\mathcal{T}}$ be a solution of Hamilton equations of motion; then, the time derivative of a generic function $A(t) = A(\widetilde{\mathbf{X}}(t), t)$ reads

$$\frac{dA(t)}{dt} = \frac{\partial A(\mathbf{X}, t)}{\partial \mathbf{X}}\dot{\mathbf{X}} + \frac{\partial A(\mathbf{X}, t)}{\partial t} = \{A, \mathcal{H}\} + \frac{\partial A}{\partial t}. \tag{70}$$

It is natural to identify the internal energy of the system with the value of the Hamiltonian $E(t) = \mathcal{H}(\widetilde{\mathbf{X}}(t), t)$ and compute its time derivative via Eq. (70)

$$\frac{dE(t)}{dt} = \{\mathcal{H}, \mathcal{H}\} + \frac{\partial \mathcal{H}}{\partial t} = \left.\frac{\partial \mathcal{H}}{\partial t}\right|_{\widetilde{\mathbf{X}}(t)}. \tag{71}$$

Therefore, if the Hamiltonian depends on an external varying parameter, the total energy of the system changes and it is not difficult to see that, from a thermodynamic point of view, this change corresponds to the time derivative of the work $\dot{W}(t)$, leading to

$$\dot{W} = \frac{\partial \mathcal{H}}{\partial t}. \tag{72}$$

It is important to remark that this convention implies that, whenever the energy of the system increases, the work is positive, whereas, in the opposite case, the work is negative: this is in contrast with the usual thermodynamic convention, but has a far more transparent energetic interpretation.

Suppose now that the explicit time dependence of the Hamiltonian is given by an additional term, namely $\mathcal{H} = \mathcal{H}_0 + h(t)$, with $h(t) = \lambda(t)X_i$, X_i being one of the component of the phase space variable $\mathbf{X}$ and $\lambda(t)$ a time-dependent parameter; in this case one has

$$\dot{W}(t) = \widetilde{X}_i(t)\dot{\lambda}(t), \tag{73}$$

which is equivalent to $dW = Vdp$, but differs from the standard definition $dW = -pdV$. The explanation of this result was reported in Ref. [76]: assume that, generalizing the above situation, the Hamiltonian depends upon a certain number of external parameters $\lambda_k(t)$, with $k = 1, \dots, M$:

$$\mathcal{H} = \mathcal{H}_0(\mathbf{X}) + \sum_k \lambda_k(t) g_k(\mathbf{X}), \tag{74}$$

where $g_k(\mathbf{X})$ are functions of $\mathbf{X}$, which define the macroscopic states. In this case one can apply an alternative definition of internal energy, $E(t) = \mathcal{H}_0(t)$, whose time derivative reads

$$\frac{d\mathcal{H}_0}{dt} = \{\mathcal{H}_0, \mathcal{H}\} = -\sum_k \lambda_k(t)\{g_k, \mathcal{H}\} = -\sum_k \lambda_k(t)\dot{g}_k(\mathbf{X}(t)). \tag{75}$$

Therefore, using this definition where all the time-dependent terms are considered *external*, the work takes the form

$$\dot{W} = -\sum_k \lambda_k(t)\dot{g}_k(\mathbf{X}(t)). \tag{76}$$

In particular, when $k = 1$ and $g(\mathbf{X}) = X_i$, we recover the usual thermodynamic definition of work

$$\dot{W}(t) = -\lambda(t)\dot{X}_i, \tag{77}$$

that is equivalent to $dW = -pdV$. It is important to remark that this definition gives a nonzero work also when the external parameters are fixed, $\dot{\lambda} = 0$. This occurs because some energy may be exchanged between the internal energy $\mathcal{H}_0$ and the external terms appearing in the Hamiltonian, despite the fact that the value of the Hamiltonian $\mathcal{H}(\mathbf{X}(t))$ does not change over time. In the rest of this section we will use the first definition of work, Eq. (72).

It is not possible to define the heat exchange in the context of purely Hamiltonian systems, since these systems do not transfer energy with the external environment. Moreover, in general, there are several different ways to define the interaction of a system with an external thermostat at temperature T (stochastic, deterministic, etc…). For this reason, to keep the discussion on general terms, it is important to give a definition of heat that does not rely on the specific model. In the following we will discuss this topic in the context of coarse-grained stochastic differential equations.

When a time-dependent Hamiltonian system is coupled to an external thermostat, the variation of the total energy $E(t) = \mathcal{H}(\mathbf{X}(t), t)$ is due to different causes: indeed, a part of energy is funneled through the external parameter that varies in time, whereas another part is exchanged with the thermostat to which the system is attached. It is customary to denote by the term heat all the energy that is not exchanged in "Hamiltonian manner", i.e.

$$\dot{Q}(t) = \dot{E}(t) - \dot{W}(t), \tag{78}$$

where $\dot{W}(t)$ is the quantity defined in Eq. (72). This last equation is the microscopic equivalent of the first principle of thermodynamics, when the appropriate sign convention is chosen. From a practical point of view, there may be some ambiguity in the definition of $\dot{Q}$ in the context of stochastic differential equations: in particular, as we will see later, it is very important to specify whether the derivative is taken according to the Itô or the Stratonovich convention. To avoid such ambiguities it can be useful to report the integrated version of Eq. (78):

$$Q(\mathcal{T}) = \Delta E - \int_0^{\mathcal{T}} \frac{\partial \mathcal{H}(t)}{\partial t} dt, \tag{79}$$

where $\mathcal{T}$ is the total time of the measurement, and $\Delta E = E(\mathcal{T}) - E(0)$ is the total energy variation in such an interval. This last equation does not present any ambiguity, since the integration variable of the integral appearing on the r.h.s. is the time t (and not the phase space position $\mathbf{X}$), and therefore $E(t)$ is a well-defined function of time.

Analogous definitions of heat and work can be given in the framework of stochastic differential equations. In particular, following Ref. [74], we will examine the simple case of a unidimensional Brownian particle, with mass m, position x and velocity v, in contact with a thermal bath at temperature T, and moving in an external time-dependent potential $V(x, t)$. The stochastic differential equation describing this system in the underdamped regime reads

$$\begin{aligned} \dot{x} &= v \\ \dot{v} &= -\gamma v - \frac{\partial_x V(x,t)}{m} + \sqrt{\frac{2k_B T \gamma}{m}}\eta, \end{aligned} \tag{80}$$

where η is white noise with $\langle \eta(t)\eta(t')\rangle = \delta(t-t')$ and γ a constant parameter.

From the natural choice for the energy of the particle $E(t)$

$$E(t) = \frac{1}{2} m v(t)^2 + V(x(t), t), \tag{81}$$

there follows that the work performed on the system is

$$\dot{W}(t) = \left.\frac{\partial V(x,t)}{\partial t}\right|_{x=x(t)}. \tag{82}$$

Those definitions, despite their apparent coherence, conceal some inconsistencies due to the fact that Eq. (80) is a coarse grained equation. It is very easy to show that, in the simple case $\partial_t V = 0$, the (equilibrium) invariant distribution of the stochastic system is

$$\rho(x, v) \propto \exp\left\{-\beta\left(\frac{m}{2}v^2 + V(x)\right)\right\}. \tag{83}$$

On the other hand, when considering x as a single component of a much larger Hamiltonian system $\mathbf{X} = (x, v, x_1, v_1, x_2, v_2 \dots, x_N, v_N)$ with Hamiltonian $\mathcal{H}(\mathbf{X})$, we have, at equilibrium,

$$\rho^{eq}(x, v) = \int \frac{dx_1 dv_1 \dots dx_N dv_N}{Z} \; e^{-\beta \mathcal{H}(\mathbf{X})}, \tag{84}$$

where Z is the partition function. Whenever the Hamiltonian can be split into the sum of a kinetic term of the particle and another part involving all the remaining degrees of freedom of the system,

$$\mathcal{H}(\mathbf{X}) = \frac{mv^2}{2} + \mathcal{H}_{int}(x, x_1, v_1, \dots, x_N, v_N), \tag{85}$$

it is possible to recast Eq. (84) in the following form

$$\rho^{eq}(x, v) = \frac{Z(x)}{Z_0} e^{-\beta m \frac{v^2}{2}}, \tag{86}$$

where $Z(x) = \int \exp\{-\beta\mathcal{H}_{int}\}dx_1dv_1\dots dx_Ndv_N$, and Z_0 is the normalizing constant. Therefore, by comparing the last expression with Eq. (83), it is easy to see that

$$V(x) = -\frac{1}{\beta}\ln Z(x), \tag{87}$$

which is interpreted by many authors (see [74]) as a conditional free energy function, rather than a proper potential energy. The simplest case is when $\mathcal{H}_{int}(x, x_1, v_1, \dots, x_N, v_N)$ can be split in an external potential $V(x)$ depending only on x, and another contribution with all the remaining variables.

The above considerations show that the microscopic definition, Eq. (72), and the coarse-grained one Eq. (82), are, in general, not equivalent. Therefore one should take some care in doing energetic considerations when starting from a Langevin equation, without having an underlying microscopic description of the system [77].

When Eq. (82) is adopted, the heat Q is the difference between energy and work (first principle of thermodynamics). An explicit formula for heat can be readily obtained:

$$\begin{aligned}\dot{Q} &= \frac{dE}{dt} - \dot{W} = (\partial_v E)\dot{v} + (\partial_x E)\dot{x}\\ &= mv\left(-\gamma v - \frac{\partial_x V}{m} + \sqrt{\frac{2\gamma k_B T}{m}}\eta\right) + v\partial_x V\\ &= m\left(-\gamma v + \sqrt{\frac{2\gamma k_B T}{m}}\eta\right)v,\end{aligned} \tag{88}$$

where, since we applied the usual calculus rules, the differential equation must be interpreted with the Stratonovich convention [78,66]. Nevertheless, in order to compute $\langle\dot{Q}\rangle$, it is useful to derive the equivalent result with the Itô convention:

$$\dot{Q} = m\left(-\gamma v + \sqrt{\frac{2\gamma k_B T}{m}}\eta\right)v + \gamma k_B T. \tag{89}$$

Of course, the average of Eqs. (89) and (88) must give the same result, the Itô expression being more explicit:

$$\langle\dot{Q}\rangle = -\gamma m\langle v^2\rangle + k_B T\gamma = -2\gamma\left(\frac{m\langle v^2\rangle}{2} - \frac{k_B T}{2}\right). \tag{90}$$

It is clear that the quantities $\dot{Q}$ and $\dot{W}$, and thus the integrated heat and work, are fluctuating quantities because they depend upon the single trajectories $\{x(t), v(t)\}_{t=0}^{\mathcal{T}}$.

The stochastic equation (80) gives a description of the system at the level of single trajectories: naturally, an equivalent description can be given in terms of the probability distribution function $\rho(x, v, t)$, i.e. the probability density of finding the particle at time t with position x and velocity v. The time evolution of this quantity is given by a partial differential equation, the Fokker–Planck equation [66]:

$$\partial_t\rho(x, v, t) = -\boldsymbol{\nabla}\cdot\mathbf{J}(x, v, t), \tag{91}$$

where the two components of the current $\mathbf{J} = (J_x, J_v)$ are

$$J_x = v\rho(x, v, t), \tag{92}$$

$$J_v = -\gamma v\rho(x, v, t) - \frac{\partial_x V}{m}\rho(x, v, t) - \frac{k_B T\gamma}{m}\partial_v\rho(x, v, t). \tag{93}$$

The average values of the thermodynamic quantities introduced above can be obtained by taking the time derivative of the average energy of the system, i.e.

$$\langle E(t)\rangle = \int dxdv\left(\frac{1}{2}mv^2 + V(x, t)\right)\rho(x, v, t), \tag{94}$$

that yields

$$\begin{aligned}\langle\dot{E}\rangle &= \int dxdv\,\partial_t V\rho(x, v, t) + \int dxdv\,E(x, v, t)\partial_t\rho(x, v, t)\\ &= \langle\dot{W}\rangle + \langle\dot{Q}\rangle.\end{aligned} \tag{95}$$

The identification of the first term of the r.h.s. in the first line with the average mechanical power is immediate, since this quantity trivially coincides with Eq. (82). The other term of the sum is associated with the average heat rate, because, in agreement with the first principle of thermodynamics, the sum of the two terms must represent the total (internal) energy variation of the system. In order to show that this second definition, i.e.

$$\langle\dot{Q}\rangle = \int dxdvE(x, v, t)\partial_t\rho(x, v, t), \tag{96}$$

is consistent with Eq. (90), it is necessary to perform some algebra:

$$\begin{aligned}\langle\dot{Q}\rangle &= -\int dxdv\, E(x,v,t)\nabla\cdot\mathbf{J}(x,v,t) = \int dxdv\,\mathbf{J}(x,v,t)\cdot\nabla E(x,v,t)\\ &= \int dxdv\,(-\gamma v)\,(mv + k_BT\partial_v\ln\rho)\,\rho(x,v,t).\end{aligned}\tag{97}$$

By performing one last integration by parts, one gets Eq. (90) from the above expression. It is important to remark that it is very useful to have two different formalisms describing the stochastic thermodynamics of one-particle systems: in fact, on the one hand, Eqs. (82) and (89) give a recipe on how to measure the work and heat exchanged on a single trajectory. Therefore, e.g. in numerical simulations where the state of the system is accessible at every time t, one can integrate the two expressions and obtain the (fluctuating) heat and work exchanged in a single realization of the experiment. On the other hand, the expressions involving the distribution $\rho(x,v,t)$ and its derivatives are more useful in an analytic context, and, as we will show in the following subsection, are necessary to obtain a connection between these quantities and the entropy production.

3.2.2. Connection with standard thermodynamics and entropy production

Let us briefly recall that in thermodynamics the entropy $S(A)$ of a state A is well defined only if A represents a set of thermodynamic variables identifying an equilibrium state. In particular, the entropy is a state function obtained through the formula

$$\Delta S = S(B) - S(A) = \int_A^B \frac{dQ}{T},\tag{98}$$

where dQ is the heat exchanged with the exterior, and T the temperature of the system on any quasi-static transformation, i.e. a generic path consisting in a succession of equilibrium states that connects A to B. The second principle of thermodynamics, in the form of Clausius inequality, reads

$$\oint \frac{dQ}{T} \leq 0,\tag{99}$$

i.e. $\Delta S \geq \int_B^A \frac{dQ}{T}$, and the equality only holds in the case of quasi-static transformations. Assuming that the system interacts with a thermostat at constant temperature T, when considering the system of interest and the thermostat attached to it, one simply gets

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{therm} \geq 0\tag{100}$$

or, equivalently,

$$\Delta S_{sys} = -\Delta S_{therm} + \Sigma.\tag{101}$$

Here Σ is a positive quantity which, with an evident meaning, is called total entropy production (it is the increase of entropy in an isolated system due only to the irreversibility of the dynamics), and the other term of the sum is

$$\Delta S_{therm} = -\frac{Q}{T},\tag{102}$$

where Q is the heat *absorbed* by the system, i.e. $Q = \int_A^B dQ$. This last quantity has been called in recent years *entropy production of the medium* [79], since it is the variation of the entropy of the thermostat, as explained below.

These quantities can be reinterpreted in the framework of stochastic thermodynamics as follows. The entropy function in this the context is provided by the Gibbs entropy, previously defined in Eq. (26),

$$S_\Gamma(t) = -k_B\int dxdv\;\rho(x,v,t)\ln\rho(x,v,t).\tag{103}$$

It is possible to compute the derivative of the Gibbs entropy and express it as a sum of different terms:

$$\begin{aligned}\frac{dS_\Gamma(t)}{dt} &= -k_B\int dxdv\;[\partial_t\rho(x,v,t)\ln\rho(x,v,t) + \partial_t\rho] = -k_B\int dxdv\,\frac{\mathbf{J}\cdot\nabla\rho}{\rho}\\ &= -k_B\int dxdv\left[v\partial_x\rho - \gamma v\partial_v\rho - \frac{\partial_x V}{m}\partial_v\rho - \frac{k_BT\gamma}{m}\frac{(\partial_v\rho)^2}{m}\right]\\ &= k_B\int dxdv\left[\gamma v\partial_v\rho + \frac{k_BT\gamma}{m}\frac{(\partial_v\rho)^2}{\rho}\right],\end{aligned}\tag{104}$$

where, in the last line, we used an integration by parts. Carrying on the calculations further, one can identify two contributions in the entropy variation

$$\begin{aligned}\frac{dS_\Gamma(t)}{dt} &= k_B \int dxdv\, \left(2\gamma v \partial_v \rho + \frac{k_B T \gamma}{m} \frac{(\partial_v \rho)^2}{\rho}\right) - k_B \int dxdv\, \gamma v \partial_v \rho \\ &= k_B \int dxdv\, \frac{1}{\rho}\left(\sqrt{\frac{k_B T\gamma}{m}}\partial_v \rho + \sqrt{\frac{\gamma m}{k_B T}} v\rho\right)^2 \\ &\quad - \frac{1}{T}\int dxdv\, \left(\gamma m v^2 \rho + \gamma v k_B T \partial_v \rho\right) \equiv \dot{A}(t) + \frac{\langle \dot{Q}\rangle}{T},\end{aligned} \tag{105}$$

where $\dot{A}(t)$ is a positive quantity. The identification of the two contributions with their thermodynamic counterparts is immediate: $\dot{S}_\Gamma(t)$ is the entropy production of the system, $\dot{A}(t) = \dot{\Sigma}$ is the total entropy production (i.e. of the system and the thermostat), and the last term is the entropy production of the medium $\dot{S}_{therm}$.

This calculation also allows us to obtain a single-trajectory, fluctuating entropy variation of the system. The state-dependent entropy of the system is defined as

$$s(x, v, t) = -k_B \ln \rho(x, v, t), \tag{106}$$

so that its average gives the Gibbs entropy in Eq. (103). This quantity can be measured once the state of the system x and the probability distribution function $\rho(x, v, t)$, i.e. the solution of the Fokker–Planck equation, are known. For instance, in every trajectory that originates at time t_0 in (x_0, v_0) and finishes at time t_f in (x_f, v_f) one can measure the entropy difference:

$$\Delta s = -k_B \ln \frac{\rho(x_f, v_f, t_f)}{\rho(x_0, v_0, t_0)}. \tag{107}$$

Averaging on all the possible trajectories one gets $\langle \Delta s\rangle = \Delta S_\Gamma$. Moreover, the single-trajectory equivalent of the total entropy production $\dot{\Sigma}$ can be obtained as the sum of the two terms

$$\dot{\Sigma}(x, v, t) = \dot{s}(x, v, t) - \frac{\dot{Q}}{T}(x, v, t). \tag{108}$$

The value of this observable depends on the single realization of the process, while $\langle \dot{\Sigma}\rangle$ is positive on average. This observation constitutes a probabilistic interpretation of the second principle of the thermodynamics: from the point of view of the single realization, there may happen "violations" of the second principle, i.e. trajectories on which the entropy production is negative, but on average this occurrences must been compensated in order to give a positive average. Fluctuation Relations are obeyed by the above quantities, as discussed below in Section 4.

Let us recall that, whenever the dynamics is conservative, i.e. a Liouville theorem holds, the value of the Gibbs entropy is always constant, for every initial distribution $\rho(x, v, 0)$, as already discussed: for this reason this entropy is not appropriate to describe some irreversible processes like the free expansion of a gas in a container, as discussed in detail in [26]. In the present context, on the other side, the system has a stochastic dynamics and – in addition – because of the very few degrees of freedom, the criticisms to the use of S_Γ, discussed in Section 2.3, are not relevant.

3.3. *Negative temperature*

In Section 2 we already mentioned that in equilibrium statistical mechanics one can introduce two different definitions of temperature. Such a topic has been recently the subject of an intense debate [18,64,80–86]. This new interest is due to the publication of experimental measurements of a negative absolute temperature [17,87]: it was demonstrated the possibility to prepare a state where the observed distribution of the modified kinetic energy *per atom* appeared to be inverted, i.e. with the largest population in the high energy states, yielding a *de facto* negative absolute temperature.

The possibility of a negative absolute temperature is well known since the work by Onsager on the statistical hydrodynamics of point vortices [88] and the results on nuclear spin systems by Pound, Ramsey and Purcell (see [89–91] for a review and discussion). In those investigations, it was clear that an inverse temperature parameter β_B ranging in the full infinite real line $(-\infty, \infty)$ did not lead to any inconsistency or paradox.

It is interesting that T_G appears in the theory of Helmholtz monocycles, which had an important role in the development of Boltzmann's ideas for the ergodic theory, for one-dimensional systems [34,65], see Section 2.4. Therefore one could conclude that the "correct" temperature is T_G. However the approach based on the Helmholtz monocycle can be used only in systems whose Hamiltonian contains a quadratic kinetic term and a potential part. For such systems in the limit $N \gg 1$ one has $T_G = T_B + O(1/N)$. Since in the reasoning in terms of monocycles the temperature is defined via the average of the kinetic energy, in a generic system it is not possible to follow the argument discussed in Section 2.4.

In the following we present a line of reasoning where Boltzmann temperature T_B (positive or negative), in systems with many degrees of freedom and short range interaction, is the (unique) proper parameter which is relevant for the statistical properties of the energy fluctuations, as well as in determining the flux of energy between two systems at different temperatures, in addition it is measurable, without the appearance of any evident inconsistency. Let us remark that the systems discussed in [64], from which the authors try to show that only T_G is the "correct" temperature, are small ($N = \mathcal{O}(1)$) and/or with long-range interactions.

In our discussion, we assume that $S_B(E, N)$ is always convex, i.e. $d^2S_B(E, N)/dE^2 \leq 0$. This is certainly true in the limit of vanishing interaction and in short-range-interacting systems for large N, since S_B is strictly related to the large deviation function associated with the density of states, see Section 2.2.2.

3.3.1. *Point-vortex systems*

One of the first, and very important, systems showing negative temperature has been studied by Onsager in a seminal paper at the origin of the modern statistical hydrodynamics [92]. Because of its historical and technical relevance we briefly summarize the main results.

Consider a two-dimensional incompressible ideal flow ruled by Euler equation

$$\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\frac{\nabla p}{\rho_0}, \;\; \nabla \cdot \mathbf{u} = 0, \tag{109}$$

where ρ_0 is the constant density and p the pressure. The vorticity can be written as $\nabla \times \mathbf{u} = \omega\hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is the unitary vector perpendicular to the plane of the flow, and ω evolves according to

$$\partial_t\omega + (\mathbf{u} \cdot \nabla)\omega = 0. \tag{110}$$

The previous equation expresses the conservation of vorticity along fluid-element paths [93]. From the incompressibility we can write the velocity in terms of the stream function, $\mathbf{u} = \nabla^{\perp}\psi = (\partial_y, -\partial_x)\psi$, while the vorticity is given by $\omega = -\Delta\psi$. Therefore, the velocity can be expressed in terms of ω

$$\mathbf{u}(\mathbf{x}, t) = -\nabla^{\perp} \int d\mathbf{x}' \mathcal{G}(\mathbf{x}, \mathbf{x}')\omega(\mathbf{x}', t),$$

where $\mathcal{G}(\mathbf{r}, \mathbf{r}')$ is the Green function of the Laplacian operator Δ, e.g. in the infinite plane $\mathcal{G}(\mathbf{r}, \mathbf{r}') = -1/(2\pi) \ln|\mathbf{r} - \mathbf{r}'|$. Consider now an initial condition at $t = 0$ such that the vorticity is localized on N point-vortices

$$\omega(\mathbf{r}, 0) = \sum_{i=1}^{N} \Gamma_i \delta(\mathbf{r} - \mathbf{r}_i(0)),$$

where Γ_i is the circulation of the ith vortex. The Kelvin theorem ensures that the vorticity remains localized at any time, and therefore

$$\omega(\mathbf{r}, t) = \sum_{i=1}^{N} \Gamma_i \delta(\mathbf{r} - \mathbf{r}_i(t)),$$

which, plugged in Eq. (110), implies that the vortex positions $\mathbf{r}_i = (x_i, y_i)$ evolve according to

$$\frac{dx_i}{dt} = \frac{1}{\Gamma_i}\frac{\partial H}{\partial y_i}, \quad \frac{dy_i}{dt} = -\frac{1}{\Gamma_i}\frac{\partial H}{\partial x_i},$$

with

$$H = \sum_{i \neq j} \Gamma_i \Gamma_j \mathcal{G}(\mathbf{r_i}, \mathbf{r}_j).$$

So the N point-vortices constitute a N degrees of freedom Hamiltonian system [94] with canonical coordinates

$$q_i = \sqrt{|\Gamma_i|}x_i, \quad p_i = \sqrt{|\Gamma_i|}sign(\Gamma_i)y_i.$$

Consider now N point-vortices confined in a bounded domain Ω of area A. Since for each point-vortex $\mathbf{r}_i \in \Omega$ one has

$$\Sigma(E) = \int_{H<E} dq_1 \cdots dq_N dp_1 \cdots dp_N \leq C_N A^N, \quad C_N = \prod_{i=1}^{N} |\Gamma_i|.$$

Therefore $\omega(E) = d\Sigma(E)/dE$ must approach to zero for $E \to \pm\infty$, and must attain its maximum at a certain value E_M, so that for $E > E_M$ the entropy $S_B(E) = k_B \ln \omega(E)$ is a decreasing function and hence $T_B(E)$ is negative.

The states at large energy, $E \gg E_M$, are those in which the vortices are crowded in special way. Since in any domain Ω for $\mathbf{r} \sim \mathbf{r}'$ we have $\mathcal{G}(\mathbf{r}, \mathbf{r}') \simeq -1/(2\pi) \ln|\mathbf{r} - \mathbf{r}'|$, the configurations with very large energy are those where point vortices, whose Γ_i have the same sign, are close. Therefore in a system with positive and negative Γ_i, negative temperature states correspond to the presence of well separated clusters of vortices with the same vorticity sign. On the contrary for $E < E_M$ (positive temperature) the vortices of opposite Γ_i tend to remain close [92–94]. Such a clustering phenomenon has been observed also in simulations of quasi-2d superfluid Bose–Einstein condensates [95], see Fig. 6.

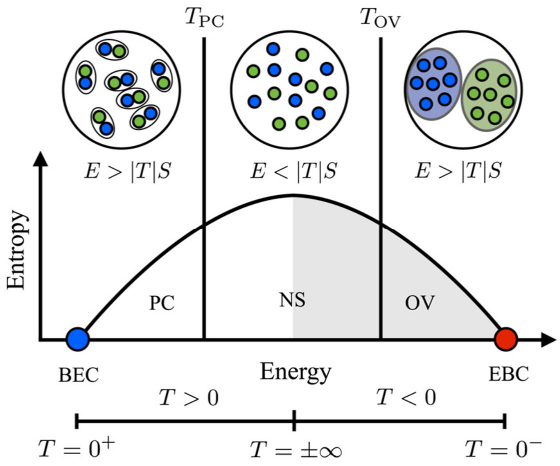

Fig. 6. A schematic plot of entropy versus energy for the point-vortex model of [95]. Blue and green colors correspond to vortices and anti-vortices respectively. The vortex binding–unbinding phase transition separates the normal state (NS) from the pair-collapse (PC) state at positive temperature, whereas there is a transition to the coherent Onsager vortex (OV) state at a vortex-number-dependent negative temperature.
Source: Reprinted Fig. 2 with permission from [T. Simula, M.J. Davis and K. Helmerson, Phys. Rev. Lett., 113, 165302 (2014)].

3.3.2. *Systems with negative temperature are not pathologic*

The Hamiltonian of the point-vortex system contains a long range interaction, however the presence of negative T_B does not depend on such a peculiarity. Replacing $\mathcal{G}(\mathbf{r}_i, \mathbf{r}_j)$ with a bounded function with a maximum for $\mathbf{r}_i = \mathbf{r}_j$ and fastly decreasing to zero for large values of $|\mathbf{r}_i - \mathbf{r}_j|$, we have a short range system and it is straightforward to show the presence of negative temperature.

In Section 2 we already discussed the second law and energy flux between two systems in contact. The energy flux obviously goes from smaller β_B (hotter) to larger β_B (colder), and a negative T_B does not lead to any ambiguity. Confusion may arise from the fact that $T_B < 0$ is, for the purpose of establishing the energy flux, hotter than $T_B > 0$. However using the variable β_B, the confusion is totally removed [89]. Let us now briefly discuss a particularly interesting case of two systems with different Hamiltonians. Suppose that for the system $\mathcal{A}$ negative temperatures can be present, whereas system $\mathcal{B}$ has only positive temperatures; it is quite easy to see that the coupling of the system $\mathcal{A}$ at negative temperature with the system $\mathcal{B}$ at positive temperature always produces a system with final positive temperature. Indeed, at the initial time the total entropy is

$$S_I = S^{\mathcal{A}}(E_{\mathcal{A}}) + S^{\mathcal{B}}(E_{\mathcal{B}}), \tag{111}$$

while, after the coupling, it will be

$$S_F = S^{\mathcal{A}}(E'_{\mathcal{A}}) + S^{\mathcal{B}}(E'_{\mathcal{B}}), \tag{112}$$

where $E'_{\mathcal{A}} + E'_{\mathcal{B}} = E_{\mathcal{A}} + E_{\mathcal{B}}$ and, within our assumptions, $E'_{\mathcal{A}}$ is determined by the equilibrium condition [96] that S_F takes the maximum possible value, i.e.

$$\beta_{\mathcal{A}} = \frac{\partial S^{\mathcal{A}}(E'_{\mathcal{A}})}{\partial E'_{\mathcal{A}}} = \beta_{\mathcal{B}} = \frac{\partial S^{\mathcal{B}}(E'_{\mathcal{B}})}{\partial E'_{\mathcal{B}}}. \tag{113}$$

Since $\beta_{\mathcal{B}}$ is positive for every value of $E'_{\mathcal{B}}$, the final common temperature must also be positive. The above result, which can also be found, without a detailed reasoning, in some textbooks [97,98], helps to understand why it is not easy to observe negative temperature for a long time. Experiments showing negative temperatures have been recently realized, by means of an efficient isolation of the system of interest [17].

3.3.3. *The generalized Maxwell–Boltzmann distribution*

In systems whose Hamiltonian contains the kinetic term $\sum_n p_n^2/(2m)$, we know the probability distribution density for the momentum of a single particle:

$$P(p) \propto e^{-\beta \frac{p^2}{2m}}, \tag{114}$$

in such a case, for $N \gg 1$, $\beta = \beta_B = \beta_G$. Let us wonder about the same problem in the case with

$$H = \sum_{n=1}^{N} g(p_n) + \sum_{n,k}^{N} V(q_n, q_k), \tag{115}$$

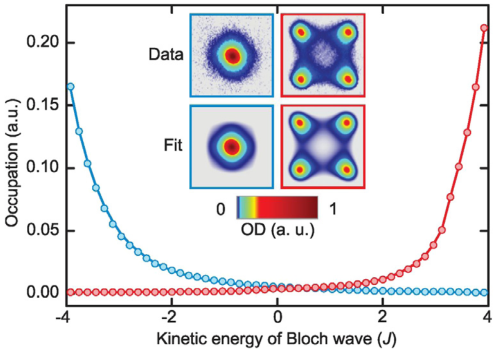

Fig. 7. Probability distribution of the "kinetic energies" in the cold atoms experiment of [17]. The blue and red circles are data at two different energies (red is with higher energy). The blue line is a fit through a Bose–Einstein distribution with positive temperature, while the red one is with a negative temperature. The inset shows the distributions of (p_x, p_y) in the two situations (left for the low energy, or positive temperature).
Source: From S. Braun et al., Science 339, 52 (2013) [17]. Reprinted with permission from AAAS.

where the variables $\{p_n\}$, as well as the function $g(p)$, are limited. With standard arguments one may compute the probability density for the distribution of a single momentum p, obtaining the generalized Maxwell–Boltzmann distribution:

$$P(p) \propto e^{-\beta_B g(p)}, \tag{116}$$

which is valid for both positive and negative β_B. We mention that in the experiment in [17], the above recipe has been applied to measure both positive and negative system's temperatures.

From (116) and the PdF of the energy in the canonical ensemble, the deep meaning of the (Boltzmann) temperature is quite transparent: it is a quantity which rules the statistical features of energy of a subsystem (as well as the "momentum" of a single particle). Let us stress again that since T_B is associated with the large microcanonical system (in physical terms, the reservoir) it is a non-fluctuating quantity [50] also for each sub-system and, in general, for non-isolated systems, see Section 3.1.

It is remarkable that (a quantum version of) Eq. (116) has been observed in [17] in an experiment with a bosonic system of cold atoms in 2d. The generalized kinetic energy as a function of quasi-momenta (p_x, p_y) – in the first Brillouin zone – is $g(p_x, p_y) = -2J[\cos(p_x\lambda) + \cos(p_y\lambda)]$ where λ is the lattice constant and J a coupling strength. The experimental result is shown in Fig. 7.

3.3.4. About the measurement of T_B and T_G

The definitions of β_B and β_G discussed in Section 2 are based on the functional dependence of $\omega(E)$ and $\Sigma(E)$ upon the energy. In a real or numerical experiment it is pretty impossible to make use of such an approach. On the other hand, after the work of Rugh [35], we know that, assuming the ergodicity, β_B can be computed with a molecular dynamics simulation, and, at least in principle, by a long-time series from an experiment.

Coming to β_G, a way, even discussed in textbooks and considered sometimes rather important [64], to determine its measurement is via the equipartition theorem, which states

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} T_G. \tag{117}$$

However the usual derivation of Eq. (117) implies the possibility to neglect boundary terms in an integration by parts. Such a possibility is challenged in the class of systems with bounded energy and phase space that we are considering. In particular it is easy to show that (117) does not hold under the simultaneous realization of the following conditions:

- bounded space of the canonical variables;
- bounded derivatives of the Hamiltonian $\frac{\partial H}{\partial x_j}$;
- bounded energy from above and below: $E_m \leq E \leq E_M$;
- vanishing density of states at the boundaries, i.e. $\omega(E_M) = 0$.

Given such conditions, one has that, on the one side, $T_G(E) = \Sigma(E)/\omega(E)$ diverges when $E \to E_M$. On the other side, $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle$ is limited, resulting in a contradiction.

We note that a failure of (117) is possible even in the absence of negative temperatures, i.e. $T_G \simeq T_B > 0$ for all E. Consider, for instance, the following Hamiltonian

$$H = \sum_{n=1}^{N} \frac{p_n^2}{2} + \epsilon \sum_{n=1}^{N} [1 - \cos(\phi_n - \phi_{n-1})] \tag{118}$$

where $\phi_n \in [-\pi, \pi)$. For large E, i.e. $E \gg \epsilon N$, the contribution to $\Sigma(E)$ of the variables $\{\phi_n\}$ does not depend too much on the value of E, so that $\Sigma_\epsilon(E) \simeq \Sigma_0(E) \propto E^{N/2}$, and $T_G \simeq 2E/N$ and, for large N, $T_B = T_G + O(1/N)$. On the other hand, it is easy to see that

$$\left| \phi_n \frac{\partial H}{\partial \phi_n} \right| \le 2\pi\epsilon, \tag{119}$$

and, therefore, the formula (117) cannot hold for large value of E and N.

3.3.5. A case study for negative temperatures

In order to discuss how systems with negative T_B are not atypical at all, we treat a system composed of N "rotators" with canonical variables $\phi_1, \dots, \phi_N, p_1, \dots, p_N$ with all ϕ_i and p_i defined in $[-\pi, \pi)$, and with Hamiltonian

$$H(\phi_1, \dots, \phi_N, p_1, \dots, p_N) = \sum_{n=1}^{N} [1 - \cos(p_n)] + \epsilon \sum_{n=1}^{N} [1 - \cos(\phi_n - \phi_{n-1})]. \tag{120}$$

Choosing, as boundary condition, $\phi_0 = 0$ guarantees that the only conserved quantity by the dynamics is the total energy E. Let us note that the shape of the kinetic part in the previous Hamiltonian is a one-dimensional version of the model used in [17].

It is immediate to verify that the energy has a maximum value $E_M = 2N(1+\epsilon)$ which is realized when $p_n = \pi$ and $\phi_n - \phi_{n-1} = \pi$ for every n. When $\epsilon = 0$ it is easy to see that Hamiltonian in Eq. (120) implies negative Boltzmann temperatures. Indeed at small energy one has $1 - \cos(p_n) \simeq p_n^2/2$ so that

$$\Sigma(E) \simeq C_N E^{N/2}, \quad \omega(E) \simeq \frac{N}{2} C_N E^{N/2-1},$$

with $C_N = (2\pi)^N \frac{\pi^{N/2}}{\Gamma(N/2+1)}$. Close to $E_M = 2N$ one has

$$\omega(E) \simeq \frac{N}{2} C_N (E_M - E)^{N/2-1} \ . \tag{121}$$

In conclusion we have that $\omega(E) = 0$ if $E = 0$ and $E = E_M$, which implies a maximum in between and a region (at high energies) with negative β_B. The previous scenario is expected to hold also in the presence of a small interaction among the rotators, this can be numerically confirmed with a sampling of the phase-space (see [99]): the density of states $\omega(E)$ has a maximum in $\tilde{E} \approx E_M/2$; it is an increasing function for $E < \tilde{E}$ whence $T_B > 0$; it decreases for $E > \tilde{E}$ whence $T_B < 0$.

Let us now discuss some statistical features of systems with negative temperature, stressing in particular the differences, and the analogies, with the more common cases with $T_B > 0$.

A rather natural way to determine T_B is via Eq. (116): computing the following average (over a single long trajectory of the system)

$$\rho(p) = \lim_{\tau \to \infty} \frac{1}{N\tau} \int_0^\tau dt \ \sum_{i=1}^{N} \delta\left[p_i(t) - p\right], \tag{122}$$

for different values of p, and assuming that the system is ergodic, it is possible to recover the single-particle-momentum probability density function $P(p)$. The result of such a measure is reported in Fig. 8: for two different values of energy $E_+ < \tilde{E}$ and $E_- > \tilde{E}$ the measured $\rho(p)$ is plotted as a function of the "kinetic energy" of the individual rotator $g(p) = 1 - \cos(p)$. The presence of a negative temperature at $E = E_-$ can be readily identified. Of course the clear positive slope of the function at $E = E_-$ is due to the fact that $T_B(E_-) < 0$: the opposite situation is encountered at $E = E_+$, where the decreasing behavior of $\rho(p)$ indicates a temperature $T_B(E_+) > 0$. These conclusions can also be drawn by measuring the time average of the function $\phi(X)$ (see Section 2); in the inset of Fig. 8 we report the temperature obtained with the Rugh's method.

3.4. Equivalence of ensembles and the equipartition formula

Following the usual treatment of textbooks, assuming that $S_B(E, N) = Ns(e)$, where $e = E/N$ and $s(e)$ is convex and performing a steepest descent analysis, for large N, one obtains the canonical functions from the (Boltzmann) microcanonical ones, e.g.:

$$T_B(e)s(e) = e - f(T_B(e)), \tag{123}$$

where $f(T)$ is the free energy per particle in the canonical ensemble. In such a derivation, the relevant point is the convexity of $S(e)$ and nothing about its first derivative is required. Therefore, the equivalence of ensembles naturally holds under our hypothesis even for negative T_B. Since T_B and T_G can be different even for large N, as in our model defined with Eq. (35), it is evident that T_G is not relevant for the ensemble equivalence.

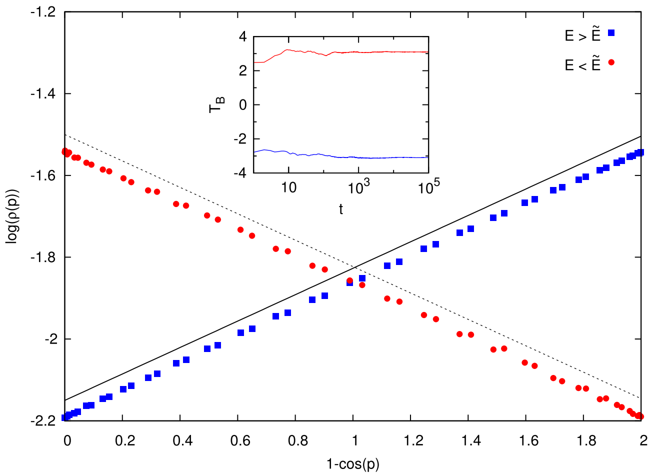

Fig. 8. Measure of the Boltzmann temperature in the rotators chain for $N = 100$ and $\epsilon = 0.5$. Probability distribution function of the momentum of the rotators as a function of their "kinetic energy" $g(p) = 1 - \cos(p)$ at energy $E = E_- = 170$ (blue squares) and $E = E_+ = 130$. The slopes of the two black straight lines are $-1/T_B^\infty(E)$, where $T_B^\infty(E)$ is the asymptotic value of the corresponding curve in the inset. Inset: The T_B obtained from the cumulated average of the observable $\phi(\mathbf{X}(t))$ (see Eq. (36)) over a trajectory up to time t at $E = 170$ (blue line) and $E = 130$ (red line).

A proposal [64] to measure the Gibbs temperature is by means of the equipartition formula, Eq. (117): for the Hamiltonian in Eq. (120) one should get

$$\langle p_n \sin p_n \rangle_E = T_G(E), \tag{124}$$

for every $1 \leq n \leq N$. Here we use the notation $\langle \, \rangle_E$ to denote the average in the microcanonical ensemble, in order to distinguish it from a canonical average $\langle \, \rangle_\beta$ which is useful to get some analytic expressions and better investigate the validity of Eq. (124).

An explicit expression (see details of analogous calculations in Ref. [100]) can be derived for the mean energy

$$U(\beta) = \langle H \rangle_\beta = -\frac{\partial}{\partial \beta} \ln Z(\beta) = N \left(1 + \epsilon - \frac{I_1(\beta)}{I_0(\beta)} - \frac{\epsilon I_1(\beta\epsilon)}{I_0(\beta\epsilon)} \right), \tag{125}$$

where $I_0(x)$ and $I_1(x)$ are, respectively, the zeroth and the first modified Bessel function of the first kind. Analogously, one can get an analytic formula for the equipartition function

$$\langle p \sin(p) \rangle_\beta = \frac{1}{\beta} - \frac{e^{-\beta}}{\beta I_0(\beta)}. \tag{126}$$

Let us remark that Eqs. (125) and (126) hold for both positive and negative β.

In Fig. 9 we report the plot of the parametric curve $(U(\beta), \langle p \sin(p) \rangle_\beta)$ obtained by varying β both in the positive and in the negative region of the real axis. This curve can be compared with measures of $\langle p \sin(p) \rangle_E$ computed from molecular dynamics simulations in the microcanonical ensemble at different values of the energy E (Fig. 9). Such a comparison clearly shows that the results obtained in the two different ensembles are identical, a transparent evidence that the equivalence of ensemble already exists for this system quite far from the thermodynamic limit ($N = 100$).

In addition Fig. 9 shows that the equipartition formula cannot be used to measure the Gibbs temperature: indeed, as already pointed out, the equipartition theorem can fail if the density of states $\omega(E)$ vanishes. This is the case of our system where $T_G = \Sigma(E)/\omega(E)$ should diverge for $E \to 2N(1 + \epsilon)$: on the other hand the results obtained in the canonical and in the microcanonical ensemble clearly indicate that $\langle p \sin(p) \rangle_E \to 0$ as $E \to 2N(1 + \epsilon)$.

3.4.1. Spatial coherence

In analogy with systems of point vortices previously discussed, as well as in other systems e.g. discrete non-linear Schrödinger equation [101], the rotators model in Eq. (120) possesses a spatially ordered phase at large values of E: this can be easily understood by noting that the density of states $\omega(E)$ vanishes in $E = E_M$, i.e. that there is a small number of microscopic configurations corresponding to large values of E. In particular, the maximum of the energy $E_M = 2N(1 + \epsilon)$ is attained by the unique microscopic state where, for every n, $p_n = \pi$ and $\phi_n - \phi_{n-1} = \pi$; that is, where all the rotators are fixed ($\dot{\phi} = \sin \pi = 0$) and the distance among two consecutive rotators is $\Delta\phi = \pi$. As a consequence, since $\phi_0 = 0$, all the particles with even index ($n = 0, 2, 4 \ldots$) must be at $\phi = 0$ and the others ($n = 1, 3, \ldots$) in $\phi = \pi$. At smaller values of $E \lesssim E_M$, such considerations can be extended, yielding a very similar situation: even and odd rotators must be close, respectively, to $\phi = 0$ or $\phi = \pi$.

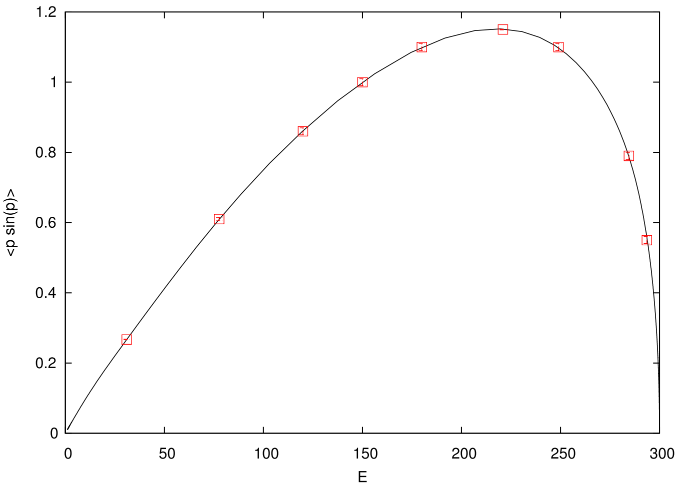

Fig. 9. Black line: $\langle p\sin(p)\rangle_\beta$ vs $U(\beta)$ in the canonical ensemble and as parametric functions of $\beta \in (-\infty,\infty)$. Red squares: time averages of the equipartition function in molecular dynamics simulations at fixed energy E (microcanonical ensemble). The values for the parameters of the model are $N = 100$ and $\epsilon = 0.5$.

3.5. *Temperature in small isolated systems?*

Let us briefly discuss about the possibility to introduce, or not, the concept of temperature in small systems. As already mentioned, such a topic, beyond its interest in the general context of the statistical physics, can be relevant in the treatment of nanosystems which can involve just few particles. As discussed in Section 2, for Hamiltonian systems, following the elegant approach introduced by Rugh, we can define (and compute) the temperature T_B in terms of time average $\langle(\ldots.)\rangle_t$ of a suitable observable $\phi(\mathbf{X})$:

$$\frac{1}{T_B} = \langle\phi(\mathbf{X})\rangle_t \ . \tag{127}$$

In a similar way one can compute (at least for a certain class of systems) the T_G using the relation

$$k_B T_G = \left\langle x_i \frac{\partial H}{\partial x_i}\right\rangle_t \ . \tag{128}$$

A quite natural, and general, question is the possible dependence of the time averages on the initial condition $\mathbf{X}(0)$. If the number of degrees of freedom is very large, one can invoke a well know important result due to Khinchin [69] which can be summarized as follows: the physically relevant observables (i.e. that ones involving all the degrees of freedom) are selfaveraging; they are practically constant (except in a region of small measure) on a constant-energy surface. More precisely in system with $N \gg 1$ the ergodicity is not a real problem, at least at a physical practical level: the time average of "physical observables" (e.g. the kinetic energy) is very close to the microcanonical average, with the exception of initial conditions in a (small) region whose measure is $O(N^{-1/4})$, and therefore goes to zero a $N \to \infty$.

Unfortunately such a result does not hold in small systems. Some authors computed numerically T_B and T_G in small Hamiltonian systems, e.g. the celebrated Hénon–Heiles model, or systems with quartic nonlinearity, usually with $N = 2$ or $N = 4$ [102–104]. They observed that $T_G \neq T_B$ and in addition, as expected from very general results of the Hamiltonian systems, the results depend on the initial conditions. Let us note that the investigated systems do not show negative temperature, the difference between T_G and T_B are just a consequence of the small value of N.

In our opinion the results in [102–104] show, in a rather clear way, that in small isolated systems the concept of temperature (both T_B and T_G) is rather misleading: its value can depend on the initial condition, and more important, does not have a clear physical relevance.

In Section 3.2 we discussed small systems interacting with a thermal bath. We saw how, in spite of the limited value of N, the temperature is well defined and rules the statistical features, e.g. it appears in the probability distribution of the energy. In an analogous way also for a class of Langevin equations with detailed balance (see Section 4.1) e.g. modeling the evolution of a colloidal particle interacting with a thermal bath, it is not difficult to introduce the temperature.

The mathematical reason of such a difference is quite transparent: at variance with the deterministic case previously discussed, because of the presence of a bath (noise) we are dealing with stochastic systems: the problem of the validity of the ergodicity is solved. So we have that for small, but non isolated, systems we can introduce in a coherent way the concept of temperature which is a property of the reservoir, and rules the statistical features of the system.

4. Temperature and response theory

In the present Section we discuss the role played by temperature in the behavior of a system which is driven out of equilibrium. A weak perturbation is treated by means of the close-to-equilibrium linear response theory, summarized in the Equilibrium Fluctuation–Dissipation Relation (EFDR), where temperature has a clear status of proportionally factor between response function and correlation of fluctuations (see Section 4.1). Far from equilibrium, things are much more complex and – in general – temperature loses its preeminent role. Nevertheless, several theoretical results in far-from-equilibrium statistical systems have been obtained, in the last twenty years, chiefly ascribable to two lines of research: linear response of systems which are already out of equilibrium (see Section 4.2), and relations between asymmetric fluctuations of entropy production (partially discussed in both Sections 4.1 and 4.2). In the close-to-equilibrium limit all those results coincide with the EFDR. In particular cases, as in systems with well-separated timescales, it is possible to extend the notion of temperature-like quantities to the non-equilibrium realm (see Section 4.3).

4.1. Close to equilibrium: Temperature from Kubo relation in Hamiltonian systems and Langevin equations

In Section 1.4 we have seen the Einstein theory for the fluctuations of macrostates, repeated here for convenience:

$$P(\alpha_1, \dots, \alpha_m) \sim e^{[S\{\alpha_k\}-S_e]/k_B}. \tag{129}$$

Eq. (129) expresses the probability of a spontaneous fluctuation as the exponential of the entropy difference with respect to equilibrium. Such a formula leads, by means of a simple perturbative expansion, to Eq. (16) which relates the amplitude of macro-fluctuations, quantified by the covariances $\langle \delta\alpha_i \delta\alpha_j \rangle$, to the second derivatives of the entropy which involve temperature. The latter represent, in general, the susceptibilities, i.e. the long time responses of the system to external perturbations.

Summarizing, Eq. (129) teaches us that in statistical mechanics – under equilibrium conditions – three fundamental concepts, i.e. spontaneous fluctuations, responses to a perturbation and temperature, are connected in a unique relation. One of the simplest examples of such a threefold connection is the textbook formula

$$\langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_v, \tag{130}$$

where the variance of the energy distribution is proportional to the heat capacity (a susceptibility, i.e. a response function) and to the square of the temperature. An analogous formula, due to Einstein, relates the diffusivity D to the mobility μ for a Brownian particle dispersed in a solvent fluid:

$$D = k_B T \mu, \tag{131}$$

where again the temperature appears as the constant of proportionality relating a measure of fluctuations (D) and a measure of response (μ).

The above examples involve quantities which do not depend upon time and, for this reason, are often referred to as *static* EFDR. In the first half of the 20th century a series of important results, with different physical systems and observables, showed that many other similar relations exist, tying in the same way those three ingredients: spontaneous fluctuations, response and temperature [97,14]. The generalization to a time-dependent – or dynamic – relation with the same form was stated in universal terms for the first time by Onsager in 1931 [105,106]. For instance, by recalling the general relation between diffusivity and the velocity autocorrelation, i.e. that

$$D = \int_0^\infty dt \langle v(t)v(0) \rangle, \tag{132}$$

it is seen that Eq. (131) is equivalent to

$$\langle v(t)v(0) \rangle = k_B T R_{vF}(t), \tag{133}$$

with the identification

$$\mu = \int_0^\infty dt R_{vF}(t). \tag{134}$$

In the r.h.s. of Eq. (133) it appears the so-called response function, $R_{vF}(t)$, which is the mean variation at time t to an impulsive perturbation at time 0: in our examples $R_{vF}(t)$ relates the rate of variation of colloidal (tracer) particle's velocity and a perturbation of the external force applied at time 0. In order to discuss in full generality the Fluctuation–Dissipation Relation (FDR), it is useful to recall the definition of response functions which is the central object of linear response theory. For simplicity we restrict the discussion to the linear perturbation of stationary states, i.e. states which are invariant under translations of time. For this reason time-dependent correlation functions and response functions only depend on differences of times. The general case is treated in Section 4.2.

The response function $R_{\mathcal{O}\mathcal{F}}(t)$ for an observable $\mathcal{O}(t)$ to a time-dependent perturbation of a parameter or degree of freedom $\delta\mathcal{F}(t)$ is implicitly defined in the following relation

$$\overline{\Delta\mathcal{O}(t)} = \int_{-\infty}^{t} dt' R_{\mathcal{O}\mathcal{F}}(t-t')\delta\mathcal{F}(t'), \tag{135}$$

where $\overline{\Delta\mathcal{O}(t)} = \overline{\mathcal{O}(t)} - \langle\mathcal{O}(t)\rangle_0$ represents the average deviation, at time t, of the observable $\mathcal{O}$ with respect to its average value in the unperturbed stationary system. Here we use $\overline{f(t)}$ to denote a time-dependent (perturbed) average of the observable f, and $\langle f\rangle_0$ to denote its stationary unperturbed average. It is clear that, taking an impulsive shape for the external perturbation i.e. $\delta\mathcal{F}(t) = \Delta\mathcal{F}\delta(t)$ (with $\delta(t)$ the Dirac delta distribution), one has

$$\frac{\overline{\Delta\mathcal{O}(t)}|_{imp}}{\Delta\mathcal{F}} = R_{\mathcal{O}\mathcal{F}}(t), \tag{136}$$

which gives a more operational definition to the response function.[2] It is also useful to see what happens when the perturbation takes the shape of a Heaviside unit step function, i.e. $\delta\mathcal{F}(t) = \delta\mathcal{F}_0\Theta(t)$:

$$\frac{\overline{\Delta\mathcal{O}(t)}|_{step}}{\delta\mathcal{F}_0} = \int_0^t dt' R_{\mathcal{O}\mathcal{F}}(t'). \tag{137}$$

If $\mathcal{O}(t)$ is the tracer velocity along one axis and $\mathcal{F}(t)$ is the external force applied from time 0 to time ∞ to the tracer (parallel to that axis), the final velocity reached by the tracer is exactly $\delta\mathcal{F}_0\int_0^\infty dt' R_{vF}(t')$, which explains the connection with the identification made in Eq. (134).

Equipped with the response function definition, it is possible to enunciate the FDR for Hamiltonian $\mathcal{H}$ systems at equilibrium with a thermostat at temperature T [107]:

$$R_{\mathcal{O}\mathcal{F}}(t) = \frac{1}{k_B T}\langle\mathcal{O}(t)\dot{A}(0)\rangle_0 = -\frac{1}{k_B T}\langle\dot{\mathcal{O}}(t)A(0)\rangle_0, \tag{138}$$

where A is the observable (or degree of freedom) which is coupled to $\mathcal{F}(t)$ in the Hamiltonian to produce the perturbation, i.e. $\mathcal{H}(t) = \mathcal{H}_0 - \mathcal{F}(t)A$. We immediately see that if $\mathcal{O}$ is the tracer's velocity and $\mathcal{F}(t)$ is an external force applied to its x coordinate, Eq. (138) is nothing but Eq. (133). In conclusion the Einstein relation is a particular case of the EFDR.

From Eq. (138) one may get several possible variants, which are useful in different physical situations. A large amount of remarkable results concern, for instance, the time-Fourier transform of Eq. (138), as well as the relation connecting currents and conductivities (the so-called Green–Kubo relations, see below) [97,14].

An interesting generalization of the EFDR concerns the realm of stochastic processes. For instance, the so-called Klein–Kramers model, for a single particle in 1 dimension [66], well describes the dynamics of a system at thermal equilibrium:

$$\frac{dx(t)}{dt} = v(t) \tag{139a}$$

$$m\frac{dv(t)}{dt} = -\frac{dU(x)}{dx} - \gamma v(t) + \sqrt{2\gamma k_B T}\xi(t), \tag{139b}$$

where $\xi(t)$ is a white Gaussian noise with $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = \delta(t-t')$, γ is the viscosity, $U(x)$ is an external potential. The model can be easily generalized to $N > 1$ interacting particles in any dimensions. In the absence of the external potential, Eq. (139) coincides with the original Langevin equation proposed a few years after the theories of Einstein [10] and Smoluchowski [108] to explain diffusion in Brownian motion [109]. Eq. (139) actually describes more than spatial diffusion (which is the *long time* behavior of Eq. (139)), as it includes short times "ballistic" effects. From a mathematical point of view, it describes a Markovian time-continuous process.

Most importantly, the distribution of its stationary states (achieved with the condition $\gamma > 0$ and confining potential) is given by the Gibbs measure $P(x, v) \propto e^{-\mathcal{H}(x,v)/(k_B T)}$ with $\mathcal{H}(x, v) = mv^2/2 + U(x)$: such a stationary state satisfies detailed balance, which is equivalent to say that the unconditioned probability of observing a trajectory is equal to the unconditioned probability of the time-reversed trajectory [78]. Linear response theory, when applied to the Klein–Kramers model in its stationary state, gives exactly the same result as Eq. (138) [78,14].

The Klein–Kramers process is Markovian with respect to the variables (x, v), usually such a property is just a rough approximation for the dynamics of a tracer which interacts with other particles in a fluid. For instance the Langevin equation - i.e. the Kramers equation with $U(x) = 0$ - must be generalized to take into account retarded hydrodynamic effects, by the introduction of linear memory terms, e.g. by writing a Generalized Langevin Equation (GLE) [97]:

$$m\frac{dv(t)}{dt} = -\int_{-\infty}^{t} dt' \Gamma(t-t')v(t') + \eta(t), \tag{140}$$

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[2] Be careful that $\Delta\mathcal{F}$ has the dimensions of a time-integral of $\mathcal{F}(t)$.

where $\Gamma(t)$ is a memory kernel representing retarded damping, and $\eta(t)$ is a stationary stochastic process with zero average $\langle\eta(t)\rangle = 0$ and time-correlation which – at equilibrium – satisfies the so-called FDR of the second kind:

$$\Gamma(t) = \frac{1}{k_B T}\langle\eta(t)\eta(0)\rangle. \tag{141}$$

It is clear that Eq. (141) has the same structure of Eq. (138) and this motivates the name of the relation. The Markovian case (damping with zero memory) is obtained when $\Gamma(t) = 2\gamma\delta(t)$ (recalling that $\int_{-\infty}^{t} dt' 2\gamma\delta(t')v(t') = \gamma v(t)$).

In the discussion of the Fluctuation–Dissipation theorem of the second kind, Kubo put in evidence that such a result is necessary to guarantee the equipartition theorem and this is the reason why it is a signature of thermodynamic equilibrium. A condition for (Markovian) microscopic dynamics which is necessary and sufficient for thermodynamic equilibrium is detailed balance [110], commonly assumed in stochastic thermodynamics [73,111]. It is interesting to discuss a simple example which connects the concept of detailed balance to the FDR of the second kind.

Let us consider the following bivariate Ornstein–Uhlenbeck process

$$m\frac{dv(t)}{dt} = -\gamma v(t) + \sqrt{M\Gamma_0}z(t) + \sqrt{2\gamma k_B T_0}\phi_1(t) \tag{142a}$$

$$M\frac{dz(t)}{dt} = -\sqrt{M\Gamma_0}v(t) - \frac{M}{\tau}z(t) + \sqrt{2\frac{M}{\tau}k_B T_\tau}\phi_2(t), \tag{142b}$$

where $v(t)$ is the velocity of a Brownian particle and $\sqrt{M\Gamma_0}z(t)$ represents an effective fluctuating force[3] induced by the surrounding solvent upon the particle: we assume that it evolves according to a separate Ornstein–Uhlenbeck process with characteristic relaxation time τ, effective mass M, effective "temperature" T_τ and feedback from the particle itself (with ϕ_1 and ϕ_2 Gaussian white noises with unitary variances). Recently such a model has been used to study a massive tracer diffusing through a moderately dense granular material [113] (we discuss this case below, in Section 5.3). A similar model has also been proposed to represent a kind of active Brownian particles, where $z(t)$ represents self-propulsion [114] (this model is briefly described in Section 5.4). The system in Eqs. (142) is linear and therefore fully solvable. The stationary state is characterized by a bivariate Gaussian distribution

$$p_{st}(\mathbf{X}) \propto \exp\left(-\frac{1}{2}\mathbf{X}\Sigma^{-1}\mathbf{X}^T\right), \tag{143}$$

where $\mathbf{X} = (v, z)$ with covariance matrix Σ given by

$$\Sigma_{vv} = \langle v^2\rangle = k_B T_0/m + \langle vz\rangle\sqrt{\Gamma_0 M}/\gamma \tag{144}$$

$$\Sigma_{zz} = \langle z^2\rangle = k_B T_\tau/M - \langle vz\rangle\sqrt{\Gamma_0 M}\tau/M \tag{145}$$

$$\Sigma_{vz} = \Sigma_{zv} = \langle vz\rangle = \frac{\Gamma_0\tau\gamma}{(\gamma+\Gamma_0\tau)(m+\gamma\tau)\sqrt{\Gamma_0 M}}k_B(T_\tau - T_0). \tag{146}$$

The probability of a trajectory going from time 0 to time t, denoted as $\{v(s), z(s)\}_{s=0}^{t}$, conditioned to the initial point $(v(0), z(0))$ is given by the Onsager–Machlup expression [115]

$$\ln P(\{v(s), z(s)\}_{s=0}^{t}) = \\ \mathcal{C} - \int_0^t ds\left\{\frac{[m\dot{v}(s) + \gamma v(s) - \sqrt{M\Gamma_0}z(s)]^2}{\gamma k_B T_0} + \frac{[M\dot{z}(s) + \sqrt{M\Gamma_0}v(s) + z(s)M/\tau]^2}{k_B T_\tau M/\tau}\right\}, \tag{147}$$

where $\mathcal{C}$ is a constant. According to the above expression, the probability (with the condition of starting at $(-v(t), z(t))$) of the time-reversed trajectory reads

$$\ln P(\{-v(t-s), z(t-s)\}_{s=0}^{t}) = \\ \mathcal{C} - \int_0^t ds\left\{\frac{[m\dot{v}(s) - \gamma v(s) - \sqrt{M\Gamma_0}z(s)]^2}{\gamma k_B T_0} + \frac{[-M\dot{z}(s) - \sqrt{M\Gamma_0}v(s) + z(s)M/\tau]^2}{k_B T_\tau M/\tau}\right\}. \tag{148}$$

The ratio between the probabilities of the forward (Eq. (147)) and backward (Eq. (148)) trajectories is obtained straightforwardly, by noting that many terms cancel out and some of the remaining ones are integral of exact time-differentials. In few passages it is verified that

$$\frac{P(\{v(s), z(s)\}_{s=0}^{t})}{P(\{-v(t-s), z(t-s)\}_{s=0}^{t})} = \frac{p_{st}[-v(t), z(t)]}{p_{st}[v(0), z(0)]}, \tag{149}$$

if and only if $T_\tau = T_0$. Eq. (149) shows, in this case, the equivalence between thermodynamic equilibrium and detailed balance.

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[3] Therefore we assume that $z(t)$ is a variable with even parity under time-reversal. The parity of coarse-grained variables is, in general, a subtle problem, see for instance [112,77].

The linear response of variable $v(t)$ in Eqs. (142) to an infinitesimal perturbation of v of intensity $\delta v(0)$ (which is equivalent to an impulsive force $m\delta v(0)\delta(t)$), can be obtained by recalling that — if the average dynamics is linear, i.e.

$$\dot{\overline{\mathbf{X}}} = A\overline{\mathbf{X}}, \tag{150}$$

as it is in this case, then the linear response is obtained straightforwardly as

$$\overline{\delta\mathbf{X}(t)} = e^{At}\delta\mathbf{X}(0), \tag{151}$$

while the covariance matrix (at positive time-delay t) in the steady state reads

$$\langle\mathbf{X}(t)\mathbf{X}(0)\rangle = \Sigma e^{At}. \tag{152}$$

Putting together results (151) and (152) we get

$$mR_{vF}(t) = \frac{\overline{\delta v(t)}}{\delta v(0)} = \Sigma^{-1}_{vv}\langle v(t)v(0)\rangle + \Sigma^{-1}_{vz}\langle v(t)z(0)\rangle. \tag{153}$$

Again it is immediate to see that the Einstein relation, Eq. (133), is recovered when $T_\tau = T_0$ which coincides with $\Sigma^{-1}_{vz} = 0$ and $\Sigma^{-1}_{vv} = m/(k_B T_0)$.

It is interesting to note [116,117,112]that a formal solution of $z(t)$ from Eq. (142b), put into Eq. (142a), leads to a GLE of the kind in Eq. (140) with memory kernel given by

$$\Gamma(t) = 2\gamma\delta(t) + \Gamma_0 \exp(-t/\tau) \quad (t > 0), \tag{154}$$

and noise made of two uncorrelated terms: $\eta(t) = \eta_0(t) + \eta_\tau(t)$, with both terms having zero average and time-correlations

$$\langle\eta_0(t)\eta_0(t')\rangle = 2k_B\gamma T_0\delta(t-t') \tag{155}$$

$$\langle\eta_\tau(t)\eta_\tau(t')\rangle = k_B T_\tau \Gamma_0 \exp(-|t-t'|/\tau). \tag{156}$$

Again we see that Eq. (141) is satisfied only when $T_0 = T_\tau$. This clarifies the deep connection between the symmetry under time-reversal, thermodynamic equilibrium and the Fluctuation–Dissipation theorem of the second kind.

To conclude this succinct summary of a wide topic of non-equilibrium statistical mechanics (close to equilibrium), it is interesting to discuss the case of currents, which has been mentioned a few pages above. Currents are physically relevant *responses* to external perturbations: examples include the electrical current in a conductor under an external electrical potential, the heat flow in a material under a temperature gradient, or the transverse momentum current in a fluid under shear. Most importantly, a measurement in a finite sample, observed for a finite time, will result in a *fluctuating* current: this has become a real possibility in the last decades, with the advent of experiments at micro or nano scale, as well as with the increase in the time-resolution of instruments [118,68]. The typical quantity which is measured is a finite-time (over a duration τ) averaged current, i.e.

$$J_\tau(t) = \frac{1}{\tau}\int_t^{t+\tau} ds j(s), \tag{157}$$

where $j(s)$ is an instantaneous current at time s, defined over a finite volume of the system: for instance, in the case of a simple current of mass of a certain species of molecules (e.g. tracers in a mixture), it is proportional to the empirical average (in the volume) of the instantaneous velocity of such molecules. The situation, and the following discussion, is greatly simplified under the assumption of stationarity.

Physical currents have the property of changing sign under the action of the operation of time-reversal. Indeed if a given trajectory of the system (in the full phase space) corresponds to observing a value x for $J_\tau(t)$, the time-reversed trajectory corresponds to observing $-x$ for $J_\tau(t)$. In the mentioned example, where the current is related to a flow of massive tracers, a time-reversed microscopic trajectory corresponds to observe – in a chronologically inverted order – all tracers' velocities with a change of sign, i.e. $j(s) \to -j(s)$ and therefore $J_\tau \to -J_\tau$.[4]

A system in equilibrium does not contain net physical currents, i.e. the stationary average of $J_\tau(t)$ is zero. A stationary state with a small non-zero average current $\langle j\rangle$ is, therefore, understood as the $t \to \infty$ response to a small external perturbation $\delta\mathcal{F}_0\Theta(t)$, applied since time 0, in an equilibrium system. For this reason it has to satisfy the Fluctuation–Dissipation theorem near equilibrium, Eq. (138), that in this particular case takes the form

$$\langle j\rangle = \delta\mathcal{F}_0\int_0^\infty dt' R_{J\mathcal{F}}(t') = \frac{\delta\mathcal{F}_0}{k_B T}\int_0^\infty dt'\langle j(t')\dot{A}(0)\rangle_0, \tag{158}$$

with $A(t)$ the observable conjugated to the perturbation $\mathcal{F}$. An interesting simplification comes by observing that the observable conjugate to the perturbation needed to produce a current J is the time-integral of the current itself [97], which leads to the classical Green–Kubo relation

$$\langle j\rangle = \langle J_\tau\rangle = \frac{\delta\mathcal{F}_0}{k_B T}\int_0^\infty dt'\langle j(t')j(0)\rangle_0. \tag{159}$$

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[4] The change of time-ordering does not affect the integral in Eq. (157) as ds changes sign together with an inversion of the extremes of integration.

What happens to the fluctuations, e.g. the variance, of the τ-averaged current J_τ? At equilibrium (when $\langle j\rangle = 0$), and for large τ, it is always possible to write

$$\tau^2\langle J_\tau^2\rangle_0 = \left\langle \left[\int_0^\tau dt' j(t')\right]^2 \right\rangle_0 \approx 2\tau \int_0^\tau dt' \langle j(t')j(0)\rangle_0. \tag{160}$$

In the framework of linear response theory, where $O(\delta\mathcal{F}^2)$ and higher order terms are neglected, the variance of a current is not changed too much by the perturbation, that is $\langle J_\tau^2\rangle - \langle J_\tau\rangle^2 \approx \langle J_\tau^2\rangle_0$. In conclusion, putting together Eqs. (159) and (160), it is found for large τ

$$\langle J_\tau^2\rangle - \langle J_\tau\rangle^2 \approx 2\frac{k_BT\langle J_\tau\rangle}{\tau\delta\mathcal{F}_0}. \tag{161}$$

At equilibrium, and close to it (at first order in the perturbation), the statistics of J_τ is well described by a Gaussian probability density function [111], which – according to the last result – reads at large τ

$$p(J_\tau) \propto \exp\left[-\tau\frac{(J_\tau - \mu\delta\mathcal{F}_0)^2}{4\mu k_BT}\right], \tag{162}$$

where we have defined the generalized mobility $\mu = \langle J_\tau\rangle/\delta\mathcal{F}_0$.

Remarkably, Eq. (162) - which is a mere consequence of the Fluctuation–Dissipation relation (and the limit $\tau \to \infty$) appears to be the particular form, when close to equilibrium, of a more general "Fluctuation Relation" which establishes a symmetry between time-reversed values of the current, i.e. J_τ and $-J_\tau$. Indeed it is immediate to verify that Eq. (162) satisfies

$$p(J_\tau)/p(-J_\tau) = \exp\left(\tau\frac{\dot{S}_\tau}{k_B}\right), \tag{163}$$

where we have introduced the "fluctuating entropy production rate" $\dot{S}_\tau$ averaged over the time τ, defined as

$$\dot{S}_\tau = \frac{J_\tau\delta\mathcal{F}_0}{T}. \tag{164}$$

In the following sections, together with some relevant non-equilibrium generalization of the Fluctuation–Dissipation theorem, we discuss the universality of Eq. (163), which also applies to cases with a large perturbation $\delta\mathcal{F}_0$, where $p(J_\tau)$ is no more guaranteed to be Gaussian, and even to cases without a single thermostat, where Eq. (164) has to be replaced by a more general definition of fluctuating entropy production.

In conclusion it is rewarding, after a journey through linear response theory, stochastic processes, time-reversal symmetry and current fluctuations, to arrive to relation Eq. (163) which is reminiscent of the starting point, Eq. (129). It is important to underline that the coherence among the many concepts touched in the last pages is a *gift* of thermodynamic equilibrium, where temperature is a well defined concept.[5]

4.2. Extension to far-from-equilibrium systems: a generalized fluctuation–dissipation relation

The significance of an equation is somehow determined by the difference of definition between the concepts underlying the left and right hand sides of the equality sign [119]. The FDT discussed in the previous Section represents a clear instance of such a deep connection between different quantities: spontaneous fluctuations and response to external stimuli. On the one hand, the theoretical interest in deriving such kind of relations relies on the possibility to go deep into the mechanisms governing a given phenomenon, uncovering hidden links between its facets and shedding further light on its nature. On the other hand, from the experimental perspective, such relations allow us to obtain information about a certain quantity by measuring a related one, which could be more easily accessible in the lab.

Unfortunately, the particularly elegant and simple forms of the FDT, Eqs. (133) and (138), do not hold when the considered system is in nonequilibrium conditions, for instance when it is coupled to thermostats at different temperatures, or during the relaxation from an initial to a final state. In these cases, due to the presence of currents (of energy, entropy or particles) crossing the system, the dynamics is not invariant under time reversal. Nevertheless, fluctuation–dissipation relations (FDRs) between the response function to an external perturbation in a nonequilibrium state and the correlation functions computed in the unperturbed dynamics, can still be derived for a large class of systems. The price to pay is that such relations do not share the same generality of the EFDR, and their explicit forms depend on the system under investigation. Several efforts have been devoted to give an intelligible physical meaning to the extra (nonequilibrium) contributions appearing in the FDRs, but a clear and shared understanding in terms of macroscopic thermodynamic quantities is still lacking.

The literature on the generalized FDRs has rapidly increased in the last decades and we refer the interested reader to the very accurate reviews recently appeared on this wide topic [14,120,68,121]to have a complete overview. In this section we present a concise perspective, identifying two main classes of FDRs:

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[5] All along the present Subsection we have always considered stochastic processes whose invariant probability distribution is the canonical one. For this reason there is no ambiguity in the definition of temperature.

- (A) FDRs involving the explicit shape of the invariant probability distribution of the process;
- (B) FDRs involving quantities defined in terms of the microscopic dynamical rules (transition rates) of the model.

These two classes may have applications in complementary cases, depending on the problem at hand.

4.2.1. Class A

The first kind of nonequilibrium FDR we consider expresses the average response of the observable $\mathcal{O}$, in terms of correlation functions, which involve (derivatives of) the stationary distribution of the system. As shown in [122,123], for a system with states $\mathbf{X}$, the response of $\mathcal{O}(t)$ to an impulsive perturbation applied at time s, defined in Eq. (136), takes the form

$$R_{\mathcal{O}\mathcal{F}}(t-s) = -\sum_j \left\langle \mathcal{O}(t) \frac{\delta \log p_{st}(\mathbf{X})}{\delta X_j}\bigg|_s \right\rangle, \tag{165}$$

where $p_{st}(\mathbf{X})$ is the invariant probability distribution of the system. This result can be obtained both for deterministic and stochastic dynamics. Similar formulae derived following different approaches, and generalized even to non-stationary conditions, have been proposed recently [124–126].

From Eq. (165), the EFDR is immediately recovered replacing p_{st} with the equilibrium distribution. In general conditions, however, if the explicit form of p_{st} is known or if some physical assumptions can be made on it, then Eq. (165) gives information on the coupling among degrees of freedom that have to be taken into account out of equilibrium to reconstruct the response function from unperturbed correlators. In the following, we will discuss an explicit example where this formalism can be applied, in the context of granular systems (see Section 5).

4.2.2. Class B

Let us consider a stochastic continuous variable α evolving according to the following stochastic differential equation

$$\dot{\alpha}(t) = \mathcal{A}[\alpha(t)] + \eta(t), \tag{166}$$

where $\mathcal{A}[\alpha]$ is a known function of the variable α and η is a Gaussian noise, with zero mean and variance $\langle \eta(t)\eta(t')\rangle = 2D\delta(t-t')$. Then, expressing the response function as a correlation with the noise [127,128], one obtains the following FDR

$$R_{\mathcal{O}\mathcal{F}}(t,s) = \frac{1}{2D}\left\{\langle \mathcal{O}(t)\dot{\alpha}(s)\rangle - \langle \mathcal{O}(t)\mathcal{A}[\alpha(s)]\rangle\right\}, \tag{167}$$

where $\langle \cdots \rangle$ denotes an average over initial conditions and noise realizations. The above result is valid in general non-equilibrium conditions, in stationary or transient regimes, where an explicit dependence on the two times (t, s) appears in the response function, and can be easily generalized to vectorial variables or field theories [129].

From the general expression Eq. (167), one obtains the FDR for the Klein–Kramers model (139), with the following substitutions: $\alpha = v$, $\mathcal{A} = -\gamma v - dU(x)/dx$ and $D = \gamma T$, which yields

$$R_{\mathcal{O}\mathcal{F}}(t,s) = \frac{1}{2\gamma T}\left\{\langle \mathcal{O}(t)\dot{v}(s)\rangle - \left\langle \mathcal{O}(t)\left[-\gamma v(s) - \frac{dU(x)}{dx}\right]\right\rangle\right\}. \tag{168}$$

The equilibrium form of the FDT, Eq. (138), can be recovered from Eq. (168) exploiting time translation invariance and causality. Indeed, the first term in the r.h.s. of Eq. (168) can be rewritten as

$$\begin{aligned} \langle \mathcal{O}(t)\dot{v}(s)\rangle &= -\langle \dot{v}(t)\mathcal{O}(s)\rangle = -\left\langle [-\gamma v(t) - \frac{dU(x)}{dx} + \eta(t)]\mathcal{O}(s)\right\rangle \\ &= \gamma\langle v(t)\mathcal{O}(s)\rangle + \left\langle \frac{dU(x)}{dx}\mathcal{O}(s)\right\rangle \\ &= \gamma\langle \mathcal{O}(t)v(s)\rangle - \left\langle \mathcal{O}(t)\frac{dU(x)}{dx}\right\rangle, \end{aligned} \tag{169}$$

where we used the Onsager relations and we have assumed that $\mathcal{O}$ is odd under time inversion. Finally, substituting Eq. (169) into Eq. (168) one gets Eq. (138).

Analogously, the FDR for an overdamped Langevin system is obtained from the relation (167) by taking $\alpha = x$, $\mathcal{A} = F(x)/\gamma$ and $D = T/\gamma$, which yields

$$R_{\mathcal{O}\mathcal{F}}(t,s) = \frac{\gamma}{2T}\left\{\langle \mathcal{O}(t)\dot{x}(s)\rangle - \langle \mathcal{O}(t)\mathcal{A}[x(s)]\rangle\right\}. \tag{170}$$

These kinds of relations (and their generalizations) have been derived in different contexts and with different approaches [68,128,130–132], providing several physical interpretations for the nonequilibrium contributions, in terms of stochastic entropy, entropy production, dynamical activity, etc. We will briefly discuss some of these concepts below.

The generalization of Eq. (167) to systems with a discrete state space, such as the Ising model or spin glasses, is non-trivial and requires the solution of some technical problems. For instance, the FDR for discrete variables $\sigma = \pm 1$ evolving according to a Master Equation with transition rates $w(\sigma \to \sigma')$, in contact with a reservoir at temperature T, takes the following form [133]

$$R_{\mathcal{O}\mathcal{F}}(t,s) = \frac{1}{2T}\left\{\frac{\partial}{\partial s}\langle \mathcal{O}(t)\sigma(s)\rangle - \langle \mathcal{O}(t)B(s)\rangle\right\}, \tag{171}$$

where the quantity $B[\sigma]$ is defined by

$$B[\sigma(s)] = \sum_{\sigma'}[\sigma' - \sigma(s)]w[\sigma(s) \to \sigma']. \tag{172}$$

From the relation (171), the equilibrium FDT (138) is immediately obtained exploiting the property

$$\left\langle \mathcal{O}(t)\sum_{\sigma''}[\sigma'' - \sigma(s)]w[\sigma(s) \to \sigma'']\right\rangle_{eq} = -\frac{\partial}{\partial s}\langle \mathcal{O}(t)\sigma(s)\rangle_{eq}, \tag{173}$$

valid when the average is taken in the equilibrium state [133]. A unified formalism for the derivation of FDRs including both the cases of continuous and discrete variables is presented in [134].

In order to illustrate with an explicit example the form assumed by the FDRs in a specific case, let us consider the two-variable model introduced previously in Eq. (142). For this system one can apply both the FDR of class A, Eq. (165), and the FDR of class B, Eq. (167). Using the known stationary distribution Eq. (143), from Eq. (165) one immediately gets the expression (153). Alternatively, applying Eq. (167), one has

$$R_{v\mathcal{F}}(t) = \frac{1}{2\gamma T_0}\left[-\frac{d}{dt}\langle v(t)v(0)\rangle + \frac{\gamma}{m}\langle v(t)v(0)\rangle - \frac{\sqrt{M\Gamma_0}}{m}\langle v(t)z(0)\rangle\right], \tag{174}$$

where the variable $z(t)$ is an effective field velocity, defined in the model (142). Obviously the two formulae are equivalent, as it can be checked.

4.2.3. Nonlinear FDRs

The FDRs in the form (167) or (171) can be generalized to nonlinear orders, providing a relation between nonlinear response functions and multi-point correlation functions. These cases are relevant for instance in the context of disordered systems, where usually growing characteristic lengths near critical points cannot be measured through linear response functions or two-point correlators, which remain always short-ranged. The problem of deriving nonlinear FDRs in this context has been addressed initially in [135], and the general formalism valid for arbitrary order has been set in [136,134]. As an example we report here the form of the second order response function for a system of discrete variables σ perturbed by two fields $\mathcal{F}_1$ and $\mathcal{F}_2$ at times t_1 and t_2 [134]

$$\begin{aligned} R^{(2)}_{\mathcal{O}\mathcal{F}}(t,t_1,t_2) &\equiv \left.\frac{\delta\langle\mathcal{O}(t)\rangle_{\mathcal{F}}}{\delta\mathcal{F}_1(t_1)\delta\mathcal{F}_2(t_2)}\right|_{h=0} \\ &= \frac{1}{4T^2}\left\{\frac{\partial}{\partial t_1}\frac{\partial}{\partial t_2}\langle\mathcal{O}(t)\sigma(t_1)\sigma(t_2)\rangle - \frac{\partial}{\partial t_1}\langle\mathcal{O}(t)\sigma(t_1)B(t_2)\rangle\right. \\ &\quad \left. - \frac{\partial}{\partial t_2}\langle\mathcal{O}(t)B(t_1)\sigma(t_2)\rangle + \langle\mathcal{O}(t)B(t_1)B(t_2)\rangle\right\}, \end{aligned} \tag{175}$$

that in equilibrium, exploiting the property (173), simplifies to

$$R^{(2)}_{\mathcal{O}\mathcal{F}}(t,t_1,t_2) = \frac{1}{2T^2}\left\{\frac{\partial}{\partial t_1}\frac{\partial}{\partial t_2}\langle\mathcal{O}(t)\sigma(t_1)\sigma(t_2)\rangle - \frac{\partial}{\partial t_2}\langle\mathcal{O}(t)B(t_1)\sigma(t_2)\rangle\right\}, \tag{176}$$

with $t > t_1 > t_2$. Note that even at equilibrium there remains a dependence on the quantity B, which explicitly involves the transition rates of the model, making the second order FDR less general than the linear one. This result has several consequences, implying that kinetic effects (combined in the quantity B), irrelevant at linear order, have to be taken into account for the nonlinear behavior of the system, even in equilibrium conditions. This can be exploited to obtain information on the dynamical rules governing the system from the study of the equilibrium second order response, as proposed in [137]. Experiments on colloidal particles in anharmonic potentials confirm the validity of this theoretical approach [138].

Another interesting result recently derived in [139], shows that the second order response function to an external force, in a form similar to Eq. (175), can be related to the thermal response of the system. More specifically, in the case of models described by an overdamped Langevin dynamics, the linear response to perturbations of the noise intensity can be expressed as a nonlinear response to a constant force, leading to the study of nonequilibrium heat capacities and thermal expansions coefficients.

Finally, let us mention that nonlinear response functions also play a crucial role in nonlinear optics and quantum spectroscopy. In particular, in this context, the lack of a unique nonlinear FDR is responsible for the differences between classical and quantum response [140–142].

4.2.4. Applications

The exact relations derived above find many applications in different contexts. Here we briefly discuss some of them, referring the interested reader to the abundant literature on the subject [14,120,68,121].

Zero-field algorithms. In general, in statistical systems, the numerical measure of the linear response function is a very time-demanding task, due to a poor signal to noise ratio. Moreover, the linear regime has always to be checked with repeated measures in a range of different values of the external field. This problem is overcome by FDRs, which allow one to obtain information on the response by the measure of suitable correlation functions, without applying any external perturbation. Moreover, the linear regime is already "built-in" and does not need any further check. These kinds of algorithm have been used in several nonequilibrium contexts, from spin systems showing aging dynamics [143–145,133,146], to glasses [147] and active matter [148]. Note that some of the relations derived for the purpose of a numerical implementation [144,145,147] cannot be applied to real systems because the terms appearing in the unperturbed correlators are only accessible in numerical protocols (e.g. measurement of attempted, but rejected, moves in Monte Carlo simulations) and do not correspond to physical quantities experimentally observable. On the contrary, the form of FDR reported in Eq. (171) involves the quantity B defined in (172), which only depends on the state of the system at a give time, and therefore is an observable quantity (see [146] for an accurate discussion of this issue in the context of spin models).

Harada–Sasa relation. Analogously to the numerical studies, in real experiments, the use of FDRs can simplify the measurement of some quantities which are otherwise not directly accessible. A major example is the Harada–Sasa relation [149–151], where the stationary heat dissipated in the system J_x, is expressed in terms of the violations of the equilibrium FDT in the frequency domain. For the Langevin equation (139), this relation reads

$$J_x = \gamma \left\{ \langle \dot{x} \rangle^2 + \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} [\tilde{C}(\omega) - 2T\tilde{R}'(\omega)] \right\}, \tag{177}$$

where $\tilde{C}(\omega)$ and $\tilde{R}'(\omega)$ are the Fourier transforms of the velocity autocorrelation and the real part of the response function, respectively. This result has been recently generalized to systems evolving according to a Master Equation and in non-stationary states [152], and with separate time scales [153]. These relations turned out to be very useful in different experimental contexts; for instance to evaluate the single-molecule energetics of a rotary molecular motor F1-ATPase [154], or to measure the heat dissipated by an optically confined colloidal particle in an aging gelatin droplet after a fast quench [155,156].

Nonequilibrium extra-terms. More generally, from a theoretical perspective, the off equilibrium FDRs highlight the coupling of the system variables with new quantities, which play a central role in the nonequilibrium dynamics.

A recently proposed line of research focuses on the FDR of class B, pointing out the symmetry properties under time reversal of the different terms [131,132,121,137,157]. In particular, using a path integral formalism, Maes and coworkers have shown that the part of the action functional which is symmetric under time reversal, called dynamical activity (traffic, or "frenesy"), enters the nonequilibrium FDR and plays a role complementary to the entropy production (that is antisymmetric for time reversal). The dynamical activity, which for instance for discrete spin systems takes the explicit form given in Eq. (172), is responsible for the nonequilibrium behaviors [131]. In particular, it is shown that kinetic factors, such as details of the coupling between the system and the environments or symmetric prefactors appearing in the transition rates, play a central role in the characterization of nonequilibrium response.

On the other hand, following the approach of the FDRs of class A, the appearance of extra terms singles out the coupling arising out of equilibrium among degrees of freedom and can be exploited to validate phenomenological models introduced to describe the system under study. An enlightening example of such an approach in the context of granular fluids will be discussed in Section 5.

4.3. Effective temperature: a subtle concept

Within the context of non equilibrium phenomena, the first natural attempts to formulate a general theory start from the concepts well defined in the consolidate equilibrium theory. In particular, the possibility that also out of equilibrium a characterization of the statistical features of the system in terms of a few variables is still feasible, leads to extend familiar concepts as temperature to the non equilibrium realm. As a matter of fact, the question of whether and in what way such a quantity can be properly defined in this context is a fundamental issue in the construction of a general theory of nonequilibrium systems [158,159]. This topic is really vast and we refer the interested reader to the reviews [160,120] for a wider discussion.

In the next subsections we recall how the effective temperature can be introduced via the linear FDR and discuss some specific issues. Explicit applications in the framework of granular systems, turbulence and active matter, will be discussed in Section 5.

4.3.1. Definition of effective temperature

One of the first attempts to define the concept of an effective temperature T_{eff} in systems out of equilibrium is based on the linear FDR [158]. Considering the case of an Ising spin system, let us start by writing the linear susceptibility, using the

FDR (171)

$$\chi(t,t_w) \equiv \int_{t_w}^{t} ds R_{\sigma\mathcal{F}}(t,s) = \frac{\beta}{2}\int_{t_w}^{t} ds \left[\frac{\partial}{\partial s}C(t,s) - \langle\sigma(t)B(s)\rangle\right], \tag{178}$$

where $C(t,s) = \langle\sigma(t)\sigma(s)\rangle$ and t_w is a reference waiting time. We then introduce the quantity

$$\psi(t,t_w) = \int_{t_w}^{t} ds \frac{\partial}{\partial s}C(t,s) = 1 - C(t,t_w), \tag{179}$$

which, for fixed t_w, is a monotonously increasing function of time. Then, it allows us to reparametrize t in terms of ψ and to write $\chi(t,t_w)$ in the form $\chi(\psi,t_w)$, with a little abuse of notation.

In equilibrium, where time translation invariance holds, the dependence on t_w disappears and the parametric representation becomes linear, yielding

$$\chi(\psi) = \beta\psi, \tag{180}$$

with the obvious consequence

$$\beta = \frac{d\chi(\psi)}{d\psi}. \tag{181}$$

Out of equilibrium, the parametric representation is not linear and an effective temperature can be defined by the generalization of the above relation

$$\beta_{eff}(\psi,t_w) = \frac{\partial\chi(\psi,t_w)}{\partial\psi}, \tag{182}$$

with $\beta_{eff} = 1/T_{eff}$.

The underlying idea for the introduction of an effective temperature can be precisely illustrated within the picture of coarsening systems, which after a sudden quench to a low temperature T, evolve from the disordered initial condition at high temperature, via the growth of domains of positive and negative magnetic order [161]. These systems are characterized by a slow relaxation due to the time dependent correlation length which typically increases with a power-law behavior. In order to give a full description of the non equilibrium dynamics, two-time observables have to be considered. In particular, the spin–spin autocorrelation $C(t,t_w)$ and the linear response $R(t,t_w)$ to an external field, in the off-equilibrium aging regime show a separation of time scales. This means that, for t_w sufficiently large, such quantities display quite different behaviors in the short and in the long time regimes, defined by the conditions $t - t_w \ll t_w$ and $t - t_w \gg t_w$, respectively. More specifically, $C(t,t_w)$ first approaches a plateau at M_{eq}^2 in a stationary manner, M_{eq} being the equilibrium magnetization, and then it decays below this value with an explicit dependence on t_w. At fixed t_w, it decays to zero for sufficiently large t.

Such a phenomenology reflects the existence of *fast* and *slow* degrees of freedom in the system. For ordering kinetics, the fast degrees of freedom represent the thermal fluctuations within ordered domains, while the slow ones are the labels of domains, like the spontaneous magnetization within each domain. In this context the off-equilibrium behavior observed during the slow dynamics can be accounted for by the separation of the time scales for different subsets of degrees of freedom. Then, each of these is regarded as in equilibrium with a different virtual thermostat at some appropriate effective temperature, which depends on the time scale and is different from the physical temperature of the real thermostat driving the relaxation. The value of T_{eff} can be therefore inferred by forcing the off-equilibrium linear FDR in the form of the equilibrium FDT, as in Eq. (182). Since in coarsening systems the full response function obeys the asymptotic form

$$\lim_{t_w\to\infty} \chi(\psi,t_w) = \begin{cases} \beta\psi, & \text{for } 0 \le \psi \le 1 - M_{eq}^2 \\ \beta(1 - M_{eq}^2), & \text{for } 1 - M_{eq}^2 < \psi \le 1, \end{cases} \tag{183}$$

from Eq. (182) one obtains

$$\lim_{t_w\to\infty} \beta_{eff}(\psi,t_w) = \begin{cases} \beta, & \text{for } 0 \le \psi \le 1 - M_{eq}^2 \\ 0, & \text{for } 1 - M_{eq}^2 < \psi \le 1. \end{cases} \tag{184}$$

Namely, the effective temperature coincides with the temperature of the thermostat in the short time regime, where the system seems to be equilibrated, while it is drastically different from it in the out of equilibrium regime, at long times, where it takes the value $T_{eff} = \infty$. This result suggests that in the quench below the critical point, while the fast degrees of freedom thermalize, the slow ones do not interact at all with the thermal bath and keep on remaining to the temperature of the initial condition.

In disordered glassy systems the above scenario can show different, more complex behaviors [143]. For instance, in models of fragile structural glasses the effective temperature takes two values: T in the stationary regime, but $T < T_{eff} < \infty$ in the aging one [158,162,163,147,164], see Fig. 10 showing a typical parametric plot χ vs. C. Models of spin glasses are instead characterized by the presence of a continuous range of temperatures in the aging regime, extending from a lower bound $T^* > T$ up to infinity [143].

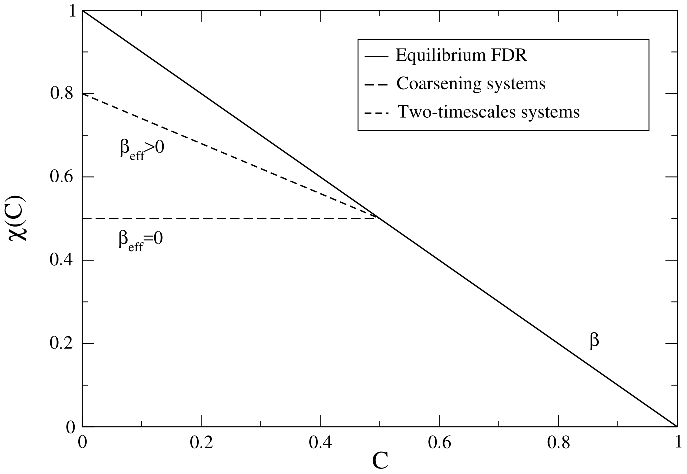

Fig. 10. Schematic example of a parametric plot χ vs. C showing effective temperatures in different systems.

4.3.2. *Effective temperature and Fluctuation Relations*

Fluctuation Relations include recent theoretical results on general symmetry properties of the density probability of quantities such as entropy production, heat and work in non-equilibrium systems. Initially discovered in numerical simulations of molecular fluids under shear [165], these relations have been proven for a large class of models [71,73,166–168], and represent an important step forward in the construction of a general theory for off equilibrium processes (see [68] for a recent review).

We have already encountered an example of these relations, when studying some general properties of non-equilibrium currents in stationary states, see Eq. (163) above. For a system in contact with a single thermostat at temperature T, a small external perturbation $\delta\mathcal{F}_0$ produces a current J_τ, which is proportional to the entropy production associated with the driving via the temperature T, see Eq. (164). In this simple case, the asymmetry function, defined as

$$R(J_\tau) = \frac{1}{\tau}\log\frac{p(J_\tau)}{p(-J_\tau)}, \tag{185}$$

shows a linear behavior $R(J_\tau) = J_\tau\delta\mathcal{F}_0/k_BT$, with slope $\delta\mathcal{F}_0/k_BT$.

In more general situations, defining the fluctuating entropy production Σ_τ as

$$\Sigma_\tau = \log\frac{\mathcal{P}(\{\mathbf{X}\}_0^\tau)}{\mathcal{P}(\mathcal{I}\{\mathbf{X}\}_0^\tau)}, \tag{186}$$

where $\mathcal{P}(\{\mathbf{X}\}_0^\tau)$ represents the probability to observe the trajectory $\{\mathbf{X}\}_0^\tau$ in the time interval $[0,\tau]$, and $\mathcal{I}$ denotes the time-inversion operator, one can prove, under quite general assumptions, that the density distribution of Σ_τ, $p(\Sigma_\tau)$, satisfies the following relation

$$\log\frac{p(\Sigma_\tau)}{p(-\Sigma_\tau)} = \Sigma_\tau. \tag{187}$$

The properties of Σ_τ have been investigated in great detail in several cases. In particular, the study of the distribution $p(\Sigma_\tau)$, in many experiments and numerical works, revealed a non-universal form and the thermodynamic interpretation in terms of macroscopic heat, work and entropy is, in general, an open issue. For practical purposes, a central point relies on the fact that the definition in Eq. (186) is not always useful, due to the difficulty to get access directly to Σ_τ (for instance in experiments, where usually measures are constrained to somehow coarse-grained quantities), and one has to resort to an expression based on phenomenological grounds. In these cases, a possible way out is to assume that the entropy production is the heat exchanged by the system with the environment (or the work applied on the system), divided by a parameter playing the role of an effective temperature. However, extreme care must be used, because "reasonable" candidates for this parameter, such as the bath temperature or the (rescaled) kinetic energy of some degrees of freedom, could be misleading. Therefore, an accurate analysis of the model is necessary, as highlighted in different non-equilibrium situations, where, for instance, the system is coupled with thermostats at different temperatures, or where the action of the thermal bath is irrelevant, as in athermal systems [113,169–172]. An explicit example in the context of granular fluids will discussed in Section 5.3.

In the context of non-stationary, slow relaxing systems, which cannot equilibrate even in the absence of external driving, the issue of the relation between the effective temperature defined through the FDR and the Fluctuation Relations for the entropy production has been addressed in [173] for kinetically constraint models, and in [174] for mean-field glassy models and coupled Langevin equations. Other studies focused on the symmetry properties of the distribution of the heat exchanged by the system with the bath during the relaxation after a quench to the low temperature phase, in spin glass models and for Brownian oscillators [175–177].

4.3.3. Some caveats on effective temperature

The real usefulness of the concept of effective temperature and its range of applicability is still under debate [120]. The first issue is concerned with the properties satisfied by the standard equilibrium temperature. In fact, in order to get the status of temperature, the new quantity ought to satisfy the properties imposed by thermodynamics. For non-equilibrium stationary systems, characterized by the presence of currents due to the simultaneous action of driving and dissipation, forces of non-thermal origin are also present, and one wonders whether the observed fluctuations of the relevant quantities under investigation can be described through a single parameter playing the role of an effective temperature. For instance, granular media – as discussed in Section 5 – are usually subjected to vibration and dissipate energy in the particle–particle collisions, whereas systems of active particles present an internal conversion of energy into directed motion. In these cases, an equilibrium-like description of the system is then reliable if this parameter satisfies some requirements, dictated by the equilibrium picture for Brownian fluctuations. In particular, it should appear (i) in the amplitude of the effective noise in the system, (ii) in the proportionality constant between the linear response of an observable and the corresponding correlation function, (iii) in the variance of the distribution probability of relevant quantities (such as energy), if Gaussian. In Section 5 we will discuss in more details these issues.

Another important requirement is that the effective temperature ought to be independent of the observable used to construct the correlations and responses functions appearing in the FDR. This condition seems quite strong and turns out to be not satisfied in different systems [178–180]. However, within the mean-field theory, the effective temperature has been shown to display many of the required properties [158]. In particular, within a time sector, it is the reading which would be shown by a thermometer tuned to respond on that timescale. Moreover, it is independent of the observable used to construct the FDR. Conversely, in non-mean field models, such properties are not yet well established. Nonetheless, the concept remains quite useful and suggestive.

The presence of a separation of time scales in the system is certainly a necessary (but not sufficient) condition for the application of the concept of effective temperature. For instance, it is possible to chose the parameters in the model introduced in Eqs. (142) in order to have a scenario with time-scale separations which is quite different from that observed in aging glassy systems, as accurately discussed in [116]. In the general case, the response–correlation parametric plot may be more difficult to read, showing intermediate "effective temperatures", as well as a more complex nonlinear shape.

A preliminary exploration of another open end in the important question of how general the effective temperature can be, focused on whether it is possible to extend this definition to the nonlinear FDR, consistently with what it is done in the linear case. In fact, if such a concept actually provides important information in the characterization of the off-equilibrium behavior, one expects it to be independent of the order of the FDR used to construct it. In [134], it has been shown that the concept of effective temperature can be extended to the second order, drawing a consistent picture with that obtained in the linear case, within the context of non disordered coarsening systems. The results obtained provide a further support to the idea that the effective temperature can play an interesting role in the description of the off equilibrium dynamics of such systems. It would be very interesting to apply the same line of reasoning presented in [134] to the case of disordered systems, such as structural or spin glasses.

Finally, let us note that the concept of effective temperature has also been revisited within the theoretical framework for linear response proposed by Maes and coworkers [181]. From this perspective, the effective temperature is given by the ratio between the dynamical activity and the entropic terms, measuring the weight of "active states" in the dynamics.

Explicit examples of the application of an effective temperature, together with a critical analysis of its practical relevance, will be discussed in Section 5 in different contexts, from granular systems to turbulence and active matter.

5. Toward a temperature for non-Hamiltonian systems?

5.1. Thermodynamics and chaos

About three decades ago, large deviations theory inspired a sort of "thermodynamic formalism" for chaotic systems and fully developed turbulence [182–186]. For sake of completeness we briefly discuss, avoiding too technical details, such a topic stressing its relation with statistical mechanics [187].

5.1.1. Multifractal measures for chaotic attractors

Let us consider a smooth measure $\mu(\mathbf{y})$. For any $\mathbf{x}$, one has

$$\int_{|\mathbf{x}-\mathbf{y}|<\ell} d\mu(\mathbf{y}) \sim \ell^{d},$$

where d is the (integer) dimension of the phase space. In the case of a chaotic attractor one has a singular behavior: in the simplest case (homogeneous fractal measure) one has

$$\int_{|\mathbf{x}-\mathbf{y}|<\ell} d\mu(\mathbf{y}) \sim \ell^{D_F},$$

where **x** belongs to the attractor, and D_F is the fractal dimension. On the other hand, usually the measure on a chaotic attractor (as well as in fully developed turbulence) is not homogeneous, and a single fractal dimension is not enough to give a complete description of the singularities.

Consider a partition of the attractor in cells (boxes) $\{\Lambda_i(\ell)\}$ of size ℓ, and introduce the probability to stay in the ith cell:

$$P_i(\ell) = \int_{\Lambda_i(\ell)} d\mu(\mathbf{x}). \tag{188}$$

Let us now introduce Renyi's dimensions d_q (where q is a real number) [184,186]:

$$\mathcal{M}_q(\ell) = \sum_i P_i(\ell)^q \sim \ell^{(q-1)d_q}, \tag{189}$$

or, in a more formal way

$$d_q = \lim_{\ell\to 0} \frac{1}{q-1} \frac{\ln \mathcal{M}_q(\ell)}{\ln \ell}.$$

It is possible to show that d_q must be a non increasing function, and, in addition, for $q = 0$ one has $d_0 = D_F$. Of course if the measure is homogeneous one has $d_q = D_F$, and more d_q is far from the horizontal line D_F, more the dishomogeneity of the measure is strong.

The information dimension d_1 is the most relevant one: for almost any **x** on the attractor one has

$$\int_{|\mathbf{x}-\mathbf{y}|<\ell} d\mu(\mathbf{y}) \sim \ell^{d_1}.$$

There exists a nice way to describe the singularities of the measure using a procedure which follows an approach in terms of the large deviation theory and quite similar to that one used in statistical mechanics. Such an approach is called multifractal [184–186]: the starting point consists in grouping all the boxes having the same singularity index α, i.e. all the i such that $P_i(\ell) \sim \ell^\alpha$. Let $dN(\alpha, \ell)$ be the number of boxes with crowding index in the infinitesimal interval $[\alpha, \alpha + d\alpha]$, we can rewrite the quantity (189) as an integral over α

$$\mathcal{M}_q(\ell) \sim \int \ell^{\alpha q} dN(\alpha, \ell), \tag{190}$$

where we have used the scaling relation $P_i(\ell) \sim \ell^\alpha$. Let us now introduce the multifractal spectrum of singularities, i.e. the fractal dimension $f(\alpha)$ of the subset with singularity α: in the limit $\ell \to 0$ the number of boxes with crowding index α, scales as

$$dN(\alpha, \ell) \sim \ell^{-f(\alpha)} d\alpha. \tag{191}$$

Therefore we have

$$\mathcal{M}_q(\ell) \sim \int_{\alpha_m}^{\alpha_M} \ell^{[q\alpha - f(\alpha)]} d\alpha, \tag{192}$$

where α_m and α_M are the minimum and maximal value of α respectively, corresponding to the strongest (α_m) and weakest (α_M) singularity. In the limit $\ell \to 0$ one has

$$d_q = \frac{1}{q-1} min_\alpha \{q\alpha - f(\alpha)\} = \frac{1}{q-1}[q\alpha_*(q) - f(\alpha_*(q))],$$

where $\alpha_*(q)$ is the solution of

$$\frac{d}{d\alpha}[q\alpha - f(\alpha)] = 0.$$

It is easy to see that for $q \gg 1$ one has $\alpha_*(q) \simeq \alpha_m$, i.e. the strongest singularity, while for $q \ll -1$ the weakest singularity is selected $\alpha_*(q) \simeq \alpha_M$. At varying q, from the value d_q we are able to understand the weight of the singularities α.

5.1.2. Fluctuation of the finite time Lyapunov exponent

A quite similar approach has been used to describe the statistical features of the fluctuations of the finite time Lyapunov exponent [183,184,186]. Let us introduce the fluctuating quantity γ defined as

$$\gamma(\tau, t) = \frac{1}{\tau} \ln \left[\frac{|\mathbf{w}(t+\tau)|}{|\mathbf{w}(t)|} \right],$$

where $\mathbf{w}(t)$ is the tangent vector in phase space (basically the difference between two very close trajectories when such a difference is very small); $\gamma(\tau, t)$ indicates the local, growth rate of the tangent vectors within the time interval $[t, t + \tau]$. The large fluctuations of γ can be quantitatively characterized in terms of the so called generalized exponents $L(q)$:

$$\langle e^{q\gamma\tau} \rangle \sim e^{L(q)\tau},$$

where τ is large. It is easy to show that the Lyapunov exponent can be expressed in terms of $L(q)$:

$$\lambda = \lim_{\tau\to\infty} \langle \ln \gamma \rangle = \left.\frac{dL(q)}{dq}\right|_{q=0}.$$

The large deviation theory suggests the shape, at large τ, of the probability distribution density:

$$P(\gamma, \tau) \sim e^{-S(\gamma)\tau}, \tag{193}$$

where $S(\gamma)$ is a Cramer's function (see Section 2.2), with $S(\lambda) = 0,\ S(\gamma \neq \lambda) > 0$ and $d^2S/d\gamma^2 > 0$. Using Eq. (193) we have

$$\langle e^{q\gamma\tau}\rangle = \int e^{\tau q\gamma} P(\gamma, \tau) d\gamma \sim \int e^{\tau[q\gamma - S(\gamma)]} d\gamma,$$

and the Laplace's method shows how the generalized Lyapunov exponents are given by a Legendre transformation [183,184,188,189]

$$L(q) = max_\gamma [q\gamma - S(\gamma)].$$

Of course for $L(q)$ and $S(\gamma)$ we can repeat in a straightforward way the same remarks previously discussed for d_q and $f(\alpha)$.

5.1.3. Analogies with the equilibrium statistical mechanics

Let us now briefly remind that from the statistical mechanics of a system of $N \gg 1$, we can write the partition function $\mathcal{Z}$ as

$$\mathcal{Z}(\beta, N) = \int e^{-N[\beta e - s(e)]} d\, e = e^{-N\beta F(\beta)}\ ,$$

being $e = E/N$ the energy for particle, $s(e)$ the microcanonical entropy and $F(\beta)$ the free energy per particle. We have $F(\beta) = e_* - Ts(e_*)$, where e_* depends on the temperature, and is selected by the minimum of $e - Ts(e)$. We can say that varying the temperature T, we can "explore" the phase space of the Hamiltonian.

It is not difficult to realize the strong analogies among the multifractal description of singular measure, fluctuations of Lyapunov exponent and equilibrium statistical mechanics [184,186,189]. The following table summarizes the correspondences.

Correspondences among multifractal measures (MM), fluctuations of the Lyapunov exponent (FL), and statistical mechanics (SM)

MM	FL	SM
$\ell \to 0$	$\tau \to \infty$	$N \to \infty$
α	γ	e
$\mathcal{M}_q(\ell)$	$e^{L(q)\tau}$	$\mathcal{Z}(\beta, N)$
$f(\alpha)$	$S(\gamma)$	$s(e)$
q	q	β
$(q-1)d_q$	$L(q)$	$\beta F(\beta)$

We conclude this subsection noting that in MM (as well in FL) q is a free parameter, which does not appear in $\mu(\mathbf{x})$ (as well as in $P(\gamma, t)$), and can be changed in order to explore the typical statistical features (for $|q| < O(1)$), or extreme ones (for $|q| \gg 1$). Since in SM β appears in the probability distribution of e, one could conclude that the above analogies are just formal.

On the contrary even in SM it is possible, following a procedure quite similar to that one used in MM (as well as FL), to investigate the statistical features at any β computing the mean value of suitable observables at a given β_0. For instance it is possible to compute the free energy per particle $F(\beta)$ performing an average with the canonical probability density at β_0. For $\beta = \beta_0 + \Delta\beta$ a trivial computation gives

$$e^{-\beta NF(\beta)} = \int e^{-\beta H(\mathbf{x})} d\,\mathbf{x} = \int e^{-\beta_0 H(\mathbf{x})} e^{-\Delta\beta H(\mathbf{x})} d\,\mathbf{x} = e^{-\beta_0 NF(\beta_0)} \langle e^{-\Delta\beta H(\mathbf{x})}\rangle_{\beta_0}\ ,$$

where $\langle(\ )\rangle_{\beta_0}$ indicates the average according to the canonical distribution at β_0:

$$\rho_{\beta_0}(\mathbf{x}) = e^{\beta_0 NF(\beta)}\, e^{-\beta_0 H(\mathbf{x})}\ .$$

The idea of the previous result is the so called *data reweighting* technique used in Monte Carlo numerical computations [190].

5.2. Statistical hydrodynamics

In Section 3 we already discussed the statistical mechanics of a system of point vortices in $2d$ incompressible fluids. Such a system is Hamiltonian, therefore, although the Hamiltonian has not the usual shape (37), it is enough to use the standard statistical mechanics.

5.2.1. Perfect fluids

Usually, apart from a few special cases, a fluid (even in the absence of viscosity) does not obey Hamiltonian equations. In spite of this, one can easily build an equilibrium statistical mechanical approach to the Euler equation: it is enough to follow straightforwardly the path used to obtain the micro-canonical formalism [191,93,185].

Let us consider a $3d$ perfect fluid, i.e. with zero viscosity, and without external forcing, in a cube of edge L with periodic boundary conditions, so that the velocity field $\mathbf{u}(\mathbf{x}, t)$ can be expanded in Fourier series as

$$u_j(\mathbf{x}, t) = \frac{1}{L^{3/2}} \sum_{n_1,n_2,n_3} e^{i(k_1x+k_2y+k_3z)} v_j(\mathbf{k}, t), \tag{194}$$

where

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3),$$

being n_j integer numbers. In addition we introduce an ultraviolet truncation $v_j(\mathbf{k}) = 0$ for $|\mathbf{k}| > K_M$, being K_M the maximum allowed wave vector.

Because of the incompressibility condition ($\nabla \cdot \mathbf{u} = 0$) and the fact that the velocity field is real, the variables $\{v_j(\mathbf{k}, t)\}$ are not independent, and indeed one has

$$\sum_{j=1}^{3} k_j v_j(\mathbf{k}, t) = 0 \quad \text{and} \quad v_j(-\mathbf{k}, t) = \left[v_j(\mathbf{k}, t)\right]^{\star}, \tag{195}$$

where $\star$ denotes complex conjugation. Therefore it is useful to introduce a new set of real variables $\{X_n(t)\}$ which replace $\{v_j(\mathbf{k}, t)\}$, and obey an ordinary differential equation:

$$\frac{dX_n}{dt} = \sum_{m,\ell} M_{n,m,\ell} X_m X_\ell, \; n = 1, 2, \ldots, N. \tag{196}$$

From Euler's equation we have the following properties: $M_{n,m,\ell} = M_{n,\ell,m}$ and $M_{n,m,\ell} + M_{m,\ell,n} + M_{\ell,n,m} = 0$: for details see [93]. Because of the introduction of the ultraviolet truncation, we have a finite system of equations, and therefore one avoids the infinite energy problems of the classical field theory.

Since Eq. (196) conserves the volume in the phase space (Liouville theorem)

$$\sum_n \frac{\partial}{\partial X_n} \frac{dX_n}{dt} = 0, \tag{197}$$

and in addition one has the (energy) conservation law

$$\frac{1}{2} \sum X_n^2 = E.$$

It is straightforward, following the usual approach of equilibrium statistical mechanics, i.e. assuming that ergodicity holds, to obtain the microcanonical distribution:

$$P_{mc}(\{X_n\}) \propto \delta\left(\frac{1}{2} \sum X_n^2 - E\right). \tag{198}$$

In addition, the $N \to \infty$ limit yields the canonical distribution

$$P_c(\{X_n\}) \propto \exp\left[-\left(\frac{\beta}{2} \sum X_n^2\right)\right], \tag{199}$$

and therefore

$$\langle X_n^2 \rangle = \frac{2E}{N} = \frac{1}{\beta}. \tag{200}$$

Let us note that, although the system is not Hamiltonian, we have a well defined temperature (which can be identified with $1/\beta$), which, as in the usual statistical mechanics for Hamiltonian systems, is the relevant parameter for the probability distribution in phase space.

It is remarkable that for perfect fluids one has a rather simple fluctuation–dissipation relation. From the general result discussed in Section 4, one has

$$\overline{\delta X_n(t)} = \sum_j R_{n,j}(t) \delta X_j(0),$$

and, in the limit $N \gg 1$,

$$R_{n,j}(t) = \frac{\langle X_n(t) X_n(0) \rangle}{\langle X_n^2 \rangle} \delta_{nj}. \tag{201}$$

Let us stress an important technical aspect: although the probability density distribution for $\{X_n\}$ is Gaussian, the dynamics is not linear and the shape of each correlation $\langle X_n(t)X_n(0)\rangle$ is not trivially exponential [192,14].

The previous procedure, used for 3d perfect fluids, can be easily generalized to the two-dimensional case. In such a system, in addition to the energy, there is a second conserved quantity, the enstrophy:

$$\Omega = \frac{1}{2}\sum_n k_n^2 X_n^2. \tag{202}$$

Therefore the microcanonical distribution should be defined on the surface in which both energy and enstrophy are constant:

$$P_{mc}(\{X_n\}) \propto \ \delta\Big(\frac{1}{2}\sum X_n^2 - E\Big)\,\delta\Big(\frac{1}{2}\sum k_n^2 X_n^2 - \Omega\Big), \tag{203}$$

and, in the large N limit, we have the canonical distribution

$$P_c(\{X_n\}) \propto \exp\left[-\Big(\frac{\beta_1}{2}\sum X_n^2 + \frac{\beta_2}{2}\sum k_n^2 X_n^2\Big)\right], \tag{204}$$

with

$$\langle X_n^2\rangle = \frac{1}{\beta_1 + \beta_2 k_n^2}. \tag{205}$$

Now, due to the presence of two conservation laws, we have two "temperatures", $1/\beta_1$ and $1/\beta_2$.

Let us open a short parenthesis on the possibility to have "more than one temperature": the presence of a unique temperature in the typical cases of the statistical mechanics is due to the fact that usually one considers systems with only one conservation law (energy). However in the presence of another conservation law, a "second temperature" appears in a quite natural way [193]. For instance in a system with central forces among particle pairs in a cylindrical vessel with elastic walls, the energy and the angular momentum along the axis of the cylinder are constant, resulting in a microcanonical distribution similar to Eq. (203).

Beyond 3d and 2d Euler equations, in hydrodynamics there are other interesting systems described by inviscid ordinary differential equations, such as Eq. (196), with quadratic invariants, for which the Liouville theorem holds (e.g. in magnetohydrodynamics and geostrophic flows). Detailed numerical simulations show that such systems are ergodic and mixing if N is large: arbitrary initial distributions of $\{X_n\}$ evolve toward the Gaussian (199) or (204), and the statistical mechanics predictions are in perfect agreement with the actual results, see [93].

5.2.2. *Viscous fluids*

In the presence of viscosity $\nu > 0$, Eq. (196) must be modified:

$$\frac{dX_n}{dt} = \sum_{m,\ell} M_{n,m,\ell} X_m X_\ell - \nu k_n^2 X_n + f_n, \qquad n = 1, 2, \dots, N. \tag{206}$$

The external forcing f_n is necessary in order to have a statistical steady state. Apparently in the limit $\nu \to 0$, and $f_n \to 0$, the system (206) can sound rather similar to the perfect fluids. The actual situation is rather different: as paradigmatic example we can remind that in 3d the limit $\nu \to 0$ of the Navier–Stokes equations, is singular and cannot be interchanged with the limit $K_M \to \infty$. Therefore the statistical mechanics of an inviscid fluid has a rather limited relevance for the Navier–Stokes equations at very high Reynolds numbers [194].

Let us briefly remind the basic phenomenology of the fully developed turbulence: in the $\nu \to 0$ limit and in the presence of forcing at large scale (small k), one has an intermediate range, called the inertial range, where practically there are neither pumping nor dissipation. In addition there is a strong departure from equipartition (200): instead of $\langle X_n^2\rangle = const.$ one has $\langle X_n^2\rangle \sim k_n^{-\gamma}$ where $\gamma \simeq 11/3$, the value $\gamma = 11/3$ corresponding to the Kolmogorov spectrum.

Let us stress that while the statistical mechanics of perfect fluids has an equilibrium behavior, the statistical features of turbulence belongs to the non equilibrium realm. There is an energy flux (cascade in the turbulent jargon) from large scale, i.e. small k where the energy is injected, to small scale, where the energy is dissipated by the molecular viscosity [194,195,185].

Because of viscosity, the system (206) is dissipative, and therefore the measure on the attractor is singular, see [185]. On the other hand the above point is not the main difficulty: one can avoid the mathematical trouble of the singular measure simply by adding a small noise. With the introduction of a noisy term, which is quite natural from a physical point of view, we have a Langevin equation, and therefore a Fokker–Planck equation whose stationary solution for the PdF is surely non singular and continuous with respect to the Lebesgue measure, but, unfortunately its shape is not known.

Although from the generalized fluctuation–dissipation relation, see Section 4, we can say that there exists a relation linking response and a (suitable) correlation, i.e.

$$R_{n,j}(t) = \langle X_n(t) F_j(\mathbf{X}(0))\rangle,$$

where the functions $F_j(\,)$ depend on the shape of the stationary PdF, as a matter of fact the statistical mechanics of turbulence is still a difficult open problem and also the existence of an FDR is not particularly useful at a practical level.

5.2.3. Difficulties for the introduction of temperature

Let us note that in all the cases where we are able to introduce, in a consistent way, the temperature, such a quantity plays the role of the (unique) parameter appearing in the probability distribution, with a known specific functional shape. For equilibrium Hamiltonian systems one has

$$\rho(\mathbf{x}) = \frac{1}{Z} e^{-\beta H(\mathbf{x})} \ .$$

In a similar way in systems ruled by a Langevin equation with a gradient drift $-\nabla V(\mathbf{x})$,

$$\frac{dx_n}{dt} = -\frac{\partial V}{\partial x_n} + \sqrt{\frac{2}{\beta}}\eta_n \, , \tag{207}$$

one has

$$\rho(\mathbf{x}) = \frac{1}{Z} e^{-\beta V(\mathbf{x})} \ .$$

The possibility to introduce a temperature from the comparison between response functions and correlation function is a consequence of the specific shape of the PdF, e.g. for Langevin equation (207) one has

$$R_{n,j}(t) = -\beta \frac{d}{dt} \langle x_n(t) x_j(0) \rangle = -\beta \left\langle x_n(t) \frac{\partial V(\mathbf{x}(0))}{\partial x_j(0)} \right\rangle \ . \tag{208}$$

On the contrary, for turbulence the introduction of the concept of temperature does not appear as an easy task even assuming a simple relation between response function and correlations. For instance in the direct-interaction-approximation (DIA) developed by Kraichnan [196–198] one assumes:

$$R_{n,n}(t) = \frac{\langle X_n(t) X_n(0) \rangle}{\langle X_n^2 \rangle} \, , \tag{209}$$

as a consequence, in such an approximation, the PdF is a Gaussian function. In spite of the fact that the above relation appears identical to (201) for the perfect fluid, there is an important difference. For the perfect fluids $\langle X_n^2 \rangle = 1/\beta$, so β is the unique parameter in the (Gaussian) PdF. On the contrary in turbulent flows the scenario is rather different, even assuming the validity of the DIA, we have a Gaussian PdF for the $\{X_n\}$ where $\langle X_n^2 \rangle$ depend on k_n, e.g. in the inertial range $\langle X_n^2 \rangle \sim k_n^{-\gamma}$. Therefore also the validity of a fluctuation–response relation and a Gaussian PdF does not imply the possibility to introduce a temperature-like quantity. Of course we can introduce a sort of "effective temperature" T_n for each n, simple writing the relation (209) in the form

$$R_{n,n}(t) = \frac{\langle X_n(t) X_n(0) \rangle}{T_n} \, , \tag{210}$$

in other words $\langle X_n^2 \rangle = T_n$, now the "temperatures" T_n have a rather trivial role: they are the variance of the $\{X_n\}$.
Let us stress that the above difficulty does not originate from the "complexity" of the turbulence. This is quite clear noting that the same difficulty is present also in the case of a generic linear Langevin equation, i.e. different from Eq. (207), whose PdF is Gaussian but the relation (208) does not hold, and therefore it is not possible to introduce a temperature, see the discussion in Section 4. In such a system the PdF is a multivariate Gaussian

$$P(\mathbf{X}) = \frac{1}{(2\pi)^{N/2} \sqrt{Det\ \sigma}} e^{-\frac{1}{2}\sum_{ij} (\sigma^{-1})_{ij} x_i x_j} \ ,$$

and, since the matrix $\boldsymbol{\sigma}$ is symmetric we can perform a linear transformation:

$$Z_j = \sum_{i=1}^{N} C_{ji} X_i$$

in such a way that the PdF is

$$P(\mathbf{Z}) = \frac{1}{(2\pi)^{N/2} \sqrt{Det\ \sigma}} e^{-\sum_{ij} \frac{Z_i^2}{2a_i}}$$

where $\{a_i\}$ are the eigenvalues of $\boldsymbol{\sigma}$. Of course Eq. (210) holds, and one as that each a_i can be (naively) considered as the "effective temperature", but we are not able to see any physical meaning in the above result.

5.3. Granular systems

Granular materials are important systems which appear in our everyday life as well as in many industrial applications, posing interesting and partly unanswered questions to statistical physics, geophysics and technology [61,199–201]. One of those questions is the possibility of defining a suitable and meaningful concept of "granular temperature" [202].

A granular medium is an ensemble of "grains", which are macroscopic objects interacting among each other, and with the surroundings, through non-conservative forces. Being almost undeformable, a granular particle is fairly described by a solid of mass m, for instance a sphere of radius r, and fully characterized by the position and velocity of its center of mass, and (possibly) angular momentum. In a collision, a fraction of the kinetic energy associated with such macroscopic variable is transferred into internal degrees of freedom and is irreversibly lost. Several orders of magnitude separate the average energy of internal thermal fluctuations at room temperature - $k_B T \sim 5 \cdot 10^{-21}$ J - and the macroscopic energy of a grain: for instance $mgr \sim 10^{-5}$ J for a steel sphere with $r = 2$ mm, g being the gravity acceleration. For this reason, until a few decades ago, granular matter was commonly described as athermal. Recently a different point of view has been accepted, where fluctuations have a role and can be characterized by some kind of temperature, which is however very different – in nature and in value – from the temperature associated with a reservoir at equilibrium, such as the surrounding environment (air, walls of the container, etc.).

Granular media can be in very different "phases", depending on boundary conditions, including external forcing: under violent shaking and with enough allowed volume, one may realize a granular "gas", but when allowed volume and/or the intensity of shaking are reduced, the observed regime is much closer to dense liquids or even slowly deforming solids [203]. Temperature can be defined in different ways, or may have different meaning, depending upon the dominant regime: for this reason we separate the discussion in three sections.

5.3.1. Granular gases

A granular gas is realized when the packing fraction (percentage of container volume which is occupied by grains) is small, typically of the order of 1% or less. In such a situation one can assume for the interactions instantaneous inelastic binary collisions. In the most common model in a collision between particles of mass m_1 and m_2, the velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ are changed into $\mathbf{v}'_1$ and $\mathbf{v}'_2$ with the rule

$$\mathbf{v}'_1 = \mathbf{v}_1 - m_2 \frac{1+\alpha}{m_1+m_2}[(\mathbf{v}_1 - \mathbf{v}_2)\cdot \hat{\mathbf{n}}]\hat{\mathbf{n}} \tag{211}$$

$$\mathbf{v}'_2 = \mathbf{v}_2 + m_1 \frac{1+\alpha}{m_1+m_2}[(\mathbf{v}_1 - \mathbf{v}_2)\cdot \hat{\mathbf{n}}]\hat{\mathbf{n}}, \tag{212}$$

where $\hat{\mathbf{n}}$ is the unit vector joining the center of particle 1 to the center of particle 2 and $\alpha \in [0, 1]$ is the restitution coefficient, which is 1 in the limit of elastic interactions [61].

Since experiments are usually done under gravity, in order to keep the packing fraction small everywhere in the allowed volume it is necessary to shake the container with accelerations much larger than gravity [61,204,205]. Many theoretical models (in simulations or analytical calculations, for instance kinetic theories) of granular gases exist. Here we list three main categories:

(1) cooling granular gases, which are obtained by initializing the velocities and positions of the particles as in a gas (for instance at equilibrium) and leaving the total kinetic energy dissipate under the effect of inelastic collisions [206–208];

(2) boundary driven granular gases, obtained by considering the presence of at least one wall which injects energy into the gas (e.g. in the fashion of a thermostat, or by a periodic vibration, etc.);

(3) bulk driven granular gases, where each particle is constantly in contact with some source of energy, for instance a monolayer of grains hopping above a vibrating rough plate [209,210].

The first category is in the class of non-stationary states (the ultimate fate is a gas of non-colliding particles, possibly at rest) and is considered very difficult to be observed in a laboratory. The second category is close to many experimental realizations with shaken containers, and has the peculiarity of leading to steady states which are non-homogeneous in the spatial distribution of positions and velocities of grains, with interesting emerging patterns [211–213]. The third category results in spatially homogeneous steady states and has been recently realized in experiments [214–216].

In all those examples the lack of a Hamiltonian structure (due to the presence of non-conservative interactions) is the main obstacle to the realization of an equilibrium-like description and therefore of a statistical mechanics definition of temperature. The easiest and effective replacement is the kinetic temperature [202,217–219], often called "granular temperature"

$$k_B T_g = \frac{m\langle|\mathbf{v}|^2\rangle}{d}, \tag{213}$$

with $\mathbf{v}$ the velocity of each particle, d the dimensionality of space and k_B is usually replaced with 1, as we do in the following. The average can have several possible meanings, depending on the considered case: in an experimental steady state it can be the empirical average cumulating observations made upon many particles and many different instants; in a theoretical study it can be realized with a theoretical probability distribution which can be time-dependent (as in cooling cases) or steady (as in driven systems), and in the latter case is naturally replaced by an average over time.

The concept of kinetic granular temperature is grounded in kinetic theory, which gives a description of granular gases through the inelastic Boltzmann equation [208,220] and its hydrodynamic limit (slow variations of the fields in space and time) [221]. The study of inelastic Boltzmann equation shows that deviations from a Maxwellian are inevitable in the presence of inelastic collisions, but are small in many practical situations: therefore one may characterize the statistics of velocities through a second moment (proportional to granular temperature T_g) and a kurtosis excess (or second Sonine coefficient) which is small in many regimes [208,220]. Granular hydrodynamics introduces a field $T_g(\mathbf{x},t)$ which is assumed to change slowly in space and time (with respect to mean free path and mean free time) obeying an equation which is similar to the analogous equation for molecular (elastic) gases, but with two crucial differences: (1) a sink term representing the loss of kinetic energy due to collisions, and (2) a conduction term which is proportional to the *density* gradient (in addition to the usual Fourier term) [222]. While energy is globally conserved in molecular gases, the same is not true in granular gases, and for this reason the assumption of slow variation of the temperature field has a smaller range of validity, restricting the application of granular hydrodynamics to small inelasticities.

Another challenge to the concept of granular temperature, even in granular gases, is posed by the breakdown of the validity of the equipartition of energy among degrees of freedom. This has been observed comparing the granular temperature of different species in a granular mixture, as well as comparing the kinetic energy along different Cartesian components in a single species gas under non-isotropic conditions [223–228]. Primarily for this reason, it is not believed that granular temperature contains more information than just a description of the (local) average kinetic energy. In the following we discuss some exception to this general view.

The role of granular temperature in the description of energy fluctuations has solicited further questions about its role in linear response relations [116,229–238]. While in cooling granular gases linear response is not described by the equilibrium Fluctuation–Dissipation relation [230,235], the case is considerably simpler in driven granular gases, where such a relation is satisfied, provided that the canonical temperature is replaced with granular temperature T_g [116,229,231,232,236]. For instance, a granular tracer under the action of a weak perturbing force in a dilute driven granular system satisfies the Einstein relation

$$R_{vF}(t) = \frac{\langle v(t)v(0)\rangle}{T_g}. \tag{214}$$

Such a result is quite interesting as, on the basis of the generalized Fluctuation–Response relation (see Section 4.2) and of the non-Gaussian distribution of velocities, one would expect a correction to it. Nevertheless, in many different dilute cases, such corrections are not observed or – in certain solvable models – can even be proven to vanish [116]. A possible explanation to such a general result is the following. In the dilute limit, *molecular chaos* is likely to be valid, which – for statistical purposes (and provided that the gas is in a bulk-driven steady state) – is equivalent to say that a particle 1 meets particle 2 only once. As a matter of fact the inelastic rule in Eq. (211), if restricted only to particle 1 (that is, disregarding the fate of particle 2) is equivalent to an *elastic* collision with effective masses m_1' and m_2' such that [239]

$$\frac{m_1'}{m_2'} = \frac{2}{1+\alpha}\left(\frac{m_1}{m_2}+1\right) - 1. \tag{215}$$

This is equivalent to say that – if the information about the second particle is lost – then for the first particle it is irrelevant if the collision is elastic or not.

A phenomenology which is consistent with the above observation has been seen studying the dynamics of a massive intruder [240], i.e. a (spherical) granular particle with mass M diffusing in a stochastically driven granular gas of particles of mass $m \ll M$. It is not important the exact mechanism of driving, provided that it guarantees in a finite time a relaxation to a dilute and spatially homogeneous steady state of the gas at granular temperature T_g, as it occurs for instance in the model introduced in [210]. For simplicity we assume that the intruder does not interact directly with the driving mechanism (in the more realistic case of interaction with the bath, additional terms appear in the following formula). In appropriate limits (large number of granular bath particles and dilute limit) the massive tracer does not influence appreciably the statistics of the surrounding granular gas and therefore its statistics is governed by a Lorentz–Boltzmann equation. Such an equation may be further simplified in the limit of large intruder's mass, i.e. basically truncating an expansion in powers of (small) m/M [241]. This procedure, which has given results in fair agreement with numerical simulations, has shown that the dynamics of the intruder's velocity $\mathbf{V}(t)$ is fairly described (in the large mass limit) by the following Ornstein–Uhlenbeck process:

$$M\dot{\mathbf{V}}(t) = -\Gamma\mathbf{V}(t) + \mathcal{E}(t), \tag{216}$$

with $\mathcal{E}(t)$ an unbiased white Gaussian noise and

$$\Gamma = (1+\alpha)mf_c, \tag{217}$$

$$\langle \mathcal{E}_i(t)\mathcal{E}_j(t')\rangle = 2\Gamma\frac{1+\alpha}{2}T_g\delta_{ij}\delta(t-t'), \tag{218}$$

where α is the restitution coefficient for the intruder–particle collisions, f_c is the frequency of collisions experienced by the intruder and T_g is the granular temperature of the surrounding gas. Both f_c and T_g are determined by the average number density of the gas, the dimension of the particles and the parameters of the external driving mechanism [240]. Note that Eq. (216) leads to

$$T_{tr} = M\frac{\langle |V|^2\rangle}{d} = \frac{1+\alpha}{2}T_g, \tag{219}$$

where we have defined the tracer granular temperature T_{tr}. Interestingly, formula (219) is equivalent to *equipartition*

$$M'\frac{\langle |V|^2\rangle}{d} = T_g, \tag{220}$$

with $M' = \frac{2}{1+\alpha}M$ which is the large M limit of formula (215) (with replacing $m_1 \to M$ and $m_2 \to m$).

Another observation that gives relevance and usefulness to the concept of granular temperature, again in the dilute limit, comes from the study of "granular ratchets". Changing the shape of the intruder, one can break a spatial symmetry (for instance $x \to -x$, which also requires some constraint to prevent rotation of the object), a large mass expansion shows the appearance of an additional constant force in Eq. (216), which is known as motor or ratchet effect [242,243]. The role of granular temperatures is evident in the observation that the motor force is proportional to $T_{tr} - T_g = \frac{1-\alpha}{2}T_g$ [242,244,245].

The departure from the dilute limit changes many of the above results and make deviations from an equilibrium description emerge: as a consequence the effective meaning of granular temperature is drastically reduced.

5.3.2. Granular liquids

The first experiment focusing on a Brownian-like description of a large intruder in a granular liquid, i.e. a shaken granular material in a non-dilute but rapidly evolving regime, is discussed in Ref. [246]. The validity of an equilibrium-like Fluctuation–Dissipation relation was observed, with an effective temperature which – as orders of magnitude – was "related to the granular temperature", a fact which is reminiscent of the observations discussed in the previous paragraphs, but cannot be fully evaluated since the real granular temperature was not measured. Most recent studies, both theoretical [247]and experimental [237], have shown that when the granular is a liquid and not a gas, deviations from the equilibrium Fluctuation–Dissipation relation are observed: most importantly, such deviations are not well described by an effective temperature. In granular liquids, as a matter of fact, granular temperature is much less useful than in gases, and cannot be replaced by some other temperature for the purpose of an effective description.

A simple example is provided, again, by the case of a massive intruder $M \gg m$ [113,247]. For the purpose of describing the velocity autocorrelation of the tracer and its linear response, the model in Eqs. (142) has revealed to give an excellent description. A particularly clear re-formulation of that model, using the notation of the present section, and restricting to a single dimension for the purpose of clarity, reads

$$M\dot{V}(t) = -\Gamma[V(t) - U(t)] + \sqrt{2\Gamma T_{tr}}\mathcal{E}_v(t) \tag{221a}$$

$$M'\dot{U}(t) = -\Gamma' U(t) - \Gamma V(t) + \sqrt{2\Gamma' T_b}\mathcal{E}_U(t), \tag{221b}$$

where Γ' and M' are parameters to be determined, for instance from the measured autocorrelation function, and T_b is the value of T_g in the elastic case: for instance if the steady state is guaranteed by an external "bath", it is the bath temperature [210] (a more detailed discussion is given below). The dilute limit, Eq. (216), can be obtained with $\Gamma' \sim M' \to \infty$, which implies small U. In the elastic limit ($T_{tr} = T_b = T_g$), on the other side, the coupling with U can still be important (as a first approximation for the breakdown of Molecular Chaos), but the equilibrium Fluctuation–Dissipation relation is recovered, as seen in Section 4.1. The model in Eqs. (221) is, of course, an approximation which is seen to work for packing fractions smaller than 40%: its advantage is in its particular simplicity and analytical solvability. Interestingly, numerical simulations have shown that the auxiliary field $U(t)$ is a local average of the velocities of the particles surrounding the intruder (in an *persistence* radius which has been discussed in [113]). A striking confirmation of the usefulness of Eqs. (221) came also from a measurement of the fluctuating entropy production, which is proportional to the work done by the force $\Gamma U(t)$ upon the intruder,

$$\Sigma_t \approx \Gamma\left(\frac{1}{T_{tr}} - \frac{1}{T_b}\right)\int_0^t dsV(s)U(s), \tag{222}$$

and which satisfies very well the Fluctuation Relation [113], see Fig. 11. The latter is quite a remarkable result, in particular if compared with previous attempts to define and measure a granular entropy production [169,170,239,248–250].

A few words are in order about the temperatures T_{tr} and T_b appearing in the "thermostats" of the $V(t)$ and $U(t)$ fields in Eqs. (221). As discussed above, in the dilute limit $T_{tr} \to \frac{1+\alpha}{2}T_g$. On the contrary, when the density increases numerical simulations suggest $T_{tr} \to T_g$, likely due to a reduction of effective inelasticity in recolliding particles. The appearance of T_b is also interesting: the fact that the temperature of the local velocity field U is equal to the bath temperature comes as a consequence of the conservation of momentum in collisions, implying that the average velocity of a group of particles is not changed by collisions among themselves and is only affected by the external bath and a (small) number of collisions with outside particles. Summarizing, model (221) suggests that in a granular liquid – at some level of approximation – *two* temperatures are relevant, one related to the single particle scale and another one related to a many-particle, or collective, scale.

Such a conclusion is consistent with a series of recent results about spatial velocity correlations, typically measured as structure factors of the velocity field. The question about velocity structure factors has been initially addressed – through numerical studies and models of fluctuating hydrodynamics [251,252] - for the case of cooling granular gases [253–255] or bulk-driven gases with an infinite relaxation time [209]. In those studies the large scale behavior of velocity structure factors appeared to be unbounded and therefore useless for the definition of a large-scale granular temperature. More recently, the

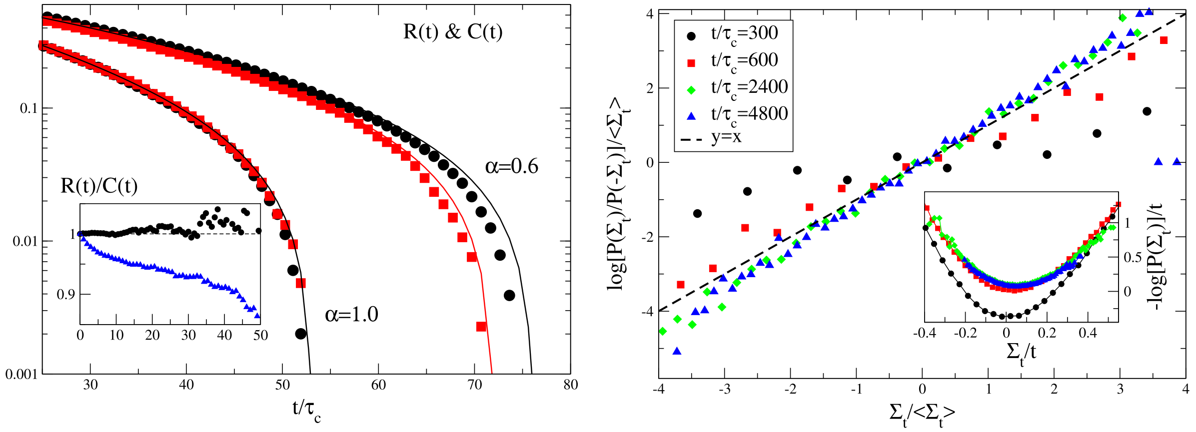

Fig. 11. Left: response function $R_{vF}(t)$ and auto-correlation function $C(t) = \langle V(t)V(0)\rangle / \langle V(0)V(0)\rangle$ as a function of time, measured in molecular dynamics simulations of a system composed of a massive intruder interacting with a driven granular fluid. Right: fluctuation relation satisfied at large times by the fluctuating entropy production measured in the same system, using the definition (222).

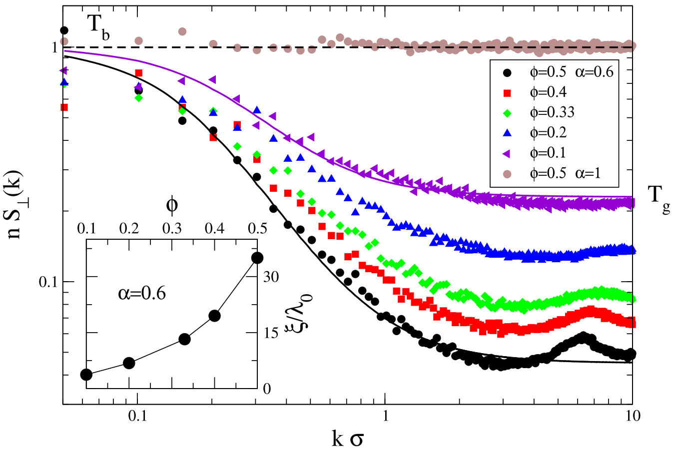

Fig. 12. Transverse velocity structure factor for simulations of a 2d driven granular gas at different packing fractions ϕ and restitution coefficients α [215]. In the graph $n = N/V$ is the average number density, σ is the diameter of the disks and λ_0 is the mean free path.

velocity correlations for a bulk-driven model of granular particles interacting at a finite frequency, proportional to γ_b, with the external bath [210] has been studied under some theoretical approximation and in experiments [215,216,256–258]. The key finding is represented by a study of the steady transverse velocity structure factor, which can be defined – for instance – as

$$S_\perp(k) = \sum_{n,j=1}^{N} v_{n,y} v_{j,y} e^{-ik\pi(x_n - x_j)}, \tag{223}$$

where x_n and $v_{n,y}$ are the x-component of the position and the y-component of the velocity of the nth particle respectively. The structure factor was found to be given by the following expression for a large range of packing fractions in the liquid regime (0–40%)

$$S_\perp(k) \approx \frac{\gamma_b T_b + \nu k^2 T_g}{\gamma_b + \nu k^2}, \tag{224}$$

where ν is the kinematic viscosity of the granular fluid. Such an expression clearly shows the dependence upon the two temperatures which appear at large scales, $\lim_{k\to 0} S_\perp(k) = T_b$, and at small scale $\lim_{k\to\infty} S_\perp(k) = T_g \le T_b$. The structure factor becomes flat, as it should, at equilibrium ($T_g = T_b$). Out-of-equilibrium, on the contrary, a finite correlation length $\xi \sim \sqrt{\nu/\gamma_b}$ appears. In the numerical studies [215,256], where full control of T_b was available, it was possible to put in evidence that (at fixed T_b) the value of T_g decreases with the packing fraction: this implies a larger contrast $T_b/T_g = S_\perp(k \to 0)/S_\perp(k \to \infty)$, which is equivalent to more pronounced correlations between velocities, see Fig. 12. A strict analogy with the several intruder's examples discussed above is recovered [234,113].

5.3.3. Dense granular materials

When packing fraction is further increased, the granular liquid typically falls in a more complicate regime which is associated with a very slow relaxation dynamics, often known as "glassy" granular state. A dynamics can still be observed, for instance in the presence of low-frequency tapping, but on time-scales much longer than in the previously considered collisional or liquid states. Schemes of deduction of the constitutive relations starting from the microscopic dynamics can hardly be applied to such a regime, unless at the cost of uncontrolled approximations. Phenomenological descriptions [200] are more common and useful, at least as a descriptive tool or for industrial applications. In these models, see [259,260,200]for reviews, macroscopic stresses are related to strains and/or strain rates through empirical formulae inspired by viscoelasticity (e.g. the so-called Maxwell model or the Kelvin–Voigt model) or Bingham materials (e.g. mayonnaise, which is characterized by the presence of a yield – or threshold – stress), or Herschel–Buckley models, which are fully non-linear in the strain/shear rate, or to more recent friction-like theories [261–265]. A noticeable exception to the phenomenological approach is the so-called Edwards theory of compactivity, which is an elegant attempt to build a theory of dense granular states, formally equivalent to equilibrium statistical mechanics [266–273].

The essence of Edwards' idea is to reproduce the observables attained dynamically by a sort of *ergodicity hypothesis*. In the theoretical approach one fixes the density of the system (which in real tapping experiment is not constant), and then calculates the value of the observables in an ensemble consisting of all the *"blocked" configurations* at that density. The blocked configurations are defined as those in which every grain is unable to move.

It is clear that configurations with low mobility are relevant in a jammed situation, while it is a much stronger hypothesis that the configurations reached dynamically are *the typical ones* of given energy and density. Had we restricted averages to blocked configurations having *all* macroscopic observables coinciding with the dynamical ones, the construction would exactly, and trivially, reproduce the dynamic results. The fact that conditioning averages to the observed energy and density suffices to give (even if maybe only as an approximation) other dynamical observables is highly non-trivial [273].

This "Edwards ensemble" leads naturally to the definition of an entropy S_{Edw}, given by the logarithm of the number of blocked configurations of given volume, energy, etc. Associated with this entropy are state variables which play a role similar to the usual thermodynamics quantity (as temperature), e.g. "compactivity"

$$\frac{1}{X_{Edw}} = \frac{\partial}{\partial V} S_{Edw}(V), \tag{225}$$

and "Edwards temperature"

$$\frac{1}{T_{Edw}} = \frac{\partial}{\partial E} S_{Edw}(E). \tag{226}$$

A series of interesting results helped to clarify and support Edwards' proposal. In particular several points of contact emerged with linear response theory of glassy systems, which is quite a different framework with respect to Edwards' approach. As discussed in Section 4.3, in the presence of a large separation of timescales, it is meaningful to define an effective temperature T_{dyn} as the one replacing the bath temperature in the Equilibrium Fluctuation–Dissipation Relation, for instance in the Einstein-like relation between diffusion and mobility [143]. In several mean-field models of disordered systems exhibiting glassy dynamics, it was possible to identify all the energy minima (the blocked configurations in a gradient descent dynamics), and calculate $1/T_{Edw}$ as the derivative of the logarithm of their number with respect to energy. Explicit computations showed that T_{Edw} coincides with T_{dyn} obtained from linear response of the out of equilibrium dynamics of the models, i.e. during a slow aging transient in contact with an almost zero temperature bath [274–281]. Moreover, given the energy $E(t)$ at long times, the value of any other macroscopic observable is also given by the flat average over all blocked configurations of energy $E(t)$. In some simplified models of dense granular media the Edwards configurational entropy can be computed and a negative temperature can arise in certain ranges of packing fraction [282]. Within the same approximation, one can also treat systems that, like granular matter, present a non-linear friction and different kinds of energy input, and the conclusions remain the same [283], despite the fact that there is no thermal bath temperature. Edwards' scenario then seems to be correct within mean-field schemes and for very weak vibration or forcing. The problem that remains is to what extent it carries through to more realistic models [284]. Recently, this approach has been revitalized due to the development of efficient algorithms for computing granular entropy [285,286].

5.4. Active matter

The study of active matter embraces systems composed by many elementary constituents with a common fundamental ingredient: self propulsion [287,62]. Typical examples are found in biology, ranging from aggregates of macroscopic living beings [288] (e.g. bird flocks, insect swarms, fish schools, etc.) to ensembles of microscale entities (e.g. interacting cells or bacteria) and, even smaller, sub-cellular unities such as actuated biopolymers (actin filaments, kinesin molecules etc.). Another important category of active matter is that of non-living – often man-made – systems, for instance self-propelled colloids at the micro-scale (typical example are the Janus particles, which propel due to asymmetric interactions with the solvent induced by inhomogeneous chemical properties of their surfaces), driven granular particles at the scale of millimeters [289] (asymmetrically manufactured granular objects may crawl due to friction asymmetries along a vibrating surface), and – at larger scales – swarming robots [290,291].

The most salient aspect of self-propulsion is an intrinsic lack of thermodynamic equilibrium with the surrounding environment, with a net transfer of energy from the "active reservoir" (a source of self-propulsion energy) to the "thermal reservoir" (the environment, usually a liquid solvent or air) [292–294]. Moreover the number of elementary constituents of an active system is large but not too much: hundreds or thousands are the most common figures. This makes active systems very interesting for the study of fluctuations, which are rarely negligible [295,296].

There is a plethora of collective phenomena observed in real active systems as well as in theoretical models. Two major ordering modes in active systems – which can also combine together – are phase separation [297] and swarming [298,299]: the former is typically a dilute–dense transition (often simply called clustering, or in the most extreme cases, jamming and crystallization), the latter consists in a macroscopic fraction of the particles moving in the same direction. In the presence of polar or chiral particles, the number of symmetries to break increases and so do the observable ordered phases [62]. Turbulent phases with whirls, jets and vortices have also been observed [300]. Other rich fields of study are that of confined active systems, where the interaction between self-propelled particles and complex geometries are considered, and that of active–passive mixtures, where the transport of passive particles is affected by the presence of self-propelled particles [290].

5.4.1. *Modeling active particles*

The motion of an active "particle" is usually modeled through simple dynamical equations, i.e. neglecting the details of the self-propulsion mechanism. Given the huge variety of systems under the label "active", a homogeneous and agreed classification is lacking. According to a recent review [290], a major distinction concerns the interaction between the self-propelled agent and its surrounding fluid: with respect to that, one can distinguish between

(1) active Brownian particles (ABP), which feel just viscous damping as a "simplified" effect of their solvent, and

(2) microswimmers (MS), which are more sophisticate models taking into account the modification of the surrounding fluid due to momentum transfer: indeed the self-propelled particle acts as a localized source of momentum in the fluid.

This difference of course reverberates into the complexity of particle–particle interactions: ABP interact through short-range forces (unless an additional long-range interaction of external origin is considered, e.g. in the case of electrically charged particles); MS are subject to hydrodynamic interactions, which – in incompressible fluids – are typically long-range. Apart from the fluid–particle mode of interaction, another discriminating property is the shape of the particle or of its self-propulsion mechanism. Shape may induce some kind of chirality, which is relevant for the possible observable collective behaviors.

Irrespective of their range – short or long – particle–particle interactions for active systems can be placed into two main categories: aligning and non-aligning. Non-aligning forces include all the kinds which are already known to act in passive (equilibrium) systems, such as excluded volume, charge repulsion, liquid-like interactions (e.g. Lennard-Jones), depletion forces, etc. Aligning forces usually involve some dissipative mechanism, the most common being a force which depends upon the velocity of the interacting particles which tends to reduce the misaligned component. The ancestor of aligning self-propelled particles is the Vicsek model, where the aligning mechanism is collective: at each time-step all particles in a given radius take as new orientation (which determine the direction of motion) their average orientation plus a small amount of noise [298].

Notwithstanding the simplicity of the models, emergent collective behaviors can be surprisingly rich. The theoretical tools most often adopted to analyze such collective behaviors are numerical simulations and coarse-graining techniques. Interestingly, a role of a certain relevance has been played by *equilibrium-like* or *equilibrium-inspired* models, where the intrinsic non-equilibrium condition of active systems has been neglected or drastically reduced [301,297]. This occurred for two main reasons: (1) equilibrium is deeply rooted in statistical mechanics and offers well-established approaches to explain complex phase diagrams in the presence of non-trivial broken symmetries (active particles, such as microswimmers, spermatozoa, bacteria, etc., but also birds in flocks, are elongated "polar" particles which can display many kinds of order, in analogy – for instance – with liquid crystals); (2) in several cases – for instance in low-Reynolds situations, e.g. in viscous solvents and at the micro-scale – the lack of thermodynamic equilibrium affects the dynamics of the self-propelled particles only at short time-scales, while on long time scales the difference between equilibrium and nonequilibrium is much harder to be observed [293,294].

5.4.2. *Toward a temperature for active matter*

The simplest way of defining a temperature for active systems is considering active diffusivity $D_{eff} = \lim_{t\to\infty}\langle|\mathbf{X}|^2(t)\rangle/(2dt)$, where $\mathbf{X}$ indicates the particle's position in d dimensions, and the viscous damping γ exerted on the particle by the surrounding solvent:

$$k_B T_{eff} = \gamma D_{eff}. \tag{227}$$

This is perfectly analogous to the definition of effective temperatures based upon linear response theory (see Section 4.1).

For several basic models of non-interacting ABPs, e.g. the so-called "active Brownian motion", "run-and-tumble" and the "Gaussian colored noise" model (also known as Ornstein–Uhlenbeck ABP), the mean-squared displacement (considering $d = 2$ for the sake of simplicity) reads [290]

$$\langle|\mathbf{X}|^2(t)\rangle = [4D_T + v^2\tau_R]t + \frac{v^2}{2}\tau_R^2\left[e^{-2t/\tau_R} - 1\right], \tag{228}$$

where $D_T = k_B T/\gamma$ is the passive translational diffusion coefficient due to Brownian motion at the thermal temperature T, v is the typical velocity of self-propulsion, and τ_R is the mean re-orientation time, related to rotational diffusion (the rotational diffusion coefficient is τ_R^{-1}). Even without entering into the details of the mentioned ABP models, the expression in Eq. (228) already gives an idea of the difference between ABP and passive Brownian motion: in the latter the rotational diffusion is not coupled to translational diffusion and therefore τ_R does not appear in the expression of $\langle|\mathbf{X}|^2(t)\rangle$. The translational movement of an ABP, on the contrary, occurs preferentially along a direction parallel to its orientation, for instance marked by its flagellum, and therefore the rotational dynamics affects translations. Eq. (228) also shows that at small times $t \ll \tau_R$ (of course still larger than the very small average time between collisions with the fluid-molecules) one has $\langle|\mathbf{X}|^2(t)\rangle \approx 4D_T t$, i.e. the short-time behavior is equivalent to the thermal diffusion of passive Brownian particles.

As a consequence of Eq. (228), the effective (long-time) translational diffusion coefficient of an ABP reads

$$D_{\mathit{eff}} = D_T + \frac{1}{4}v^2\tau_R \tag{229}$$

and therefore its "effective temperature" takes the expression

$$k_B T_{\mathit{eff}} = k_B T + \frac{\gamma\tau_R}{4}v^2. \tag{230}$$

Typical velocities v of biological or artificial micro-scale active particles are in the range of 1–100 $\mu\mathrm{m\,s}^{-1}$, while their translational and rotational diffusivities are (in water) $D_T \sim 0.1\ \mu\mathrm{m}^2 s^{-1}$ and $\tau_R \sim 5$ s. For such particles, the ratio T_{eff}/T is commonly of the order of 10^3 or larger. This is the reason why ABP may be considered as "hot colloids", a scenario which is also observed in some experiments. However, when interactions or external (inhomogeneous) fields become important, this simple picture based upon a single equilibrium-like temperature breaks down.

Numerical studies of the linear-response-theory-based effective temperature in active models with relevant particle–particle interactions (e.g. active liquids) have been performed in [302–305]. These results, however, are not conclusive. Some of them [302,305] indicate a certain robustness in the definition of T_{eff}, which can also be measured by coupling "thermometers" (e.g. tracer particles whose mass selects time-scales and therefore degrees of freedom) or which can be relevant for a liquid–glass transition. The measured T_{eff}/T is however of order 1 (typically between 1 and 2), which suggests that the adopted models are not very close to real active systems. Other studies [303,304], apparently enforcing stronger self-propulsions, indicate that a temperature based upon linear response or diffusivity/mobility ratios is not a useful concept.

Recent theoretical and experimental studies have also tested the concept of effective temperature in different active systems, such as hair bundle's spontaneous oscillations [306], biopolymers in an active medium [307], red-blood-cell membranes [308], DNA hairpins [309], and active colloid suspensions [310,311] and mixtures [312].

5.4.3. *Effective temperature in the Gaussian colored noise model*

An interesting alternative to effective temperatures based upon response has emerged, recently, in the study of the Gaussian colored noise model for active systems [313,314]. Even the simple one-dimensional case with no particle–particle interactions, but only in the presence of an external inhomogeneous field, is interesting [315]. In this case each active particle obeys the following equation of motion:

$$\dot{x}(t) = v(t) \tag{231a}$$

$$m\dot{v}(t) = -\gamma v(t) + \sqrt{2\gamma T}\xi(t) - U'(x) + \gamma v_a(t) \tag{231b}$$

$$\dot{v}_a(t) = -\frac{v_a(t)}{\tau_R} + \sqrt{2\frac{D_{\mathit{eff}}}{\tau_R^2}}\xi_a(t), \tag{231c}$$

where γ, T, τ_R and D_{eff} have the same qualitative meaning as above, m is the particle's mass, $U(x)$ is an external potential and both $\xi(t)$ and $\xi_a(t)$ are Gaussian white noises with zero average and unitary variance. The model in (231) has three main timescales:

(1) $\tau_m = m/\gamma$, which is the momentum relaxation timescale due to interaction with fluid molecules;

(2) τ_R, which is the persistence timescale of the active force;

(3) τ_U, the characteristic time needed by the particle to see the variations of the potential $U(x)$: for instance, it can be defined as $\tau_U = \Delta x/V$, with Δx a characteristic length-scale (e.g. periodicity) of the external potential and V the typical particle's velocity, which in the presence of activity is of the order of $\sqrt{D_{\mathit{eff}}/\tau_R}$ while in the passive case is $\sqrt{T/m}$. Apart from atypical choices of the potential (e.g. $U(x)$ varying over very small lengthscales) and in the low-Reynolds regime ($Re \sim \tau_m/\tau_R$), the order of the three timescales is $\tau_m \ll \tau_R \ll \tau_U$.

In the literature, the model is usually presented in its overdamped limit [313–315], i.e. disregarding the time-scales of order τ_m or smaller, that is equivalent to consider $\dot{x} \approx \frac{x(t+\Delta t)-x(t)}{\Delta t}$ with $\tau_R \gg \Delta t \gg \tau_m$. The overdamped equation reads:

$$\dot{x}(t) = \sqrt{2\frac{T}{\gamma}}\xi(t) - \frac{U'(x)}{\gamma} + v_a(t) \tag{232a}$$

$$\dot{v}_a(t) = -\frac{v_a(t)}{\tau_R} + \sqrt{2\frac{D_{\mathit{eff}}}{\tau_R^2}}\xi_a(t). \tag{232b}$$

In view of the quite large difference between thermal and active diffusivities, it is reasonable to neglect thermal noise, the first term in the r.h.s. of Eq. (232a). This has the advantage of leading to a differentiable dynamics for $\dot{x}(t)$. Indeed, upon time-differentiation of Eq. (232a) (and few more passages), one gets

$$\dot{v}(t) = -\frac{1}{\tau_R}\left(1 + \frac{\tau_R}{\gamma}U''(x)\right)v(t) - \frac{1}{\tau_R\gamma}U'(t) + \sqrt{\frac{2D_{eff}}{\tau_R^2}}\xi_a(t). \tag{233}$$

Of course this equation is different from Eq. (231b), because of the overdamped approximation considered to derive it: basically $v(t)$ in Eq. (233) is not the same velocity as in Eq. (231b). Interestingly, a second level of coarse-graining is available, that is looking at larger time-scales Δt, with $\tau_U \gg \Delta t \gg \tau_R$. This is the so-called uniform color noise approximation (UCNA),[6] which reads

$$\dot{x}(t) = -\frac{1}{\gamma\Gamma(x)}U'(x) + \sqrt{\frac{2D}{\Gamma^2(x)}}\xi_a(t), \tag{234}$$

where the Stratonovich convention is assumed and $\Gamma(x) = 1 + (\tau_R/\gamma)U''(x)$. The stationary distribution for Eq. (234) is known and reads

$$p_{ucna}(x) = \mathcal{N}|\Gamma(X)| \exp\left(-\frac{U(x)}{\gamma D_{eff}} - \frac{\tau_R}{2\gamma^2 D_{eff}}[U'(x)]^2\right). \tag{235}$$

Most importantly, a joint position–velocity stationary distribution

$$p(x,v) = p_{ucna}(x)\sqrt{\frac{\Gamma(x)\tau_R}{2\pi D_{eff}}} \exp\left(-\frac{\Gamma(x)\tau_R}{2D_{eff}}v^2\right) \tag{236}$$

is an approximate solution of the stationary Fokker–Planck equation associated with Eq. (233). Among the properties of the joint probability density function in Eq. (236), a remarkable one is that it satisfies a coarse-grained form of detailed balance: more precisely, the first three velocity moments of the irreversible probability current are zero [294].

The above considerations suggest an interesting interpretation of the quantity $T_a(x) = D_{eff}/(\tau_R\Gamma(x)) \equiv T_{eff}/(\tau_R\gamma\Gamma(x))$ as the local temperature of the active bath. Two additional arguments support such an interpretation:

(1) an equation of state of the kind $p(x) \approx \rho(x)T_a(x)$ (with local density $\rho(x) = \int dv p(x,v)$) fairly explains anomalous density fluctuations due to activity in the presence of confining potentials [315];

(2) a generalized Clausius inequality can be demonstrated involving a local heat flux normalized by $T_a(x)$ [294]:

$$\int dx \frac{\dot{q}(x)}{T_a(x)} \leq 0, \tag{237}$$

where $\dot{q}(x)$ represents the local density of heat flux from the system to the active bath:

$$\dot{q}(x,t) = \frac{\Gamma(x)}{\tau_R}\left[T_a(x)\rho(x,t) - \int dv v^2 p(x,v,t)\right]. \tag{238}$$

The interpretation of $T_a(x)$ as a temperature with some thermodynamic meaning is still a conjecture. Nevertheless it has interesting fascinating consequences, including a possible connection with the issue of negative temperatures.

Another open question strictly connected to the previous considerations on heat fluxes is that of entropy production. Only few studies have addressed such a problem, adopting – to represent self-propulsion – the Gaussian colored noise model [293,294] or a velocity-dependent force [317]. The latter approach has been seen to raise ambiguities in the equivalence between zero entropy production and equilibrium [77].

6. Conclusions

In this review we have revisited the notion of temperature, focusing on some difficult aspects that arise when one tries to extend such a concept beyond the standard cases covered by thermodynamics and equilibrium statistical mechanics. The need for such a critical analysis is motivated also by new experimental achievements, allowing us to study the non-equilibrium statistical properties of "small systems", at the micro and nano-scales, such as macromolecules (like DNA, proteins and molecular motors), colloidal suspensions, granular media and active matter, just to name a few examples. Our main purpose was to provide the reader with the basic aspects and the open issues related to a mindful use of the concept of temperature, from different perspectives.

We have followed a line of reasoning that, starting from the two possible definitions of temperature (Boltzmann *vs* Gibbs) in the well-established framework of equilibrium statistical mechanics, led us to clarify some debated points, such as the

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[6] A rigorous discussion of the UCNA, see for instance [316], shows that it can be obtained in the limit $\tau_R \to 0$ but also in the opposite limit $\tau_R \to \infty$, provided that one focuses in the regions of stable potential $U'' > 0$.

problem of "temperature fluctuations" and the existence of negative temperatures, related to cases of systems with few degrees of freedom or with a limited phase space, respectively.

Our journey, then, crossed the realm of non-equilibrium systems, where a notion of effective temperature can be introduced via the generalization of the fluctuation–dissipation relation. We critically discussed its physical meaning and usefulness in the description of non-equilibrium states, focusing on some specific examples of non-Hamiltonian systems, such as statistical hydrodynamics, granular media and active matter.

In particular, we have discussed how, in dilute granular fluids, an effective temperature can be safely introduced, while, in dense regimes, a good description cannot be obtained with a single macroscopic parameter, due to the presence of not well-separated time-scales in the system. On the contrary, a statistical approach based on few macroscopic parameters, directly inspired by the equilibrium theory, seems to be effective for describing the slow dynamics of very dense granular systems, as suggested by Edwards. In the context of active matter, we have focused our attention on a specific model characterized by colored noise, where a local temperature of the active bath can be introduced, consistently with the thermodynamic requirements. Another rich field of research where similar issues naturally arise, is represented by systems characterized by aging dynamics, such as glassy and disordered models, or colloidal suspensions, for reviews of such aspects see [143,120].

In conclusion, some questions related to the notion of temperature, at least in the context of equilibrium statistical mechanics, seem to have been by now sufficiently clarified. Others remain largely open, in particular in the field of out of equilibrium and non-Hamiltonian systems. Here, the search for general theories based on few macroscopic parameters, in analogy with the equilibrium approach, is far from being completed. Despite some important recent results, such as the Fluctuation Relations or the extensions of the fluctuation–dissipation theorem [165,71,318], general methods to treat non-equilibrium dynamics are not available. From this perspective, the generalization of the notion of temperature to characterize non-equilibrium behaviors seems to play a central role. To pursue such an ambitious program, further efforts have to be devoted, in particular, to the study of the effects of typical non-equilibrium features, such as coarse-graining, memory terms, or mixed time-scales in the system.

Acknowledgments

We warmly thank Luca Cerino for many fruitful discussions and close collaboration on the topics of this review. We are grateful to M. Baldovin, M. Falcioni, L. Peliti and H. H. Rugh for remarks, suggestions and correspondence. We also thank the Authors of Refs. [17] and [95] for allowing us to use their figures.

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