Chapter 2
Non-Equilibrium Steady States

Abstract In this chapter a brief collection of the results present in literature and used in this work is described. We starts with a derivation of the Langevin equation in a way that makes clear the assumptions on the basis of equilibrium dynamics. Then, generalized response relations are presented and the role of entropy production is discussed. Since a large part of this work regards the study of granular gases, the second part of the chapter is entirely devoted to them, paying attention to the still open problems in dense regimes. This is not a chapter of a review article, and for this reason it could appear incomplete. However, it must be seen as an occasion to present the common ground where there are the basis of our research, and it proposes some questions which are developed and, at least partially, solved in the rest of the work.

The fluctuations of a system at equilibrium are characterized by strong symmetries that connect dissipation and noise. In this way, it is possible to have a prediction of the response to an external perturbation by only measuring a coniugated correlation function in the unperturbed system. As soon as non conservative forces are present, this symmetries are broken. In this case, the complete characterization of fluctuation and response is still an open problem of statistical mechanics.

In this chapter we start from a derivation of the Langevin equation from first principles, as example of equilibrium dynamics. From this example it appears evident that the fluctuating part and the dissipative part are both linked to the projection of fast degrees of freedom and are then connected. Using this case as a starting point, we present a derivation of the generalized response relations and the fluctuation relations for generic stochastic processes. Some specific phenomena typical of non-equilibrium states are then deduced from this general theory, like the connection between entropy production and the arrow of time, the ratchet effect of an asymmetric object in a non-equilibrium environment and finally the concept of effective temperature for aging systems. In the last part of the chapter, granular gases are introduced. In this class of models the presence of dissipation due to inelastic collisions, when balanced by an external energy injection mechanism, produces a striking example of non-equilibrium steady state. In granular gases, the description of non-thermal

D. Villamaina, *Transport Properties in Non-Equilibrium and Anomalous Systems*,
Springer Theses, DOI: 10.1007/978-3-319-01772-3_2,

fluctuations, the response mechanism and the entropy production are still unclear from a theoretical point of view. These open questions are here briefly presented in a general context, and the search for a proper answer will be the central issue in the rest of the work.

2.1 Historical Notes: The Central Role of the Fluctuations

The study of fluctuations has a great importance in statistical mechanics. Historically, it is common and appropriate to start from the work of the botanist Robert Brown [16]. In 1827, by using a microscope, he observed grains of pollen of the plant *Clarkia pulchella* suspended in water moving in a very irregular way. Contrary to the common thinking, Robert Brown was not the first one to discover the Brownian motion (in a paper [17] he mentions several precursors) but his main contribution was to unveil the pure mechanical origin of this phenomena. As written in a review of that period [18]:

This motion certainly bears some resemblance to that observed in infusory animals, but the latter show more of a voluntary action. The idea of vitality is quite out of the question. On the contrary, the motions may be viewed as of a mechanical nature, caused by the unequal temperature of the strongly illuminated water, its evaporation, currents of air, and heated currents...

Thirty years after the work of Brown, the French physicist Louis Georges Gouy, supporting kinetic theory, pointed out several peculiarities of this motion, as reported in Perrin's book [73]. Among others, the most relevant are:

- the motion is very irregular, it appears that the trajectory has no tangent, and close particles move in independent way
- by increasing the temperature of the solvent, the motion is "more active"
- the motion never ceases or change qualitatively.

These features could be explained via kinetic arguments, and a direct test of it resides in the equipartition law. However, before the celebrated Einstein's work, several experimentalists failed to estimate the velocity of the tracer particle because of its irregularity and confirmation of kinetic theory was not possible (see [67] and references therein).

The breakthrough in understanding this phenomena arrived independently from Smoluchowski [81] and Einstein [29]. The conceptual relevant point of the work of Einstein is the assumption of the statistical equilibrium of the particle with the surrounding medium, together with the Stokes law experienced by a particle immersed in a fluid.

Based on this intuition, Langevin [58] proposed a stochastic differential equation for the velocity of a Brownian particle:

$$\frac{dV}{dt} = f_s + \xi(t) = -\gamma V + \xi(t), \tag{2.1}$$

where f_s is the Stokes law with $\gamma = 6\pi\eta a$, a is the radius of a molecule, η is the viscosity and $\xi(t)$ is a fluctuating force, whose variance is fixed by the equipartition law. The importance of fluctuations is now clear: a computation with only the Stokes term would produce an exponential relaxation and no movement would be predicted. From (2.1) an expression for the diffusion coefficient is obtained

$$D = \lim_{t\to\infty} \frac{\langle [x(t) - x(0)]^2 \rangle}{2t} = \frac{RT}{6N_A \pi\eta a}, \tag{2.2}$$

where N_A is the Avogadro number and R is the gas constant. The evocative aspect of Eq. (2.2) is given by the possibility of counting molecules, by observing the macroscopic fluctuations of the position $x(t)$ of a tracer particle, whose measure is clearly easier than velocity estimations, as tried in the past.

This relation was experimentally confirmed by Svendberg and Perrin, dispelling any doubt on the atomic theory.

On the other side, the dynamical equations introduced by Langevin have a wide range of applicability and have been generalized and deduced in several contexts.

2.1.1 The Origin of the Langevin Equation: Noise and Friction

Let us consider a system coupled to a thermal bath, for example a massive intruder in a fluid, and let us suppose we are interested in obtaining its dynamical equations. The basic idea is to start from a full description of the variables present in the system, and then to obtain an effective dynamical equation by reducing the number of degrees of freedom. Generally speaking, the Hamiltonian of the system can be split into three parts:

$$H_{tot} = H_{system} + H_{bath} + H_{int}, \tag{2.3}$$

where H_{int} is the interaction term. A standard projection recipe consists in integrating over the bath variables and then in obtaining some dynamical equations for the "slow" variables of the system of interest. In this section, we will describe, as particular case, a harmonic model introduced for the first time by Zwanzig [88], which has the advantage of being analytically tractable. In this case one has

$$H_{system}(X, P) = \frac{P^2}{2M} + U(X) \tag{2.4}$$

$$H_{bath} + H_{int} = \sum_j \left[\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left(x_j - \frac{\gamma_j}{\omega_j^2} X \right)^2 \right]. \tag{2.5}$$

where the capital letters refer to the tracer particle and the bath is described by the collection of variables $\{x, p\}$. Note that the strength of the interaction term is ruled

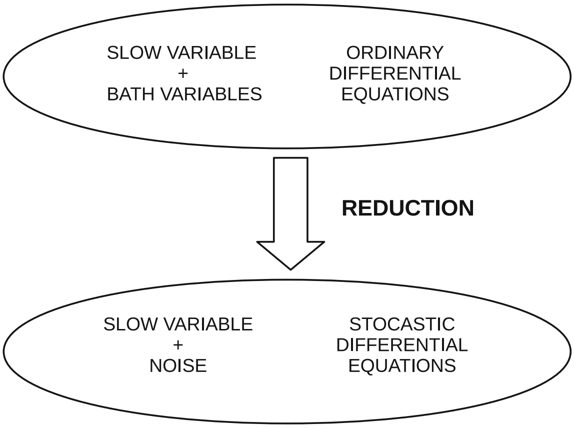

Fig. 2.1 Scheme of the reduction process

by γ_i. The equations of motion read

$$M\frac{dX}{dt} = P \quad \frac{dP}{dt} = \quad -U'(X) + \sum_j \gamma_j (x_j - \frac{\gamma_j}{\omega_j^2} X) \tag{2.6}$$

$$\frac{dx_j}{dt} = p_j \quad \frac{dp_j}{dt} = \quad -\omega_j^2 x_j + \gamma_j X. \tag{2.7}$$

Now, thanks to the harmonic choice of the bath variables, it is evident that the Eq. (2.7) can be integrated and substituted in (2.6), yielding an equation for the variables (P, X) depending only on the initial conditions $\{q(0), p(0)\}$. The equation for the variable P can be recast into:

$$\frac{dP}{dt} = -U'(x) - \int_0^{+\infty} ds K(s) \frac{P(t-s)}{M} + F_p(t), \tag{2.8}$$

where

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos \omega_j t \tag{2.9}$$

$$F_p(t) = \sum_j \gamma_j p_j(0) \frac{\sin \omega_j t}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) \cos \omega_j t. \tag{2.10}$$

Up to now, no approximation has been done: these equations are indeed a simple rewriting and the level of the description is still Hamiltonian, with a deterministic evolution depending on the initial conditions. Clearly, for a large numbers of oscillators, for instance of the order of the Avogadro number, referring to the initial condition in order to maintain the deterministic nature of the analysis is ingenuous and useless, and a probabilistic approach is necessary.

The statistical ingredient in the description is implemented by considering an equilibrium canonical distribution at a well defined temperature[1] $T = \frac{1}{\beta}$ for the initial conditions of the bath oscillators:

$$\rho(x, p) \propto e^{-\beta(\mathcal{H}_{bath}+\mathcal{H}_{int})}. \tag{2.11}$$

The statistical averages of the initial conditions are

$$\left\langle \left(x_j(0) - \frac{\gamma_j}{\omega_j^2} X(0) \right)^2 \right\rangle = \frac{T}{\omega_j^2} \qquad \langle p_j(0)^2 \rangle = T, \tag{2.12}$$

and clearly the first moments and the cross correlation vanishes. With this operation the scenario changes completely, and from a deterministic approach one passes to a stochastic one. As a consequence, the variable $F_p(t)$ depends on the initial condition of the bath, and plays the role of a noise [25]. A central relation in this model is given by:

$$\langle F_p(t) F_p(t') \rangle = T K(t - t'), \tag{2.13}$$

which is called fluctuation dissipation relation of the second kind [50, 52]. Let us conclude this example with some remarks. Thanks to the peculiar form of H_{int}, one obtains that the correlation of the noise does not depend on x. It is possible to show, indeed, that if one introduces a non linear coupling term between the variable X and the bath variables, a multiplicative noise term appears [38]. In some non linear cases, like in some pure kinetic models, some approximations must be taken into account, like the large mass of the intruder, inducing some time scales separation. We will return largely on this point in Chap. 4 with the work, among the others, of Mori and Zwanzig [66, 89], the theory of the Brownian motion and of the generalized Langevin equation has been extended to slow observables, via a projection technique, under very general hypothesis. A central aspect is that, also in these more general approaches, the proportionality between the correlation of noise and the memory term is always verified. One must notice that, as evident from this simple example, both the noise and the memory have the same origin and, as a consequence, a relation connecting them is expected. We will point out in Chap. 3 that (2.13) is substantially equivalent to have taken equilibrium conditions.

In this work we will focus on the classical aspect of non-equilibrium statistical mechanics but it is worth to mention that extensions to the quantum or relativistic case have been developed [28, 39].

[1] In this thesis we always measure the temperature in scales of energy, namely we set the Boltzmann constant k_B equal to one.

2.2 General Aspects of Non-Equilibrium Steady States

2.2.1 The Linear Response Relations

The study of the response properties plays a central role in this work. Historically, response theory has been developed first in equilibrium, namely for system described by Hamiltonian dynamics or where the ensemble theory is correct. For this reason, in quite all the textbooks, response theory is presented as a synonymous of the so-called fluctuation dissipation theorem.[2] A consequence of this important theorem was anticipated by Lars Onsager. With the regression hypothesis, he argued that a system cannot "know" if a small fluctuation from equilibrium is caused by an internal fluctuation or by an external field: as a consequence the regression of microscopic thermal fluctuations at equilibrium follows the macroscopic law of relaxation of small non-equilibrium disturbances [70]. Actually there is no apparent reason to apply this "causality principle" only to equilibrium systems: it is possible, indeed, to define the response of a system at a more general level [64], and as we will see, it is always possible to connect it to a suitable correlation. At equilibrium, it assumes well known and tractable forms.

In order to fix ideas, let us suppose that some noise is present. Therefore we consider cases in which it is possible to associate a probability to the trajectories. Let us then consider the space $\{\omega\}$ of trajectories of length t and its probabilities $P_0(\omega)$. Let us consider the effect of an external perturbation: it changes the dynamics and the relative probability of the trajectories in $P_h(\omega)$ (for simplicity in what follows we consider that the space of perturbed trajectories $\{\omega\}$ remain the same). The average value of any observable in presence of the perturbation is easy computed as[3] $\langle O(t)\rangle_h = \sum_\omega O(\omega)P_h(\omega)$. Within this definition, the following identity trivially holds:

$$\langle O(t)\rangle_h = \left\langle O(t)\frac{P_h(\omega)}{P_0(\omega)}\right\rangle_0, \tag{2.14}$$

where, with $\langle \ldots \rangle_0$ we denote the average over the unperturbed trajectories. By taking the functional derivative with respect to $h(t')$, the response function is easily obtained:

$$\left.\frac{\overline{\delta O(t)}}{\delta h(t')}\right|_{h=0} = \left\langle O(t)\frac{1}{P_0(\omega)}\left.\frac{\delta P_h(\omega)}{\delta h(t')}\right|_{h=0}\right\rangle_0, \tag{2.15}$$

where we have introduced $\overline{(\ldots)} \equiv \langle \ldots \rangle_h$, in order to lighten notation. Equation (2.15) is, as anticipated above, a generalization of the Onsager's sentence, for a general system: the response of an observable to an external perturbation is equal to a suitable correlation computed in the unperturbed system. As it appears

[2] We will omit the expression "of the first kind" When the kind is not specified we always refer to this relation.

[3] We consider a numerable set of trajectories for simplicity of notation.

clear, Eq. (2.14) and its linearized version (2.15) are somehow too general: the knowledge of the full phase space probability is required in order to compute the correlation, which is clearly strongly dependent by the details of the model. In equilibrium statistical mechanics, a great outcome is that it is possible to recast, under general conditions, the second member of (2.15) in a clear way, as described in Sect. 2.2.1.3. In other words, this is another example of how, at equilibrium, it is possible to get rid of the dynamical details of the model, as it happens for ensemble theory.

In order to fix notation, consider $\mathbf{x}$ as the collection of the phase space variables, then the probability distribution of a trajectory can be written as:

$$\mathcal{P}_0(\omega) = \rho_0(\mathbf{x}) K_0(\omega), \tag{2.16}$$

where ρ_0 is the distribution of the initial conditions. In the following we will present two ways of calculating the response of a generic system: the formal expressions are different, but they are evidently equal, as we will show explicitly at equilibrium. Depending on the model under analysis, it can be convenient to use one expression instead of the other.

2.2.1.1 Linear Response and Steady State Distribution

At the first step we study the behavior of one component of $\mathbf{x}$, say x_i, described by $\rho_{inv}(\mathbf{x})$, which is a non-vanishing and smooth enough invariant measure. When such a system is subjected to an initial perturbation such that $\mathbf{x}(0) \to \mathbf{x}(0) + \Delta\mathbf{x}_0$. We consider the case in which the system is prepared in its steady state, therefore $\rho_0(\mathbf{x}) = \rho_{inv}(\mathbf{x})$. This instantaneous kick modifies the initial density of the system but does not affect the transition rates, therefore one has:

$$\begin{aligned} h &= \Delta\mathbf{x}_0 \\ \rho_h(\mathbf{x}) &= \rho_0(\mathbf{x} - \Delta\mathbf{x}_0) \\ K_h(\omega) &= K_0(\omega). \end{aligned} \tag{2.17}$$

For an infinitesimal perturbation $\delta\mathbf{x}(0) = (0, \ldots, \delta x_j(0), \ldots, 0)$, by substituting (2.17) inside (2.15) one arrives straightforward to[4]

$$R_{i,j}(t) \equiv \overline{\frac{\delta x_i(t)}{\delta x_j(0)}} = -\left\langle x_i(t) \left. \frac{\partial \ln \rho(\mathbf{x})}{\partial x_j} \right|_{t=0} \right\rangle, \tag{2.18}$$

which is the response function of the variable x_i with respect to a perturbation of x_j. This is a first example of a generalized fluctuation response relation, derived for the first time in [32]. The information requested to compute the response in terms of unperturbed correlations is now reduced to the knowledge of the steady state

[4] We put $\rho \equiv \rho_{inv}$ for simplicity.

distribution but can be still non-trivial. However the nature of the perturbation can be easily implemented in numerical experiments: we will describe an application to granular materials in Sect. 2.3.2.

With similar passages, it is also possible to derive the relaxation to finite time perturbation, defining $\overline{\Delta x_i} = \langle x_i \rangle_h - \langle x_i \rangle_0$, from (2.17) and (2.14) one has

$$\overline{\Delta x_i}\,(t) = \Big\langle x_i(t)\ F(\mathbf{x}_0, \Delta\mathbf{x}_0)\Big\rangle, \tag{2.19}$$

where

$$F(\mathbf{x}_0, \Delta\mathbf{x}_0) = \left[\frac{\rho(\mathbf{x}_0 - \Delta\mathbf{x}_0) - \rho(\mathbf{x}_0)}{\rho(\mathbf{x}_0)}\right]. \tag{2.20}$$

In this example, the dependence on the perturbation parameter is highly non linear; this is important in different situations, such as in geophysical or climate investigations: in these contexts, understanding the relaxation to a finite perturbation due to a sudden external change is quite common and represents a challenging issue in comparison to the infinitesimal perturbation required by the linear response theory [9, 57], which can never be applied in practical situations.

2.2.1.2 Linear Response from Transition Rates

In some cases the distribution function is not known and the perturbation enters directly in the equations of motion in form of external field. In these cases a computation from dynamics can be tempted.

Let us define $A(\omega) \equiv -\ln \frac{P_h(\omega)}{P_0(\omega)}$. This functional can be decomposed in two contributions

$$\mathcal{A}(\omega) = \frac{1}{2}(\mathcal{T} - \mathcal{S}), \tag{2.21}$$

where

$$\begin{aligned} \mathcal{T} &= \mathcal{A}(\mathcal{I}\omega) + \mathcal{A}(\omega), \\ \mathcal{S} &= \mathcal{A}(\mathcal{I}\omega) - \mathcal{A}(\omega). \end{aligned} \tag{2.22}$$

The ω dependence in $\mathcal{T}$ and $\mathcal{S}$ is omitted and the time reversal operator $\mathcal{I}$ is introduced. With this formal operation one has:

$$\begin{aligned} \frac{\delta\langle O(t)\rangle_h}{\delta h(t')} &= \frac{\delta\langle O(t)e^{-\mathcal{T}/2+\mathcal{S}/2}\rangle}{\delta h(t')} \\ &= \frac{1}{2}\Big\langle O(t)\ \frac{\delta\mathcal{S}}{\delta h(t')}\Big|_{h=0}\Big\rangle - \frac{1}{2}\Big\langle O(t)\ \frac{\delta\mathcal{T}}{\delta h(t')}\Big| h=0\Big\rangle. \end{aligned} \tag{2.23}$$

It is clear that (2.23) is exactly the same of (2.15), apart from a different notation. In order to go beyond on this result one must restrict to the Markovian case with transition rates $W(x \to y)$ and introduce a prescription for the perturbed transition rates W_h

$$W_h(x \to y) = W(x \to y)e^{\beta/2h(t)[y-x]}. \tag{2.24}$$

Equation (2.24) is called "local detailed balance condition". From this particular assumption, one can derive this expression (see Appendix A.1 for details)

$$R_{Ox}(t,t') = \frac{\beta}{2}[\langle O(t)\dot{x}(t')\rangle - \langle O(t)B(t')\rangle], \tag{2.25}$$

where

$$B(t) \equiv \sum_{y \neq x} W(x \to y)[y - x]. \tag{2.26}$$

Let us stress again that formula (2.25) holds for non-stationary, aging processes, even in absence of detailed balance [3, 22, 63].

At a first sight the two formulas (2.25) and (2.18) appear very different. Actually such a difference can be exploited: we will see in this work how can be convenient one of the two forms with respect to the other, depending on the model under analysis [80].

2.2.1.3 The Equilibrium Case

As mentioned above, linear response theory historically has been developed in an equilibrium context, and many results have been obtained. Let us show how the usual forms of fluctuation dissipation theorems can be deduced from the dynamical versions of the linear response. The advantage of this derivation is that the main features of an equilibrium system must be taken into account and it appears clear how the fluctuation dissipation theorem is a signature of equilibrium.

Let us start from the following identity (see Appendix A.1 for the details of the calculations):

$$\frac{d}{dt}C(t,t') \equiv \langle \dot{x}(t)O(t')\rangle = \langle B(t)O(t')\rangle \quad \text{for } t > t'. \tag{2.27}$$

Moreover, let us consider that:

- if the system is time translational invariant $\frac{d}{dt}C(t,t') = -\frac{d}{dt'}C(t-t')$
- if the system is also invariant for time reversal symmetry $\langle B(t)O(t')\rangle = \langle O(t) B(t')\rangle$.

Within these assumptions from (2.27) and (2.25)

$$R_{Ox}(t) = \beta\langle O(t)\dot{x}(0)\rangle, \tag{2.28}$$

which is nothing but the celebrated fluctuation dissipation theorem. The predictive power of (2.28) is evident especially if compared with the more general relations (2.18) and (2.25): the response of a generic observable is predicted by a suitable correlator, which contains only the observable conjugated to the applied force and is not dependent on the dynamical details of the system under investigation.

It is instructive to recover this result starting also from (2.18). In Hamiltonian systems, taking the canonical ensemble as the equilibrium distribution, one has

$$\ln \rho = -\beta H(\{p\}, \{q\}) + const. \tag{2.29}$$

Then, from the Hamilton's equations ($dq_k/dt = \partial H/\partial p_k$) and from (2.18) one has the differential form of the usual fluctuation dissipation relation [50, 51]:

$$\overline{\frac{\delta O(t)}{\delta p_k(0)}} = \beta \left\langle O(t) \frac{dq_k(0)}{dt} \right\rangle = -\beta \frac{d}{dt} \left\langle O(t) q_k(0) \right\rangle. \tag{2.30}$$

Apart from some differences in the notations, it is evident that (2.28) and (2.30) are completely equivalent.

Moreover, let us suppose to make a perturbation on the momenta p_0. From (2.18), if the distribution of velocities is Maxwell-Boltzmann, one has

$$\overline{\frac{\delta v(t)}{\delta v(0)}} = \beta \langle v(t) v(0) \rangle, \tag{2.31}$$

where, for simplicity of notations, we have introduced the velocity $v \equiv p_0/m$ where m is the mass. Equation (2.31) is most known in its integrated version: if a perturbation like $F\Theta(t)$ acting on the particle is considered,[5] the well known Einstein relation is derived:

$$\mu = \beta D, \tag{2.32}$$

where we have introduced the mobility $\mu \equiv \lim_{t\to\infty} \frac{\overline{\delta v(t)}}{F}$ and the diffusion coefficient

$$D \equiv \int_0^{+\infty} \langle v(t) v(0) \rangle dt. \tag{2.33}$$

We will return largely on (2.32) in Chap. 5, dealing with system exhibiting anomalous diffusion.

In both these derivations, it emerges that when equilibrium dynamics is considered, the response function appears in a compact and general form, involving only the correlation of the observable of interest and the one coupled to the external field. On the contrary, when some currents are flowing into the system and it is driven out of equilibrium, this forms simply fail and no general prescriptions for the response are available. In order to stress this crucial point let us note that, as well clear even

[5] Θ is the Heavyside step function.

in the case of Gaussian variable, the knowledge of a marginal distribution

$$p_i(x_i) = \int \rho(x_1, x_2, ...) \prod_{j \neq i} dx_j \tag{2.34}$$

is not enough for the computation of the autoresponse:

$$R_{i,i}(t) \neq -\left\langle x_i(t) \left. \frac{\partial \ln p_i(x_i)}{\partial x_i} \right|_{t=0} \right\rangle. \tag{2.35}$$

On the contrary, as shown above, the equality in (2.35) holds for the velocities in the case of Maxwell-Boltzmann distribution.

2.2.1.4 The Effective Temperature

In this work we will quite always consider driven systems, with the assumption that they are ergodic and that they reach a steady state in a reasonable time. There is another class of systems where dissipative forces are absent, but they start form an initial configuration which is not the equilibrium one and are, then, characterized by a non-time translational invariant dynamics. In some cases the transient regime has very interesting properties like in domain growth [26], polymers [83], structural glasses [20, 61] and spin glasses [19], where a dramatic slowing down of the relaxation process appears as soon as some parameter is opportunely changed. In these cases the memory of the initial condition is not completely lost and the system "ages": the observables depend non-trivially also by the waiting time, namely the time elapsed since the system is prepared. This "aging regime" is then non stationary and the fluctuation dissipation theorem is not expected to hold; both response and correlation, indeed, decays slower as the system gets older. The analysis of this "fluctuation dissipation violations" has been largely studied in literature (for a review see [24]). In order to give an interpretation of these violations, the concept of effective temperature has been introduced:

$$T^{eff}(t, t_w) = \frac{1}{R(t, t_w)} \frac{\partial C(t, t_w)}{\partial t_w}. \tag{2.36}$$

Note that, up to this moment, (2.36) is just a rewriting and it is obviously true.[6] However, for slow enough dynamics, it is assumed that $T^{eff}(t, t_w) \equiv T^{eff}(C(t, t_w))$, namely the correlation is assumed as a clock of the dynamics. This assumption is verified in mean field glasses. In particular, one can distinguish two well definite regimes: when $(t - t_w)/t_w \ll 1$ one has that $C(t, s) \simeq C_{st}(t - s)$ and the fluctuation dissipation theorem holds, namely $T^{eff}(C)$ is equivalent to the temperature of

[6] A similar definition is often introduced also in the frequency domain conjugated to the variable t [27].

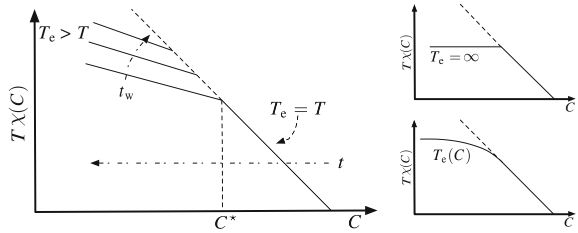

Fig. 2.2 *Left* Integrated response versus correlation in a glass former. For small times (i.e. high values of the correlation) the slope is equal to T and for a value C^* which increases with the waiting time, the slope corresponds to an higher temperature associated to the slow modes. *Right* behavior expected for coarsening (*top*) and spin glasses (*bottom*). The image is taken from [62]

the dynamics T. On the contrary, when $(t - t_w)/t_w > 1$ the fluctuation dissipation theorem is violated and different scenarios are possible, as shown in Fig. 2.2.

It is well established that structural glasses, when quenched below their Mode-Coupling temperature, display an out-of-equilibrium dynamics customarily described within a two-temperature scenario [11, 49, 86]. Fast modes are equilibrated at the bath temperature while slow modes remember, in a sense, the higher temperature determined by the initial condition.

An important question is whether this "violation factor" can be considered a temperature in a thermodynamic sense. This question is still on debate [27, 61], and it has some limits. For instance, it has been shown that, for a generalized version of the trap model of Bouchaud [12], this definition of temperature is observable dependent [35]. Moreover, in some stationary systems like granular gases, the effective temperature meets some conceptual problems, for instance it is negative for vibrated dry granular media [68] and, in case of mixtures, the two components have different temperatures in the steady state [6].

However, it must be noticed that for the class of structural glasses, the interpretation of the fluctuation dissipation ratio (2.36) as an "effective temperature" seems to be well posed, considering also some detailed analysis made on a Leonard-Jones binary mixture showing evidences that the so-defined temperature is observable independent and constant on a long time interval [8].

We will return on the "effective temperature" interpretation on a "two temperature" driven model in Chap. 4.

2.2.2 A Measure of Non-Equilibrium: The Entropy Production

In the previous section we discussed how, when one deals with response theory, it is quite crucial to distinguish between equilibrium and out of equilibrium dynamics. Up to now, we just have stated that non equilibrium regimes are always characterized by some sort of current flowing across the system. Actually, this definition appears quite vague. In this section we go beyond this consideration by introducing a family of observables which somehow can give a sort of distance from equilibrium.

In general, when one deals with non-equilibrium dynamics, very few results, independent from the details of the model, are available. Actually in the last decades a group of relations, known with the name of "fluctuation relations" have captured the interest of the scientific community, especially for their generality and the vast range of applicability. Initially, a numerical evidence given by Evans and Searles [30] showed a particular symmetry in the Cramer function ruling the large deviation of an observable of a molecular fluid under shear. On the other hand, a theorem has been proved by Gallavotti and Cohen [36], under quite general hypothesis, for deterministic systems. This result has been then generalized to stochastic processes by Kurchan [55] and by Lebowitz and Spohn [59]. In a second moment, Jarzinski [45] and Hatano and Sasa [42] have derived other equalities, regarding irreversible transformations: we will return on these last group of identities in Sect. 2.2.3.

Apart from the differences among the various forms of fluctuation relations, it is possible to present these results under an unitary point of view [56], as evidence that the physical ground underlying these results is the same.

According to the description here adopted we will focus on systems in which some noise is present. Thanks to this assumption, it is possible to skip several technical problems and some forms of fluctuation theorems for stochastic systems can be used. We will not enter in the description of the huge literature related to these relations (the interested reader can see, among others [31]) but we will focus on the description of the Lebowitz-Sphon functional, since it is applied to the models presented in the following chapters.

2.2.2.1 The Lebowitz-Sphon Functional

It was shown in Sect. 2.2.1.3 that equilibrium response formula can be derived in a steady state, by assuming time reversal symmetry. This condition is translated on a symmetry property of the probability distribution

$$\mathcal{P}(\omega_t) = \mathcal{P}(\mathcal{I}\omega_t), \tag{2.37}$$

where $\mathcal{I}$ denotes the time reverse operator. Let us consider a transition rate from a generic state x to the state y, from (2.37) the well-known detailed balance condition is obtained

$$\rho_{inv}(x)W(x \to y) = \rho_{inv}(y)W(y \to x). \tag{2.38}$$

where ρ_{inv} is the invariant measure. When a current is present, (2.38) is violated and the time reversal symmetry is broken. From these considerations it appears natural to introduce the following functional for a trajectory of length t:

$$\Sigma_t = \ln \frac{P(\omega_t)}{P(\mathcal{I}\omega_t)}. \tag{2.39}$$

Within this definition, Σ_t is identically equal to zero for each trajectory separately, if detailed balance condition (2.38) is satisfied. Moreover it easy to show, by exploiting the properties of the Kullback-Leibler divergence [53], that $\langle \Sigma_t \rangle$ is always non-negative. Quantity (2.39) is very difficult to be measured, for instance, in an experimental setup [87]. However, in some cases, the entropy production is related to the power injected by external non conservative forces, let us then discuss with a pedagogical example how the entropy production is related to non-equilibrium currents.

Consider a Markov process where the perturbation of an external force F induces non-equilibrium currents. Let us assume that it enters in the transition rates according to local detailed balance condition (2.24), that we rewrite here for clarity

$$\frac{W_F(x \to y)}{W_F(y \to x)} = \frac{W_0(x \to y)}{W_0(y \to x)} e^{2\beta F j(x \to y)}, \tag{2.40}$$

where $j(x \to y)$ is the current associated to the transition $x \to y$, which obey the symmetry property $j(x \to y) = -j(y \to x)$. According to the definition of entropy production (2.39) one finds, for large times,

$$\frac{\Sigma_t}{t} \simeq 2\beta F \frac{1}{t} \sum_{n=1}^{t} j(x(n-1) \to x(n)) = 2\beta F J(t), \tag{2.41}$$

where $J(t)$ is the time-averaged current over a time window of duration t. The fluctuation relation for the probability distribution of the variable $y = \Sigma_t / t$ reads:

$$\frac{P(y)}{P(-y)} = e^y \Longrightarrow \frac{P(2\beta F J(t))}{P(-2\beta F J(t))} = e^{2\beta F J(t)}. \tag{2.42}$$

Namely the fluctuation relation describes a symmetry in probability distribution of the fluctuations of currents. Also, for large times we can assume a large deviation hypothesis $P(y) \sim e^{-tS(y)}$, with $S(y)$ a Cramer function. For small fluctuations around the mean value of y the Cramer function can be approximated to $S(y) = S(2\beta F J) \simeq \beta^2 F^2 (J - \overline{J})^2 / \sigma_J^2$, where σ_J is the variance. The fluctuation relation reads as

$$S(y) - S(-y) = y. \tag{2.43}$$

In the Gaussian limit (y close to $\overline{y}$) the previous constraint can be easily demonstrated to be equivalent to $\overline{J}/F = \beta \sigma_J^2$, which is nothing but the standard fluctuation dissipation relation. Therefore the fluctuation relation, which in the simplest case can be directly related to the fluctuation dissipation relation, is a more general symmetry to which we expect to obey the fluctuating entropy production. For a more general discussion of the link between the Lebowitz-Spohn entropy production and currents, see [1, 59]. The remarkable fact appearing in Eq. (2.42) is that it does not contain any free parameter, and so, in this sense, is model-independent.

It is instructive to calculate the entropy production for a simple Langevin equation of a particle in a force field [2]:

$$\dot{v} = -\Gamma v + F(x,t) + \eta(t) \tag{2.44}$$

with, as usual, the noise is Gaussian with $\langle\eta\rangle = 0$, $\langle\eta(t)\eta(t')\rangle = 2T\Gamma\delta(t-t')$, and where $F(x,t) = F_c + F_{nc}$ is a sum of a conservative force $F_c = -U'(x)$ and a non-conservative force $F_{nc}(t)$. The path probability can be written down by introducing the Onsager-Machlup functional [71]:

$$\mathcal{P}(\omega \equiv \{v\}_t) \propto \exp(-L), \tag{2.45}$$

where

$$L = \frac{1}{4\Gamma T}\int_0^t ds\,(\dot{v} + \Gamma v - F)^2\,. \tag{2.46}$$

The entropy production reads:

$$\Sigma_t = \ln\frac{P(\omega)}{P(\mathcal{I}\omega)} = \frac{\Delta H}{T} + \frac{\int_0^t F_{nc}(s)v(s)ds}{T}, \tag{2.47}$$

where $\Delta H = \frac{v^2(t)-v^2(0)}{2} + U[x(t)] - U[x(0)]$. Equation (2.47), for large times, allows one to identify the work $w_{nc}(t) = \int_0^t F_{nc}(t)v(t)dt$ done by the external non-conservative force (divided by T) as the entropy produced during the time t. This is an example of the result by Kurchan [54] and by Lebowitz and Spohn [59] about the fluctuation relation for stochastic systems. We will return on this functional in Chap. 3 and 4.

2.2.3 Entropy Production and the Arrow of Time

The previous class of fluctuation relations are a sort of extensions of the second law of thermodynamics to small or non-equilibrium systems. In order to see this similarity, let us consider a system $\mathbf{x}$ which moves from the state A to the state B by a variation of a parameter α. Then Hatano and Sasa, showed that

$$\langle e^{-\int dt\,\frac{\partial\phi(\mathbf{x};\alpha)}{\partial\alpha}\dot{\alpha}}\rangle = 1, \tag{2.48}$$

where $\phi(\mathbf{x};\alpha) = \ln\rho_{inv}(\mathbf{x};\alpha)$, being ρ_{inv} the invariant measure at constant α. By applying the Jensen inequality to (2.48), one has

$$\left\langle -\int dt\,\frac{\partial\phi(\mathbf{x};\alpha)}{\partial\alpha}\dot{\alpha}\right\rangle \geq 0. \tag{2.49}$$

It is simple to see that the equality is reached only if the transformation is, in a sense, reversible, namely one must assume that, for each value of the control parameter α, the system is in the corresponding stationary state: Eq. (2.48) can be interpreted as a generalization of the second principle of thermodynamic to generic steady states [72]. A relevant question regarding steady states rises again: the quantity $\phi(\mathbf{x}; \alpha)$, present in Eq. (2.48) has not a clear thermodynamic meaning, when some currents are present. On the contrary if the system is in equilibrium and the canonical probability density can be assumed, one has

$$\langle e^{-\beta W} \rangle_{A \to B} = e^{-\beta \Delta F}, \tag{2.50}$$

which is named Jarzinski relation, where ΔF is the free energy change between A and B. Also in this case, by means of the Jensen inequality one has that $\langle W \rangle_{A \to B} \geq \Delta F$, which is exactly the second law in thermodynamics. The main message that emerges from this example is that the fluctuation relations of the kind (2.42) are a sort of extension of the second law when fluctuations are relevant. Different connections between these formulas and information theory has been proposed. Let us discuss, for instance, the problem of the arrow of time. In order to fix ideas, let us suppose to observe a trajectory generated by the dynamics of (2.44) and we do not know *apriori* if we are observing it in the right temporal sequence. Clearly if we had an ensemble of trajectories from the same initial condition we could work with the averaged trajectory $\langle v(t) \rangle$ to find easily the answer. On the contrary, because of fluctuations, we cannot be sure of the direction of the time and it becomes a problem of estimation theory. Let be H_0 the hypothesis that the trajectory observed does follow the real time-line and H_1 its negation, a straightforward application of the Bayes formula gives

$$P(H_0|\{V\}) = \frac{P(\{V\}|H_0)P(H_0)}{P(\{V\}|H_0)P(H_0) + P(\{V\}|H_1)P(H_1)}. \tag{2.51}$$

We consider now the case in which there is no reason to prefer as prior an hypothesis respect to the other: then we have $P(H_0) = P(H_1) = \frac{1}{2}$. Moreover $P(\{V\}|H_1) \equiv P(\mathcal{I}\{V\}|H_0)$. Finally, by recalling Eq. (2.47) one has

$$P(H_0|\{V\}) = \frac{1}{1 + e^{-\beta(\Delta H + W_d)}}, \tag{2.52}$$

where the dissipative work has been introduced $W_d = \int_0^t F_{nc}(s)v(s)ds$. Despite of this simplicity, the result (2.52) is really evocative: if the work of the dissipative forces, without sign, is sensibly greater than the thermal fluctuations it is possible to find the correct direction of the time (see Fig. 2.3). Remarkably, if conservative forces are absent, namely if an equilibrium limit is obtained, the probability collapses to the value $\frac{1}{2}$, as a consequence of the detailed balance condition (2.37). This example can by easily generalized to a generic Hamiltonian system showing the same results [10, 46]. Other works have also shown similar connections with the Landauer principle [48].

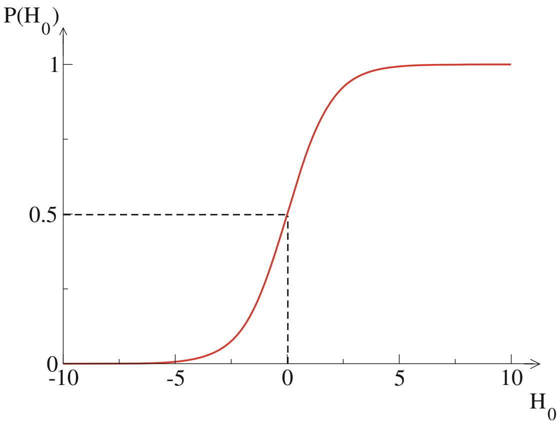

Fig. 2.3 Qualitative behavior of Eq. (2.52) in function of the entropy production, where $\Sigma = \beta(\Delta H + W_d)$. If the dissipative work differs appreciably from zero, it is possible to distinguish the arrow of time of the trajectory. An equilibrium system corresponds to the case $\Sigma = 0$

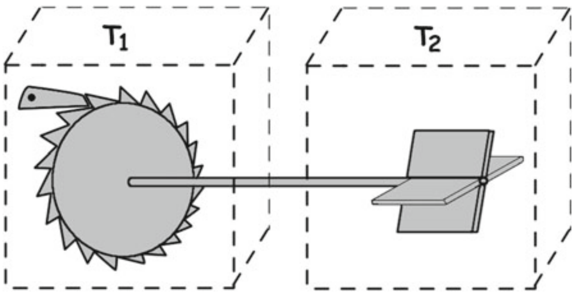

Fig. 2.4 Schematic representation of the Feynman-Smoluchowski ratchet. If the two temperatures are equal, i.e. $T_1 = T_2$, a net drift cannot be observed. The picture is taken from Wikimedia Foundation

These simple arguments are a reflection of the dualism entropy/information. We will return on this subject in Sect. 3.3.

2.2.4 The Ratchet Effect: A Pure Non-Equilibrium Phenomena

Let us conclude this part of the chapter by describing a pure non-equilibrium feature, known with the name of ratchet effect. The first one to focus on this problem was Smoluchowski with a *Gedanken experiment* [82], then recovered by Feynman in his popular lectures [34].

As shown in Fig. 2.4, the machine described by Feynman is composed by two compartments. In one of these there is a spring connected with a pawl, while a symmetric rotor is present in the second compartment. Both the compartments are filled with a gas. At a first glance, the machine seems to rotate, since the particles of the gases are supposed to strike uniformly all the faces of the pawl, but it is able to move only in one direction, also if the two temperatures in the compartments are equal. On the contrary, as pointed out by Feynman, the pawl, in order to be sensible to the fluctuation induced by the particles, must be of a similar order of magnitude. Therefore, the dynamics of the pawl is sensible to the thermal fluctuations. Taking into account of this, it is possible to show that there is not a drift. From this example one can conclude that from equilibrium fluctuations is not possible to observe a directed motion. Such a result can be understood in terms of the second law of thermodynamics or, from a kinetic point of view, observing that, from detailed balance condition (2.37), it is not possible to distinguish between past and future. On the contrary, if the two containers of the model are kept at different temperatures ($T_1 \neq T_2$), the system is out of equilibrium and, as commented in Sect. 2.2.2, time reversal symmetry is broken. Under these conditions it is possible to extract work, as derived by Van Den Broeck et al. [15], via kinetic theory, in a simplified version of the model. Note that, in this case, we are not creating work without putting energy into the system: the two reservoirs, indeed, are in contact. Therefore, in a energy balance calculation, also the power injected in order maintain the two temperature different must be taken into account.

As this simple example shows, the necessary ingredient to have a ratchet effect are:

- a spatial symmetry breaking, obtained by an asymmetric shape of intruder or by a non-symmetric external potential acting on the probe particle
- a time symmetry breaking, obtained with non equilibrium conditions.

Even if only one of this two conditions is lacking, a directed motion cannot be observed. This mechanism is also described as a "rectification of non equilibrium fluctuations": let us illustrate this point with a simple overdamped Langevin model [41]:

$$\gamma \dot{x} = -V'(x) + \xi(t), \tag{2.53}$$

where $V(x) \equiv V(x + L)$ is a periodic asymmetric potential with period L and $\xi(t)$ is the usual Gaussian noise with $\langle \xi(t)\xi(t') \rangle = 2\gamma T(t)\delta(t - t')$. Note that the time dependence in the correlation of noise is necessary in order to break the detailed balance condition since the fluctuation dissipation theorem of the second kind is not satisfied. Two typical shapes of the potential and of the temperature are

$$V(x) = V_0 \langle [\sin(2\pi x) + \frac{1}{4}\sin(2\pi x/L)] \rangle \tag{2.54}$$

$$T(t) = T(1 + A\text{sgn}[\sin(\omega t)]). \tag{2.55}$$

where the coefficients in the potential are properly fixed in order to avoid a trivial drift. Within the choice (2.55) the conditions described above are satisfied and a ratchet effect occurs [40]. Given the simplicity of this model, it is not difficult to understand how a proper choice of the shape of $T(t)$ is able to rectify the asymmetries induced by the asymmetric potential, as commented in Fig. 2.5.

In the case above discussed the scales of energy are put by hand and fixed as external parameters, like the two temperatures in Fig. 2.4. On the contrary, there is another class of ratchet whose "second temperature" breaking the detailed balance

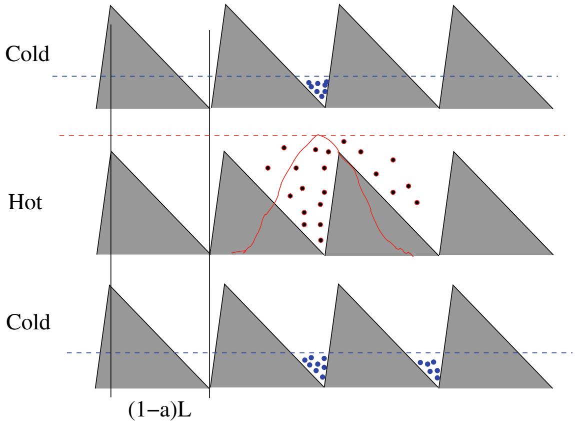

Fig. 2.5 Schematic explanation of a ratchet effect of the kind (2.53). In the hot phase, particle diffuses and, given the asymmetry of the potential, the diffusive motion is rectified in a neat drift. From this example it is clear that the intensity of the drift does non-trivially depend on the other parameters

is, in a sense, generated by non-equilibrium dynamics. The first example in this direction is obtained by substituting the gas with a granular material, characterized by inelastic collisions [23, 65]. Another elegant example has recently experimentally produced by using a thermal bath made of bacteria [60]. In Chap. 4 we will see another application of this kind, by studying an intruder in a fragile glass former. Such an application sounds new for two main reasons: first, it happens in the presence of anomalous transport, and as a consequence, the position of the intruder does not increase linearly in time, secondly the system under investigation is neither stationary nor periodic, as in the other cases here presented.

2.3 An Example of Out of Equilibrium Systems: The Granular Gases

Granular materials are a good candidate to study the non equilibrium effects described up to this point. The main ingredients necessary to have a granular material are essentially the inelastic nature of the collisions and the presence of an excluded volume, due to the macroscopic dimensions of its constituents [47]. Despite of this simplicity there is a huge variety of phenomena that has interested the physicist in the last decades, both in applied and theoretical contexts. It is quite usual to divide granular materials in two main classes: stable or metastable systems and flowing granular systems. One of the first examples of the peculiar properties of the granular material, the quite popular Janssen effect [44], belongs to the first class and describes the deviation from the Stevino's law in such a material. The study of the distribution of avalanches led to introduce the concept of self organized criticality [4]. On the contrary, as the name suggests, in the case of flowing granular systems an uninterrupted flow is present. Also in this regime, several non-equilibrium effects may arise and have been largely studied, like segregation phenomena, pattern formations and convection [37, 43].

In this work, we do not touch the interesting issue of non-ergodic properties related to granular materials, but we always refer to a "granular gas regime", in a steady state condition. In order to reach a steady state it is necessary to balance the dissipation due to collisions with an energy injection mechanism. There are several models of external energy sources that can be applied such that the system rapidly forgets the initial condition and reaches a steady state [75]. We will focus on a specific model, that is the one used in Chaps. 4 and 5, but it must be noticed that, apart from some details, in quite all the models of driven granular gases the scenario described in Sect. 2.3.1 is qualitatively similar.

2.3.1 A Model of a Granular Gas with Thermostat

Let us consider a d-dimensional model for driven granular gases [69, 76, 77, 85]: N identical disks (in $d = 2$) or rods of diameter 1 (in $d = 1$) in a volume $V = L \times L$ or total length L with inelastic hard core interactions characterized by an instantaneous velocity change

$$\mathbf{v}_i' = \mathbf{v}_i - \frac{1+r}{2}[(\mathbf{v}_i - \mathbf{v}_j) \cdot \hat{\sigma}]\hat{\sigma}, \tag{2.56}$$

where i and j are the label of the colliding particles, $\mathbf{v}$ and $\mathbf{v}'$ are the velocity before and after the collision respectively, $\hat{\sigma}$ is the unit vector joining the centers of particles and $r \in [0, 1]$ is the restitution coefficient which is equal to 1 in the elastic case. Each particle i is coupled to a "thermal bath", such that its dynamics (between two successive collisions) obeys

$$m\frac{d\mathbf{v}_i}{dt} = -\frac{1}{\tau_b}\mathbf{v}_i + \sqrt{\frac{2T_b}{\tau_b}}\phi_i(t), \tag{2.57}$$

where τ_b and T_b are parameters of the "bath" and $\phi_i(t)$ are independent normalized white noises. As anticipated before, we restrict ourselves to the dilute or liquid-like regime, excluding more dense systems where the slowness of relaxation prevents clear measures and poses doubts about the stationarity of the regime and its ergodicity.

Note that, with the choice of this kind of thermostat, the equilibrium limit is well defined: if $r = 1$ particles interact each other with elastic collisions and the distribution of velocity is Maxwell-Boltzmann.

Two important observables of the system are the mean free time between collisions τ_c, and the packing fraction ψ. Moreover, it is common to introduce the granular temperature

$$T_g = \frac{m\sum_i \langle v_i^2 \rangle}{N}, \tag{2.58}$$

which is a quite involved function of the parameters, as we will see in the next section.

In this model is possible to recover two different regimes:

- When $\tau_c \gg \tau_b$ grains thermalize, on average, with the bath before experiencing a collision and the inelastic effects are negligible. This is an "equilibrium-like" regime, similar to the elastic case $r = 1$, where the granular gas is spatially homogeneous, the distribution of velocity is Maxwellian and $T_g = T_b$.
- When $\tau_c \ll \tau_b$, non-equilibrium effects can emerge such as deviations from Maxwell-Boltzmann statistics, spatial inhomogeneities and $T_g < T_b$ [69, 76, 77, 85]. This "granular regime", easily reached when packing fraction or inelasticity are increased, is characterized by strong correlations among different particles.

2.3.1.1 Granular Temperature of the Gas

In this section, in order to see an example of a kinetic calculation, we will see how to obtain, in some limit, an expression for the granular temperature T_g.

Multiplying Eq. (2.57) by $\mathbf{v}(t)$ and averaging, one gets[7]

$$\frac{1}{2}m\frac{d}{dt}\langle \mathbf{v}^2(t)\rangle = -\gamma_b\langle \mathbf{v}(t)^2\rangle + \langle \mathbf{v}(t)\mathbf{f}(t)\rangle + \langle \mathbf{v}(t)\boldsymbol{\eta}(t)\rangle. \tag{2.59}$$

Where, for simplicity, we have introduced $\gamma_b = \frac{1}{\tau_b}$ and $\eta_i = \frac{2T_b}{\tau_b}\phi_i$. At stationarity, the left hand side of the above equation vanishes and $\langle \mathbf{v}(t)\boldsymbol{\eta}(t)\rangle = 2\gamma_b T_b/m$. The term $\langle \mathbf{v}(t)\mathbf{f}(t)\rangle$ represents the average power dissipated by collisions:

$$\langle \mathbf{v}(t)\mathbf{f}(t)\rangle = -\langle \Delta E\rangle_{col}, \tag{2.60}$$

where $\Delta E = 1/8m(1-\alpha^2)[(\mathbf{v}_1 - \mathbf{v}_2)\cdot\hat{\boldsymbol{\sigma}}]^2$ is the energy dissipated per particle and the collision average is defined by

$$\langle \ldots\rangle_{col} = \int d\hat{\boldsymbol{\sigma}}\int d\mathbf{v}_1\int d\mathbf{v}_2 \ldots p(\mathbf{v}_1,\mathbf{v}_2)\Theta[-(\mathbf{v}_1-\mathbf{v}_2)\cdot\hat{\boldsymbol{\sigma}}]|(\mathbf{v}_1-\mathbf{v}_2)\cdot\hat{\boldsymbol{\sigma}}|.$$

This integral contains the joint distribution of the collisional particle velocity. It can be solved with the Enskog correction, a slight modification of the molecular chaos assumption [21]:

$$p(\mathbf{v}_1,\mathbf{v}_2) = \chi p(\mathbf{v}_1)p(\mathbf{v}_2), \tag{2.61}$$

where $\chi = \frac{g_2'(2r)}{l_0}$ and l_0 is the mean free path and $g_2'(2r)$ is the pair correlation function for two gas particles at contact. Equation (2.61) is expected to hold in a dilute system, but fails in denser regimes, because of recollisions and memory effects.

Thanks to this approximation, the integral in Eq. (2.60) can be computed by standard methods [13], and, in two dimensions within the Gaussian approximation, yields

[7] The index i has been removed for simplicity.

$$\langle \Delta E \rangle_{col} = \chi_g \frac{\sqrt{\pi}(1-r^2)}{\sqrt{m}} T_g^{3/2}. \tag{2.62}$$

Substituting this result into Eq. (2.59) and recalling that $T_g = m\langle \mathbf{v}^2 \rangle/2$, one finally obtains the implicit equation

$$T_g = T_b - \chi_g \frac{\sqrt{\pi m}(1-r^2)}{2\gamma_b} T_g^{3/2}, \tag{2.63}$$

which can be solved to obtain T_g. Note that, from (2.63), when $\gamma_b \to \infty$, the equilibrium-like limit is recovered and $T_b = T_g$.

2.3.2 Response Analysis

For the model presented above, and for other similar steady state granular gases, a response analysis has been performed [5, 7, 14, 74, 78, 84].

We will focus on the numerical experiments on the model described in Sect. 2.3.1. The protocol used in numerical experiments cited above is the following:

1. The gas is prepared in a "thermal" state, with random velocity components extracted from a Gaussian with zero average and given variance, and positions of the particles chosen uniformly random in the box, avoiding overlapping configurations.
2. The system is let evolve until a statistically stationary state is reached, which is set as time 0.
3. A copy of the system is obtained, identical to the original but for one particle, whose x (for instance) velocity component is incremented of a fixed amount $\delta v(0)$.
4. Both systems are let evolve with the unperturbed dynamics. For the random thermostats, the same noise realization is used. The perturbed tracer has velocity $v'(t)$, while the unperturbed one has velocity $v(t)$, so that $\delta v(t) = v'(t) - v(t)$.
5. After a time t_{max} large enough to have lost memory of the configuration at time 0, a new copy is done with perturbing a new random particle and the new response is measured. This procedure is repeated until a sufficient collection of data is obtained.
6. Finally the autocorrelation function $C_{vv}(t) = \langle v(t)v(0)\rangle$ in the original system and the response $R_{vv}(t) \equiv \frac{\overline{\delta v(t)}}{\delta v(0)}$ are measured.

In dilute cases, it is numerically observed that the phase space distribution can be factorized, namely:

$$\rho(\{\mathbf{v}_i, x_i\}) = n^N \prod_{i=1}^{N} \prod_{\alpha=1}^{d} p_v(v_i^{(\alpha)}), \tag{2.64}$$

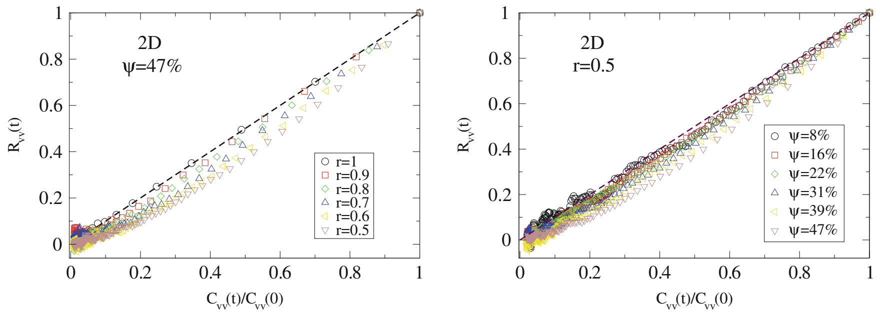

Fig. 2.6 Parametric plots to check the Einstein Relation, for $d = 2$ models of inelastic hard-core gases with thermal bath. Different choices of parameters r (restitution coefficient), $\alpha = \tau_c/\tau_b$ and ψ (packing fraction) are shown: note that one can change α at ψ or r fixed (changing τ_b), but - in general - changes in ψ or r determine also changes in α (because of changes in τ_c). In all plots, the dashed line marks the Einstein relation $R_{vv} = C_{vv}(t)/C_{vv}(0)$

with n the spatial density $n = N/V$ and $p_v(v)$ the one-particle velocity component probability density function, $v_i^{(\alpha)}$ the α-th component of the velocity of the i-th particle and d the system dimensionality. Exploiting isotropy, we will denote with v an arbitrary component of the velocity vector: the results do not change if v is the x or y component.

From (2.18), it is expected that an instantaneous perturbation $\delta v(0)$, at time $t = 0$ on a particle of the gas will result in an average response of the form

$$R(t) = \frac{\overline{\delta v(t)}}{\delta v(0)} = -\left\langle v(t) \frac{\partial \ln p_v(v)}{\partial v}\bigg|_0 \right\rangle \neq C_1(t), \tag{2.65}$$

having defined $C_1(t) = \langle v(t)v(0)\rangle/\langle v^2\rangle$. On the contrary it is observed that noticeable deviations form Einstein relation do not occur, therefore non-Gaussianity alone is not sufficient to produce violations. Indeed it has been shown in simplified models that all the higher order correlations are proportional [74]

$$C_f(t) = \frac{\langle v(t) f[v(0)]\rangle}{\langle v(0) f[v(0)]\rangle} \approx C_1(t), \tag{2.66}$$

which is shown to be valid also in the model here described, by numerical inspection. In conclusion, in the dilute limit the two conditions (2.64) and (2.66) are sufficient to verify the Einstein relation.

On the contrary, when the system is denser, the Molecular chaos approximation is no more valid and Eq. (2.64) fails; as a consequence, one can observe strong deviations from linearity between response and autocorrelation.
In addiction, there are same remarkable points: the violation is more and more pronounced as the inelasticity increases (lower values of r), the importance of the bath is reduced (lower values of τ_b/τ_c) or the packing fraction is increased, as shown in

Fig. 2.6. In correspondence of such variations of parameters, the correlation between velocities of adjacent particles is also enhanced, a phenomena which is ruled out in equilibrium fluids. We will return on this aspect in Chap. 5 by observing a similar behavior in a one dimensional model.

2.3.3 Entropy Production in Granular Gases: A Challenge

An experiment has been performed by Menon and Feitosa [33] using a granular gas shaken in a container at high frequency. The setup consisted of a $2D$ vertical box containing N identical glass beads, vertically vibrated at frequency f and amplitude A. The authors observed the kinetic energy variations ΔE_τ, over time windows of duration τ, in a central sub-region of the system characterized by an almost homogeneous temperature and density. They subdivided this variation into two contributions:

$$\Delta E_\tau = W_\tau - D_\tau, \tag{2.67}$$

where D_τ is the energy dissipated in inelastic collisions and W_τ is the energy flux through the boundaries, due to the kinetic energy transported by incoming and outgoing particles. The authors of the experiment have conjectured that W_τ, being a measure of injected power in the sub-system, can be related to the entropy flow or the entropy produced by the thermostat constituted by the rest of the gas (which is equal to the internal entropy production in the steady state). They have measured its probability distribution $f(W_\tau)$ and found that

$$\ln \frac{f(W_\tau)}{f(-W_\tau)} = \beta W_\tau, \tag{2.68}$$

with $\beta \neq 1/T_g$. By lack of a reasonable explanation for the value of β, the authors have concluded to have experimentally verified the fluctuation relation with an "effective temperature" $T_{eff} = 1/\beta$, suggesting its use as a possible non-equilibrium generalization of the usual granular temperature. The same results have been found in molecular dynamics simulations of inelastic hard disks with a similar setup [79]. This "effective temperature" interpretation is not convincing for different reasons. Among others, in the elastic limit one should expect that this definition of temperature should coincide with the external one, on the contrary it diverges, since the function $f(W_\tau)$ is symmetric. A different explanation has been proposed in [79], and it shows no connection with the fluctuation relation. It appears that the injected power measured in the experiment can be written as

$$W_\tau = \frac{1}{2}\left(\sum_{i=1}^{n_+} v_{i+}^2 - \sum_{i=1}^{n_-} v_{i-}^2\right), \tag{2.69}$$

where n_- (n_+) is the number of particles leaving (entering) the sub-region during the interval of time τ. In this case the authors assume n_- and n_+ being Poisson-distributed, neglecting correlations among particles entering or leaving successively the central region. The key ingredient due to inelasticity is that, as confirmed by simulations, the velocities $\mathbf{v}_{i+}$ and $\mathbf{v}_{i-}$ are assumed to originate from two distinct populations with different temperatures T_+ and T_- respectively. Within this assumptions, the left member of (2.68) can be exactly calculated, showing a non linear behavior in W_τ. The linear expression (2.68) found in the experiments is consistent with the expansion up to the third order[8] and can then be explained with lack of statistics.

2.3.4 Some Remarks

As underlined in the previous sections, both the response properties and the entropy production in granular gases are non completely clarified issues.

Regarding response properties, the lack of factorization of the phase space distribution produces a failure of the Einstein relation. A tentative modelling of the response was tried in [74] by assuming an effective distribution for the perturbed particle

$$p_v(v, \mathbf{x}, t) \sim \exp\left\{-\frac{(v - u(\mathbf{x}, t))^2}{2T_g}\right\}, \tag{2.70}$$

where $u(\mathbf{x}, t)$ is an effective fluctuating local velocity field coupled to the tracer (one can think to the average velocity of the surrounding particles). Using (2.18) one has

$$\overline{\frac{\delta v(t)}{\delta v(0)}} \propto \langle v(t)\,[v(0) - u(\mathbf{x}, t)]\rangle. \tag{2.71}$$

This formula has the merit to catch the main non-equilibrium source of the syste; for this reason, indeed, there is a partial agreement with simulations. On the other hand, assumption (2.70) has two main problems. First of all, a local velocity field can be defined only with an associated length, and, at this level, there is not an operative definition of it. Second, for the elastic limit the Einstein relation must be recovered and the distribution of velocities must approach to a Maxwell-Boltzmann; such a limit is not straightforward in Eq. (2.70), since a local velocity field does also exist in a dense elastic case, but is uncoupled to the tracer. Noticeably, one of the major criticism that can be moved to the "effective temperature interpretation" (2.68) is that the elastic limit is not well defined.

Given the considerations above, it appear necessary to work in a more controlled setup, where the correlations and the corresponding coupling with a velocity field emerge as soon as dissipation due to inelasticity is turned on, and a proper elastic limit can be recovered, together with the validity of the fluctuation dissipation theorem

---

[8] The second order term trivially vanishes for functions of the form $g(x) = \ln[f(x)/f(-x)]$.

and with a vanishing entropy production. This issue is a central point in this work and it will be discussed in Chaps. 3 and 4.

References

1. Andrieux, D., Gaspard, P.: Fluctuation theorem for currents and schnakenberg network theory. J. Stat. Phys. **127**, 107 (2007)
2. Astumian, R.D.: The unreasonable effectiveness of equilibrium theory for interpreting non-equilibrium experiments. Am. J. Phys **74**, 683 (2006)
3. Baiesi, M., Maes, C., Wynants, B.: Nonequilibrium linear response for markov dynamics, i: jump processes and overdamped diffusions. J. Stat. Phys. **137**, 1094 (2009)
4. Bak, P., Tang, C., Wiesenfeld, K.: Self-organized criticality. Phys. Rev. A **38**, 364 (1988)
5. Baldassarri, A., Barrat, A., D'Anna, G., Loreto, V., Mayor, P., Puglisi, A.: What is the temperature of a granular medium? J. Phys. Condens. Matter **17**, S2405 (2005)
6. Barrat, A., Trizac, E.: Lack of energy equipartition in homogeneous heated binary granular mixtures. Granular Matter **4**, 57 (2002)
7. Barrat, A., Loreto, V., Puglisi, A.: Temperature probes in binary granular gases. Phys. A. **334**, 513 (2004)
8. Berthier, L., Barrat, J.L.: Shearing a glassy material: numerical tests of nonequilibrium mode-coupling approaches and experimental proposals. Phys. Rev. Lett. **89**, 095702 (2002)
9. Boffetta, G., Lacorata, G., Musacchio, S., Vulpiani, A.: Relaxation of finite perturbations: Beyond the fluctuation-response relation. Chaos **13**, 806 (2003)
10. Boksenbojm, E., Wynants, B., Jarzynski, C.: Nonequilibrium thermodynamics at the microscale: work relations and the second law. Stat. Mech. Appl. Phys A **389**, 4406 (2010)
11. Bouchaud, J.P., Cugliandolo, L.F., Kurchan, J., Mezard. M.: Spin Glasses and Random Fields. World Scientific, singapore (1998)
12. Bouchaud, J., Dean, D.: Aging on parisi's tree. J. Phy. **I**(5), 265 (1995)
13. Brilliantov, N.K., Poschel, T.: Kinetic Theory of Granular Gases. Oxford University Press, Oxford (2004)
14. Brilliantov, N.V., Poschel, T.: Self-diffusion in granular gases: green-kubo versus chapman-enskog. Chaos **15**, 026108 (2005)
15. Van den Broeck, C., Kawai, R., Meurs, P.: Microscopic analysis of a thermal brownian motor. Phys. Rev. Lett. **93**, 90601 (2004)
16. Brown, R.: A brief account of microscopical observations made.. on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies. Phil. Mag. Ser. 2 **4**, 161 (1828)
17. Brown, R.: Additional remarks on active molecules. Phil. Mag Ser. 2 **6**, 161 (1829)
18. Brown's microscopical observations on the particles of bodies. Philos. Mag. N. S., **8**, 296 (1830)
19. Castellani, T., Cavagna, A.: Spin-glass theory for pedestrians. J. Stat. Mech. Theor. Exp. **2005**, P05012 (2005)
20. Cavagna, A.: Supercooled liquids for pedestrians. Phys. Rep. **476**, 51 (2009)
21. Chapman, S., Cowling, T.: The mathematical theory of non-uniform gases. The mathematical theory of non-uniform gases, vol. 1. Cambridge University Press, Cambridge (1991).
22. Corberi, F., Lippiello, E., Sarracino, A., Zannetti, M.: Fluctuation-dissipation relations and field-free algorithms for the computation of response functions. Phys. Rev. E **81**, 011124 (2010)
23. Costantini, G., Marconi, U., Puglisi, A.: Granular brownian ratchet model. Phys. Rev. E **75**, 061124 (2007)
24. Crisanti, A., Ritort, F.: Violation of the fluctuation-dissipation theorem in glassy systems: basic notions and the numerical evidence. J. Phys. A **36**, R181 (2003)

25. Cugliandolo, L.: Disordered systems. Lecture notes, Cargese (2011)
26. Cugliandolo, L.F.: Weak-ergodicity breaking in mean-field spin-glass models. Phil. Mag. **71**, 501–514 (1995)
27. Cugliandolo, L., Kurchan, J., Peliti, L.: Energy flow, partial equilibration, and effective temperatures in systems with slow dynamics. Phys. Rev. E **55**, 3898 (1997)
28. Dunkel, J., Hänggi, P.: Relativistic brownian motion. Phys. Rep. **471**, 1 (2009)
29. Einstein, A.: On the movement of small particles suspended in a stationary liquid demanded by the molecular-kinetic theory of heat. Ann. d. Phys. **17**, 549 (1905)
30. Evans, D.J., Searles, D.J.: Equilibrium microstates which generate second law violating steady states. Phys. Rev. E **50**, 1645 (1994)
31. Evans, D.J., Searles, D.J.: The fluctuation theorem. Adv. Phys. **52**, 1529 (2002)
32. Falcioni, M., Isola, S., Vulpiani, A.: Correlation functions and relaxation properties in chaotic dynamics and statistical mechanics. Phys. Lett. A **144**, 341 (1990)
33. Feitosa, K., Menon, N.: Fluidized granular medium as an instance of the fluctuation theorem. Phys. Rev. Lett. **92**, 164301 (2004)
34. Feynman, R., Leighton, R., Sands, M., et al.: The Feynman lectures on physics, vol. 2. Addison-Wesley Reading, MA (1964)
35. Fielding, S., Sollich, P.: Observable dependence of fluctuation-dissipation relations and effective temperatures. Phys. Rev. Lett. **88**, 50603 (2002)
36. Gallavotti, G., Cohen, E.G.D.: Dynamical ensembles in stationary states. J. Stat. Phys. **80**, 931 (1995)
37. Goldhirsch, I.: Rapid granular flows. Ann. Rev. Fluid Mech. **35**, 267 (2003)
38. Hänggi, P.: Generalized langevin equations: a useful tool for the perplexed modeller of non-equilibrium fluctuations? Stochastic, dynamics, p. 15. Springer, Berlin (1997)
39. Hänggi, P., Ingold, G.: Fundamental aspects of quantum brownian motion. Chaos: an Interdisciplinary. J. Nonlinear Sci. **15**, 026105 (2005)
40. Hänggi, P., Marchesoni, F., Nori, F.: Brownian motors. Ann. Phys. **14**, 51 (2005)
41. Hänggi, P., Marchesoni, F.: Artificial brownian motors: controlling transport on the nanoscale. Rev. Mod. Phys. **81**, 387 (2009)
42. Hatano, T., Sasa, S.: Steady-state thermodynamics of Langevin systems. Phys. Rev. Lett. **86**, 3463 (2001)
43. Jaeger, H.M., Nagel, S.R.: Physics of the granular state. Science **255**, 1523 (1992)
44. Janssen, H. Versuche uber getreidedruck in silozellen. z. ver deut. Ing. **39** 1045 (1895)
45. Jarzynski, C.: Nonequilibrium equality for free energy differences. Phys. Rev. Lett. **78**, 2690 (1997)
46. Jarzynski, C.: Nonequilibrium work relations: foundations and applications. Eur. Phys. J. B Condens. Matter Complex Syst. **64**, 331 (2008)
47. Kadanoff, L.P.: Built upon sand: theoretical ideas inspired by granular flows. Rev. Mod. Phys. **71**, 435 (1999)
48. Kawai, R., Parrondo, J., den Broeck, C.: Dissipation: the phase-space perspective. Phys. Rev. Lett. **98**, 80602 (2007)
49. Kob, W., Barrat, J., Sciortino, F., Tartaglia, P.: Aging in a simple glass former. J. Phys. Condens. Matter **12**, 6385 (2000)
50. Kubo, R.: The fluctuation-dissipation theorem. Rep. Prog. Phys. **29**, 255 (1966)
51. Kubo, R.: Brownian motion and nonequilibrium statistical mechanics. Science **32**, 2022 (1986)
52. Kubo, R., Toda, M., Hashitsume, N.: Statistical physics II Nonequilibrium Stastical Mechanics. Springer, Berlin (1991)
53. Kullback, S., Leibler, R.: On information and sufficiency. Ann. Math. Stat. **22**, 79 (1951)
54. Kumaran, V.: Temperature of a granular material "fluidized" by external vibrations. Phys. Rev. E **57**, 5660 (1998)
55. Kurchan, J.: Fluctuation theorem for stochastic dynamics. J. Phys. A **31**, 3719 (1998)
56. Kurchan, J.: Non-equilibrium work relations. J. Stat. Mech. Theor. Exp. **2007**, P07005 (2007)
57. Lacorata, G., Puglisi, A., Vulpiani, A.: On the fluctuation-response relation in geophysical systems. Int. J. Mod. Phys. B **23**, 5515 (2009)

58. Langevin, P.: Sur la theorie du mouvement brownien. C. R. Acad. Sci. (Paris) **146** 530 (1908) (Translated in. Am. J. Phys. **65**, 1079 (1997))
59. Lebowitz, J.L., Spohn, H.: A Gallavotti-Cohen-type symmetry in the large deviation functional for stochastic dynamics. J. Stat. Phys. **95**, 333 (1999)
60. Di Leonardo, R., et al.: Bacterial ratchet motors. Proc. Nat. Acad. Sci. **107**, 9541 (2010)
61. Leuzzi, L., Nieuwenhuizen, T.M.: Thermodynamics of the Glassy State. Taylor & Francis, New York (2007)
62. Leuzzi, L.: A stroll among effective temperatures in aging systems: limits and perspectives. J. Non-Cryst. Solids **355**, 686 (2009)
63. Lippiello, E., Corberi, F., Zannetti, M.: Off-equilibrium generalization of the fluctuation dissipation theorem for Ising spins and measurement of the linear response function. Phys. Rev. E **71**, 036104 (2005)
64. Marconi, U., Puglisi, A., Rondoni, L., Vulpiani, A.: Fluctuation-dissipation: response theory in statistical physics. Phys. Rep. **461**, 111 (2008)
65. Van Der Meer, D., Reimann, P., Van Der Weele, K., Lohse, D.: Spontaneous ratchet effect in a granular gas. Phys. Rev. Lett. **92**, 184301 (2004)
66. Mori, H.: Transport, collective motion, and brownian motion. Progress Theoret. Phys. **33**, 423 (1965)
67. Nelson, E. Dynamical theories of Brownian motion. Citeseer **17** (1967)
68. Nicodemi, M.: Dynamical response functions in models of vibrated granular media. Phys. Rev. Lett. **82**, 3734 (1999)
69. van Noije, T.P.C., Ernst, M.H., Trizac, E., Pagonabarraga, I.: Randomly driven granular fluids: large-scale structure. Phys. Rev. E **59**, 4326 (1999)
70. Onsager, L.: Reciprocal relations in irreversible processes. I. Phys. Rev. **37**, 405 (1931)
71. Onsager, L., Machlup, S.: Fluctuations and irreversible processes. Phys. Rev. **91**, 1505 (1953)
72. Perez-Espigares, C., Kolton, A. B., Kurchan, J.: An infinite family of second law-like inequalities. Phys. Rev. **85**(3), 031135 (2012)
73. Perrin, J.: Les Atomes. Alcan, Paris (1913)
74. Puglisi, A., Baldassarri, A., Vulpiani, A.: Violations of the einstein relation in granular fluids: the role of correlations. J. Stat. Mech. P08016 (2007)
75. Puglisi, A.: Granular fluids, a short walkthrough (2010)
76. Puglisi, A., Loreto, V., Marconi, U.M.B., Petri, A., Vulpiani, A.: Clustering and non-gaussian behavior in granular matter. Phys. Rev. Lett. **81**, 3848 (1998)
77. Puglisi, A., Loreto, V., Marconi, U.M.B., Vulpiani, A.: A kinetic approach to granular gases. Phys. Rev. E **59**, 5582 (1999)
78. Puglisi, A., Baldassarri, A., Loreto, V.: Fluctuation-dissipation relations in driven granular gases. Phys. Rev. E **66**, 061305 (2002)
79. Puglisi, A., Visco, P., Barrat, A., Trizac, E., van Wijland, F.: Fluctuations of internal energy flow in a vibrated granular gas. Phys. Rev. Lett. **95**, 110202 (2005)
80. Seifert, U., Speck, T.: Fluctuation-dissipation theorem in nonequilibrium steady states. EPL (Europhys. Lett.) **89**, 10007 (2010)
81. Smoluchowski, M.: Zur kinetischen theorie der brownschen molekularbewegung und der suspensionen. Ann. d. Phys. **21**, 756 (1906)
82. Smoluchowski, M.: Experimentell nachweisbare, der üblichen thermodynamik widersprechende molekularphänomene. Physik. Zeitschr **13**, 1069 (1912)
83. Struik, L.: Physical Aging in Amorphous Polymers and Other Materials. Elsevier, Amsterdam (1978)
84. Villamaina, D., Puglisi, A., Vulpiani, A.: The fluctuation-dissipation relation in sub-diffusive systems: the case of granular single-file diffusion. J. Stat. Mech. L10001 (2008)
85. Williams, D.R.M., MacKintosh, F.C.: Driven granular media in one dimension: correlations and equation of state. Phys. Rev. E **54**, R9 (1996)
86. Zamponi, F., Bonetto, F., Cugliandolo, L. F., Kurchan, J.: A fluctuation theorem for non-equilibrium relaxational systems driven by external forces. J. Stat. Mech. P09013 (2005)

87. Zamponi, F.: Is it possible to experimentally verify the fluctuation relation? a review of theoretical motivations and numerical evidence. J. Stat. Mech. P02008 (2007)
88. Zwangzig, R.: Nonequilibrium statistical mechanics. Oxford University Press, Oxford (2001)
89. Zwanzig, R.: Time-correlation functions and transport coefficients in statistical mechanics. Ann. Rev. Phys. Chem. **16**, 67 (1965)

Springer

http://www.springer.com/978-3-319-01771-6

Transport Properties in Non-Equilibrium and Anomalous Systems
Villamaina, D.
2014, XII, 125 p. 31 illus., 17 illus. in color., Hardcover
ISBN: 978-3-319-01771-6