Focus on some Nonequilibrium Issues

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Abstract

A mathematical framework for the physics of nonequilibrium phenomena is gradually being developed. This review is meant to shed light on some aspects of Response Theory, on the theory of Fluctuation Relations, on the so-called *t-mixing* condition, and on the use of Large Deviation techniques in the description of stochastic diffusion processes.
I. INTRODUCTION

Statistical Mechanics provides a mathematical formalism to bridge different scales of investigation of natural phenomena: a) the microscopic scale, concerning the statistical or collective behaviour of large assemblies of atoms and molecules, approached e.g. in terms of statistical ensembles; b) the mesoscopic scale, commonly described by the Boltzmann equation and its variations, or by more general and abstract stochastic processes; c) and the macroscopic level, by and large the realm of Thermodynamics and Irreversible Thermodynamics which consider matter as a continuum.

Equilibrium phenomena have been investigated and understood much more thoroughly than non-equilibrium ones. At present, the theory may be considered complete, for what concerns the microscopic foundations of equilibrium thermodynamics, including the theory of phase transitions and critical phenomena. Differently, in spite of its celebrated history and of the countless and deep results obtained so far, Statistical Mechanics has not produced yet a comprehensive theoretical framework for non-equilibrium phenomena. These, indeed, are much more numerous, diverse and complex than equilibrium phenomena.

Nevertheless, problems posed, in particular, by the modern bio- and nano-technologies, have turned the attention of a large fraction of the Statistical Mechanics community towards the non-equilibrium phenomena. This has been possible also thanks to the progress of dynamical systems theory, which becomes necessary when the classical hypotheses of local equilibrium \[1\] or kinetic theory fail, as well as in describing macroscopic chaotic phenomena such as those of turbulence \[1\]. Indeed, in equilibrium there is no need to deal with the microscopic dynamics equations of motion, because the classical ensembles have been proven by experience to accurately capture the statistics for the macroscopic quantities and their fluctuations. On the contrary, the classical ensembles do not properly describe systems which are not in equilibrium, in which finite size effects and the persistence of space and time correlations may play a crucial role. Therefore, new hypotheses and novel approaches are required to describe these systems; in particular, understanding the dynamics of the microscopic constituents seems to be unavoidable to shed light even on the properties of stationary states.

As a matter of fact, the study of the macroscopic dynamics of dissipative particle systems, such as those of nonequilibrium molecular dynamics, has produced a number of results of direct inter-

\[1\] Which take place in local equilibrium.
est in nonequilibrium statistical mechanics, including relations between transport coefficients and Lyapunov exponents, which are presently part of a rather satisfactory theory of nonequilibrium liquids.

Twenty years ago, the first fluctuation relation for reversible deterministic dynamics was proposed, and remains one of the few exact and microscopic results for nonequilibrium systems. This led to new response formulae, which generalize the classical response theory to states far from the equilibrium, and to large perturbations of interest, e.g. in climate studies. Interestingly, various results obtained within the deterministic framework coincide with those obtained within the stochastic framework, which is reassuring, because in many situations the two frameworks aim at describing the same phenomenon.

Investigations of Fourier’s law of heat conduction have continued along these dynamical lines since the early days of molecular dynamics and the Fermi-Pasta-Ulam problem, and today they have gained momentum thanks to the discovery of anomalies in the transport of matter, energy, charge etc. at the nanometric scales, which is of interest to bio- and nano-technology.

Dynamics and stochastics together may thus advance our understanding of the fundamental principles which are believed to be common to the incredibly wide spectrum of nonequilibrium phenomena, which ranges from microscopic to macroscopic scales and includes hydrodynamics and turbulence, biology, atmospheric physics, granular matter, nanotechnology, etc.

The wealth of techniques developed to tackle the problems of nonequilibrium physics can also be considered as a theoretical playground for many questions of foundational nature, such as determinism, chaos and randomness, or emergence and complexity, which find in the problem of irreversibility one of their earliest examples.

In this paper, we provide a review of some of the cornerstones of nonequilibrium statistical mechanics in order to clarify the corresponding physical mechanisms. This work is structured as follows.

In Sec. II we analyze the evolution of probability distributions, through the prism of Dynamical Systems theory.

In Sec. III we address the theory of Linear Response, whose origin can be traced back to the pioneering work of R. Kubo [2].

Section IV focuses on the Onsager-Machlup theory, which concerns the regime of small fluctuations around equilibrium.

In Sec. V we review the theory of Fluctuation Relations.

Section VI is devoted to the analysis of the t-mixing condition.
Section VII presents some results concerning the use of large deviations techniques in stochastic diffusion processes.

Conclusions are drawn in Sec. VIII.

II. EVOLUTION OF PROBABILITY DISTRIBUTIONS

This section recalls basic notions of dynamical systems theory, introducing our notation. Consider a dynamical system defined by an evolution equation on a phase space $\mathcal{M}$:

$$\dot{\Gamma} = F(\Gamma), \quad \Gamma \in \mathcal{M}$$

whose trajectories for each initial condition $\Gamma$ are given by $\{S^t \Gamma \}_{t \in \mathbb{R}}$, where $S^t$ is the operator that moves $\Gamma$ to its position after a time $t$ (e.g. $S^0 \Gamma = \Gamma$). We will consider time reversal invariant dynamics, i.e. dynamics obeying

$$IS^t \Gamma = S^{-t} I \Gamma, \quad \forall \Gamma \in \mathcal{M}$$

holds, where the linear operator $I : \mathcal{M} \to \mathcal{M}$ is an involution ($I^2 = \text{identity}$) representing a time reversal operation $^2$. Furthermore, we will consider evolutions such that $\{S^t \}_{t \in \mathbb{R}}$ satisfies the group property $S^t S^s = S^{t+s}$. The time averages of a phase variable $\phi : \mathcal{M} \to \mathbb{R}$, along a trajectory starting at $\Gamma$, will be denoted by:

$$\overline{\phi}(\Gamma) = \lim_{t \to \infty} \frac{1}{t} \int_0^t \phi(S^s \Gamma) \, ds$$

If the dynamics represents a thermodynamic system, in which $\Gamma$ is a single microscopic phase, the time average should not depend on this phase, and could be obtained as a phase space average, with respect to a given probability distribution $\mu$ $^3$:

$$\overline{\phi}(\Gamma) = \int_{\mathcal{M}} \phi(X) \, d\mu(X) = \langle \phi \rangle_\mu, \quad \text{for } \mu\text{-almost every } \Gamma \in \mathcal{M}$$

This is the case if the dynamical system $(S, \mathcal{M}, \mu)$ is ergodic (cf. Subsection II A), which is a very strong property, not verified by most of the systems of physical interest. It can be however safely assumed to hold very often, because physics is often concerned with a small set of observables and with systems made of exceedingly large numbers of particles, c.f. $^3$.

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$^2$ For instance, in simple cases one may take $\Gamma = (q, p)$, and $I(q, p) = (q, -p)$.

$^3$ Mathematically this condition is verified if the $\Gamma \in \mathcal{M}$ that yield different values for $\overline{\phi}(\Gamma)$ constitute a set of vanishing probability. This is a sufficient, not necessary, condition.
Once $\mathcal{M}$ is endowed with a probability distribution $\mu_0$, $\mu_0(\mathcal{M}) = 1$ and $\mu_0(E) \geq 0$ for all allowed events $E \subset \mathcal{M}$, the dynamics in $\mathcal{M}$ may be used to induce an evolution in the space of probabilities. One may assume that the subsets of the phase space have a certain probability, which they carry along where the dynamics moves them. As a consequence, the probability distribution on $\mathcal{M}$ changes in time, and one may introduce a set of distributions $\{\mu_t\}_{t \in \mathbb{R}}$ as follows:

$$\mu_t(E) = \int_E d\mu_t = \int_{S^{-t}E} d\mu_0 = \mu_0(S^{-t}E) \quad (5)$$

where $S^{-t}E$ is the preimage of $E$ an earlier time $t$. This equation simply means that the probability of $S^{-t}E$ at the initial time, is assumed to pertain to $E$ at time $t$. With this definition, probability is conserved in phase space and in general it flows like a compressible fluid. Taking much care, the evolution of the probability distributions may be used to define an evolution of the observables, introducing

$$\langle \phi \rangle_t = \int_{\mathcal{M}} \phi \, d\mu_t \quad (6)$$

Under certain conditions, the mean values of the phase functions completely characterize the system, therefore one often refers to $\mu_t$ as to the state of the system at time $t$, which is to be distinguished from the microscopical phase $\Gamma \in \mathcal{M}$. A probability measure $\mu$ is called invariant if $\mu(E) = \mu(S^{-t}E)$ for all $t$ and all measurable sets $E$.

At times $\mu_t$ has a density $f_t$, i.e. $d\mu_t(\Gamma) = f_t(\Gamma)d\Gamma$. In that case, the evolution of $\mu_t$ follows from the evolution of the normalized non-negative function $f_t$, determined by Eq.(5). Operating in Eq.(5) the change of coordinates $Y = S^tX$, i.e. $X = S^{-t}Y$, in the last integral of the following expression

$$\mu_t(E) = \int_E f_t(X) \, dX = \int_{S^{-t}E} f_0(X) \, dX \quad (7)$$

and:

$$\int_E f_t(X) \, dX = \int_E f_0(Y)J^{-t}(Y) \, dY \quad (8)$$

where $J^{-t}(Y) = |(\partial S^{-t}X/\partial X)|_Y$ is the Jacobian of the transformation. As Eqs.(5-8) hold for all allowed subsets of $\mathcal{M}$, one can write

$$f_t(X) = f_0(S^{-t}X)J^{-t}(X) \quad (9)$$

In case of Hamiltonian dynamics, probabilities flow like incompressible fluids.
For Hamiltonian dynamics, $J^{-t}(X) = 1$, hence $f_t(X) = f_0(S^{-t}X)$. In general, for the evolution of the observables one obtains:

$$\langle \phi \rangle_t = \int_M \phi(\Gamma)f_t(\Gamma)d\Gamma = \int_M \phi(\Gamma)f_0(S^{-t}\Gamma)J^{-t}(\Gamma)d\Gamma$$  \hspace{1cm} (10)

Introducing $Y = S^{-t}\Gamma$ in the last integral, so that $d\Gamma = J^t(Y)dY$, one finds:

$$\langle \phi \rangle_t = \int_M \phi(S^tY)f_0(Y)J^{-t}(S^tY)J^t(Y)dY$$  \hspace{1cm} (11)

Under suitable smoothness conditions for the dynamics and $M$, probability is transported by the phase space points like the mass of a fluid, whose density $f$ obeys the formal continuity equation:

$$\frac{\partial f}{\partial t} = -\nabla_{\Gamma} \cdot (Ff) , \quad \frac{df}{dt} = \frac{\partial f}{\partial t} + \nabla_{\Gamma} f \cdot F = -f \nabla_{\Gamma} \cdot F = -f \Lambda$$  \hspace{1cm} (12)

Here $\Lambda = \nabla_{\Gamma} \cdot F$, called phase space expansion rate, is the divergence of the vector field $F$ on $M$, cf. Eq. (11). Introducing the total time derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + F \cdot \nabla_{\Gamma}$$,  \hspace{1cm} (13)

Eqs. (12) may also be written as

$$\frac{d}{dt} \ln f = -\Lambda$$  \hspace{1cm} (14)

Because the global existence and uniqueness of solutions of the equations of motion is practically assured for particle systems of physical interest, one may safely assume that the solutions of the Liouville equation also exist and can be constructed by means of formal calculations. Various procedures are available for this purpose. For example, let us introduce the $f$-Liouvillean operator $\mathcal{L}$:

$$\mathcal{L} = -i(\nabla_{\Gamma} \cdot F + F \cdot \nabla_{\Gamma})$$, so that $\frac{\partial f}{\partial t} = -i\mathcal{L}f$$  \hspace{1cm} (15)

and let us express $\partial f_t/\partial t$ to first order in the time increment $\Delta t$:

$$\frac{\partial f_t}{\partial t}(\Gamma) = -i(\mathcal{L}f_t)(\Gamma) = \frac{f_{t+\Delta t}(\Gamma) - f_t(\Gamma)}{\Delta t} + O(\Delta t)$$  \hspace{1cm} (16)

It follows that

$$f_{\Delta t}(\Gamma) = (1 - i\mathcal{L}\Delta t) f_0(\Gamma) + O(\Delta t^2)$$  \hspace{1cm} (17)

$$f_{2\Delta t}(\Gamma) = (1 - i\mathcal{L}\Delta t) f_{\Delta t}(\Gamma) + O(\Delta t^2) = (1 - i\mathcal{L}\Delta t)^2 f_0(\Delta) + O(\Delta t^2)$$  \hspace{1cm} (18)

$$\vdots$$  \hspace{1cm} (19)

$$f_{n\Delta t}(\Gamma) = (1 - i\mathcal{L}\Delta t)^n f_0(\Gamma) + nO(\Delta t^2)$$  \hspace{1cm} (20)

Global solution means that particles do no cease to exist after a while; Uniqueness implies that the same particles do not exist at once along distinct trajectories. If these properties are violated, the model under investigation must be discarded.
Taking $\Delta t = t/n$, so that $\Delta \to 0$ and $nO(\Delta t^2) \to 0$ as $n \to \infty$, one obtains:

$$f_t(\Gamma) = \lim_{n \to \infty} \left(1 - \frac{itL}{n}\right)^n f_0(\Gamma) = \sum_{n=0}^{\infty} \frac{(-itL)^n}{n!} f_0(\Gamma) \equiv e^{-itL} f_0(\Gamma) \quad (21)$$

The question is now to connect Eq. (21) with Eq. (9). One can write

$$Y = S^t X = S^{t/n} \left( S^{t/n} \left( \cdots S^{t/n} (X) \cdots \right) \right) \quad (22)$$

Hence, the chain rule yields

$$\frac{\partial Y}{\partial X} \bigg|_{X_i} = \left( \frac{\partial S^{t/n} X}{\partial X} \bigg|_{X_{n-1}} \right) \left( \frac{\partial S^{t/n} X}{\partial X} \bigg|_{X_{n-2}} \right) \cdots \left( \frac{\partial S^{t/n} X}{\partial X} \bigg|_{X_0} \right) \quad (23)$$

where $X_j = S^{jt/n} X_0$, and $X_0$ is the initial point of a trajectory. One can expand to first order each derivative in brackets as follows:

$$\left. \frac{\partial (S^{t/n} X)}{\partial X} \right|_{X_j} = \frac{\partial}{\partial X}(X + F \Delta t + O(\Delta t^2)) \bigg|_{X_j} \quad (24)$$

and further

$$\left. \frac{\partial (S^{t/n} X)}{\partial X} \right|_{X_j} = 1 + \left. \frac{\partial F}{\partial X} \right|_{X_j} \Delta t + O(\Delta t^2) = e^{\frac{\partial F}{\partial X} |_{X_j} \Delta t} + O(\Delta t^2) \quad , (25)$$

$1$ being the identity matrix. Substituting Eq. (25) in Eq. (23), and noting that the exponential operators do not commute in general, the $n \to \infty$ limit leads to a so-called left ordered exponential, which can also be expressed as a Dyson series:

$$e^{\int_0^t T(S^s X) ds} = 1 + \int_0^t dt_1 T(S^{t_1} X) + \int_0^t dt_1 \int_0^{t_1} dt_2 T(S^{t_1} X) T(S^{t_2} X)$$

$$+ \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 T(S^{t_1} X) T(S^{t_2} X) T(S^{t_3} X) + \ldots$$

where the time dependent matrix

$$T(S^s X) = \left. \frac{\partial F}{\partial X} \right|_{S^s X} \quad (26)$$

is the Jacobian matrix of $F$ computed at the point $S^s X$. Considering that the identity $\det(e^L) = \exp(\text{Tr} L)$ holds for left ordered exponentials as well, one obtains:

$$\det \left( e^{\int_0^t T(S^s X) ds} \right) = \exp \left\{ \int_0^t \nabla_\Gamma \cdot F(S^s X) \, ds \right\} = \int_0^t \Lambda(S^s X) \, ds \quad (27)$$

Which implies that:

$$J^t(X) = e^{\int_0^t \Lambda(S^u X) du} = e^{\int_0^1 \Lambda(S^{t+u} X) du} = \frac{1}{J^{-t}(S^t X)} = \frac{1}{J^{-t}(Y)} \quad (28)$$
where we have taken \( u = t + s \) in the second integral. Equation (28) is obvious for compressible fluids: a fluid element about \( X \) varies in a time \( t \) by a factor which is the inverse of the variation of the fluid element about \( Y \), when tracing backwards its trajectory. Consequently \( J^{-t}(S^{t}X)J^{t}(X) = 1 \), and Eq. (29) may be rewritten as:

\[
f_{t}(X) = f_{0}(S^{-t}X)e^{-\int_{0}^{t} \Lambda(s^{t}X)ds}
\]

while Eq. (30) takes the interesting form

\[
\langle \phi \rangle_{t} = \int_{\mathcal{M}} (\phi \circ S^{t})(X) f_{0}(X) \, dX = \langle \phi \circ S^{t} \rangle_{0}
\]

A. Ergodicity and mixing

Let \( \mu \) be one invariant probability distribution and \( \phi \) an integrable phase function. The following statements are equivalent:

\begin{enumerate}
  \item \( \overline{\phi}(\Gamma) = \langle \phi \rangle_{\mu} \), except for a set of vanishing \( \mu \) probability;
  \item except for a set of vanishing \( \mu \) probability, \( \tau_{E}(\Gamma) = \mu(E) \), where \( E \subset \mathcal{M} \) is a \( \mu \)-measurable set and
    \[
    \tau_{E}(\Gamma) = \lim_{t \to \infty} \frac{1}{t} \int_{0}^{t} \chi_{E}(S^{s}\Gamma) \, ds ; \quad \text{with} \quad \chi_{E}(\Gamma) = \begin{cases} 1 & \text{if } \Gamma \in E \\ 0 & \text{else} \end{cases}
    \]
    is the the mean time in \( E \);
  \item let \( \phi \) be \( \mu \)-integrable and let \( \phi \) be a constant of motion (i.e. \( \phi(S^{t}\Gamma) = \phi(\Gamma) \) for all \( t \) and all \( \Gamma \)). Then \( \phi(\Gamma) = C \mu \)-almost everywhere, for a given \( C \in \mathbb{R} \);
  \item the dynamical system \((S, \mathcal{M}, \mu)\) is metrically indecomposable, i.e. given the invariant set \( E \) (which means \( S^{-t}E = E \)), either \( \mu(E) = 0 \) or \( \mu(E) = 1 \).
\end{enumerate}

We call ergodic the dynamical systems that verify these statements. This is a very strong property because \( \phi \) can be any integrable function. Physics concerns, instead, only a few phase variables that are physically relevant.

The following statements are equivalent too:

\begin{enumerate}
  \item \( \mu \left( S^{-t}D \cap E \right) = \mu(D)\mu(E) \quad (32) \)
\end{enumerate}

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M2. for all $\phi, \psi \in L_2(M, \mu)$ the following holds:

$$\lim_{t \to \infty} \langle (\phi \circ S^t) \psi \rangle_\mu = \langle \phi \rangle_\mu \langle \psi \rangle_\mu$$  \hspace{1cm} (33)

We call mixing the dynamical systems that verify these two statements. Mixing is an even stronger property than ergodicity, in the sense that mixing systems are also ergodic, whereas not all ergodic systems are mixing.

For dynamics, which are mixing with respect to a probability measure with density $h$, $d\mu = hd\Gamma$ say, one can prove that an initial state characterized by a probability density $f_0$ eventually converges to the state of density $h$. To prove that, consider the phase functions $\phi$ and $\psi$, for which one can write:

$$\lim_{t \to \infty} \langle (\phi \circ S^t) \cdot \psi \rangle_h = \lim_{t \to \infty} \langle \phi \circ S^t \rangle_h \langle \psi \rangle_h$$

$$= \langle \psi \rangle_h \int d\Gamma \phi(S^t\Gamma)h(\Gamma) = \langle \psi \rangle_h \int d\Gamma \phi(\Gamma) S^{*t} h(\Gamma) = \langle \psi \rangle_h \langle \phi \rangle_h$$

where the superscript * denotes the distribution function propagator for a period time $t$. Then, for a time dependent probability distribution $f_t$ which vanishes at least where $h$ does, let us introduce $R_t = f_t/h$:

$$\int R_t(\Gamma)h(\Gamma)d\Gamma = \int f_t(\Gamma)d\Gamma = 1; \quad \int \frac{1}{R_t(\Gamma)} f_t(\Gamma)d\Gamma = \int h(\Gamma)d\Gamma = 1$$ \hspace{1cm} (34)

for all times $t$, and we obtain:

$$\langle \phi \rangle_t = \int \phi(\Gamma)f_t(\Gamma)d\Gamma = \int \phi(\Gamma)R_t(\Gamma)h(\Gamma)d\Gamma = \langle \phi \cdot R_t \rangle_h$$ \hspace{1cm} (35)

We can also write, by definition:

$$\langle \phi \rangle_t = \int \phi(\Gamma)f_t(\Gamma)d\Gamma = \int \phi(S^t\Gamma)f_0(\Gamma)d\Gamma = \int \phi(S^t\Gamma)R_0(\Gamma)h(\Gamma)d\Gamma$$ \hspace{1cm} (36)

from which, the mixing condition produces the convergence to the steady state of density $h$:

$$\lim_{t \to \infty} \langle \phi \rangle_t = \int \phi(S^t\Gamma)R_0(\Gamma)h(\Gamma)d\Gamma = \langle (\phi \circ S^t) R_0 \rangle_h \to \langle \phi \rangle_h \langle R_0 \rangle_h = \langle \phi \rangle_h$$ \hspace{1cm} (37)

In other words, probability densities for finite systems, if they are both stationary and mixing, are attractors in the space of probability densities.

However, this proof of convergence to a mixing stationary state is deceitfully simple. Although it is a very strong property, in general mixing does not suffice to prove convergence to a steady state, because it amounts to the decay in time of the microscopic correlations within already stationary macroscopic states and not to the decorrelation of the initial state from the final state.
III. LINEAR RESPONSE

Let us address the response of a given system to external actions. As an example, consider a system of \( N \) particles in contact with a thermal bath at inverse temperature \( \beta \), described by the following Hamiltonian:

\[
H(\Gamma) = H_0(\Gamma) + \lambda A(\Gamma) ,
\]

where \( \lambda \) is a small parameter and \( A \) perturbs the canonical equilibrium:

\[
f_0 = \exp(-\beta H_0) / \int d\Gamma \exp(-\beta H_0)
\]

After some time, a new canonical equilibrium is established which, to the first order in \( \lambda \), is given by:

\[
f = \frac{e^{-\beta H_0}e^{-\beta \lambda A}}{\int d\Gamma e^{-\beta H_0}e^{-\beta \lambda A}} = \frac{e^{-\beta H_0} [1 - \beta \lambda A + O(\beta^2 \lambda^2 A^2)]}{\int d\Gamma e^{-\beta H_0} [1 - \beta \lambda A + O(\beta^2 \lambda^2 A^2)]} \\
\simeq f_0 \frac{1 - \lambda \beta A}{1 - \lambda \beta \langle A \rangle_0} \simeq f_0(\Gamma) [1 - \lambda \beta (A(\Gamma) - \langle A \rangle_0)]
\]

where, \( \langle \cdot \rangle_0 \) denotes averaging with respect to \( f_0 \). The effect of the perturbation on a given observable \( \phi \), is then expressed by:

\[
\langle \phi \rangle_\lambda - \langle \phi \rangle_0 = \int d\Gamma \phi(\Gamma) [f(\Gamma) - f_0(\Gamma)] \simeq -\lambda \beta [\langle \phi A \rangle_0 - \langle \phi \rangle_0 \langle A \rangle_0]
\]

which is the correlation of the observable \( \phi \) with the perturbation \( A \), with respect to the state expressed by \( f_0 \). Taking \( \phi = A = H_0 \), one obtains an expression for the heat capacity at constant volume \( C_V \), which expresses the response of the system to temperature variations. Indeed, defining \( C_V \) as

\[
C_V = \frac{\partial \langle H_0 \rangle_0}{\partial T} = \frac{d\beta}{dT} \frac{\partial \langle H_0 \rangle_0}{\partial \beta} = \frac{\langle H_0^2 \rangle_0 - \langle H_0 \rangle_0^2}{k_B T^2}
\]

Eqs (41,42) yield:

\[
\left. \frac{\partial \langle H_0 \rangle_0}{\partial \lambda} \right|_{\lambda=0} = \lim_{\lambda \to 0} \frac{\langle H_0 \rangle_\lambda - \langle H_0 \rangle_0}{\lambda} = -\beta \left( \langle H_0^2 \rangle_0 - \langle H_0 \rangle_0^2 \right) = -k_B T^2 C_V
\]

More in general, consider time dependent perturbations of form \(-\mathcal{F}(t)A(\Gamma)\):

\[
H(\Gamma, t) = H_0(\Gamma) - \mathcal{F}(t)A(\Gamma)
\]

and split the corresponding evolution operator in two parts:

\[
i\mathcal{L}_0 f = \{f, H_0\} , \quad i\mathcal{L}_{\text{ext}}(t)f = -\mathcal{F}(t) \{f, A\}
\]
where \( \{ \cdot \} \) are the Poisson brackets. One has \( i\mathcal{L}_0 f_0 = 0 \), which means that \( f_0 \) is invariant for the unperturbed dynamics. Then, the solution of the Liouville equation

\[
\frac{\partial f}{\partial t} = -i (\mathcal{L}_0 + \mathcal{L}_{\text{ext}}(t)) f
\]

(46)
can be expressed by:

\[
f_t(\Gamma) = e^{it\mathcal{L}_0} f_0(\Gamma) - i \int_0^t dt' e^{-it'(t-t')} \mathcal{L}_0 \mathcal{L}_{\text{ext}}(t') f_{t'}(\Gamma)
= f_0(\Gamma) - i \int_0^t dt' e^{-it'(t-t')} \mathcal{L}_0 \mathcal{L}_{\text{ext}}(t') f_0(\Gamma) + \text{higher order in } \mathcal{L}_{\text{ext}}
\]
as proved by inspection. If the deviations from the unperturbed system are considered small, the higher orders in \( \mathcal{L}_{\text{ext}} \) can be omitted. Then Eq. (41) implies:

\[
\langle \phi \rangle_t - \langle \phi \rangle_0 \simeq \int \! d\Gamma \phi(\Gamma) \int_0^t \! dt' e^{-it'(t-t')} \mathcal{F}(t') \{ f_0, A \}
\]

(47)

where

\[
\{ f_0, A \} = \{ H_0, A \} \frac{\partial f_0}{\partial H_0} = \beta f_0 \frac{dA}{dt}
\]

(48)

Eventually, one obtains:

\[
\langle \phi \rangle_t - \langle \phi \rangle_0 \simeq \int_0^t \! dt' R(t-t') \mathcal{F}(t')
\]

(49)

where \( R(t) \) is the response function:

\[
R(t) = \beta \left\langle \dot{A} \left( \phi \circ S^t \right) \right\rangle_0 = \beta \int \! d\Gamma f_0(\Gamma) \frac{dA}{dt}(\Gamma) e^{it\mathcal{F}_0} \phi(\Gamma)
\]

(50)

Once again, the macroscopic nonequilibrium behaviour of a given system has been related solely to the correlations of microscopic fluctuating quantities, computed with respect to the relevant equilibrium ensemble.

Equation (49) suggests that even the linear response is in general affected by memory effects, hence the Markovian behaviour appears to be either very special or only approximately valid. This implies, for instance, that all nonequilibrium fluids have a viscoelastic behaviour. In practice, however, in normal fluids this behaviour arises only exceedingly far from equilibrium.

Recently, it has been shown that this approach applies to the case of perturbation of nonequilibrium steady states, if they are represented by a regular probability density, as in the presence of noise, cf. Refs. [4, 5].

Differently, the invariant phase space probability distribution \( \mu \) of a dissipative system is singular and supported on a fractal attractor. Consequently, it is not obvious anymore that the statistical
features induced by a perturbation can be related to the unperturbed statistics. The reason is that even very small perturbations may lead to microscopic phase whose probability vanishes in the unperturbed state. In such a case, the information contained in $\mu$ is irrelevant.

Indeed, Ruelle showed that in certain cases a perturbation $\delta\Gamma$ about a microstate $\Gamma$ and its evolution $S^t\delta\Gamma$ can be decomposed in two parts, $(S^t\delta\Gamma)\parallel$ and $(S^t\delta\Gamma)\perp$, respectively perpendicular and parallel to the fibres of the attractor:

$$S^t\delta\Gamma = (S^t\delta\Gamma)\parallel + (S^t\delta\Gamma)\perp$$

The first addend can be related to the dynamics on the attractor, while the second may not.

Later, it has been pointed out that this difficulty should not concern systems of many interacting particles. In those cases, rather than the full phase space, one considers the much lower dimensional projections concerning the few physically relevant observables, i.e. the marginals of singular phase space measures, on spaces of sufficiently lower dimension, which are usually regular. These facts can be briefly recalled as follows. Ruelle showed that the effect of a perturbation $\delta F(t) = \delta F\parallel(t) + \delta F\perp(t)$ on the response of a generic (smooth enough) observable $\phi$ is given by:

$$\langle \phi \rangle_t - \langle \phi \rangle_0 = \int_0^t R^{(\phi)}_{\parallel}(t-\tau)\delta F\parallel(\tau)d\tau + \int_0^t R^{(\phi)}_{\perp}(t-\tau)\delta F\perp(\tau)d\tau$$

where the subscript 0 denotes averaging with respect to $\mu$, $R^{(\phi)}_{\parallel}$ may be expressed in terms of correlation functions evaluated with respect to $\mu$, while $R^{(\phi)}_{\perp}$ depends on the dynamics along the stable manifold, hence it may not.

Let us adopt the point of view of Ref. Since for a $d$-dimensional dissipative dynamical system consider, for simplicity, an impulsive perturbation $\Gamma \rightarrow \Gamma + \delta\Gamma$, such that all components of $\delta\Gamma$ vanish except one, denoted by $\delta\Gamma_i$. The probability distribution $\mu$ is correspondingly shifted by $\delta\Gamma$, and turns into a non-invariant distribution $\mu_0$, whose evolution $\mu_\ell$ tends to $\mu$ in the $t \rightarrow \infty$ limit. For every measurable set $E \subset \mathcal{M}$, $\mu_0(E)$ equals $\mu(E - \delta\Gamma)$, and $\mu(E)$ is computed as explained in Sec. Taking $\phi(\Gamma) = \Gamma_i$, one obtains:

$$\langle \Gamma_i \rangle_t - \langle \Gamma_i \rangle_0 = \int \Gamma_i \, d\mu_\ell(\Gamma) - \int \Gamma_i \, d\mu(\Gamma)$$

Let us now approximate the singular $\mu$, coarse graining $\mathcal{M}$ with an $\epsilon$-partition made of a finite set of $d$-dimensional hypercubes $\Lambda_k(\epsilon)$ of side $\epsilon$ and centers $\Gamma_k$. The corresponding approximations of

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6 Concerning certain smooth, uniformly hyperbolic dynamical systems.

7 The set $E - \delta\Gamma$ is defined by $\{ \Gamma \in \mathcal{M} : \Gamma + \delta\Gamma \in E \}$. 

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\(\mu\) and of \(\mu_t\) are given by the probabilities \(P_k(\epsilon)\) and \(P_{t,k}(\epsilon; \delta \Gamma)\) of the hypercubes \(\Lambda_k(\epsilon)\), where:

\[
P_k(\epsilon) = \int_{\Lambda_k(\epsilon)} d\mu(\Gamma), \quad P_{t,k}(\epsilon) = \int_{\Lambda_k(\epsilon)} d\mu_t(\Gamma).
\]

The coarse grained invariant density \(\rho(\Gamma; \epsilon)\) is given by:

\[
\rho(\Gamma; \epsilon) = \sum_k \rho_k(\Gamma; \epsilon), \quad \text{with} \quad \rho_k(\Gamma; \epsilon) = \begin{cases} 
P_k(\epsilon)/\epsilon & \text{if } x \in \Lambda_k(\epsilon) \\
0 & \text{else} \end{cases}
\]

If \(Z_i\) is the number of one-dimensional bins of form \([\Gamma_i^{(q)} - \epsilon/2, \Gamma_i^{(q)} + \epsilon/2]\), \(q \in \{1, 2, ..., Z_i\}\), in the \(i\)-th direction, marginalizing the approximate distribution yields the quantities:

\[
p_i^{(q)}(\epsilon) = \int_{\Gamma_i^{(q)} + \epsilon/2}^{\Gamma_i^{(q)} - \epsilon/2} \left\{ \int \rho(\Gamma; \epsilon) \prod_{j \neq i} d\Gamma_j \right\} d\Gamma_i,
\]

each of which is the invariant probability that the coordinate \(\Gamma_i\) of \(\Gamma\) lie in one of the \(Z_i\) bins. Similarly, one gets the marginal of the evolving approximate probability:

\[
p_{i,t}^{(q)}(\epsilon) = \int_{\Gamma_i^{(q)} + \epsilon/2}^{\Gamma_i^{(q)} - \epsilon/2} \left\{ \int \rho_t(\Gamma; \epsilon) \prod_{j \neq i} d\Gamma_j \right\} d\Gamma_i,
\]

Dividing by \(\epsilon\), one obtains the coarse grained marginal probability densities \(\rho_i^{(q)}(\epsilon)\) and \(\rho_{i,t}^{(q)}(\epsilon)\), as well as the \(\epsilon\)-approximate response function:

\[
B_i^{(q)}(\Gamma_i, \delta \Gamma_i, t, \epsilon) = \frac{1}{\epsilon} \left[ p_{i,t}^{(q)}(\epsilon) - p_i^{(q)}(\epsilon) \right] = \rho_{i,t}^{(q)}(\epsilon) - \rho_i^{(q)}(\epsilon)
\]

Reference \[7\] shows that the right hand side of Eq.(57) tends to a regular function of \(\Gamma_i\) under the \(Z_i \to \infty, \epsilon \to 0\) limits. Consequently, \(B_i^{(q)}(\Gamma_i, \delta \Gamma_i, t, \epsilon)\) yields an expression similar to that of standard response theory, in the sense that it depends solely on the unperturbed state, although that is supported on a fractal set. There are exceptions to this conclusion, most notably those discussed by Ruelle. But for most systems of physical interest, such as systems of many interacting particles, this is the expected result. The idea is that the projection procedure makes unnecessary the explicit calculation of \(R_{\perp}(\phi)\) in Eq.(51), although \(R_{\perp}^{(q)}(\phi)\) does not need to be negligible \[10\]. Therefore, apart from peculiar situations, the response may be referred only to the unperturbed dynamics, as in the standard theory.

IV. ONSAGER-MACHLUP: RESPONSE FROM SMALL DEVIATIONS

The classical theory of fluctuations, developed by Onsager and Machlup \[11, 12\] to quantify the probability of temporal fluctuations paths, is based on the following assumptions:
A1. Onsager regression hypothesis: the decay of a system from a nonequilibrium state produced by a spontaneous fluctuation, obeys on average the macroscopic law describing the decay from the same state produced by a macroscopic constraint that has been suddenly removed;

A2. the observables are Gaussian random variables (i.e. the probability density of \( m \) values taken at \( m \) consecutive instants of time is an \( m \)-dimensional Gaussian);

A3. the probability density \( P(\Gamma) \) of the microstate \( \Gamma \) obeys Boltzmann’s principle:

\[
k_B \log P(\Gamma) = S(\Gamma) + \text{const} \quad (58)
\]

A4. the state \( S^t \Gamma \) is statistically independent of the state \( S^{t'} \Gamma \) for \( |t - t'| > \tau_d \), \( \tau_d \) being the decorrelation time;

A5. the microscopic dynamics is time reversal invariant;

A6. the vector of observables \( \alpha = (\alpha_1, ..., \alpha_n) \) is chosen so that its evolution is Markovian. This is possible if \( n \) is neither too small nor too large in such a way that:

- \( \alpha_i \) represents a macroscopic quantity referring to a subsystem containing very many particles;
- \( \alpha_i \) is an algebraic sum of molecular variables, so that by the Central Limit Theorem its fluctuations are Gaussians centered on its average (equilibrium) value;
- \( \alpha_i \) must be an even function of the molecular variables that are odd under time reversal (microscopic time reversal invariance);

A7. the system is in local thermodynamic equilibrium;

A8. the fluxes \( \dot{\alpha}_i \) depend linearly on the thermodynamic forces \( X_i \):

\[
\dot{\alpha}_i = \sum_{j=1}^{n} L_{ij} X_j , \quad X_i = \sum_{j=1}^{n} R_{ij} \dot{\alpha}_j ; \quad (59)
\]

A9. the process is stationary: i.e. given the times \( t_1, t_2, ..., t_p \) and the \( n \)-dimensional vectors \( \alpha^{(1)}, \alpha^{(2)}, ..., \alpha^{(p)} \), the probabilities \( F_{i,p} \), \( i = 1, ..., n \), that each component of the observable vector is smaller by value than the corresponding component of the vector sequence \( \alpha^{(k)} \) at the corresponding times \( t_k \) satisfy:

\[
F_{i,p} \left( \alpha_i \leq \alpha_i^{(k)} , t_k , k = 1, ..., p \right) = F_{i,p} \left( \alpha_i \leq \alpha_i^{(k)} , t_k + \tau , k = 1, ..., p \right) \quad (60)
\]
for all $\tau$ and, analogously, the corresponding probability densities $f_{i,p}$, satisfy

$$f_{i,p} \left( \alpha_i = \alpha_i^{(k)}, t_k, k = 1, \ldots, p \right) = f_{i,p} \left( \alpha_i = \alpha_i^{(k)}, t_k + \tau, k = 1, \ldots, p \right)$$  \hspace{1cm} (61)$$

where

$$F_{i,p} \left( \alpha_i \leq \alpha_i^{(k)}, t_k, k = 1, \ldots, p \right) = \int_{-\infty}^{\alpha_i^{(1)}} d\alpha_i^{(1)} \cdots \int_{-\infty}^{\alpha_i^{(p)}} d\alpha_i^{(p)} f_{i,p} \left( \alpha_i = \alpha_i^{(k)}, t_k, k = 1, \ldots, p \right)$$

For simplicity, let $\alpha$ be the vector of the deviations from the equilibrium values. Then, the entropy $S$ is a function of the observables $\alpha$, which can be expanded about its equilibrium value $S_0$ as:

$$S = S_0 - \frac{1}{2} \sum_{i,j=1}^{n} s_{ij} \alpha_i \alpha_j + \text{higher order in } \alpha$$  \hspace{1cm} (62)$$

There is no linear term in $\alpha$ because $S_0$ is the maximum of $S$. Correspondingly, the thermodynamic forces are expressed by

$$X_i = \frac{\partial S}{\partial \alpha_i} = -\sum_{j=1}^{n} s_{ij} \alpha_j , \quad i = 1, \ldots, n$$  \hspace{1cm} (63)$$

which implies

$$\sum_{j=1}^{n} \left[ R_{ij} \dot{\alpha}_j + s_{ij} \alpha_j \right] = 0 , \quad i = 1, \ldots, n$$  \hspace{1cm} (64)$$

To compute the evolution of $\alpha$, let us introduce the functions

$$\Phi \left( \dot{\alpha}, \dot{\beta} \right) = \frac{1}{2} \sum_{i,j=1}^{n} R_{ij} \dot{\alpha}_i \dot{\alpha}_j , \quad \Psi \left( X, Y \right) = \frac{1}{2} \sum_{i,j=1}^{n} L_{ij} X_i X_j$$  \hspace{1cm} (65)$$

Which characterize the real evolution only when $\dot{\alpha} = \dot{\beta}$ are the real evolving fluxes and when $X = Y$ are the real thermodynamic forces, in which cases we have:

$$\dot{S} = 2\Phi \left( \dot{\alpha}, \dot{\alpha} \right) = 2\Psi \left( X, X \right)$$  \hspace{1cm} (66)$$

The molecular chaos may be accounted for by a random perturbation, which turns Eq. (64) into

$$\sum_{j=1}^{n} \left[ R_{ij} \dot{\alpha}_j + s_{ij} \alpha_j \right] = \epsilon_i , \quad \langle \epsilon_i \rangle = 0 , \quad i = 1, \ldots, n$$  \hspace{1cm} (67)$$

where $\epsilon_i$ is a random force which allows different paths with different probabilities and which does no net work.
Let \( f_{i,1} (\alpha_i^{(1)}, t_1) \) be the probability density for the \( i \)-th observable to take values close to \( \alpha_i^{(1)} \) at time \( t_1 \). By assumption A3, \( f_{i,1} \) is independent of \( t_1 \). Let \( f_{i,1} (\alpha_i^{(k)}, t_k | \alpha_{i-1}^{(k-1)}, t_{k-1}) \) be the conditional probability density for the \( i \)-th observable to take values close to \( \alpha_i^{(k)} \) at time \( t_k \), given that it was \( \alpha_{i-1}^{(k-1)} \) at time \( t_{k-1} \). Because of the Markov property and of A3, one has:

\[
f_{i,p} (\alpha_i = \alpha_i^{(k)}, t_k, k = 1, \ldots, p) \]

\[
= f_{i,1} (\alpha_i^{(p)}, t_p | \alpha_{i-1}^{(p-1)}, t_{p-1}) \cdots f_{i,1} (\alpha_i^{(2)}, t_2 | \alpha_i^{(1)}, t_1) f_{i,1} (\alpha_i^{(1)}, t_1) \tag{68}
\]

\[
= f_{i,1} (\alpha_i^{(p)}, t_p | \alpha_{i-1}^{(p-1)}, t_{p-1}) \cdots f_{i,1} (\alpha_i^{(2)}, t_2 | \alpha_i^{(1)}, t_1) e^{S(\alpha_i^{(1)})/k_B} \tag{69}
\]

with two constraints

\[
a) \lim_{\tau \to 0} f_{i,1} (\alpha_i, t_1 + \tau | \alpha_i^{(1)}, t_1) = K\delta (\alpha - \alpha^{(1)}) \tag{71}
\]

due to the fact that \( \tau \to 0 \) is the limit in which \( \alpha \) deterministically approaches \( \alpha^{(1)} \), and

\[
b) \lim_{\tau \to \infty} f_{i,1} (\alpha_i, t_1 + \tau | \alpha_i^{(1)}, t_1) = e^{S(\alpha_i^{(1)})/k_B} \tag{72}
\]

representing the loss of correlations between the time \( t_1 \) and the time \( t_1 + \tau \). Solving the Langevin equation (73), \( f_{i,1} (\alpha_i, t_1 + \tau | \alpha_i^{(1)}, t_1) \) can be explicitly given. Let us now turn to the case with \( n = 1 \):

\[
R \dot{\alpha} + s\alpha = \epsilon \tag{73}
\]

this process is described by:

\[
f_1 (\alpha, t + u | \alpha^{(0)}, t) = \frac{s \exp \left\{ - \frac{s(\alpha - \alpha^{(0)})}{2 k_B (1 - e^{-2 u / R})} \right\}}{\sqrt{2\pi k_B} \sqrt{1 - e^{-2 u / R}}} \tag{74}
\]

With this information and with Ito’s discretization convention [11], one eventually obtains:

\[
f_1 (\alpha, t + \tau | \alpha^{(0)}, t) = \left( \frac{1}{2k_B} \right)^p \left( \frac{sR}{\pi \delta \tau} \right)^{p/2} \times \int d\alpha^{(1)} \cdots \int d\alpha^{(p)} \exp \left\{ - \frac{R}{4k_B} \sum_{k=1}^{p} \left[ \dot{\alpha}^{(k)} + \frac{s}{R} \alpha^{(k+1)} \right]^2 \delta \tau \right\} \tag{75}
\]

\[
\int d\alpha^{(1)} \cdots \int d\alpha^{(p)} \exp \left\{ - \frac{R}{4k_B} \sum_{k=1}^{p} \left[ \dot{\alpha}^{(k)} + \frac{s}{R} \alpha^{(k+1)} \right]^2 \delta \tau \right\} \tag{76}
\]

Under the \( p \to \infty \), \( \delta \tau \to 0 \) limits, with \( \tau = p \delta \tau \), the sum in the exponential tends to the integral along the path:

\[
\int_t^{t+\tau} \left[ \dot{\alpha}(t') + \frac{s}{R} \alpha(t') \right]^2 dt' \tag{77}
\]
which must be minimized to maximize the probability. Analogously, the \( n \)-dimensional case requires the minimization of:

\[
\int_{t}^{t+\tau} \sum_{i=1}^{n} \left( \dot{\alpha}_i(t') + \frac{s_i}{R_i} \alpha_i(t') \right)^2 dt'.
\]  

(79)

Here, the integrand can be expressed as

\[
\mathcal{L}(\alpha, \dot{\alpha}) = 2\Phi(\dot{\alpha}, \dot{\alpha}) - 2s_s(\alpha) + 2\Psi(X(\alpha), X(\alpha))
\]  

(80)

and the path of minimum integral follows from the Lagrange equation:

\[
\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\alpha}} - \frac{\partial \mathcal{L}}{\partial \alpha} = 0,
\]

which yields

\[
R_j \ddot{\alpha}_j - \frac{s^2_j}{R_j} \alpha_j = 0, \quad j = 1, \ldots, n
\]  

(81)

These second order differential equations are equivalent to pairs of first order equations. Indeed, their general solution

\[
\alpha_j(t) = C_{j1} e^{-s_j t/R_j} + C_{j2} e^{s_j t/R_j}
\]  

(82)

requires \( C_{j2} = 0 \) when the \( t \to \infty \) limit is considered—in which case we have relaxation to equilibrium from a nonequilibrium initial condition—while it requires \( C_{j1} = 0 \) when the previous history, beginning with an equilibrium state at \( t = -\infty \), is considered. The first case is solution of the differential equation

\[
\dot{\alpha}_j + \frac{s_j}{R_j} \alpha_j = 0
\]  

(83)

and the second case corresponds to

\[
\dot{\alpha}_j - \frac{s_j}{R_j} \alpha_j = 0.
\]  

(84)

We thus have two evolutions, which are symmetric under time reversal: one describes the relaxation to equilibrium, in accord with hydrodynamics; the other treats fluctuations away from equilibrium, and is the first example of the so-called adjoint hydrodynamics [13]. In the large \( n \) limit, the most probable path becomes the only path of positive probability and a justification of hydrodynamics is obtained, starting from a mesoscopic description.

*These results are crucially based on the Gaussian distributions, hence they are restricted to small deviations, from which the linear response about equilibrium states is derived.*

Considering large deviations, this theory has been generalized to fluctuations about nonequilibrium steady states, which are not symmetric under time reversal [13]. For dissipative deterministic particle systems, that are time reversal invariant, it has been shown that similar asymmetries may arise, when particles interact [14].
V. FLUCTUATION RELATIONS: RESPONSE FROM LARGE DEVIATIONS

In 1993, the paper [15] addressed the question of the fluctuations of the entropy production rate in a pioneering attempt towards a unified theory of a wide range of nonequilibrium phenomena. In particular, a Fluctuation Relation (FR) was there derived and tested. Obtained on purely dynamical grounds, it constitutes one of the few general exact results for systems almost arbitrarily far from equilibrium, while close to equilibrium it is consistent with the Green-Kubo and Onsager relations. This FR reads:

$$\frac{\text{Prob}_\tau(\sigma \approx A)}{\text{Prob}_\tau(\sigma \approx -A)} = e^{\tau A}$$  \hspace{1cm} (85)

where $A$ and $-A$ are average values of the normalized power dissipated in a long time $\tau$ in a driven system, denoted by $\sigma$ and $\text{Prob}_\tau(\sigma \approx \pm A)$ is the steady state probability of observing values close to $\pm A$.

This relation constitutes a large deviation result: for large $\tau$, any $A \neq \langle \sigma \rangle$ lies many standard deviations away from the mean. In other words, $A$ corresponds to a large (macroscopic) deviation from the macroscopically observable value $\langle \sigma \rangle$.

The FR (85) was derived for the following isoenergetic model of a 2-dimensional shearing fluid:

$$\begin{align*}
\frac{d}{dt} q_i &= \frac{p_i}{m} + \gamma y_i \hat{x} \\
\frac{d}{dt} p_i &= F_i(q) + \gamma p_i^y \hat{x} - \alpha_{th} p_i
\end{align*}$$  \hspace{1cm} (86)

where $\gamma$ is the shear rate in the $y$ direction, $\hat{x}$ is the unit vector in the $x$-direction, and the friction term $\alpha_{th}$, called “thermostat”, takes the form

$$\alpha_{th}(\Gamma) = -\frac{\gamma}{\sum_{i=1}^{N} p_i^2} \sum_{i=1}^{N} p_i^{(x)} p_i^{(y)}$$  \hspace{1cm} (87)

as prescribed by Gauss’ principle of least constraint, in order to keep the internal energy fixed.

This molecular dynamics model was chosen by the authors of [15] because its phase space expansion rate $\Lambda$ is proportional to $\alpha_{th}$. Hence a dynamical quantity, could be related to the energy dissipation rate divided by $\sum p_i^2$. The FR is parameter-free and, being dynamical in nature, it applies almost arbitrarily far from equilibrium as well as to small systems.

Gallavotti and Cohen clearly identified the mathematical framework within which Ref. [15] had been developed, introducing the following [16–19]:

18
Chaotic Hypothesis: A reversible many-particle system in a stationary state can be regarded as a transitive Anosov system for the purpose of computing its macroscopic properties.

Anosov systems can indeed be proven to have probability distributions of the kind assumed in [15]. The result is a steady state FR for the fluctuations of Λ, which we call Λ-FR and which will be described below. As the Anosov property practically means a high degree of randomness, analogous results have been obtained first for finite state space Markov chains and later for many other stochastic processes [20–22]. Stochastic processes are easier to handle than deterministic dynamics, but ambiguities affect their observables, except for special cases. The reader is addressed to the numerous existing review papers, such as Refs. [4, 23, 24]. We focus now on some specific results for deterministic dynamics.

A. The Gallavotti-Cohen approach

The idea proposed by Gallavotti and Cohen is that dissipative, reversible, transitive Anosov maps, \( S : \mathcal{M} \rightarrow \mathcal{M} \), are idealizations of nonequilibrium particle systems [17]. That the system evolves with discrete or continuous time was thought to be a side issue [17]. The Λ-FR for Anosov maps relies on time reversibility and on the fact that these dynamical systems admit arbitrarily fine Markov partitions [25]. These are subdivisions of \( \mathcal{M} \) in cells with disjoint interiors and with boundaries forming invariant sets, which in two dimensions consist of pieces of stable and unstable manifolds. Gallavotti and Cohen further assumed that the dynamics is transitive, i.e. that a typical trajectory explores all regions of \( \mathcal{M} \), as finely as one wishes. This structure justifies the probability (Lyapunov) weights of Eq.(1) in Ref. [15], from which the Λ-FR emerges.

Let the dynamics be given by \( X_{k+1} = SX_k \) and introduce the phase space expansion rate

\[
\Lambda(X) = \log J(X),
\]

where \( J \) is the Jacobian determinant of \( S \). The dynamics is called dissipative if \( \langle \Lambda \rangle < 0 \), where \( \langle . \rangle \) is the steady state phase space average. Then, consider the dimensionless phase space contraction rate \( e_\tau \), obtained along a trajectory segment \( w_{X,\tau} \) with origin at \( X \in \mathcal{M} \) and duration \( \tau \), defined by:

\[
e_\tau(X) = \frac{1}{\tau \langle \Lambda \rangle} \sum_{k=-\tau/2}^{\tau/2-1} \Lambda(S^k X) \tag{88}
\]

Let \( J^u \) be the Jacobian determinant of \( S \) restricted to the unstable manifold \( V^+ \), i.e. the product of the asymptotic separation factors of nearby points, along the directions in which distances asymptotically grow at an exponential rate. If the system is Anosov, the probability that \( e_\tau(X) \in \)
\( B_{p, \epsilon} \equiv (p - \epsilon, p + \epsilon) \) equals, in the fine Markov partitions and long \( \tau \) limits, with the sum of weights of form

\[
w_{X, \tau} = \prod_{k=-\tau/2}^{\tau/2} \frac{1}{J_{\nu}(S^k X)}
\]

(89)
of the cells containing the points \( X \) such that \( e_\tau(X) \) lies in \( B_{p, \epsilon} \). Then, denoting by \( \pi_\tau(B_{p, \epsilon}) \) the corresponding probability, one can write

\[
\pi_\tau(e_\tau(X) \in B_{p, \epsilon}) \approx \frac{1}{M_{\epsilon}} \sum_{X, e_\tau(X) \in B_{p, \epsilon}} w_{X, \tau}
\]

(90)
where \( M_{\tau} \) is a normalization constant. If the support of the physical measure is \( M \), as in the case of moderate dissipation [26], time-reversibility and dissipation guarantee that the range of possible fluctuations includes a symmetric interval \([-p^*, p^*] \), with \( p^* > 0 \), and one can consider the ratio

\[
\frac{\pi_\tau(B_{p, \epsilon})}{\pi_\tau(B_{-p, \epsilon})} \approx \frac{\sum_{X, e_\tau(X) \in B_{p, \epsilon}} w_{X, \tau}}{\sum_{X, e_\tau(X) \in B_{-p, \epsilon}} w_{X, \tau}}
\]

(91)
where each \( X \) in the numerator has a counterpart in the denominator. Denoting by \( I \) the involution which replaces the initial condition of a given trajectory with the initial condition of the reversed trajectory, time-reversibility yields:

\[
\Lambda(X) = -\Lambda(IX), \quad w_{IX, \tau} = w_{X, \tau}^{-1} \quad \text{and} \quad \frac{w_{X, \tau}}{w_{IX, \tau}} = e^{-\tau(\Lambda)p}
\]

(92)
if \( e_\tau(X) = p \). Taking small \( \epsilon \) in \( B_{p, \epsilon} \), the division of each term in the numerator of (91) by its counterpart in the denominator approximately equals \( e^{-\tau(\Lambda)p} \), which then equals the ratio in (91). Therefore, in the limit of small \( \epsilon \), infinitely fine Markov partitions and large \( \tau \), one obtains the following:

**Gallavotti-Cohen Theorem.** Let \( (M, S) \) be dissipative and reversible and assume that the chaotic hypothesis holds. Then, in the \( \tau \to \infty \) limit, one has

\[
\frac{\pi_\tau(B_{p, \epsilon})}{\pi_\tau(B_{-p, \epsilon})} = e^{-\tau(\Lambda)p}.
\]

(93)
with an error in the argument of the exponential which can be estimated to be \( p \)- and \( \tau \)-independent.

If \( \Lambda \) can be identified with a physical observable, the \( \Lambda \)-FR is a parameter-free statement about the physics of nonequilibrium systems. Unfortunately, \( \Lambda \) differs from the dissipated power in general, [27], hence alternative approaches have been developed.
B. Fluctuation relations for the dissipation function

One different approach from above consists in posing a different question in order to remain closer to the interest of physics: if the FR has been observed to hold for the energy dissipation of a given system, which mechanisms are responsible for that? To answer this question, various results have been achieved and others clarified. In particular:

1. transient, or ensemble, FRs have been derived;
2. classes of infinitely many identities have been obtained to characterize equilibrium and nonequilibrium states;
3. a novel ergodic notion, known as \textit{t-mixing}, has been introduced;
4. a quite general response formula has been derived.

These developments began with a paper by Evans and Searles [28], who proposed the first transient fluctuation relation for the \textit{Dissipation Function} $\Omega$, which is formally similar to Eq. (85). In states close to equilibrium, $\Omega$ can be identified with the \textit{entropy production rate}, $\sigma = JV F^\text{ext} / k_B T$, where, $J$ is the (intensive) flux due to the thermodynamic force $F^\text{ext}$, $V$ and $T$ are the volume and the kinetic temperature, respectively [28, 29]. This relation, called transient $\Omega$-FR, is obtained under virtually no hypothesis, except for \textit{time reversibility}; it is transient because it concerns non-invariant ensembles of systems, instead of the steady state. The approach stems from the belief that the complete knowledge of the invariant measure implied by the Chaotic Hypothesis is not required to understand the few properties of physical interest, like thermodynamic relations do not depend on the details of the microscopic dynamics [30].

Let $\mathcal{M}$ be the phase space of the system at hand, and $S^\tau : \mathcal{M} \to \mathcal{M}$ be a reversible evolution corresponding to $\dot{\Gamma} = F(\Gamma)$. Take a probability measure $d\mu_0(\Gamma) = f_0(\Gamma)d\Gamma$ on $\mathcal{M}$, and let the observable $\mathcal{O} : \mathcal{M} \to \mathbb{R}$ be odd with respect to the time reversal, \textit{i.e.} $\mathcal{O}(\Gamma) = -\mathcal{O}(\Gamma)$. Denote its time averages by

$$\overline{\mathcal{O}}_{t,t+\tau}(\Gamma) \equiv \frac{1}{\tau} \mathcal{O}_{t_0,t_0+\tau}(\Gamma) \equiv \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \mathcal{O}(S^s \Gamma) ds . \quad (94)$$

For a density $f_0$ that is even under time reversal [$f_0(\Gamma) = f_0(\Gamma)$], define the

\textbf{Dissipation function:}

$$\Omega(\Gamma) = -\frac{d}{d\Gamma} \ln f_0 \bigg|_{\Gamma} \cdot \dot{\Gamma} - \Lambda(\Gamma) , \quad \text{so that} \quad (95)$$

$$\overline{\Omega}_{t,t+\tau}(\Gamma) = \frac{1}{\tau} \left[ \ln \frac{f_0(S^\tau \Gamma)}{f_0(S^{t+\tau} \Gamma)} - \Lambda_{t,t+\tau} \right] . \quad (96)$$
For a compact phase space, the uniform density $f_0(\Gamma) = 1/|\mathcal{M}|$ implies $\Omega = \Lambda$, which was the case of the original FR. The existence of the logarithmic term in (95) is called ergodic consistency, a condition met if $f_0 > 0$ in all regions visited by all trajectories $S^\Gamma$.

For $\delta > 0$, let $A_\delta^\pm = (\pm A - \delta, \pm A + \delta)$, and let $E(\mathcal{O} \in (a, b))$ be the set of points $\Gamma$ such that $\mathcal{O}(\Gamma) \in (a, b)$. Then, we have $E(\Omega_0, \tau \in A_\delta^-) = IS^\tau E(\Omega_0, \tau \in A_\delta^+)$ and:

$$
\frac{\mu_0(E(\Omega_0, \tau \in A_\delta^+))}{\mu_0(E(\Omega_0, \tau \in A_\delta^-))} = \frac{\int_{E(\Omega_0, \tau \in A_\delta^+)} f_0(\Gamma) d\Gamma}{\int_{E(\Omega_0, \tau \in A_\delta^-)} f_0(S^\tau X) e^{-\Lambda_0, \tau(X)} dX} = \frac{\int_{E(\Omega_0, \tau \in A_\delta^+)} f_0(\Gamma) d\Gamma}{\int_{E(\Omega_0, \tau \in A_\delta^-)} e^{-\Omega_0, \tau(X)} f_0(X) dX} = \langle e^{-\Omega_0, \tau} \rangle_{\Omega_0, \tau \in A_\delta^+}^{-1}
$$

where by $\langle \cdot \rangle_{\Omega_0, \tau \in A_\delta^+}$ we mean the average computed with respect to $\mu_0$ under the condition that $\Omega_0, \tau \in A_\delta^+$. This implies the

**Transient $\Omega$-FR:**

$$
\frac{\mu_0(E(\Omega_0, \tau \in A_\delta^+))}{\mu_0(E(\Omega_0, \tau \in A_\delta^-))} = e^{[\cdot + \epsilon(\delta, A, \tau)] \tau}, \quad (97)
$$

with $|\epsilon(\delta, A, \tau)| \leq \delta$, an error due to the finiteness of $\delta$.

**Remarks:**

i. *The transient $\Omega$-FR refers to the non-invariant probability distribution $\mu_0$. Time reversibility is basically the only ingredient of its derivation.*

ii. *Its similarity with the steady state FR is misleading: rather than expressing a statistical property of fluctuations of a given system, it expresses a property of the initial ensemble of macroscopically identical systems.*

iii. *In order for $\Omega$ to be the energy dissipation, $f_0$ has to be properly chosen. For instance, in simple molecular dynamics models, $\Omega$ is the energy dissipation if $f_0$ is the equilibrium ensemble dynamics, which is obtained when the external driving is switched off, while the thermostats keep acting.*

iv. *Consequently, the transient $\Omega$-FR yields a property of the equilibrium state by means of nonequilibrium experiments, thus complementing the FDR, which yields non equilibrium properties from equilibrium experiments.*

The steady state $\Omega$-FR requires further hypotheses. In the first place let averaging begin at time $t$, i.e. consider

$$
\frac{\mu_0(E(\Omega_{t,t+\tau} \in A_\delta^+))}{\mu_0(E(\Omega_{t,t+\tau} \in A_\delta^-))}. \quad (98)
$$
Taking $\hat{t} = t + \tau + t$, the transformation $\Gamma = IS^{\hat{t}}W$ in $M$ and some algebra yield:

$$
\frac{\mu_0(E(\Omega_{t,t+\tau} \in A_\delta^+))}{\mu_0(E(\Omega_{t,t+\tau} \in A_\delta^-))} = \left\langle \exp \left( -\Omega_0,\tilde{t} \right) \right\rangle_{\tilde{\Omega}_{t,t+\tau} \in A_\delta^+}^{-1} = e^{[A+\epsilon(\delta,t,A,\tau)]\tau} \left\langle e^{-\Omega_0,\tilde{t}-\Omega_{t+t+\tau},2\tau+\tau} \right\rangle_{\tilde{\Omega}_{t,t+\tau} \in A_\delta^+}^{-1} \tag{99}
$$

where $|\epsilon(\delta,t,A,\tau)| \leq \delta$. Here, the second line follows from the first because $\Omega_0,\tilde{t} = \Omega_0,\tilde{t} + \Omega_{t+t+\tau}$, with the central contribution made approximately equal to $A$ by the condition $\tilde{\Omega}_{t,t+\tau} \in A_\delta^+$.

Recall that $\mu_0(E) = \mu_t(S^tE)$, where $\mu_t$ is the evolved probability distribution, with density $f_t$.

Then, taking the logarithm and dividing by $\tau$ Eq. (100) produces:

$$
\frac{1}{\tau} \ln \frac{\mu_t(E(\Omega_{0,\tau} \in A_\delta^+))}{\mu_t(E(\Omega_{0,\tau} \in A_\delta^-))} = A + \epsilon(\delta,t,A,\tau) - \frac{1}{\tau} \ln \left\langle e^{-\Omega_0,\tilde{t}-\Omega_{t+t+\tau},2\tau+\tau} \right\rangle_{\tilde{\Omega}_{t,t+\tau} \in A_\delta^+}^{-1} \equiv A + \epsilon(\delta,t,A,\tau) + M(A,\delta,t,\tau) \tag{101}
$$

because $E(\Omega_{0,\tau}) = S^tE(\tilde{\Omega}_{t,t+\tau})$.

If $\mu_t$ tends to a steady state $\mu_\infty$ when $t \to \infty$, the exact relation (101) changes from a statement on the ensemble $f_t$, to a statement on the statistics generated by a single typical trajectory. In particular one could have the analogous of the $A$-FR:

**Steady State $\Omega$-FR.** For any tolerance $\epsilon > 0$, there is a sufficiently small $\delta > 0$ such that

$$
\lim_{\tau \to \infty} \frac{1}{\tau} \ln \frac{\mu_\infty(E(\Omega_{0,\tau} \in A_\delta^+))}{\mu_\infty(E(\Omega_{0,\tau} \in A_\delta^-))} = A + \eta , \quad \text{with} \quad \eta \in (-\epsilon,\epsilon) \tag{102}
$$

For this to be the case, one needs some assumption. Indeed, $M(A,\delta,t,\tau)$ could diverge with $t$ at fixed $\tau$, making Eq. (101) useless. If on the other hand $M(A,\delta,t,\tau)$ remains bounded by a finite $M(A,\delta,\tau)$, $\lim_{\tau \to \infty} M(A,\delta,\tau)$ could still exceed $\epsilon$.

The first difficulty is simply solved by the observation that the divergence of $M(A,\delta,t,\tau)$ implies that one of the probabilities on the left hand side of Eq. (101) vanishes, i.e./ that $A$ or $-A$ are not observable in the steady state. If no value $A$ is observable, there are no fluctuations in the steady state and there is no need for a steady state FR. Therefore, let us assume that $A$ and $-A$ are observable. To proceed, observe that Eqs. (95,96) lead to

$$
f_s(\Gamma) = f_0 \left( S^{-s}\Gamma \right) e^{-A,s,0(\Gamma)} = f_0(\Gamma) e^{\Omega_{-s,0}(\Gamma)} \tag{103}
$$

which implies the following relation:

$$
\left\langle e^{-\Omega_{0,s}} \right\rangle_0 = 1 , \quad \text{for every} \quad s \in \mathbb{R} . \tag{104}
$$
Suppose now that the $\Omega$-autocorrelation with respect to $f_0$ decays instantaneously in time, so that one can write:

$$1 = \langle e^{-\Omega_{0,s}} \rangle_0 = \langle e^{-\Omega_{0,s}} \rangle_0 \langle e^{-\Omega_{s,t}} \rangle_0,$$  \hspace{1cm} (105)

hence

$$\langle e^{-\Omega_{s,t}} \rangle_0 = 1, \quad \text{for all } s \text{ and } t \quad (106)$$

under the same condition, the conditional average of eq.(101) does not depend on the condition $\Pi_{t,t+\tau} \in A^+_\delta$, so that:

$$\langle e^{-\Omega_{t,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \rangle_{\Pi_{t,t+\tau} \in A^+_\delta} = \langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \rangle_0 = 1. \quad (107)$$

Then, the logarithmic correction in Eq. (101) identically vanishes for all $t, \tau$, and the steady state $\Omega$-FR is verified at all $\tau > 0$. This idealized situation does not need to be realized, but molecular dynamics indicates that the typical situation is similar to this [32]; for $\tau$ much larger than a characteristic time $\tau_M$, one may write:

$$\langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \rangle_{\Pi_{t,t+\tau} \in A^+_\delta} \approx \langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \rangle_{\Pi_{t,t+\tau} \in A^+_\delta} \approx \langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \rangle_0 \approx \langle e^{-\Omega_{0,t}} \rangle_0 \langle e^{-\Omega_{t+\tau,2t+\tau}} \rangle_0 = O(1) \quad (108)$$

with improving accuracy for growing $t$ and $\tau$. If these scenarios are realized, $M(A, \delta, \tau)$ vanishes as $1/\tau$ for growing $\tau$.

The assumption that Eqs.(108)- (111) hold is a kind of mixing property which, however, refers to non-invariant probability distributions, differently from the standard notion of mixing.

Various other relations can be obtained following the same procedure. For instance, for each odd $O$, any $\delta > 0$, any $t$ and any $\tau$ the following transient FR holds:

$$\frac{\mu_0(\overline{O}_{0,\tau} \in A^+_\delta)}{\mu_0(\overline{O}_{0,\tau} \in A^-_\delta)} = \langle \exp (-\Omega_{0,\tau}) \rangle^{-1}_{\overline{O}_{0,\tau} \in A^+_\delta}, \quad (112)$$

expressed a property of the initial state by means of nonequilibrium dynamics.

VI. T-MIXING AND GENERAL RESPONSE THEORY

Observing that Eq.(30), implies:

$$\langle e^{-\Omega_{s,t}} \rangle_0 = \langle e^{-\Omega_{0,t-s}} \rangle_0 \quad (113)$$
Eqs. (108, 111) appear to be one special case of the following property:

$$\lim_{t \to \infty} \left[ \langle \psi (\phi \circ S^t) \rangle_0 - \langle \psi \rangle_0 \langle \phi \rangle_t \right] = 0$$ (114)

In the case that $\psi = \Omega$, Eq. (114) becomes

$$\lim_{t \to \infty} \langle \Omega (\phi \circ S^t) \rangle_0 = 0$$ (115)

because $\Omega$ is odd and $f_0$ is even under time reversal, hence $< \Omega >_0 = 0$.

If the convergence of this limit is faster than $O(1/t)$, one further has:

$$\int_0^\infty \langle \Omega (\phi \circ S^t) \rangle_0 \ dt \in \mathbb{R}$$ (116)

a condition which has been called $t$-mixing.

To obtain the response of observables, starting from an equilibrium state, we have:

$$\langle \phi \rangle_t - \langle \phi \rangle_0 = \int_0^t \frac{d}{ds} \langle \phi \rangle_s \ ds = \int_0^t ds \frac{d}{ds} \int d\Gamma f_s(\Gamma) \phi(\Gamma)$$ (117)

Where Eq. (103) yields:

$$\frac{d}{ds} \int d\Gamma f_s(\Gamma) \phi(\Gamma) = \int d\Gamma f_0(\Gamma) e^{\Omega_s(\Gamma)} \Omega (S^{-s}) \phi(\Gamma)$$ (118)

Introducing the coordinate change $X = S^{-s} \Gamma$, $\Gamma = S^s X$, with Jacobian determinant $|\partial \Gamma/\partial X| = \exp(\Lambda_{0,s}(X))$ and observing that:

$$\Omega_{-s,0}(S^s X) = \int_{-s}^0 du \ \Omega (S^u S^s X) = \int_0^s dz \ \Omega (S^s X) = \Omega_{0,s}(X)$$ (119)

so we finally obtain:

$$\frac{d}{ds} \langle \phi(\Gamma) \rangle_s = \int dX \ \phi (S^s X) \Omega(X) e^{\Omega_0,s(X)} e^{\Lambda_0,s(X)} f_0(S^s X)$$ (120)

$$= \int dX \ \Omega(X) \phi (S^s X) f_0(X) = \langle \Omega (\phi \circ S^s) \rangle_0$$ (121)

which is the integrand of Eq. (116). Therefore, we have the following Response Formula:

$$\langle \phi \rangle_t = \langle \phi \rangle_0 + \int_0^t ds \ \langle \Omega (\phi \circ S^s) \rangle_0$$ (122)

Moreover, if the $t$-mixing condition holds for $\phi$, we get

$$\langle \phi \rangle_t \xrightarrow{t \to \infty} \langle \phi \rangle_0 + \int_0^\infty ds \ \langle \Omega (\phi \circ S^s) \rangle_0 \in \mathbb{R}$$ (123)
and the ensemble under investigation converges to what appears to be a steady state.

One interesting aspect of the relation between standard mixing and t-mixing is the following. Standard mixing concerns the decay of correlations among the evolving microscopic phases within a given steady state, t-mixing concerns the decay of correlations among evolving macrostates. For this reason, the t-mixing property implies the convergence to a steady state, whereas the mixing property in general does not.

Mixing assumes the state to be stationary, making irrelevant the issue of relaxation. The derivation of convergence to a microcanonical state, illustrated in Section [1A], is thus just a trick. That derivation is possible because one may formally interpret the evolving transient probability densities as evolving observables as well. This way one combines in one mathematical object two physically very different entities: the ensemble of microscopic phases and a macroscopic measurable observable. This will not be legitimate under most circumstances. However, even in the case of t-mixing, the convergence of the steady state has not been proved in the sense of thermodynamics. Indeed, different initial conditions \( \Gamma \in \mathcal{M} \) are allowed by t-mixing to produce different time averages. The uniqueness of the time average is currently under investigation.

VII. STOCHASTIC DIFFUSIONS AND LARGE DEVIATIONS

Let us now turn our attention to stochastic dynamics. In general, the presence of noise allows one to characterize the steady state dynamics, even in presence of dissipation, by regular probability densities, thus overcoming the problem posed e.g. by fractal structures. Hence, one may safely rely, in this case, on perturbative approaches in the description of perturbations of a given (possibly dissipative) reference state. In particular, a detailed analysis of the response formulae valid for Markovian Langevin-type stochastic differential equations is presented in Ref. [33], where Ruelle clarifies the conditions under which the zero noise limit leads the various terms of the perturbation theory to reproduce their counterparts in the deterministic dynamics, cf. Refs. [34, 35]. In Ruelle’s case, this is made possible by the stability of the SRB states under small random perturbations [36, 37].

A different approach based on the large deviations method is presented in Refs. [38, 39]. Let us focus, for simplicity, on stochastic diffusion processes described by overdamped Langevin equations, in which one disregards inertial effects, letting forces to be proportional to velocities rather than to

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8 Something similar happens when the equilibrium thermodynamic entropy of a physical object is expressed by the equilibrium average of the logarithm of the equilibrium density, which is the Gibbs entropy.
These processes correspond to the high damping limits of the underdamped (or inertial) stochastic dynamics. Let us start considering overdamped diffusion processes for $x \in \mathbb{R}^n$, in the Itô sense expressed by:

$$\dot{x}_t = \chi \cdot [F(x_t) + F^p_t(x_t)] + \nabla \cdot D(x_t) + \sqrt{2D(x_t)}\xi_t,$$

(124)

where $\xi_t$ denotes standard white noise and $F^p$ denotes the perturbation to the reference dynamics. The mobility $\chi$ and the diffusion constant $D$ are strictly positive (symmetric) $n \times n$-matrices, which, provided the system is in contact with a thermostat at inverse temperature $\beta > 0$, are connected by the Einstein relation $\chi = \beta D$. The force $F$ denotes the drift of the reference unperturbed dynamics, and can be expressed as:

$$F = F_{nc} - \nabla U,$$

(125)

where $F_{nc}$ denotes a nonconservative force pulling the reference dynamics out of equilibrium, while $U$ is the energy of the system. The Fokker-Planck equation for the time dependent density $f_t$, related to the diffusion process described by (124), reads

$$\frac{\partial f_t}{\partial t}(x_t) = -\nabla \cdot j_f, \quad \text{with} \quad j_f = [\chi(F + F^p_t)f_t(x_t) - \frac{\chi}{\beta} \nabla f_t(x_t)],$$

(126)

where $j_f$ denotes the probability current. Rather than attempting a direct solution of Eq. (126), one may tackle Eq. (124) from the point of view of large deviations theory. The key idea, cf. Refs. [38, 45], is to determine the perturbed probability density through its embedding in the path-space distribution. That is, given the (random) paths $\omega = (x(s), s \in [0, t])$, one may connect the distribution $P$ on paths starting from $f_0$ and subjected to the perturbation $F^p_t$, with the reference distribution $P^0$ pertaining to paths starting from $f_0$ and undergoing the reference dynamics, via the formula:

$$P(\omega) = e^{-A(\omega)}P^0(\omega).$$

(127)

The relation (127) defines the action $A(\omega)$, which is typically local in space-time and is, thus, similar to the Hamiltonians or Lagrangians of equilibrium statistical mechanics, see e.g. [46]. One can also decompose, in terms of its time symmetric components $t$ and its time antisymmetric components:

$$A = (T - S)/2,$$

where

$$S(\omega) = A(g\omega) - A(\omega), \quad T(\omega) = A(g\omega) + A(\omega).$$

(128)
and \( g \) is the time reversal operator:

\[
g\omega = \left((\pi x)_{t-s}, 0 \leq s \leq t\right),
\]

(129)

with \( \pi x \) equal to \( x \) except for flipping any other variable with negative parity under time reversal.

The quantity \( S(\omega) \), under the assumption of local detailed balance \[44\], is the entropy flux triggered by the perturbation and released into the environment \[38\]. On the other hand, the quantity \( T(\omega) \) is referred to, in the literature, as \textit{dynamical activity} \[40, 41\], as it measures the reactivity and instability of a trajectory. Dynamical activity is thus much more concerned with kinetics than with thermodynamics but it allows us to explore response around equilibrium beyond the linear regime. This shows also that the noise along in- and outgoing trajectories is crucial for the determination of state plausibilities \[47–49\].

A simple calculation yields the following general expression for the action pertaining to the process described by Eq. (124):

\[
A(\omega) = \frac{\beta}{2} \int_0^t ds \left[ F_s^p \cdot \chi F + \nabla \cdot (DF_s^p) + \frac{1}{2} F_s^p \cdot \chi F_s^p \right] - \frac{\beta}{2} \int_0^t dx_s \circ F_s^p
\]

(130)

where the stochastic integral with the \( \circ \) is in the sense of Stratonovich. From (128) and (130), one can derive the following expressions for \( S(\omega) \) and \( T(\omega) \):

\[
S(\omega) = \beta \int_0^t dx_s \circ F_s^p \quad \text{and} \quad T(\omega) = T_1 + T_2,
\]

with

\[
T_1 = \beta \int_0^t ds \left[ F_s^p \cdot \chi F + \nabla \cdot (DF_s^p) \right] \quad \text{and} \quad T_2 = \frac{\beta}{2} \int_0^t ds F_s^p \cdot \chi F_s^p.
\]

If the chosen observable \( \phi \) is endowed with an even kinematical parity, the following linear response formula can be thus established \[40\]:

\[
\langle \phi \rangle_t - \langle \phi \rangle_0 \simeq \langle \phi(x_t)S(\omega) \rangle_0 = - \langle \phi(x_0)S(\omega) \rangle_0 = - \int dx_0 f_0(x_0) \phi(x_0) \langle S(\omega) \rangle_{x_0}^t.
\]

(131)

The expression (131) looks similar to the response formula (122) obtained for deterministic systems, with the entropy flux \( S(\omega) \) taking the role of the observable \( \Omega \) defined in Eq. (95) \[9\]. The quantity

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\[9\] This is not surprising and indeed it is common. The fact is that both derivation are very formal and general and only the evolution operators and the observables must appear.
\( \langle S \rangle^0_{0} \), in Eq. [131], denotes the conditional expectation of the entropy flux \( S(\omega) \) over \([0, t] \) given that the path started from the state \( x_0 \). Its instantaneous flux is defined as [38, 45]:

\[
\langle S \rangle^0_{x_0} = \beta \int_0^t \langle w(x_s) \rangle^0_{x_0} ds ,
\]

where \( w(x_s) \) corresponds to the instantaneous (time-antisymmetric, random) work made by the perturbation \( F^p \).

**A. Nonequilibrium steady states**

By setting \( F_{nc} \neq 0 \), in Eq. [124], one spoils the time-reversibility of the reference dynamics. Therefore, given enough time, the reference dynamics settles on a nonequilibrium steady state described by an invariant density \( f_0 \) (usually not known). In the steady state, one can use the definition of the probability current given in Eq. [126], to define the information potential \( I_f \) as:

\[
I_f = -\nabla (\log f_0) = (\beta/\chi)u - \beta F \quad ,
\]

where \( u \equiv j_f / f_0 \) denotes a probability velocity. From Eq. [133], the large deviations method detailed in Ref. [35] leads to the following general response function for nonequilibrium overdamped diffusion processes:

\[
R(t - s) = \chi \langle [-\nabla \cdot F^p_s(x_s) + I_f(x_s) \cdot F^p_s(x_s)] \phi(x_t) \rangle_0 \quad .
\]

In particular, if the perturbation takes the (time-independent) gradient form \( F^p = \nabla V \), an easy calculation yields:

\[
R(t - s) = \beta \langle (u(x_s) \cdot \nabla V(x_s)) \phi(x_t) \rangle_0 - \beta \langle LV(x_s) \phi(x_t) \rangle_0 \quad ,
\]

with \( L = \chi F \cdot \nabla + \chi/\beta \nabla^2 \). Next, by using the adjoint generator \( L^* = L - 2u \cdot \nabla \), one can suitably cast Eq. [135] into the equivalent form [35]:

\[
R(t - s) = -\beta \langle (u(x_s) \cdot \nabla V(x_s)) \phi(x_t) \rangle_0 + \beta \frac{d}{ds} \langle \phi(x_t)V(x_s) \rangle_0 \quad .
\]

It is worth remarking that the function \( u(x) \), in [133], is unknown in general. Nevertheless, Eq. [135] is relevant at a formal level, because it shows that the response function can be expressed in

---

10 \( L^* \) is defined with the help of the stationary distribution \( f_0 \): for any two state functions \( a \) and \( b \), \( L^* \) is such that 
\[
\int dx f_0(x)a(x)L^*b(x) = \int dx f_0(x)b(x)La(x).
\]
For detailed balance dynamics, in particular, one has \( L^* = \pi L \pi \), where \( \pi \) flips the variables which are odd under time reversal.
terms of a suitable correlation function computed wrt reference stationary density characterizing
the nonequilibrium steady state.
One also readily notices that Eq. (136) produces the classical Kubo formula (48) for $F_{nc} = 0$ (i.e.
$u = 0$) or when describing the response in a reference frame moving with drift velocity $u$.

VIII. CONCLUDING REMARKS

We have summarised some of the main results of the theory of nonequilibrium systems. We
emphasized the physical questions and mechanisms lying behind the formalism presenting the var-
ious results in their historical order. Research has, in fact, gradually moved from the analysis of
equilibrium systems to dissipative ones, from the regime of small fluctuations to large deviations.
Along this challenging route, we also stressed similarity and difference between the different math-
ematical frameworks. In particular we noted the reassuring fact that (microscopic) deterministic
dynamics, discussed in Sec. [VI], give rise to similar linear response formulae as those of the (meso-
scopic) stochastic dynamics, reviewed in Sec. [VII]. The resulting thermodynamic behavior of the
observable under consideration is indeed expected not to depend on the mathematical framework
used in the modelling, as long as the different frameworks describe the same phenomena.
Although a comprehensive understanding of the physics of nonequilibrium systems is still missing,
we thus believe that a unifying framework is gradually emerging.

[1] M. Colangeli, From Kinetic Models to Hydrodynamics. Some Novel Results (Springer, 2013).
[2] R. Kubo, Statistical-mechanical theory of irreversible processes: I. General theory and simple applica-
tions to magnetic and conduction problems J. Phys. Soc. Japan 12, 570 (1957).
[3] A. I. Khinchin, Mathematical Foundations of Statistical Mechanics, Dover Publications, New York
(1949).
[4] U. Marini Bettolo Marconi, A. Puglisi, L. Rondoni, A. Vulpiani, Fluctuation - dissipation: Response
theory in statistical physics Phys. Rep., 461, 111 (2008)
[5] G. Boffetta and G. Lacorata and S. Musacchio and A. Vulpiani, Relaxation of finite perturbations:
Beyond the fluctuation-response relation, Chaos, 13, 806 (2003).
[6] D. Ruelle, General linear response formula in statistical mechanics, and the fluctuation-dissipation
theorem far from equilibrium, Phys. Lett. A 245, 220 (1998).
[7] M. Colangeli, L. Rondoni, A. Vulpiani, Fluctuation-dissipation relation for chaotic non-Hamiltonian
systems, J. Stat. Mech. L04002 (2012).
[8] D. J. Evans, L. Rondoni, Comments on the entropy of nonequilibrium steady states, J. Stat. Phys. 109, 895 (2002).
[9] F. Bonetto, A. Kupiainen, J. L. Lebowitz, Absolute continuity of projected SRB measures of coupled Arnold cat map lattices, Ergod. Th. Dyn. Syst. 25, 59 (2005).
[10] B. Cessac, J.-A. Sepulchre, Linear response, susceptibility and resonances in chaotic toy models, Physica D 225, 13 (2007).
[11] L. Onsager and S. Machlup, Fluctuations and irreversible processes, Phys. Rev., 91, 1505 (1953).
[12] S. Machlup and L. Onsager, Fluctuations and irreversible process. II. Systems with kinetic energy, Phys. Rev., 91, 1512 (1953).
[13] L. Bertini, A. D. Sole, D. Gabrielli, G. Jona-Lasinio, C. Landim, Macroscopic fluctuation theory for stationary non-equilibrium states, J. Stat. Phys. 107, 635 (2002).
[14] A. Gamba, L. Rondoni, Current fluctuations in the nonequilibrium Lorentz gas, Physica A 340, 274 (2004). C Giberti, L Rondoni, C Vernia, Asymmetric fluctuationrelaxation paths in FPU models, Physica A 365, 229 (2006). C Paneni, D J Searles, L Rondoni, Temporal asymmetry of fluctuations in nonequilibrium states, J. Chem. Phys. 124, 114109 (2006). C Paneni, D J Searles, L Rondoni, Temporal asymmetry of fluctuations in nonequilibrium steady states: Links with correlation functions and nonlinear response, J. Chem. Phys. 128, 164515 (2008).
[15] D. J. Evans and E. G. D. Cohen and G. P. Morriss, Probability of second law violations in shearing steady flows, Phys. Rev. Lett., 71, 2401 (1993).
[16] G. Gallavotti and E. G. D. Cohen, Dynamical ensembles in nonequilibrium statistical mechanics, Phys. Rev. Lett., 94, 2694 (1995).
[17] G. Gallavotti and E. G. D. Cohen, Dynamical ensembles in stationary states, J. Stat. Phys., 80, 931 (1995).
[18] G. Gallavotti, Reversible Anosov diffeomorphisms, large deviations, Math. Phys. Electronic J., 1, 1 (1995).
[19] G. Gallavotti, Fluctuation theorem revisited, http://arXiv.org/cond-mat/0402676 (2004).
[20] J. Kurchan, Fluctuation theorem for stochastic dynamics, J. Phys. A 31, 3719 (1998).
[21] J. L. Lebowitz, H. Spohn, A GallavottiCohen-type symmetry in the large deviation functional for stochastic dynamics, J. Stat. Phys. 95, 333 (1999).
[22] C. Maes, it The fluctuation theorem as a Gibbs property, J. Stat. Phys. 95, 367 (1999).
[23] L. Rondoni, C. Mejía-Monasterio, Fluctuations in nonequilibrium statistical mechanics: models, mathematical theory, physical mechanisms Nonlinearity, 20, R1 (2007).
[24] R. Chetrite and K. Gawedzki, Fluctuation Relations for Diffusion Processes Comm. Math. Phys. 282, 469 (2008).
[25] Ya. G. Sinai, Lectures in Ergodic Theory, Lecture Notes in Mathematics (Princeton University Press) (1977).
[26] D. J. Evans, G. D. Cohen, D. J. Searles and F Bonetto, Note on the Kaplan-Yorke dimension and
linear transport coefficients, J. Stat. Phys., 101, 17 (2000).

[27] D. J. Evans and D. J. Searles and L. Rondoni, On the application of the Gallavotti-Cohen fluctuation relation to thermostatted steady states near equilibrium, Phys. Rev. E, 71, 056120 (2005).

[28] D. J. Evans and D. J. Searles, Equilibrium microstates which generate second law violating steady states, Phys. Rev. E, 50, 1645 (1994).

[29] D. J. Evans and D. J. Searles, Steady states, invariant measures, response theory, Phys. Rev. E, 52, 5839 (1995).

[30] D. J. Evans, D. J. Searles, L. Rondoni, The steady state fluctuation relation for the dissipation function, J. Stat. Phys. (2007).

[31] D. J. Evans and G. P. Morriss, Statistical Mechanics of Nonequilibrium Liquids New York: Academic Press (1990).

[32] B. Johnston, D. J. Evans, D. J. Searles, L. Rondoni (2012, submitted).

[33] D. Ruelle, Nonequilibrium statistical mechanics near equilibrium: computing higher order terms, Nonlinearity 11, 5 (1998).

[34] D. Ruelle, Smooth Dynamics and New Theoretical Ideas in Nonequilibrium Statistical Mechanics, J. Stat. Phys. 95, 1094 (2009).

[35] M. Colangeli, V. Lucarini, Elements of a unified framework for response formulae, J. Stat. Mech. (2014) P01002.

[36] W. Cowieson, L.S. Young, SRB measures as zero-noise limits, Erg. Th. and Dyn. Syst. 25, 1115 (2005).

[37] Yu. Kifer, Random perturbations of dynamical systems (Birkhäuser, Boston, 1988).

[38] M. Colangeli, C. Maes, B. Wynants, A meaningful expansion around detailed balance, J. Phys. A: Math. and Theor. 44, 095001 (2011).

[39] M. Baiesi, C. Maes, An update on the nonequilibrium linear response, New Journal of Physics 15, 013004 (2013).

[40] M. Baiesi, C. Maes, B. Wynants, Nonequilibrium linear response for Markov dynamics, I: jump processes and overdamped diffusions, J. Stat. Phys. 137, 1094 (2009).

[41] C. Maes, K. Netočný, B. Wynants Steady state statistics of driven diffusions, Physica A 387, 2675 (2008).

[42] H. Risken, The Fokker-Planck Equation, 2nd edn. (Springer Berlin, 1989).

[43] A. Dembo, O. Zeitouni, Large Deviations Techniques and Applications (Springer-Verlag, New York, 1998).

[44] S. Katz, J. L. Lebowitz, and H. Spohn, Phase transitions in stationary nonequilibrium states of model lattice systems, Phys. Rev. B, 28 1655 (1983).

[45] C. Maes, K. Netočný, Rigorous meaning of McLennan ensembles, J. Math. Phys. 51, 015219 (2010).

[46] C. Maes, On the origin and the use of fluctuation relations for the entropy, Séminaire Poincaré 2, 29 (2003).

[47] R. Landauer, Inadequacy of entropy and entropy derivatives in characterizing the steady state,
Phys. Rev. A 12, 636-638 (1975).

[48] R. Landauer, Stability and entropy production in electrical circuits, J. Stat. Phys. 13, 1-16 (1975).

[49] R. Landauer: Motion Out of Noisy States, J. Stat. Phys. 53, 233-248 (1988).

[50] J. Prost, J. F. Joanny, J. M. Parrondo, Generalized fluctuation-dissipation theorem for steady-state systems, Phys. Rev. Lett. 103, 090601 (2009).