

Fluctuation-Dissipation Theorems and Entropy Production in Relaxational Systems

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We show that for stochastic dynamical systems out of equilibrium the violation of the fluctuation-dissipation equality is bounded by a function of the entropy production. The result applies to a much wider situation than “near equilibrium,” comprising diffusion as well as glasses and other macroscopic systems far from equilibrium. For aging systems this bounds the age-frequency regimes in which the susceptibilities satisfy the fluctuation-dissipation theorem in terms of the rate of decay of the H function, a question intimately related to the reading of a thermometer placed in contact with the system. [S0031-9007(97)04030-1]

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Many systems encountered in nature have slow dynamics but are not “near equilibrium” in any obvious sense. Typical examples are (i) glassy systems a long time after the preparation procedure has finished, e.g., long after a temperature quench; (ii) domain growth and phase separation; (iii) systems that can be kept “far” from equilibrium by a *small* external power input done by stationary nonconservative forces and/or periodically time-dependent forces; and (iv) diffusion in noncompact spaces.

A slow, persistent, out of equilibrium regime is possible because in the thermodynamic limit the ergodic time is very large compared to the experimental time scales—this is the case of the first three examples—or due to the absence of confining potentials in the case of diffusion. Indeed, in contrast with the usually studied situation [1,2], none of the cases we mentioned can be viewed as a small perturbation about equilibrium such that the systems would return quickly to equilibrium as soon as the perturbation is removed.

Moreover, these systems may not be regarded in general as “metastable.” Specifically, one cannot consider a glass or a system undergoing domain growth to be completely equilibrated within a fixed sector of phase space, as in the case of, e.g., diamond, because the probability distribution in phase space changes continually. Indeed, by measuring two-time correlation or response functions one can at any time determine the age of a glass [3–6].

Bearing this in mind, a relevant question is whether some specifically equilibrium properties are also present in these systems. In this paper we concentrate on the study of the fluctuation-dissipation theorem (of the “first kind,” FDT [1]). A physical interpretation of this FDT is that its validity is a necessary condition for a thermometer in contact only with the system to register the bath’s temperature [7].

Working with dissipative dynamics, we show that the violations of the fluctuation-dissipation equalities vanish with a quantity that can be identified with the entropy production rate.

This leads us to suggest that there are unifying features in situations with small entropy production rate, whatever its origin (aging, work done by nonconservative and/or time-dependent forces, temperature gradients, etc). This comprises a much wider class of systems than the conventionally studied linear regime.

Let $C(t, t') = \langle A(t)B(t') \rangle$ be a correlation between observables A and B , $R(t, t') = \delta \langle A(t) \rangle / \delta h(t')$ the associated response to a field conjugate to B , and $\chi(t, t') \equiv \int_{t'}^t R(t, s) ds$ the integrated response. The “differential” violation V of FDT at (t, t') is

$$V(t, t') \equiv \frac{\partial C}{\partial t'} - TR = [1 - X(t, t')] \frac{\partial C(t, t')}{\partial t'}, \quad (1)$$

which also defines the “fluctuation-dissipation ratio” $X(t, t')$ [4]. Here, and in what follows, $t \geq t'$. A stronger and more physical form of the violation is the integrated version $I(t, t') \equiv \int_{t'}^t V(t, s) ds$:

$$I(t, t') = C(t, t) - C(t, t') - T\chi(t, t'). \quad (2)$$

The static (zero-frequency) violation is $I^{\omega=0} \equiv \lim_{t \rightarrow \infty} \times I(t, t')$. We can now be more precise about what is meant by far from equilibrium. In the systems we consider, $I(t, t')$ is (very) different from zero for certain large t, t' even in the limit of vanishing entropy production and, in particular, static susceptibilities do *not* coincide with their equilibrium value ($I^{\omega=0} \neq 0$) [4,5,8,9].

We assume a Langevin dynamics with an inertial term

$$m\ddot{x}_i + \gamma\dot{x}_i + \partial_{x_i} E + f_i = \Gamma_i, \quad (3)$$

where $i = 1, \dots, N$. f_i are velocity-independent nonconservative or time-dependent forces. Γ_i is a delta-correlated white noise with variance $2\gamma T$. This relation between the friction coefficient and the noise correlation is the “fluctuation-dissipation relation” (or FDT of the “second kind”); it expresses the fact that the bath itself is and stays in equilibrium. We encode x_i in an N vector \mathbf{x} . For simplicity, we have set the Boltzmann constant $k_B = 1$ and all masses m_i to be equal to m . We briefly describe the

massless case at the end of this Letter. We shall not consider purely Hamiltonian systems with $\gamma = 0$, for reasons which will become evident.

The probability distribution at time t for the process (3) is given by $P(\mathbf{x}, \mathbf{v}, t) = \mathcal{T} \exp(\int_0^t L_K) P(\mathbf{x}, \mathbf{v}, 0)$ with \mathcal{T} denoting time ordering and L_K the Kramers operator given by [10]

$$L_K = -\partial_{x_i} v_i + \frac{1}{m} \partial_{v_i} \left(\gamma v_i + \partial_{x_i} E + f_i + \gamma \frac{T}{m} \partial_{v_i} \right), \quad (4)$$

where we have used the summation convention. An H function may be defined as [1,2]

$$H(t) = \int d\mathbf{x} d\mathbf{v} P \left(T \ln P + E(\mathbf{x}) + \frac{m\mathbf{v}^2}{2} \right) \quad (5)$$

and may be interpreted as a “generalized free energy.”

Using the equation for P and some integrations by parts one finds

$$\dot{H}(t) = -\langle \mathbf{f}(t) \cdot \mathbf{v}(t) \rangle - \sum_i g_i(t), \quad (6)$$

where the first term is the power done by the forces \mathbf{f} and g_i are the entropy production terms

$$g_i(t) = \gamma \int d\mathbf{x} d\mathbf{v} \frac{(m v_i P + T \partial_{v_i} P)^2}{m^2 P} \geq 0. \quad (7)$$

Equations (6) and (7) imply that in the purely relaxational $\mathbf{f} = 0$ case with bounded energy, $H(t)$ is monotonically decreasing (and constant if $\gamma = 0$ —Liouville’s theorem for Hamiltonian dynamics) and its time derivative must tend to zero since the equilibrium free energy is finite. They also imply that a *stationary* ($\dot{H} = 0$) driven system does negative external work on average.

We describe below a number of situations in which the differential FDT violation V vanishes and the integral FDT violation I , which can be finite, takes a restricted form.

(i) Purely relaxational systems [5] as the total entropy production rate tends to zero when $t' \rightarrow \infty$. This can be satisfied in *two ways*, depending on the large-times sector we consider. For infinitely separated times, “aging regime,” one may have $X(t, t') \neq 1$ and $\partial_{t'} C \rightarrow 0$. Instead, in the regime of smaller time separations $X(t, t') \rightarrow 1$ and $\partial_{t'} C \neq 0$ (more like ordinary FDT). We also show that the asymptotic rate of decay of $H(t)$ determines the extent of both regimes.

(ii) Stationary driven systems with $\dot{H} = 0$ in the limit of small driving power $\langle \mathbf{f} \cdot \mathbf{v} \rangle \rightarrow 0$. For time separations that are larger for smaller driving powers one can have [11] $V(t - t') \rightarrow 0$ with $X(t - t') \neq 1$ and $\partial_{t'} C(t - t') \rightarrow 0$, while for time differences that remain finite in the weak driving limit $V(t - t') \rightarrow 0$ with $X(t - t') \rightarrow 1$ and $\partial_{t'} C(t - t') \neq 0$.

(iii) Periodically driven systems of period τ that have achieved a stationary (period τ) regime [12] in the limit of vanishing work per cycle. The FDT violation over a cycle $\int_{t'}^{t'+\tau} ds V(t, s)$ vanishes with $\int_{t'}^{t'+\tau} ds \langle \mathbf{f}(s) \cdot \mathbf{v}(s) \rangle$.

In these three cases X can be different from one precisely for pairs of times such that the correlation evolves slowly. The fact that for large, widely separated times one can (and often does [4]) have $X \neq 1$ is crucial, because it ultimately leads to the violation of the integral form of FDT: $I(t, t') \neq 0$ in certain large-time sectors.

(iv) Diffusion (with or without nonconservative forces) [13] for times such that the root mean squared displacement at later time t times the entropy production rate at the earlier time t' vanishes.

Derivation.—We prove the result for macroscopic correlations and responses constructed as follows. Let $\{A_i(\mathbf{x})\}$ and $\{B_i(\mathbf{x})\}$ be two sets of operators. We assume that each A_i (B_i) depends only upon the subset C_i^A (C_i^B) of the degrees of freedom of the system. We denote $C_{A_i, B_i}(t, t')$ the correlation, $R_{A_i, B_i}(t, t')$ the response of A_i to a field conjugate to B_i in the energy and $V_{A_i, B_i}(t, t') \equiv \partial_{t'} C_{A_i, B_i} - T R_{A_i, B_i}$ the corresponding FDT violation. We calculate the total FDT violation $V_{AB}(t, t')$ associated with $NC_{AB} \equiv \sum_i^N C_{A_i, B_i}$ and $NR_{AB} \equiv \sum_i^N R_{A_i, B_i}$.

Using Eq. (4), one can easily show that

$$\begin{aligned} V_{A_i, B_i}(t, t') &= \sum_l \theta(l, i) \int d\mathbf{x} d\mathbf{v} d\mathbf{x}' d\mathbf{v}' A_i(\mathbf{x}') \\ &\quad \times P(\mathbf{x}', \mathbf{v}', t | \mathbf{x}, \mathbf{v}, t') \partial_{x_l} B_i(\mathbf{x}) \\ &\quad \times \left(\frac{T}{m} \partial_{v_l} + v_l \right) P(\mathbf{x}, \mathbf{v}, t'), \end{aligned} \quad (8)$$

where $P(\mathbf{x}', \mathbf{v}', t | \mathbf{x}, \mathbf{v}, t') \equiv \langle \mathbf{x}', \mathbf{v}' | \mathcal{T} e^{\int_{t'}^t L_K} | \mathbf{x}, \mathbf{v} \rangle$. We have made explicit the nonzero terms by introducing $\theta(l, i) = 1$ if $l \in C_i^B$ and zero otherwise.

Identifying each term on the right as $\langle \Phi_{il} | \Psi_{il} \rangle \equiv \int d\mathbf{x} d\mathbf{v} d\mathbf{x}' d\mathbf{v}' \Phi_{il} \Psi_{il}$ with

$$\Phi_{il} \equiv A_i(\mathbf{x}') P^{1/2}(\mathbf{x}', \mathbf{v}', t | \mathbf{x}, \mathbf{v}, t') P^{1/2}(\mathbf{x}, \mathbf{v}, t') \partial_{x_l} B_i(\mathbf{x})$$

and using the Cauchy-Schwartz inequality $|\langle \Phi_{il} | \Psi_{il} \rangle| \leq \sqrt{\langle \Phi_{il} | \Phi_{il} \rangle \langle \Psi_{il} | \Psi_{il} \rangle}$ one can bound separately each integral in (8) as

$$|\langle \Phi_{il} | \Psi_{il} \rangle| \leq \langle A_i^2(t) (\partial_{x_l} B_i)^2(t') \rangle^{1/2} g_l^{1/2}(t') \theta(l, i) \quad (9)$$

with $g_l(t')$ given by Eq. (7).

The “macroscopic” FDT violation is

$$NV_{AB}(t, t') \equiv \left| \sum_i V_{A_i, B_i}(t, t') \right|. \quad (10)$$

The Cauchy-Schwartz inequality applied on the sum yields

$$\begin{aligned} NV_{AB}(t, t') &\leq \sum_{il} |\langle \Phi_{il} | \Psi_{il} \rangle| \\ &\leq \sqrt{N} D_{AB}(t, t') \left(\sum_{i'l'} g_{l'}(t') \theta(l', i') \right)^{1/2}, \end{aligned} \quad (11)$$

where we have defined D_{AB} through

$$\sqrt{N} D_{AB}(t, t') \equiv \left(\sum_{il} \langle A_i^2(t) (\partial_{x_i} B_i)^2(t') \rangle \theta(l, i) \right)^{1/2}.$$

The last factor is $\sum_{l'} g_{l'}(t') \sum_{i'} \theta(l', i') = \sum_{l'} g_{l'}(t') \mathcal{N}_{l'}$, where $\mathcal{N}_{l'}$ is the number of different $A_{i'}$ that depend on $x_{l'}$. Assuming all the \mathcal{N}_i to be finite, we can again bound the last factor using $\mathcal{N}_i \leq \mathcal{N} \equiv \max_i \mathcal{N}_i$. If in addition C_i^A has a finite number of elements, D_{AB} is $O(1)$. Thus

$$V_{AB}(t, t') \leq \sqrt{\mathcal{N}} D_{AB}(t, t') \left(\frac{1}{N} \sum_i g_i(t') \right)^{1/2}. \quad (12)$$

Both sides of the inequality are $O(1)$. This is the basic result of this Letter. We shall explore its consequences below.

For a purely relaxational system, this yields

$$V_{AB}(t, t') \leq \sqrt{\mathcal{N}} D_{AB}(t, t') \left(-\frac{1}{\gamma N} \frac{dH(t')}{dt'} \right)^{1/2}. \quad (13)$$

Note that this proof breaks down in the nondissipative limit $\gamma = 0$.

For stationary nonconservative systems we have

$$V_{AB}(t - t') \leq \sqrt{\mathcal{N}} D_{AB}(t - t') \left\langle \frac{\mathbf{v} \cdot \mathbf{f}}{N} \right\rangle^{1/2}, \quad (14)$$

while for a ‘‘stationary’’ periodically driven system such that $H(t) = H(t + \tau)$,

$$\int_{t'}^{t'+\tau} ds V_{AB}(t, s) \leq \left(\mathcal{N} \int_{t'}^{t'+\tau} ds D_{AB}^2(t, s) \right)^{1/2} \times \left(\frac{W}{N} \right)^{1/2}.$$

$W(t') \equiv \int_{t'}^{t'+\tau} ds \langle \mathbf{v}(s) \cdot \mathbf{f}(s) \rangle$ is the work per period.

These results can be generalized to establish a relation for multiple point correlations between operators A_i^k depending on the coordinates in C_i at times $t_1 > \dots > t_k$, $C_i^{1, \dots, k} \equiv \langle A_i^1 \dots A_i^k \rangle$, and the corresponding responses $R_i^{1, \dots, k}$ to a perturbation applied to A_i^k at time t_k .

Applications.—As a particular simple case of Eq. (13) we obtain a bound for the variation of a single-time quantity in a relaxational case. Setting $A_i = 1$ and taking a single operator B , $R_{AB} = 0$ and we obtain

$$\left| \frac{d\langle B \rangle}{dt} \right| \leq \left(\sum_i^N \langle (\partial_{x_i} B)^2 \rangle \right)^{1/2} \left(-\frac{1}{\gamma} \frac{dH(t)}{dt} \right)^{1/2}. \quad (15)$$

Another typical application of the formulas above is when x_i are lattice variables, with i denoting the site. The fluctuation-dissipation theorem associated with the two-point correlation $C(r, t, t')$ and response $R(r, t, t')$ is obtained by putting $B_i = x_i$ and $A_i = x_{i+r}$. Similarly, one can study the energy-energy correlations $C^E(r, t, t')$ with $B_i = E_i - \langle E_i \rangle$ and $A_i = E_{i+r} - \langle E_{i+r} \rangle$, provided

that the energy E_i of site i depends on a finite number of neighbors (and hence \mathcal{N} is finite).

One can extend the derivation to the calculation of total correlations if the corresponding spatial dependencies fall fast enough. For example, for the energy

$$\frac{1}{N} \langle E(t) E(t') \rangle - \frac{1}{N^2} \langle E(t) \rangle \langle E(t') \rangle = \sum_r C^E(r, t, t'), \quad (16)$$

one can use the bounds obtained previously provided one can cut off the sum at some maximum distance r_{\max} .

Another interesting bound is obtained by writing $\langle \mathbf{f}(\mathbf{x}) \cdot \mathbf{v} \rangle = \int d\mathbf{x} d\mathbf{v} \mathbf{f}(\mathbf{x}) \cdot (\mathbf{v} + T \partial_{\mathbf{v}}) P$ and by proceeding as from Eq. (8) to Eq. (11):

$$\langle \mathbf{f} \cdot \mathbf{v} \rangle^2 \leq \langle |\mathbf{f}|^2 \rangle \sum_i g_i. \quad (17)$$

Integrated bounds for purely relaxational systems.—In glassy systems it is known [4,5,9] that the integral form of FDT is violated in certain two (large) time sectors. We can bound the extent of these sectors as follows.

Assuming that the factor D_{AB} is finite for all times, $D_{AB}(t, t') < K$, on integrating (13) and applying once again Cauchy-Schwartz, we obtain

$$|I_{AB}(t, t')| \leq K \int_{t'}^t \left(-\frac{1}{N} \frac{dH(s)}{ds} \right)^{1/2} ds,$$

where $I_{AB}(t, t') = C_{AB}(t, t) - C_{AB}(t, t') - T \chi_{AB}(t, t')$. Hence, there can be no integral violation of FDT for *any* long times if H falls faster than t^{-1} . Interestingly enough, if $H(t)$ can be written as an average over exponential processes $H(t) = \int d\tau \rho(\tau) \exp(-t/\tau)$, this result implies that there can be FDT violation at large times only if $\langle \tau \rangle$ diverges [14].

For H falling slower than or as t^{-1} , we can still bound the region in which FDT holds. First of all, we have that for $t' \rightarrow \infty$ and $t - t' = O(1)$ FDT will always hold. More generally, consider the limit $t' \rightarrow \infty$ with $t - t' = O(t'^a)$ with $0 < a < 1$. A simple calculation gives

$$|I_{AB}(t, t')| \leq K \left(-\frac{1}{N} \frac{dH(t')}{dt'} \right)^{1/2} t'^a.$$

If $H(t) = H_\infty + kt^{-\alpha}$, then there will be no FDT violation in the time sectors defined by a provided $2a < (\alpha + 1)$. In particular, if H falls as any inverse power of a logarithm, FDT holds for $t - t' < O(t'^{1/2})$.

Massless case.—One can treat the case with $m = 0$ (i.e., without inertial term) in the same way. One defines an H function as in (5), without the kinetic term and with $P(\mathbf{x}, t)$ depending only on space. Using the Fokker-Planck equation, one may derive an expression for the fluctuation-dissipation violation analogous to (8), which can be bounded in terms of the entropy production, which in this case reads

$$g_i = \int d\mathbf{x} \frac{[P \partial_{x_i} E(\mathbf{x}) + T \partial_{x_i} P]^2}{P} \geq 0. \quad (18)$$

Diffusion.—A simple application of the massless case is to Brownian motion in D dimensions, if we set the diffusion constant to be equal to a temperature T , and take $A_i = X_i$ and $B_i = X_i$. The application of the inequality for the massless case yields

$$|V(t, t')| \leq (2Dt)^{1/2} [TD/(2t')]^{1/2} = TD(t/t')^{1/2}.$$

Note that here $D_{AB}(t, t') = 2Dt$ and is therefore not bounded. Since in this case neither R nor $\partial_{t'} C$ are small, this equation tells us that FDT can be violated [15]. The exact calculation gives $V(t, t') = TD$; hence the inequality is clearly obeyed but with equality only at $t = t'$.

A more interesting example of the applications of our study is to the problem of Sinai diffusion in one dimension [13,16,17]. If one assumes that $\overline{H}(t)$ scales in the same way as the energy $\overline{E}(t)$, then one may deduce the scaling of the energy via the Arrhenius law $t \sim \tau_0 \exp[c\overline{E}(X_t)]$, with c and τ_0 constants and $\overline{}$ representing an average over disorder. In this problem the particle is subject to a white noise force and therefore is diffusing in a Brownian potential; hence $\overline{E}(x) \sim x^{1/2}$. From this one deduces the results $\langle X_t^2 \rangle \sim \log^4(t)$ and $H(t) \sim \overline{E}(t) \sim \log(t)$ (where we emphasize the relation between \overline{E} and \overline{H} is justified only on the grounds of physical intuition). We therefore obtain $|V(t, t')| \leq c \log^2(t)/\sqrt{t'}$, which implies that the integrated form of FDT must hold at least up to time differences scaling as $t - t' \sim ct'^{1/2}$.

In conclusion we have shown that there is a direct connection between FDT violations and entropy production in systems with stochastic dynamics. This connection allows one to obtain results even in the interesting cases in which in the limit of small entropy production the systems are still far from equilibrium, as may happen in macroscopic (or diffusive) systems. It is important, though probably tougher, to extend these results to deterministic systems with a thermostat [18] in the thermodynamic limit; it would be surprising if these results did not carry through to this case.

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- [1] R. Kubo, M. Toda, and N. Hashitume, *Statistical Physics II. Nonequilibrium Statistical Mechanics* (Springer-Verlag, Berlin, 1992).
- [2] S.R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
- [3] L.C.E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Houston, 1978); I. Hodge, *Science* **267**, 1945 (1996).
- [4] L.F. Cugliandolo and J. Kurchan, *Phys. Rev. Lett.* **71**, 173 (1993); *Phil. Mag. B* **71**, 50 (1995); *J. Phys. A* **27**, 5749 (1994).
- [5] For a review on recent progress in theoretical aspects of glass models, see J.-P. Bouchaud, L.F. Cugliandolo, J. Kurchan, and M. Mézard, in *Spin-Glasses and Random Fields*, edited by A.P. Young (World Scientific, Singapore, 1997), cond-mat/9702070.
- [6] For a review on aging simulations in spin glasses, see, e.g., H. Rieger, *Annual Reviews of Computational Physics*, edited by D. Stauffer (World Scientific, Singapore, 1995), Vol. II. Aging simulations in glasses are beginning to appear: E. Andrejew and J. Baschnagel, *Physica (Amsterdam)* **233A**, 117 (1996); G. Parisi, cond-mat/9701015; W. Kob and J.-L. Barrat, cond-mat/9704006.
- [7] L.F. Cugliandolo, J. Kurchan, and L. Peliti, *Phys. Rev. E* **55**, 3898 (1997).
- [8] See [7,11] for examples of stationary systems that violate FDT in the limit of vanishing drive.
- [9] S. Franz and H. Rieger, *J. Stat. Phys.* **79**, 749 (1995); G. Parisi, cond-mat/9701100; cond-mat/9703219.
- [10] H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1984).
- [11] A. Crisanti and H. Sompolinsky, *Phys. Rev. A* **36**, 4922 (1987); H. Horner, *Z. Phys. B* **100**, 243 (1996); L.F. Cugliandolo, J. Kurchan, P. Le Doussal, and L. Peliti, *Phys. Rev. Lett.* **78**, 350 (1997).
- [12] Physical systems where strong periodic time-dependent applied forces are relevant are, e.g., sandpiles; see M. Jaeger, S.R. Nagel, and R.P. Behringer, *Rev. Mod. Phys.* **68**, 1259 (1996).
- [13] J.-P. Bouchaud and A. Georges, *Phys. Rep.* **195**, 127 (1990).
- [14] J.-P. Bouchaud (private communication).
- [15] L.F. Cugliandolo, J. Kurchan, and G. Parisi, *J. Phys. I (France)* **4**, 1641 (1994).
- [16] J.-P. Bouchaud, A. Comtet, A. Georges, and P. Le Doussal, *Ann. Phys. (N.Y.)* **201**, 285 (1990).
- [17] L. Laloux and P. Le Doussal, cond-mat/9705249.
- [18] The exploration of the consequences of a chaotic hypothesis in thermostated systems is a very fruitful field at the moment. See, for example, G. Gallavotti and D. Ruelle, cond-mat/9612002, and references therein.