Power spectra for both interrupted and perennial aging processes

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We study the power spectrum of a random telegraphic noise with the distribution density of waiting times τ given by $\psi(\tau)\propto 1/\tau^{\mu}$, with $\mu\approx 2$. The condition $\mu<2$ violates the ergodic hypothesis, and in this case the adoption of Wiener–Khintchine (WK) theorem for the spectrum evaluation requires some caution. We study this problem theoretically and numerically and we prove that the power spectrum obeys the prescription $S(f)=K/f^{\eta}$, with $\eta=3-\mu$, namely, the $1/f$ noise lives at border between the ergodic $\mu>2$ and nonergodic $\mu<2$ condition. We study sequences with the finite length L. In the case $\mu<2$ the adoption of WK theorem is made legitimate by two different kinds of truncation effects: the physical and observation-induced effect. In the former case $\psi(\tau)$ is truncated at $\tau\approx T_{\max}$ and $L\gg T_{\max}$ ensures the condition of interrupted aging. In this case, we find that K is a number independent of L. The latter case, $L\ll T_{\max}$, is more challenging. It was already solved by Margolin and Barkai, who used time asymptotic arguments based on the ergodicity breakdown and obtained $K\propto 1/L^{2-\mu}$, proving that the out-of-equilibrium nature of the condition $\mu<2$ is signaled by the decrease of K with the increase of L. We use a generalized version of the Onsager principle that leads us to the same conclusion from a somewhat more extended view valid also for the transient out-of-equilibrium case of $\mu>2$. We do not limit our treatment to the time asymptotic case, thereby producing a prediction that accounts for the transition from the $1/f^{\eta}$ to the $1/f^2$ regime, recently observed in an experiment on blinking quantum dots. Our theoretical approach allows us to discuss some other recent experiments on molecular intermittent fluorescence and affords indications that should help to assess whether the spectrum is determined by the $L\ll T_{\max}$ or by the $L\gg T_{\max}$ condition. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3006051]

I. INTRODUCTION

Intermittent fluorescence is a widespread phenomenon of single quantum systems that has triggered an enormous interests in both physics and chemistry since the pioneer paper by Cook and Kimble.[1] The resulting fluorescence signal gets the form of a random telegraphic noise, with two waiting time distribution densities, one for the "light on" and one for the "light off" state. In the case of semiconductor nanocrystals the interest was stimulated also by the observation that the durations of bright and dark periods follow the inverse power law statistics,[2,3]

$$\psi(\tau) \propto \frac{1}{\tau^{\mu}}, \tag{1}$$

with $\mu<2$.[2,3] The inverse power law with $\mu<2$ has also been observed in the fluorescence of organic molecules.[4–7]

In the case of semiconductor nanocrystals the hypothesis was made that the time of sojourn in a given state, either "on" or "off," does not have any correlation with the other sojourn times.[8] This property, referred to as *renewal* condition, has been confirmed by the careful statistical analysis of real data made by the authors of Ref. 9. The renewal and the inverse power law condition with $\mu<2$ generate perennial aging[10] and consequently a conflict with the ergodic assumption,[11] thereby posing a challenge to the adoption of the prescriptions of ordinary statistical physics. Ergodicity breakdown has been recently observed also with the spectroscopy of single organic molecules.[12] In the case of blinking fluorescence in nanocrystal quantum dots, the authors of Refs. 13 and 14 found that these fluctuations have the spectral form of $1/f$ (flicker) noise. The phenomenon of flicker noise has been known for a long time.[15] It describes the deviation of the noise spectral density $S(f)$ from the flat condition, through the form

$$S(f) \propto \frac{1}{f^{\eta}}, \tag{2}$$

where f is the frequency and η ranges from $\eta=0.5$ to $\eta=1.5$. The authors of Refs. 13 and 14 found $\eta=1.3$ and $\eta=1.1$, respectively.

In the literature of $1/f$ noise no adequate attention has been devoted so far by the majority of the authors to the fact that, although $\eta<1$ is compatible with the ergodic assumption, $\eta>1$ (Refs. 13 and 14) may imply ergodicity breakdown, in spite of the fact that $\eta>1$ is frequently found in the literature. For another example where $\eta>1$ see, for instance, the flicker noise emerging from the scanning tunnelling microscopy[16] with $\eta\approx 1.08$. The theoretical approaches to $1/f$ noise are based on the Wiener–Khintchine theorem, and

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consequently, on the stationary assumption: see, for instance, the theory of Voss and Clarke.[17] This may raise therefore doubts on the claim that intermittent fluorescence is associated to the emergence of nonergodic properties. According to Chung *et al.*[18] the power law statistics of the laser induced fluorescence intermittence of quantum dots is limited to a finite time interval $[T_{\min}, T_{\max}]$, with $\psi(\tau)$ dropping to 0 for $\tau > T_{\max}$. As a consequence, the $1/f$ noise is expected to hold in the frequency region $1/T_{\max} < f$, and the aging process, which in the case $\mu < 2$ should be perennial, is interrupted, as explained by Witkoskie and Cao.[19]

The only example of theoretical treatment of an extension of the WK theorem, without requiring the condition $T_{\max} < \infty$, is the recent work of Margolin and Barkai.[20] The authors of this remarkable work did succeed in extending the WK theorem to the nonergodic case with both single realizations and averages over the Gibbs ensemble. In this paper we shall address the same problem, using a different approach that is limited to the conventional averaging over the Gibbs ensemble. However, the generalization of the WK theorem proposed in this article applies to the nonequilibrium process generated by the preparation at $t=0$ in both the $\mu < 2$ and $\mu > 2$ case, although, as we shall see, the nonstationary effects in the latter case are not significant. We shall make more transparent than in Ref. 20 the important fact that $\eta = 1$, the ideal condition of $1/f$ noise, is the boundary between the ergodic and nonergodic regime. Furthermore, we shall not confine our attention to the time asymptotic regime and we shall shed light into the transition from the regime $\eta \approx 1$ to the regime $\eta = 2$.

The outline of this paper is as follows. In Sec. II we use surrogate sequences to evaluate the power spectrum $S(\omega)$ in both cases: $T_{\max} < \infty$ and $T_{\max} = \infty$. The next four sections are theoretical and serve the purpose of explaining the numerical results of Sec. II with theoretical arguments compatible with the nonequilibrium nature of these processes. In Sec. III we illustrate an approach to the power spectrum based on the Onsager principle, which suggests a way to extend the WK theorem to the non-ergodic case resting on the survival probability, thought of as a nonstationary form of correlation function. To make a proper comparison with the stationary approach to $1/f$ noise, in Sec. IV we illustrate the derivation of $1/f$ noise using a non-Ohmic bath. The non-stationary WK theorem of Sec. V is based on a nonstationary correlation function. We devote Sec. VI to deriving an approximated analytical expression for the aging waiting time distribution $\psi(\tau)$ that is expected to be very accurate for $\mu \approx 2$. In Sec. VII we prove with both heuristic and rigorous arguments that the age of a finite size sequence coincides with the sequence length L. In Sec. VIII we make a comparison with the earlier work of other groups. Finally, in Sec. IX we draw the conclusions of this article.

II. NUMERICAL EXPERIMENT ON A DICHOTOMOUS SIGNAL $\xi(t)$, WITH FINITE AND INFINITE $T_{\max}$

Let us consider a sequence of events occurring at times t_i with $i = 1, 2, \ldots$. Let us make the assumption that these events are renewal and that the histogram of the waiting times between two consecutive events is an inverse power law with index $\mu \approx 2$. We generate a dichotomous signal simulating the real intermittent fluorescence by using the following procedure, derived by the earlier work of Refs. 21 and 22. The quiescent region between two consecutive events, occurring at times t_i and t_{i+1}, is filled with the sign $\pm$, according to a coin tossing prescription. The time distances between two consecutive events $\tau_i = t_{i+1} - t_i$ is derived by using the prescription

$$\tau = T\left[\frac{1}{w^{1/(\mu-1)} - 1}\right], \tag{3}$$

where w is a random number of the interval $I = [0, 1]$.[23] The assumption that the outcomes of the random variable w are equiprobable,[23] makes the resulting waiting time distribution density acquire the form

$$\psi(\tau)(\mu - 1)\frac{T^{\mu-1}}{(t+T)^{\mu}}. \tag{4}$$

When $\mu > 2$, the mean waiting time is given by

$$\langle\tau\rangle = \frac{T}{(\mu - 2)}. \tag{5}$$

When $\mu < 2$, the mean waiting time is divergent thereby generating ergodicity breakdown.[10,11] The corresponding survival probability $\Psi(t)$ has the following analytical expression:

$$\Psi(t) = \left(\frac{T}{t+T}\right)^{\mu-1}. \tag{6}$$

We call $\xi(t)$ the resulting dichotomous signal. This corresponds to $T_{\max} = \infty$. To generate the condition corresponding to $T_{\max} < \infty$ we set $\tau = 0$ if the prescription of Eq. (3) generates a number τ exceeding $T_{\max}$.

It is important to notice that the coin tossing assumption apparently generates a theory where some of the renewal events responsible for the process may be invisible, because when an event occurs the signal $\xi(t)$ does not necessarily make a jump. Actually, if we prepare a Gibbs ensemble with all the realizations characterized by an event occurrence at $t=0$, and we create at the same time an out of equilibrium fluctuation by selecting the set of systems with $\xi = 1$ at $t = 0$, the relaxation of this out-of-equilibrium fluctuation decays in time as the survival probability of Eq. (6). In fact, when the first event after the preparation event occurs, half of the systems remain in the state + and half jump to the state −, thereby annihilating the out-of-equilibrium condition. This property, which can be experimentally observed, is related to $\psi(\tau)$ of Eq. (4) by the renewal relation $\Psi(\tau) = -d\psi(\tau)/d\tau$. In this article we shall discuss how to extend this way of proceeding to the case where the out-of-equilibrium fluctuation is created at an arbitrary time distance from the preparation, thereby taking aging effects into account. For more details we refer the interested reader to the work of Allegrini *et al.*[22]

It is also important to notice that the parameter T is introduced for the fundamental purpose of ensuring that $\psi(\tau)$

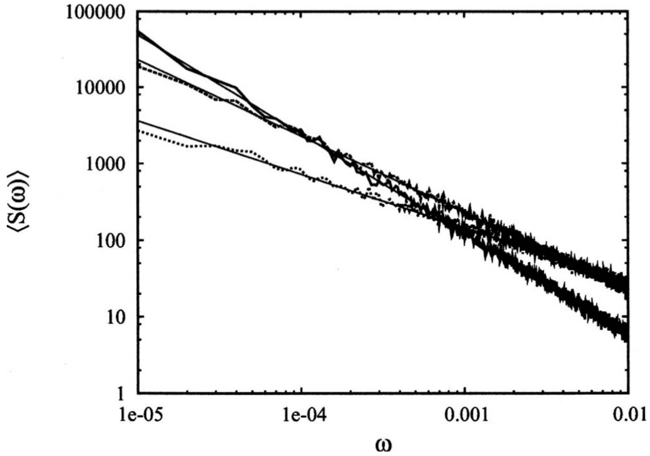


FIG. 1. Comparison of power spectra of systems with different μ. Each curve was obtained by using an ensemble of 100 realizations of length $L=10^6$ time units. The curves represent the power spectra of processes with $\mu=2.3$ (dotted curve), $\mu=2.0$ (dashed curve) and $\mu=1.7$ (full curve). The straight lines are the corresponding fits: $1.15\omega^{-0.7}$, $0.23\omega^{-1}$, $0.0155\omega^{-1.3}$.

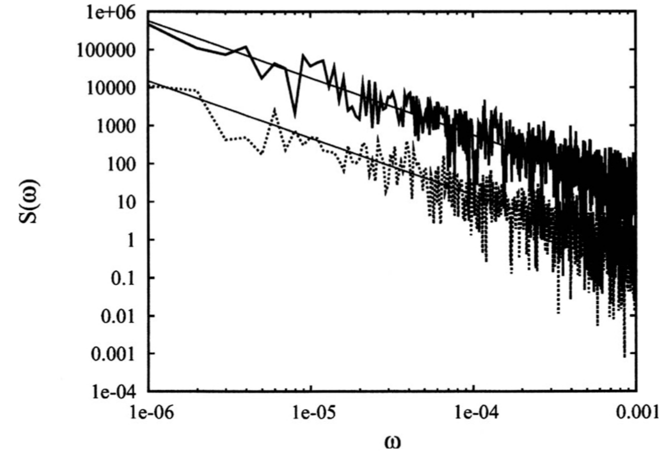


FIG. 2. Single realization. We used $\mu=1.5<2$ for the two curves. The upper curve represents the power spectrum of a single realization of length $L=1\times 10^7$ units. Increasing the length of the realization to $L=1\times 10^9$ units makes the entire power spectrum drop to lower values. This is shown by the lower curve. The function that fits the upper curve is $0.000\,57\omega^{-1.5}$ and the one that fits the lower curve is $1.5\times 10^{-5}\omega^{-1.5}$. This figure shows that the power spectrum of a single realization is the same as the power spectrum of an ensemble of realizations. For a more accurate treatment of the spectra of single realizations, see Fig. 10 of Ref. 20.

remains finite also at $\tau=0$. The analytical expression of the distribution density of Eq. (4) fits the normalization condition

$$\int_0^\infty dt'\,\psi(t')=1, \tag{7}$$

in accordance with the condition $\Psi(0)=1$ obeyed by the survival probability of Eq. (6). It is also important to notice that the parameter T has an important physical meaning: it defines the time span within which the system does not produce yet an inverse power law distribution density of waiting times. In this article we do not discuss the physical origin of the intermittent fluorescence: we limit ourselves to afford the theoretical prescriptions to evaluate the spectrum $S(\omega)$, in such a way as to ensure the possibility of defining the parameters T and μ from the comparison between theoretical predictions and experimental results. In Sec. VIII we shall discuss a physical effect produced by $T>0$.

We evaluate the spectrum $S(\omega)$ by using the standard prescription

$$S(\omega)=\lim_{L\to\infty}\frac{1}{L}\left|\int_0^L \exp(i\omega t)\xi(t)dt\right|^2, \tag{8}$$

where $\xi(t)$ denotes a sequence produced with the earlier algorithm. We have to point out that all the single realizations are characterized by an event occurring at $t=0$, namely, $t_0=0$. This is the preparation condition that, as we shall see, plays an important role in the nonstationary case discussed in this article. The results of the numerical treatment are illustrated in Figs. 1–7. All of the figures were created by simulations using the prescription of Eq. (8). It should be noted that $S(\omega)$ is the power spectrum of a single realization whereas $\langle S(\omega)\rangle$ is the average out of a set of many power spectra of different realizations with the same index μ.

The numerical results show that for $2<\mu<3$, in agreement with the WK theorem,

$$S(\omega)\propto\frac{T^{\mu-2}}{\omega^{3-\mu}}, \tag{9}$$

and that for $1<\mu<2$, in accordance with the generalized WK theorem of Ref. 20 and with their numerical calculations [see Eq. (33) and Fig. 10 of Ref. 20],

$$S(\omega)\propto\frac{1}{L^{2-\mu}}\frac{1}{\omega^{3-\mu}}, \tag{10}$$

thereby implying that a range of values close to $\mu=2$ generates $1/f$ noise. The proportionality factors in Eqs. (9) and (10) are of the order of unity.

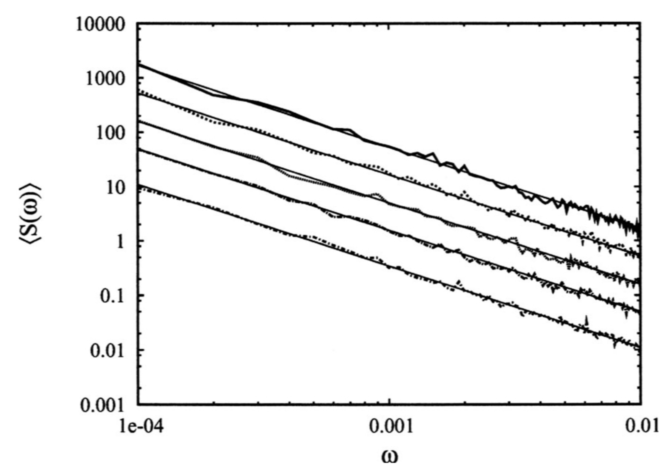


FIG. 3. Power spectrum—$\mu<2$. We used $\mu=1.5$ for all five curves in this figure—we are dealing with a nonstationary condition. To each curve there corresponds a different realization length L. Each curve was obtained by using an ensemble of 1000 realizations. The topmost curve was realized using a realization of length 10^6. The one immediately below corresponds to $L=10^7$. As we move further below, the lengths of the realizations used were 10^8, 10^9, and 10^{10}. The straight lines are functions of the form $K\omega^{-1.5}$, where K is a constant factor (see Fig. 7). From top to bottom, $K=1.7\times 10^{-3}$, 5.3×10^{-4}, 1.6×10^{-4}, 5×10^{-5}, 1.1×10^{-5}.

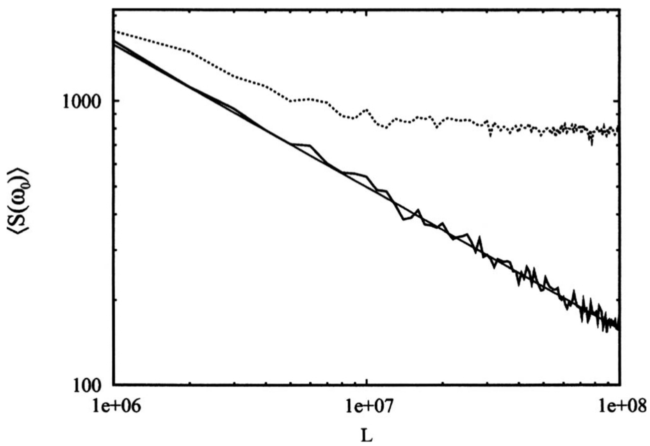


FIG. 4. Amplitude as a function of realization length at a constant frequency. We used $\mu=1.5$ and 1000 realizations. We fixed the angular frequency at $\omega_0=10^{-4}$ and calculated the corresponding amplitude $\langle S(\omega_0=10^{-4})\rangle$ for different realization lengths L. The dashed curve is the result obtained when the waiting time distribution, $\psi(\tau)$ is truncated at $\tau=10^7$. We see that after about $L=10^7$ units, the power spectrum stops dropping as the realization length increases. The full curve is the result obtained in the absence of truncation. The straight line corresponds to the function $K/L^{0.5}$, where $K=1.58\times10^6$.

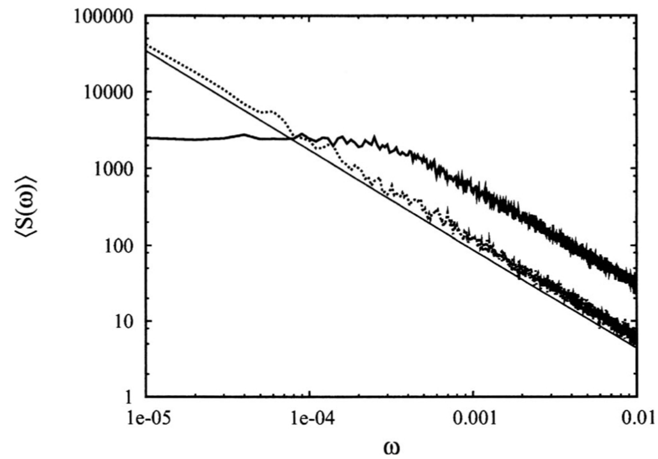


FIG. 6. Effect of truncating the waiting time distribution. We used $\mu=1.7$ for this figure and an ensemble of 100 realizations for the curves. The waiting time distribution $\psi(\tau)$ was truncated at $\tau=10^4$. In that case $T_{\max}=10^4$. The figure shows the power spectrum before and after truncation. The curve with the plateau corresponds to the truncated waiting time distribution. The straight line in the middle is $0.011\omega^{-1.3}$. Both curves were obtained using realizations of length $L=10^6$.

With the help of 100 realizations Fig. 1 shows that this is indeed the condition that emerges from the numerical evaluation of $S(\omega)$. Following Pelton *et al.*,[13] we compared the power spectrum of an ensemble of realizations to that of single realizations. Figure 2 shows that the $1/f$ noise behavior is maintained also at the level of single realizations although in this case there are fluctuations around the $1/f$ behavior that become larger and larger with larger frequencies. The average over an ensemble of many realizations has the effect of reducing the intensity of these fluctuations, as shown by Fig. 3. Figure 3 shows also another interesting effect: The intensity of $1/f$ noise is a decreasing function of L if $\mu<2$. All these properties have been already found numerically by the authors of Ref. 20 and interpreted by them theoretically, on the basis of their ergodicity breakdown arguments. We shall reach the same conclusions by focusing on the perennial aging condition that is in fact closely related to the ergodicity breakdown. Figure 4 shows that $S(\omega)$, for $\mu<2$, follows Eq. (10), whereas for $\mu>2$, after a weak intensity decrease at lower values of L, it tends to a final intensity value that is independent of L for larger sequences. This is a consequence of the fact that, as we shall see, the preparation of the sequences at $t=0$ generates a nonequilibrium process in the whole interval $1<\mu<3$. The process is transient in the case $\mu>2$, generating effects much less significant than in the case $\mu<2$, where the nonequilibrium condition is perennial. The weak dependence of the $1/f$ intensity of L is confirmed by Fig. 5, where the slight differences among realizations with different lengths, are perhaps due to the fact that with the same number of realizations the accuracy of the result decreases with L. Figures 6 and 7 show the effect of setting $T_{\max}<\infty$. Figure 6 shows that for $\omega<1/T_{\max}$ the time sequence is perceived as white noise. As expected,[19] $T_{\max}<\infty$ generates interrupted aging, and as a consequence also the interruption of the reduction of $1/f$ noise intensity, which is known[20] to be a manifestation of the nonstationary behavior of the case $\mu<2$.

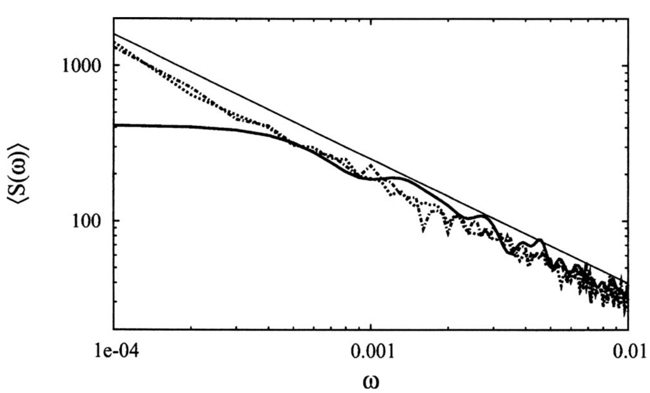


FIG. 5. Power spectrum—$\mu>2$. We used $\mu=2.2$ for all three curves in this figure. To each curve there corresponds a different realization length L. Each curve was obtained by using an ensemble of 100 realizations. The full curve corresponds to an ensemble of realizations of length $L=10^4$ units. The other two correspond to lengths $L=10^5$ units and $L=10^6$ units. The straight line is the function $\omega^{-0.8}$. The power spectrum does not depend on L, of the realizations.

III. ONSAGER PRINCIPLE APPROACH TO THE SPECTRUM

Let us consider a Gibbs ensemble of sequences $\xi(t)$ and let us prepare this ensemble at time $t=0$. As we have seen in Sec. II, preparation at $t=0$ is a special out of equilibrium condition where all the realizations have an event at $t=0$. We assume also that half of the Gibbs systems are in the "on" state, $\xi(0)=1$, and half in the "off" state, $\xi(0)=-1$, thereby yielding $\langle\xi(0)\rangle=0$. Note that the vanishing mean value of ξ should not be confused with real equilibrium[22] that is never reached if $\mu<2$. After preparation, we let the ensemble evolve up to time $t=t_a$. At this time we select all the sequences characterized by $\xi(t_a)=1$. The sum over all these realizations corresponds to a macroscopic out-of-equilibrium fluctuation whose value is M, with $M\approx N/2$ and N is the total number of realizations. According to the Onsager

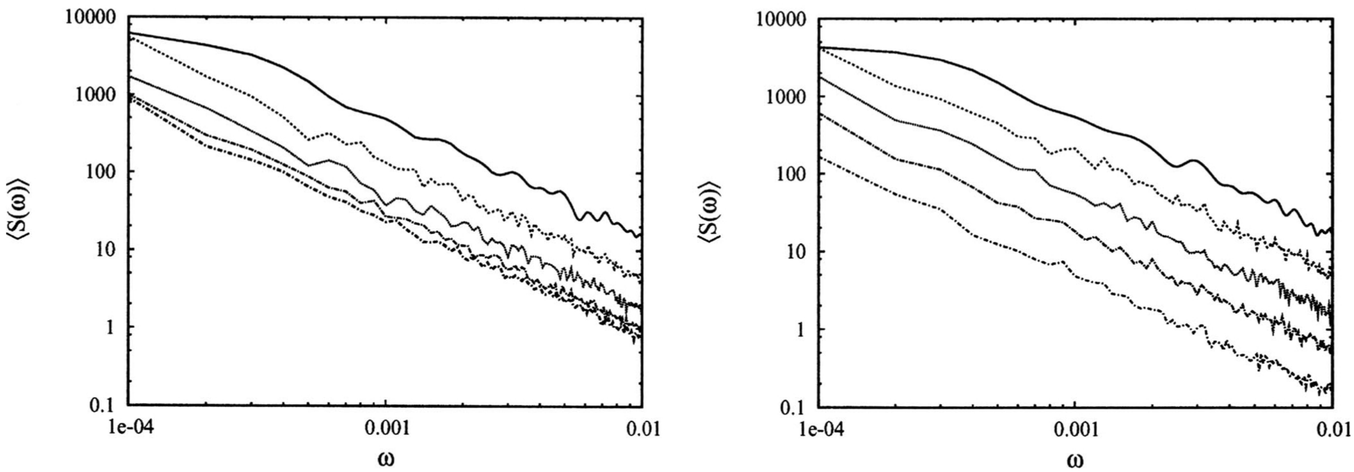


FIG. 7. Effect of truncating the waiting time distribution and changing L. Each curve in this figure is a result of averaging over 100 realizations. We used $\mu=1.5<2$ for all the curves in these two figures. Figure on the left: we can see the effect of truncating the waiting time distribution $\psi(t)$. The topmost curve is the one created using the shortest realization length L. As the length is increased, the curves drop. From top to bottom, the length of the realizations used is $L=10^4$, 10^5, 10^6, 10^7, and 10^8 units. We can see that they cease to do so after a certain limit (in Fig. 7 this limiting value can be measured). Unlike in Fig. 5, here we do not see a plateau because $\psi(\tau)$ was truncated at $\tau=10^7 \gg 1/10^{-4}$. Figure on the right: it shows the result that is obtained under the same conditions as those used in the figure on the left, but without truncating the waiting time distribution.

principle[24] this macroscopic out-of-equilibrium property is expected to regress to the vanishing value as the corresponding correlation function of the fluctuation $\xi(t)$. Here we adopt the theoretical perspective of Ref. 22. The authors of this paper proved that the Onsager principle can be extended to the case of non-Poisson renewal processes, and that the survival probability of age t_a is nothing but the nonstationary correlation function of the same age.

The single realizations are the systems of the Gibbs ensemble, and have the ordinary form of a dichotomous fluctuation, with the only condition that $\xi(t_a)=1$. We evaluate the Fourier transform of each of these realizations and, for simplicity sake, we set t_a as the new origin of time. Let us define

$$\hat{\xi}(\omega) \equiv \int_{-\infty}^{\infty} \Theta(t)\xi(t)\exp(i\omega t)dt, \tag{11}$$

where $\Theta(t)$ is the Heaviside step function. From the Fourier transform procedure we get

$$\hat{\xi}(\omega) = \frac{1}{\omega}\sin(\omega t_1) + \frac{i}{\omega}[1-\cos(\omega t_1)] + R(t_2,t_3,\ldots), \tag{12}$$

where t_i are the times when the events occur. We do not write the explicit expression of $R(t_2,t_3,\ldots)$ because due to the sign random choice it will not contribute to the Gibbs mean value of $\hat{\xi}(\omega)$. Thus, we obtain

$$\langle\hat{\xi}(\omega)\rangle = \frac{1}{\omega}\int_0^{\infty}\sin(\omega\tau)\psi_{t_a}(\tau)d\tau + \frac{i}{\omega}\int_0^{\infty}[1-\cos(\omega\tau)]\psi_{t_a}(\tau)d\tau, \tag{13}$$

where $\psi_{t_a}(\tau)$ denotes the distribution density of the time distance between the observation beginning and the first event occurrence. The age of this distribution density is t_a, because, as earlier pointed out, the Gibbs system preparation has been done at an earlier time, with t_a denoting the time distance between the observation beginning and the preparation phase.

Let us define

$$\Lambda(\omega) \equiv \Re[\langle\hat{\xi}(\omega)\rangle], \tag{14}$$

where $\Re[\cdots]$ denotes the real part of $[\cdots]$. Thus, using Eq. (13) we get

$$\Lambda(\omega) = \frac{1}{\omega}\int_0^{\infty}\sin(\omega\tau)\psi_{t_a}(\tau)d\tau. \tag{15}$$

To establish a connection with the traditional WK theorem, let us notice that

$$\psi_{t_a}(t) = -\frac{d}{dt}\Psi_{t_a}(t). \tag{16}$$

By using the method of integration by parts we turn Eq. (15) into

$$\Lambda(\omega) = \int_0^{\infty}\cos(\omega\tau)\Psi_{t_a}(\tau)d\tau. \tag{17}$$

The connection with the ordinary WK theorem is established by noticing that, when $\mu>2$,

$$\Psi_{\infty}(\tau) = \left[\frac{T}{(\tau+T)}\right]^{\mu-2}, \tag{18}$$

which is the equilibrium correlation function of the fluctuation $\xi(t)$. Thus, Eq. (19) coincides with the traditional form of the WK theorem, when $t_a=\infty$.

In conclusion, the adoption of the generalized Onsager principle, with the help of Eqs. (15) and (17) suggests that the WK can be generalized through the expression

$$\langle S(\omega)\rangle = \int_0^\infty \cos(\omega\tau)\Psi_{t_a}(\tau)d\tau. \tag{19}$$

In Sec. V we shall recover the same result from the direct use of the power spectrum prescription of Eq. (8).

IV. A COMPLEX SYSTEM AS A SUPERPOSITION OF INFINITELY MANY INDEPENDENT AND HARMONIC COMPONENTS

The key results of the numerical calculations illustrated in Sec. II [see Eqs. (9) and (10)] are expressed by the power spectrum $S(\omega)\propto 1/\omega^\eta$ with η given by

$$\eta = 3 - \mu. \tag{20}$$

The parameter μ, which is the power index of the distribution density of Eq. (4), can be determined in principle from the experimental observation of the process of intermittent fluorescence.[9] As we have seen in Sec. II, the fluctuation $\xi(t)$ is generated by filling the time intervals between two consecutive times, t_i and t_{i+1}, with the values ± 1, according to a coin tossing prescription. More in general, the power spectrum $S(\omega)\propto 1/\omega^\eta$ with η given by Eq. (20) can be obtained by assigning to the events occurring at times t_i the role of producing the decorrelation of the fluctuation $\xi(t)$ without producing abrupt jumps. An example of this kind is given by the EEG fluctuations of Ref. 25. In this case, however, we may have the legitimate doubt that the origin of $1/f$ noise spectrum is given by the slow decay of the autocorrelation function of the fluctuation $\xi(t)$ with no need of renewal event occurrence. In Sec. I we have remarked that $\eta > 1$ involves the action of renewal events with $\mu < 2$. To substantiate this remark we show here in action a model with no renewal events, and we show that it is confined in fact to the condition $\eta < 1$.

Following Weiss[26] let us consider the fluctuation $\xi(t)$ defined by

$$\xi(t) = \sum_i^N c_i\left[x_i(0)\cos(\omega_i t) + \frac{v_i(0)}{\omega_i}\sin(\omega_i t)\right]. \tag{21}$$

We interpret $\xi(t)$ as the sum of the coordinates $x_i(t)$ of infinitely many independent and linear oscillators. The initial positions and the initial velocities of these oscillators are uncorrelated. As a consequence, when we evaluate the correlation function $\langle\xi(t)\xi(t')\rangle$, we obtain

$$\Phi_\xi(t,t') \equiv \langle\xi(t)\xi(t')\rangle = \sum_i^N c_i^2\left[\langle x_i^2(0)\rangle\cos(\omega_i t)\cos(\omega_i t') + \frac{\langle v_i^2(0)\rangle}{\omega_i^2}\sin(\omega_i t)\sin(\omega_i t')\right]. \tag{22}$$

The equipartition theorem yields

$$\langle v_i^2\rangle = \langle x_i^2\rangle\omega_i^2 = k_B T. \tag{23}$$

Thus, we obtain

$$\langle\xi(t)\xi(t')\rangle = k_B T\sum_i^N \frac{c_i^2}{\omega_i^2}\cos(\omega_i(t-t')). \tag{24}$$

Under the assumption[26]

$$c_i \propto (\delta+1)/2^i_\omega, \tag{25}$$

the normalized correlation function of $\xi(t)$, $\Phi_f(t)$, becomes

$$\Phi_f(t-t') = \frac{\sum_i \omega_i^{\delta-1}\cos(\omega_i(t-t'))}{\sum_i \omega_i^{\delta-1}}. \tag{26}$$

This is an attractive way to go beyond ordinary statistical mechanics, or, using the terminology of Ref. 26, beyond the Ohmic condition, $\delta=1$. In fact, following Pottier[27] we have

$$\lim_{t\to\infty}\Phi_f(t) \propto \frac{1}{t^\delta}, \tag{27}$$

for $0<\delta<1$, and

$$\lim_{t\to\infty}\Phi_f(t) \propto -\frac{1}{t^\delta}, \tag{28}$$

for $1<\delta<2$.

From a formal point of view the same results is obtained by setting

$$\xi(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\exp(-i\omega t)\hat{\xi}(\omega), \tag{29}$$

with the condition

$$\hat{\xi}(\omega) = |\xi(\omega)|\exp(i\phi(\omega)), \tag{30}$$

with

$$|\xi(\omega)| = \chi|\omega|^{(\delta-1)/2} \tag{31}$$

and

$$\langle\exp(\phi(\omega)+\phi(\omega'))\rangle = \tfrac{1}{2}\delta(\omega+\omega'). \tag{32}$$

This random phase assumption is the key ingredient of the approach to $1/f$ noise proposed by Voss and Clarke.[17] Following Voss and Clarke, let us define the power spectrum $S(\omega)$ as the Fourier transform of the correlation function $\Phi_f(t)$,

$$S(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\Phi_f(t)\exp(-i\omega t)dt. \tag{33}$$

Using the technique of Ref. 17, we get

$$S(\omega) \propto \frac{1}{\omega^\eta}, \tag{34}$$

yielding

$$\eta = 1-\delta < 1. \tag{35}$$

Note that the case $1<\delta<2$ is of no interest here because it does not yield $1/f$ noise.

If the origin of the fluctuation $\xi(t)$ is not known, the emergence of the spectrum $S(\omega)$ with $\eta<1$ leaves open the possibility that the decorrelation of $\xi(t)$ is determined by renewal events. In fact, in this case we obtain[25] the correlation function of Eq. (27) with

$$\delta = \mu - 2, \tag{36}$$

which makes Eq. (35) identical to Eq. (20) with $\mu > 2$. Thus, if $\eta < 1$, it is not necessary to make the assumption that the decorrelation of ξ is determined by renewal events, even if their existence cannot be ruled out. In the case $\eta > 1$, on the contrary, the approach of Voss and Clarke to $1/f$ noise cannot be used, and the hypothesis of the existence of renewal events with $\mu < 2$ becomes necessary.

We reiterate that the adoption of the stationary approach to $1/f$ noise requires the random phase assumption of Eq. (32) that, in turn, suggests that the dynamic process under study emerges from the superposition of infinitely many independent oscillations, each of which with a given frequency. It is expected that perturbing the system with a harmonic stimulus will have the effect of producing a steady response with the same frequency as that of the stimulus. If the $1/f$ noise is generated by renewal events, as shown by the Fourier analysis of Eq. (12), there exists a close correlation between phase and frequency that generates a deeply different dynamic process, thereby implying that an external harmonic perturbation cannot influence only one component of the system. It has been recently shown[28] that systems driven by renewal and nonergodic events do not respond to external harmonic perturbation and that the response with the same frequency as the perturbing stimulus dies out. We see therefore that there exists a close connection between the lack of response to harmonic stimuli, and the renewal nature of the events leading to the $1/f$ noise spectrum with $\eta > 1$ of Eq. (20).

V. THE WK THEOREM IN THE NONSTATIONARY CASE μ<2

Let us assume that $t_a = L$, where L is the length L of the sequence under study. In Sec. VII we shall explain why this assumption is correct. Here, we limit ourselves to remarking that in the case $\mu < 2$ aging is an unavoidable property that we take into account by identifying t_a with L. Thus, we turn Eq. (19) into

$$\langle S(\omega)\rangle = \int_0^\infty \cos(\omega\tau)\Psi_L(\tau)d\tau, \tag{37}$$

which is equivalent to

$$\langle S(\omega)\rangle = \frac{1}{\omega}\int_0^\infty \sin(\omega\tau)\psi_L(\tau)d\tau. \tag{38}$$

Actually, the standard prescription of Eq. (8) allows us to write the Gibbs average on the spectrum $S(\omega)$ as

$$\langle S(\omega)\rangle = \frac{1}{L}\int_0^L dt_1 \int_0^L dt_2 \Phi_\xi(t_1,t_2)\exp[-i\omega(t_1 - t_2)], \tag{39}$$

where

$$\Phi_\xi(t_1,t_2) = \langle \xi(t_1)\xi(t_2)\rangle \tag{40}$$

is not a stationary correlation function. The result of Sec. III suggests that for $L \to \infty$

$$\Phi_\xi(t_1,t_2) = \Psi_L(|t_1 - t_2|). \tag{41}$$

Thus, by adopting the new integration variables $\tau = t_1 - t_2$ and $\sigma = t_1 + t_2$, we obtain, after some easy algebra,

$$\langle S(\omega)\rangle = \frac{1}{L}\int_0^L d\tau \cos(\omega\tau)\Psi_L(\tau)(L-\tau), \tag{42}$$

which, for $L \to \infty$ becomes identical to Eq. (37).

VI. AGING CORRELATION FUNCTION

To complete our discussion we have to find a proper expression for $\psi_{t_a}(\tau)$. The exact expression is[29]

$$\psi_{t_a}(\tau) = \psi(\tau + t_a) + \int_0^{t_a} dt' P(t')\psi(\tau + t_a - t'), \tag{43}$$

where $P(t)$ is the mean number of events occurring per unit of time in the Gibbs system prepared at $t=0$. The exact expression of $P(t)$ is given by

$$P(t) = \sum_{n=1}^{\infty} \psi_n(t), \tag{44}$$

where $\psi_n(t)$ is the probability density for the occurrence of the nth event at time t. Note that $\psi_n(t)$ can be expressed in terms of $\psi_1(t) = \psi(t)$ and that using the Laplace transform technique described in detail in Ref. 30, it is proven that, for $1 < \mu < 2$ and for $t \to \infty$,

$$P(t) = \frac{1}{\Gamma(2-\mu)\Gamma(\mu-1)}\frac{1}{T^{\mu-1}}\frac{1}{t^{2-\mu}} \tag{45}$$

and that for $2 < \mu < 3$ and for $t \to \infty$,

$$P(t) = \frac{(\mu-2)}{T}\left[1 + \frac{T^{\mu-2}}{(3-\mu)}\frac{1}{t^{\mu-2}}\right]. \tag{46}$$

The results of Eqs. (45) and (46), which have been originally obtained by Feller in Refs. 31 and 32, respectively, suggest that in the region close to $\mu = 2$ the time dependence of $P(t)$ becomes critically slow, namely, proportional to $1/\log(t)$. For simplicity's sake we adopt the approximation

$$P(t) = K, \tag{47}$$

with K being a constant to define according to the normalization constraint. This approximation has not to be mistaken for the Poisson condition, where K would define the constant rate of event production. Let us assume $t_a \gg T$. In this case we neglect the first term on the right-hand side of Eq. (43), which is expected to be much faster than the second term, and we write

$$\psi_{t_a}(\tau) = K\int_0^{t_a} dt' \psi(\tau + y)dy, \tag{48}$$

with K determined by the normalization condition. Thus, we obtain

$$\psi_{t_a}(\tau) = (2-\mu)\frac{(\tau+T)^{1-\mu} - (\tau+T+t_a)^{1-\mu}}{(T+t_a)^{2-\mu} - T^{2-\mu}}, \tag{49}$$

which for $\tau \ll t_a$ becomes

$$\psi_{t_a}(\tau) = (2-\mu)\frac{(r+T)^{1-\mu}}{(T+t_a)^{2-\mu} - T^{2-\mu}}. \tag{50}$$

Let us identify t_a with the sequence length,

$$t_a = L \gg T. \tag{51}$$

This allows us to write Eq. (50) as

$$\psi_L(\tau) = \frac{2-\mu}{L^{2-\mu}} \frac{1}{(\tau+T)^{\mu-1}}, \tag{52}$$

with $\psi_L(\tau)=0$ for $\tau > L$.

Using Eq. (16) we find for the correlation function of age $t_a=L$, the following expression:

$$C_\xi(\tau) = \Psi_L(\tau) = \frac{(T+L)^{2-\mu} - (T+\tau)^{2-\mu}}{(T+L)^{2-\mu} - T^{2-\mu}}. \tag{53}$$

Note that Eq. (53) agrees with Eq. 4 of Ref. 33. Note also that the approximation yielding Eq. (53) makes the aged correlation function $\Psi_L(\tau)$ vanish at $\tau=L$. In the case of a set of Gibbs systems prepared at $t=0$, with the Onsager out-of-equilibrium condition generated at $t=t_a$ the correlation function cannot vanish at $\tau=t_a$ and values of τ larger than t_a are admitted. This requires the adoption of infinitely extended sequences. In the case of sequences of finite size L, it is no longer an approximation; the vanishing of the correlation function at $\tau=L$ is a compelling consequence of L being finite, and $\psi_L(\tau)=0$ for $\tau > L$.

For an analytical treatment of the power spectrum it is convenient to use the waiting time distribution $\psi_L(\tau)$, rather than the aged correlation function $\Psi_L(\tau)$. We note that $\psi_L(\tau)$ at $\tau=L$ undergoes an abrupt jump to 0, so as to fit Eq. (53). Thus, Eq. (38) has to be expressed as

$$\langle S(\omega)\rangle = \frac{1}{\omega}\int_0^L \sin(\omega\tau)\psi_L(\tau)d\tau. \tag{54}$$

By plugging Eq. (52) into Eq. (54), we get

$$\langle S(\omega)\rangle = \frac{1}{\omega^{3-\mu}}\frac{1}{L^{2-\mu}}A(\omega,L), \tag{55}$$

where

$$A(\omega,L) \equiv (2-\mu)\int_0^{\omega L} dx(x+\omega T)^{1-\mu}\sin x, \tag{56}$$

which is a slow function of ω. We see that this formula accounts very well for the numerical results of Sec. II. In fact, we see that

$$\eta = 3-\mu, \tag{57}$$

and that the power spectrum is proportional to $1/L^{2-\mu}$. For $\mu > 2\langle S(\omega)\rangle$ is independent of L. We recover Eqs. (9) and (10), which are the two important results of our numerical simulations. It is worth reiterating that the same numerical results were already obtained by Margolin and Barkai[20] who also afforded a theoretical explanation resting on the ergodicity breakdown. The theory of this paper yields the same result on the basis of the renewal aging effects. This is in line with the theoretical arguments of Ref. 20 insofar as perennial aging is a consequence of $\mu < 2$ as is the ergodicity breakdown.

VII. AGE OF A SEQUENCE OF FINITE LENGTH

The theoretical arguments that we have adopted to explain the numerical results of this article, rests on the key assumption that

$$t_a = L \tag{58}$$

and

$$\tau \ll t_a = L. \tag{59}$$

Let us see why these assumptions are correct. Let us consider the ideal condition where we have at our disposal infinitely many realizations of the fluctuation $\xi(t)$ of infinite length. Let us assume that all these trajectories are prepared at $t=0$. It is not necessary to locate all the trajectories in the "on" state at $t=0$. We assume that in all the realizations the system is found at the beginning of the laminar region, regardless of whether it corresponds to the "on" or to the "off" state. We set the beginning of the observation process at $t=t_a>0$. This is the condition that we use to derive Eq. (49). Note that the Gibbs average on a set of infinitely many realizations of infinite length does not force us to adopt the condition $\tau \ll t_a$. Actually, once t_a is fixed, we can move from the condition $\tau \ll t_a$ to the condition where τ is comparable to t_a and we can also explore the condition $\tau \gg t_a$. In this latter case, the Taylor series expansion of Eq. (49) with respect to the small value $\epsilon = t_a/\tau$ yields the emergence of a rejuvenation effect[29] making the distribution density ψ, which for $\tau \ll t_a$ has the power index $\mu-1$, recover the original power index μ.

Let us consider now the more delicate case of infinitely many realizations of length L. Let us focus our attention on the time interval $I(L,\Delta) \equiv [L-\Delta, L]$. Both L and Δ are large numbers, fitting the condition

$$\Delta \ll L. \tag{60}$$

The interval $I(L,\Delta)$ contributes to the numerical results through a large number of mobile windows of size τ moving within its borders. Each window corresponds to observing all the trajectories that at the beginning of the window have either the value 1 or -1. The numerical result, as shown in Sec. III, is determined by the probability density of finding an event located at the window end. It is evident that

$$\tau < \Delta. \tag{61}$$

Thanks to the condition (60), this inequality yields

$$\tau \ll L. \tag{62}$$

The windows moving within the interval $I(L,\Delta)$ have different ages, ranging from $L-\Delta$ to values very close to L. However, thanks to condition (60) we can safely assign to all of them the same age, thereby justifying Eqs. (58) and (59).

Note that the numerical results depend also on contributions violating the condition of Eq. (60). There are windows of age much smaller than L, and these windows generate spectral contributions proportional to $1/f^{\eta}$ with $\eta=2-\mu<3-\mu$. There are also windows of intermediate age that generate intermediate values of η. In conclusion, we have a set of windows with the same time size τ and different ages, ranging from $t_a=0$ to $t_a=L$. The windows of maximum age, $t_a=L$ have the largest statistical weight, with $\eta=3-\mu$, thereby determining the observed index $\eta=3-\mu$. For the theoretical discussion of the case of a single realization, we refer the reader to the work of Ref. 20. Here we limit ourselves to observe that due to the nonergodic nature of the condition $\mu<2$,[20] the smaller the number of realizations, the larger the fluctuations around $\eta=3-\mu$. Figure 2, which refers to the case of a single realization, with $\mu<2$, illustrates the case of largest fluctuation.

VIII. COMPARISON WITH EARLIER WORK IN THE FIELD OF INTERMITENT FLUORESCENCE

It is important to notice that the authors of Ref. 34 developed an interesting approach to the spectrum $S(\omega)$ generated by the intermittent fluorescence of arrays of semiconductor nanocrystals, based on Lévy statistics. Using the notation of this article, their prediction is that, after a small frequency plateau, the spectrum $S(\omega)$ is given by

$$S(\omega) \propto \frac{1}{\omega^{\eta}}, \tag{63}$$

with

$$\eta = \mu - 1 \tag{64}$$

that has to be compared to Eq. (57). These authors find $\mu=1.72$, thereby yielding $\eta=0.72<1$, a condition that according to the theoretical approach of this article corresponds to the ergodic condition. The discussion of the experiment of Ref. 34 is beyond the purpose of this article. We limit ourselves to noticing that the theory of Ref. 34 is based on the assumption that the time duration of the "off" state is negligible. In their calculations, they bypass the difficulties with the non-ergodic properties generated by $\mu<2$ without involving the correlation function of the fluctuation $\xi(t)$. It is worth noticing that the assumptions made by these authors correspond to a sequence of pulses of negligible time duration as in the theoretical approach to $1/f$ noise developed by Kaulakys and co-workers.[35]

In this article we made the assumption that the state "on" has the same statistics as the state "off," and this led us to theoretical predictions that are compatible with the theoretical approach of Refs. 13 and 14. However, the results of our article allow us to clarify two important aspects of the earlier papers of Refs. 13 and 14. As for the former aspect, concerning Ref. 13, we notice that it adopts the theory of Zumofen and Klafter[36] which is based on the form

$$\Phi_{\xi}(t) = \frac{1}{\langle t\rangle}\int_t^{\infty} dt'(t-t')\psi(t')dt'. \tag{65}$$

When $\mu>2$, this theoretical prescription yields

$$\Phi_{\xi}(t) = \left[\frac{T}{(t+T)}\right]^{\mu-2}, \tag{66}$$

in accordance with Eq. (18). In the case $\mu<2$, adopted by Ref. 13, this formula is made legitimate by the assumption that $T_{\max}<\infty$ and $L \gg T_{\max}$ so as to ensure the condition of infinite aging that is essential for the adoption of the WK theorem. Of course, this approach implies the condition of interrupted aging illustrated by the authors of Ref. 19. The theory developed in this article allows us to go beyond the condition of interrupted aging and to evaluate the spectrum in the nonequilibrium condition, regardless of whether it is transient $T_{\max}<\infty$ or perennial $T_{\max}=\infty$.

As already pointed out in Sec. I, the extension of the WK theorem to the case where $T_{\max}=\infty$ has been made by Margolin and Barkai.[20] However, we note that the authors of Ref. 20 focus on the time asymptotic properties, thereby disregarding the multi-η phenomenon. The emergence of the multi-η effect depends on the parameter T of the distribution density of Eq. (4). To explain the multi-η effect, with an example borrowed from the blinking quantum dots, we notice that the parameter T can be identified with the critical time t_c of the model of Ref. 14. This can be realized by comparing our Fig. 8 to Fig. 4 of Ref. 14. We see, in fact, that at $f=1/T$ the transition occurs from the $1/\omega^{\eta}$ regime, with $\eta=3-\mu$, to the $1/\omega^2$ regime.

It is straightforward to account for this experimentally assessed transition with the help of the theoretical approach of this article. The algorithm of Eq. (3) is equivalent to using for the aged-specific failure rate,[37]

$$g(t) = \frac{\psi(t)}{\Psi(t)}, \tag{67}$$

the analytical expression

$$g(t) = \frac{r_0}{1+r_1 t} \tag{68}$$

with

$$r_1 = \frac{1}{T} \tag{69}$$

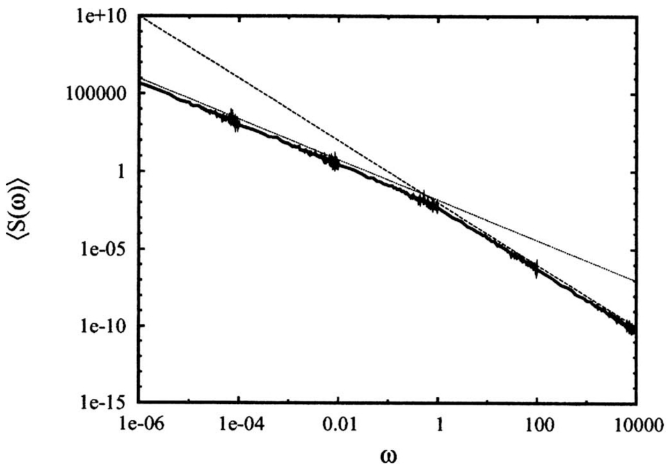
and

$$r_0 = \frac{\mu-1}{T}. \tag{70}$$

It is straightforward to derive (68) and (69) by substituting Eqs. (4) and (6) into Eq. (67). In the time scale $\tau \ll Tg(t) \sim (\mu-1)/T$ thereby yielding a Poisson process with

$$\Psi(t) \approx \exp\left(-\frac{\mu-1}{T}t\right). \tag{71}$$

In the time region $t<T$, the waiting times τ of the "on" and "off" states have the same probabilities. Thanks to the coin-tossing prescription for the sign selection, the fluctuation $\xi(t)$ in this time region is virtually equivalent to the velocity fluctuations of the Langevin equation $dv/dt = -\gamma v(t)+f(t)$, with $f(t)$ denoting white noise and $\gamma \approx 1/T$, thereby yielding[17] $1/\omega^2$.



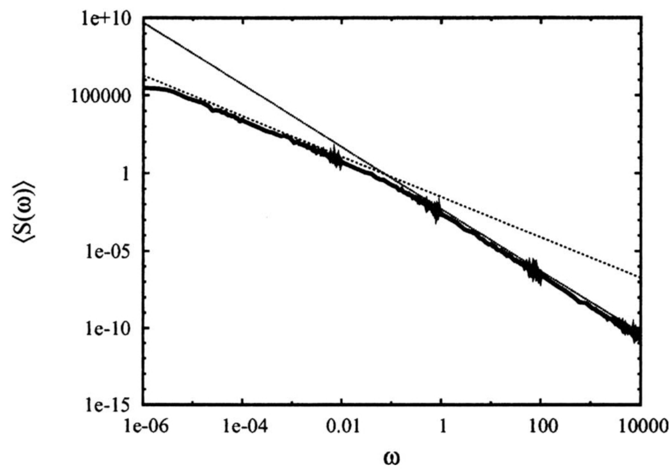


FIG. 8. Average power spectrum. We used $\mu=1.7$ and 100 realizations of length $L=10^7$ units. The figure shows the two regimes. Figure on the left: We used $T=1$. The thick line is the numerical result. For $\omega<1$, $\langle S(\omega)\rangle \propto 1/\omega^{3-\eta}$ and for $\omega>1$, $\langle S(\omega)\rangle \propto 1/\omega^2$. The two finer lines that fit the numerical data are $0.015/\omega^{1.3}$ for $\omega<1$ and $0.01/\omega^2$ for $\omega>1$. The transition frequency is approximately equal to 1. Figure on the right: Same as the figure on the left the only difference being that $T=10$. It shows that the transition frequency has moved to a lower value, approximately $\omega=1/10=1/T$. The two finer lines that fit the numerical data are $0.03/\omega^{1.3}$ for $\omega<1$ and $0.005/\omega^2$ for $\omega>1$.

IX. CONCLUDING REMARKS

This article makes a new perspective emerge in the $1/f$ noise literature: the ideal $1/f$ condition is a singularity corresponding to $\mu=2$. This is the border between the ergodic ($\mu>2$) and nonergodic[11] condition and the accurate evaluation of η, see Eq. (57), is expected to be a reliable criterion to establish which condition applies. It is worth noting that Eq. (49) applies to both the case of μ slightly larger as well as slightly smaller than 2. Thus, the age dependent WK theorem of this article, see Eq. (54), yields a small dependence of the spectrum on L also in the case $\mu>2$, in good agreement again with the numerical results. This is a consequence of temporary aging of the condition $2<\mu<3$,[38] which fades away with increasing L until it recovers the ordinary ergodic prediction, independent of L.

The main theoretical result of this article, Eq. (55), is derived from Eq. (19), which is not limited to the case $\mu<2$ where the perennial aging condition is generated when $T_{\max}=\infty$; it applies more in general to all cases characterized by large Deborah numbers.[39,40] The Deborah number is given by[39]

$$D=\frac{\tau_{\text{int}}}{\tau_{\text{ext}}}, \tag{72}$$

where τ_{int} denotes the internal scale on which the dynamics of the system occur, and τ_{ext} is the external scale on which properties are measured. The theory developed in the present paper refers to a condition where the internal time scale is defined by the correlation time of the equilibrium correlation function of Eq. (18),

$$\tau_c=\frac{T}{\mu-3}, \tag{73}$$

which is finite only for $\mu>3$. We identify τ_{ext} with L. As a consequence, if $T_{\max}=\infty$, the Deborah number is infinite not only for $\mu<2$, but it diverges also for $2<\mu<3$. Thus, the ordinary WK theorem is violated in principle in the whole interval $1<\mu<3$, even if for $\mu>2$, its breakdown does not produce significant effects. The key prescription of Eq. (19) can be safely applied to the whole range of values of μ between $\mu=1$ and $\mu=3$.

It is plausible that $T_{\max}<\infty$ in all the physical processes generating intermittent fluorescence,[18,19] thereby yielding the condition of interrupted aging[19] that ensures the validity of the traditional version of WK theorem. However, the results of this article are expected to bring useful indications also in this case, insofar as the dependence of the spectral intensity on L that should be experimentally assessed for $L<T_{\max}$, can be used to confirm the physical truncation of the waiting time distribution $\psi(\tau)$ at $\tau=T_{\max}$. For this reason we hope that the theoretical work of this article may help the progress of the experimental and theoretical research work in the field of intermittent fluorescence.

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