Strong Correlations Between Fluctuations and Response in Aging Transport

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Once the problem of ensemble averaging is removed, correlations between the response of a single molecule to an external driving field $F$, with the history of fluctuations of the particle, become detectable. Exact analytical theory for the continuous time random walk and numerical simulations for the quenched trap model give the behaviors of the correlation between fluctuations of the displacement in the aging period $(0, t_a)$, and the response to bias switched on at time $t_a$. In particular in the dynamical phase where the models exhibit aging we find finite correlations even in the asymptotic limit $t_a \rightarrow \infty$, while in the non-aging phase the correlations are zero in the same limit. Linear response theory gives a simple relation between these correlations and the fractional diffusion coefficient.

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Originally the fluctuation–dissipation theorem was formulated by Einstein using simple Brownian motion, i.e. the well known Einstein relation between the diffusivity of an ensemble of identical particles and their mobility $D$. Modern optical techniques enable experimentalists to track single molecules undergoing either normal diffusion, or non Markovian diffusion, and in some cases anomalous diffusion in a very wide variety of Physical and biological conditions [2, 3, 4, 5]. An issue overlooked so far are the correlations between the response of individual particles to an external bias and their history of fluctuations. We will soon define these correlations precisely, however for the time being consider chemically identical single molecules under going a diffusion process in some random medium. In the time period $(0, t_a)$, called the aging period, different particles may exhibit different fluctuations, for example if the particles sample different realizations of disorder in the system. Then an external driving field is switched on at time $t_a$. We realize that the response of different particles might be correlated with their diffusivity in the aging period. For example if a particle happens to sample a region in space with deep traps in the aging period, it is expected to diffuse slowly and then also respond weakly compared with another particle which happened to sample relatively shallow traps. However if the aging period is long $t_a \rightarrow \infty$ and the process ergodic, we may expect that diffusivity of the particles in the aging period becomes de-correlated from their response, since the particles had enough time to sample the full random energy landscape in which they are moving.

Here we investigate the correlations between diffusion (fluctuations) and mobility (response), found when single particle trajectories are analyzed. We use two well known models: the Montroll-Weiss continuous time random walk (CTRW) model [6, 7] and Bouchaud’s quenched trap model [8]. These models are known to exhibit anomalous diffusion [6, 7] and aging [8, 9, 10, 11, 12, 13, 14], i.e. the ensemble averaged response to an external field switched on at time $t_a$ depends on the aging time $t_a$ (see details below). We show that in the phase where the models exhibit aging and even in the limit where $t_a \rightarrow \infty$ correlations between fluctuations and response are finite, in complete contrast to non-aging dynamics. Besides the theoretical interest in correlations in aging transport, the existence of such correlations can be used in principle to predict which members of an ensemble of diffusing particles will respond strongly (or weakly) to a driving force. Our work also indicates that data analysis of the aging fluctuation-dissipation relations must be made with care, since the response and the fluctuations are generally correlated.

There are many examples of systems where such correlations might become important, we mention the recent experiments on the diffusion of single LacI repressor proteins on DNA [3], where a wide distribution of diffusion coefficients of the proteins was found. This distribution is likely due to the random DNA sequence the single protein explores. Since the single molecules have widely distributed diffusion constants, their response to an external field is likely correlated with their history of diffusion, e.g. particles with small (or large) diffusion constants have a weak (strong) response respectively. Other single particle experiments of micro-beads diffusing in actin networks [4] exhibit power law waiting times and anomalous diffusion, very much reminiscent of the trap and CTRW models. Hence these single particle systems are candidates for the investigation of the new correlations we consider in this manuscript, correlations which go beyond the Einstein relations between the ensemble average diffusion coefficient and mobility.

Model 1 We consider the well known one dimensional CTRW on a lattice $\{0,1,2\}$. The lattice spacing is $a$ and the jumps are to nearest neighbors only. Waiting times between jump events are independent identically distributed random variables with a common probability density function (PDF) $\psi(\tau)$. After waiting the particle has a probability $1/2 + h/2$ or $1/2 - h/2$ to jump to the right or left respectively. In the aging period $(0, t_a)$ $h = 0$ and the particles follow an unbiased motion, while in the
response period \( t_a < t \) the bias is \( 0 < h < 1 \). The total measurement time is \( t = t_a + t_r \) where \( t_r \) is called the response time. To define the response one has to define the field which is responsible for the bias. For example, if the particle is coupled to a thermal heat bath with temperature \( T_c \) and driven by a uniform force field \( F \), standard detailed balance conditions give \( h = aF/2k_bT \), when \( h \ll 1 \) [13, 17]. We consider later the generic case

\[
\psi(\tau) \sim A\tau^{-(1+\alpha)} \frac{\Gamma(-\alpha)}{\Gamma(\alpha+1)} \quad (1)
\]

when \( \tau \to \infty \) and \( 0 < \alpha < 1 \), \( A > 0 \). Specific values of \( \alpha \) for a wide range of physical systems and models are given in [6, 7]. For example for the annealed version of the trap model \( \alpha = T/T_c < 1 \) [4]. In this case the average waiting time is infinite.

The position of the particle at time \( t_a + t_r \) is \( X = X_a + X_r \), where \( X_a \) (\( X_r \)) is the displacement in the aging (response) periods respectively. More specifically \( X_a = \sum_{i=1}^{n_a} \Delta x^{(a)} \) and \( X_r = \sum_{i=1}^{n_r} \Delta x^{(r)} \), where \( \Delta x^{(a)} \) and \( \Delta x^{(r)} \) are the random jump lengths (of length \( a \)) in the aging \((0, t_a)\) and response periods \((t_a, t_a+t_r)\) respectively. While \( n_a \) and \( n_r \) are the random number of jumps in the aging and response periods respectively.

We investigate the correlation function \( \langle (X_a)^2 X_r \rangle \) which is a measure for the correlation between the fluctuations in the aging period \( (X_a)^2 \), and the response to the driving force switched on at time \( t_a \). We define a dimensionless fluctuation-response (FR) parameter

\[
\text{FR}(t_a, t_r) = \frac{\langle (X_a)^2 X_r \rangle}{\langle (X_a)^2 \rangle \langle X_r \rangle} - 1, \quad (2)
\]

which is equal zero when correlations vanish. For the CTRW under investigation one can show that

\[
\langle (X_a)^2 \rangle = a^3 \langle n_a n_r \rangle \quad \text{and} \quad \text{FR}(t_a, t_r) = \frac{\langle n_a n_r \rangle}{\langle n_a \rangle \langle n_r \rangle} - 1. \quad (3)
\]

Thus \( \langle n_a n_r \rangle \), the correlations of the number of steps in the aging period with the number of steps in the response period gives a measure for the correlations between the fluctuations in the displacement in the aging period and the response to the bias.

Let \( P_{u,t} (n_a, n_r) \) be the probability of making \( n_a \) jumps in the aging period and \( n_r \) jumps in the response period. Knowledge of this function is needed for the calculation of the FR parameter and other high order correlation functions which we will discussed in a future publication. The paths with \( n_a \) (\( n_r \)) jump events in the aging period (response period) clearly satisfy \( t_a < t < t_{a+1} \) and \( (t_{a+n} < t_r + t_a < t_{a+n+r+1}) \) respectively, where the subscript \( n \) in \( t_n \) is for the jump number. Hence

\[
P_{u,t} (n_a, n_r) = \frac{\langle I(t_a < t < t_{a+1}) I(t_{a+n} < t_r + t_a < t_{a+n+r+1}) \rangle}{\langle \int_0^\infty dt_a e^{-\varphi(t)} P_{u,t} (n_a, n_r) \rangle}
\]

where \( I(x) = 1 \) if the event in the parenthesis is true otherwise it is zero. Us-usual we make use of the double Laplace transform \( t_a \to u \) and \( t_r \to s \) of \( P_{u,t} (n_a, n_r) \),

\[
P_{u,s} (n_a, n_r) = \int_0^\infty dt_a e^{-ut_a} \int_0^\infty dt_r e^{-st_r} P_{u,t} (n_a, n_r).
\]

For the sake of space we do not discuss the details of the calculation (which will be published later). We use the model assumption of independent identically distributed waiting times, namely the renewal property of the CTRW, and find

\[
P_{u,s} (n_a, n_r = 0) = \frac{1}{s} \left[ \frac{1}{u} \hat{\psi} (u) - \frac{\hat{\psi} (s) - \hat{\psi} (u)}{u-s} \right],
\]

while for \( n_r \geq 1 \)

\[
P_{u,s} (n_a, n_r) = \frac{1}{s} \left[ \frac{1}{u} \hat{\psi} (u) - \frac{\hat{\psi} (s) - \hat{\psi} (u)}{u-s} \right] \quad (6)
\]

In Eqs. (5,6) \( \hat{\psi} (u) \) and \( \hat{\psi} (s) \) are Laplace transforms of the waiting time PDF. Note that Eqs. (5,6) give the proper normalization since \( \sum_{n_a=0}^\infty \sum_{n_r=0}^\infty P_{u,s} (n_a, n_r) = 1/(us) \). Using Eq. (6) and \( \langle n_a n_r \rangle_{u,s} = \sum_{n_a=0}^\infty \sum_{n_r=0}^\infty n_a n_r P_{u,s} (n_a, n_r) \) we find

\[
\langle n_a n_r \rangle_{u,s} = \frac{\hat{\psi} (s) - \hat{\psi} (u)}{s(u-s)} \left[ 1 - \hat{\psi} (u) \right]^2 \quad (7)
\]

and the averages

\[
\langle n_a \rangle_{u,s} = \frac{\hat{\psi} (u)}{s(u-s)} \left[ 1 - \hat{\psi} (u) \right] \quad (8)
\]

In principle once the double Laplace inversion of Eqs. (7,8) is made, we can calculate the FR parameter.

If the dynamics is Markovian, namely the waiting time PDF is exponential \( \psi(t) = R \exp(-Rt) \)

\[
\langle n_a n_r \rangle = \langle n_a \rangle \langle n_r \rangle = R t_a R t_r, \quad (9)
\]

and \( \text{FR}(t_a, t_r) = 0 \). For any non-Markovian process with a non-exponential waiting time PDF the FR parameter is generally not equal zero.

If the average waiting time \( \langle \tau \rangle = \int_0^\infty \tau \psi(\tau) d\tau \) is finite and in the limit \( t_a \to \infty \) the fluctuation-response parameter Eq. (2) satisfies

\[
\lim_{t_a \to \infty} \text{FR}(t_a, t_r) = 0, \quad (10)
\]

and the correlations are lost in this limit. To see this use Eq. (7) in the \( u \to 0 \) limit, the small \( u \) expansion \( \psi(u) \to 1 - u(\psi) \) to find \( \langle X_a^2 \rangle \sim a^3 \frac{1}{\varphi''(\tau)} \frac{1}{\varphi'(\tau)} \). Interestingly this result is valid for any \( s > 0 \), namely both for short and long response times \( t_r \). Hence when \( t_a \to \infty \) we find
The figure illustrates that the correlations between finite period is much larger than the finite time between jumps the response is not correlated with the fluctuations, since the particles had enough time to equilibrate.

A very different behavior is found in the common situation \[1, 2, 3\] where the average waiting time is infinite namely when \(0 < \alpha < 1\) in Eq. \(1\). Then using Eq. \(2\), in the limit of small \(s\) and \(u\)

\[
\langle (X_o)^2 X_r \rangle \sim \frac{a^3}{A^2} \frac{u^\alpha - s^\alpha}{(u - s) u^{2\alpha} s^{1 + \alpha}},
\]

where the expansion \(\hat{\psi}(u) \sim 1 - A u^\alpha\) was used. Skipping the technical details, we analytically invert the double Laplace transform in Eq. \(13\) to the double time domain and find

\[
\langle (X_o)^2 X_r \rangle \sim \frac{a^3}{A^2} \frac{u^\alpha}{t_a} g \left( \frac{t_a}{t_r} \right),
\]

which is valid in the limit of long times \(t_a\) and \(t_r\). The scaling function in Eq. \(12\) is a hypergeometric function

\[
g(x) = \frac{x^{2\alpha} 2F_1(1, -\alpha; 1 + \alpha; -x)}{\Gamma^2(1 + \alpha)} - \frac{x^{2\alpha}}{\Gamma(1 + 2\alpha)}.
\]

Eq. \(12\) is a main result of this paper, since it shows that even in the long aging time limit a non-trivial correlation between fluctuation and response exists. The hypergeometric function in Eq. \(13\) is tabulated in Mathematica hence the solution is not a formal expression. Using \(\langle (X_o)^2 \rangle \sim a^2 \frac{t_a^\alpha}{t_a^{1 + \alpha}},\) and the aging response of the model \( \langle X_r \rangle \sim \frac{a^3}{A t_a} \frac{t_a^\alpha}{(1 + \alpha)}\), the dimensionless fluctuation-response parameter is

\[
FR(x) = \frac{2F_1(1, -\alpha; 1 + \alpha; x)}{(1 + x)^\alpha - x^\alpha} - 1,
\]

where \(x = t_a/t_r\). If \(\alpha = 1\) we have \(FR(x) = 0\) indicating that the non-trivial correlations are found in the limit of long times, only for anomalous processes with \(\alpha < 1\). Eq. \(14\) is valid in the limit \(t_a \rightarrow \infty\) and \(t_r \rightarrow \infty\) their ratio \(x\) remaining finite.

Comparison between simulations of the CTRW process and Eq. \(14\) for \(\alpha = 1/2\) and \(\alpha = 3/4\) is made in Fig. \(4\). The figure illustrates that the correlations between fluctuations and response becomes larger as \(x = t_a/t_r\) is increased. This is the expected behavior, the larger is the aging time \(t_a\) compared with the response time \(t_r\) the stronger is the correlation, since if \(t_r \gg t_a\) the particle already “forgot” its behavior in the aging period. The Fig. also demonstrates that as \(\alpha\) is decreased the correlations get stronger. In the simulation \(t_a = 3 \times 10^6\), \(\psi(\tau) = \alpha^{-1(1+\alpha)} \tau\) for \(\tau > 1\) otherwise it is zero.

Using Eq. \(14\) we find in the limit \(x = t_a/t_r < < 1\)

\[
FR(x) \sim \left(1 - \frac{\Gamma^2(1 + \alpha)}{\Gamma(1 + 2\alpha)}\right) x^\alpha + O(x),
\]

namely weak correlations between fluctuations and response. In the opposite limit, of the aging regime of \(x > > 1\) the correlations are stronger, and we find

\[
FR(x) \sim \frac{\alpha \Gamma(\alpha)^2}{\Gamma(2\alpha)} - 1 - \frac{1}{1 + \alpha x^\alpha} \quad x \rightarrow \infty.
\]

The leading term gives the non-trivial behavior of the fluctuation-response parameter when \(t_a/t_r \rightarrow \infty\). We find the bounds \(0 \leq \lim_{x \rightarrow \infty} FR(x) \leq 1\) where the lower bound with zero correlations corresponds to \(\alpha \rightarrow 1\) and the upper bound of strong correlations is found when \(\alpha \rightarrow 0\).

Applying linear response theory to Eq. \(12\), yields the connection between the correlation function and physically observable parameters. In this same limit aging Einstein relations between the ensemble average response and the fluctuations in the absence of the field are valid \[15, 17\]. We find using \(h = aF/2k_b T \rightarrow 0\)

\[
\langle (X_o)^2 X_r \rangle \sim \frac{2FD^2_{\alpha}t_a}{k_b T} g \left( \frac{t_a}{t_r} \right),
\]

where \(D_{\alpha} = a^2/2A\) is the fractional diffusion coefficient, which according to its definition is \(\langle X^2 \rangle \sim 2D_{\alpha} t^\alpha/\Gamma(1 + \alpha)\) \[5, 20\]. Eq. \(17\) is important since it shows that the transport coefficient \(D_{\alpha}\) and the exponent \(\alpha, \text{ describing the fluctuations in the absence of the external driving field, are the only system parameters needed for the determination of the correlation between fluctuations and the response.}\)

Model 2 As shown by Feigelman and Vinokur \[21\] transport in disordered systems with quenched disorder may exhibit aging effects. Hence it is natural to check
if fluctuations and response are correlated for models of quenched disorder, and if so how do they compare with those we obtained analytically in the annealed CTRW model? In particular do quenched models also exhibit a transition between an aging regime with strong correlations to a regime with vanishing correlations when \(t_a \to \infty\)? For that aim we consider the quenched trap model on a one dimensional lattice \([10, 17]\). Each lattice site \(i\) has a fixed random energy \(E_i > 0\), which is the energy barrier the particle has to cross in order to jump from \(i\) to \(i + 1\) or \(i - 1\). The energy barriers are all independent identically distributed random variables with a common PDF \(\rho(E) = (T_g)^{-1}e^{-E/T_g}\). The PDF of escape times from site \(i\) is exponential with a mean escape time \(\tau_i = \exp(E_i/T)\). Notice that according to this Arrhenius law small fluctuations in the energy may lead to exponentially large fluctuations in the waiting time in site \(i\). After waiting in the trap for a random time the particle has a probability 1/2 of jumping left or right if the system is not biased. It has a probability \((1 \pm h)/2\) of jumping left or right when the bias is not zero. In simulations one lets the system evolve without bias in the aging period, \((0, t_a)\) and then a bias is switched on.

It is well known that the model exhibits aging behaviors when \(T < T_g\) \([8]\). Bertin and Bouchaud showed that the aging exhibits linear and non-linear types of response, depending on the magnitude of \(h\) \([17]\). Here we consider only the linear response regime of \(h \to 0\). The trap model is not an exactly solvable model since the effect of the quenched disorder is to induce non-independent waiting times in the random walk. Hence we investigate the trap model using numerical simulations.

Simulation result for the FR parameter are shown in Fig. 2. We choose a parameter set which is known to exhibit aging behavior \([17]\) \(t_a = 10^6, h = 0.008\), and vary \(t_r\). We choose two values of temperature \(T\) the first is in the high temperature ergodic phase \(T/T_g = 5/2\), in this case we see that the FR parameter is practically zero with some small deviations due to the finite time of simulation. For \(T/T_g = 1/2\), namely in the aging phase, we see strong correlations between the fluctuations and the response especially when \(t_r < t_a\). We also plot the FR(\(x\)) parameter for the CTRW model using the exponent \(\alpha = 2T/T_g/(1 + T/T_g) = 2/3\) (\(\alpha\) is the exponent describing the averaged response function \([17]\)). The Fig. clearly demonstrates that the FR parameter in the CTRW theory is smaller than the corresponding FR parameter of the quenched trap model. In the quenched trap model, unlike the CTRW process, the diffusion is strongly correlated in the sense that a particle once returning to a specific trap will recall its waiting time for that trap, hence the FR parameter for the quenched model is larger than the one found for the CTRW.

To conclude we showed that for any non-Markovian CTRW, correlations between the fluctuations in the aging period and the response are finite if the aging period is finite. Both for the CTRW with \(\alpha < 1\) and for the quenched trap model with \(T < T_g\) a non-trivial FR parameter was found, even in the limit of large aging times. These correlations are found in the phase where the models exhibit aging transport, and hence we suspect that generally systems which exhibit aging may exhibit similar correlations between fluctuations and response. The advance of single molecule tracking makes this research timely, since we showed that the response of individual particles to an external field depends on their history of fluctuations.

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