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# Non-equilibrium linear response of micron-sized systems

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**Abstract.** - The linear response of non-equilibrium systems with Markovian dynamics satisfies a generalized fluctuation-dissipation relation derived from time symmetry and antisymmetry properties of the fluctuations. The relation involves the sum of two correlation functions of the observable of interest: one with the entropy excess and the second with the excess of dynamical activity with respect to the unperturbed process. We illustrate this approach in the experimental determination of the linear response of the potential energy of a Brownian particle in a toroidal optical trap. The overdamped particle motion is effectively confined to a circle, undergoing a periodic potential and driven out of equilibrium by a non-conservative force. Independent direct and indirect measurement of the linear response around a non-equilibrium steady state are performed in this simple experimental system. The same ideas are applicable to the non-equilibrium linear response of more general micron-sized systems immersed in Newtonian fluids either in stationary or non-stationary states and possibly including inertial degrees of freedom.

**Introduction.** – The linear response of systems in thermodynamic equilibrium is generally described by the fluctuation-dissipation theorem [1]. This theorem provides a simple relation between the equilibrium fluctuations of a given observable  $Q$  with the response of the system due to a small external perturbation  $h_s$  changing the potential at time  $s$  as  $U \rightarrow U - h_s V$ :

$$R_{QV}(t-s) = \beta \frac{d}{ds} \langle Q(t)V(s) \rangle_0. \quad (1)$$

In eq. (1)  $R_{QV}(t-s) = \delta \langle Q(t) \rangle_h / \delta h_s|_{h=0}$  is the linear response function of  $Q$  at time  $t \geq s$ ;  $\langle Q(t)V(s) \rangle_0$  is the two-time correlation function between  $Q$  and  $V$  measured at equilibrium; the brackets  $\langle \dots \rangle_h$  denote the ensemble average in the state perturbed by  $h_s$  so that  $\langle \dots \rangle_0$  corresponds to the ensemble average at equilibrium ( $h_s = 0$ ). The inverse temperature of the equilibrium system,  $\beta = 1/k_B T$ , appears as a multiplicative factor. Hence, eq. (1) represents a useful tool in experiments and simulations to explore indirectly the linear response regime from fluctuation measurement completely performed at thermal equilibrium. Vice versa, one can obtain information on microscopic fluctuations from non-equilibrium macroscopic measurements of response functions or susceptibilities by applying sufficiently weak external fields.

In general, eq. (1) fails to describe the linear response

of systems already prepared in a non-equilibrium state. This situation is relevant in real mesoscopic systems that usually operate far from equilibrium due to either non-conservative/time-dependent forces exerted by the experimental apparatus or external flows and gradients applied at the boundaries. For instance, the development of micro and nano techniques (*e.g.* optical tweezers and atomic force microscopes) has allowed one to mechanically manipulate colloidal particles, living cells and single molecules of biological interest with forces ranging from pN to fN. In this kind of experiments, thermal fluctuations can be comparable or larger than the typical external perturbations necessary to determine  $R_{QV}$ . Then, for these systems it is more reliable in practice to measure non-equilibrium fluctuations than linear response functions.

On the theoretical side, several works have recently dealt with the problem of the extension of the fluctuation-dissipation theorem around non-equilibrium steady states [2–11]. In most of the formulations, an additive extra term on the right-hand side of eq. (1) appears as a non-equilibrium correction of the fluctuation-dissipation relation due to the broken detailed balance. Different physical interpretations of the corrective term are provided in the literature. We specially highlight the roles of the non-vanishing probability current [6] and the conjugate variables to the total entropy production [5, 11] in the

analytical expression of the corrective term, leading independently to a Lagrangian interpretation for Langevin systems with first-order Markovian dynamics. Following these two approaches an equilibrium-like fluctuation-dissipation relation can be restored in the Lagrangian frame of the local mean velocity of the system for the right choice of observables [5,12]. An alternative interpretation has been proposed in terms of time-symmetric and time-antisymmetric properties of the fluctuations [13–15]. This formulation holds even in more general situations including non-steady states and inertial degrees of freedom provided that the dynamics is Markovian [15].

**Generalized approach to linear response.** –

We briefly present the formulation of the fluctuation-dissipation relation developed in [13–15] for the special case of stochastic systems described by a finite number of degrees of freedom  $\{q\}$  with overdamped Markovian Langevin dynamics, in presence of a potential  $U(q)$ . The systems are in contact with a thermal bath at temperature  $T$  and driven into a non-equilibrium steady state by a non-conservative force. We focus on the average value of an observable  $Q(q)$  at time  $t$ , denoted by  $\langle Q(q_t) \rangle_0$ . We are also interested in the mean value  $\langle Q(q_t) \rangle_h$  of  $Q(q)$ , when a small time dependent perturbation  $h_s$  is applied to  $U(q)$ , namely  $U(q) \rightarrow U(q) - h_s V(q)$ . As formally shown in [13, 14],  $\langle Q(q_t) \rangle_h$  is given at linear order in  $h_s$  by

$$\langle Q(q_t) \rangle_h = \langle Q(q_t) \rangle_0 + \int_{-\infty}^t R_{QV}(t, s) h_s ds, \quad (2)$$

where the linear response function  $R_{QV}$  obeys the generalized fluctuation-dissipation relation

$$R_{QV}(t, s) = \frac{\beta}{2} \frac{d}{ds} \langle V(q_s) Q(q_t) \rangle_0 - \frac{\beta}{2} \langle LV(q_s) Q(q_t) \rangle_0. \quad (3)$$

In eq. (3),  $L$  is the generator of the unperturbed Langevin dynamics which determines the time evolution of any single-time observable  $O(q)$ :  $d\langle O(q_t) \rangle_0/dt = \langle (LO)(q_t) \rangle_0$ .

It should be noted that  $R_{QV}(t, s)$  is operationally obtained by applying an instantaneous delta perturbation at time  $s$  and measuring  $\langle Q(q_t) \rangle_h - \langle Q(q_t) \rangle_0$ . In experiments it is always more reliable to apply a Heaviside perturbation ( $h_s = 0$  for  $s < 0$ ,  $h_s = h = \text{const.}$  for  $s \geq 0$ ) instead. This procedure directly yields the integrated response function

$$\chi_{QV}(t) = \int_0^t R_{QV}(t, s) ds = \frac{\langle Q(q_t) \rangle_h - \langle Q(q_t) \rangle_0}{h}, \quad (4)$$

defined over the time interval  $[0, t]$ . Therefore, in the following we consider the integral form of eq. (3)

$$\chi_{QV}(t) = \frac{\beta}{2} [C(t) + K(t)], \quad (5)$$

where the term

$$C(t) = \langle V(q_t) Q(q_t) \rangle_0 - \langle V(q_0) Q(q_t) \rangle_0, \quad (6)$$

can be interpreted as a correlation between the observable  $Q(q_t)$  and the excess in entropy produced by the Heaviside perturbation during the interval  $[0, t]$ :  $[hV(q_t) - hV(q_0)]/T$ . On the other hand, the term

$$K(t) = - \int_0^t \langle LV(q_s) Q(q_t) \rangle_0 ds, \quad (7)$$

can be interpreted as minus the correlation between the observable  $Q(q_t)$  and the integrated excess in dynamical activity or *frenesy*:  $\beta \int_0^t LV(q_s) h ds$ , which quantifies how frenetic the motion is due to the perturbation with respect to the unperturbed process. The frenesy  $\beta LV(q)$  can be regarded as a generalized escape rate of a trajectory from a given phase-space point  $q$ . In refs. [13–15] it has been widely discussed that the origin of the entropic  $C(t)$  and the frenetic  $K(t)$  terms can be traced back to time-antisymmetric and symmetric properties of the fluctuations, respectively.

**Colloidal particle in a toroidal optical trap.** – In the present paper we apply the previous ideas to a simple experimental micron-sized system driven away from thermal equilibrium. Our aim is to show that the generalized fluctuation-dissipation formula (5) is suitable for the description of the non-equilibrium linear response of micron-sized systems immersed in Newtonian fluids and subjected to time-dependent or non-conservative forces. Under this conditions all the unperturbed terms on the right-hand side of eq. (5) are measurable. Viscoelastic environments are excluded from this formulation because they imply non-Markovian dynamics.

Specifically we study the linear response of a single colloidal particle driven out of equilibrium by a non-conservative force in presence of a non-linear potential. We recall the main features of the experiment, described in detail in ref. [16], where this experimental set-up has been used in the context of a modified fluctuation dissipation relation, but with a different interpretation of the one described in the present letter. In our experiment the Brownian motion of a spherical silica particle (radius  $r = 1 \mu\text{m}$ ) immersed in water is confined on a thin torus of major radius  $a = 4.12 \mu\text{m}$  by a tightly focused laser beam which rotates at 200 Hz (see fig. 1). The rotation frequency of the laser is so high that it is not able to trap continuously the colloidal particle in the focus because the viscous drag force of the surrounding water quickly exceeds the optical trapping force. Consequently, at each rotation the beam only kicks the particle a small distance along the circle of radius  $a$ . During the absence of the beam ( $\approx 5$  ms), the particle undergoes free diffusion of less than 40 nm in the radial and perpendicular direction to the circle. Thus, the particle motion is effectively confined on a circle: the angular position  $\theta$  of its barycenter is the only relevant degree of freedom of the dynamics. In addition, a static light intensity profile is created along the circle by sinusoidally modulating in time the laser power which has a mean value of 30 mW and a modulation am-

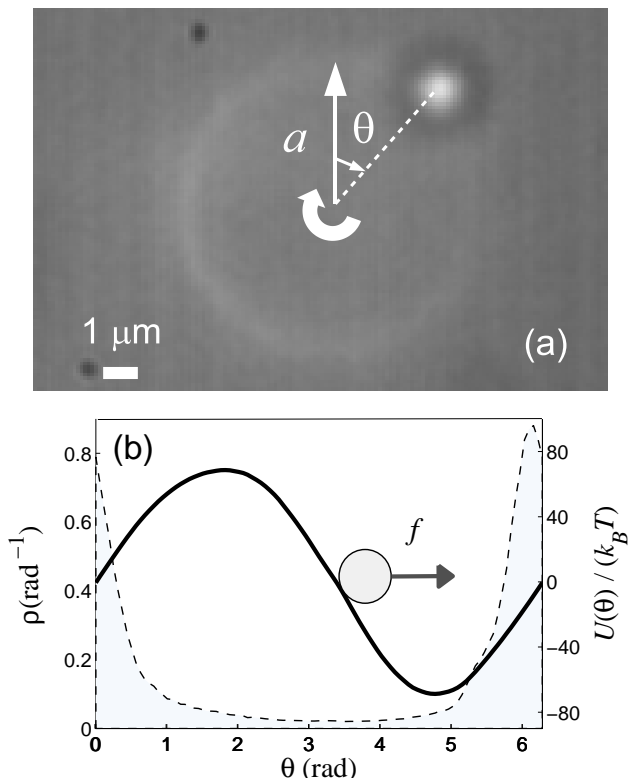


Fig. 1: (a) Snapshot of the colloidal particle in the toroidal optical trap. The straight vertical arrow indicates the position  $\theta = 0$  whereas the curled arrow shows the direction of the rotation of the laser beam. (b) Experimental potential profile (solid line) and the corresponding probability density function of  $\theta$  (dashed line) for the non-equilibrium steady state generated by the non-conservative force  $f$ .

plitude of 4.2 mWpp at the same frequency as the rotation frequency of the beam. Fig. 1(a) sketches this experimental configuration on a snapshot of the colloidal particle in the toroidal optical trap. The water reservoir acts as an equilibrium thermal bath at fixed temperature ( $T = 20 \pm 0.5^\circ\text{C}$ ) providing thermal fluctuations to particle. The viscous drag coefficient at this temperature is  $\gamma = 1.89 \times 10^{-8} \text{ kg s}^{-1}$ .

For the experimentally accessible length and time scales the dynamics of  $\theta$  is modeled by the first-order Langevin equation [16, 17]

$$\dot{\theta} = -A\phi'(\theta) + F + \xi, \quad (8)$$

where  $A\phi(\theta)$  is a periodic non-linear potential [ $A\phi(\theta) = A\phi(\theta + 2\pi)$ ] of amplitude  $A = 0.87 \text{ rad}^2 \text{ s}^{-1}$  created by the laser intensity modulation;  $F = 0.85 \text{ rad s}^{-1}$  is a constant force acting in the direction of the laser rotation which is associated to the mean kick of the beam;  $\xi$  is a white noise process of zero mean and covariance  $\langle \xi_t \xi_s \rangle = 2D\delta(t - s)$  with bare diffusivity  $D = k_B T / (\gamma a^2) = 1.26 \times 10^{-2} \text{ rad}^2 \text{ s}^{-1}$ , which models the thermal fluctuating force exerted by the water molecules.  $F$  is non-conservative

( $\int_0^{2\pi} F d\theta = 2\pi F > 0$ ) since the motion takes places on a circle, driving the system out of equilibrium. The physical non-conservative force and the potential are  $f = \gamma a F = 66 \text{ fN}$  and  $U(\theta) = \gamma a^2 A \phi(\theta) = 68.8 k_B T \phi(\theta)$ , respectively. The experimental potential profile  $U(\theta)$  is plotted as a continuous black line in fig 1(b). Note that at thermal equilibrium ( $F = 0$ ) the particle motion would be tightly confined around the potential minimum with the stochastic variable  $\theta$  distributed according to the Boltzmann density  $\rho_{eq}(\theta) \propto \exp[-\beta U(\theta)]$ . However, due to the thermal fluctuations and the non-conservative force  $F > 0$ , the particle is able to go beyond the potential barrier and explore the whole circle. In the non-equilibrium situation with constant  $F, A, D > 0$ , the angular position  $\theta$  settles in a stationary probability density  $\rho(\theta) \neq \rho_{eq}(\theta)$  that admits an analytical expression found in [18]. The experimental non-equilibrium density  $\rho(\theta)$  is shown in fig. 1(b) as a dashed line. A constant probability current  $j = \langle \dot{\theta}(t) \rangle_0 / (2\pi) = [F - A\phi'(\theta)]\rho(\theta) - D\partial_\theta \rho(\theta) > 0$ , in the direction of  $F$  appears reflecting the broken detailed balance of the dynamics. For the experimental conditions one finds  $j = 3.76 \times 10^{-2} \text{ s}^{-1}$  corresponding to a mean rotation period of 26.6 s for the particle. Both  $\rho(\theta)$  and  $j$ , determined from 200 independent experimental time series of the angular position of the particle  $\{\theta_t, 0 \leq t \leq 66.67 \text{ s}\}$ , allow one to precisely compute the value of the non-conservative force  $f$  and the potential profile  $U(\theta)$ , as described in [16].

Now we proceed to determine the linear response of the particle motion when slightly perturbing the non-equilibrium steady state previously described. For experimental simplicity we consider a perturbation to the potential amplitude  $A \rightarrow A + \delta A$ , so that the perturbation and its conjugate variable are  $h = -\delta A$  and  $V(q) = \phi(\theta)$ , respectively. In order to illustrate the meaning of the non-equilibrium linear response relation of eq. (5) in this case, we perform two different kinds of independent measurements: *direct* and *indirect*, as explained in the following.

**Direct measurement of the linear response function.** — First, we consider the *direct* measurement of the integrated response function  $\chi_{QV}$  for the periodic observable  $Q(q) = \phi(\theta) = \phi(\theta + 2\pi)$ . This observable times  $\gamma a^2 A$  represents the instantaneous potential energy of the particle. This is experimentally accomplished by applying a step perturbation to the amplitude of the sinusoidal laser power modulation,  $4.2 \text{ mWpp} \rightarrow 4.4 \text{ mWpp}$ , but keeping constant the power offset at 30 mW so that  $F$  remains constant. This results in a perturbation of the potential amplitude  $\delta A = 0.05A$ . Then, the integrated response function of  $\phi(\theta)$  at time  $t \geq 0$  due to the perturbation  $-\delta A$  applied at time 0 is given by

$$\chi_{QV}(t) = \frac{\langle \phi(\theta_t) \rangle_{\delta A} - \langle \phi(\theta_t) \rangle_0}{-\delta A}, \quad (9)$$

where  $\langle \dots \rangle_{\delta A}$  and  $\langle \dots \rangle_0$  denote the ensemble averages of the perturbed  $\theta_{t, \delta A}$  and unperturbed  $\theta_t$  trajectories, re-

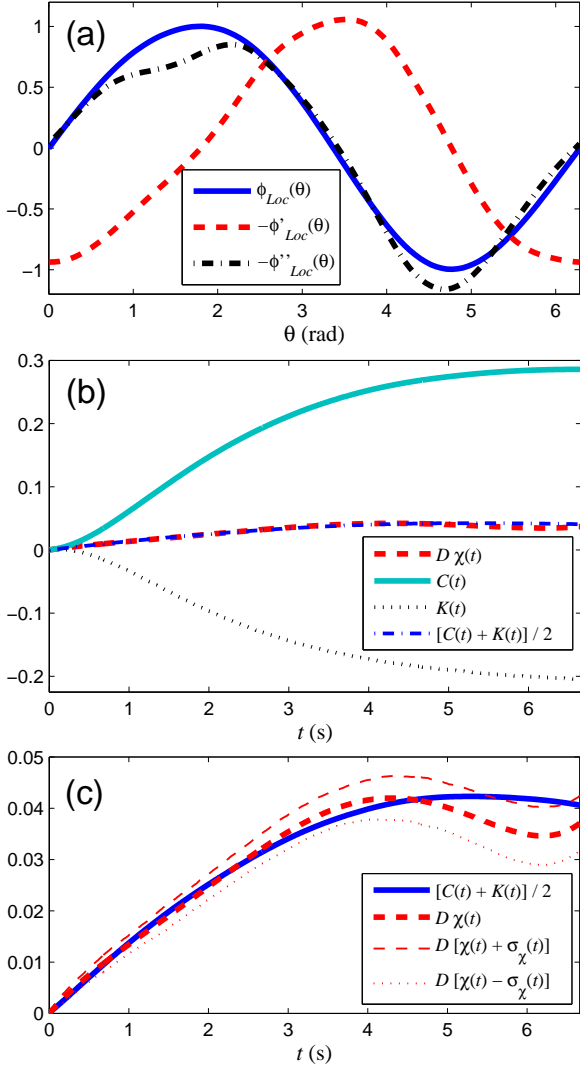


Fig. 2: (a) Potential profile  $\phi(\theta)$  locally fitted as a third-order polynomial  $\phi_{Loc}(\theta)$  around each value of  $\theta$ . Their derivatives are computed from  $\phi_{Loc}(\theta)$ . (b) Integrated linear response function  $\chi_{QV}(t)$ , entropic  $C(t)$  and frenetic  $K(t)$  terms and the corresponding indirect measurement  $[C(t) + K(t)]/2$  for  $Q = \phi(\theta)$ ,  $h = -\delta A$  and  $V = \phi(\theta)$ , as functions of the integration time  $t$ . (c) Expanded view of (b).

spectively. In order to decrease the statistical errors in comparison of the terms in eq. (9), for a given perturbed trajectory  $\theta_{t,\delta A}$  we look for as many unperturbed ones  $\theta_t$  as possible starting at time  $t^*$  such that  $\phi(\theta_{t^*}) = \phi(\theta_{0,\delta A})$ . Then we redefine  $t^*$  as  $t = 0$  in eq. (9). The unperturbed trajectories found in this way allow us to define a subensemble over which the average  $\langle \dots \rangle_0$  is computed. On the other hand, the average  $\langle \dots \rangle_{\delta A}$  is performed over 500 independent realizations of  $\delta A$  that are enough for a fair determination of the integrated response. The resulting curve  $\chi_{QV}(t)$  and its corresponding error bars  $\pm \sigma_\chi(t)$  as functions of the integration time  $t$  starting at the in-

stant of the application of the step perturbation are shown in figs. 2(b) and 2(c).

**Indirect measurement of the linear response function.** – The same response information can be obtained *indirectly* from correlation measurements of the unperturbed non-equilibrium steady-state fluctuations ( $\delta A = 0$ ) when properly using eq. (5). For the Langevin dynamics of  $\theta$  described by eq. (8) the analytical expression of the generator  $L$  is

$$L = (F - A\phi'(\theta))\partial_\theta + D\partial_\theta^2. \quad (10)$$

Hence, in this case eq. (5) reads

$$D\chi_{QV}(t) = \frac{C(t) + K(t)}{2}, \quad (11)$$

where the entropic and frenetic terms are

$$C(t) = \langle \phi(\theta_t)\phi(\theta_t) \rangle_0 - \langle \phi(\theta_0)\phi(\theta_t) \rangle_0, \quad (12)$$

$$K(t) = - \int_0^t ds \langle [D\phi''(\theta_s) + (F - A\phi'(\theta_s))\phi'(\theta_s)]\phi(\theta_t) \rangle_0, \quad (13)$$

respectively. At this point it is clear the need of a precise knowledge of the potential profile  $\phi(\theta)$  for the indirect method. The integrand of eq. (13) involves the instantaneous values of  $\phi(\theta)$  and its derivatives  $\phi'(\theta)$  and  $\phi''(\theta)$ . Otherwise a cumulative error would appear when computing  $K(t)$ . As a first approximation  $\phi(\theta) \approx \sin \theta$  according to the sinusoidal modulation of the laser power. However, due to unavoidable experimental static defects of the toroidal optical trap (*e.g.* optical aberration) the resulting profile  $\phi$  is slightly distorted. In order to take into account the distortion, we perform a local polynomial fit  $\phi_{Loc}$  of  $\phi$  around each value of  $\theta \in [0, 2\pi)$ . Then the instantaneous value of the observable  $\phi(\theta_t)$  at time  $t$  is approximated by  $\phi_{Loc}(\theta_t)$  either for an unperturbed or a perturbed trajectory. The local polynomial approximation  $\phi_{Loc}$  and its derivatives  $\phi'_{Loc}$ ,  $\phi''_{Loc}$  are plotted in fig. 2(a) showing the non-sinusoidal distortion. The resulting curves  $C(t)$  and  $K(t)$  as functions of the integration time  $t$  are plotted in fig. 2(b). At thermal equilibrium ( $F = 0$ ) one should find that  $C(t) = K(t)$  for all  $t \geq 0$  because of the time reversibility and stationarity of the two-time correlations leading to the equilibrium fluctuation-dissipation relation  $D\chi_{QV}(t) = C(t)$ . Meanwhile, in the present case  $K(t)$  reaches negative values of the same order of magnitude as the positive values of  $C(t)$ . This reflects the experimental conditions far from thermal equilibrium of the system. The average of these two quantities  $[C(t) + K(t)]/2$  is one order of magnitude smaller. This average, which is an indirect measurement of the integrated response function according to eq. (11), agrees very well with the direct measurement of  $\chi_{QV}$  within the experimental error bars, as shown in fig. 2(c). It is consistent with the experimental results presented in ref. [16] since the entropic-frenetic approach followed in the present



paper reduces to the Lagrangian interpretation of ref. [6] for non-equilibrium steady states of overdamped diffusion on a circle, as shown in [13].

We remark that for this kind of micron-sized system the relation (5) actually represents a feasible indirect method to access the linear response regime far from thermal equilibrium. This is because all the parameters of the unperturbed dynamics are known a priori or can be determined in situ without any external perturbation of the non-equilibrium state. On the other hand, the direct measurement of the linear response function exhibit a number of technical difficulties in practice. First, a vanishingly small Heaviside perturbation  $-hV(q)$  to the initially unperturbed potential  $U(q)$  is ideally required. Otherwise spurious effects quickly bias the measurement of  $\chi_{QV}$ , specially when the system is strongly non-linear. Second, even when  $h$  is small enough to be within the linear response regime, its finiteness restricts the available integration time range to determine  $\chi_{QV}(t)$ . This occurs because when  $t$  increases,  $Q$  approaches a new non-equilibrium state at the new potential  $U(q) - hV(q)$  whose probability density may depend non-linearly on  $h$ . Third, one requires an extremely large number of independent realizations of  $h$  to resolve  $\chi_{QV}$  as the perturbation  $-hV(q)$  must be chosen very weak, typically smaller than the thermal fluctuations of the energy injected by the environment. The last two limitations are evident on the results of the direct measurement of  $\chi_{QV}$  for the colloidal particle, see fig. 2(c). For integration times  $t \lesssim 3$  s the agreement between  $D\chi_{QV}(t)$  and  $[C(t) + K(t)]/2$  is excellent. Then, for  $t \gtrsim 3$  s the combined effects of the non-linear dependence of the new steady-state on  $-\delta A$  and the finite sampling lead to deviations between the two methods and increasingly large error bars for the direct measurement of  $\chi_{QV}$ . These drawbacks are skipped when implementing the indirect method measuring the unperturbed quantity  $[C(t) + K(t)]/2$ . In addition, for a steady state like the one experimentally studied here one can improve dramatically the statistics by performing an additional time average over a window  $[0, t_{max}]$ :  $C(t) = \int_0^{t_{max}} C(t+u)du/t_{max}$ ,  $\bar{K}(t) = \int_0^{t_{max}} K(t+u)du/t_{max}$ , as actually done for the curves  $C$ ,  $K$  and  $(C+K)/2$  in figs. 2(b) and 2(c). However, one must be careful when performing the time average. This is because the value of  $t_{max}$  may affect the resulting values of  $[C(t) + K(t)]/2$  as  $t$  increases, specially for correlation functions involving strongly fluctuating quantities such as velocities, as recently discussed in [19]. For the curves shown in figs. 2(a) and 2(b) we verified that their shapes are not significantly influenced by  $t_{max}$ .

Finally, we illustrate the use of eq. (5) to study the behavior of the mean potential energy of the particle  $\langle U(\theta_t) \rangle_h$  when slightly perturbing in time either the phase or the amplitude of the potential around the non-equilibrium steady state associated to eq. (8). We concentrate on a sinusoidal perturbation starting at time  $s = 0$

$$h_s = h_0 \sin 2\pi f_0 s. \quad (14)$$

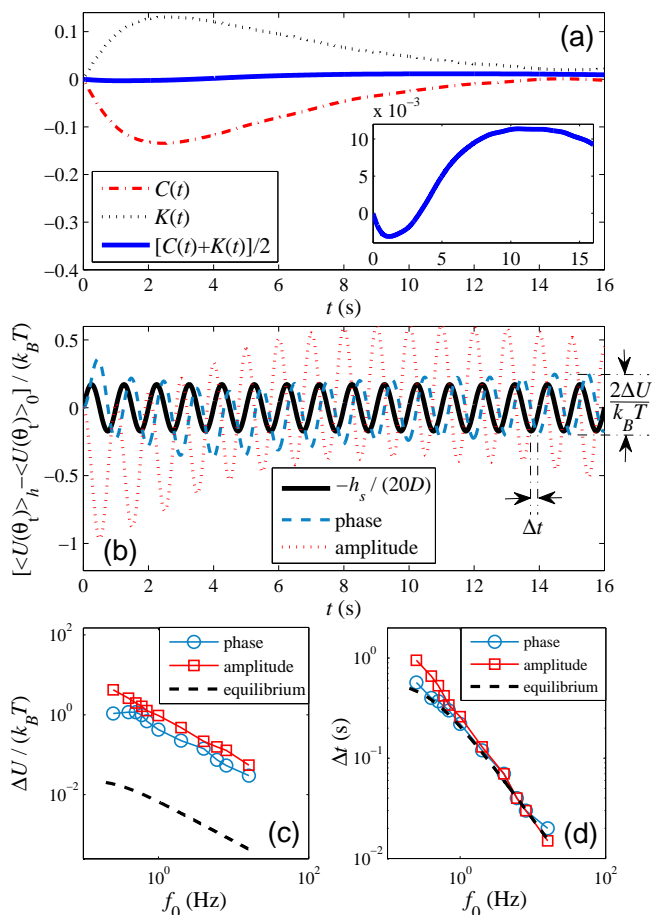


Fig. 3: (a) Integrated response function of the observable  $Q = \phi(\theta)$  for a small perturbation of the potential phase as a function of the integration time  $t$ . Inset: expanded view of  $[C(t) + K(t)]/2$ . (b) Sinusoidal time-dependent perturbation  $-h_s$  (solid black line) of the static potential  $A\phi$ . Resulting mean potential energy of the Brownian particle for a phase perturbation (dashed blue line) and an amplitude perturbation (dotted red line) for  $-h_0/A = 0.05$  and  $f_0 = 1$  Hz. (c) Asymptotic values of oscillation amplitude of the potential energy and (d) the delay time with respect to  $-h_s$  for each kind of perturbation. The black dashed lines represent the values around thermal equilibrium, given by eqs. (17) and (18).

First, we consider the case of a small phase perturbation  $\alpha_s = \alpha_0 \sin 2\pi f_0 s$  with  $\alpha_0 \ll 1$ :  $A\phi(\theta) \rightarrow A\phi(\theta + \alpha_s) \approx A\phi(\theta) + A\phi'(\theta)\alpha_s$  so that  $h_0 = -A\alpha_0$  in Eq. (14) and  $V = \phi'(\theta)$ . One must compute first the integrated response function of  $Q = \phi(\theta)$  given by  $[C(t) + K(t)]/(2D)$  by inserting the right  $V$  and  $Q$  in eqs. (6) and (7). The resulting curves  $C(t)$ ,  $K(t)$  and  $[C(t) + K(t)]/(2D)$  are plotted in fig. 3(a). Next, using eq. (2) the experimental impulse response function  $[\partial_t C(t-s) + \partial_t K(t-s)]/(2D)$  must be convolved with  $h_s$  given by eq. (14). In this way one finds that the mean potential energy of the particle oscillates around the non-equilibrium steady state value  $\langle U(\theta) \rangle_0 = -4.7k_B T$  as shown by the dashed blue line in

fig. 3(b) for  $\alpha_0 = 0.05$  rad and  $f_0 = 1$  Hz. The oscillations exhibit a delay time ( $\Delta t \approx 0.23$  s) with respect to  $\alpha_s$  and a slow transient ( $\sim 15$  s) corresponding to the decay of the non-equilibrium stationary correlations. As  $t$  increases the oscillations settle around  $\langle U(\theta) \rangle_0$  with a constant amplitude  $\Delta U \approx 0.2k_B T$ . Now, we consider a sinusoidal time-dependent perturbation to the potential amplitude:  $\delta A_s = \delta A_0 \sin 2\pi f_0 s$  with the same strength ( $-h_0/A = 0.05$ ) and frequency as before. In this case  $h_0 = -\delta A_0$  and  $V = \phi(\theta)$ . Following the same procedure with  $[C + K]/(2D)$  shown in fig. 2(c), one finds a different qualitative behavior of  $\langle U(\theta_t) \rangle_h$ , as depicted by the dotted red line in fig. 3(b). At the beginning the mean potential energy responds in the opposite direction to  $\delta A_s$ . Then, as  $t$  becomes larger than the slow non-equilibrium transient  $\langle U(\theta) \rangle_h$  oscillates around  $\langle U(\theta) \rangle_0$  with a constant amplitude  $\Delta U \approx 0.5k_B T$  and a delay time  $\Delta t \approx 0.26$  s. For both types of perturbations one can write the asymptotic dependence of  $\langle U(\theta_t) \rangle_h$  on  $t \gtrsim 15$  s as

$$\langle U(\theta_t) \rangle_h = \langle U(\theta_t) \rangle_0 \pm \Delta U \sin[2\pi f_0(t - \Delta t)], \quad (15)$$

where the positive and negative signs stand for the phase and amplitude perturbations, respectively. The values of  $\Delta U$  and  $\Delta t$  depend on the frequency  $f_0$ . In figs. 3(c) and 3(d) we show this dependence. We now compare these far-from-equilibrium results with those that would be obtained when applying  $h_s$  around thermal equilibrium ( $F = 0$ ). In such a case the particle motion is tightly confined to the harmonic part of the potential around the minimum  $\theta_m = 3\pi/2$ :  $\phi(\theta) \approx -1 + (\theta - \theta_m)^2/2$ . After some algebra using this approximation one finds the expression for  $\langle U(\theta_t) \rangle_h$  when perturbing thermal equilibrium

$$\langle U(\theta_t) \rangle_h = \langle U(\theta_t) \rangle_0 \pm \Delta U \{ \sin[2\pi f_0(t - \Delta t)] + e^{-2At} \sin 2\pi f_0 \Delta t \}, \quad (16)$$

where  $\langle U(\theta_t) \rangle_0 = -68.3k_B T$  and

$$\Delta U = -\frac{h_0}{A} \frac{k_B T}{2(1 + \pi^2 f_0^2 / A^2)^{1/2}}, \quad (17)$$

$$\Delta t = \frac{1}{2\pi f_0} \arctan \left( \frac{\pi f_0}{A} \right), \quad (18)$$

either for a phase (positive sign) or an amplitude (negative sign) perturbation. Note that for  $t \gg (2A)^{-1}$ , eq. (16) exhibits the same qualitative behavior as (15). We plot the curves given by eqs. (17) and (18) in figs. 3(a) and 3(b), respectively, for the same values of the parameters  $h_0$  and  $A$  as before. Unlike the behavior close to equilibrium, the oscillation amplitude  $\Delta U$  strongly depends on the perturbed parameter around the non-equilibrium steady state: it is more sensitive to amplitude perturbations than to phase perturbations. In addition, the far-from-equilibrium values are two orders of magnitude larger than that given by eq. (17). By contrast, the delay time  $\Delta t$  is not significantly affected by the far-from-equilibrium nature of the system. It is almost independent of  $F$  and of the type of perturbation and it converges to eq. (18) as  $f_0$  increases.

**Concluding remarks.** – We have experimentally studied the non-equilibrium linear response of the potential energy of a Brownian particle in a toroidal optical trap. We gain insight into the application of the fluctuation-dissipation relations far from thermal equilibrium in this non-linear system with a single relevant degree of freedom. In particular, we show that the entropic-frenetic approach is appropriate and feasible for the study of the non-equilibrium linear response of micron-sized systems with a small number of degrees of freedom immersed in simple fluids. Non-trivial linear response information can be obtained from purely unperturbed measurements of the non-equilibrium fluctuations provided that the parameters describing the dynamics are known. Our experiment reveals that the indirect determination of the linear response function is less time-consuming, more accurate and more flexible than the direct perturbation of the non-equilibrium system. Similar ideas are expected to be applicable to more complex micron-sized systems such as atomic-force microscopy experiments and ensembles of colloidal particles in simple non-equilibrium conditions.

## REFERENCES

- [1] H. B. CALLEN and T. A. WELTON, *Phys. Rev.*, **83** (34) 1951.
- [2] G. S. AGARWAL, *Z. Phys.*, **252** (25) 1972.
- [3] T. HARADA and S.-I. SASA, *Phys. Rev. Lett.*, **95** (130602) 2005.
- [4] E. LIPPIELLO, F. CORBERI, and M. ZANNETTI, *Phys. Rev. E*, **71** (036104) 2005.
- [5] T. SPECK and U. SEIFERT, *Europhys. Lett.*, **74** (391) 2006.
- [6] R. CHETRITTE, G. FALKOVICH, and K. GAWEDZKI, *J. Stat. Mech.*, (2008) P08005.
- [7] K. MARTENS, E. BERTIN, and M. DROZ, *Phys. Rev. Lett.*, **103** (260602) 2009.
- [8] A. PUGLISI and D. VILLAMAINA, *EPL*, **88** (30004) 2009.
- [9] D. VILLAMAINA, A. BALDASSARRI, A. PUGLISI, and A. VULPIANI, *J. Stat. Mech.*, (2009) P07024.
- [10] J. PROST, J.-F. JOANNY, and J. M. R. PARRONDO, *Phys. Rev. Lett.*, **103** (090601) 2009.
- [11] U. SEIFERT and T. SPECK, *EPL*, **89** (10007) 2010.
- [12] R. CHETRITTE, and G. GAWEDZKI, *J. Stat. Phys.*, **137** (890) 2009.
- [13] M. BAIESI, C. MAES and B. WYNANTS, *Phys. Rev. Lett.*, **103** (010602) 2009.
- [14] M. BAIESI, C. MAES and B. WYNANTS, *J. Stat. Phys.*, **137** (1094) 2009.
- [15] M. BAIESI, E. BOKSENBOJM, C. MAES and B. WYNANTS, *J. Stat. Phys.*, **139** (492) 2010.
- [16] J. R. GOMEZ-SOLANO, A. PETROSYAN, S. CILIBERTO, R. CHETRITTE, and K. GAWEDZKI, *Phys. Rev. Lett.*, **103** (040601) 2009.
- [17] V. BLICKLE, T. SPECK, U. SEIFERT, and C. BECHINGER, *Phys. Rev. E*, **75** (060101(R)) 2007.
- [18] C. MAES, K. NETOCNY, and B. WYNANTS, *Physica A*, **387** (2675) 2008.
- [19] J. MEHL, V. BLICKLE, U. SEIFERT, and C. BECHINGER, *arXiv:1003.1029v1*, () .