Nonequilibrium fluctuations of a Brownian particle

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Motivation

Recent progress in statistical mechanics of nonequilibrium processes during the 90s and 2000s:

Fluctuation Relations [FR]

(Gallavotti-Cohen, Evans-Searles, Jarzynski, Crooks, Hatano-Sasa, Seifert, etc.): **Symmetry properties of fluctuating energy exchanges and entropy production.**

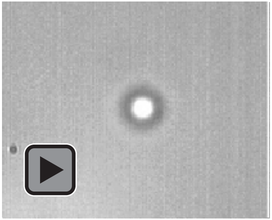
Generalized Fluctuation-Dissipation Relations [GFDR]

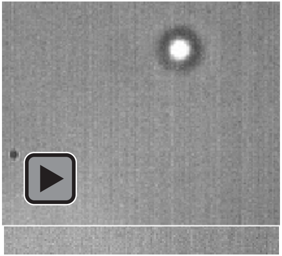
(Cugliandolo-Kurchan, Harada-Sasa, Speck-Seifert, Chetrite-Gawedzki, Maes-Baiesi-Wynants, Joanny-Prost-Parrondo, etc.): **Linear response around an unperturbed state far from thermal equilibrium.**

Application

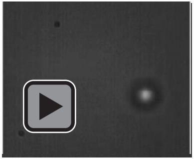
Experiments on micron- and nano-sized systems:

- **Fluctuations** exerted by the surrounding molecules are significant.
- **Nonequilibrium conditions** due to time-dependent drivings, nonconservative forces, nonstationary conditions, energy/mass fluxes.

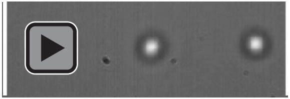




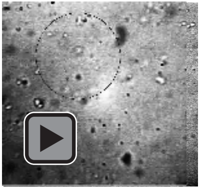
Experiments of a Brownian particle in nonequilibrium conditions



1) Generalized fluctuation-dissipation relation for nonequilibrium *steady* states



2) Fluctuations and linear response in an *aging* colloidal glass



3) Heat fluctuations and linear response in an *aging* gel after a quench

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Outline

- Experimental setup

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- Microrheology

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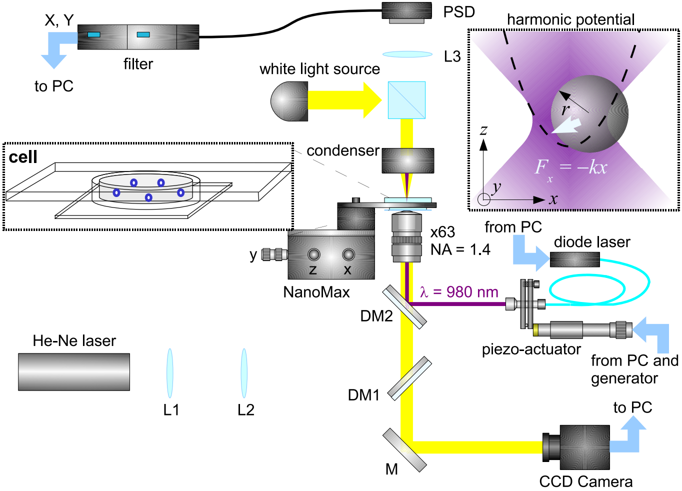
- Single colloidal particle (silica, $r = 1\,\mu$m) embedded in a fluid (heat bath) and trapped by **optical tweezers**.



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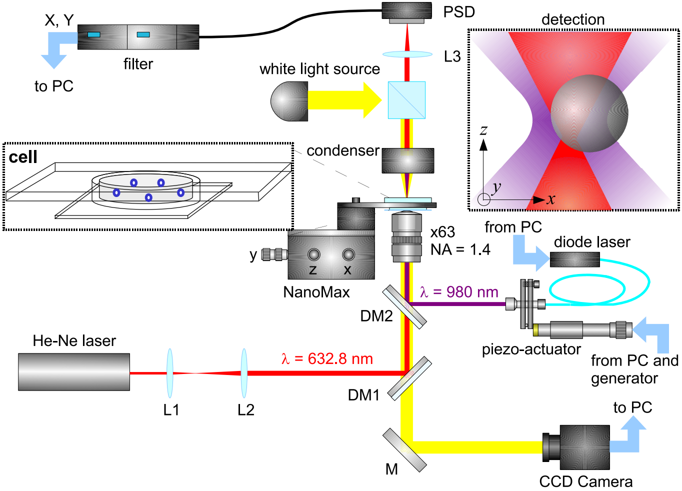
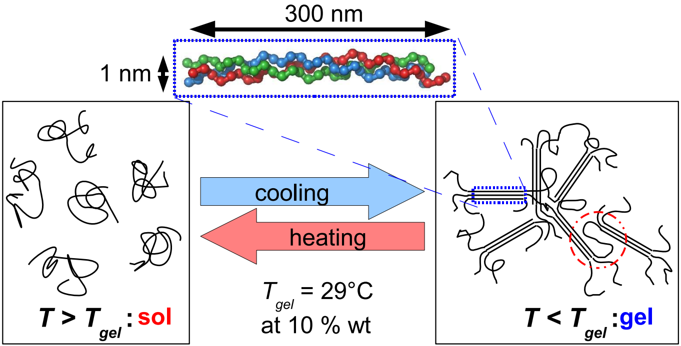


Nonstationary heat bath: Gelatin in aqueous solution

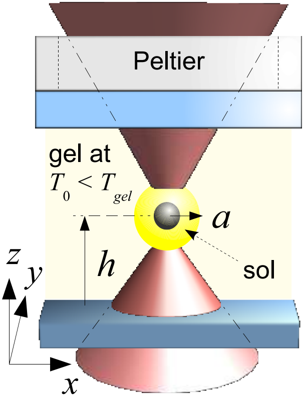
- Thermoreversible gel obtained from denatured collagen.



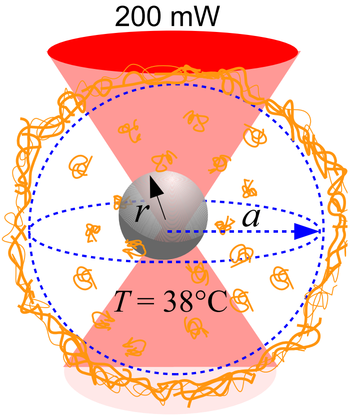
- Existence of a critical (gelation) temperature T_{gel}.
- After a quench $T > T_{gel} \rightarrow T < T_{gel}$: physical aging.

Experimental configuration: laser heating

- Gelatin bulk kept in the gel phase at 26°C.
- Local heating around a trapped particle by laser power absorption by water: sol droplet at $T = 38^\circ$ C $> T_{gel}$ at 200 mW.



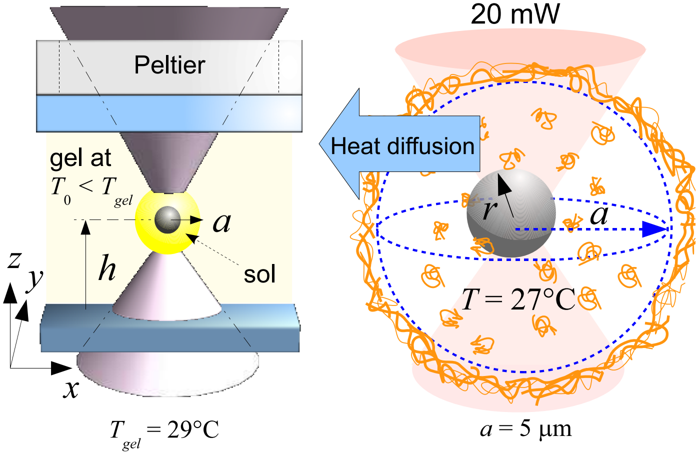
$T_{gel} = 29°C$



$a = 5$ µm

Experimental configuration: fast quench

- Sudden laser power decrease from 200 mW to 20 mW.
- Local temperature quench from $T = 38^\circ$ C $> T_{gel}$ to $T = 27^\circ$ C $< T_{gel}$ by heat diffusion into the gel bulk in $\lesssim$1 ms.



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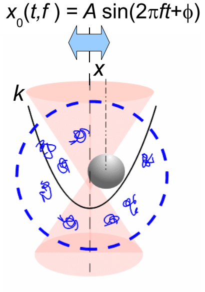
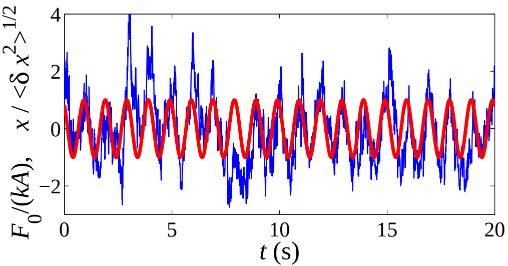
Active microrheology during gelation

Measurement of shear modulus $G(f)$ by oscillatory displacement $x_0(t, f)$ of the optical trap

- Force applied to the particle: $F_0(t) = kx_0(t, f)$.
- Response R of the particle: $x(t) = x(0) + (R * F_0)(t)$
- Shear modulus of gelatin droplet: $G(f) = G'(f) + \mathrm{i}G''(f)$

$$G'(f) = \frac{1}{6\pi r}[\mathrm{Re}[\hat{R}(f)^{-1}] - k], \quad G''(f) = \frac{1}{6\pi r}\mathrm{Im}[\hat{R}(f)^{-1}].$$





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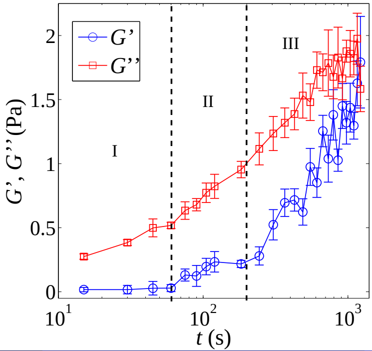
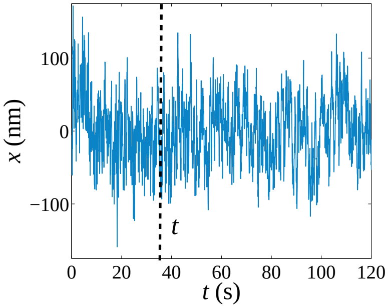
Aging time evolution of shear modulus

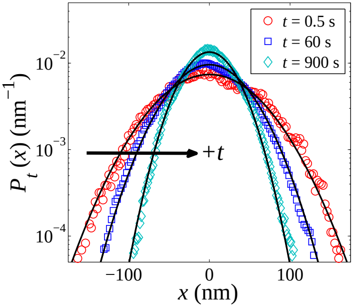
- I Purely viscous fluid: $G'(f) = 0$ (0 s $\leq t \leq$ 60 s).
- II Purely viscous fluid or negligible low frequency elasticity: $G'(f) \ll G''(f)$ as $f \to 0$ (60 s$\leq t \leq$ 200 s).
- III Non-negligible low frequency elasticity G'. Logarithmic growth G', $G'' \sim \log t$ similar to bulk measurements (200 s $\leq t$).



Particle motion during the gelation process $[F_0(t) = 0]$

- **Nonstationarity**: Probability density $P_t(x)$ of x computed at each t over an ensemble of independent quenches.
- Fluctuations of x are **Gaussian** for all $t \geq 0$: the **variance** $\sigma_x(t)^2$ is enough to characterize the statistical properties of the particle motion.

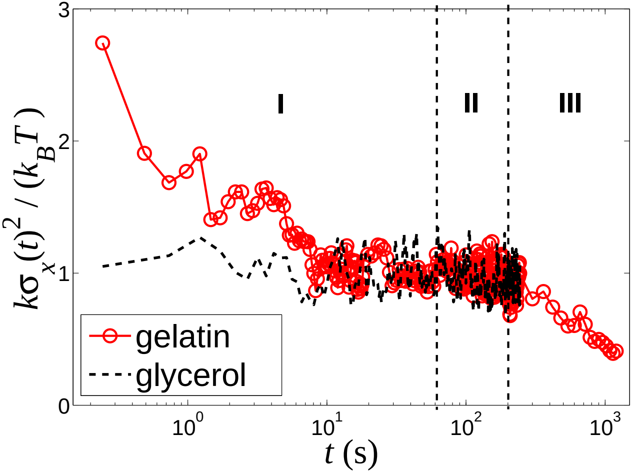




How does $\sigma_x(t)^2$ behave during the gelation process and what information does it provide?

Particle motion during the gelation process $[F_0(t) = 0]$

Time evolution of the variance of the fluctuations of x (normalized by $k_B T/k$) during the three different aging regimes



Particle motion during the gelation process $[F_0(t) = 0]$

- Potential energy of the particle

$$U = \frac{1}{2}kx^2 + U_{stored}.$$

- At thermal equilibrium at T, U satisfies equipartition:

$$\langle U \rangle = \frac{1}{2}k_B T,$$

- which implies that σ_x^2 is fixed:
  - If negligible elasticity of the bath ($U_{stored} = 0$):

$$\sigma_x^2 = \frac{2\langle U \rangle}{k} = \frac{k_B T}{k},$$

  - If non-negligible elasticity ($U_{stored} > 0$):

$$\sigma_x^2 = \frac{2\langle U - U_{stored} \rangle}{k} < \frac{k_B T}{k}.$$

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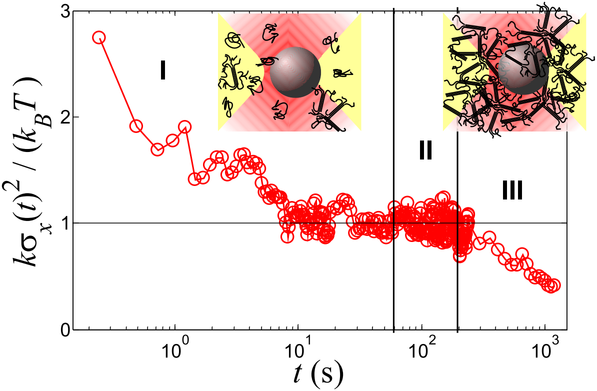
Particle motion during the gelation process [$F_0(t) = 0$]

- Three different regimes of Brownian particle motion:
  - I Nonthermal fluctuations due to the transient assemblage of the gel network.
  - II Relaxation to equilibrium-like behavior, negligible elasticity.
  - III Continuous increase of network elasticity.



How to interpret nonequilibrium fluctuations of x due to the assemblage of the gel, within the framework of FT and GFDRs?

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Stochastic thermodynamics (regimes I and II)

- Energy stored by gelatin chains is negligible:

$$\langle U_{stored} \rangle \leq 0.05 \langle U \rangle.$$

- Then, total potential energy of the particle at time $t \geq 0$:

$$U_t \approx \frac{1}{2} k x_t^2.$$

- First law applied to a single stochastic trajectory x_t [Sekimoto, PTPS 130, 17 (1998)]: direct measurement of **heat** exchanged between particle and gelatin during $[t, t+\tau]$ for $t+\tau \leq 200$ s:

$$Q_{t,\tau} = U_{t+\tau} - U_t = \frac{1}{2} k (x_{t+\tau}^2 - x_t^2).$$

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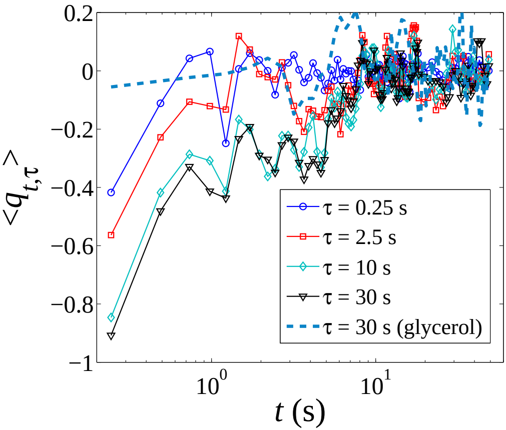
Mean heat flux

- Mean heat flux from particle to the surroundings due to the relaxation of σ_x^2:

$$\langle Q_{t,\tau} \rangle = \frac{k}{2}[\sigma_x(t+\tau)^2 - \sigma_x(t)^2] \leq 0.$$

- Broken detailed balance due to gel formation.
- $\langle Q_{t,\tau} \rangle$ slows down as the bath ages: experimentally undetectable for $t \gtrsim 20$ s.

Time evolution of mean heat flux (normalized by $k_B T$ for different time lags τ).

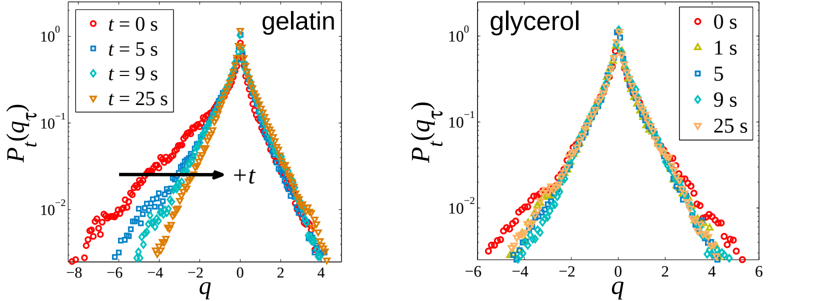


Probability density function P_t of heat fluctuations

- Asymmetric non-Gaussian profile of P_t of normalized heat

$$q_{t,\tau} = \frac{Q_{t,\tau}}{k_B T}.$$

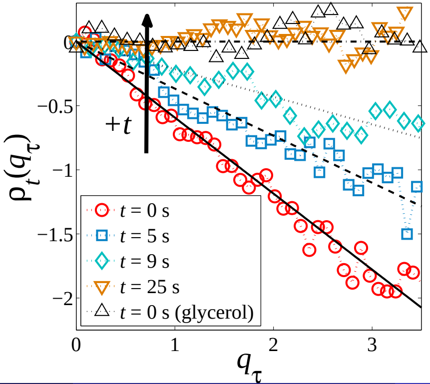
- Real heat flux in gelatin due to the assemblage of the gel network: no asymmetry detected in simple Newtonian fluid.



- Asymmetry function of heat fluctuations

$$\rho_t(q_\tau) = \ln \frac{P_t(q_\tau)}{P_t(-q_\tau)}.$$

- **Heat fluctuations satisfy FT!:** $\rho_t(q_\tau) = -\Delta\beta_{t,\tau} q_\tau$.



Model

- Using the fact that fluctuations of x are Gaussian, for $\tau \gg \tau_k = 65$ ms, analytical expression of $P_t(q_\tau)$ for $0 \leq t \leq 200$ s:

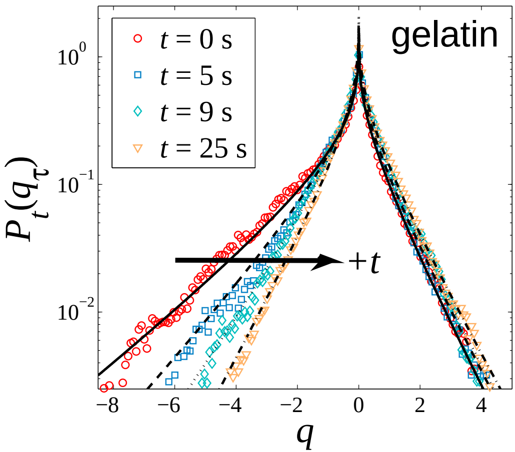
$$P_t(q_\tau) = \frac{A_{t,\tau}}{\pi} K_0\left(B_{t,\tau}|q_\tau|\right) \exp\left(-\frac{\Delta_{t,\tau} A_{t,\tau}}{2} q_\tau\right),$$

where

$$\begin{aligned}
\Delta_{t,\tau} &= \frac{\sigma_x(t)}{\sigma_x(t+\tau)} - \frac{\sigma_x(t+\tau)}{\sigma_x(t)}, \\
A_{t,\tau} &= \frac{k_B T}{k\sigma_x(t)\sigma_x(t+\tau)}, \\
B_{t,\tau} &= A_{t,\tau}\sqrt{1 + \frac{\Delta_{t,\tau}^2}{4}}.
\end{aligned}$$

- Asymmetry of $P_t(q_\tau)$ completely determined by $\Delta_{t,\tau} A_{t,\tau}$.

- The analytical expression of $P_t(q_\tau)$ perfectly fits the experimental data

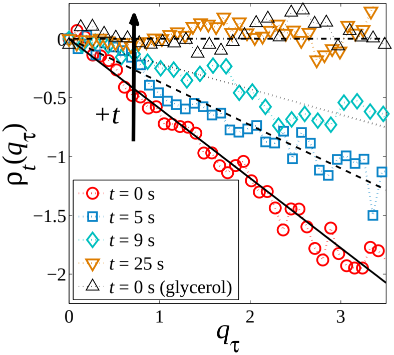


- Analytical expression of $\rho_t(q_\tau)$:

$$\rho_t(q_\tau) = -\Delta\beta_{t,\tau} q_\tau,$$

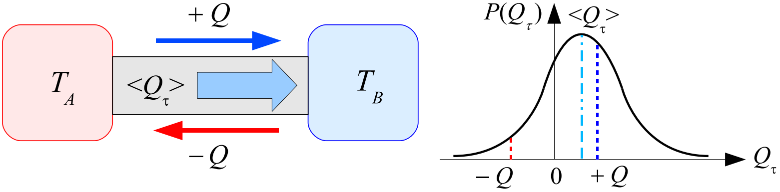
where

$$\Delta\beta_{t,\tau} = \frac{k_B T}{k}\left[\frac{1}{\sigma_x(t+\tau)^2} - \frac{1}{\sigma_x(t)^2}\right].$$



Fluctuation Theorem for stationary heat conduction

- Fluctuations of entropy production for conductive system between two reservoirs in a nonequilibrium steady state.



$$\ln \frac{P(Q)}{P(-Q)} = \frac{1}{k_B}\left(\frac{1}{T_B} - \frac{1}{T_A}\right) Q,$$

$\rightarrow$Second law of thermodynamics: $\left\langle \left(\frac{1}{T_B} - \frac{1}{T_A}\right) Q \right\rangle \geq 0.$

Interpretation

Introducting equipartition-like relation for particle motion:

$$\frac{1}{2}k_B T_{eff}(t) = \frac{1}{2}k\sigma_x(t)^2,$$

the aging time dependent prefactor can be written as

$$\Delta\beta_{t,\tau} = \left[\frac{1}{T_{eff}(t+\tau)} - \frac{1}{T_{eff}(t)}\right] T.$$

- **Similar to system in contact with two thermostats at unequal temperatures $T_{eff}(t) \geq T_{eff}(t+\tau) \to T$.**
- **Entropy produced by breakdown of time reversal symmetry due to the nonstationarity of the bath:**

$$\Delta S_{t,\tau} = -k_B \Delta\beta_{t,\tau} q_{t,\tau} = \left(\frac{1}{T_{eff}(t)} - \frac{1}{T_{eff}(t+\tau)}\right) Q_{t,\tau}.$$

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Fluctuations and linear response

- Power spectrum of fluctuations of x ($F_0 = 0$): information on timescales of particle coupled to the aging bath

$$S_x(f,t) = \langle |\hat{x}(f)|^2 \rangle,$$

- Linear response of particle position to external oscillatory force ($F_0 \neq 0$): related to shear modulus $G(f)$

$$\hat{R}(f,t) = \frac{1}{6\pi r G^*(f) + k},$$

- At thermal equilibrium at T, fluctuation-dissipation relation

$$S_x(f,t) = \frac{2k_B T}{\pi f} \mathrm{Im}\{\hat{R}(f,t)\},$$

Relation between S_x and $\hat{R}$ during nonequilibrium gelation?

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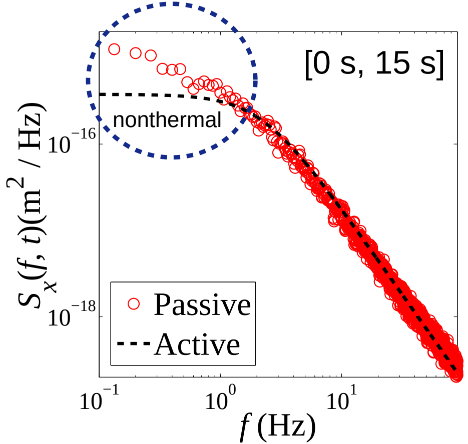
Fluctuations and linear response

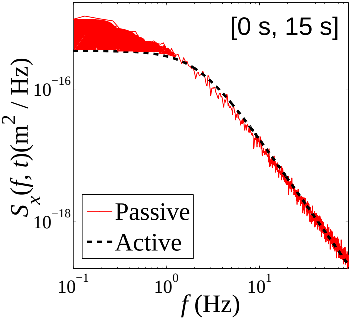


- Significant violation of FDT when $\langle Q_{t,\tau} \rangle$ is non-negligible (0 s$\leq t \leq 60$ s).

GFDR for a Brownian particle in an aging bath

- **Violation of FDT quantifies broken detailed balance: heat $Q_{t,\infty}$ that must flow from particle to bath in order to reach thermal equilibrium at T.**

$$\int_0^\infty \left[\langle |\hat{x}(f,t)|^2 \rangle - \frac{2k_B T}{\pi f} \mathrm{Im}\{\hat{R}(f,t)\} \right] \mathrm{d}f = \frac{2|\langle Q_{t,\infty} \rangle|}{k}.$$



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Analogy with GFDR for nonequilibrium steady states

- GFDR for Brownian particle in a **nonstationary** heat bath relaxing towards thermal equilibrium

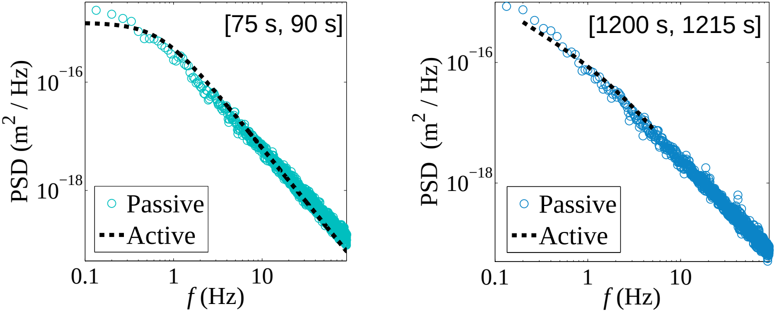
$$\int_0^{\infty} \left[\langle |\hat{x}(f,t)|^2 \rangle - \frac{2k_B T}{\pi f} \mathrm{Im}\{\hat{R}(f,t)\} \right] \mathrm{d}f = \frac{2|\langle Q_{t,\infty} \rangle|}{k}.$$

- GFDR for Brownian particle driven into a nonequilibrium **steady** state by a nonconservative force [Gomez-Solano et al., PRL 103, 040601 (2009)]

$$\partial_s \langle O(\theta_t) \phi(\theta_s) \rangle_0 - k_B T R(t-s) = \langle O(\theta_t) v_0(\theta_s) \partial_\theta \phi(\theta_s) \rangle_0.$$

Violation of FDT quantifies broken detailed balance: probability current, total entropy production.

- Relaxation to equilibrium-like behavior as the bath ages



- FDT apparently holds for $t \geq 20$ s because of the smallness of the total entropy production rate as t increases.

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Summary

- Measurement of energy fluctuations in a nonequilibrium system relaxing towards thermal equilibrium.
- Experimental setup allows one to perform very fast local quenches and probe the length and time scales of the nonequilibrium gelatin.
- Direct measurement of microrheological properties of the medium: three different aging regimes.
- Nonequilibrium assemblage of the gel probed by the Brownian particle: heat flux from particle to the surroundings.
- Spontaneous heat fluctuations satisfy FT even when the system is undriven and in a nonstationary state.
- Violation of FDT quantifies irreversible heat flux from particle to bath similar to GFDRs for NESS.

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Perspectives

- Detailed study of the gelation process of the quenched gelatin droplet by means of free Brownian tracers.
- Study of heat fluctuations in other kind nonstationary systems, e.g. glasses.
- Fluctuations and linear response in small complex systems far from equilibrium:
  - Interacting multiparticle systems.
  - Non-Markovian dynamics.

Thank you for your attention!