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Extended fluctuation-dissipation theorem for soft matter in stationary flow

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For soft matter systems strongly driven by stationary flow, we discuss an extended fluctuation-dissipation theorem (FDT). Beyond the linear-response regime, the FDT for the stress acquires an additional contribution involving the observable that is conjugate to the strain rate with respect to the dissipation function. This extended FDT is evaluated both analytically for Rouse polymers and in numerical simulations for colloidal suspensions. More generally, our results suggest an extension of Onsager's regression principle to nonequilibrium steady states.

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I. INTRODUCTION

The fluctuation-dissipation theorem (FDT) holding for all systems slightly perturbed around their equilibrium state is one of the cornerstones of equilibrium statistical physics [1]. Specifically, for a system coupled to a heat bath at temperature T and setting Boltzmann's constant to unity throughout the Rapid Communication,

$$TR_{A,h}(t-\tau) = \langle A(t)\dot{B}(\tau)\rangle \equiv C_{A\dot{B}}(t-\tau) \tag{1}$$

relates the response $R_{A,h}(t-\tau) \equiv \delta\langle A(t)\rangle / \delta h(\tau)$ of an observable A to a small perturbation h to equilibrium correlations. Crucially, these correlations involve the same observable A and the time-derivative $\dot{B}$ of another observable that is conjugated to the perturbation h in the sense that upon a perturbation the energy U of the system transforms as $U \mapsto U - Bh$. In a stationary state, due to time-translational invariance both response and correlation function can only depend on the difference $t-\tau > 0$. The physical picture behind the FDT can be expressed by Onsager's regression principle: the decay of fluctuations created by a small external perturbation cannot be distinguished from the decay of spontaneous thermal fluctuations.

Beyond the linear-response regime, the FDT in form (1) no longer holds. However, more than 30 years ago, Agarwal [2] noted that any stationary Markov process obeys a generalized FDT. This generalized FDT is obtained through linear-response theory of stochastic processes where the probability distribution $\psi(t)$ obeys $\partial_t \psi = \mathcal{L}\psi$ with some time evolution operator $\mathcal{L}$ [2,3]. In the presence of a perturbation, one can decompose the evolution operator $\mathcal{L} = \mathcal{L}_0 + h\delta\mathcal{L}$ into an unperturbed part $\mathcal{L}_0$ and a perturbation operator $\delta\mathcal{L}$. The stationary solution of the unperturbed system obeys $\mathcal{L}_0\psi_s = 0$. The generalized FDT then has the form of Eq. (1) with $\dot{B}$ replaced by $B^* \equiv T\psi_s^{-1}\delta\mathcal{L}\psi_s$. This form appears to be less useful than its equilibrium counterpart because the new conjugate variable B^* has no independent physically significant meaning. In order to equip the involved variables with such a physical interpretation, we can take the effect of the driving into account as an additive excess function. The general structure of such an extended FDT reads

$$TR_{A,h}(t) = \langle A(t)[\dot{B}(0) - \bar{B}(0)]\rangle \equiv C_{A\dot{B}}(t) - I_{A\bar{B}}(t). \tag{2}$$

Interpreted in the spirit of Onsager's regression principle, the FDT now states that the decay of forced fluctuations *out of a nonequilibrium steady state* cannot be distinguished from the decay of spontaneous fluctuations *around* $\bar{B}$. Such a statement becomes physically significant only if the variable $\bar{B}$ carries a transparent physical meaning as an observable. One purpose of the present Rapid Communication is to show that for shear flow driven soft matter systems governed by stochastic dynamics, the extended FDT [Eq. (2)] acquires such a transparent form: for a perturbation caused by a change in the strain rate the observable $\bar{B}$ becomes the stress that is conjugated to the strain rate with respect to the dissipation function, the mean of which is related to the total entropy production. Such a characterization generalizes the identification of $\bar{B}$ as the local mean velocity in our previous study of a driven Langevin-type dynamics with h a small additional force [4]. A change in the frame of reference from the laboratory frame to the frame moving with this local mean velocity then restores the equilibrium form of the FDT [4,5]. The extended FDT in its integrated form leads to an experimentally tested generalized Einstein relation [6].

Our approach is complementary to the strategy of introducing an effective temperature to restore the equilibrium form (1) of the FDT even in nonequilibrium. The latter approach has been developed over the last decade for systems with a small heat flow into the reservoir corresponding to a small entropy production rate [7–10]. With such an effective temperature concepts from equilibrium statistical mechanics could be applied to driven systems even though a full microscopic understanding on the range of validity of this concept does not seem to have been reached yet.

For the restricted but paradigmatic class of shear driven systems on which we will focus, quantitative progress has been achieved using the framework of mode-coupling theory. This includes the constitutive equation [11] using integration through transients [12] and an FDT for the diffusion of a tagged particle [13]. Invariant quantities [14] constitute an exact result for systems driven through the boundaries with

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an unchanged bulk Hamiltonian, whereas in this Rapid Communication the system is driven through an imposed external flow.

II. SOFT MATTER UNDER SHEAR

We consider soft matter systems such as colloidal suspensions or polymers that can be described as N interacting Brownian particles. The system is driven into a nonequilibrium steady state by shearing with a strain rate γ, resulting in an imposed flow profile $\mathbf{u}(\mathbf{r})=\gamma y\mathbf{e}_x$ of the solvent with unit vector $\mathbf{e}_x$. Picking out the ith particle, the force exerted by all other particles is $\mathbf{F}_i\equiv-\nabla_i U$, where the potential energy $U(\Gamma)=\Sigma_{(ij)}u(|\mathbf{r}_{ij}|)$ is given by the sum over all pairs (ij), with $\mathbf{r}_{ij}\equiv\mathbf{r}_i-\mathbf{r}_j$. The particles interact via an isotropic pair potential $u(r)$ and the set of particle positions is denoted as $\Gamma\equiv\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}$ [15].

The response of an observable $A(\Gamma)$ to a small time-dependent variation in the strain rate is $R_{A,\gamma}(t-\tau;\gamma)$, where the dependence on γ emphasizes that such a response can be defined for any steady state, not only for $\gamma=0$ corresponding to equilibrium. The mean $\langle A(t)\rangle\equiv\int d\Gamma A(\Gamma)\psi(\Gamma,t)$ involves the time-dependent probability distribution $\psi(\Gamma,t)$. The perturbation operator with respect to a small change in the strain rate is $\delta\mathcal{L}=-\Sigma_i y_i\partial/\partial x_i$. In the linear-response regime, the FDT

$$TR_{A,\gamma}(t-\tau;0)=\langle A(t)\sigma_{xy}(\tau)\rangle \tag{3}$$

relates the response to a correlation function involving the stress

$$\dot{B}=\sigma_{xy}=\sum_{(ij)}\frac{x_{ij}y_{ij}}{|\mathbf{r}_{ij}|}\frac{\partial u(|\mathbf{r}_{ij}|)}{\partial r}=-\sum_{i=1}^{N}y_i\mathbf{e}_x\cdot\mathbf{F}_i \tag{4}$$

due to particle interactions. The resulting generalized fluctuation-dissipation relation reads

$$TR_{A,\gamma}(t-\tau;\gamma)=\langle A(t)\sigma^*_{xy}(\tau)\rangle \tag{5}$$

with conjugate stochastic variable

$$\sigma^*_{xy}\equiv T\psi_s^{-1}\delta\mathcal{L}\psi_s=-\sum_{i=1}^{N}y_i\mathbf{e}_x\cdot T\nabla_i\ln\psi_s. \tag{6}$$

Applying the generalized Onsager principle by following Eq. (2), we split $\sigma^*_{xy}=\sigma_{xy}-\bar{\sigma}_{xy}$ into the stress [Eq. (4)] and

$$\bar{\sigma}_{xy}\equiv-\sum_{i=1}^{N}y_i\mathbf{e}_x\cdot\mathcal{F}_i, \tag{7}$$

which involves the thermodynamic force $\mathcal{F}_i\equiv-\nabla_i[U+T\ln\psi_s]$. Both stresses have the same mean $\langle\sigma_{xy}\rangle=\langle\bar{\sigma}_{xy}\rangle$. In equilibrium, $\bar{\sigma}_{xy}=0$ vanishes and hence Eq. (5) reduces to Eq. (3) as expected.

We now provide for $\bar{\sigma}_{xy}$ a clear physical meaning connecting it to the entropy production caused by the external flow $\mathbf{u}(\mathbf{r})$. For overdamped dynamics, the dissipation function [16]

$$\mathcal{W}(\Gamma,\{\mathbf{v}_i\};\gamma)=\frac{1}{2\mu_0}\sum_{i=1}^{N}[\mathbf{v}_i-\mathbf{u}(\mathbf{r}_i)]^2 \tag{8}$$

is related to the mean total entropy production rate through $T\langle\dot{s}_{\mathrm{tot}}\rangle=2\langle\mathcal{W}\rangle$ [17]. In a nonequilibrium steady state, the sum $\langle\mathcal{W}\rangle+\dot{\mathcal{A}}$ of mean dissipation function and time derivative of the "dynamical free energy" $\mathcal{A}\equiv\int d\Gamma\psi[U+T\ln\psi]$ attains a minimum with respect to the local mean velocities $\{\mathbf{v}_i\}$, which then obey $\mathbf{v}_i=\mathbf{u}(\mathbf{r}_i)+\mu_0\mathcal{F}_i$. A variation in $\mathcal{W}$ with respect to the strain rate leads to

$$\frac{\partial\mathcal{W}}{\partial\gamma}=-\frac{1}{\mu_0}\sum_{i=1}^{N}[\mathbf{v}_i-\mathbf{u}(\mathbf{r}_i)]\cdot\frac{\partial\mathbf{u}(\mathbf{r}_i)}{\partial\gamma}=\bar{\sigma}_{xy}.$$

In this sense, $\bar{\sigma}_{xy}$ is the variable conjugate to the strain rate γ with respect to the dissipation function in analogy to B being the variable conjugate to h with respect to the energy.

In the remainder of this Rapid Communication, we concentrate on response and correlation functions of $A=\dot{B}=\sigma_{xy}-\langle\sigma_{xy}\rangle$ and $\bar{B}=\bar{\sigma}_{xy}-\langle\sigma_{xy}\rangle$, e.g., $C(t)=\langle\sigma_{xy}(t)\sigma_{xy}(0)\rangle-\langle\sigma_{xy}\rangle^2$. To ease the notation we drop the subscripts denoting the observables. We first consider a Rouse polymer which allows for analytic expressions and then turn to numerical results for a colloidal suspension with nontrivial interactions.

III. ROUSE POLYMER

Analytic expressions for correlation and response functions can be obtained for systems with quadratic interaction energies of the form $U(\Gamma)=\frac{1}{2}\Sigma_\alpha k_\alpha\mathbf{q}_\alpha^2$ with amplitudes $\{\mathbf{q}_\alpha\}$ of normal modes. The stress through interactions is $\sigma_{xy}=\Sigma_\alpha k_\alpha x_\alpha y_\alpha$. Inserting the explicit form of ψ_s, Eq. (7) becomes

$$\bar{\sigma}_{xy}=\sum_\alpha\frac{k_\alpha}{1+\kappa_\alpha^2}(\kappa_\alpha^2x_\alpha y_\alpha+\kappa_\alpha y_\alpha^2). \tag{9}$$

A straightforward calculation [18] based on the Smoluchowski operator leads to a closed equation of motion for the correlation function

$$C(t)=T^2\sum_\alpha[1+\kappa_\alpha^2(3+2t/\tau_\alpha)]e^{-t/\tau_\alpha}, \tag{10}$$

where $\kappa_\alpha\equiv\gamma\tau_\alpha$ and $\tau_\alpha\equiv(2\mu_0k_\alpha)^{-1}$ is half the relaxation time of the corresponding mode. The response function $R(t)=T\Sigma_\alpha e^{-t/\tau_\alpha}$ is independent of the driving. The excess $I=C-TR\propto\gamma^2$ is a quadratic function of the shear rate. While such quadratic behavior is expected universally at small shear rates, for the Rouse polymer its persistence for large γ depends on the Gaussian form of ψ_s.

To obtain the universal expressions for a large number of modes, we replace the summation by an integration, $\Sigma_\alpha\mapsto\int_1^\infty d\alpha$, and set the relaxation times $\tau_\alpha=\tau_1/\alpha^2$, where the time scale is determined by the fundamental relaxation time τ_1. In addition, we consider integrated response $\chi(t)\equiv\int_0^t d\tau R(\tau)$ and correlation $K(t)\equiv\int_0^t d\tau C(\tau)$. In Fig. 1(a) the normalized integrated response $\chi(K)$ is plotted against the value of the correlation function (parametrized by time). If the equilibrium FDT [Eq. (3)] holds then this curve is a

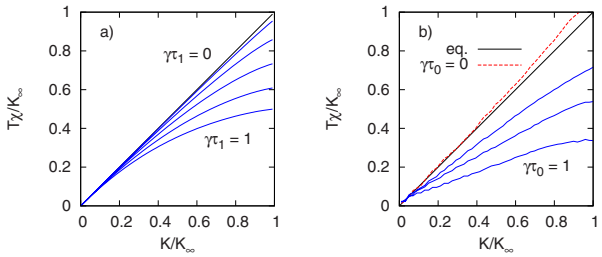

FIG. 1. (Color online) Integrated response χ vs integrated correlation function K for (a) a Rouse polymer and (b) a colloidal suspension (see main text). Both functions have been normalized by $K_\infty \equiv K(t\to\infty)$. The straight solid line corresponds to the equilibrium FDT [Eq. (3)].

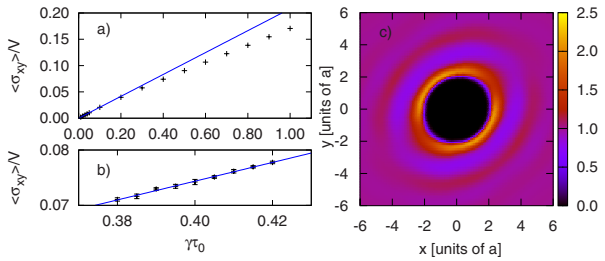

FIG. 2. (Color online) (a) Mean stress $\langle\sigma_{xy}\rangle$ of a colloidal suspension vs the strain rate γ. The solid line indicates the linear-response regime. (b) Mean stress in the vicinity of $\gamma\tau_0=0.4$. The solid line is a fit indicating the linear response of the nonequilibrium steady state. The error bars have been obtained as standard deviation by splitting the trajectory into eight segments. (c) Pair distribution function $g(\mathbf{r})$ for $\gamma\tau_0=1$ in the xy plane with $z=0$. For parameters, see main text.

straight line. For increasing strain rates the deviation, and therefore the excess, increases. Moreover, for the Rouse polymer no regimes with constant slope corresponding to an effective temperature can be discerned.

IV. COLLOIDAL SUSPENSION

We consider N colloidal particles with diameter a suspended in a fluid. We assume the particles to interact through a repulsive screened Coulomb pair potential,

$$u(r) = TZ^2\lambda_B \frac{e^{\kappa a}}{(1+\kappa a/2)^2}\frac{e^{-\kappa r}}{r}, \tag{11}$$

where $\lambda_B \simeq 7$ nm is the Bjerrum length in water at room temperature, Z is the effective surface charge, and κ^{-1} is the screening length.

Response and correlation functions are obtained through simulations of a sheared dilute colloidal suspension in a cubic box with side length $L=25a$ and volume $V=L^3$. We are interested in the bulk behavior, and therefore we employ periodic Lees-Edwards boundary conditions in the simulation. The particle number is $N=1000$ corresponding to a volume fraction of $\phi \simeq 0.034$. The screening length is set to $\kappa^{-1}=0.15a$ and the effective surface charge is $Z=12000$. The natural time scale $\tau_0 \equiv a^2/D_0$ is set by the time a particle needs to diffuse a distance equal to its diameter. To make contact with physical units, we choose $a=1$ μm. In Fig. 2(a), the mean stress is shown for different Péclet numbers $\gamma\tau_0$. The straight line indicates the linear-response behavior. The deviation of the mean stress from this line for large strain rates corresponds to shear thinning of the suspension [19]. Mean values and correlation functions are obtained from single runs with constant strain rate. The response function is determined as $R(t)=\partial_t\langle\sigma_{xy}(t)\rangle/\varepsilon$ after a jump $\gamma\mapsto\gamma+\varepsilon$ of the strain rate. Figure 2(b) shows the linear response of the nonequilibrium steady state corresponding to $\gamma\tau_0=0.4$. In the simulation, we have chosen a step of $\varepsilon\tau_0=0.01$.

The strong violation of the FDT can been seen in Figs. 3(a)–3(c), where response and correlation functions are plotted as functions of time for equilibrium ($\gamma=0$) and two driven nonequilibrium steady states. For increasing strain rate, the deviation of the correlation function $C(t)$ from the response function $R(t)$ becomes larger, too. In Fig. 1(b), the normalized integrated response $\chi(K)$ is shown as function of the integrated correlations. The small deviation between response and correlation function in Fig. 3(a) is responsible for the fact that in Fig. 1(b) the equilibrium curve for $\gamma=0$ lies slightly above the expected straight slope. Overall, the structure is comparable to the Rouse polymer in Fig. 1(a). Following Ref. [7], one might even be tempted to identify a linear slope in the intermediate range corresponding to an effective temperature even though this is not the focus of the present work.

V. APPROXIMATE EXCESS FUNCTION

So far, we have obtained the excess as difference $I=C-TR$. In principle, we need the complete distribution $\psi_s(\Gamma)$ to determine I independently using Eq. (7). Such complete information is, however, neither available experimentally nor in computer simulations. Hence, approximate schemes will become important in future applications of the extended FDT. As a first step, we discuss here an approximation to $\bar{\sigma}_{xy}$. Since the suspension is homogeneous, the one-point density $\rho^{(1)}(\mathbf{r}_1)=\rho=N/V$ is constant and the two-point density,

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int d\mathbf{r}_3\cdots d\mathbf{r}_N \psi_s(\Gamma) \equiv \rho^2 g(\mathbf{r}),$$

becomes a function of the displacement $\mathbf{r}\equiv\mathbf{r}_1-\mathbf{r}_2$ only. The factor $N(N-1)$ accounts for the possible permutations of the identical particles. The pair distribution $g(\mathbf{r})$ as obtained from the simulation for the parameters introduced above is shown in Fig. 2(c) (for hard spheres, cf. Ref. [20]).

We approximate the stationary distribution as $\tilde{\psi}_s(\Gamma)=\exp\{-\alpha\Sigma_{(ij)}w(\mathbf{r}_{ij})/T\}$ with potential of mean force $w(\mathbf{r})\equiv -T\ln g(\mathbf{r})$ [19]. This approximation effectively factorizes the probability distribution by using the correct pair correlations and neglecting correlations between three and more particles. It is motivated by the fact that the stress is determined by pair interactions only. In the parameter range we have studied we found $\alpha\simeq 0.5$. Inserting the pair approximation into Eq. (6) leads to

$$\tilde{\sigma}^*_{xy} = \alpha\sum_{(ij)} y_{ij}\frac{\partial w(\mathbf{r}_{ij})}{\partial x_{ij}} + \text{const.} \tag{12}$$

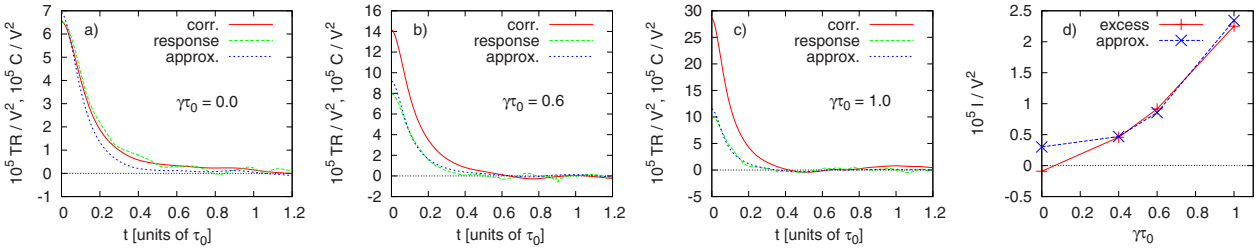

FIG. 3. (Color online) Correlation function $C(t)$, response function $R(t)$, and approximated response function $\tilde{R}(t)$ over time for (a) equilibrium and [(b)–(c)] two different nonequilibrium steady states. (d) Comparison of integrated excess (through $I=C-TR$) and integrated approximated excess [using Eq. (12)] vs strain rate.

The constant offset is adjusted for every strain rate such that $\langle\tilde{\sigma}^*_{xy}\rangle=0$. We also employ a cutoff taking into account only neighboring particles within the first shell. Using this approximation, we can then both calculate the response function through Eq. (5) and access the stress [Eq. (7)] in the simulation. In Figs. 3(a)–3(c) the approximated response function $\tilde{R}(t)$ is shown together with $R(t)$ and the correlation functions. In Fig. 3(d), both the integrated excess $\int_0^\infty d\tau I(\tau)$ as well as the integrated approximate excess based on Eq. (12) are shown for different strain rates. For moderate to large strain rates, the pair approximation works quite well. In the limit of vanishing strain rate, even though the volume fraction of the colloidal particles is low, the potential of mean force still deviates from the pair potential resulting in a breakdown of this type of approximation for equilibrium.

VI. CONCLUDING PERSPECTIVE

For strongly driven soft matter systems, we have discussed an extended FDT. Beyond the analytical and numerical data for two case studies, our general insight is twofold. First, beyond the linear-response regime, the FDT acquires an additive contribution which involves the stress that in the dissipation function is conjugate to the strain rate. This result suggests more generally that the nonequilibrium form of the FDT involves the observable that is conjugate to the perturbation in the dissipation function. Such a scheme could be analogous to the pairing of observables conjugate with respect to energy in the equilibrium form of the FDT. Second, the additive contribution allows an interpretation in the spirit of Onsager's regression principle: the decay of a spontaneous fluctuation around a nonequilibrium steady state cannot be distinguished from the decay of a fluctuation forced by a small external perturbation. Whether these observations can be generalized to an even larger class of nonequilibrium systems remains to be investigated both by further case studies and, more ambitiously, by an attempt to formulate a more formal theory for nonequilibrium steady states along these lines.

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