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Statistical mechanics far from equilibrium: Prediction and test for a sheared system

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We report the application of a far-from-equilibrium statistical-mechanical theory to a nontrivial system with Newtonian interactions in continuous boundary-driven flow. By numerically time stepping the force-balance equations of a one-dimensional model fluid we measure occupancies and transition rates in simulation. The high-shear-rate simulation data reproduce the predicted invariant quantities, thus supporting the theory that a class of nonequilibrium steady states of matter, namely, sheared complex fluids, is amenable to statistical treatment from first principles.

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Complex fluids relax slowly so their structure is radically reordered by flow, as in shear-aligning liquid crystals [1], jamming suspensions [2], or liposome creation [3]. In processing and using complex fluids, a state of flux is the rule rather than the exception, e.g., molten plastic flowing into a mold, blood flowing within capillaries, or grease lubricating a rotating axle. Under continuous shear flow, these systems exhibit statistically steady states with intriguing similarities to equilibrium phase behavior. For example, in "shear banding" of wormlike micelles [4,5], the fluid itself partitions the applied shear into a region of low-viscosity *oriented* material at high strain rate, coexisting with a slower more viscous region. The parameters controlling this structural phase transition include shear rate in addition to temperature and concentration.

Sheared fluids consist of particles following the same Newtonian equations of motion as at equilibrium since no field is applied to drive them; only the boundary conditions differ. Nevertheless, they violate equilibrium statistical mechanics [6]. Without knowledge of the fundamental statistical principles governing nonequilibrium Newtonian systems (notwithstanding nonequilibrium generalizations of *thermodynamics* [7] and the appealing concept of a nonequilibrium temperature [8]), models of driven fluids typically employ simplified artificial dynamics [9], assumptions about microscopic noise or rates [10], or near-equilibrium approximations [11]. Equivalently, it has become a common practice to assume that noise obeys the *equilibrium* fluctuation-dissipation theorem (FDT) or some other *ad hoc* criterion (such as colored noise). Only the distributions of entropy and work have been rigorously analyzed for realistic systems [12–15].

A system's dynamics can be fully summarized by a set $\{\omega_{ab}\}$ of transition rates between every possible pair of microstates a and b that the system can adopt. Here, ω_{ab} is the probability per unit time that the system, currently in microstate a, will be found in microstate b an instant later (so $\omega_{ab}=0$ for transitions that would violate the laws of motion). In the presence of random impulses from a heat bath, the latter microstate is not uniquely determined. Thus, the set $\{\omega_{ab}\}$ describes *both* the system's dynamics *and* the probability distribution of forces from the reservoir.

Arbitrary invention of the rates is forbidden for equilibrium models, by the principle of detailed balance (DB), which states that, due to the statistical properties of an equilibrium heat bath, the ratio of forward to reverse transition rates between any pair of microstates must equal the Boltzmann factor of their energy difference, $\omega_{ab}^{\text{eq}}/\omega_{ba}^{\text{eq}}=\exp(E_a-E_b)$, with microstate energies E_i measured in units of the thermal energy k_BT. (Equivalently, in a Langevin description of the equilibrium dynamics, the added noise must obey a FDT [16].) One might expect rules to exist also in sheared fluids. Indeed, a nonequilibrium counterpart to DB (NCDB) was recently derived [17–19] by considering a macroscopic region of fluid under shear, *the system*, embedded in a larger volume of the same sheared fluid, which acts as a *heat bath* or *reservoir* and exerts time-dependent random stresses on the system's boundary, with a nonzero mean. The statistics of this *nonequilibrium* heat bath yield DB-like constraints on the rates $\{\omega_{ab}\}$ of stochastic events in the system (the NCDB). Those constraints are clearly important, as they represent a nonequilibrium extension to the theory of statistical mechanics. Of course, no theory can describe *all* nonequilibrium steady states since such states are even more diverse than equilibrium ones. Systems to which NCDB does *not* apply include molecular motors, convection cells, granular media, and traffic flow. It *is* hypothesized to govern the microscopic stochastic dynamics of every continuously sheared fluid with nondiverging correlation length. The theory has particular relevance for the nontrivial sheared states of complex fluids since their preferred macrostates are radically altered by shear flow. Here, we report a numerical test of that theory.

The predictions of NCDB [18,20] that we test are some remarkably simple relationships between the transition rates in a fluid in contact with the sheared nonequilibrium reservoir, and the same fluid (with the same equations of motion) in contact with an equilibrium reservoir. The relationships are expected to be valid arbitrarily far from equilibrium and apply to any state space with arbitrary connectivity between any set of microstates:

(1) The total exit rate from any given microstate differs from its equilibrium value by a shear-rate-dependent constant that is the same for all microstates, i.e., $\Sigma_b(\omega_{ab}-\omega_{ab}^{\text{eq}})=Q\ \ \forall a$.

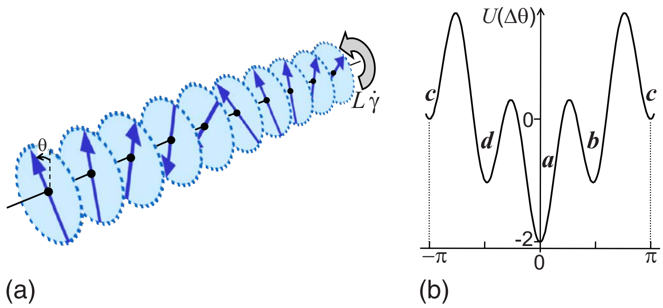

FIG. 1. (Color online) (a) The one-dimensional rotor model of length L. Each of the L rotors is characterized by its angle θ and angular velocity $\dot{\theta}$. (b) The potential of interaction between neighbors, $U(\Delta\theta)=-\cos\Delta\theta-\cos 4\Delta\theta$, a symmetric periodic function of their angular difference $\Delta\theta$, with four wells, labeled a,b,c,d.

(2) The product of forward and reverse transition rates is the same in the equilibrium and sheared ensembles, i.e., $\omega_{ab}\omega_{ba}=\omega_{ab}^{\mathrm{eq}}\omega_{ba}^{\mathrm{eq}}\ \forall a,b$.

In common with early tests of equilibrium statistical mechanics, we use an idealized one-dimensional model since, for reasons discussed below, acquisition of statistically significant data is a formidable task even in the simplest cases. The model is nevertheless capable of exhibiting complex behavior [21] mimicking inhomogeneous flow regimes of real complex fluids. For simplicity, in the present study we visit only the regime of homogenous mean flow.

Unlike other idealized models, designed for the measurement of macroscopic observables such as heat flux [22], the system in this case must not be defined in terms of a set of notional DB-respecting rates, as the rates are what we want to *measure*. Our test system is a one-dimensional model "fluid" of rotors [see Fig. 1(a)], each interacting with its neighbors via torsional forces, and *respecting Newton's laws of motion*. The angular acceleration of each rotor (with moment of inertia I) is proportional to its net unbalanced torque, which is the difference between the torques applied by its two neighbors: $I\ddot{\theta}_i=\tau_i-\tau_{i-1}$. The torque $\tau_i=\tau_i^{\mathrm{c}}+\tau_i^{\mathrm{d}}+\tau_i^{\mathrm{r}}$ between rotors i and $i+1$ has three contributions: conservative, dissipative, and random. The conservative part τ_i^{c} is the gradient of the four-well potential $U(\Delta\theta_i)$ shown in Fig. 1(b), which is a function of the angular difference between the rotors $\Delta\theta_i=\theta_{i+1}-\theta_i$. Thus, the model's zero-temperature equilibrium ground state has all rotors parallel, but antiparallel and perpendicular configurations are also moderately favorable. The uncorrelated random contribution to the torque τ_i^{r} (representing any microscopic degrees of freedom that are independent of shear strain, e.g., Brownian forces from solvent molecules) has a uniform distribution with zero mean, and width $\sigma/\sqrt{\Delta t}$ (that scales with time step Δt in the usual way for a stochastic force). The dissipative part τ_i^{d} is proportional to the difference between the rotors' angular velocities, with a constant of proportionality Γ playing a role akin to solvent viscosity in a complex fluid. Neighbors experience equal and opposite torques, so that angular momentum is exactly conserved in the model. The boundary conditions are periodic, and the equations of motion are numerically time stepped.

As described thus far, this is an equilibrium model. Once initial transients have died away, it exhibits Boltzmann statistics in the occupancies of the potential $U(\Delta\theta)$. At sufficiently low noise strength, the relative angles between neighbors are mostly confined close to the local potential minima, with only occasional transitions between potential wells. The *measured* rates of those transitions respect DB. Note that DB is not imposed *a priori*; it emerges from the dynamics at equilibrium.

We model a fluid under (angular) shear by *twisting* the model [see Fig. 1(a)]. The twist is imposed via the periodic boundary condition by introducing an offset in the angle measured between rotors on either side of the boundary and increasing that offset linearly in time, at a rate $L\dot{\gamma}$, so that the twist rate per rotor is $\dot{\gamma}$. Thus, the angle between boundary rotors is defined to be $\Delta\theta_L\equiv L\dot{\gamma}+\theta_1-\theta_L$. This is an angular analog of the Lees-Edwards boundary condition [23]. It has almost the same effect as holding rotor 1 fixed and continuously twisting rotor L but, as with ordinary periodic boundaries, our condition avoids introducing edge effects. Rotors 1 and L experience the same conditions as any other rotor.

To apply NCDB, some region of the model must be defined as the system, while the large remainder is the reservoir, supplying unpredictable nonequilibrium forces to it. The system should be much larger than any correlation length to ensure *weak* coupling to an *uncorrelated* reservoir. Unfortunately, a large system implies a high-dimensional phase space (θ and $\dot{\theta}$ for each rotor), so that acquiring a statistically significant sample of all the transition frequencies becomes prohibitively time consuming (this was also our motivation, alluded to above, for choosing as simple a model as possible). We take two steps to reduce the size of the phase space. First, we take the limit of small moment of inertia, so that momenta are no longer independent, and the phase space reduces to the set of inter-rotor angles $\Delta\theta$. This has the added advantage, in a one-dimensional force chain, of reducing the correlation length to zero since, with vanishing rate of change of angular momentum, the torques now balance globally ($\tau_i=\tau_{i-1}\ \forall i$). We are therefore able, second, to treat every inter-rotor gap (with its single characteristic variable $\Delta\theta$) as a system, each surrounded by a nonequilibrium reservoir. Note that NCDB is expected to apply to systems with nonvanishing correlation lengths, but we are compelled to examine a special case only to make data acquisition feasible.

To obtain data on the rates of transitions between potential wells in our stochastic model, we have numerically integrated the force-balance equations forward in time. Those equations can be expressed, in terms of the spatially constant torque $\tau_i=c$, as $U'(\Delta\theta_i)+\Gamma\Delta\dot{\theta}_i+\tau_i^{\mathrm{r}}=c$. In the absence of inertia, the friction coefficient Γ can be set to unity without loss of generality, leaving the noise strength σ and shear rate $\dot{\gamma}$ as the model's only parameters. The constant c is determined from the constraint $\Sigma_{j=1}^{L}\Delta\dot{\theta}_j=L\dot{\gamma}$ that follows from the boundary condition, giving

$$\Delta\dot{\theta}_i=\dot{\gamma}-U'(\Delta\theta_i)-\tau_i^{\mathrm{r}}+\frac{1}{L}\sum_{j=1}^{L}\left[U'(\Delta\theta_j)+\tau_j^{\mathrm{r}}\right].$$

This was numerically time stepped using a simple Euler scheme, $\Delta\theta(t+\Delta t)=\Delta\theta(t)+\Delta\dot{\theta}(t)\Delta t$, with a time step chosen to be $\Delta t = 10^{-4}$, which was found to be sufficiently small that all results are independent of it. Data are reported for a number of rotors L between 200 and 400. To check for finite-size effects, at many different values of σ and $\dot{\gamma}$, simulations were repeated with different values of L in this range and the results were found to be independent of the system size. To ensure steady-state behavior, each simulation was run for a time t of order 3000 before data were collected, well in excess of the duration of any observed starting transients. Data were subsequently collected until at least a few hundreds of the slowest transitions had been observed. The durations of the simulations therefore depended strongly on the parameter values.

We first analyze the predicted relationship between total exit rates. The required quantity $\Sigma_b \omega_{ab}^{\mathrm{eq}}$ implicitly depends on the unknown temperature of the compared equilibrium system. However, we can eliminate that unknown by appealing to a symmetry of $U(\Delta\theta)$ [Fig. 1(b)]. Since wells b and d are identical at equilibrium, they have equal total exit rates, $\omega_{ba}^{\mathrm{eq}} + \omega_{bc}^{\mathrm{eq}} = \omega_{da}^{\mathrm{eq}} + \omega_{dc}^{\mathrm{eq}}$. So relationship (1) predicts them also to have equal total exit rates in the driven case: $\omega_{ba} + \omega_{bc} = \omega_{da} + \omega_{dc}$ *for all* imposed shear rates $\dot{\gamma}$. This equality is not obvious since the equilibrium symmetry is broken in the driven case, where one of the potential wells is upstream of the other. Measurements of the four rates in question are plotted against shear rate in Fig. 2(a) for a particular noise strength. The rates vary considerably with $\dot{\gamma}$ and depart significantly from their equilibrium values. Nevertheless, the ratio of sums, as anticipated, remains very close to unity.

Next we test the second predicted relationship, between products of rates. Again, we exploit the symmetries of the hypothetical equilibrium state to obtain a relationship between the measured rates in the actual driven system only. At equilibrium, symmetry of $U(\Delta\theta)$ (together with DB) implies $\omega_{ab}^{\mathrm{eq}} = \omega_{ad}^{\mathrm{eq}}$ and $\omega_{ba}^{\mathrm{eq}} = \omega_{da}^{\mathrm{eq}}$. Substitution into the proposed relationship (2) implies a constraint on the measured rates in the driven system: $\omega_{ab}\omega_{ba} = \omega_{ad}\omega_{da} \;\; \forall \dot{\gamma}$. This prediction is tested in Fig. 2(b): as before, while the individual rates vary significantly across the range of driving speeds, the prediction is obeyed to an excellent approximation. Similarly, the equilibrium symmetry about well c gives rise to a third nonequilibrium prediction, $\omega_{cd}\omega_{dc} = \omega_{cb}\omega_{bc} \;\; \forall \dot{\gamma}$, verified in Fig. 2(c).

To quantify the accuracy of the nonequilibrium theory across the model's whole parameter space, contours of the measured ratio $(\omega_{ba} + \omega_{bc})/(\omega_{da} + \omega_{dc})$ are plotted in Fig. 2(d). The NCDB theory predicts a value of unity everywhere and, significantly, our measurements are *close* to unity for all values of the model's parameters, even at high shear rates $\dot{\gamma}$ where we have driven the model very far from equilibrium. The small but not negligible discrepancies between theory and data may indicate that the ergodic hypothesis, on which NCDB relies, fails at low noise strength σ. The theory shares this hypothesis with equilibrium statistical mechanics, which also fails for low-temperature nonergodic systems such as glasses. Alternatively, the discrepancies may be due to an unavoidable imperfection in our test: NCDB applies to transitions between microstates, whereas we measure the rates of transitions between potential wells a, b, c, and d that cover a finite range of angles. If these four *continuous sets* of microstates are sufficiently analogous to true microstates, then

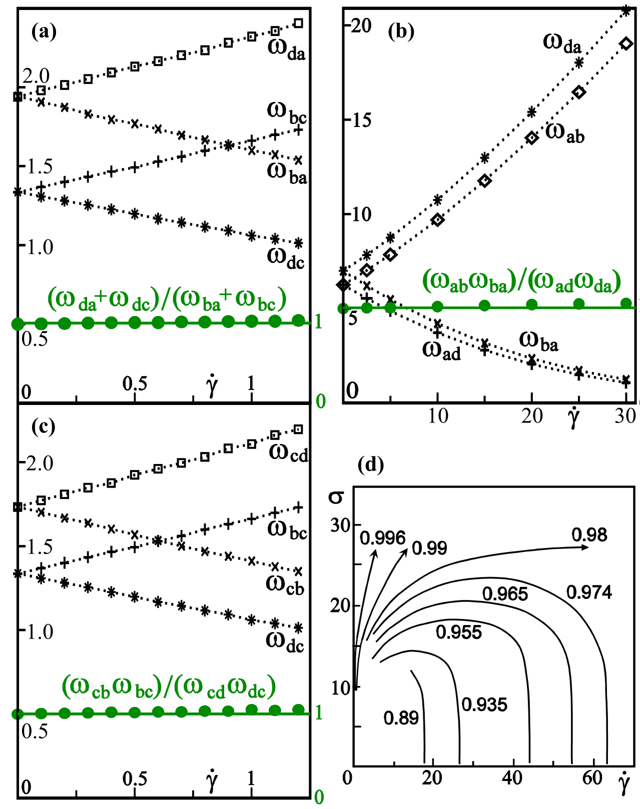

FIG. 2. (Color online) (a) Test of the prediction $\omega_{da} + \omega_{dc} = \omega_{ba} + \omega_{bc} \;\; \forall \dot{\gamma}$ with noise strength $\sigma = 10$. The left-hand ordinate measures rates, using the same units as the abscissa, while the right-hand ordinate measures the dimensionless ratio. (b) Test of the predicted relationship $\omega_{ab}\omega_{ba} = \omega_{ad}\omega_{da} \;\; \forall \dot{\gamma}$, with $\sigma = 20$. At this higher noise strength, higher shear rates are numerically accessible because of the greater number of observed backward transitions. (c) Test of the prediction $\omega_{cd}\omega_{dc} = \omega_{cb}\omega_{bc} \;\; \forall \dot{\gamma}$, for the same parameters as in (a). (d) Contours of the measured ratio $(\omega_{ba} + \omega_{bc})/(\omega_{da} + \omega_{dc})$, predicted to be unity across the whole parameter space of shear rate $\dot{\gamma}$ and noise strength σ. Data acquisition time limited simulations in the bottom left-hand corner. See supplementary material for more data [24].

the theory applies to transition rates between the potential wells in our model. Subject to that qualification, the nonequilibrium rotor model can be used to test the theory's predictive power. Although the model constitutes an imperfect test, preventing us from drawing rigorous conclusions as to the exactness of the theory in this case, NCDB performs strikingly well here. Importantly, the discrepancies between measurements and theory do not increase with $\dot{\gamma}$, confirming that NCDB is not a near-equilibrium approximation. We can conclude that the theory is either exact or at least captures much of the statistical physics of sheared systems, exceeding the predictive power of approximate methods.

While the logistics of data acquisition have restricted our study of the rotor model to the zero-mass zero-correlation-length limit, NCDB is expected to apply to the more general case with momentum degrees of freedom, thus encompassing phases with nonzero correlation lengths as well as nonzero correlation times as exhibited here. However, even the testable model studied here exhibits highly nontrivial behavior, in reasonable agreement with the nonequilibrium statistical-mechanical theory. Our results support the proposal that NCDB governs the steady-state motion of sheared systems on which work is done by a weakly coupled ergodic nonequilibrium reservoir. These findings are significant since such systems include all flowing complex fluids, whose phenomenology is as important to future technologies as it is to our understanding of nonequilibrium physics.

A proper appreciation of the rules governing stochastic dynamics in sheared complex fluids will give us the potential to explain the universal features of nonequilibrium phenomena, like the jamming transition, on an equal footing with equilibrium phase transitions. With this improved understanding we may find, for instance, the origin of the very high effective temperature required to model soft glassy materials in flow [25], or predict complex nonequilibrium phenomena such as shear banding from variational principles rather than macroscopic constitutive relations and interfacial properties [5]. Indeed, models created using the correct rates will predict *all* fluid properties (e.g., viscoelastic moduli, birefringence, dielectric susceptibility, universality class, etc.) with a veracity that is unattainable by models that incorrectly treat the effects of global shear on local activated processes. Moreover, since DB is the foundation on which equilibrium statistical mechanics rests, discovering the principles that replace DB away from equilibrium *should* be the most pressing topic of investigation for statistical physicists. In this paper, we have brought data to that debate.

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