How Far is Far from Equilibrium? A Deeper Understanding in the Presence of Noise

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Nonequilbrium systems have both fundamental and technological interest as they usually provide a richer behavior than their equilibrium counterparts. For example, driven systems are those acted on by a time-dependent generalized force. In spite of the present research interest in nonequilibrium systems across different scientific disciplines, little research effort has been devoted to the diagnosis of how far a system has been pulled away from its equilibrium state. Addressing such an issue is both scientifically and technologically relevant, as well as challenging. Understanding how far a system has moved away from its equilibrium state benefits not only the overall understanding of driven systems, but also equilibrium ones.

Consider a particle of mass m in contact with a heat reservoir, at temperature T, evolving in a basin of attraction provided by a potential $V(x)$. The coupling to the heat reservoir is achieved using the well-known Langevin dynamics [1]. Langevin dynamics adds a noise term to Newton's equation of motion so that the dynamics accounts for the presence of the heat reservoir. Two initial conditions, namely, $x(0) \equiv \mathrm{x}_0$ and $\dot{x}(0) \equiv \dot{x}_0$, are required to describe the motion of the particle. Let us consider a parabolic potential depicted in Fig. 1 by the solid line with a natural frequency ν_0. Now, consider two trajectories $x_1(t)$ and $x_2(t)$ evolving according to Langevin dynamics. It has been shown [1] that if the provided random noise sequence is common to both trajectories, they merge into a single trajectory, the so-called master trajectory. This *synchronization* effect is illustrated in Fig. 2a for a pair of undriven trajectories.

Now consider the case of a particle being kept away from its equilibrium state under the influence of a time-dependent parabolic potential basin with an initial frequency ν_i. The rate at which the initial frequency changes in time sets a natural time scale that we denote as the driving rate, α. Similar to the static trajectories, Fig. 2b shows a schematic of a pair of driven trajectories also merging into a (driven) master trajectory. We were able to obtain an exact, closed-form, analytical solution for the case of a pair of trajectories in a time-dependent parabolic potential. At the instant the frequency of the driven system takes the value ν_0 at time t^*, one can also measure the mismatches between the driven and undriven (master) trajectories. Of course, one does not expect the driven and undriven master trajectories to exactly coincide at t^*, so this mismatch represents a measure of how far the driven system has been pulled away from its equilibrium state as it crosses ν_0. One expects the synchronization level to be dependence on the driving rate, a. The idea can easily be grasped by noticing that at vanishingly small driving rates, the synchronization level must match that of a static system. The dependency on the driving rate α can actually be observed in the log-log plot shown in Fig. 3, where the mismatch in the synchronization increases with increasing values of the driving rate. At high driving rates, comparable to the natural frequency ν_0 of the basin, nonlinear terms become relevant.

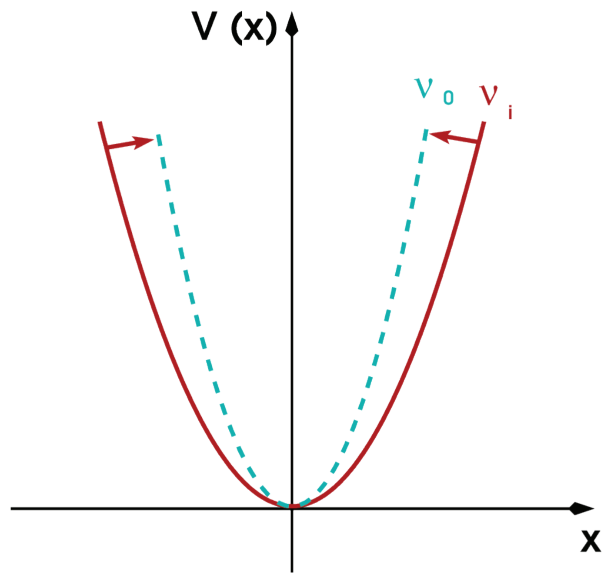

Fig. 1. Plot of the parabolic potential. The dashed line represents the potential felt by a static system of frequency ν_0. The time-dependent potential has an initial frequency ν_i (solid line) and crosses the ν_0 value (dashed line) at time t^*.

In summary, studying the synchronization of pairs of trajectories evolving accordingly to Langevin dynamics and sharing the same noise sequence allows an understanding of the timescale required for their thermalization in a particular basin, as well as the degree of departure from equilibrium for a driven system. As Fig. 3 shows, for driving rates comparable to the natural frequency of the basin, nonlinear terms become relevant, which can help define more elaborate ways to classify departure from equilibrium. Even at extremely low driving rates, there is deviation from perfect equilibrium, which we can quantify with this approach. We are also exploring the connection between this disruption of synchronization and the deviations in the instantaneous rate constants in the system. This in turn will give us a simple way to quantify and control errors in the application of parallel replica dynamics [2] to driven systems [3]. In driven parallel replica dynamics, it is assumed that there are well-defined instantaneous rate constants that are independent of the driving rate. Finally, we point out that the present methodology can be straightforwardly extended to more realistic systems with complex potentials and larger numbers of particles.

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[3] B.P. Uberuaga et al., *J. Chem. Phys.* **120,** 6363 (2004).

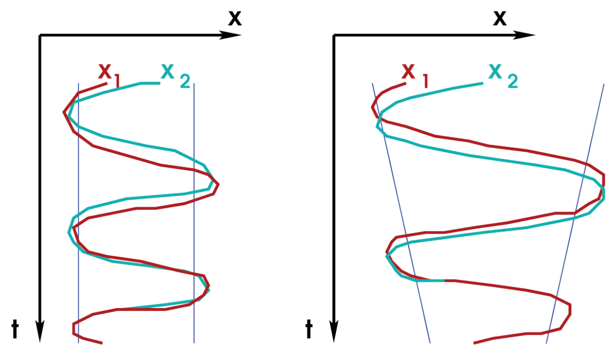

Fig. 2. Schematic examples of pairs of trajectories merging into a master trajectory for the (a) time-independent and (b) time-dependent potentials. Jagged lines represent a way of cartooning the effect of Langevin dynamics. Both the static and driven pairs of trajectories synchronize into a master trajectory at a time $t_s < t^*$. Notice that t_s does not have to be the same for the driven and static systems. The synchronization level is computed as the driven system crosses ν_0 at time t^*.

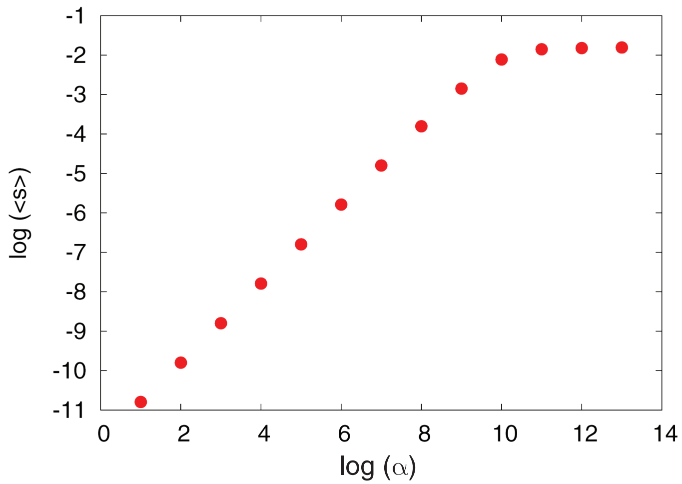

Fig. 3. Mismatch (deviation from perfect synchronization) between the positions of the driven and undriven trajectories $\nu(t) = \nu_0$, averaged over 10^4 pairs of trajectories. The coupling strength to the heat reservoir is $\gamma = 10^{12}\ s^{-1}$.

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