Time-Reversal Symmetry and Thermodynamic Forces

Dissipation affects the time asymmetry of fluctuations in systems out of thermodynamic equilibrium. A newly discovered inequality elucidates that connection.

By **Hyun-Myung Chun**

The emergent field of stochastic thermodynamics uses random variables to investigate the dynamics of microscopic systems that operate out of thermodynamic equilibrium, such as active matter and metabolic pathways. Now Naruo Ohga and two colleagues at the University of Tokyo have applied tools from stochastic thermodynamics to uncover a universal law that could find broad applications in the description of active matter, cell metabolism, and other systems whose continuous supply of energy keeps them out of equilibrium [**1**] (Fig. **1**.)

When a thermodynamic system is close to equilibrium, the fluxes of physical quantities, such as energy and electric charge, are linearly proportional to thermodynamic forces, such as temperature gradients and voltage differences. The coefficients connecting the fluxes and forces are symmetric, meaning that the one relating flux A to force B is the same as the one relating flux B to force A. Such symmetries are known as Onsager's reciprocal relations [**2**]. At the microscopic level, their origin can be attributed to the time-reversal symmetry of the cross-correlation function between two physical quantities at equilibrium.

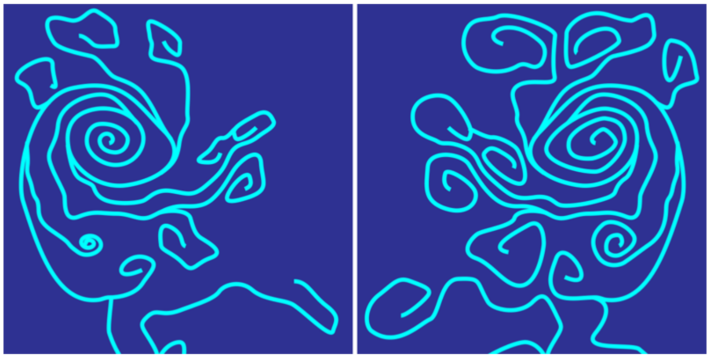

Figure 1: A system driven out of equilibrium breaks time-reversal symmetry, which is represented here by reflection symmetry.

Credit: APS/Alan Stonebraker

In the presence of significant thermodynamic forces, however, a system deviates from its equilibrium state, rendering Onsager's insight inapplicable. Time-reversal symmetry is broken, leading to various phenomena that are absent in equilibrium. The broken symmetry is manifested as incessant flows of physical quantities or state variables, and the resulting sustained dissipation keeps the system in a nonequilibrium steady state. In particular, the time-reversal symmetry of the cross-correlation function between two physical quantities is no longer preserved. The centrality of time-reversal symmetry raises an intriguing question: How does the extent to which symmetry is broken relate to the thermodynamic forces that drive the system out of equilibrium?

Ohga and his colleagues have addressed this question. Their new work has revealed the existence of an inequality between the asymmetry of cross-correlations and thermodynamic forces. This research combined established techniques from stochastic thermodynamics with their own innovative ideas. Other researchers applying stochastic thermodynamics have revealed universal laws—among them, fluctuation theorems that uncover symmetry in the statistics of entropy production [**3**] and thermodynamic uncertainty relations that uncover trade-offs between current fluctuations and dissipation [**4**]. Ohga and colleagues' recent discovery represents yet another fundamental law in the realm of nonequilibrium thermodynamics.

The dynamics of nonequilibrium open systems are often modeled as stochastic processes, in which randomness is introduced to describe the system's interaction with the fast-relaxing thermal environment. Ohga and colleagues focused on general nonequilibrium systems, which they modeled as a continuous-time Markov chain. (In a Markov chain the probability of a particle moving or other event depends only on the state of the previous event.) They arranged the events on a graph made up of a finite number of vertices, each representing mesoscopic states of the system. They then connected the vertices by edges that denote transitions between these states. In this description, thermodynamic forces can be identified by examining the imbalance of transition rates along opposite directions of cyclic sequences of events within the graph [**5**]. The presence of thermodynamic forces gives rise to unbalanced "currents" of transitions along cycles; the currents serve as indicators of broken time-reversal symmetry.

Ohga and colleagues introduced an ingenious idea into this concept: they represented the asymmetry of the cross-correlation function between two physical quantities as the area of a polygon in an auxiliary vector space. They went on to employ the isoperimetric inequality—a mathematical theorem that relates the area and perimeter of a polygon—to establish rigorous bounds on the degree of asymmetry. In doing so, they demonstrated that the extent of broken time-reversal symmetry, as quantified by the asymmetry of the cross-correlation function, is bounded from above by a monotonically increasing function of the strength of the thermodynamic forces.

The discovered inequality between the asymmetry of cross-correlations and thermodynamic forces has yielded remarkable outcomes. Ohga and colleagues have harnessed it to shed light on a seemingly unrelated problem concerning coherent oscillations in biochemical systems. The conjecture that the number of coherent oscillations is bounded by the chemical potential released from the hydrolysis of chemical fuel, such as ATP, has intrigued researchers but has until now remained unproven [**6**, **7**]. Through the use of their novel inequality and a clever selection of quantities involved in cross-correlations, Ohga and his colleagues have provided a proof of this conjecture, thereby elucidating how the thermodynamic cost limits the stability of the coherent oscillations. This surprising application of the inequality underscores both the inequality's power and its potential to uncover hidden connections across diverse scientific domains.

The fundamental bound on broken time-reversal symmetry carries broad implications. For example, odd viscosity and other anomalous transport coefficients of active matter are closely linked to the asymmetry of cross-correlations [**8**]. Active matter refers to a class of systems composed of self-propelled entities. The self-propulsion breaks the dynamics' time-reversal symmetry, introducing antisymmetric transport coefficients absent in equilibrium fluids. Ohga and his colleagues' work now provides a way of estimating the values of anomalous transport coefficients in terms of thermodynamic forces that drive active matter out of equilibrium, a development that holds both theoretical and practical significance.

Multiple avenues for future research can be envisioned. Generalizing the results to encompass stochastic processes with continuous system variables, and even quantum regimes, presents an exciting opportunity for future investigation. What's more, these possibilities pose challenges that transcend the graph-theoretical approaches employed by Ohga and colleagues.

Lastly, it is worth mentioning that the inequality for the asymmetry of cross-correlations has been derived under the condition of a short interval between the two times involved in cross-correlations. Extending the inequality to longer time intervals would be a valuable and challenging extension of the current work. Indeed, Ohga and his collaborators have already provided numerical evidence supporting this extension in their work's supplemental materials.

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