Far-From-Equilibrium Physics: An Overview

Heinrich Jaeger, James Franck Institute and Department of Physics, University of Chicago Andrea J. Liu, Department of Physics and Astronomy, University of Pennsylvania

Isolated systems tend to evolve towards equilibrium, a special state that has been the focus of many-body research for a century. Yet much of the richness of the world around us arises from conditions far from equilibrium. Phenomena such as turbulence, earthquakes, fracture, and life itself occur only far from equilibrium. Subjecting materials to conditions far from equilibrium leads to otherwise unattainable properties. For example, rapid cooling is a key process in manufacturing the strongest metallic alloys and toughest plastics. Processes that occur far from equilibrium also create some of the most intricate structures known, from snowflakes to the highly organized structures of life. While much is understood about systems at or near equilibrium, we are just beginning to uncover the basic principles governing systems far from equilibrium.

THE IMPORTANCE OF FAR-FROM-EQUILIBRIUM PHENOMENA

We live in a world of evolving structures and patterns. When energy is continually supplied to systems with many interacting constituents, the outcome generally differs strikingly from the unchanging state that characterizes equilibrium. From the molecular processes on the nanoscale that form the basis of life to the dynamically changing climate on this planet to the clustering of matter within the universe as a whole, a myriad of phenomena owe their existence to being not just slightly away from equilibrium, but far from it (Fig. 1). Far-fromequilibrium conditions also strikingly alter the behavior of ordinary fluids and solids. Dramatic examples occur when fluid flow turns turbulent or when solids give way and fracture (Fig. 2). Both turbulence (Falkovich et al. 2001) and fracture (Carlson et al. 1994; Freund 1998) generate patterns of amazing complexity that not only completely change the materials properties but also redistribute energy across a whole hierarchy of nested structures ranging from the microscopic to the macroscopic scale. Far-from-equilibrium processes span a similarly immense range of time scales, from electronic transitions at the sub-nanosecond scale, to glassy relaxation too slow to measure with any technique, to the age of the universe.

Far-from-equilibrium behavior is not confined to special conditions or certain types of materials. Instead, it arises across the entire spectrum of physics in a host of problems of fundamental interest. Far-from-equilibrium phenomena also benefit and plague us in technology and in everyday life (Ennis *et al.* 1994; Marder and Fineberg 1996) (Fig. 2).

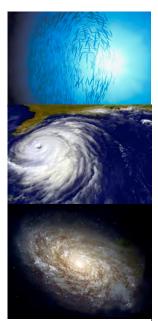


Fig.1. Swarming schools of fish, swirling storms and galaxies (top to bottom) are all examples of systems formed and evolving far from equilibrium. Indeed, some of the most complex outcomes of behavior far from equilibrium emerge in situations we are familiar with from daily experience. We can see turbulence in cloud patterns as well as in a bath tub; we take advantage of glassy behavior in nearly all plastics but suffer from it in traffic jams; we exploit the breaking-up of a stream of fluid into droplets with fuel injection and ink jet printing but also find it in every leaky faucet. The reach of far-from-equilibrium phenomena extends

even further to many systems of profound societal importance. In the last decade, researchers from the condensed-matter physics community have begun to tackle far-fromequilibrium behavior governing the workings of systems ranging from the economy to ecosystems and the environment (Wu and Loucks 1995; Ghashghaie *et al.* 1996; Mantegna and Stanley 2000; Sornette 2003; McCauley 2004; Moritz *et al.* 2005).

Two important themes define the scope of the challenge, and they run as persistent motifs through a description of the current status of physics far from equilibrium. First, *far-from*-





Fig.2. The need to control far-from equilibrium behavior. Top: Turbulent airflow produced by the wingtips of a small airplane (visualized by red smoke). Bottom: Disastrous effect of materials fatigue and eventual fracture.

equilibrium behavior is ubiquitous. The breadth of phenomena investigated makes the study of far-from-equilibrium systems an inherently interdisciplinary field that forges connections between the physics community and researchers in biology, chemistry, applied mathematics, geology, meteorology and engineering. Far-from-equilibrium physics is connected intimately to both fundamental scientific challenges and cutting-edge materials processing. Finally, far-from-equilibrium physics underlies a wide range of phenomena outside the traditional boundaries of condensed matter physics, including earthquakes, hurricanes, galaxy formation, and consciousness. As a result, breakthroughs in the area have potential for far-reaching impact.

The second key theme is that far-from-equilibrium behavior is not a simple extension of equilibrium or near-equilibrium physics. Instead, it corresponds to qualitatively different types of behavior and response, typically associated with crossing some threshold into a new regime. In some specific cases we have been able to unearth the microscopic origins of far-from-equilibrium phenomena, but we are still lacking the understanding necessary to develop more comprehensive frameworks. Therefore, despite its importance, *far-from-equilibrium behavior still remains largely uncharted territory*. The reasons why far-from-equilibrium phenomena often resist understanding are described below. The is followed by a discussion of problems for which we have been able to identify robust features, both in experiment and in theory, that can serve as starting points for future work. Except for small modifications and for the addition of references, this article corresponds to Chapter 5 of the CMMP2010 report released by the National Research Council (NRC *et al.* 2007). In order to provide entering researchers a starting point, we focused primarily on reviews, when available, in selecting the references. Clearly this

glosses over much of the relevant literature. For a more exhaustive treatment we ask the reader to turn to the more specialized reviews in the references.

What Condensed Matter Physicists Bring to the Table

Researchers trained in condensed matter physics are well-positioned to spearhead progress in the field of far-from-equilibrium behavior. As one of the forefront areas of interdisciplinary research, condensed matter physics has long been a focal point for new approaches that bring together ideas from physics and other science and engineering disciplines, and that connect basic science with applied research. Condensed matter physics also specializes in developing new theoretical, numerical, and experimental tools and techniques for systems of many interacting constituents. Experimental techniques that have been especially useful for probing far-from-equilibrium behavior include novel imaging tools, spectroscopic and particle tracking methods, and optical Many powerful theoretical and numerical techniques for studying the emergent tweezers. behavior of many-particle systems near equilibrium have been generalized to systems far from equilibrium; for example, techniques originally developed for studying magnets have been extended to the flocking of birds (Toner et al. 2005). Perhaps the field's most valuable characteristic, however, is its penchant for searching for commonalities in wildly disparate systems. This focus led to the spectacular success of condensed matter physics in realizing that the enormous variety of equilibrium phase transitions can be understood in terms of a few classes of behavior. This history motivates researchers to search for similar organizing principles in the even vaster array of far-from-equilibrium phenomena.

Far-from-equilibrium behavior is an important component in several of the challenges discussed in the CMMP2010 report (NRC *et al.* 2007). It underlies many emergent phenomena in systems ranging from the nanoscale to the macroscale, and it plays an essential role in the physics of living systems. Because many far-from-equilibrium phenomena require energy in order to be driven, they are also inevitably implicated in energy consumption and conversion. In quantum computing, the challenge is to prepare qubits in prescribed pure quantum states. Such systems are necessarily far from equilibrium. Finally, because far-from-equilibrium phenomena are so common in everyday life and underlie so many societal concerns, they provide a rich context for education and learning, for the next generation of scientists as well as for the general public.

HOW DO SYSTEMS REACH THE FAR-FROM-EQUILIBRIUM REGIME AND WHAT MAKES FAR-FROM-EQUILIBRIUM PHYSICS DIFFICULT?

One way to keep a system from its natural state of rest and push it into the far-from-equilibrium regime is to subject it to continual and sufficiently strong forcing. For example, the energy that continually strikes the earth from the sun gives rise to far-from-equilibrium behavior ranging from chaotic weather patterns to the staggering diversity of life. If solar energy were no longer supplied, many systems on earth would revert to equilibrium. Driven systems such as these not only give rise to rich and unanticipated phenomena but are also of tremendous importance to technological applications. For example, in molecular or nano-scale electronics, new phenomena arise from the response to large electromagnetic fields, currents and mechanical stresses

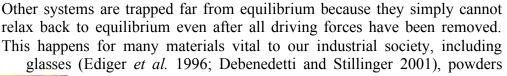
(Gaspard 2006). As one scales the physical dimensions of matter to the nanometer scale, the applied fields that drive the system away from its equilibrium state are amplified while the scattering that allows relaxation back to equilibrium is suppressed (Huang *et al.* 2007). As a result, such devices often operate in the far-from-equilibrium regime, unlike conventional semiconductor devices at the micron scale, which typically operate much closer to equilibrium. On somewhat larger scales, far-from-equilibrium processes such as grinding and milling have

been key to many industries for a long time, and newer techniques such as mechanical alloying of powders are gaining attention for novel materials synthesis (Murty and Ranganathan 1998; Suryanarayana 2001).

Conditions far from equilibrium also provide a route for controlling a larger variety of patterns and for assembling structures from the nanoscale on up at growth rates much faster than would be possible with near-equilibrium approaches (Stoldt *et al.* 1998; Lopes and Jaeger 2001; Rabani *et al.* 2003). Importantly, far-from-equilibrium processes can achieve structural and dynamical richness even with the simplest of ingredients, such as the intricate dendritic growth realized in snowflakes (Langer 1980) (Fig.3).



Fig.3. Farfrom-equilibrium growth in nature: the snowflake

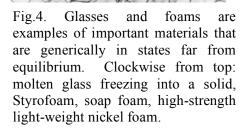


(Knowlton *et al.* 1994; Shinbrot and Muzzio 2000), foams (Weaire and Hutzler 1999; Banhart 2001) and polymeric packaging materials (Auras *et al.* 2004), which attain their properties from being intrinsically caught in far-fromequilibrium states. These materials exhibit structural properties

that, under equilibrium conditions, would identify them as liquids; yet they can behave like solids (Fig. 4).

Processes that occur far from equilibrium are beginning to force us to rethink some of the foundations of condensed matter and materials physics. Yet even today, most of our knowledge about how systems with many constituent particles behave and evolve is based on considerations valid only close to equilibrium. We know much more about systems near equilibrium and have developed a powerful formalism, statistical mechanics, to

predict the emergent, collective behavior of manyparticle systems. This framework has allowed condensed matter researchers to understand a large number of phases of matter, the origins of many of their properties and the nature of transitions between them. However, this framework applies only to situations where a system is thermally and mechanically in balance with its surroundings, and thus it covers only a small subset of



the phenomena we observe around us and that we confront in applications.

One conceptual difficulty posed by systems far from equilibrium thus arises from the absence of established theoretical frameworks. By virtue of being far from equilibrium, such systems pose numerous challenges. They are typically *nonlinear*; *i.e.* their response to perturbation is often not proportional to the magnitude of the perturbation, as for systems near equilibrium. They are often *disordered*; *i.e.* their structure is typically not crystalline, as equilibrium solids generally are. Finally, they are often *non-ergodic*; *i.e.* they do not necessarily explore a large subset of the states available to them, as equilibrium systems must. As a result, even characterizing their behavior and structure leads one onto largely unfamiliar ground from the standpoint of most of condensed matter physics.

Far-From-Equilibrium Materials

Certain classes of materials almost always exist under conditions far from equilibrium. Many materials investigated by soft condensed matter researchers fall into this category, including glasses, foams, granular materials and dense colloidal suspensions (Liu and Nagel 2001). In all these examples, the thermal energy supplied by the surroundings is too small to allow the

systems explore many configurations. Instead, they are trapped in configurations that structurally resemble a liquid (they are dense and highly disordered), but are unable to flow and thus behave as solids. This glassy behavior, a hallmark of many far-from-equilibrium materials, is observed for constituents ranging from molecules in glass-forming liquids to grains of sand in dunes. Since these materials cannot relax to equilibrium, they typically retain a memory of the preparation or processing conditions, a key for many technological innovations such as molded plastic parts and shape memory polymers (Gunes and Jana 2008). Transitions from far-from-equilibrium glassy states to near-equilibrium crystalline states are the basis for chalcogenide glass optical disks (Zakery and Elliott 2003) and phase-change memory devices (Wuttig and Yamada 2007).

Over the last decade, granular matter has emerged as a key prototype of a far-from-equilibrium material (Jaeger *et al.* 1996; de Gennes 1999; Kadanoff 1999) (Fig. 5). In its simplest form, granular matter consists of nothing more than a large number of non-cohesive, macroscopic hard spheres interacting only at contact; yet it exhibits all the characteristics of far-from-equilibrium behavior, as discussed in the subsequent sections. Furthermore, several ideas



Fig.5. Granular materials consist of individually solid grains, interacting only at contact; yet large assemblies of such grains exhibit a rich set of complex behaviors. Left[.] ripples in a sand dune. Right: while fluids mix when stirred, materials granular sizeseparate. MRI of interior of lavered granular system, showing upward motion of large particle (dotted circle) in a bed of smaller ones.

developed originally within the context of granular materials have by now been successfully "exported" into other areas; for example, the concept of jamming gives insight into glassy phenomena (Liu and Nagel 2001). Similarly, ideas about avalanche statistics in driven

dissipative systems, investigated early on in sand piles, have been applied to the dynamics of traffic (Helbing 2001), earthquakes (Carlson *et al.* 1994) and friction (Nasuno *et al.* 1997; Bretz *et al.* 2006), and have been connected to magnetic-flux-bundle motion in superconductors (Jaeger and Nagel 1992; Field *et al.* 1995; Nowak *et al.* 1997; Olson *et al.* 1997; Altshuler and Johansen 2004; Aranson *et al.* 2005). Beyond fundamental research, a large number of industrial processes depend on the handling and transport of granular matter, from seeds and fertilizer pellets in agriculture to ore and gravel in mining operations to powders and pills in the pharmaceutical industry (Ennis *et al.* 1994; Knowlton *et al.* 1994; Shinbrot and Muzzio 2000). Yet the inherently far-from-equilibrium behavior of these materials is still poorly understood and controlled. For example, in North America, new plants designed for processing granular materials initially operate at only about 50-60% of design capacity, while those designed for the handling of liquids immediately operate at nearly full efficiency (Merrow 1985; Merrow 1988).

Far-From-Equilibrium Processing and Assembly

Many materials processing techniques exploit far-from-equilibrium conditions for the growth and manufacture of materials that otherwise could not be fabricated. High-strength alloys are often formed by the same rapid dendritic growth that underlies the formation of snowflakes. Some of the very strongest materials available are metallic alloy glasses, made by rapid cooling into amorphous states far from equilibrium (Inoue 2000; Wang *et al.* 2004) (Fig. 6). Lightweight, strong and tough plastics for car bumpers and aircraft are produced by similar processes. The understanding and control of out-of-equilibrium behavior are also important for interface growth processes, for example during the mechanical alloying already mentioned above (Murty and Ranganathan 1998; Suryanarayana 2001) or the fabrication of large, defect-free crystalline domains for silicon thin film devices by laser-induced melting and solidification (Sposili and Im 1996; Hatano *et al.* 2000).

Far-from-equilibrium processing conditions can be used to drive a system towards unique final configurations in very efficient and speedy ways. On the nanoscale this offers new advantages. For example, certain polymers (diblock-copolymers) spontaneously organize themselves into extended patterns with repeat spacings in the 10-50nm range (Park et al. 2003; Hawker and Russell 2005). Such feature sizes are difficult to achieve with conventional lithographic methods and are desirable for applications ranging from drug delivery (Allen et al. 1999) to high-density magnetic storage (Park et al. 1997; Ross et al. 1999; Kim et al. 2003; Terris and Thomson

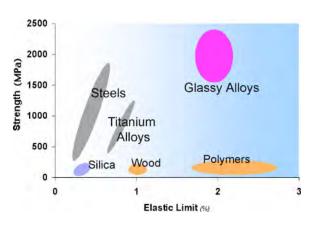


Fig.6. Far-from-equilibrium processing produces some of the highest strength materials (glassy metal alloys).

2005). Unprocessed, these polymeric structures are often fairly disordered and contain a large number of defects. If the systems are sheared, however, the defects can be removed and the structures can order over extremely large distances (Chen *et al.* 1997; Angelescu *et al.* 2004).

An advantage of far-from-equilibrium processing conditions is that small differences in the physical or chemical properties of neighboring regions in a material can be amplified; in equilibrium, diffusion tends to smooth out such differences. This property can be exploited to aggregate inorganic components, such as metallic, magnetic or semiconducting particles, on selective polymer domains, leading to new nanoscale-structured hybrid materials (Lopes and Jaeger 2001; Thompson *et al.* 2001). Another important area where far-from-equilibrium conditions can be used to control morphologies is drying-mediated assembly of nanoparticles. Here pathways have been developed for the creation of both densely packed but disordered thin film aggregates (Rabani *et al.* 2003; Sztrum and Rabani 2006; Lee *et al.* 2007) and highly ordered superlattices (Bigioni *et al.* 2006; Xu *et al.* 2007).

WHAT DETERMINES THE BEHAVIOR FAR-FROM-EQUILIBRIUM?

In equilibrium, minimization of a free energy determines the preferred state, and the system reaches this state independent of the initial conditions. Far from equilibrium, systems typically exhibit a very rich set of characteristic behaviors that are not generally described by a minimization principle. What physics governs the state a system chooses? We have made considerable progress in a number of specific cases. This section discusses advances in the areas of fluids and dynamical systems, and looks at the use of singularities in understanding and controlling far-from-equilibrium behavior.

Systems with Hydrodynamic Equations of Motion

In many cases, far-from-equilibrium systems exhibit a convenient separation of length and time scales. In order to understand many fluid-flow problems, such as the vortex of a tornado, it is not necessary to describe the motions of individual molecules. Experience with systems at or near equilibrium teaches us that it is often fruitful to focus on the long length scale, long time scale behavior (Chaikin and Lubensky 1995). This so-called "hydrodynamic" approach has been the basis of success in describing a number of systems far from equilibrium. Once we know the basic differential equations that describe long length and time scale properties we can tackle an astounding range of far-from-equilibrium, nonlinear behaviors. The prototypical example is the Navier-Stokes equation for incompressible fluid flow:

$$\rho\left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v}\right) = -\nabla p + \eta \nabla^2 \vec{v} \tag{1}$$

Like other typical hydrodynamic equations of motion, the Navier-Stokes equation is a nonlinear partial differential equation that describes long length and time scale properties and can be used to tackle an astounding range of far-from-equilibrium, nonlinear behaviors, including erratic fluttering of flags in the wind (Zhang *et al.* 2000) (Fig. 7), the flapping of a bird's wing (Vandenberghe *et al.* 2004), and the breaking of water waves on a beach (Lin and Liu 1998). The difficulty lies in solving the equation. Similar descriptions also apply to complex fluids

under flow, a frontier area that is only beginning to be explored (Morozov and van Saarloos 2007; White and Mungal 2008). Finally, the hydrodynamic approach can be applied to a wide range of phenomena not immediately associated with fluids, such as collapsing white dwarves (Plewa et al. 2004; Fisker et al. 2006), the flocking of birds and other organisms (Toner et al. 2005), and the development of single-celled amoebae into multicellular organisms (Ben-Jacob et al. 2000). Another example is found in semiconductor heterostructures in which electron density waves are confined to the sample edge. There, when dissipation plays no role, strong electronic correlations are predicted (Bettelheim et al. 2006) to produce dispersive shock waves that resemble roll clouds in the atmosphere (Christie 1989). Many more examples are provided by the physical, chemical and biological systems that exhibit pattern formation, in which a uniform system develops patterns in space and/or time by being driven out of equilibrium (Cross and Hohenberg 1993).

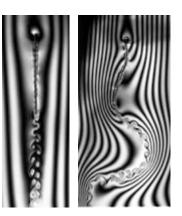


Fig.7. The transition from steady (left) to fluttering (right) motion, visualized by imaging the fluid flow around a filament tied to a post (circle at the top).

The idea that the dynamics of a system with many degrees of freedom can be dominated by the interaction of only a few (such as those at long length and time scales) is an important concept that motivates the study of simple dynamical models to gain insight into complex phenomena. For example, the Lorenz model is a set of nonlinear coupled equations for three variables:

$$\frac{dx}{dt} = \sigma(y - x)$$

$$\frac{dy}{dt} = x(\rho - z) - y$$

$$\frac{dz}{dt} = xy - \beta z$$
(2)

where σ , ρ and $\beta>0$ are adjustable parameters. The Lorenz model was originally developed to describe convection rolls in the atmosphere and includes only a few degrees of freedom yet successfully capture qualitatively many features of the earth's climate (Palmer 1993). Similar approaches are used to gain insight into the origin of the earth's magnetic field (Roberts and Glatzmaier 2000), mantle convection (Ogawa 2008), Jupiter's red spot (Marcus 1993), and the cycle of solar flares (Low 2001).

The challenges in tackling this class of problems lie in the identification of the few crucial degrees of freedom that must be retained and in the complexity of the resulting equations of motion. Much progress has come from a close coupling of analytic theory with large-scale computer simulations, informed by experiments.

Turbulence and fracture

Many far-from-equilibrium phenomena pose special challenges because they involve a multitude of length and time scales that interact and thus all become important. Large-scale turbulence is connected directly to flow behavior at scales many orders of magnitude smaller (Mellor and Yamada 1974; Falkovich et al. 2001); macroscopic fracture patterns depend intimately on the local configuration of molecular bonds in front of the crack tip (Marder and Fineberg 1996; Freund 1998). In problems such as turbulence, hydrodynamic equations apply but become impossible to solve. Theoretical techniques used in condensed matter physics to study equilibrium critical phase transitions, such as the renormalization group, can be useful here. These techniques are designed to understand how physics at small length or time scales

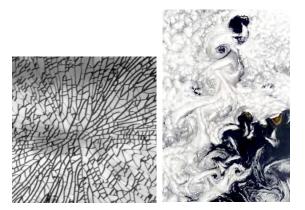


Fig. 8. Far-from-equilibrium behavior often involves processes interacting over a large range of length (and time) scales, leading to characteristic patterns such as the ones observed in the fracture of a glass (left) and in turbulent cloud formations (right; over the Canary Islands).

affects behavior at somewhat larger length or time scales, and so on, ultimately leading to an understanding of how a wide range of length scales or time scales interact with one another.

We will focus here on turbulence as one of the most common far-from-equilibrium phenomena in the environment and in industrial processes. Turbulence produces complex flow structures that modify the transport of momentum, mass and heat, thereby creating a wide variety of both wanted and unwanted effects: a means for rapid mixing of reagents in industrial processes but also parasitic drag in pipe flow and, on a larger scale, catastrophic weather patterns such as hurricanes. Very similar unstable flow structures are produced during the extrusion of polymers or pastes through an orifice (Meulenbroek et al. 2003), in flows of complex fluids such as polymer solutions ("elastic turbulence") (Groisman and Steinberg 2000), and in slow sedimentation of particles at high concentration in a fluid (Segre et al. 2001). Thus, the mechanisms underlying turbulence appear to be remarkably general. Ideas from turbulence have even been applied to finance (Ghashghaie *et al.* 1996; Mantegna and Stanley 2000). Despite the ubiquity and importance of turbulence, however, we do not understand how it develops well enough to control or prevent it in many cases. The onset flow rate and the nature of the onset of turbulence are still puzzling; turbulence often sets in gradually, in stages, but in many cases, including simple pipe flows, turbulence sets in prematurely for reasons that remain vexingly elusive (Hof et al. 2003; Faisst and Eckhardt 2004). Finally, despite much progress during the last decade or two, the nature of the fully-turbulent state still poses many open problems (Siggia 1994; Kadanoff et al. 1995; Lewis and Swinney 1999; Sreenivasan 1999; La Porta et al. 2001; Tabeling 2002; Benzi et al. 2008). In this state, long-lived, large-length-scale coherent structures play an important but still poorly understood role. In the next decade, particle-tracking techniques (Ott and Mann 2000; Ouellette et al. 2006) for imaging fluid elements during turbulent flow should shed light on many of these longstanding questions.

Singularities

In many circumstances, especially under extreme mechanical loading or shearing conditions, materials are driven so far from equilibrium that they change their shape irreversibly. This happens every time a liquid splashes and breaks up into droplets, a piece of glass fractures, a sheet of paper crumples, or a car crashes. Such catastrophic events are typically connected with deformations or failure modes that act at the smallest possible scales and yet affect the overall

shape. Consider a slowly dripping faucet with water that is just about to pinch off into a drop. What sets the shape of drop and of the neck by which it hangs just before breaking off? It turns out that, in many cases, these shapes are controlled completely and at every stage by only one spot along the neck, namely where the neck is thinnest (Cohen et al. 1999; Eggers and Villermaux 2008). This type of behavior is scale invariant-an image of a neck gives no clue as to the overall size of the neck. In other words, the breakingapart into a drop is controlled by a local singularity, in this case the divergence of the neck curvature. One important recent realization has been that there are two classes of singular break-up events: one in which the neck shape is universal since it does not remember the initial conditions, and one where there is memory of the early stages of neck formation and thus no universality. An everyday example of the latter one is

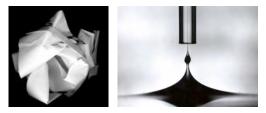


Fig.9. Using singularities to control materials' properties. Left: crumpling a piece of paper stiffens it and allows it to absorb shock. Right: entraining particles, for encapsulation purposes, into the near-singular flow when an interface between two fluids (here: oil and water) is deformed by extruding the oil with a pipette.

an air bubble breaking off and then rising inside a highly viscous medium such as honey (Doshi *et al.* 2003; Keim *et al.* 2006). Similarly, the overall behavior of a crumpled piece of paper is determined by small number of local spots, sharp points of very high curvature connected by a network of ridges (DiDonna and Witten 2001; Witten 2007). Such singular spots instantly transform an otherwise floppy sheet into a structure that can bear loads and absorb shocks (Fig. 9). Similar stress focusing has also been observed at the nanoscale, in crumpled sheets of nanoparticles (Lin *et al.* 2003).

Similar scale invariance occurs at singularities such as those at critical phase transitions in equilibrium systems. Over the last decade, researchers have built upon the conceptual foundation of equilibrium phase transitions to identify and tackle far-from-equilibrium materials under extreme conditions. These systems were previously intractable precisely because of their singularities; the triumph in the last decade has been to *exploit* singularities to understand how they control the behavior of such systems over a broad range. Extensions of this approach have demonstrated how the unique behavior in the vicinity of a singularity can be used to achieve unprecedented levels of processing control, which can be used, for example, to uniformly encapsulate live cells prior to transplantation (Fig. 9, right) (Cohen *et al.* 2001; Wyman *et al.* 2007). The extreme mechanics associated with singularities are likely to become increasingly important. They also are prime examples of how, far from equilibrium, the evolution of structure and dynamics are often inseparable.

Robustness as a Design Principle

In the last decade, ideas from engineering and biology have led physicists to explore a mechanism of state selection very different from equilibrium free energy minimization. Many far-fromequilibrium systems have been designed, either by deliberate engineering or through evolution and natural selection, to be robust to perturbations (Barkai and Leibler 1997; Carlson and Doyle 2002; Gao et al. 2003). For example, cars are now designed with complicated internal networks involving many components, backup mechanisms and adaptive feedback loops to ensure reliable operation under a wide range of environmental conditions. Likewise, biological networks, such as those that enable white blood cells to pursue invading bacteria, have evolved to be insensitive to biochemical changes in their components (Barkai and Leibler 1997; Alon et al. 1999). Recently, researchers have used maximization of robustness as a mechanism of state selection in interacting networks (Albert et al. 2000; Strogatz 2001; Albert and Barabasi 2002; Milo et al. 2002; Newman 2003) (Fig. 10). This opens up a vast array of systems that can be studied using the tools of condensed matter physics, ranging from circadian clocks (Tyson et al. 2008)to the Internet (Albert and Barabasi 2002; Newman 2003)and from our immune systems (Jerne 1974) to the environment (Proulx et al. 2005). One interesting common feature of systems designed for robustness is that their complexity renders them vulnerable to rare, unexpected perturbations (Carlson and Doyle 2002). For example, the network of

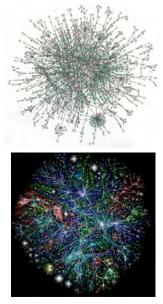


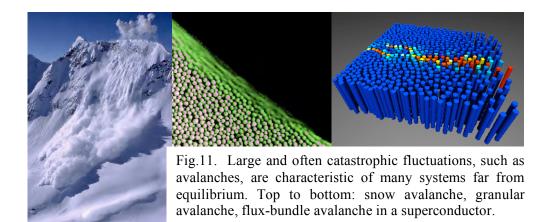
Fig. 10. Examples of evolving network structures far from equilibrium. Top: map of interacting yeast proteins. Bottom: Internet nodes.

interconnected species in the world's oceans has adapted over millennia to be remarkably stable to the vast number of perturbations that can occur. Yet a small change of acidity in ocean waters produced by increased carbon dioxide in the atmosphere may trigger mass extinctions of species (Orr *et al.* 2005; Guinotte and Fabry 2008). Even far-from-equilibrium systems, such as materials under stress, which have not evolved or been specifically designed, can exhibit similar vulnerabilities, such as fracture, due to the history of their formation and the complexity of interactions among the many atoms or molecules that constitute them.

Predictability and Control: What can we learn from fluctuations?

For systems comprised of many particles in or near equilibrium, statistical mechanics tells us that fluctuations of observable quantities around their average values tend to be small and to have a Gaussian (bell-shaped) distribution. For systems far from equilibrium, there is no general framework such as statistical mechanics, and fluctuations tend to be distributed rather differently. The distributions are often broader than simple Gaussian "bell curves", exhibiting for example slower, exponential decays, power-laws or additional peaks, so that catastrophic, but rare, events can dominate behavior. This is the case in avalanches involving sudden magnetic domain reorientations or flux bundle motion in superconducting magnets (Jaeger and Nagel 1992; Field *et al.* 1995; Olson *et al.* 1997; Aranson *et al.* 2005) (Fig. 11). Similar fluctuations that include

large, catastrophic events occur in granular materials, as in landslides or mudslides, or during earthquakes (Carlson *et al.* 1994; Jaeger *et al.* 1996; Bretz *et al.* 2006). Turbulence and spatiotemporal chaos also produce characteristic fluctuations in the measured quantities (Lewis and Swinney 1999; Falkovich *et al.* 2001; La Porta *et al.* 2001; Ouellette *et al.* 2006; Benzi *et al.* 2008). In sheared granular materials, where stresses propagate along highly branched networks of "force chains", the characteristic distribution of inter-particle contact-force magnitudes around their mean can give valuable information about incipient failure, the transition from jammed to unjammed behavior, and the nature of the flowing state (Liu *et al.* 1995; Howell *et al.* 1999; Brujic *et al.* 2003; Corwin *et al.* 2005; Majmudar and Behringer 2005; Behringer *et al.* 2008). Quite generally, the spectrum of fluctuations thus can serve as a key signature of far-from-equilibrium behavior and a powerful tool to analyze the underlying mechanism.



One of the most important questions one can ask about a many-particle system is how it will respond to perturbations. For systems in thermal equilibrium, the fluctuation-dissipation theorem provides the answer: we know that if the perturbation is small, the system will respond just as it does to naturally occurring fluctuations. The relationship between correlation and response depends on temperature;. For example, the second law of thermodynamics states that fluctuations of any extensive thermodynamic variable X are related to the response of the average value of X to its thermodynamic conjugate ξ by:

$$\left\langle \left(X - \left\langle X \right\rangle\right)^2 \right\rangle = -k_B T \frac{\partial \left\langle X \right\rangle}{\partial \xi} \tag{3}$$

Thus, temperature measures the size of fluctuations relative to the response, which quantifies how hard it is to create a fluctuation. In other words, one could define temperature by

$$k_{B}T = \frac{\left\langle \left(X - \langle X \rangle\right)^{2} \right\rangle}{-\partial \langle X \rangle / \partial \xi}$$
(4)

For systems far from equilibrium temperature no longer plays such a role. However, in analogy to the thermal case it is possible, in some cases, to define an *effective* temperature from the relationship between correlation and response. For certain classes of driven dissipative systems, such as sheared glasses, foams, or fluidized granular materials such as vibrated or gas-fluidized

granular beds, there is evidence that the notion of an effective temperature can be useful in predicting behavior (Cugliandolo and Kurchan 1993; Cugliandolo *et al.* 1997; Berthier *et al.* 2001; Makse and Kurchan 2002; Ono *et al.* 2002; Abou and Gallet 2004; Feitosa and Menon 2004; Ojha *et al.* 2004; Haxton and Liu 2007). Important issues are to elucidate the conditions under which effective temperatures provide a reasonable description, and extent of the analogy to ordinary temperature.

Formal Theoretical Developments

One of the great challenges of far-from-equilibrium systems is to develop a theoretical framework, akin to equilibrium and near-equilibrium thermodynamics and statistical mechanics, for tackling these systems. In the last decade, there has been substantial progress in generalizing thermodynamics and statistical mechanics to far-from-equilibrium systems. Steady-state thermodynamics takes into account the heat that is continually generated in steadily-driven systems to generalize the second law of thermodynamics (Oono and Paniconi 1998; Taniguchi and Cohen 2008). Other approaches generalize the concept of entropy to zero-temperature systems (Barrat *et al.* 2001; Blumenfeld and Edwards 2003; Edwards 2004; Henkes *et al.* 2007), while still others generalize the fluctuation-dissipation theorem to far-from-equilibrium systems (Falcioni *et al.* 1990; Ruelle 1999; Crisanti and Ritort 2003; Harada and Sasa 2005; Speck and Seifert 2006). A new thermodynamic result has made it possible to extract equilibrium free energy differences from far-from-equilibrium processes (Jarzynski 1997): the Jarzynski equality states that

$$\exp(-\Delta F/k_B T) = \langle \exp(-W/k_B T) \rangle$$
(5)

where ΔF is the free energy difference between two thermodynamic states A and B, k_B is the Boltzmann constant, T is the temperature, and W is the work done during a non-equilibrium process that takes the system from A to B. The angular brackets denote an average over all realizations of this process. This equality has been tested experimentally (Liphardt *et al.* 2002; Cohen and Mauzerall 2004) and promises to be an especially useful tool for studying free energy differences in biological systems. Fluctuation theorems have been used to show how irreversibility can emerge from underlying reversible dynamics (Evans and Searles 2002; Sevick *et al.* 2008). Due to these developments, the field of nonequilibrium thermodynamics and statistical mechanics is gathering additional momentum.

Getting (Un-)Stuck: Jammed States and Jamming Transitions

The prototypical example of a jammed state is a glass, a state that has both fluid- and solid-like attributes: it has the amorphous structure of a liquid, yet responds to an applied stress like a solid (Ediger *et al.* 1996). All liquids will form glasses upon cooling if crystallization can be avoided (for example, by cooling rapidly enough), and for complex fluids such as polymers, the transition to a glass (plastic) is nearly impossible to avoid. As a liquid is cooled, the time required to reach equilibrium, the relaxation time, increases and the response of the system to perturbations turns more and more sluggish until it becomes immeasurably slow. At this point, the system is now

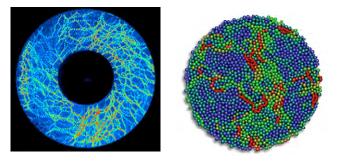


Fig.12. In systems at or near the jamming transition, network-like structures are formed dynamically, such as chains of particles experiencing high contact forces in slowly sheared granular systems (left; (Howell *et al.* 1999)) and strings of particles whose motion is correlated in a gas-fluidized granular bed (right; (Keys *et al.* 2007)).

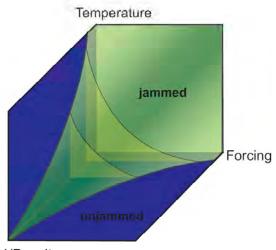
called a glass. The increase of relaxation time is continuous but occurs over an incredibly narrow range of temperature, so that lowering the temperature by 10-20K can increase viscosity and relaxation time by ten or more orders of magnitude. Because the relaxation time exceeds any measurable time scale as the glassy state is approached, a glass by definition is a system far from equilibrium.

Similar glassy states are found not only in ordinary liquids, but in many electronic systems in the presence of disorder, including interacting electron spin systems (spin glasses) or systems of interacting

magnetic flux bundles (vortex glasses) (Edwards and Anderson 1975; Blatter *et al.* 1994; Nattermann and Scheidl 2000; Salamon and Jaime 2001). They also occur whenever particles of any size congregate at sufficiently high concentrations (Liu and Nagel 2001)(Fig. 12). For example, micelles or colloids in dense suspensions (Kegel and van Blaaderen 2000; Weeks *et al.* 2000; Trappe *et al.* 2001; Anderson and Lekkerkerker 2002), lubricants trapped between surfaces (Thompson *et al.* 1992; Hu and Granick 1998), bubbles in foams (Durian *et al.* 1991; Sollich *et al.* 1997; Gopal and Durian 1999; Weaire and Hutzler 1999; Banhart 2001), and candies in a jar (Donev *et al.* 2004) all get trapped in glassy states. The onset of glassy behavior is easily observed in an hourglass filled with sand: a fluid-like stream of grains falling through the central neck is rapidly quenched into a solid-like heap that retains the stream's amorphous structure but,

unlike a fluid, supports a finite angle of repose. However, once the particles become macroscopic as in the case of sand grains, temperature is no longer effective in facilitating escape from the glassy state. Instead, mechanical fields such as stress or vibration can take over this role and unjam the system (Jaeger et al. 1996). The suggestion that temperature and stress can act similarly in systems close to the onset of rigidity has led to the introduction of a more general framework, the concept of jamming (Cates et al. 1998; Liu and Nagel 1998; Liu and Nagel 2001; Trappe et al. 2001; O'Hern et al. 2003). This concept describes the cooperative phenomenon of jamming in terms of the interplay of three key parameters: random thermal motion, applied forcing, and geometrical constraints (Fig. 13).

The idea of a general jamming transition, applying to both thermal and non-thermal systems, has put the spotlight onto some of the most longstanding problems in condensed matter physics, such as the



1/Density

Fig.13. Jamming phase diagram, delineating the conditions under which a multitude of systems become rigid and solid-like. Inside the jammed region (green), these systems are far from equilibrium.

glass transition. Because the jammed state is out of equilibrium, even the most basic questions about any jamming transition remain intensely controversial. Is there a true thermodynamic transition, at which the relaxation time diverges? Or is there a dynamical transition to the jammed state, where the relaxation time diverges with no thermodynamic signature? Or is there no transition at all, so that the relaxation time only truly diverges at zero temperature or mechanical driving? It is because these fundamental questions remain unresolved that the onset of glassy behavior is generally considered one of the most intriguing unsolved problems in condensed matter physics.

SUMMARY

Far-from-equilibrium behavior is emerging as one of the major challenges within condensed matter physics and beyond. The importance of making progress in this field is underlined by several key facts: First, far-from-equilibrium behavior is not rare but ubiquitous, occurring from the nanometer scale on up, in daily life as well as high-tech applications. Second, it connects directly to critical, national needs for the next decade, affecting a large fraction of the manufacturing base as well as our economy, climate and environment. Third, we emphasize that far-from-equilibrium behavior cannot be understood simply through small modifications of equilibrium physics. Because it differs so strikingly and at the same time represents largely uncharted intellectual territory, it provides exciting opportunities for major scientific breakthroughs.

The field of far-from-equilibrium physics is vast, and it is unlikely that any one organizing principle will work for all far-from-equilibrium systems. Nonetheless, there is great value in identifying *classes* of systems that might have common underlying physics or that might be tackled by common methods. Recent work within the condensed matter community has set the stage for fresh approaches to longstanding problems concerning far-from-equilibrium behavior by introducing new model systems, such as granular matter, new unifying paradigms, such as jamming, new organizing principles, such as robustness, and new formal approaches, such as steady-state thermodynamics. We are also finding important connections to a wide range of other fields, both within and outside physics. These connections are likely to amplify the impact of advances in far-from-equilibrium physics even further.

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Image Credits for Figures

Figure 1

Top: school of fish, <u>http://imagecache2.allposters.com/images/PTGPOD/603809.jpg</u> Middle: hurricane Francis, <u>http://www.shnorth.com/Hurricane.htm</u> Bottom: spiral galaxy NGC4414, <u>http://en.wikipedia.org/wiki/File:NGC_4414_(NASA-med).jpg</u>

Figure 2

Top: wing tip turbulence produced by small agricultural plane,

http://en.wikipedia.org/wiki/File:Airplane vortex edit.jpg

Bottom: Aloha Airlines cabin top peeled off during flight, from Michale Marder's web page on "How things

break",<u>http://chaos.ph.utexas.edu/~marder/fracture/phystoday/how_things_break/how_things_break/how_things_break/html</u>

Figure 3

Snow flake crystal, http://www.its.caltech.edu/~atomic/snowcrystals

Figure 4

Clockwise from top: molten glass, <u>http://srnl.doe.gov/images/pour.jpg</u> molten glass, <u>http://www.usefilm.com/image/1163585.html</u> Styrofoam, <u>http://www.aic.info.ro/styrofoam/</u> soapy foam, image courtesy of Doug Durian, University of Pennsylvania simulation of Ni foam, <u>http://www.itwm.fhg.de/mab/projects/MIKRO/nifoam.jpg</u>

Figure 5

Left: sand dune, <u>http://www.photo.net/photo/pcd0738/great-sand-dune-ridge-7</u> Right: <u>http://jfi.uchicago.edu/~jaeger/group/granular.html</u>, image adapted from Fig. 1 of Matthias E. Möbius et al., "Intruders in the Dust: Air-Driven Granular Size Separation", Phys. Rev. Lett., **93**, 198001 (2004).

Figure 6

Strength versus elastic limit of various materials, William L. Johnson, <u>http://www.its.caltech.edu/~matsci/wlj/wlj_research.html</u>

Figure 7 flapping filament flow visualizations, Jun Zhang, NYU, <u>http://physics.nyu.edu/~jz11/filaments.html</u>

Figure 8

Right: fracture in glass with nickel-sulphide inclusions, <u>http://www.picams.com.au/nickel-sulphide.html</u>
Left: turbulence in clouds over Canary Islands (NASA),
http://plus.maths.org/issue26/news/turbulence/index.html

Figure 9

Left: crumpled sheet with sharp points and ridges, taken from Tom Witten's talk given at Frontiers of Condensed Matter workshop, Snowmass Aspen, 2004, http://frontiers.physics.rutgers.edu

Right: entrainment of a small object due to (near-)singular flow at an oil/water interface, image courtesy Sid Nagel, see Jason Wyman et al., "Immunoisolating Pancreatic Islets by Encapsulation with Selective Withdrawal," Small **3**, 683–690 (2007).

Figure 10

Top: map of interacting yeast proteins, from A.-L. Barabasi and E. Bonabeau, "Scale-Free Networks," Scientific American **288** (5), 50-59 (2003), <u>http://www.nd.edu/~networks/PublicationCategories/ReviewArticles/ScaleFree_ScientificAmeri288,60-69(2003).pdf</u>

Bottom: Internet map, Date: Nov 22 2003, http://www.opte.org/maps/

Figure 11

Left: snow avalanche, http://www.avalanche.org/pictures/avalanche1.jpg

Middle: granular avalanche in pile of mustard seeds, cover image accompanying H. M. Jaeger, S. R. Nagel, and R. P. Behringer, "The Physics of Granular Materials", Physics Today **49**, 32 (1996).

Right: flux bundle avalanche in type-II superconductor, Cynthia Olson-Reichhardt, <u>http://www.t12.lanl.gov/home/olson/</u> and

http://www.t12.lanl.gov/home/olson/aval_index.html