FLUID PHASES

Going supercritical

The critical point of a fluid is defined as the point beyond which it ceases to exhibit distinct liquid- or gas-like states. A crossover between liquid-like and gas-like behaviour observed by inelastic X-ray scattering suggests subtle effects involving nanoscale fluctuations in the one-phase region above the critical point.

Paul F. McMillan and H. Eugene Stanley

As the pressure and temperature of a gas or liquid are increased beyond its critical point (P_c,T_c) the distinction between them disappears and the system is said to be in a fluid state. The nature of such supercritical fluids and how they relate to the liquid and gas states of matter has been debated for over two centuries[1]. Early observations of critical behaviour led to the development of modern statistical thermodynamics. Nowadays, supercritical fluids are recognized as possessing unique solvation properties that make them important technological materials. They probably dominate the physical behaviour within the interiors of giant gas planets, such as Jupiter, Neptune and Saturn. Writing in *Nature Physics*, Simeoni and colleagues[2] report a combination of inelastic X-ray scattering (IXS) measurements and molecular dynamics simulations of fluid argon that indicate supercritical fluids can exhibit distinct liquid-like or gas-like behaviour as a function of density. These states are manifest in nanoscale density fluctuations generated by complex interactions between particles in the fluid, an observation that will probably have important implications for understanding fluid phenomena among a variety of other materials systems.

Macroscopically, the coexistence line that separates the pure gas and pure liquid phases of a fluid ends at the critical point (Fig. 1). However the occurrence of a maximum in the specific heat (C_p) as the pressure or temperature is varied across the extension of the coexistence line is well documented. This is understood by definition of the 'Widom line' — a term introduced to define the locus of maximum correlation length that extends into the single fluid phase beyond the critical point[3]. Asymptotically near the critical point, in what is termed the scaling region, all response functions become proportional to powers of the correlation length. Thus the locus of the maximum in C_p becomes identical to maxima observed in the thermal expansion and compressibility.

IXS measurements conducted by Simeoni *et al.* of the speed and dispersion of sound in supercritical argon under high temperature and pressure indicate that these properties undergo striking changes in the fluid state. Combined with molecular dynamics simulations, they find that these changes correlate with nanoscale density fluctuations that map on to the Widom line. The IXS data thus provide a new way of probing the dynamic heterogeneities that are developed within the fluid state and to correlate the thermal heterogeneities with dynamic mechanical fluctuations. Simeoni *et al.* then build on previous work to extend the results to systems ranging from fluid-state neon, oxygen and nitrogen to molten alkali metals and water[2].

The case of water is particularly interesting. This remarkable liquid that is essential for life shows a large number of anomalies in its physical properties including the existence of different amorphous polymorphs and a density- or entropy-driven phase transition in its supercooled liquid state[4,5]. The liquid–gas transition terminates at a critical point for which the associated Widom line has been well studied. The liquid–liquid transition line also terminates at a critical point with its own associated Widom line[3]. The behaviour of water in confined spaces plays a key role in protein hydration, and nanoscale fluctuations associated with the Widom line can influence biological processes[6,7].

Polyamorphic liquid–liquid transitions are now thought to occur generally among a wide range of substances, and the liquid–gas transition might simply represent the last of a series of such transitions at the lowest densities[8]. Measurements of the electrical conductivity, molar volume and thermal properties for liquids including sulphur, selenium, tellurium or iodine indicate rapid changes extending well into the single-phase regime that have been

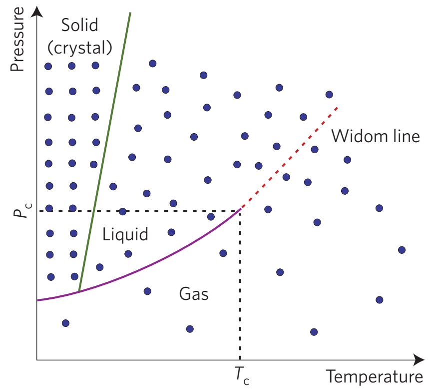

Figure 1 | The emergence of relationships between classical states of matter. The ordered crystalline solid is separated from the liquid state by the melting line (green). The liquid–gas coexistence line ends at a critical point (P_c,T_c) beyond which the system becomes a homogeneous fluid. But dynamic heterogeneities exist in the fluid owing to atomic fluctuations with a maximum correlation length expressed by the Widom line (dashed) that extends into the fluid state. Crossing the Widom line results in changes in the thermal and mechanical properties that are mapped by the new IXS measurements of Simeoni *et al.*

associated with the presence of nanoscale fluctuations. These probably indicate the location of a Widom line for each of the liquid–liquid transitions occurring among these various different systems[9]. The new IXS measurements will help us map the location and nature of dynamic heterogeneities in the density, structure and thermal properties within the one-phase regime and allow us to build a complete picture of the nanoscale fluctuations that lead to macroscopic phase changes among the liquid, gas and fluid states of matter.

In the case of polyamorphic liquid phosphorus, a transition line was proposed to occur between polymeric and molecular phases extending into the stable liquid state[10]. However, that is now shown to correspond to a transition between a high-density polymeric liquid and a low-density molecular fluid[11]. New IXS measurements of the local density fluctuations and dynamic heterogeneities will allow us to decipher the complex set of liquid–fluid transitions within this and other apparently chemically simple but often complex elements or compounds owing to their bonding, and extend the studies to the wide range of systems that might exhibit liquid–liquid and liquid–fluid polyamorphism. ❐

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COMPLEX NETWORKS

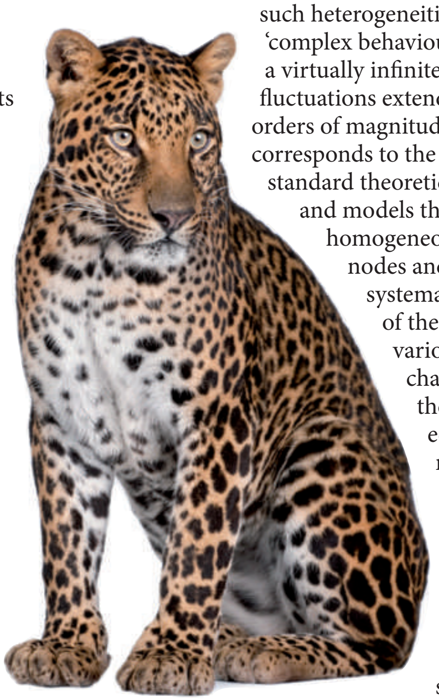
Patterns of complexity

The Turing mechanism provides a paradigm for the spontaneous generation of patterns in reaction–diffusion systems. A framework that describes Turing-pattern formation in the context of complex networks should provide a new basis for studying the phenomenon.

Romualdo Pastor-Satorras and Alessandro Vespignani

We live in the age of networks. The Internet and the cyberworld are networks that we navigate and explore on a daily basis. Social networks, in which nodes represent individuals and links potential interactions, serve to model human interaction. Mobility, ecological, and epidemiological models rely on networks that consist of entire populations interlinked by virtue of the exchange of individuals. Network science, therefore, is where we can expect answers to many pressing problems of our modern world, from controlling traffic flow and flu pandemics to constructing robust power grids and communication networks. But there is more than nodes and links. An important development of recent years has been the realization that the topology of a network critically influences the dynamical processes happening on it[1]. Hiroya Nakao and Alexander Mikhailov have now tackled the problem of the effects of network structure on the emergence of so-called Turing patterns in nonlinear diffusive systems. With their study, reported in *Nature Physics*[2], they offer a new perspective on an area that has potential applications in ecology and developmental morphogenesis.

In the past decade the physics community has contributed greatly to the field of network science, by defining a fresh perspective to understand the complex interaction patterns of many natural and artificial complex systems. In particular, the application of nonlinear-dynamics and statistical-physics techniques, boosted by the ever-increasing availability of large data sets and computer power for their storage and manipulation, has provided tools and concepts for tackling the problems of complexity and self-organization of a vast array of networked systems in the technological, social and biological realms[3–6]. Since the earliest works that unveiled the complex structural properties of networks, statistical-physics and nonlinear-dynamics approaches have been also exploited as a convenient strategy for characterizing emergent macroscopic phenomena in terms of the dynamical evolution of the basic elements of a given system. This has led to the development of mathematical methods that have helped to expose the potential implications of the structure of networks for the various physical and dynamical processes occurring on top of them.



A complex beast. The markings on leopards and other animals might be a manifestation of Turing-pattern formation during morphogenesis[8,9]. A new framework for studying the Turing mechanism on complex networks should deepen our understanding of the process and its consequences. Image credit: © iStockphoto / Eric Isselée

It has come as a surprise then to discover that most of the standard results concerning dynamical processes obtained in the early studies of percolation and spreading processes in complex networks are radically altered once topological fluctuations and the complex features observed in most real-world networks are factored in[1]. The resilience of networks, their vulnerability to attacks and their spreading-synchronization characteristics are all drastically affected by topological heterogeneities. By no means can such heterogeneities be neglected: 'complex behaviour' often implies a virtually infinite amount of fluctuations extending over several orders of magnitude. This generally corresponds to the breakdown of standard theoretical frameworks and models that assume homogeneous distributions of nodes and links. Therefore systematic investigations of the impact of the various network characteristics on the basic features of equilibrium and non-equilibrium dynamical processes are called for.

The work of Nakao and Mikhailov[2], in which they study the Turing