

Polymorphic Phase Transitions in Liquids and Glasses

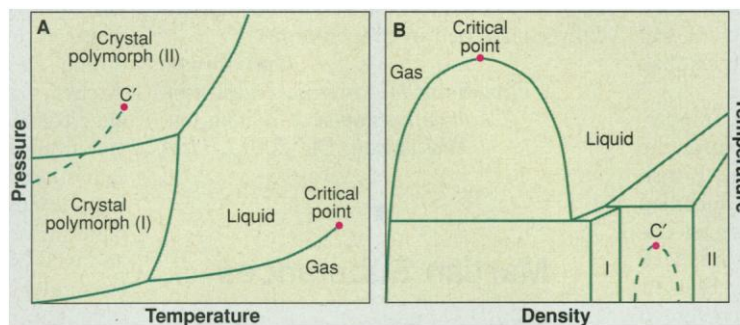
Peter H. Poole, Tor Grande, C. Austen Angell, Paul F. McMillan

At low temperatures, the thermodynamic equilibrium state of a pure substance is an ordered crystal. The crystalline portion of the pressure-temperature phase diagram is usually subdivided among several chemically identical but thermodynamically distinct polymorphs (1). Diamond and graphite are well-known examples. Such polymorphism is not restricted to crystals. Above the triple point, in the regimes of liquid and gas, distinct disordered phases are observed (see figure). Above the liquid-gas critical temperature T_c , these states merge into a single "fluid" phase. In this sense, the liquid and gas states can be regarded as "polymorphs" of the disordered fluid state (2).

The laws of thermodynamics permit the liquid region of the phase diagram for a pure substance to be subdivided into distinct phases (3). The coexistence of two distinct liquids is common in multicomponent chemical systems and also in liquid crystals, where composition and molecular orientation are the respective order parameters. However, "liquid polymorphism" for a pure, isotropic substance does not fall within our common experience. The usual microscopic picture of a liquid as a dynamic system with constantly rearranging molecular configurations makes it difficult to envisage distinct liquid phases, each with the same composition but with different thermodynamic properties and local structure. However, recent studies have revealed rich thermodynamic behaviors in a number of liquids that point to the occurrence of multiple liquid phases distinguished by density, not chemical composition. These results have

implications for liquid and glass science, as well as for the thermodynamics of systems with fixed composition.

If liquid-liquid (L-L) phase transitions can occur for pure, isotropic substances, why are they not commonly observed? First, because the density will generally be an appropriate order parameter for such transitions, the exploration of a wide range of pressure and temperature may be required for their detection.



Schematic phase diagram of a pure substance exhibiting a liquid-liquid phase transition. (A) Solid lines locate the coexistence lines between the liquid, gas, and two crystal polymorphs. The liquid-gas coexistence line terminates in the critical point. The dashed line is the coexistence line for a liquid-liquid phase transition in the supercooled liquid, terminating in a critical point C'. (B) Projection of the lines given in (A) into the plane of temperature and density.

Second, the likely temperature range of L-L transitions must be considered. Because both phases are liquid, the changes in energy, entropy, and density across the transition at a given temperature will be much smaller than those for the liquid-gas transition. The resulting L-L coexistence curve should then be much narrower, and should terminate at a much lower temperature, than the liquid-gas coexistence curve. Moreover, the freezing temperature is typically less than T_c only by a factor of 2 to 4, so that most L-L transitions will be found below the crystal-liquid coexistence line; that is, they are most likely to be metastable transitions observed in the supercooled liquid state and may be obscured by crystal nucleation.

Third, even when crystal nucleation is avoided, a supercooled liquid cannot be studied in internal equilibrium to arbitrarily low temperatures, because of the dramatic in-

crease in structural relaxation time τ . When τ exceeds the experimental observation time, the liquid properties are no longer observed in equilibrium, and the system has passed into the glassy state. Thus, a L-L transition in a supercooled liquid may also be obscured by the glass transition.

With these limitations in mind, what are the possibilities for observing liquid polymorphism? Among the most promising candidates to date are liquids having open molecular coordination environments at low pressure. Notably, these include liquids with a locally tetrahedral molecular structure, such as Si, Ge, C, SiO_2 , GeO_2 , and H_2O itself. For liquid Si, observation of a first-order glass-to-liquid transition, consistent with an underlying L-L transition, has been reported in flash-heating experiments (4) and computer simulations (5). For H_2O (6), SiO_2 (7), and GeO_2 (8), liquid polymorphism is suggested from glass studies at low temperatures. In all three cases, abrupt changes in density and glass structure with changing pressure closely resemble

behavior associated with first-order phase transitions and have been described as "polyamorphic", that is, amorphous solid analogs of crystalline polymorphism (9). Although a glass is not an equilibrium thermodynamic state, if its behavior parallels that of the corresponding supercooled liquid, then the observation of a polyamorphic transition in a glass indicates the existence of distinct liquid states.

Theoretical and computer simulation studies also provide evidence for polymorphism in tetrahedral liquids. At the critical point of an L-L transition, response functions,

such as the isothermal compressibility K_T , will diverge. On approaching this criticality from high temperatures, there will be a regime in which K_T exhibits a maximum, which is augmented on approach to T_c . Computer simulations of liquid H_2O (10) and SiO_2 (11) display K_T maxima that grow as T decreases. For H_2O , rapid crystal nucleation has so far precluded an experimental test of this prediction, but experiments on liquid SiO_2 (or, more conveniently, its structural analog BeF_2) at high pressures and temperatures should be feasible.

An intriguing report of liquid polymorphism has been recorded for the multicomponent system $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ (12). During the quenching of melts with several Y/Al ratios, two coexisting glasses were obtained that were chemically identical but had different density and molecular structure. In this case, although the system could un-

P. H. Poole is in the Department of Applied Mathematics, University of Western Ontario, London, Ontario N6A 5B7, Canada. E-mail: poole@yorkick.apmaths.uwo.ca. T. Grande is in the Department of Inorganic Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway. C. A. Angell and P. F. McMillan are in the Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA.

dergo conventional multicomponent phase separation, the dominant order parameters for the observed L-L phase change were the density and entropy of each melt phase. Here, the melt passed through the glass transition and the L-L phase transition almost simultaneously, allowing both of the (metastably) coexisting liquids to be quenched and studied in the glassy state.

Liquid polymorphism has also been reported in the organic liquid triphenyl phosphite (13). Indirect evidence for liquid polymorphism can also be found in studies of the conductivity of certain molecular liquids, such as I, Se, and S (14). During compression, abrupt increases in the conductivity have been observed and attributed to first-order L-L transitions. The L-L transitions attributed to the melt phases of Si, Ge, and C are also predicted to occur with large changes in conductivity (15).

These findings indicate that liquid polymorphism in systems with fixed composition is an observable phenomenon and that further candidates will be uncovered as we probe more deeply into liquid behavior over a wider range of pressure-temperature conditions. The occurrence of L-L transitions can lead to the synthesis of new, technologically useful families of liquids and glasses

chemically identical to currently known substances but with quite different thermodynamic, rheological, and other physical properties. Also, the complex behavior of viscous liquids and the nature of the glass transition itself are recognized as important, unsolved problems in condensed matter physics (16). The occurrence of liquid polymorphism in low-temperature liquids might be one source of this complexity. Recognition and study of L-L transitions should therefore both enrich and illuminate the phenomenology of the liquid state at low temperatures.

An enhanced version of this Perspective, with live links, can be seen in Science Online on the Web at <http://www.sciencemag.org/>

References

1. A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Oxford, 1984).
2. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, Oxford, 1971).
3. A. C. Mitus, A. Z. Patashinskii, B. I. Shumilo, *Phys. Lett. A* **113**, 41 (1985).
4. E. P. Donovan, F. Saepen, D. Turnbull, J. M.

- Poate, D. C. Jacobson, *J. Appl. Phys.* **57**, 1795 (1985).
5. W. D. Luedtke and U. Landman, *Phys. Rev. B* **37**, 4656 (1988); C. A. Angell, S. Borick, M. Grabow, in *Proceedings of the 17th Conference on Liquids and Amorphous Semiconductors*, in press.
6. O. Mishima, L. D. Calvert, E. Whalley, *Nature* **314**, 76 (1985); O. Mishima, K. Takemura, K. Aoki, *Science* **254**, 406 (1991); O. Mishima, *Nature* **384**, 546 (1996).
7. H. Sugiura, K.-I. Kondo, A. Sawaoka, in *High-Pressure Research in Geophysics*, S. Akimoto and M. H. Manghnani, Eds. (Reidel, Dordrecht, 1982), p. 551; M. Grimsditch, *Phys. Rev. Lett.* **52**, 2379 (1984).
8. K. H. Smith, E. Shero, A. Chizmeshya, G. H. Wolf, *J. Chem. Phys.* **102**, 6851 (1995).
9. G. H. Wolf *et al.*, in *High-Pressure Research: Application to Earth and Planetary Sciences*, Y. Syono and M. H. Manghnani, Eds. (American Geophysical Union, Washington, DC, 1992), p. 503.
10. P. H. Poole, F. Sciortino, U. Essmann, H. E. Stanley, *Nature* **360**, 324 (1992); F. Sciortino, P. H. Poole, U. Essmann, H. E. Stanley, *Phys. Rev. E* **55**, 727 (1997).
11. H. E. Stanley *et al.*, *Physica A* **205**, 122 (1994).
12. S. Aasland and P. F. McMillan, *Nature* **369**, 633 (1994).
13. A. Ha, I. Cohen, X.-L. Zhao, M. Lee, D. Kivelson, *J. Phys. Chem.* **100**, 1 (1996).
14. V. V. Brazhkin, R. N. Voloshin, S. V. Popova, A. G. Umnov, *Phys. Lett. A* **154**, 413 (1991); *High Pressure Res.* **6**, 363 (1992).
15. A. Ferraz and N. H. March, *Phys. Chem. Liq.* **8**, 289 (1979); E. G. Ponyatovsky and I. O. Barkalov, *Mater. Sci. Rep.* **8**, 147 (1992); M. van Thiel and F. H. Ree, *Phys. Rev. B* **48**, 3591 (1993).
16. P. W. Anderson, *Science* **267**, 1615 (1995); A. P. Sokolov, *Science* **273**, 1675 (1996).

POPULATION BIOLOGY

Chaotic Beetles

Charles Godfray and Michael Hassell

Ecologists have known since the pioneering work of May in the mid-1970s (1) that the population dynamics of animals and plants can be exceedingly complex. This complexity arises from two sources: The tangled web of interactions that constitute any natural community provide a myriad of different pathways for species to interact, both directly and indirectly. And even in isolated populations the nonlinear feedback processes present in all natural populations can result in complex dynamic behavior. Natural populations can show persistent oscillatory dynamics and chaos, the latter characterized by extreme sensitivity to initial conditions. If such chaotic dynamics were common in nature, then this would have important ramifications for the management and conservation of natural resources. On page 389 of this issue, Costantino *et al.* (2) provide the most

convincing evidence to date of complex dynamics and chaos in a biological population—of the flour beetle, *Tribolium castaneum* (see figure).

It has proven extremely difficult to demonstrate complex dynamics in populations in the field. By its very nature, a chaotically fluctuating population will superficially resemble a stable or cyclic population buffeted by the normal random perturbations experienced by all species. Given a long enough time series, diagnostic tools from nonlinear mathematics can be used to identify the telltale signatures of chaos. In phase space, chaotic trajectories come to lie on "strange attractors," curious geometric objects with fractal structure and hence noninteger dimension. As they

move over the surface of the attractor, sets of adjacent trajectories are pulled apart, then stretched and folded, so that it becomes impossible to predict exact population densities into the future. The strength of the mixing that gives rise to the extreme sensitivity to initial conditions can be measured mathematically estimating the Liapunov expo-

nent, which is positive for chaotic dynamics and nonpositive otherwise. There have been many attempts to estimate attractor dimension and Liapunov exponents from time series data, and some candidate chaotic population have been identified (some insects, rodents, and most convincingly, human childhood diseases), but the statistical difficulties preclude any broad generalization (3).

An alternative approach is to parameterize population models with data from natural populations and then compare their predictions with the dynamics in the field. This technique has been gaining popularity in recent years, helped by statistical advances in parameter estimation. Good ex-



Cannibalism and chaos. The flour beetle, *Tribolium castaneum*, exhibits chaotic population dynamics when the amount of cannibalism is altered in a mathematical model.

The authors are in the Department of Biology, Imperial College at Silwood Park, Ascot, Berks, SL5 7PZ UK. E-mail: m.hassell@ic.ac.uk