# Nonequilibrium Structures in Condensed Systems

A. S. Mikhailov and G. Ertl

At thermal equilibrium, condensed molecular systems form regular structures that become more ordered when the temperature of the system (that is, the degree of its thermal activation) is decreased. Strong external activation, however, may lead to qualitative changes in the system's behavior and to the emergence of new nonequilibrium structures. A striking example of this was recently reported by Tabe and Yokoyama for traveling waves in Langmuir-Blodgett films (*1*).

Nonequilibrium structures have long been observed in low-density systems, such as in the Belousov-Zhabotinsky reaction (*2–4*). Concentrations are low, so physical interactions between reacting molecules can be neglected. Therefore, the system resembles an ideal gas (where the reacting molecules diffuse through the solvent instead of freely moving). A similar situation is found in semiconductors, where electrons and holes represent a reactive gas-like subsystem inside a solid crystal (*5*). Pattern formation in these "ideal" systems is described by reaction-diffusion models (*6*).

But nonequilibrium structures can also appear in condensed systems of particles with attractive interaction. Here, external activation must act against cohesion, which is responsible for formation of an equilibrium thermodynamic structure; therefore, higher activation is generally needed to produce structural changes. So that kinetic processes can efficiently compete with physical interactions between the particles and thus influence the microscopic organization of a system, the system must be structurally labile.

Structural lability is a feature of "soft matter," condensed molecular systems with relatively weak interactions between particles. Examples include polymer gels and liquid crystals (*7*), lipid membranes or vesicles (*8*), Langmuir-Blodgett films (*9*), thin liquid films on solid surfaces (*10*), and adsorbate layers on metals (*11*). Nonequilibrium structures, directly interfering with the equilibrium organization, are much more likely to form.

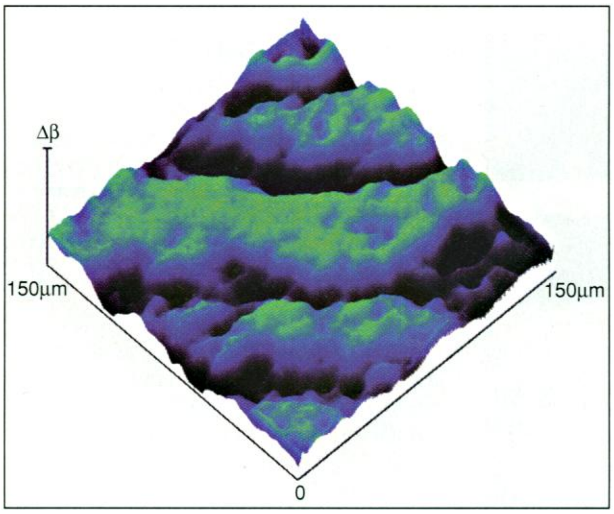
Nonequilibrium structures can generally be divided into stationary and time-dependent types. Stationary nonequilibrium structures have basically the same morphology as do equilibrium structures; that is, they represent periodic or disordered patterns of stripes or certain domain arrays (*12*). There is, however, a principal difference.

The properties of equilibrium structures, such as the spatial size of domains or the array period, are determined only by the energy of interactions between the molecules. In contrast, the properties of nonequilibrium structures are controlled by the kinetic parameters, which specify the rates of diffusion, relaxation, or reactions. Therefore, although the Turing patterns (*13*) or the spots (*14*) in reaction-diffusion systems may have the same shapes as, for example, equilibrium patterns formed by bubbles in thin films of magnetic garnets (*15*), they belong to a different class of physical phenomena. They are accompanied by dissipation of energy; therefore, their generation and maintenance requires permanent energy (or mass) supply.

Stable periodic oscillations, self-supported propagation of waves, and formation of complex wave patterns or even turbulence represent the kinds of behavior that are not possible at thermal equilibrium. Here the difference in the properties of equilibrium and nonequilibrium systems becomes most spectacular. The typical time-dependent patterns are propagating fronts or pulses (*5*), rotating spiral waves (*4*), pacemakers (*3*), or traveling spots (*16*).

Theoretical analysis and experimental investigations of nonequilibrium structures have been performed mainly for reaction-diffusion systems (that is, when attractive interactions between particles forming a structure were negligible). However, some examples of condensed systems in which nonequilibrium pattern formation is accompanied by a change in the microscopic organization or by phase transitions are already known (*17*).

Tabe and Yokoyama (*1*) reported traveling waves in illuminated Langmuir-Blodgett monolayers (see figure). Such insoluble monomolecular layers are formed at the air-water interface by amphiphilic molecules possessing a permanent electric dipole moment. At thermal equilibrium, complicated domain structures—stripes forming a labyrinthine pattern or bubbles ordered in hexagonal arrays—have previously been observed in these films (*18*).



**Traveling waves** in an illuminated Langmuir-Blodgett film. The ordinate shows the local orientation angle (Δβ) of molecules forming the film; the bright elongated bands are the excited waves characterized by a smaller tilt. The waves propagate, preserving their shapes, in the direction denoted by the arrow. [Adapted with permission from *Langmuir* **11**, 4612 (1995). Copyright 1995 American Chemical Society]

Illumination with linearly polarized light at a wavelength suitable to induce trans-cis isomerizations was found to cause a significant change in the equilibrium stripe pattern (*1*). Its spatial profile became modified, and at a sufficiently high light intensity, the pattern broke down into a nonequilibrium stationary granular texture consisting of randomly oriented domains of 10 μm or less in diameter. When the illumination was shut off, the initial equilibrium pattern of stripes was recovered.

At the light intensities preceding formation of a random granular texture, traveling periodic orientational waves were observed (*1*). The wave velocity was typically of the order 50 mm $s^{-1}$ and only slightly depended on the incident light power. Occasionally, propagating solitary waves were also seen.

The importance of this discovery goes beyond a particular experiment. It shows that the kinds of nonequilibrium spatiotemporal organization, which were previously seen for chemical reactions in liquid solutions or at catalytic surfaces, are also possible in monomolecular organic films. Their existence also poses the question whether similar nonequilibrium structures may be observed in other condensed organic systems, such as lipid membranes, playing a fundamental role in biological processes.

---

The authors are at the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin (Dahlem), Germany. E-mail: ertl@fhi-berlin.mpg.de

**References and Notes**

1. Y. Tabe and H. Yokoyama, *Langmuir* **11**, 4609 (1995).
2. B. P. Belousov "A Periodic Reaction and Its Mechanism" (1951, from his archives) [English translation in R. J. Field and M. Burger, Eds., *Oscillations and Traveling Waves in Chemical Systems* (Wiley, New York, 1985), pp. 601–613].
3. A. M. Zhabotinski and A. N. Zaikin, *Nature* **225**, 535 (1970).
4. A. T. Winfree, *Science* **175**, 634 (1972).
5. F.-J. Niedernostheide, B. S. Kerner, H.-G. Purwins, *Phys. Rev. B* **46**, 7559 (1992).
6. J. Ross, S. C. Müller, C. Vidal, *Science* **240**, 460 (1988); for a recent review of pattern formation in reaction-diffusion systems, see A. S. Mikhailov, *Foundations of Synergetics* (Springer, Berlin, ed. 2, 1994), vol. 1.
7. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, Oxford, 1974).
8. F. Julicher and R. Lipowsky, *Phys. Rev. Lett.* **70**, 2984 (1993).
9. D. Andelman, F. Brochard, J.-F. Joannny, *J. Chem. Phys.* **86**, 3673 (1987).
10. P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
11. K. Kern *et al.*, *Phys. Rev. Lett.* **67**, 855 (1991).
12. M. Seul and D. Andelman, *Science* **267**, 476 (1995).
13. Q. Quyang and H. L. Swinney, *Chaos* **1**, 411 (1991); J. J. Perraud, K. Agladze, E. Dulos, P. De Kepper, *Physica A* **188**, 1 (1992).
14. K.-J. Lee, W. D. McCormick, J. E. Pearson, H. L. Swinney, *Nature* **369**, 215 (1994).
15. A. T. Eschenfelder, *Magnetic Bubble Technology* (Springer, Berlin, 1980).
16. K. Krischer and A. S. Mikhailov, *Phys. Rev. Lett.* **73**, 3165 (1994).
17. J. Tabony, *Science* **264**, 245 (1994); D. Meinköhn and A. Mikhailov, *Phys. Lett. A* **178**, 143 (1993); *Physica A* **198**, 25 (1993); A. Joetts and R. Ribotta, *Phys. Rev. Lett.* **60**, 2164 (1988); I. Rehberg, S. Rasenat, V. Steinberg, *ibid.* **62**, 756 (1989); S. Nasuno, M. Sano, Y. Sawada, *J. Phys. Soc. Jpn.* **58**, 1875 (1989); V. Gorodetskii, J. Lauterbach, H. A. Rotermund, J. H. Block, G. Ertl, *Nature* **370**, 276 (1994); A. Mikhailov and G. Ertl, *Chem. Phys. Lett.* **238**, 104 (1995).
18. M. Lösche and H. Möhwald, *Eur. Biophys. J.* **11**, 35 (1984); W. M. Heckl and H. Möhwald, *Ber. Bunsenges. Phys. Chem.* **90**, 1159 (1986).

---

UPDATE

# Polar Clouds and Sulfate Aerosols

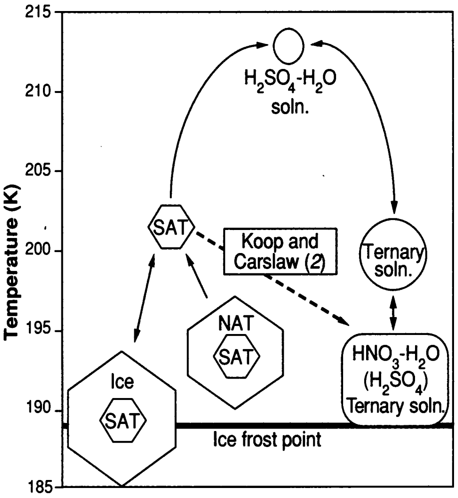
Margaret A. Tolbert

It is now well established that heterogeneous chlorine activation reactions on polar stratospheric clouds (PSCs) play a central role in polar ozone depletion. In contrast, the chemical composition and formation mechanism of the polar clouds is still a topic of considerable debate (*1*). Theoretical work by Koop and Carslaw on page 1639 of this issue (*2*) provides a piece to the puzzle of how one kind of PSC (type I) forms over and over again throughout the winter.

Several years ago, nitric acid trihydrate (NAT) was favored as the main ingredient of type I PSCs (*3*). It was thought that the global sulfate aerosols froze and formed sulfuric acid tetrahydrate (SAT) at the cold polar temperatures and that crystalline SAT then provided a good nucleating surface for NAT. However, laboratory work has shown that neither of these two steps occurs readily (*4*). In addition, some type I PSCs are not composed of NAT (*5*, *6*).

A new picture of PSC formation has recently emerged. Low-temperature liquid sulfuric acid aerosols can absorb significant quantities of $HNO_3$ (*7*), forming ternary solutions of $H_2SO_4$-$HNO_3$-$H_2O$. As temperatures plunge further, the ternary solutions absorb more $HNO_3$ and $H_2O$, forming PSC particles that are essentially binary solutions of $HNO_3$-$H_2O$. Recent work has indicated that these liquid PSCs may actually activate chlorine more efficiently than frozen NAT particles (*8*).

Although liquid sulfate aerosols do explain the presence of liquid PSCs, lidar data indicate that crystalline PSCs also exist at temperatures above the ice equilibrium temperature (or ice frost point) (*5*). It has been assumed that evaporation of crystalline PSCs (either ice or NAT) leaves a frozen sulfate core, probably in the form of SAT (see figure). Laboratory work has suggested that in the atmosphere, SAT remains frozen until a temperature of 210 to 215 K (*9*). This high temperature may never occur during the polar winter, and thus, SAT could remain frozen for the entire season. However, it has also been shown that SAT is not a good nucleating surface for PSCs (*4*). Thus, until recently, experimental results coupled with the two formation mechanisms described above implied that after crystalline PSCs formed once and left behind a frozen core, additional PSC growth would be hindered. PSCs could only form after either the temperature warmed to cause SAT melting or cooled to 189 K, where ice could condense. Neither of these possibilities occurs frequently enough to explain the observations of PSCs throughout the winter.



**Closing the loop.** Conversion of cloud particles from crystalline to liquid through the melting of SAT upon cooling (dashed line), which then permits PCSs to form again.

Koop and Carslaw (*2*) get us out of this dilemma by showing that SAT can melt upon moderate cooling in the atmosphere to form a supercooled ternary solution particle of $H_2SO_4$-$HNO_3$-$H_2O$ (see figure). They suggest that the presence of $HNO_3$ in the atmosphere can help regenerate liquid sulfate aerosols, allowing the cycle of PSC formation to begin again. Adsorption of $HNO_3$ onto SAT causes the crystal to melt at temperatures well below the temperature of 210 to 215 K measured for SAT in the absence of $HNO_3$. This melting temperature depends only on the pressures of water and nitric acid in the atmosphere and occurs at a temperature several degrees above that at which NAT was seen to grow on SAT in laboratory experiments. Thus, if SAT does form in the atmosphere, this theory predicts that it will melt back to a ternary solution before NAT can directly condense, solving the mystery of how PSCs continue to form late in the polar winters. Formation of crystalline PSCs should not prevent subsequent formation of liquid PSCs on the same sulfate particles. Still, the issue of how crystalline PSCs form in the first place is unresolved.

---

The author is in the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA. E-mail: tolbert@colorado.edu

## References

1. M. A. Tolbert, *Science* **264**, 527 (1994).
2. T. Koop and K. S. Carslaw, *ibid.* **272**, 1638 (1996).
3. D. Hanson and K. Mauersberger, *Geophys. Res. Lett.* **15**, 855 (1988); O. B. Toon *et al.*, *ibid.* **13**, 1284 (1986); P. J. Crutzen and F. Arnold, *Nature* **324**, 651 (1986); D. W. Fahey *et al.*, *J. Geophys. Res.* **94**, 11299 (1989).
4. K. D. Beyer *et al.*, *Geophys. Res. Lett.* **21**, 871 (1994); T. Koop *et al.*, *ibid.* **22**, 917 (1995); S. E. Anthony *et al.*, *ibid.*, p. 1105; L. T. Iraci *et al.*, *J. Geophys. Res.* **100**, 20969 (1995).
5. E. V. Browell *et al.*, *Geophys. Res. Lett.* **17**, 385 (1990).
6. J. E. Dye *et al.*, *J. Geophys. Res.* **97**, 8015 (1992); O. B. Toon and M. A. Tolbert, *Nature* **375**, 218 (1995).
7. A. Tabazadeh *et al.*, *Geophys. Res. Lett.* **21**, 1619 (1994); K. S. Carslaw *et al.*, *ibid.* **23**, 2479 (1996); M. J. Molina *et al.*, *Science* **261**, 1418 (1993).
8. A. R. Ravishankara and D. R. Hanson, *J. Geophys. Res.* **101**, 3885 (1996).
9. A. Middlebrook *et al.*, *ibid.* **98**, 20473 (1993).