When kinetics plays strange tricks

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Nanometer-scale ionic crystals, when immersed in an appropriate salt solution, often undergo a process of ion exchange; some atoms of the crystals are replaced by atoms from the solution. Thermodynamics dictates what will happen after the system reaches equilibrium. The concentration of the guest ions should reach a steady state dictated just by the difference in chemical potential between the ionic species. However, in some crystals (for example, cadmium sulfide immersed in a solution of silver ions) (1–3), one observes modulated concentration patterns with length scales of many lattice spacings persisting over the time of experimental observation. These patterns, according to thermodynamics, should not exist, especially in large crystals.

Frechette et al. (4) introduce a simple model capable of describing this apparently paradoxical phenomenon. The model is based on a simple lattice description, in which each site can be occupied by two kinds of ions (host or guest). Since the guest and host ions have a different size, the presence of guest ions induces an elastic strain, inducing a pair potential interaction between the sites. According to this model, the concentration waves are determined by a subtle interplay between diffusion and elastic forces. At equilibrium, the probability of observing these waves is extremely small and vanishes if the crystal is very large. However, consistent with experiments, simulations show that these transient waves are so long lived that they are practically stable. Examples of these quasistable concentration waves are shown in figure 10 in ref. 4 for model nanocrystals with a geometry that resembles the experimental geometry. Frechette et al. (4) provide a neat explanation of this observation. When the original crystal is immersed in the solvent, a very fast exchange happens close to the surface. Further diffusion of the guest ionic species toward the interior is subsequently much slower. If no further ions are exchanged with the solvent (for example, because the solvent is removed), the concentration wave close to the surface looks like an ordered stripe. At this point, long-range elastic deformation plays a key role; the lattice mismatch between the host and guest ionic species determines a coherent strain on the scale of several lattice spacings, which, in turn, favors the diffusion and the subsequent stabilization of host ions only at a specific distance from the previous concentration stripe. This effect can then propagate toward the interior of the crystal and persist for a very long time.

Kinetic Trapping Everywhere

These results suggest that highly nontrivial mesoscopic properties of ionic crystals can be achieved, and eventually controlled, by fine-tuning the protocol of their preparation. Kinetic accessibility of a configuration, rather than its thermodynamic stability, seems to be the key driving force determining the properties of these systems.

Another class of processes in which kinetics seems to play the key role is the assembly of nanocrystals from solution into ordered assemblies. As in the case of ion exchange, controlling and understanding this process have enormous technological importance, but once again, the tricks played by kinetics are subtle, and they are often poorly acknowledged and understood. It has been shown, for example, that by controlling solvent evaporation rates, it is possible to promote the arrangement of nanocrystals in mesoscopic rings (5) and honeycomb arrays (6). It has also been observed that drop-deposited nanoparticle films can form arrays with exceptional long-range order and are macroscopically compact by a nonequilibrium process, which is controlled by evaporation kinetics and particle interactions with the liquid–air interface (7). In these examples, the nanoparticles arrange in configurations that should not be likely to occur according to thermodynamics. This seems to happen by kinetic mechanisms related to subtle details of the...
interaction between the nanocrystals, the substrates, and the solvents.

By considering these examples, one might be tempted to associate the onset of exotic kinetic effects to “complexity”—for example, directional interactions induced by the shape of the nanoparticles or for the case of ionic crystals, the interplay between diffusion and long-range elastic interaction. However, one realizes that there are also many examples of such effects among inorganic crystals, even those composed of a single element. Perhaps the most prominent—and magnificent—example is diamond, which is thermodynamically metastable at ambient conditions and in principle, should convert to graphite. However, as we all know, it is pretty uncommon to see a lusty diamond turn into a homely pencil tip. A similar behavior is observed in a countless number of other cases. A nitrogen molecular crystal should convert to a polymeric one around 40 GPa, but at room temperature the transition does not happen (8). Silicon with cubic diamond structure converts to the beta tin phase upon compression to 9 GPa, but at decompression, that beta tin phase does not revert back to cubic diamond, converting instead to a metastable phase (9).

In the zoo of materials where kinetics matters, a place of honor is held by water. Pressure-induced amorphization of ice is known to be a kinetic effect (10). However, even the properties of ordinary ice are the result of kinetic trapping. Almost 90 y ago, Pauling realized that ordinary ice at absolute zero has a structure of ordinary ice are the result of kinetic trapping. Almost 90 y ago, Pauling realized that ordinary ice at absolute zero has a residual entropy. This is due to the fact that, while the oxygen atoms of each molecule form a regular diamond-like lattice, their hydrogens can point in six different directions. The disordered state is “selected” in ice simply by kinetic trapping; the thermodynamic free energy minimum, in which all the hydrogens are also ordered, cannot be reached in ordinary conditions. Even more surprisingly, the kinetic trap in this specific system is not unique but forms a continuum; according to the history of the sample, a different fraction of hydrogens is capable of ordering (11).

Kinetics effects, therefore, not only contribute to the formation of concentration patterns in ionic crystals or determine the structure of nanoparticle arrays and in ordinary crystals, such as carbon, silicon, or ice. They are also exploited by biological systems to perform their function. Arguably, life can be thought of as one of the strangest tricks played by kinetics. It is well known that the thermodynamically stable state of proteins in a crowded environment is insoluble fibrils (12). These fibrils, unfortunately, are sometimes formed in living organisms and are responsible for several infamous neurodegenerative diseases, such as Parkinson’s and Alzheimer’s diseases. However, the timescale for formation of these aggregates is of the order of hours or days in ideal conditions and, with luck, of decades in human cells. Evolution has fine-tuned the timescales of biochemistry in such a way that the lifetime of proteins, between synthesis and degradation, is much shorter than this. In this manner, proteins typically exist only in the kinetically built metastable state in which they can perform their function.

Exactly which metastable state is chosen among an infinity of possibilities is very often decided by subtle details, such as the interplay between diffusion and long-range elastic forces in the ionic crystals examined by Frechette et al. These details can be fine-tuned by evolution in living organisms or by a field expert in the case of nanoscience, but they are, in the generality of cases, poorly understood and therefore, out of control.

A Challenge for Molecular Simulators

The take-home message is that in an enormous number of systems, thermodynamics does not seem to matter too much. The “stable” state in which these systems exist on the mesoscopic or macroscopic timescale is just one of many metastable states that the system can explore and not necessarily the most stable one, reached only if one could wait an infinite time. Exactly which metastable state is chosen among an infinity of possibilities is very often decided by subtle details, such as the interplay between diffusion and long-range elastic forces in the ionic crystals examined by Frechette et al. (4). These details can be fine-tuned by evolution in living organisms or by a field expert in the case of nanoscience, but they are, in the generality of cases, poorly understood and therefore, out of control.

Scientists working on molecular and atomistic simulations are well aware of the utmost importance of metastability in determining the properties of real-world systems. However, the weapons available to the researchers to find predictive answers are still rather primitive and can be branded as brute force simulation of a model which is so simple that can be simulated for an arbitrarily long time. As underlined by Frechette et al. (4), it is currently not possible to understand ion exchange using a chemically accurate description, and one has to use a simplified model, in which the ions do not have a well-defined chemical identity. Similarly, if proton ordering in ice can be studied only by a model in which chemical bonds are treated like binary variables, we can only tell if the bond arrow points forth or back (11). We foresee that in the future the community of molecular simulators will work hard to develop tools capable of predicting kinetic accessibility with the same level of accuracy that has been achieved for thermodynamic stability.

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