

Patterns Lead the Way to Far-from-Equilibrium Materials

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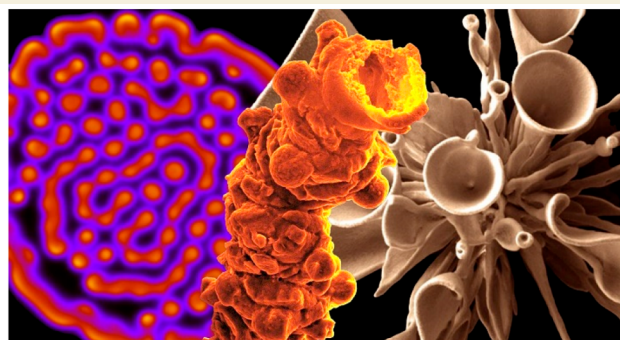
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ABSTRACT: The universe is a complex fabric of repeating patterns that unfold their beauty in system-specific diversity. The periodic table, crystallography, and the genetic code are classic examples that illustrate how even a small number of rules generate a vast range of shapes and structures. Today, we are on the brink of an AI-driven revolution that will reveal an unprecedented number of novel patterns, many of which will escape human intuition and expertise. We suggest that in the second half of the 21st century, the challenge for Physical Chemistry will be to guide and interpret these advances in the broader context of physical sciences and materials-related engineering. If we succeed in this role, Physical Chemistry will be able to extend to new horizons. In this article, we will discuss examples that strike us as particularly promising, specifically the discovery of high-entropy and far-from-equilibrium materials as well as applications to origins-of-life research and the search for life on other planets.

KEYWORDS: *self-organization, high-entropy materials, biomorphs, pattern formation, origins of life, machine learning, artificial intelligence*



Nearly all studies aimed at the elucidation of the mysterious processes in living beings were studies on the living organisms themselves. Only a few modern researchers have tried, like the alchemists, to imitate these phenomena of life with nonliving matter.

—Raphael Eduard Liesegang, 1896¹

INTRODUCTION

It is a common interpretation that the human brain evolved to minimize surprise.² This innate desire to predict future events can also be seen as the root of scientific curiosity and progress. A key building block of this reliable anticipation is our ability to recognize patterns. Patterns present themselves in various forms and contexts ranging from the rhythmic repetition of events to causal chains and spatial order. And while we might think of predators returning to a body of water at certain times of the day or a tree with delicious fruits in a particular location, these principles carry over into the realm of chemistry. Here patterns take the form of characteristic reactivities, reaction classes, and molecular structures, but they also go far beyond those important categories.

An even cursory look at the history of chemistry is a look at evolving patterns that have become so obvious that we barely recognize them as such. For physical chemists, this is apparent in the evolution of ancient ideas about matter to modern quantum chemistry. In this progression, a patternless, continuum state of infinitely divisible matter turned into atoms and molecules and

eventually wave functions so complicated that they continue to resist descriptions by modern computational methods.³ They also directly relate to concepts of determinism and the role of chance as these opposing poles affect the success of predictions and the minimization of surprise.^{4,5}

As our understanding of patterns in chemistry has evolved over the centuries, so too have the tools at our disposal to recognize and use them. Today we are at the beginning of a new era of pattern identifications that will be driven by machine learning (ML) and artificial intelligence (AI). One of the prime examples is how large language models (LLMs) recognize human language patterns and even excel in translating languages with limited digital data.⁶ Perhaps surprisingly, this ability can also be used in chemistry. For example, with the help of the simplified molecular-input line-entry system (SMILES), very similar models can predict chemical reactions by treating them as translations from one language (reactants/reagents) to another (products).⁷

In addition to these advancements, LLMs have begun to mimic our thought patterns, making them capable of answering

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complex questions such as “Why is AI so good at recognizing patterns?” When prompted with this question, OpenAI’s GPT4⁸ generates what appears to be an enthusiastic answer, stating “AI, particularly machine learning algorithms, is exceptionally good at recognizing patterns due to its underlying architecture and training process”. Considering this type of answers, it is not surprising that recent studies of GPT-4 have evoked Arthur Eddington’s quote “Something unknown is doing we don’t know what,” highlighting their intricate and elusive operations while echoing the enigma of the electron.^{8,9} Beyond their broad linguistic prowess, ML and AI systems are revolutionizing health sciences¹⁰ and accelerating mainstream materials chemistry¹¹ as exemplified by the Materials Genome Initiative.¹²

Obviously, the potential impacts of ML/AI in (bio)chemistry and chemical education will be far-reaching and are impossible to discuss in a single article. We hence focus on three, in our opinion, promising and interesting research directions: high-entropy materials, far-from-equilibrium materials, and the role of such complex matter in the origins of life. Throughout this discussion, we will review the role of patterns that offer an excellent leverage point for ML/AI methods. We will not discuss details of underlying algorithms, network architectures, and learning approaches and refer the reader to an online resource by Andrew White on deep learning for molecules and materials.¹³ We also note that this article was inspired by the *ACS Phys. Chem. Au* call for “Visions for the Future of Physical Chemistry” and this original intention permeates many of the topics and viewpoints presented in the following.

Much of our direct scientific inspiration comes from living matter which uses abundant reactants to create systems that might seem imperfect and unreliable when compared to crystalline materials and their well-defined properties. Nonetheless, living systems boast a long list of remarkable abilities that are entirely inaccessible to conventional materials. These include growth, self-reproduction, adaptation to environmental changes, learning, avoidance of destructive factors, and self-healing.

In the spirit of the opening quote by Raphael Liesegang, we suggest that these features are not intrinsically biological, but available to abiotic and inorganic processes. Instances of these life-like inorganic systems include self-organizing chemical reactions such as the oscillating Belousov–Zhabotinsky or the Turing-pattern-forming chlorite-iodide-malonic acid reaction,^{14–18} chemical gardens,¹⁹ and BaCO₃-silica biomorphs²⁰ (Figure 1). The discovery of these life-like inorganic systems has often been the result of fortuitous serendipity rather than systematic searches, which might explain why they are often viewed as anomalies. Notable exceptions include pioneering work by Irving Epstein, Patrick De Kepper, and others on the systematic design of chemical oscillators²¹ and Turing patterns.^{14,22} These captivating systems and innovative approaches hint at untapped potential to revolutionize our understanding of the world and envision new types of engineering.

What prevents us today from exploring this potential? The main stumbling block is that we only grasp a small fraction of the rules required to create these systems and struggle to chart their complex dynamic and structural phases. For interesting applications, we are further confronted with a mind-blowing combination of kinetics problems, intricate questions concerning crystal growth and unconventional crystallization, far-from-equilibrium conditions, and transport processes such as diffusion and reaction-driven convection. Often additional

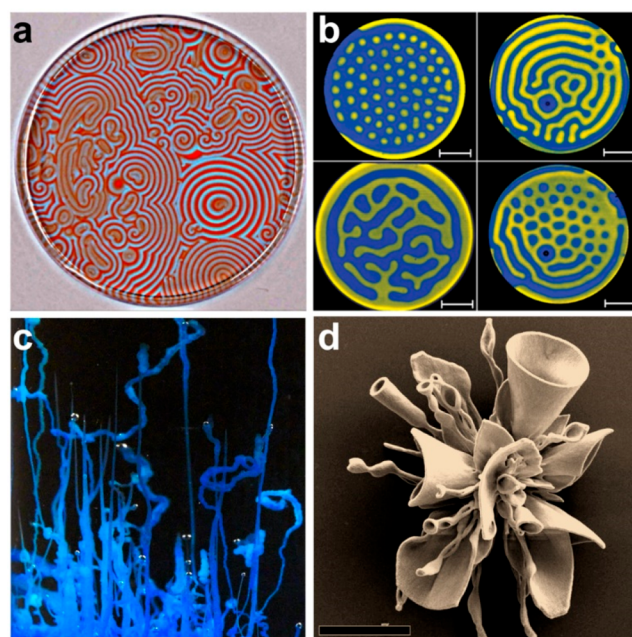


Figure 1. Self-organizing chemical system. (a) Target patterns and spiral waves in the Belousov–Zhabotinsky reaction occur due to autocatalytic reaction-diffusion processes. Contrast arises from the redox catalyst ferroin. (b) Near-stationary Turing patterns in the chlorite-iodide-malonic acid reaction. Colors result from a pH indicator. Scale bars: 4 mm. (c) Centimeter-scale chemical gardens formed by precipitation reactions of Cu²⁺ ions in a basic silicate solution. (d) Scanning electron micrograph of a BaCO₃-silica biomorph. Scale bar: 30 μm. Panel (b) reproduced with permission from ref 14. Copyright 2009 AAAS.

factors exacerbate these challenges, such as temperature gradients, phase separation, diffusio-phoresis, and poorly understood liquid precursors.

Is it naive to ask AI to come to the rescue? We believe it is not as patterns seem to organize similar behaviors in extremely different systems. If future AI can identify these ingredients and unravel their complex interactions, remarkable applications might result.

THE ALGORITHMIC ALCHEMIST

Chemical research often resembles a puzzle; some pieces are known, others are missing, and their mutual connections are often unclear. Classic examples are Mendeleev’s work that led to the periodic table of the elements and the structure elucidation of DNA, but we dare say that most chemists’ research follows this theme. At closer inspection, we also find that the main challenge often boils down to identifying an underlying pattern that can exist in real space or in some more abstract context such as a high-dimensional reaction network or phase space. And perhaps not surprisingly, the underlying physics is either far from understood or not applicable when these major and minor advances occur or fail.

Some chemical patterns manifest themselves by a predictable repetition such as atomic positions in crystals or the surprising alternating abundance of organic compounds with even and odd numbers of carbon atoms.²³ Some are more elusive as beautifully demonstrated by quasicrystals (Figure 2a) for which the atoms are perfectly ordered but not periodic.²⁴ These seemingly impossible structures only gained acceptance after Dan Shechtman’s 2011 Nobel Prize in Chemistry. (Some sources

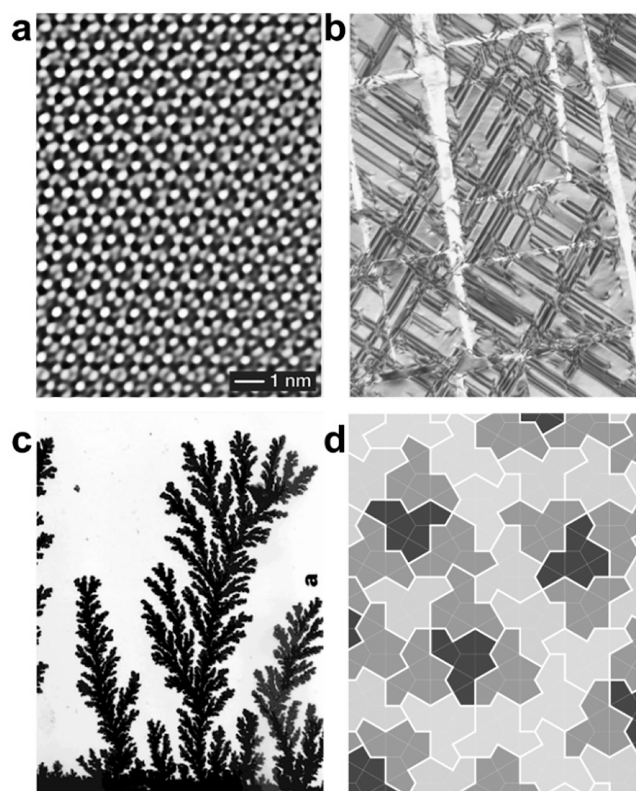


Figure 2. Unusual patterns complementing the examples in Figure 1. (a) Inverted Fourier transform of a high-resolution transmission electron microscopy (TEM) image of a quasicrystal. (b) TEM micrograph of a two-phase engine blade alloy. (c) Dendritic copper deposits obtained by electrodeposition. (d) Copies of a 13-sided shape that covers the plane but cannot form periodic tilings. Reproduced with permission from (a) ref 24 Copyright 2009 AAAS, (b) ref 25 Copyright 2016 Springer Nature, (c) ref 26 Copyright 1997 Springer Nature, and (d) adapted with permission under the Creative Commons BY 4.0 DEED Attribution 4.0 International License from ref 27 Copyright 2023 Smith, D.; Myers, J. S.; Kaplan, C. S.; Goodman-Strauss, C.

claim that Linus Pauling, who did not accept the existence of quasicrystals, said “There is no such thing as quasicrystals, only quasi-scientists.” Other puzzling patterns are only discernible by detailed analyses (Figure 2b,c) such as strange attractors in chemical chaos.^{15,16} These and other fractal structures are self-similar meaning that their appearance repeats to some extent as we magnify them more and more. In chemistry, such structures also include snowflakes and certain particle assemblies including colloidal aggregates and dust bunnies. Yet another type of pattern is the class of the “unknown unknowns”²⁸ that escape our otherwise excellent ability to spot and create patterns. They serve as a warning that patterns are not necessarily obvious. Indeed the sentiment that “it is easy to spot patterns” was prominently disproven yet again in 2023, when a hobbyist mathematician discovered the first einstein (“one stone”) tile, a single shape that forces aperiodic tiling of the plane (Figure 2d).²⁷ How many unknown patterns are woven through chemical space and nature remains a mystery and we can only speculate that many treasures remain hidden.

During the past few years, ML stepped into this world of chemical puzzles and patterns as a powerful player. For instance, in 2020/21 AlphaFold predicted about 100,000 unique protein structures with high accuracy²⁹ followed by the 2022 release of around 200 million protein structures from 1 million species.³⁰ Then in 2023, ProGen predicted numerous novel proteins with high catalytic activities that were largely confirmed experimentally.³¹ While it is beyond the scope of this article to explain the underlying transformer architectures and detailed learning and refinement methods, we do emphasize that the most successful models use enormous training sets which can create limitations for certain chemical applications.

The main advantages of ML/AI for pattern recognition include the ability to process these high volumes of data without specific model assumptions. Given sufficient inputs, AI models, particularly deep learning models, can handle and find patterns in high-dimensional spaces that would be difficult or impossible for humans to visualize or comprehend. The trained network structures of advanced AI models have millions or even billions

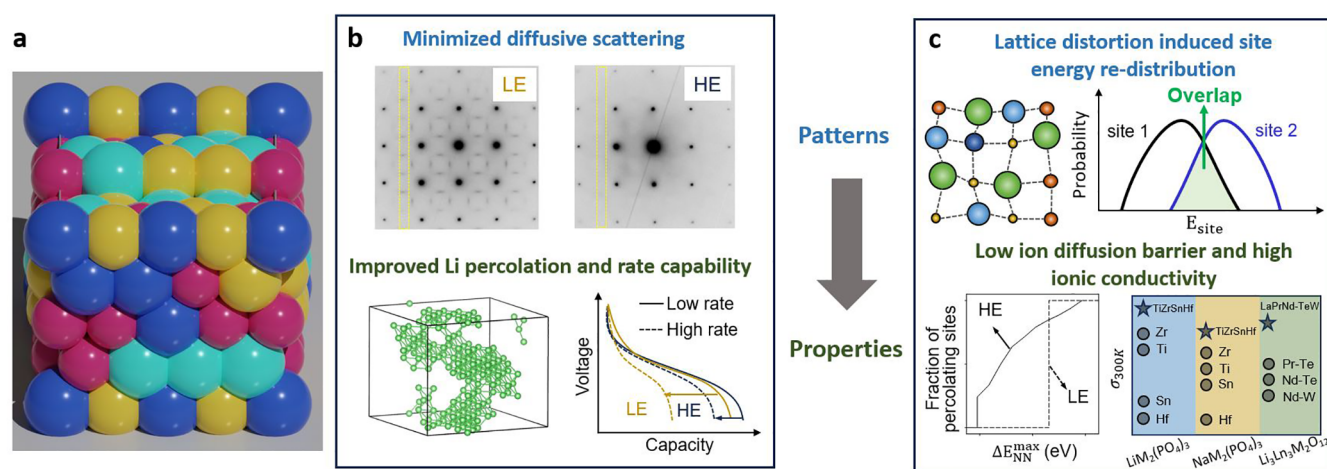


Figure 3. Patterns and pattern-induced properties in high entropy materials: (a) Illustration of the configurational disorder in high entropy materials. (b) Top panels: electron diffraction patterns of low-entropy (LE) and high-entropy (HE) disordered rocksalt (DRX) highlight the lack of short-range order in HE-DRX. Bottom panels: Schematics showing optimized Li percolation (left) and resulting higher rate capability (right). (c) Top panels: atomic patterns in HE materials show significant lattice distortion that gives rise to a distribution of site energies. Bottom panels: The resulting properties include distortion-induced low-ion-diffusion barriers and orders of magnitude improvement in ionic conductivity σ . Components of (b) and (c) are modified with permission from refs 34 Copyright 2021 Springer Nature and 35 Copyright 2022 AAAS, respectively.

of parameters that can be finely tuned to optimize performance on specific tasks, allowing for nuanced and detailed pattern detection. The following section will introduce a particular class of materials as an interesting example that illustrates the emerging pattern-finding abilities of ML/AI in materials chemistry and physics.

■ HIGH ENTROPY MATERIALS

Research on high entropy materials is an emerging area of modern chemistry and materials science. Their name is derived from attempts to create alloys of five or more elements stabilized by configurational entropy, which specifically refers to the entropy stemming from the various possible arrangements or configurations of atoms or molecules in a system with a periodic lattice (Figure 3a). They are also known as multiprincipal-element materials or compositionally complex materials. Such materials were first designed to reach a sweet spot in the trade-off game of strength and ductility in structural materials,^{32,33} as high entropy alloys show special plastic deformation mechanisms.³³ Later advancements extended these concepts to the design of energy storage materials, encompassing battery electrodes³⁴ and superionic conductors.³⁵

The rise of these applications pivots on the chemical manipulation of patterns within crystal lattices. For high entropy materials, there is a minimization of typical patterns, i.e., deviations from the commonly seen repeating positions of atoms in the lattice. In these materials, all symmetries are broken save for the translational symmetry, resulting in the formation of unique lattice patterns. This characteristic underpins their distinct functionalities. Take, for example, high entropy Li-containing disordered rocksalt materials. When used as a battery cathode, these materials limit atomic pairing, also known as the chemical short-range order, as illustrated in Figure 3b (top panels). Consequently, more efficient ion transport arises due to the maximization of fast Li diffusion channels in a fully random configuration, creating a distinct “new pattern”. This allows such battery electrodes to achieve much quicker charge/discharge rates than standard batteries.

Additionally, when designing optimal superionic conductors, the inclusion of multiple principal elements introduces significant lattice distortions. This is due to the amalgamation of elements of different sizes, creating a challenge for lattice rigidity. As the conventional lattice patterns are disrupted, a transformative ion transport channel, or “highway”, emerges. This transformation can elevate a crystalline framework from a subpar ionic conductor to a superior one, as illustrated in Figure 3c.

Accompanied by the rapid development of high entropy structural and functional materials, deciphering the underlying design pattern will be challenging due to the enormous composition and synthesis space. State-of-the-art AI algorithms can serve as a potential solution to such a high-dimensional design problem. Despite considerable progress toward machine learning of high entropy alloys, the journey of AI-driven machine learning is still in its infancy. The challenge for AI-assisted design of high entropy materials stems from two parts: (i) Unbiased harvesting of scientific data that can be used for learning the design pattern; (ii) the need for interpretable methods that can reveal the underlying physics. AI/ML techniques in other branches of materials chemistry that can potentially benefit high entropy materials, are summarized in the following two paragraphs.

Two research streams have emerged concerning the collection and effective utilization of data. To begin with, natural language processing (NLP) has been applied to text-mine or image-mine the existing literature. With a rapid increase in the number of papers on high entropy materials, a substantial amount of data is available in various styles and formats within the literature. NLP algorithms can be developed to scrape such data and reorganize them in a more accessible form by machine learning algorithms. A notable example of such initiatives is the inorganic synthesis database established by Ceder, Olivetti et al.,^{36,37} which compiles synthesis methods from millions of sources (accessible via the Materials Project³⁸). Beyond data collection, another challenge is effectively processing diverse data qualities.³⁹ Recent literature demonstrates the utility of transfer learning⁴⁰ as an effective tool to extract useful materials design patterns from diverse data sets, such as data sets from different levels of simulation and experiments. This capability facilitates the pretraining of machine learning models on more generic data sets for specific research domains including high entropy materials.

Beyond data collection and utilization, efforts are intensifying to improve interpretability in pattern recognition. A clear progression exists in the encoding of materials, evolving from early compositional deep learning models to those that encompass structural features.⁴¹ Such an evolution became evident with the development of crystal graph convolutional neural network for materials prediction, showcasing that an interpretable encoding process fosters more accurate predictive models. Additionally, symbolic machine learning stands out as a rapidly growing field.⁴² Instead of acting merely as black boxes predicting numerical outcomes, this approach aims to capture underlying principles. Symbolic machine learning predominantly seeks the optimal mathematical representation of large data sets, often producing models that align with both data-driven trends and foundational physical principles.

■ FAR-FROM-EQUILIBRIUM MATERIALS

A further leap in complexity takes us to far-from-equilibrium matter which, in the realm of inorganic chemistry, is today more a vision than an existing reality. Accordingly, applications of ML/AI are less clear here, but we suggest that underlying universalities and patterns provide evidence for potential and powerful future applications. This potential is demonstrated by model-free machine learning predictions of spatiotemporally chaotic or turbulent systems. Prominent examples include work on the Kuramoto–Sivashinsky equation which captures the dynamics of flame fronts in combustible media and drift waves in plasmas.^{43,44} Using an ML method called reservoir computing, a type of neural (“echo state”) network, the complex evolution of these systems can be predicted in both space and time for surprisingly long periods. In the following, we will first provide a very brief overview of chemical self-organization and then discuss future opportunities that could arise over the next decades.

A good starting point is to distinguish self-organization from self-assembly. Both processes are fascinating and some chemists use the terms in broad and overlapping ways. For us and many in our field, however, self-assembly is a process that occurs close to equilibrium resulting in structures that approach energy minima as they arise from the forces between different units (e.g., surface-bound polymers or colloidal aggregates). Self-organization, however, takes place far from equilibrium and neither dynamics nor patterns are controlled by energy minimization.

Indeed, much of the initial disbelief in chemical oscillations and other forms of self-organization resulted from the misconception that oscillations occurred around the equilibrium rather than far from the equilibrium.

In chemical processes, the distinction between systems that are near and those far from equilibrium is not inherently determined by the system structure; instead, it is controlled by the strength of the applied driving “forces”. These forces can encompass various factors, including external fields, rates of mass exchange, and more. An instructive analogy for this behavior is the flow of water from a tilted bottle. At gentle tilt angles, water flows out calmly, following a laminar pattern. As the tilt becomes more pronounced, the water begins to spurt, influenced by the formation of vortices and necessary adjustments in air pressure. This shift in water behavior, from laminar to turbulent, mirrors certain chemical phenomena. Specifically, the oscillations and turbulence seen in the flowing water can be paralleled to chemical concentration oscillations and deterministic chaos.¹⁶ Using further nonlinear dynamics concepts, the tilt angle, where the behavior changes, signifies a bifurcation point.¹⁵ This point is heavily influenced by the shape of the bottleneck, which in the realm of chemical systems can be likened to nonlinearities in the underlying rate laws.

Open systems can further sustain low entropic states by increasing the entropy of their surroundings. This universal feature of living systems is also a rather common aspect in chemical engineering where (continuous-stirred tank) reactors (CSTRs) are steadily fed while useful products and waste are extracted.^{15,16} This through-flow mode of operation is the driving force that establishes steady states that are not the thermodynamic equilibrium. As shown by numerous studies from the 1980s, sufficiently high flow rates can result in complex reactor dynamics including nonlinear (i.e., nonsinusoidal) oscillations, bi- and multistability, as well as deterministic chaos.^{15,21} For practical and safety reasons, these states are often deemed unwanted in engineering applications (although some might provide higher yields), but they seem to be an advantageous theme in living systems where they result in desired rhythms and flexible response possibilities. One can only wonder how many opportunities in chemistry and engineering are missed by a focus on simple reaction conditions.

Beyond these temporal patterns, continuous flow unstirred reactors (CFURs) can produce intriguing spatiotemporal concentration patterns including rotating spiral waves and stationary Turing structures (Figure 1b).^{14,15} These dissipative patterns are maintained in thin porous glass disks or gels that allow undisturbed diffusion within the self-organizing layer. Other examples include the catalytic oxidation of CO on Pt(110) surfaces for which micrometer-scale wave patterns in CO coverage can be monitored by photoelectron emission microscopy.¹⁸ This research was pioneered by the 2007 Nobel laureate Gerhard Ertl and co-workers. Even unfed (and essentially isolated) systems, such as a Petri dish with the aqueous Belousov–Zhabotinsky solution (Figure 1a), create similar patterns for hours if the key reactants (bromate and malonic acid) are present in sufficiently high concentrations.¹⁷

This fascinating class of spatiotemporal patterns in reaction-transport systems is again not limited to chemistry but arguably more widespread in living systems. Examples include calcium waves in single cells, traveling action potentials coordinating the contractions of the human heart, and even wave-like phenomena in groups of aggregating amoebae and giant honeybees. However, other types of chemical self-organization do exist.

Among them, reaction systems that create solid product structures are of particular interest to materials science. Liesegang patterns are one such system, characterized by their spatially periodic crystallization in cm-scale (or shorter) concentration gradients.⁴⁵ However, here we will introduce two other examples, namely chemical gardens and biomorphs, that help illustrate some of the particular features of solids formed under nonequilibrium conditions.

Chemical gardens are thin (inorganic) precipitate membranes that take the shape of hollow tubes and irregular spheres (Figure 1c).¹⁹ The classic experiment, which dates back over three hundred years, involves the placement of small salt particles into a sodium silicate solution. Salt dissolution and the high pH of the silicate solution result in the precipitation of metal hydroxides that form a semipermeable membrane around the salt seed. Now osmosis drives the flow of water toward the seed, builds up pressure, and bursts the delicate membrane. A resulting buoyant jet of salt solution rises in the silicate solution and templates the growth of a precipitate tube.

Additional growth modes exist, specifically fully closed tubes that expand through stretching and periodic ejection of membrane segments as well as tubes with attached gas bubbles. The resulting tubes form within seconds or minutes, reach lengths of up to several centimeters, and have tube diameters anywhere between a few micrometers and several millimeters. The tube wall is typically between 1 and 10 μm in thickness and—in the classic experiment—consists of microporous metal hydroxide with a thin outer layer of amorphous silica.

Modern research has greatly improved our understanding of these enigmatic structures. For example, we know today that the newly formed chemical garden membrane (typically at the upper tip of the precipitate tube) is remarkably dynamic and elastic in response to the expanding enclosed solution volume. This expansion increases the membrane mass and resembles living systems, which grow by increasing their number of cells.

For analogy, consider a cantaloupe: as it grows, its rind initially expands evenly through cell division. Later, as the outer layer hardens and cannot keep pace with internal growth, a net-like pattern forms due to macroscopic cracks and a protective polymer. In chemical gardens, the specific chemistry driving these patterns remains understudied, but it involves a shift from self-healing microbreaches to prominent ridges and cracks akin to those on cantaloupes.¹⁹ Aging of the material, influenced by hydration changes and silica deposition, plays a pivotal role in this transition and the resulting shapes of chemical gardens, highlighting the intricate nature of dynamic materials.⁴⁶

Furthermore, particle aggregation is an important factor in chemical garden growth. These colloidal building blocks form in solution and assemble onto the thickening precipitate walls. This attachment process can generate dendritic patterns as well as parallel bands with the latter resulting from spatially separated, steadily moving aggregation zones.⁴⁷ The resulting internal features are part of a simple hierarchical architecture and in this way relate to biomineralized structures such as the complicated skeletal silica structure of certain glass sponges that surprises the observer with distinct and optimized features spanning over seven orders of length scales.⁴⁸

Biomorphs are the second example that we will briefly discuss. They are fully inorganic polycrystalline objects that grow as leaf-like sheets, single and double helices, funnels, or urns (Figure 1d).²⁰ These and other rather fantastic structures have sizes of typically 50–100 μm , but can extend to centimeters. Biomorphs form in high pH solutions with millimolar concentrations of

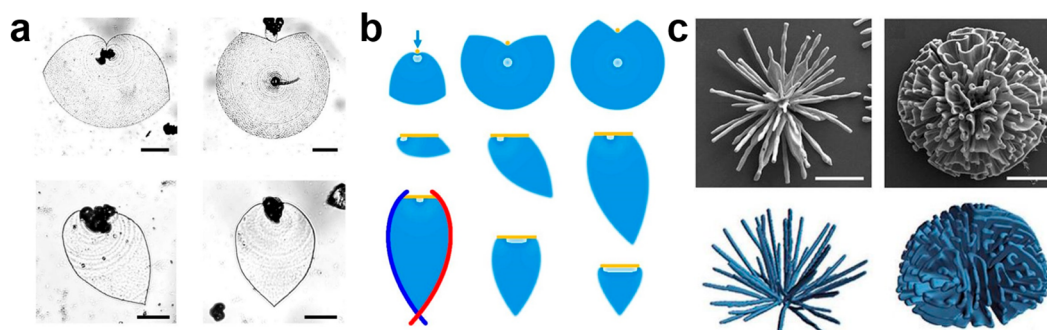


Figure 4. BaCO₃-silica biomorph shapes: experiment vs simulations based on nonlinear reaction-diffusion models. (a) Biomorph sheets observed by optical microscopy. Scale bars: 100 μm (top row), 50 μm (bottom row). (b) Simulated sheets with growth fronts that laterally shrink, match the experimental shapes in (a), especially their edges that trace logarithmic spirals (blue/red curves). (c) Top row: scanning electron micrographs of coral-shaped biomorphs. Scale bars: 20 μm . Bottom row: three-dimensional patterns formed by a nonlinear reaction-diffusion model. Reproduced with permission from (a,b) ref 53 Copyright 2017 ACS and (c) ref 54 Copyright 2019 American Institute of Physics.

barium, strontium, or calcium ions and sodium silicate when CO₂ enters the solution from the atmosphere (or carbonate is added). While the immediate interest in these structures arises from their mesoscopic shapes, they also show a surprising nanoscale architecture featuring a multitude of metal carbonate nanorods all locally aligned in the original growth direction.

Biomorph shapes were discovered by Juan Manuel Garcia-Ruiz in the 1970s, initially in experiments with silica gels rather than solutions, and since then have continued to attract interest due to their life-like appearance.⁴⁹ In 2017, it was also shown that biomorphs can form in natural spring waters such as those found at the Ney spring in Northern California which have a pH of up to 12 and a silica concentration of 4200 ppm.⁵⁰

As of today, there is no clear mechanism that would resolve the peculiar tension between the limitation to a small set of alkaline earth metal ions, restriction in the crystal system of the products (almost exclusively orthorhombic although one example in the trigonal system has been reported), and the dramatic deviation from the euhedral shape repertoire.⁵¹ Recent studies by two of us also revealed a complicated growth mechanism via solution-borne nanoparticles, particle-to-biomorph attachment, and subsequent transformations from nanodots to nanorods.⁵²

In addition, there is mounting evidence that the biomorph patterns are selected by nonlinear reaction-diffusion processes akin to those in the Belousov–Zhabotinsky reaction (Figure 1a). Simulations based on such qualitative models can reproduce and explain the logarithmic spirals traced by biomorph leaf edges, pinned constant-pitch (Archimedean) spirals formed by biomorph-on-biomorph growth, and coral-like patterns (Figure 4).^{53,54} These examples show that nonlinear reaction-diffusion patterns can produce lasting 3D structures that effectively “fossilize” certain aspects of their spatiotemporal progression as intricately patterned materials.

CHEMICAL GOLEM LESSONS

A golem is an entity crafted from lifeless materials like soil or clay, animated to life through Hebrew characters such as the word *emét* (“truth”) and deactivated by removing the letter *aleph* to yield the word for “dead”. What immediate lessons can be learned from the golem-like chemical garden and biomorph systems?

(i) Chemical self-organization is a powerful method for producing three-dimensional meso- and macroscopic structures.

These permanent products can be hierarchically structured, as in the case of nanorod-based shapes of biomorphs, and show compositional gradients as exemplified by chemical gardens that have an outer layer of silica and interior surface of various catalytic compounds. The latter feature was recently used to produce tubes capable of self-propelling in H₂O₂ solution by ejection of oxygen bubbles that primarily form in the tube cavity and not its silica-shielded outer skin.⁵⁵ Also the hierarchical architecture of (fluorescein-doped) helical biomorphs was utilized in a recent study that demonstrated highly directional light emission along their long axes with enantiomorph-specific polarization.⁵⁶

(ii) True far-from-equilibrium materials intricately depend on their surroundings, the exchange of energy and matter, as well as local gradients within and near the growing system. This requirement constitutes a clear distinction from most materials studied in chemistry today, with the possible exception of liquid crystals. Field-controlled liquid crystals are—within tight limits—rapidly reprogrammable and in this sense provide a glimpse at the possible future of reactive far-from-equilibrium materials. We envision that this class of materials will be reprogrammable in both shape and composition, respond to external changes and performance demands, potentially be capable of repositioning and exploratory motion, as well as have the ability to self-repair and reproduce.

While our vision formulated under (ii) is clearly ambitious, isolated and admittedly humble examples of many of these features do exist today. Only thorough and broad investigations will reveal the full potential and limits of this research direction. We remind the skeptical reader that the universe provides us with one exceedingly convincing example of this chemical technology: life. The surprisingly confusing line between abiotic and biotic patterns and shapes is the topic for the next two sections of this article, but before we continue, it is worth summarizing some of the problems chemistry is facing with regard to far-from-equilibrium processes and materials.

Chemical gardens and biomorphs serve as potent reminders that contemporary chemistry can struggle to elucidate and predict the emergence of life-like macrostructures and hierarchical architectures. This limitation arises even when the reaction systems consist of only a small number of inorganic reactants and bulk products are compositionally simple. One of the underlying problems is the coexistence and mechanistic coupling of self-organization and self-assembly.

We believe that it will prove difficult to untangle these interdependencies under a hard reductionist approach as they are typically inseparable without loss of pattern formation and shape generation. This situation is reminiscent of the processes in a living cell that is often discussed as a machine with parts that appear static and separable. However, this viewpoint, which has been remarkably successful, is not without controversies. It overlooks the dynamic and structural complexity of most involved players, from proteins to organelles. For a deeper dive into this debate, we recommend Daniel Nicholson's insightful review, "Is the cell really a machine?"⁵⁷

How can we unravel these messy systems and gain a deeper understanding of their nature? One important path to meaningful answers is provided by the patterns formed as well as the phase diagrams indicating structural and dynamic states. The field of nonlinear science has developed a remarkable arsenal of methods and frameworks to test and describe these patterns both in the space and time domains.^{15,16,18,21} However, these methods have not entered the common teaching canon for physical chemists and still await to be discovered by larger groups of chemists. This lack of integration might be driven by two factors: (i) a focus on molecular and crystalline systems and (ii) a lack of direct ways to apply nonlinear dynamics to complicated, poorly understood reaction systems that undergo a multitude of processes including dozens of reactions, autocatalysis, diffusion, fluid flow, osmosis, crystallization, particle aggregation, simultaneously.

The way forward appears to be a soft reductionist approach and a focus on model systems for which sufficiently accurate reaction mechanisms and transport equations can be formulated and then analyzed in terms of bifurcation analyses and direct numerical simulations. Simultaneously, physical chemistry will have to adapt and develop methods that are more suited to messy systems. One of these approaches is clearly ML/AI due to its supreme ability to detect patterns.

The possible rewards become clear as we gain the ability to contribute to the understanding of living matter, corrosion science, geochemistry, oceanography, astrobiology, and other fields that currently are at the distant periphery of physical chemistry. Moreover, truly disruptive technologies might result from this expansion of physical chemistry. In this possible revolution, adaptive materials will replace static ones just like programmable computers replaced fixed-function calculators. Perhaps, these materials and systems will even be capable of some degree of self-improvement or evolution and future generations might look at materials through the lens of Charles Darwin who wrote "... from so simple a beginning endless forms most beautiful and most wonderful have been, and are being, evolved."⁵⁸

■ LIFE'S AMBIGUOUS DAWN

...or how patterns can fool us. Let us imagine a time machine that sends us safely back four billion years. Early Earth is a wild place, most likely an ocean world, and volcanic activity is still very strong. The moon had formed, in a cataclysmic collision with the Mars-sized body Theia, a mere 500 million years earlier. Our goal is to study how life emerged and we are lucky enough to have access to the best analytical instruments of the 21st century. Where do we look and what will we see?

The rock–water interface on the seafloor is littered with hydrothermal vents where hot mineral-rich water surges into the ocean creating large precipitate towers. This place seems a promising starting point and we start to look for patterns—

molecular patterns, kinetic patterns, morphological patterns. We detect numerous molecules loosely associated with life and find high reaction rates driven by steep temperature and concentration gradients. We find porous rocks with adsorbed organic molecules acting as catalysts, and strange inorganic microshapes. Perhaps, we see that particular environments carry out reactions that purposefully remove toxic elements or notice randomly emerging cycles of autocatalytic reactions, but are the results conclusive? Is the emergence of life a unique event between dead and alive, a flickering between states, or perhaps a drawn-out, continuous process?

This little story and the concluding questions highlight several problems that to a large extent relate to the ambiguity of patterns. Short of fossilized dinosaur bones or proteins, what compounds are reliable life indicators? This intriguing question has not received much attention, partly because we have only Earth's biology as our sample base. Nonetheless, in recent years Cronin, Walker et al. have developed a method called "assembly theory" that aims to evaluate whether a molecule could be derived from a life process.⁵⁹ In order to gauge the complexity of the molecule, it is broken down into its elemental parts in a recursive manner. The molecular assembly index (MA) is then calculated as the minimal number of steps needed to reassemble the object. This process yields high indices for molecules such as adenosine triphosphate (ATP, MA = 21) and the third-generation antibiotic Ceftiofur (524 g/mol, MA = 27), but low values for glycine (MA = 4) and succinic acid (MA = 5). Combined with mass spectrometry analyses of complex biotic (e.g., yeast extracts) and abiotic samples (e.g., Miller–Urey spark discharge mixtures), this approach suggests that only living systems produced MA indices greater than ~15. (Interestingly, borosilicate glass containers increase the number of organic compounds formed in the Miller–Urey experiment compared to Teflon flasks. Several amino acids, a dipeptide, carboxylic acids, and aromatic compounds are produced only in the presence of borosilicate.⁶⁰) We also note that assembly theory has been the subject of discussion, with some likening it to aspects of the Shannon-Fano and Huffman's encoding algorithms.⁶¹

Above the molecular scale, this ambiguity continues and complicates efforts to distinguish life from life-like shapes based on morphology. To navigate this, we must delineate what constitutes the "shape of life," spanning from living organisms to their biomineral derivatives. Recognizing that living entities predominantly exhibit curvilinear shapes, while abiotic forms often present rectilinear characteristics (e.g., the flat faces and sharp edges of crystals), provides an initial guideline: Is it smoothly curved?

Historically, morphology has served as a primary indicator of life. Although this approach still persists in some areas, it is now more broadly recognized—albeit not always heeded—that relying solely on morphology can result in misidentifying early Earth life and, by extension, extraterrestrial life. A notable example of this contention centers around structures found in the Early Archean Apex Basalt in Western Australia. In a pivotal 1987 article, Schopf and Packer announced the discovery of what they believed to be the oldest known microfossils, dated between 3.3 and 3.5 billion years ago, highlighting their similarity to present-day cyanobacteria.⁶²

However, in 1999, these purported fossils underwent reevaluation by Martin Brasier, who argued that the observed patterns, resembling spheroidal cells in either globular or filamentous aggregates, were of abiotic origin.⁶³ As the

knowledge of silica–carbonate biomorphs grew, Schopf's microstructures were further reinterpreted in the light of these strikingly similar globular and worm-like shapes. The debate between Schopf and Brasier continued through 2017, spawning a series of research papers either supporting Schopf's claim or echoing Brasier's skepticism regarding the biogenicity of the structures in the Apex chert. This discourse expanded, integrating multiple chemical analysis techniques.^{62,63}

Drawing parallels, in the 1990s, a purported microfossil in Martian meteorite ALH 84001 captivated global attention as potential evidence of life on an early, wet Mars.⁶⁵ It prompted the following statement by President Clinton: "Today, rock 84001 speaks to us across all those billions of years and millions of miles. It speaks of the possibility of life. If this discovery is confirmed, it will surely be one of the most stunning insights into our universe that science has ever uncovered. Its implications are as far-reaching and awe-inspiring as can be imagined."⁶⁴ While initial carbon-residue findings seemed promising, the minute diameter (20–100 nm) of the object caused skepticism. Today, only a minority of scientists consider these structures as Martian fossils, highlighting yet again the risks of relying solely on morphology. More recently, Dodd et al. identified potential microfossils in 4-billion-year-old rocks from the Canadian Nuvvuagittuq Supracrustal Belt (Figure 5a,b). However, also these samples have faced scrutiny,⁶⁶ as they morphologically and chemically mirror small, iron-mineralized chemical garden tubes (Figure 5c,d).

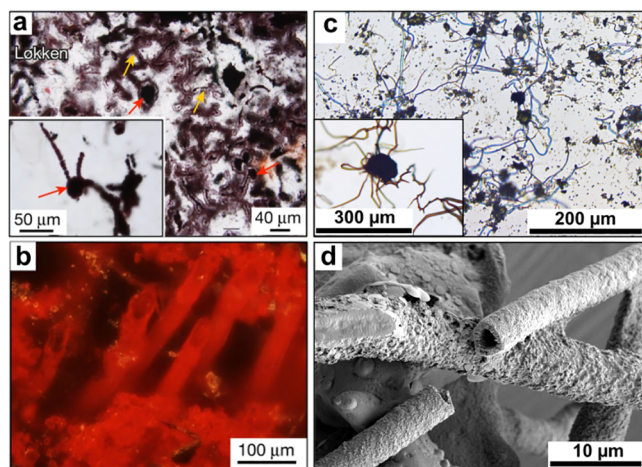


Figure 5. Comparison of (a,b) transmitted light micrographs of around four billion-year-old putative ancient microfossils extracted from sedimentary rocks interpreted as a sea-floor hydrothermal vent and (c,d) abiotic ferrous-based chemical garden tubes formed in lab experiments imaged using optical (c) and scanning electron (d) microscopy. (a,b) Reproduced with permission from ref 67 Copyright 2017 Springer Nature. (c) Reproduced with permission under a Creative Commons BY 4.0 DEED Attribution 4.0 International from ref 66 Copyright 2019 Royal Society Publishing.

Lastly, modern science is not limited to the nearby moons and planets of our solar system, but has started to expand the search for life to exoplanets of which to date more than 5000 representatives have been confirmed for our galaxy. A question of direct interest to physical chemists is whether life indicators can be detected by spectroscopic measurements of exoplanets. In 2012, this idea prompted Loeb and Turner to suggest that artificial illumination (i.e., nonblackbody radiation such as LED light) would signal the existence of extraterrestrial technolo-

gies.⁶⁸ While this suggestion still sounds ambitious a decade later, recent data from the James Webb Space Telescope provide evidence for CO₂, water, active photochemistry, and possibly clouds in the atmosphere of the exoplanet WASP-96b.⁶⁹ Another exoplanet, a Venus-like object called TRAPPIST-1c, was believed to have a dense atmosphere, but careful measurements of its heat balance revealed that the atmosphere is very thin.⁷⁰ Again the key questions return to the identification of patterns in the average and temporally resolved characteristics of thousands of planets and the study of life-markers in general. We believe that these questions are suited for ML/AI analyses and also challenge physical chemists to improve the current knowledge of interactions between bio- and atmospheres. Such research would connect us back to one of the first physical chemists, Svante Arrhenius, who in 1896 predicted rising global temperatures due to manmade CO₂ production and the greenhouse effect.⁷¹

■ LIFE-GENERATING MATERIALS

While the existence of life on other planets remains uncertain, deciphering the origins of life on Earth is one of the grand scientific challenges. Surprisingly, it is also one of the more neglected problems in chemistry, although it is not only intellectually challenging and philosophically relevant but also a perfect target for cross-disciplinary research that should greatly benefit from modern measurement and analysis techniques. For physical chemists, the origins-of-life problem appears at the top level as a problem of thermodynamics and kinetics. Diving deeper into the details, we likely require knowledge of surface chemistry, porous materials, electron transport, autocatalysis, phase separation, and many other facets of physical chemistry. And yet again, we believe that both physical and temporal patterns provide needed guidance for the identification of the enigmatic materials and conditions that started life from the abiotic.

The origins of life clearly required some level of prebiotic complexity (and possibly prebiotic evolution) to provide the molecular building blocks for information-carrying units such as RNA or other self-replicating macromolecules. One of the leading theories for the emergence of this chemical complexity was proposed by Mike Russell and others who proposed hydrothermal vents (Figure 6a) as the birthplace of life.^{73,74,77} Despite their vast size and global abundance, hydrothermal vent systems were only discovered in 1976.⁷⁷ Commonly found near volcanically active parts of the seafloor, they produce tall precipitate structures where superheated mineral-rich water surges through fissures on the seabed into the cooler ocean. So-called white smokers are rich in barium, calcium, and silicon minerals, whereas black smokers contain larger amounts of metal (e.g., Fe and Mn) sulfides and also green rust. Off-axis alkaline vents emit fluids below 100 °C and are rich in methane and hydrogen with some additional hydrocarbons formed during serpentinization, the reaction of certain silicate rocks with hot water that produces serpentine minerals (Figure 6b).⁷⁷

The potential advantages of alkaline vents for the emergence of life are intriguing. First of all, they were abundant on Earth and most vents provided, akin to the CFUR reactors discussed before, a steady supply of reactants and free energy that lasted for thousands of years.^{76,77} The precipitates formed layers of porous material that allowed for spatial confinement without the need for lipids (Figure 6c). The interior of these connected pores showed catalytic activity that possibly became more specific as small organic molecules adsorbed to the minerals. Some of these

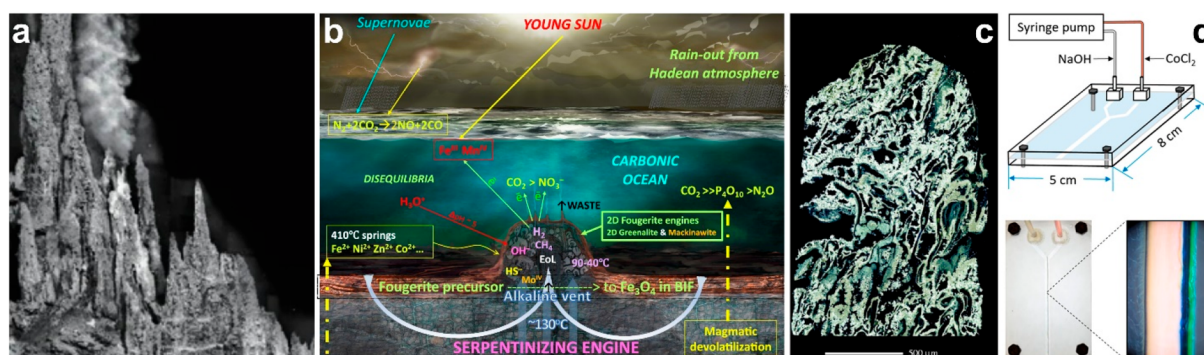


Figure 6. (a) Modern hydrothermal vent chimneys at the ocean floor. (b) Schematics summarizing the processes and chemical species responsible for the emergence of life according to the alkaline vent theory. Fougerite is a naturally occurring green rust mineral. The Hadean is the oldest of Earth's eons, ending about 3.8 billion years ago. (c) Scanning electron micrograph of a small cross-section of an alkaline vent chimney. (d) Microfluidic experiment creating similar precipitates as long membranes in microfluidic channels. Reproduced with permission (a) from ref 72 Copyright 2008 Springer Nature, (b) under a Creative Commons BY 3.0 DEED Attribution 3.0 Unported from ref 73 Copyright 2023 Frontiers Media SA, (c) ref 74 Copyright 2007 Royal Society Publishing, and (d) ref 75 Copyright 2017 ACS.

surfaces might have shared similarities to modern metalloproteins such as iron–sulfur proteins which employ small Fe–S clusters as their active sites.⁷⁸ Lastly, the precipitate walls and membranes were subject to steep gradients in temperature and various chemical species. Specifically, the pH gradients provide some intriguing resemblance to the proton gradients of modern cells and organelles.

All of this might have provided a globe-spanning set of diverse reactors that for millions of years explored a high-dimensional parameter space of flow rates, catalyst materials, gradient values, and physical conditions. Considering additional factors like cooperativity between neighboring precipitate regions and chemical exchange between different vents, it seems daunting to recreate this process in the lab. However, during the past decade, some groups have started to tackle this challenge in hopes of demonstrating specific aspects of hydrothermal vent chemistry. Many of these studies draw on parallels between chemical gardens and hydrothermal vents as both are porous, inorganic precipitates that form and exist in steep concentration gradients. In our opinion, microfluidic realizations of chemical gardens are of particular promise as they provide controlled experimental conditions, easily exclude oxygen, require small solution volumes, and are readily accessible for in situ spectroscopy (Figure 6d).^{75,79}

Of particular interest to physical chemists is how concentration gradients as steep as 1 mol/L per micron affect the growth of the porous material, its internal structure, and reactivity. These far-from-equilibrium conditions clearly have the potential to induce different forms of pattern formation. A simple example is the formation of bands of colors shown in the lower, right panel of Figure 6d. Here different colors indicate different types of cobalt precipitates that in a prebiotic context could have enriched the chemical possibilities of the material. These include the recently reported production of pyrophosphates—a possible early substitute for ATP—in similar experiments with iron oxyhydroxides.⁷⁹ Braun et al. further investigated the extreme accumulation of nucleotides by thermal gradients in simulated hydrothermal pore systems.⁸⁰ This effect is of additional importance as thin pores can concentrate only long polynucleotides, while thicker pores accumulate short and long polynucleotides equally well and, thus, could create cell-like compositional patterns within the system.

We believe that the necessary existence of an inorganic material capable of starting life from abiotic conditions should inspire more research activity than it currently attracts. This type of material will likely be a porous geochemical system and only function in the presence of appropriate gradients and feed-through conditions. We speculate that these conditions will create not only the needed prebiotic chemistry but also self-organize into patterns capable of performing different tasks.

Another example of this type of pattern formation relates to the formose reaction that, in the presence of CaCO_3 , autocatalytically generates ribose and other sugars from formaldehyde.⁸¹ The relevance of this reaction to prebiotic chemistry was criticized by Stanley Miller, who showed that at the high pH conditions needed for the formose reactions, sugars decay within minutes.⁸² However, if these processes occurred in a mineral membrane subject to pH gradients, they could generate sugars in a high-pH region and accumulate them in a nearby neutral zone of the chemical pattern. These and other examples show that it is unavoidable to consider spatial patterns when analyzing or designing complex materials and systems including those that enabled the emergence of life.

The idea that the search for the origins of life can be accelerated or solved by ML/AI approaches has been pursued by Lee Cronin.⁸³ His group develops “chemputers”, lab automation systems controlled by AI, that seek faint patterns in the high-dimensional search space that somewhere encodes emerging life. There is a certain irony if machine systems should solve the mystery of our geochemical origins and we are vaguely reminded of a collection of science fiction stories by Stanislaw Lem.⁸⁴ Lem describes a civilization of self-constructing robots that have forgotten the existence of organic life. The robots treat the notion of “fleshy” life as an ancient myth and ponder the question of their origins as they cannot comprehend the idea that soft, biological beings could have ever given rise to their metallic and silicon-based existence.

CONCLUSIONS

Recognizing and understanding patterns is fundamental to scientific inquiry because it allows us to formulate predictions, develop theories, and understand the underlying mechanisms or principles at play. Even in the absence of immediate understanding, recognizing patterns has direct implications as sufficiently reliable predictions allow for engineering applica-

tions. In this paper, we have tried to illustrate that patterns provide important information for the exploration and creation of novel types of materials, specifically complex inorganic matter such as high entropy and far-from-equilibrium materials. These patterns often share similarities with patterns found in living systems and can suggest ways to design novel functionalities ranging from hierarchical architectures to adaptability, self-pulsation, and self-healing which are common in biology but rare in chemistry.

The latter view is not common among contemporary physical chemists who frequently employ a hard reductionist approach and, over the past decades, have focused less on kinetics, transport processes, and (nonequilibrium) thermodynamics. However, we suggest that these classic subdisciplines are essential for progress toward the novel types of complex and life-like materials described here. We are also reminded of Donald Mikulecky's thought-provoking statement "The widely accepted myth that biology is special and that physics is generic is totally wrong. In fact, far more can be learned about the material world by a careful study of biology than can ever be learned from physics."⁸⁵ Perhaps, the time is right for physical chemistry to look up at biological, geological, or even planetary systems for valuable insights and inspiration that ultimately will complement the remarkable achievements inspired by atomic physics.

We further aimed to show that patterns in man-made and natural systems can be intricate, hidden, or misleading and that superficial similarities are insufficient for concluding similar underlying mechanisms. We also discussed that these patterns do not necessarily present themselves in real space or time, but that they can exist in high-dimensional phase spaces, chemical reaction networks, or even more abstract spaces such as those defined by assembly theory and related approaches. Regardless of the details, these patterns contain precious information that, in our opinion, is a terra incognita of chemistry and science in general waiting to be explored for both intellectual and technological purposes.

Considering AI's powerful ability to transmute large data sets into patterns, ML/AI appears a promising way to accelerate this exploration into the complex fabric of nature; in some cases, it might turn out to be the only path forward as AI will likely outperform human abilities as pattern detectives. However, ML/AI methods are also susceptible to biases and can learn patterns that are artifacts rather than fingerprints. We believe that physical chemists should play a major role in overseeing and guiding the AI-assisted hunt for complex inorganic matter. Lastly, we emphasize that both AI predictions as well as isolated engineering applications should not be the end goal, but rather a stepping stone toward a deeper understanding of the world in terms of physical laws and theories.

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Author Contributions

All three authors contributed equally to the manuscript with an emphasis on pattern formation (Steinbock), high-entropy materials (Ouyang), and origins-of-life-related topics (Knoll). The authors are listed in alphabetical order. CRediT: **Pamela Knoll** conceptualization, visualization, writing-original draft, writing-review & editing; **Bin Ouyang** conceptualization, visualization, writing-original draft, writing-review & editing; **Oliver Steinbock** conceptualization, visualization, writing-original draft, writing-review & editing.

Notes

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