Evolutionary Design of Granular Media and Block Copolymer Patterns

Heinrich M. Jaeger[a] and Juan J. de Pablo[b,c]

[a] James Franck Institute and Department of Physics, The University of Chicago, Chicago, IL 60637
[b] Institute for Molecular Engineering, The University of Chicago, Chicago, IL 60637
[c] Institute for Molecular Engineering, Argonne National Laboratory, Lemont, IL 60439

Abstract. The creation of new materials "by design" is a process that starts from desired materials properties and proceeds to identify requirements for the constituent components. Such process is challenging because it inverts the typical modeling approach used in physics and materials science, which starts from given micro-level components in order to predict macro-level properties. We describe how to tackle this inverse problem using concepts from evolutionary computation that make it possible to find with high efficiency component-scale parameters best adapted to given target properties. These methods have widespread applicability and open up new opportunities for design as well as discovery. In the interest of generality, we discuss examples from two, very different classes of soft materials. First we consider granular materials, which are inherently disordered and far from equilibrium, and where an important problem is to identify particle shapes that are optimized for design targets such as low aggregate porosity or high stiffness under compression. Second, we discuss thin films of block-copolymers, which have gained increasing relevance for applications in commercial nanodevice fabrication, and where a crucial engineering problem is to develop processes that coerce these materials to self-assemble into ideal, defect-free circuit-like features.

Introduction. Whether we design an object in our minds, on a piece of paper, or on the computer, we always start with an idea about the desired overall properties and then proceed to identify the necessary components, their configuration, and any associated fabrication steps required to achieve the targeted outcome. As such, the process of design maps macro-level targets onto micro-level requirements and develops strategies that implement such mapping. The same holds for the design of materials.

While this sounds conceptually simple, there are at least four reasons why it can rapidly become difficult. The first is that, as the number of constituent ingredients increases, the set of possible combinations to consider grows exponentially. More ingredients open up more choices, but properly tuning the many micro-level parameters to generate the targeted outcome becomes a major challenge [1]. Second, the mapping from the space of desired macro-level behaviors to the space of particle-level parameters does not have to be unique. In other words, there can be a multitude of valid design solutions to a given design problem. Third, a critical additional aspect of design may be identifying not only the ingredients, but also the most appropriate boundary conditions and the processing path, including the best initial conditions. This is important especially in situations where the design target is a material in a non-equilibrium configuration, such as a glass. Finally, to make a design-based solution valuable it should do more than represent a single answer to single task. What we are looking for in a useful design is that it provides a path toward solving similar problems without having to go through the full process. Ultimately we would like to obtain more generally applicable prescriptions, or rules, that apply to whole classes of related design problems.

For creating materials with novel properties, where a useful macro-to-micro level mapping has not yet been established, the design process therefore tends to involve a significant degree of trial and error. Here we ask whether this process can be guided, and perhaps even automated, through computational means.

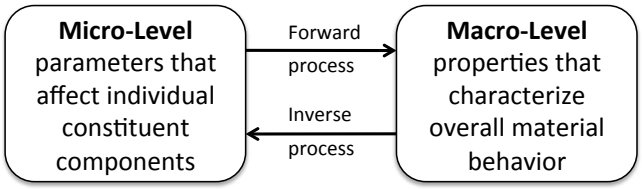

Fig. 1. Materials design involves an inverse process that starts with macroscale target properties to identify microscale constituents.

One way to think about the approach toward a desired design outcome is to delineate the iterative process that accompanies it into two closely coupled parts that we here call the forward and the inverse component (**Fig. 1**). The forward component describes the part of the process where a particular idea or implementation is tried out, i.e., where a given set of micro-scale variables is used to create a particular macro-level outcome. We label this a "forward" process, because it is the typical approach taken in materials science, physics, and chemistry (called the "direct approach" in Ref. [2]). This forward component could be an actual laboratory experiment or a virtual experiment performed via computer simulation. As long as the forward simulation engine used produces physically accurate output,

virtual experiments have the advantage that a large portion of parameter space can be explored quickly. The inverse component then compares this macro-level outcome with the targeted design goal and, assessing the difference, generates a set of new micro-level parameters to be tried out by the forward component in a subsequent iteration step.

In this way, the design process can be viewed as a search and optimization problem: the sought after micro-level parameters are those that minimize the difference between the output of the forward process and the given design target.

When we design in our mind, we perform this iterative optimization automatically and are able to close the distance to the design goal more or less effectively depending on prior experience. Yet the same process also has merits when there is little or no prior experience, except that empirical trial and error clearly is not the best design strategy and some knowledge has to be built up first about how the macro-level outcome reacts to micro-level parameter changes. When designing with the help of a computational approach this "learning" needs to be achieved by the algorithm that performs the optimization.

Since several of the above issues apply very generally to the design of any complex system or material, there has been considerable interest in developing automated, computer-based approaches to solving inverse problems of this type. Recent reviews of inverse methods for materials design, such as those by Rondinelli, Poeppelmeier and Zunger [2] or Jain, Bollinger and Truskett [3], show how computer algorithms that can guide the design of materials with targeted properties have opened up new directions for materials science.

In practice, there are numerous optimizers to choose from and generally the choice of both the optimizer and the forward simulation engine will depend on the type of problem at hand. Computer-aided design approaches have been used to predict crystal and protein structures, including super-hard materials and novel protein configurations [4-7]. Applied to polymers, such methods have paved the way towards optimizing directed self-assembly [8-11]. Similar methods have been employed to identify the crystal structures of patchy, colloidal particles [12]. For far-from-equilibrium systems like jammed, metastable aggregates of particles [13], simulation-based optimization has been used to design bulk properties such as stiffness or packing density by tuning complicated micro-scale features like particle shape [14-16].

In the following we consider one particular class of optimization algorithms, namely those based on evolutionary computation. We discuss examples from two very different classes of soft materials to demonstrate the wide range of applicability: macroscopic granular materials and nano-structured block-copolymers. Given the rather different physics and design tasks for each of these materials, the forward calculation engines are completely different, involving DEM simulations in one case, and particle-based simulations of field theory solvers [69-70] in the other, but the algorithms for the inverse process are closely related. Details can be found in Refs. [10, 11, 13-18]. In the following we provide an overview of this prior work by our

research groups.

The basic idea is to treat a materials design problem in a way that is, at least superficially, similar to biological evolution: a whole family of different trial solutions is implemented, the performance of every member of this family is evaluated in a forward simulation of the resulting macro-level material properties, and the fittest performers (in the sense of coming closest to the design target) are kept. From these, a new family of "offspring" is then constructed via suitable mutations in the space of micro-level parameters, and these offspring then compete against each other in successive generations of selection and mutation. The process is terminated once the output approximates the design goal sufficiently well.

To apply this technique, only two components are essential. The first is a genome, or means of encoding trial solutions, so that mutations can be applied freely. The second is a fitness metric, i.e., a means of determining which potential solutions are better than others. Once these two components have been established, an optimization algorithm can be constructed to search the solutions space. Much improved over older methods like genetic algorithms, the current front runners are called evolutionary strategies. Specifically, we focus here on the Covariance Matrix Adaptation Evolution Strategy (CMA-ES), originally developed by Hansen et al. [19]. Like most evolution strategies, this algorithm attempts to improve the quality of solutions by examining perturbations around a given mean solution. In an ordinary random search, a new population is obtained by perturbing the old population using Gaussian noise. In contrast, CMA-ES uses the covariance matrix to perturb the system along specific search directions. The key feature of this algorithm is that it uses information from prior iterations of the search to deterministically update the mean and covariance matrix. In particular, the mean of the distribution is updated so that the likelihood of drawing a previously found good candidate is maximized, whereas the covariance matrix is updated so as to increase the probability of a successful next step.

There are several important features of this approach worth noting. Unlike gradient-based techniques, this type of optimizer can cope easily with very rough or very flat "search-scapes". Further, the forward simulations in each generation can all be carried out in parallel, which means that large numbers of trial solutions can be tested simultaneously, speeding up convergence when searching in high-dimensional parameter spaces. Since the optimizer only operates on the space of input variables for the forward process it can be completely agnostic about the actual physics of the problem. Thus, the optimizer can operate in "black box" fashion and potentially be effective across a larger class of problems than a highly tailored optimizer. One additional point of note is that this approach allows us to go beyond incrementally improving a material's properties: we can set a design target far outside any previously established performance envelope, for example asking for *qualitatively* new behavior. As long as the method can identify the micro-level parameters required to achieve such target it will thus function as a powerful tool not only for optimization but also for discovery.

Granular Materials by Design

Granular materials are random aggregates of a large number of macroscopic, individually solid particles that interact primarily via dissipative contacts among neighboring grains [20, 21]. They come in all sizes and encompass particulate media from sand, gravel, or soil to agricultural products like grain or fertilizer, to pharmaceutical powders to pigments. Most often a bulk commodity comprised of seemingly simple ingredients, granular material can nevertheless exhibit complex behavior during storage, handling and processing, which necessitates careful choice of the constituent particles. In fact, compared to ordinary elastic solids, many of the properties of granular matter are sufficiently special that it makes sense to consider optimizing them. For example, granular materials can reversibly transform between flowing and rigid states via a jamming transition [22] and offer distinct advantages over ordinary solids in terms of their ability to withstand plastic deformation and dissipate energy without cracking, or to self-heal after impact and recover load bearing strength if suitably confined. If picked correctly, granular materials can simply be poured or dumped into place, yet the resulting, amorphous particle aggregate is solid-like rigid, can support load and withstand shear. At the same time, a granular aggregate remains highly porous: the densest possible random packing for equal spheres is only ~64% by volume; rods and odd-shaped particles pack even less dense [21, 23, 24]. On large scales, these features are important, for example, for the construction and functioning of breakwaters, railroad beds, or foundations. On smaller scales, they enable a range of unique applications for energy dissipation and vibration isolation, for additive manufacturing via laser sintering of metal powder [25-27], or as shape-adaptive, variable-compliance material for soft robotics [28-33]. In addition, the high surface area to volume ratio of granular aggregates offers advantages for applications in catalysis or as advanced battery electrodes.

For applications where either the performance of the granular material components is critical or the fabrication cost is substantial, it therefore makes sense to envision customized particle types and ask: What kind of particle should be picked in order to optimize a particular property of the aggregate? Furthermore, if there were a method for rational design of granular materials, could suitably optimized particles lead to novel aggregate properties beyond those currently known?

The availability of optimized particles would make it possible to overcome a number of bottlenecks currently limiting the use of granular materials and open up a wide range of new uses. This might include light-weight particulate materials with jamming/unjamming behavior designed to optimize soft robotics applications; high-porosity high-toughness materials for medical implants that can be poured into place during minimal incision surgery; shock absorbing materials that have designed stress-strain characteristics to protect sensitive equipment; head-conforming helmet interiors for better blast protection; or particles designed for specific settling characteristics to minimize, or tune, compaction.

With granular materials a key difficulty in achieving this is that the aggregate behavior depends not only on specific material properties of the individual particles, but critically also on their shape and their surface properties, since these control the packing arrangement among contacting neighbors. Thus, to a large extent it is the local connectivity and the "architecture" of the contact network that determine the overall response to applied stresses. In granular media, this architecture is based on particle configurations that are random. Together with the wide range of possible particle shapes this allows for tremendous structural diversity and a very rich set of dynamic responses. Compared to regular lattice structures this also makes it significantly more challenging to predict how the overall, aggregate behavior is affected by the local, particle-level properties and packing arrangements.

Prior work on granular materials has therefore mainly focused on finding and rationalizing the aggregate properties for a given particle type. Going beyond spherical particles, there has been much progress concerning the maximum achievable packing densities, together with local particle configurations and correlations among neighboring particles. This includes particle shapes such as Archimedean and Platonic solids [34-39], ellipsoids, cuboids, or 'superballs' [24, 40-45], cylinders, cones, and frustums of different aspect ratios [46-48], as well as various types of particles constructed from overlapping disks or spheres [42, 49-56]. In general, much less is known about the mechanical response of such packings and, with few exceptions, the focus has traditionally been on particles with an overall convex shape. More recently, however, increasing attention has been paid to particles that are highly non-convex (or are sufficiently flexible so they can assume concave shape during the packing process) [24, 57-66]. Significant concavity allows for interlocking or entanglement, which directly affects the mechanical response. Meanwhile, non-convex particles with sharp bends or large protrusions tend to pack less densely than convex shapes. Together, this suggests that shapes could be found that optimize trade-offs between several desirable attributes, e.g., maximize porosity together with strength, or maximize jammed rigidity together with malleability when unjammed.

The challenge in expressing the role of particle geometry in driving certain behaviors of granular material lies in the combination of two aspects: shape not only is an effectively inexhaustible parameter, but the macro-scale aggregate behavior can sensitively and non-monotonically depend on small changes in particle shape [14]. However, we found that optimizers based on evolutionary strategies vastly outperform standard search methods (such as simulated annealing) and make it possible to find optimal or at least near-optimal particle shapes for a given design task.

Fig. 2. 'Granular Molecules', each 3d-printed as one piece from hard plastic. Each sphere is ~3mm in diameter.

For simplicity, we represent particles as granular molecules, i.e., sets of equal-sized spheres that overlap a fixed distance. The main reason is that this limits the type of particle-particle interactions to sphere-sphere contacts that can be handled straightforwardly in standard DEM simulations, as shown previously in

work using such bonded-sphere compound particles as a means to explore non-sphericity and aspects of (geometric) friction [42, 49, 50, 52, 55, 67, 68]. Different particle shapes are represented by N spheres placed in configurations specified by a construction protocol we call a blueprint [14]. The blueprint expresses the genotype of each particle shape (**Fig. 2**). These configurations do not have to be planar, and for N >3 can extend in all three dimensions. The optimizer then creates and evolves a whole family of shapes by mutating the sphere configurations.

As we mentioned earlier, this approach makes it possible not only to quantitatively optimize known properties of a granular material, but also to search for particle-level attributes, here shape, that result in qualitatively new properties. An example has been the discovery of a particle shape that leads to strain stiffening material, i.e., a stress-strain curve that exhibits a positive second derivative, under constant pressure boundary conditions (**Fig. 2**, on the right) [14]. This qualitatively differs from typical jammed material, which exhibits strain weakening under similar conditions. With N = 5 this particle is just large enough to assume a 3-armed shape that combines strong non-convexity with non-planarity.

With compound particles composed of same-size spheres as in **Fig. 2** the range of addressable design tasks is limited to behavior that can be produced by highly corrugated shapes. One extension is to allow for variable radius of each sphere [15]. A further extension is letting neighboring spheres overlap. For large N this makes it possible to approximate both smooth surfaces and sharp corners or edges, thereby greatly opening up the design space. **Figure 3** shows an example using both extensions, where the design task was to find the shape that produces the densest packing for particles poured into a container (for the limit that the container is large enough to neglect wall effects) [16]. Friction in this case was turned off in the simulations, which in experiments corresponds to packings that are vibrated or tapped sufficiently to reach their asymptotic density.

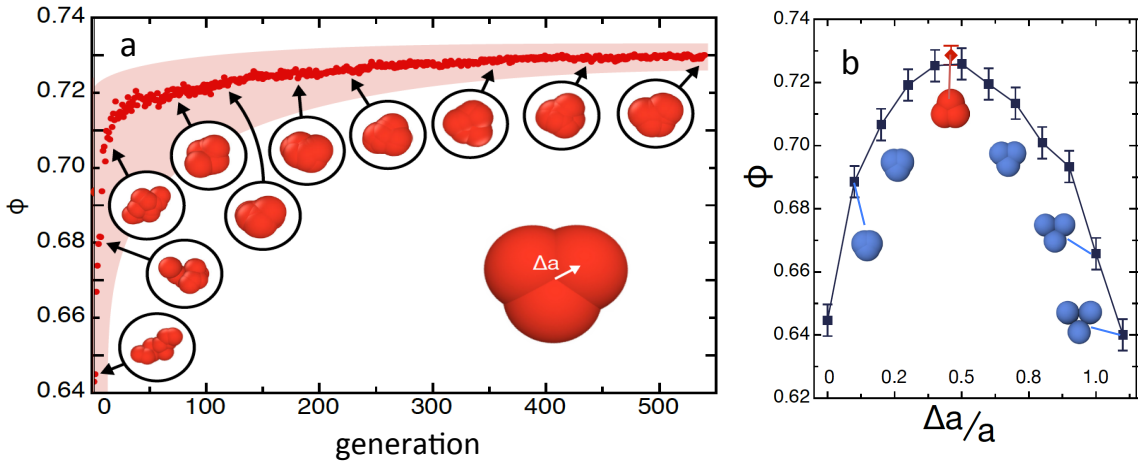

Fig. 3. Using evolutionary algorithm to find best-packing particle shape. a: Packing density ϕ as the particle shape evolves. Inset: Basic shape identified as optimal under given packing conditions. b: Effect of varying the degree of sphere overlap. Adapted from Ref. 16.

In materials such as jammed granular or glassy systems, which inherently exist in structural configurations far from (thermal) equilibrium, considering boundary and initial conditions together with the processing path is crucial in finding a proper solution to a design task. A particular advantage of the method discussed here is that these aspects are included automatically.

Design Rules. While the approach outlined above provides a way to obtain a solution for a particular design task, it does not say anything about how the solution might change if the task changes. Ideally, we would like to have more generally applicable mappings, which could provide answers for related design problems. We here call such general mappings *design rules*. For granular media, developing design rules constitutes a major challenge since the understanding of how particle shape affects the aggregate properties currently exists only in limited form for certain classes of simple particles.

Interestingly, the same search and optimization approach can also be used to construct design rules [15]. The basic idea behind this is as follows. We assume that the optimizer is able to find a solution to a specified design target by tuning a given set of particle-level parameters (understanding that we can only consider design targets that actually are achievable). In other words, we assume the optimizer can solve the inverse problem of mapping from design target (aggregate properties, vertical axis in **Fig. 4**a,b) to corresponding particle-level parameters (here shown for simplicity as a single particle shape index, horizontal axis). We then give the optimizer two very specific tasks: identify particle-level solutions that correspond to the two extrema in design-target space, i.e., that maximize or minimize the aggregate properties with respect to a whole class of related design targets (circled red in **Fig. 4**a,b).

Once the optimizer identified the particle-level parameters giving rise to the extrema in aggregate properties, any other (allowed) setting of these parameters will necessarily produce aggregate properties that are intermediate. For the purpose of design this has a very important consequence: we can sweep through design-target space by interpolating between the particle-level parameter values corresponding to the extrema. Importantly, we can use *any* interpolation, which means we are free to pick an interpolation that takes into account additional considerations, such as ease of implementation in an experiment or in industrial production.

Figure 4c,d demonstrates the power of this approach. The design task was to find the particle shape producing a desired target packing density. As before, particles were formed from up to N = 10 rigidly bonded, frictionless spheres of arbitrary radius, but in this case without overlap. Under these conditions, not the planar triangles as in **Fig. 3** but "Mouse" trimers (**Fig. 4c**) form the densest packers, while in all cases rods produce the loosest aggregates [15]. The sum of the radii of all spheres constituting a particle, $\sum_i^N r_i$, serves as a suitable particle-level "shape index".

While exploring the parameter space during the evolution process, the optimizer produced a cloud of shape/packing-density relationships (**Fig. 4**c). However, close inspection shows that similar target densities can be achieved with shapes that vary widely, so that there is no obvious way to predict how small changes in desired target density translate into shape changes.

On the other hand, based on the above considerations, we can sweep through the full range of possible packing densities by picking *any* path through shape space, as long as it starts and ends with the shapes corresponding to the two density extrema. As an example, **Fig. 4**d shows a path that starts from the largest N=10 rod (all spheres of equal size) and simply shrinks the rod length from one end by successively reducing the size of the outermost sphere, until only one single sphere is left; at this point the path switches to a second branch (shown in green) which grows two "ears" on the central sphere, attached at a 70^0 bond angle and each increasing in diameter from zero to 1/3 of the main sphere, which are the

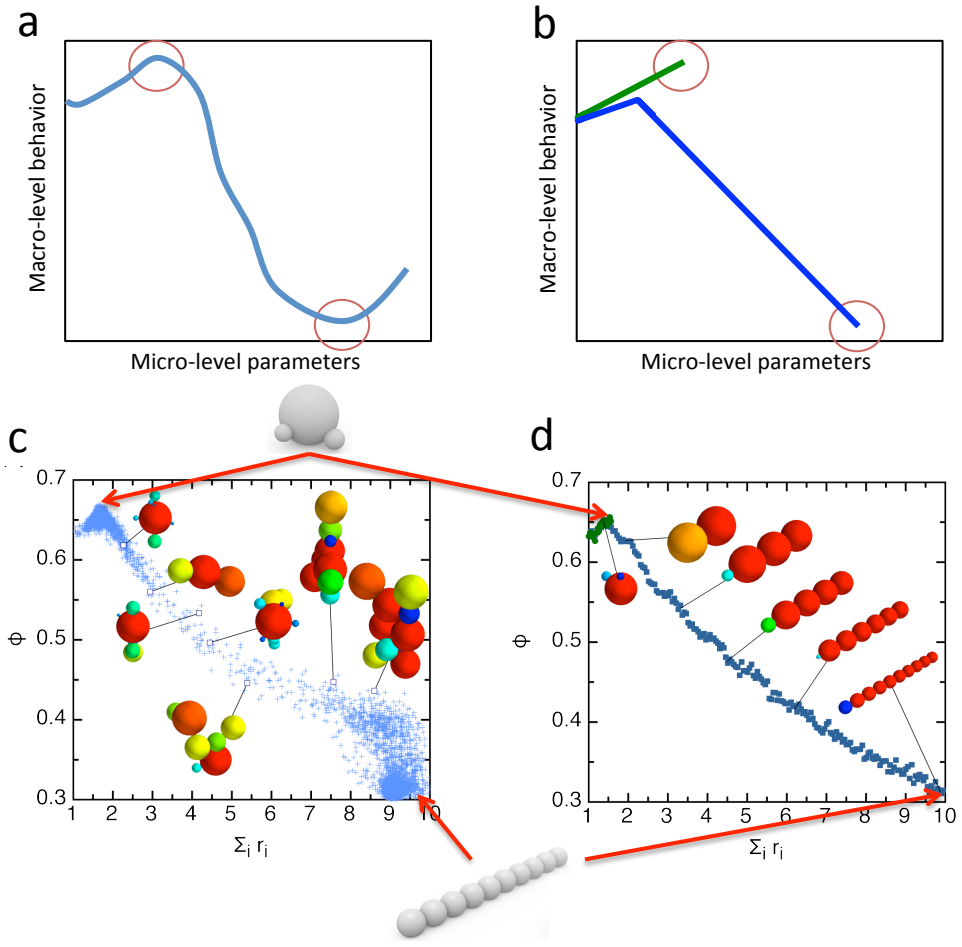

Fig. 4. Design rules for micro-to-macro-level mappings. a: Sketch of mapping. Red circles indicate extrema in design space. b: Design rules using paths (here two paths) based on additional criteria such as ease of implementation. c: Packing density ϕ vs. shape parameter. Points indicate all shapes sampled by optimizer while searching for extrema in ϕ (corresponding extremal shapes are shown in gray). d: Path for design rule developed from (c). Adapted from Ref. 15.

appropriate parameter values for the particle producing the densest packing with $\phi \approx 0.67$ under the given conditions.

This path establishes a useful *design rule* because it (a) provides a smooth mapping of target packing fraction to particle shape in the sense that small variations in ϕ correspond to small changes in shape and thus allows for interpolation, (b) covers the full range of achievable ϕ values (up to the allowed N=10 in this example), and (c) is straightforward to implement (as opposed to many of the highly complex shapes the optimizer parsed through during evolution). We note that for this design problem the design rule is not everywhere one-to-one, since the path is non-monotonic in ϕ over a small region: to generate packing densities in the range 0.64-0.65 one can choose either an asymmetric dimer or a trimer particle shape. From a practical point of view, this degeneracy is unimportant, given that both shapes provide a solution to the same packing problem.

Directed Self-Assembly of Block Copolymer Thin Films

Block Copolymers consist of two or more strands, or blocks, of different polymers covalently bonded together. Blocks containing different chemical compositions tend to repel each other and, as a consequence, in aggregate these systems tend to spontaneously micro-phase separate and self-assemble into nanoscale domain morphologies when driven below their order-disorder transition. The typical feature size of these domains, 5-100nm, the availability to easily control different domain morphologies via the relative block sizes and interaction strengths, and the ability to generate very sharp domain boundaries (of order a nm) has made block copolymers an attractive choice for a wide range of nanotechnology applications [1].

An important application has been the use of block copolymer thin films for generating highly regular patterns over large areas on substrates of interest to the semiconductor industry, and then transferring those patterns into the substrate by exploiting the differential etch resistance of the blocks. The particular advantage of this approach is that the patterns self-assemble and thus do not need to be created by lithographic techniques operating at the same, fine nanometer scale. However, in order to create patterns that are exceptionally defect-free and that are oriented along specific directions, the self-assembly process has to be guided, or directed, by topographic or chemical surface features. Such features could be holes, posts, trenches or steps, they could be local areas with distinct surface wetting properties, or they could be areas where a short brush layer has been used to attract one of the polymer blocks. In all cases they can work with high efficiency even if they are spaced apart significantly further than the inherent domain spacing of the block copolymer. Directed self-assembly thus can multiply the feature density, making it possible to create very fine patterns by using much coarser lithography to generate the guiding features. **Figure 5** shows this schematically for the case of 3x density multiplication of a striped domain morphology resulting from triblock copolymers in their lamellar phase. Such highly periodic morphologies are of interest for next generation semiconductor devices and high-density storage media.

The directed self-assembly process divides the task of creating a particular nanoscale pattern into generating the appropriate set of sparse guide features and then letting the block copolymer interpolate spatially to fill in the gaps between the features. In particular, one would like to make sure the final pattern self-assembles robustly with as few defects as possible even in the presence of some (inadvertent) variability in the pre-fabricated guide features. This immediately implies that attractive as well as repulsive interactions should not be made too strong, so that energetic penalties for accommodating such variability do not become prohibitive. The challenge therefore lies in appropriately tuning the local interaction parameters that control both the self-assembly and the proper recognition of any guide features.

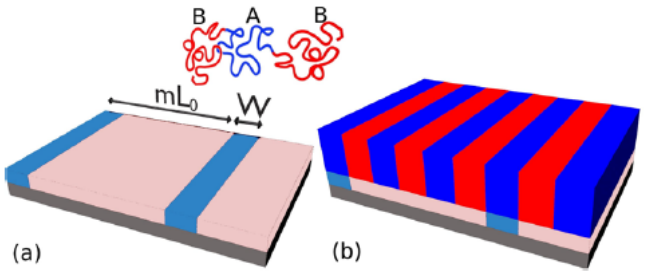

Fig. 5. Schematic representation of an approach that uses chemical markers on a substrate to direct the self-assembly of highly ordered block-copolymer patterns at very small size scales. Triblock copolymer consisting of blocks of types A and B, linked by covalent bonds, is sketched at top. a) Stripes of width W are printed at pitch mL_0. b) Block type A preferentially attach to stripes, which leads to an increase in stripe density. From Ref. 11.

These parameters include the ones that control the geometry of the guide features (such as the width W and pitch mL_0 of the guide stripes in **Fig. 5**), as well as the interaction type and strength between the various copolymer blocks, and the interactions between these blocks and the guide features or the background surface. In practice, these interactions can be tuned via the polymers' chemical structure and molecular weight, as well as by modifying the surfaces of the guide features. Traditionally, this tuning is done through empirical trial and error. More recently, design approaches using inverse methods have been implemented [8-11, 18]. In these cases, the forward simulation consists of a numerical engine to solve various trial morphologies by implementing, e.g., a self-consistent field theory [69], a mean field model based on the Cahn-Hilliard equation [10], or a theoretically informed coarse-grain model for block copolymers [70].

As before, the forward simulation is coupled to an inverse process that optimizes the parameter set in order to achieve a solution that closely approximates the targeted design. In this regard, our recent work [10, 11, 18] has shown that evolutionary strategies such as CMA-ES can be significantly faster and more efficient in finding optimized solutions than inverse methods based on Monte Carlo searches [8, 9].

In a typical design task corresponding to **Fig. 5**, the type of copolymer, and thus the block-block interactions, might be given (based on other considerations or requirements) and the goal is to optimize the guide stripe geometry together with

the block-stripe and block-background interactions such that the a regular, pristine lamellar pattern self-assembles most quickly and/or reliably at the desired density multiplication. A suitable objective function to be minimized in this case is the mean-square difference between the order parameter of the morphology tested and the order parameter of the desired target morphology. Another option for an objective function might be to consider differences in Fourier components, possibly with different weights for long and short wavelengths modes.

Variations of this design approach might involve tasks where the goal is to find the minimum number of posts and their positioning in order to self-assemble the copolymer into more complicated line patterns that can act as templates for nanoelectronic circuitry [10]. Extensions could include the molecular weights of the copolymer blocks as variables to be optimized.

A different, particularly powerful application of evolutionary algorithms is to rely on the strategies that have been outlined so far to interpret experimental data. In this case, the "target function" is an experimental measurement, and the design engine must identify the material (and material characteristics) that would generate such data in the laboratory. A concrete example is provided by scattering experiments. In the case of block copolymer self-assembly, critical dimension small angle x-ray scattering (CDSAXS) or grazing incidence small angle x-ray scattering (GISAXS) could be used to examine samples such as those shown in **Fig. 6**. The traditional approach to interpret such data, which is illustrated in the figure, has been to assume or guess a possible geometric shape for the material morphology, to calculate the scattering spectrum for such a morphology, and to compare it to the experimental measurement. The cycle is repeated until convergence, and the fitting strategy can be implemented within the framework of an inverse Monte Carlo algorithm [71].

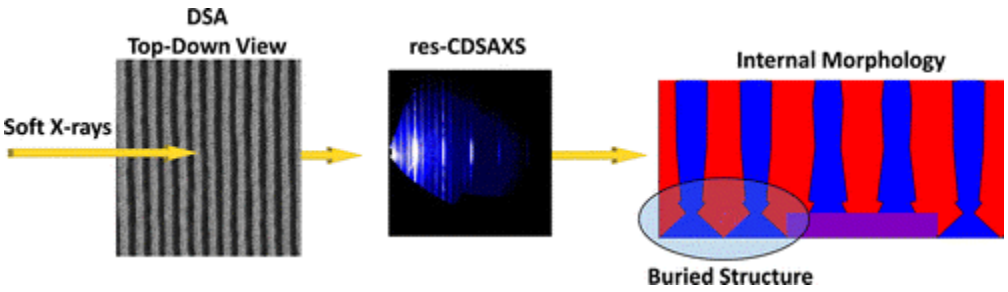

Fig. 6. Conceptual representation of physics-model based interpretation of x-ray scattering data, from [71]. The left image represents a diblock copolymer sample assembled on a pattern consisting of guiding stripes, analogous to that shown in Fig. 5. The center panel shows the spectra that is collected in CDSAXS experiments of that sample, and the right panel shows a model, based on a collection of geometric shapes, that is constructed to reproduce the experimental scattering results (center panel).

An alternative approach is to use a physics based model, be it a self-consistent field theory or a molecular simulation, to interpret the data. While such a consideration

would be overly demanding for traditional Monte Carlo-based strategies, by relying on CMA-ES versions and our more recently proposed variants [10,11,18] it is possible to interpret scattering in terms of a fully three-dimensional particle based model that includes fluctuations [72]. Again, we highlight the fact here that, from a computational point of few, a computational engine is charged with *designing* a material that scatters x-ray data in a manner dictated by the experiments. In our recent work, illustrated in **Fig. 7**, the design engine basically builds a model of the system, with as many as 15 ingredients (e.g. stripe width, stripe height and shape, interaction parameters, composition, molecular weight), that agrees with the target function, i.e. the experiment.

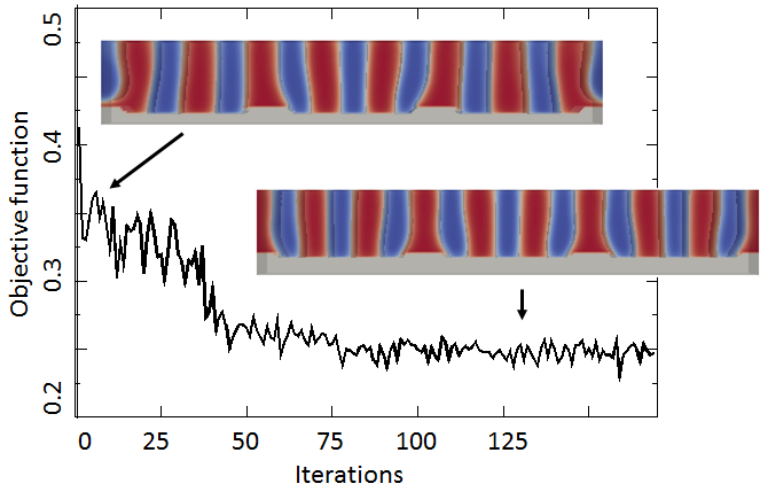

Fig. 7. Evolution of objective function during CMA-ES optimization as a function of number of iterations. A fully three-dimensional particle based model is used to interpret the scattering data (shown in Fig. 6). The two insets show representative configurations of the material in the early and late stages of the optimization process, respectively. The optimization algorithm is tasked with identifying the characteristics of the material and the pattern (e.g. size, shape, and chemistry of the guiding stripes) that lead to scattering profiles that agree with experiment. As many as fifteen material and pattern variables are explored simultaneously to arrive at the best model to describe a target (experimental) system [72].

Beyond Black Box Optimizers. Inverse methods based on either CMA-ES, Monte Carlo schemes or simulated annealing typically work in black box fashion, i.e., in their attempt to minimize the objective function they operate on the space of micro-level parameters without considering the underlying physics. Furthermore, to run successfully black box methods typically require the tuning of one or more control parameters. This brings up the question whether letting the optimizer exploit certain information about the physics makes it possible to create search engines that do not require any tuning and at the same time also speed up the optimization process. We recently were able to show that the answer is yes, at least for design problems where the underlying physics can be described by models based on

statistical mechanics [18].

Specifically, in situations where the macro-level outcome depends on the likelihood for a system to be in a particular micro-level configuration, knowledge of the probability distribution for these microstates can be used to derive an "equation of motion" for the parameters that encode these microstates. This equation deterministically calculates updates along directions of small entropy change in order to find new, improved parameter values. Since these updates depend only on expectation values calculated from the microstate statistics, the same equation can function as a highly efficient optimization algorithm. Methods like CMA-ES and adaptive simulated annealing deal with the actual configurations only through the objective function, effectively condensing a vast amount of information into one parameter. The CMA-ES then creates updates from a Gaussian distributed over all possible parameter values, while adaptive simulated annealing samples by assigning an energy value to each parameter choice. In contrast, the new approach solves the optimization problem in the space of micro-state configurations. It is able to use information about how fluctuations in configurations correspond to fluctuations in quality because it has been built to exploit the extra fact that the simulation data were generated from a known distribution [18]. Importantly, to create the probability distribution the microstate statistics have to be evaluated only once during this evolution toward the design goal.

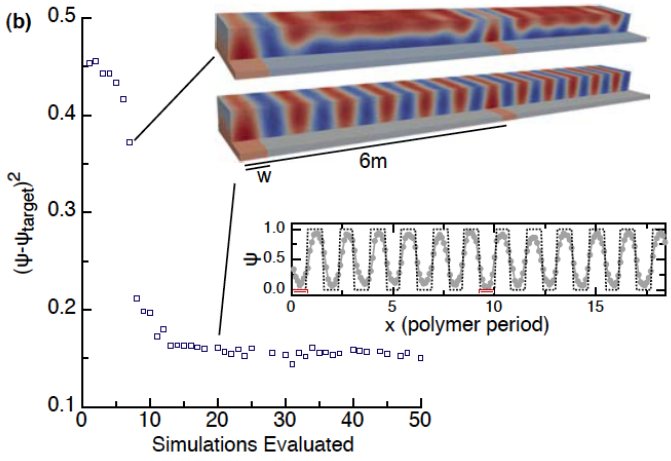

Fig. 8. Optimized design of block copolymer stripe pattern. As in Fig. 5, the design target was the identification of optimal interaction and geometric parameters, here with the goal of 6x density multiplication for a diblock system where the red block prefers the stripe printed onto the substrate. The graph demonstrates the rapid approach to the targeted "square-wave" cross-sectional concentration profile (see inset; ψ is the local concentration of the blue block). The call-outs show a rendering of intermediate and final stripe configurations. Adapted from Ref. 18.

The result is a powerful optimizer for a wide range of equilibrium as well as non-equilibrium problems. Comparing the performance of this new method to standard

CMA-ES for directed self-assembly problems, where the design task consists of identifying the optimal stripe width and interaction parameters, we find an improvement in computation speed of at least fivefold. **Figure 8** shows the results for 6x density multiplication using a PS-PMMA block copolymer.

Outlook

The ideas and algorithms outlined above are actively being pursued for design of actual processes both in academic settings and industry. Results to date have been highly encouraging, and these strategies are precursors to what we think could be a paradigm shift in how soft matter is designed. Consider, for example, designing multiblock polymer molecules that fold in predictable manners; in doing so, it would be possible to design molecules that start approaching the structural complexity and function of proteins. Or consider synthesizing a complex material as its morphology is probed in situ by scattering techniques, and having the interpretation of the data occur simultaneously. That would enable cycles of design, synthesis and characterization that, for the first time, occur truly co-currently, with potentially extraordinary increases in efficiency and productivity.

Perhaps more importantly, the approaches discussed here are not limited to equilibrium conditions. In fact, they are extremely effective also far from equilibrium, where much less is known about materials behavior and design. Not only can the materials processing pathway be included explicitly, but identifying the most suitable pathway can become the actual design target. This paves the way for creating disordered, glassy materials with performance by design. It also paves the way for macromolecular assembly processes that lead predictably and reliably towards useful, non-equilibrium morphologies. We posit that it is only by relying on such design approaches that the materials science community will be able to harness the full spectrum of structure and function that soft materials have to offer.

We end by noting that, beyond finding customized solutions that solve specific design tasks, a particular strength of these methods is that they can be extended to develop more general design rules, which then apply to whole classes of similar tasks. We showed this explicitly for the case of granular packings, but the same procedure should be applicable to a wide range of different systems. Finally, the computational approach we described makes it possible to go beyond quantitative optimization: the design target can be formulated such that it implies qualitatively new material properties, and this turns an evolutionary optimizer into a powerful tool for discovery.

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