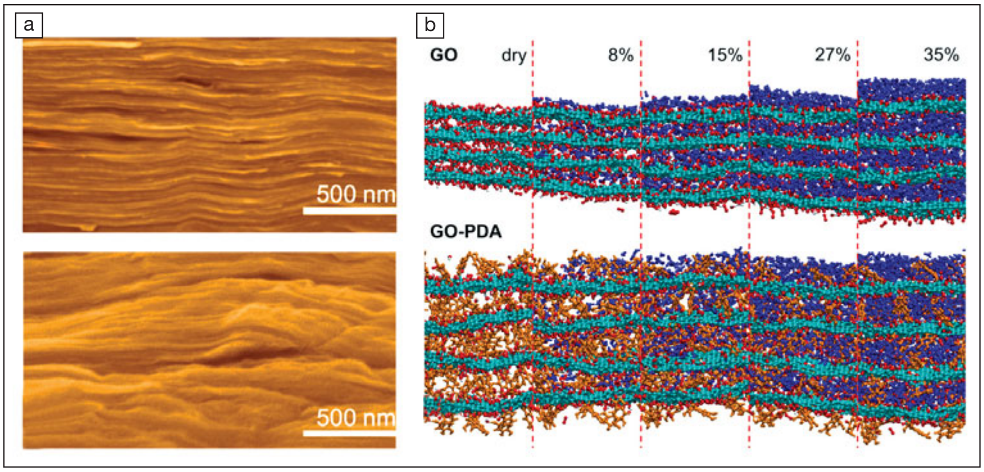
interwoven polymer. Density functional theory calculations showed that, instead of oxygen-to-oxygen functional group bonding, the polymer found reactive epoxy groups and formed carbon-to-carbon bonds, which are significantly stronger. Since the reaction simultaneously defunctionalized graphene oxide, the resulting graphene (with a 130 GPa tensile strength) was much stronger than its oxidized version (63 GPa tensile strength).

The chemical bonds were the first important element of the structure. The hydrophilic nature of the material intercalated different amounts of water in between the layers, and the researchers relied on x-ray diffraction and molecular dynamics simulations to assess the effects of this process on layer-to-layer stacking. The "dry" GO-PDA composites featured large interlayer spacings, and small amounts of water that intercalated between the sheets without pushing them apart. In contrast, water molecules used strong hydrogen bonding to bridge adjacent laminates, which pulled them together and shrunk the composite.



(a) Scanning electron microscope images of the graphene oxide-polydopamine (GO-PDA) material; (b) a snapshot of a molecular dynamics simulation for GO and GO-PDA with different water content. Credit: Chun-Teh Chen and Shengjie Ling.

Intercalated water molecules, and the resulting additional bonding reinforcement, yielded greater strength and toughness of the resulting GO-PDA composites. The researchers subjected these materials to different air moisture content levels, and an increase in relative humidity from 33% to 75% increased the toughness by 123%. The strength of the resulting composites, which had reached 170 MPa, exceeded the level of their natural nacre counterparts.

Bioinspired nanomaterials inherit designs that are the product of millions of years of evolution, and the resulting properties offer numerous improved capabilities. The work by Buehler's group shows that composite structures and laboratory-engineering materials, such as graphene composites, stand to benefit by drawing inspiration from living organisms. This work also shows the benefits of a combined approach that relies on both computational simulations and experimental results in an effort to design high-performing, commercially viable materials and composites.

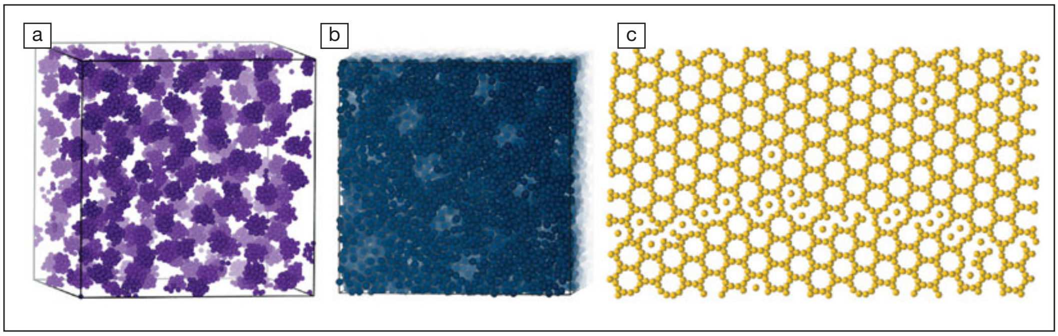
Boris Dyatkin

Intermolecular forces for self-assembly identified through simulations

The patterns that form upon molecular self-assembly are a direct consequence of interaction forces among the entities constituting the structure. Thus, the study of different intermolecular forces and the resulting self-assembled pattern is of extreme importance. Corresponding mathematical modeling has its roots in statistical mechanics. The usual practice is to modify the interparticle interaction and simulate the resulting self-assembly. A recent study led by Thomas Truskett and co-workers at The University of Texas at Austin asks an inverse question: "Can one know what sort of intermolecular forces are required to produce a desired structure upon self-assembly?" The findings were published recently in the *Journal of Chemical Physics* (doi:10.1063/1.4981796).

The simulations begin with an initial estimate of the interaction potential and a target structure. Other inputs such as number of particles (*N*), volume of the ensemble (*V*), and temperature (*T*) are specified and kept constant (for an NVT ensemble). First, molecular dynamics simulations are used to compute the equilibrium structure from the initial guess for intermolecular forces. Then based upon the difference between the current and target structures, optimization calculations are used to iteratively improve the interaction potentials ("difference of two self-assembled structures" is defined by the Kullback–Leibler measure in the present calculations). At every iteration, the researchers find a new equilibrium structure based on the most recent estimate for interaction potential. Calculations are terminated once a prescribed accuracy is achieved; in other words, when the structure based on the force field is close to the target structure.

The research team also demonstrated the applicability of the formulation by applying it to three distinct system types: cluster fluids (fluid-like particle aggregates that are roughly spherical in shape and monodisperse in size); porous mesophases (self-assembly of the conjugate inverse cluster phase); and crystals, with multiple examples of each.



Representative structures obtained with particles interacting through the inverse designed pair potentials: (a) cluster fluid, (b) porous mesophase, and (c) truncated hexagonal lattice. Credit: Thomas Truskett.

The beauty of the procedure lies in its generality. It can be easily extended to study systems with more complex molecules such as polymer chains having additional rotational and stretching degrees of freedom. Similarly, additional effects such as solvent interaction, boundary and interfacial contributions, and field effects can be straightforwardly integrated into the system's total energy potential.

Salvatore Torquato from Princeton University, a theoretician in the field of heterogeneous materials and microstructures, says, "The authors have made novel contributions to this field by applying inverse design methods to optimize for interparticle interactions that self-assemble particles into a variety of complex microstructures, including cluster fluids, porous mesophases, and crystalline lattices, by isotropic interactions. This work represents a significant advancement in inverse design of materials."

While discussing future directions, Truskett mentions "to start extending the work to more experimentally realistic systems including particles with patchy interactions, shape anisotropy, and more complicated 'many-body' interactions due to the presence of other particles (e.g., salt, small polymers, etc.)." He emphasizes the importance of these further extensions as they will make the approach more useful for experimental design, and provide information regarding the parameters that are to be tuned in a laboratory setting.

Aashutosh Mistry