A topological equilibrated configuration space analysis of nanoparticle systems

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1. Introduction

Material science is undergoing a revolution driven by the ever-increasing computational demands of a data-centric reality, coupled with an environmental crisis dictating the need for sustainable solutions and practices. Aided by machine learning and computational methods, we are searching for novel and unconventional materials with optimised properties that will define the next generation of semiconductors for (nano)electronics, thermal insulators for wearables and construction, and biodegradable materials for packaging [1, 2, 3, 4].

While algorithmically-mediated property-driven material prediction has shown promising results [5], materialising them in the lab imposes significant challenges, primarily due to our still limited understanding of the synthesis dynamics. Phase transitions, nucleation pathways, and identification of possible and viable states drastically influence the synthesisability and utility of a material. We are thus in need of methods that can analyse the dynamical behaviour of a candidate material, and robustly characterise its ground states.

Here, we propose a topology-driven unsupervised learning approach to expose the complicated phase structure and the configurational polymorphy of highly frustrated, often amorphous, systems, such as colloidal nanoparticles. Output of our method is an interactive graph, which acts as a map that enables robust inverse material design.

Traditionally, phases of matter are understood through *phase diagrams* [6], maps constructed by ground-state sampling while varying electrochemical or environmental parameters, and tracking discontinuities of thermodynamic observables. Phase classification then relies on structural observables, such as radial distribution functions and order parameters. However, the sensitivity of such methods to the observables of choice, the accuracy of the experimental data or simulation potentials [7, 8, 9, 10], and the dimensionality restrictions of projecting to only two or three dimensions at a time, deem them inadequate for characterising complex systems with phase coexistences and numerous tunable parameters defining alternative nucleation pathways.

Our method acts as a higher-dimensional alternative to phase diagrams, exploiting the enhanced expressivity of topological methods for characterising structure [11, 12]. The systems' configurations are viewed through the lens of persistent homology [13], producing noise-robust, isometric-invariant, multiscale structural summaries. Treating the totality of configurations as points sampled from the systems'

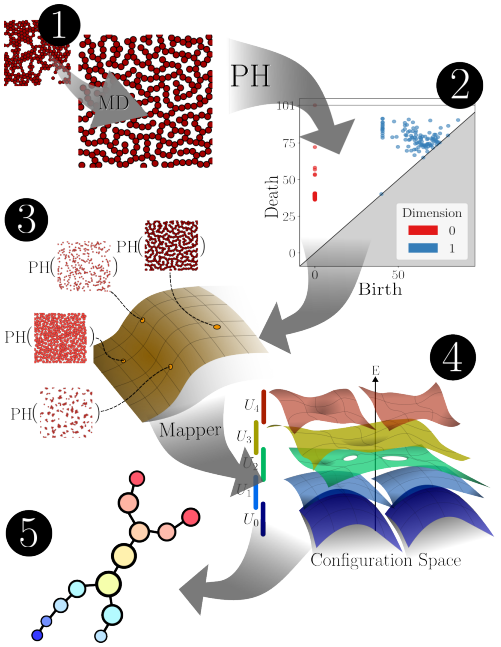

Fig. 1: The pipeline of our topological configuration space analysis. (1) 2D colloidal nanoparticles simulated under different environmental and electrochemical conditions (2) are vectorised with persistent homology (PH). (3) Each sample is a point of the high-dimensional configuration space (viewed through the lens of persistent homology). (4) The Mapper algorithm segments the configuration space into energy level sets, (5) from which the Mapper graph is derived. Each node of the Mapper graph is a cluster of similarly structured configurations that belong to the same energy level set.

high-dimensional *configuration space*, we use the Mapper algorithm [14] to dissect it into equipotential level sets, and visualise it as a simple graph which approximates its *nerve*, i.e. its fundamental connectivity in terms of independent components, loops, and voids.

Structurally-clustered configurations comprise the different nodes of the output graph, revealing phase organisation and coexistence. Node connectivity is dictated by energetic and structural criteria that implicitly define different configurational morphing pathways. The overall phase structure is then revealed by changes in the Mapper graph topology, such as bifurcation points, and by sharp changes in the topological signatures of neighbouring nodes.

We ground our approach in the *topological hypothesis* [15], according to which phase transitions induce topological changes in the equipotential level sets of the configuration space of a Hamiltonian system. This has been shown true for analytically solvable sys-

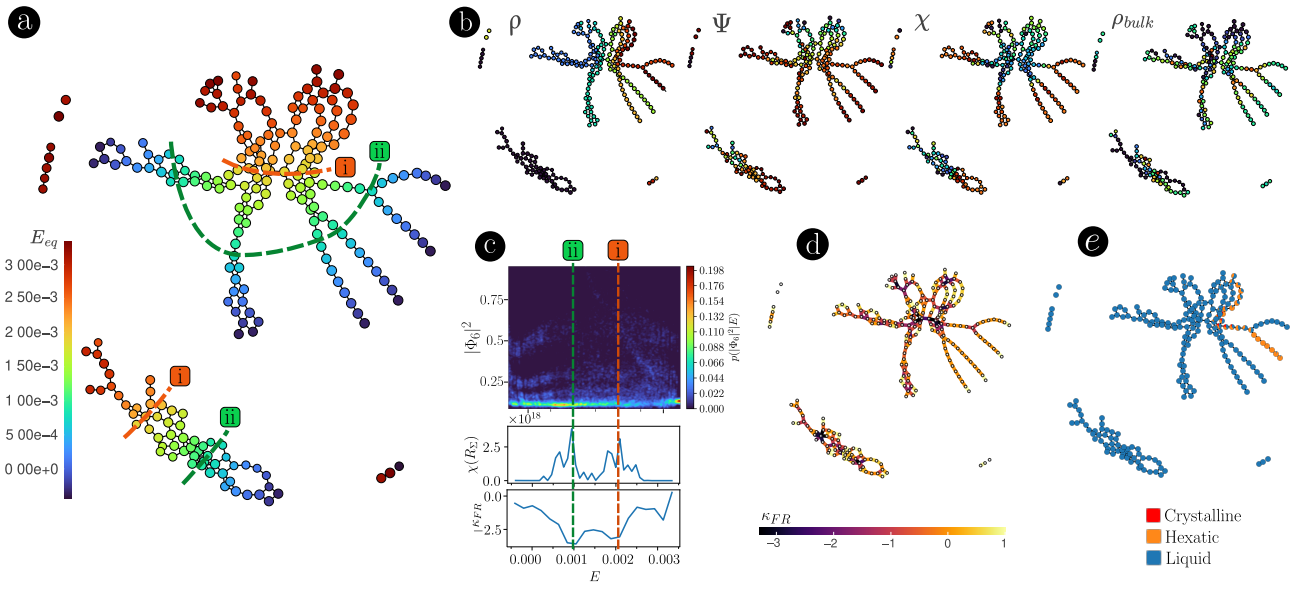

Fig. 2: (a) The Mapper graph of 2D colloidal nanoparticles, with nodes coloured according to the mean potential energy of the configurations they represent. Significant topological changes of the Mapper graph are annotated by [i] and [ii], and correspond to (c) topological changes of the configuration space and phase transitions, as signified by the susceptibility of level set sectional curvature $\chi(R_\Sigma)$, the hexatic bond orientational order parameter $|\Phi_6|^2$, and the negative peaks of the Forman-Ricci curvature of the Mapper graph κ_{FR} (d). (e) Phase clustering based on $|\Phi_6|^2$ (< 0.4 liquid, > 0.7 crystalline, hexatic otherwise) indicates high-frustration and phase coexistence. (b) Annotating the Mapper graph by the mean electrochemical parameters that produced the configurations of each node allows us to identify patterns in equilibration pathways, and do inverse design.

tems [16, 17], and for small network glass-former systems, where proxy geometrical observables of equipotential level sets were queried for inflection points and discontinuities [18].

We apply our method to a 2D colloidal nanoparticle system, as it exemplifies the complexity of modern material design. Complex dynamics, non-traditional phase-mediated pathways [19], and frustration that induces phase coexistence, all impose challenges to standard phase analysis methods. From a practical perspective, synthesis is only achievable through self-assembly, in which the system equilibrates with limited and indirect external guidance, mostly by modulating environmental and electrochemical parameters [20]. Thus, clear understanding of the colloidal system's phase structure and robust control of equilibration dynamics are critical for the fabrication of improved catalysts, optoelectronic materials, biosensors, and antimicrobial agents [21]. Our pipeline is illustrated in Fig. 1.

2. Results

We sample the equilibrated configuration space of 2D colloidal nanoparticles by running molecular dynamics simulations at the canonical ensemble (NVT) with the DLVO pairwise potential [22], augmented with steric interactions. To capture the configurational variability of the colloidal system, we vary electrochemical and environmental parameters that can be manipulated in *in vitro* experiments, namely, the particle density ρ, the surface charge Ψ, the ion concentration in the solution ρ_{bulk}, and the quality of the solvent χ, which affects steric stabilisation.

The Mapper graph of 41,731 equilibrated $200nm$ 2D colloidal nanoparticle configurations is shown in Fig. 2. Its topology, in terms of bifurcations and bottlenecks, exposes topological changes of the high-dimensional configuration space that coincide with phase transitions of the colloidal system, as the juxtaposition of Forman-Ricci curvature κ_{FR} with the susceptibility of the sectional curvature per energy level set $\chi(R_\Sigma)$, and the hexatic bond orientational order $|\Phi_6|^2$ indicate. Our analysis also reveals phase coexistence at specific energetic and parametric regions, and acts as a high-dimensional phase diagram when annotating the Mapper nodes by the different experimental parameters.

3. Discussion

We propose a topological unsupervised learning method for representing high-dimensional configuration spaces as simple graphs, whose structure exposes the dynamical behaviour of the system under study. Inverse material design is now possible as simple traversal of the Mapper graph. Albeit focusing on the configurational and dynamical complexity of 2D colloidal nanoparticle self-assembly, our analysis pipeline is directly applicable to any Hamiltonian system. As future work, we aim to exploit the symplectic structure of our construction, and the Mapper graph as a graph neural network backbone for more generalised and accurate inverse material design.

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