COMMENTARY

Machine learning provides realistic model of complex phase transition

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Nature has provided us with many more types of phases than the elementary ones—solid, liquid, and gas—that we learn in school textbooks. Some of them can be rather exotic, such as the one considered in the PNAS article by Robinson et al. (1), which deals with a remarkable but not so uncommon state of matter found in several elemental solids when they are compressed to gigapascal pressures (1 GPa = 10,000 bar). The solid in this specific case, elemental rubidium, crystallizes in a tetragonal structure composed of two interpenetrating lattices with incommensurate periodicity (Fig. 1). When heated, the “host” chain sublattice loses its long-range periodic order while the “guest” sublattice remains crystalline.

Microscopically complex state changes such as the ones observed in host–guest structures raise fundamental questions regarding how the system disorders as temperature is raised. Is chain disordering a phase transition? Why do the two interpenetrating lattices melt at different temperatures? Do different types of order, or rather disorder, appear?

Determining the nature of phase transitions, and especially temperature-induced phase transitions, is one of the most fascinating topics in statistical physics, and an area where Ehrenfest and Landau made important contributions by, among other things, providing us with the theoretical framework that we still use to classify phase transitions. Crucial ingredients of such a theoretical framework are the identification of an order parameter and the possibility to determine the free energy of the different phases by means of a microscopic model.

Simplified microscopic models have proved themselves useful in providing important insight into the nature of phase transitions, as well as for identifying universal classes of phase transitions obeying similar critical behavior as the transition is approached. The Ising model, for example, which was originally developed to describe the ferromagnetic transition and the appearance of spontaneous magnetization at low temperature, has found applications in fields as diverse as neuroscience and biology. Simplified models sometimes allow for analytical solutions and, in general, can be solved

Fig. 1. Crystal structure of the incommensurate host–guest structure observed in sodium, potassium, and rubidium at high pressure. The guest chains (dark green atoms) fill the channels of the host sublattice (light green atoms). At low temperature, the periodicity of the two sublattices is incommensurate along the chain direction. At high temperature, the chain sublattice loses long-range order. Adapted with permission from ref. 7, which is licensed under CC BY 4.0.

numerically for large enough sizes to enable the study of critical behavior and determine universality classes.

But nature, as we see in the case of host–guest structures, can be complex and hard to describe with simplified models. Chain disordering in host–guest structures requires a proper understanding of the low-temperature incommensurate solid phase. Moreover, chain disordering is most likely a second-order phase transition, as shown in the case of similar intergrown structures (2). How can we combine an accurate description of the interatomic interactions in host–guest structures with the extensive statistical sampling required to understand the nature of the phase transition?

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Author contributions: S.S. wrote the paper.

The author declares no conflict of interest.

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See companion article on page 10297.

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Published online May 8, 2019.

Huge progress has been made in the development of microscopic models for the quantitative determination of formation energies of complex arrangements of atoms, including solids, entirely from first principles (i.e., without relying on empirical data). Among the most powerful levels of theory, density functional theory (DFT) in its many approximations presently allows the determination of formation energies within an accuracy that can reach few millielectron volts per atom, for systems of several hundred up to a few thousand atoms, with arbitrary chemical composition and structural ordering. More accurate quantum-chemistry models exist, but their usefulness in the field of phase transitions is limited by the small size of the systems and, therefore, of the sampling of thermal disorder that can be studied with these models. Accuracies in the range of a few millielectron volts per atom are essential in the study of phase transitions at temperatures close to ambient, where the relevant energy scale of thermal motion is $(3/2)k_B T \sim 40$ meV per atom.

Starting from the pioneering work of Sugino and Car (3) on the melting of silicon, DFT has been applied successfully to the determination of melting temperatures of several other simple solids. In some rare cases, melting is determined by “brute force” simulations; that is, simulations in which a system of atoms moving according to DFT forces is forced to melt or to freeze as temperature is decreased or increased, mimicking the real process. In most cases, however, the DFT determination of melting proceeds via two independent steps. In the first step, statistically meaningful microscopic configurations are generated by means of an approximate (and computationally less expensive) microscopic model. In a second step, the energies are corrected to achieve DFT accuracy (4). The procedure can be made arbitrarily precise by increasing the size of the pool of sampled microscopic configurations. The closer the approximate model reproduces the DFT model, the more the procedure is efficient and fast.

The search for approximate simplified models (or force fields) that reproduce as close as possible the DFT forces has been a

prolific field of research that started concomitantly with the first large-scale DFT simulations (5). Force fields are typically based on analytical functions of the atomic positions and can be adapted to fit the DFT model (i.e., its forces, energies, and other properties) by means of adjustable parameters.

However, the increasing size and time of DFT simulations generates an incredible wealth of DFT data for a given system. Nowadays, a typical DFT simulation can generate 10^4 to 10^5 statistically uncorrelated microscopic configurations, and therefore 10^6 to 10^7 statistically independent values of the atomic forces. Optimizing a force field on such a large dataset by tuning a small set of parameters leads to a hugely overconstrained optimization problem, or the kind of problem in which machine-learning algorithms have an advantage with respect to a best-fit procedure (6).

Once built, machine-learned force fields can be so accurate as to be essentially indistinguishable from the DFT model from which they originate, or at least to be as accurate as DFT, itself an approximate model. Therefore, they can be used to study phase transitions as an alternative to DFT models, not just as a generator of statistically relevant microscopic configurations.

Having built by machine learning an accurate force field for rubidium at high pressure, Robinson et al. (1) used it to simulate the temperature-induced loss of interchain order in the rubidium host-guest structure shown in Fig. 1. By doing so, they provide bona fide evidence that chain disordering can be ascribed to a phase transition, as observed in other host-guest structures with intergrown chains (2). Whether the transition is second order and, if so, what its critical properties are, are all aspects that remain to be determined. Similarly, the intrachain loss of correlation indicates that the simulations may also offer a glimpse into the fundamental but elusive phenomenon of long-range correlations in 1D systems of particles. Both questions will benefit enormously from the availability of a computationally cheap yet realistic model of interaction between Rb atoms in phase III, such as the one developed by Robinson et al. (1).

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