Angewandte Highlights

Structure Prediction

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From Ergodicity to Extended Phase Diagrams**

Scott M. Woodley* and Alexey A. Sokol

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Is it possible to predict stable or metastable modifications of a compound starting from the chemical formula or only knowing its stoichiometry? And why include metastable structures? Higher-energy states are important in the real world, and we need to address why and for how long such metastable phases can exist. Conservation of the local stoichiometry and homogeneity is another complication considering possible phases—when is a particular stoichiometry more favorable for a solid solution or, for a given stoichiometry, will a micro- or macroscopic ordering prevail? As the state of the chemical matter will depend upon the external conditions of temperature and pressure, a partial answer would be given by the standard phase diagram drawn for thermodynamically stable phases. A more complete answer has been proposed,[1] and comes in the form of an extended phase diagram that includes the notion of *lifetimes* for metastable phases. This novel approach is applied to an example system: $Li_{1-x}Na_xBr$. Rational synthesis of new compounds and structures has been a long-term ambition of the group of Jansen,[2] which has been realized spectacularly in the synthesis of predicted lithium halide structures.[3] The extended phase diagram is generated through running simulations, yielding essential insights into the existence and stability of possible compounds from which the synthetic route could be ascertained. This work builds on the previous advances in the development of a comprehensive strategy to guiding syntheses.[4]

Although matter is continuously changing its configuration (state), at finite temperatures the average configuration over a period of time may persist in one form, typically resembling a potential local minimum, or a collection of potential energy minima separated by small energy barriers. The collection of states visited in this time on the energy landscape is called the locally ergodic region. The measurement, or observation time should be greater than the thermal equilibration time but less than the escape time for a system to leave the current ergodic region. This is the key concept the authors deploy to determine the existence and parameters of metastable phases. In the chosen example system, the solid solution between LiBr and NaBr, several possible (metastable) structures are found, even for the end members. However, all cation arrangements in these structures need to be included in the free-energy calculation. Their procedure generates structures and cation ordering, the lifetimes and the free enthalpies, and thus the free energy landscape as a function of the Li/Na ratio, temperature, and lifetime. By retaining the relevant part of the hypersurface for a given observation time, spanning each particular structure type, the authors present a novel appealing representation of the structural diversity that can be observed in nature or synthesized in a laboratory.

So how much work is involved in generating the extended phase diagram from simulations? There are three major challenges in the execution of the procedure. The first step is a global exploration of the potential energy landscape of the given chemical system. As the number of atomic coordinates increases, structure prediction, a primary subject of a very active field in materials science,[5] becomes computationally expensive. For example, there is only one local energy minimum for an isolated cluster of $(LaF_3)_1$—a planar structure with D_{3h} symmetry—but a quick search for $(LaF_3)_2$, $(LaF_3)_3$, $(LaF_3)_4$, $(LaF_3)_5$, and $(LaF_3)_6$ soon generates 3, 11, 55, 286, and over a thousand local minima configurations, respectively. The cost of computing the energy, which also increases with the number of atoms, is unavoidable and, therefore, it is important to minimize the number of configurations to assess—the discrete number of local minima are hidden within the numerous other configurations that dominate the energy landscape.

To date, great success in predicting new feasible structures has been achieved by essentially data-mining known local minimum structures (substituting the chemical elements of interest for those in known structures of compounds with the same stoichiometry)[6] or the use of certain patterns in bonding or connectivity of targeted compounds.[7] An alternative approach is, however, required to discover novel structure types, for example, by generating and quenching random configurations using suitable ab initio electronic structure techniques.[8] But such a brute force attack only works well for a small number of unknowns: the number of atomic coordinates or possible configurations of a solid solution. Global optimization techniques as applied to structure prediction have been developed since before Maddox's controversial comment on the lack of predictive ability of the community back in 1988[5] and such techniques are still being refined today.[2,4,9]

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[*] Dr. S. M. Woodley, Dr. A. A. Sokol
Department of Chemistry, University College London
20 Gordon Street, London WC1H 0AJ (UK)
E-mail: scott.woodley@ucl.ac.uk
Homepage: http://www.ucl.ac.uk/klmc

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For two decades, Jansen and Schön have successfully employed a Monte Carlo approach—a walk across the energy landscape with the Metropolis Criterion used to decide whether to accept or reject each attempted small step (random atomic and cell displacements from initially randomized coordinates).[10] The temperature parameter of the Metropolis Criterion is slowly reduced so that the process of annealing is simulated. An instructive insight into the merits and successes of competing approaches to structure prediction can be gleaned from Figure 1, which shows the evolution of the best energy for several independent walkers from a recent blind test—the crystal structure prediction of $BaMgAl_4Si_4O_{16}$.[11] At various points along each path, standard local optimization is performed to investigate the local minima. At high temperatures, a string of random configurations are investigated, and therefore the local minima near these paths are representative of the structures found from quenches of random structures. It is clear that although low-energy minima can be obtained quite quickly (see the circled data point) these are much higher in energy than many local minima found upon quenching towards the end of annealing in any of the ten runs.

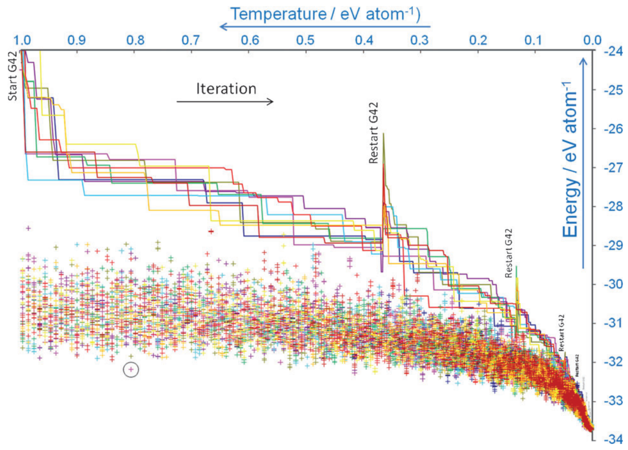

Figure 1. The trajectories of the best energy found (lines) for ten simulated annealing Monte Carlo runs (each with a unique color) for a fixed unit cell containing 26 atoms.[11] Each run starts (restarts) with a different random (the last accepted) configuration. For a number of configurations along each trajectory the local minima are reported (data points). The circled data point is the best energy found during the high-temperature phase of the simulations. Data obtained using the G42 software developed by J. C. Schön.[2]

Returning to the extended phase diagrams, the second step estimates the lifetimes of the hypothetical phases. The threshold algorithm is employed, which yields estimates of the energy barriers surrounding local minima and of the probability flows between these minima as function of energy and temperature.[12] The required computational effort is usually of the same order of magnitude or greater than that of the global search.

Finally, the free enthalpy of the various phases is evaluated. Here, the explicit treatment of the thermal excitations could be readily included but at a yet greater computational cost. Without the vibrational contributions, the enthalpy of mixing can be calculated routinely by using ab initio or molecular mechanical methods. As a function of cation ratio, free energy curves are widely reported in the literature for many solid solutions, often reporting the existence of miscibility gaps.[13] The application of global optimization techniques to structure prediction on the potential energy landscape is also becoming routine. Therefore, it is a real breakthrough to introduce the concept of local ergodicity and thus to move to the free-energy landscapes combined with the lifetimes of the distinct phases. Jansen, Pentin and Schön have, for an example of a solid solution, $Li_{1-x}Na_xBr$, demonstrated how to explore the Gibbs free energy hypersurfaces for stable and metastable phases and how to identify the parts that need to be included in the extended phase diagrams for a given observation time. These extended phase diagrams for complex systems will surely become the retort in the toolkit of the future synthetic chemist.

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