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Metastable Phase Diagrams

A Universal Representation of the States of Chemical Matter Including Metastable Configurations in Phase Diagrams

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Encoding equilibrium states of matter in the format of phase diagrams is among the basic and at the same time most fruitful concepts in solid-state and materials chemistry. The appealing stringency of these concepts is related to the fact that any equilibrium state of matter, as characterized by its phase content (defined by the phases present, their compositions, and concentrations) and the respective activities of the components, is unambiguously determined by fixing the set of independent variables of state, p (or V), T, x_{i-1} for a system constituted of i components. In many fields of science and technology, analyzing chemical processes in terms of phase diagrams and equilibrium thermodynamics has proven an invaluable tool.[1–3] In spite of the impressive success of such an approach in specific areas, it fails seriously in addressing the full “real” materials world, since most of the matter around us stays trapped in metastable, in many cases quite persistent, states. Even at demanding thermal conditions, for example, prevailing in gas or steam turbines, many of the materials employed are not in equilibrium. Quite generally, it is easy to show that metastable materials are of substantial relevance: durable diamond is metastable at ambient conditions, glasses constitute an economically significant class of matter, and (metastable) amorphous ceramics can outperform thermodynamically stable crystalline ones with respect to the overall set of properties relevant for high-temperature applications.[4,5] As a consequence, a holistic consideration of a given chemical system, for example, for the purpose of synthesis planning, needs to include both the equilibrium and the metastable states.[6,7]

Thus it would be highly desirable to address metastable states of matter in a similarly rational way as thermodynamically stable ones and to put both on a comparable footing. Regarding the most popular presentation of equilibrium phase diagrams that are obtained by projecting the lowest parts of the Gibbs energy surfaces of the competing thermodynamically stable phases onto the space spanned by the variables (p, T, x_i), such an objective would imply to perform an analogous procedure for metastable matter. After identifying all chemical compounds and phases that are capable of existence, one would determine their free energies as a function of the thermodynamic boundary conditions, and directly derive graphical representations (analogous to equilibrium phase diagrams) from this information. Noteworthy, such a procedure requires to involve the temperature-dependent lifetime of the metastable state under consideration as a further parameter.

In the past, it has been shown that known features of equilibrium phase diagrams can be extra- and interpolated, as well as checked for consistency, by the well-known CALPHAD approach.[8] Furthermore, for a known configuration, its internal energy can be calculated, and, by considering the respective thermal excitations, the free energy can be derived, $G_{\mathrm{tot}} = G_{\mathrm{vib}} + G_{\mathrm{conf}} + G_{\mathrm{el}} + G_{\mathrm{magn}} + \ldots$, where G_{el} and G_{magn} refer to the electronic and magnetic contributions, respectively. However, previous work in this direction has considered only specific known modifications and thus has failed to fully explore the respective systems.[9] This is a serious drawback, because missing phases render phase diagrams greatly incorrect, a fault that cannot be corrected by, for example, employing the CALPHAD approach. In particular in the context of our approach to planning solid-state and materials syntheses,[6,7] such a limitation would undermine the supreme objective of addressing all compounds capable of existence, that is, possible targets for synthesis, within the chemical system under consideration. Therefore, we have been performing global explorations of the potential energy landscape associated with the space of atom arrangements from the outset. The identification of the structure candidates and computation of their total energies serve as starting points for the calculation of free energies as a function of the thermodynamic boundary conditions for all thermodynamically stable and metastable phases.

Obviously, when including both, metastable and equilibrium states of matter, in the same graphical representation, the occurrence of a phase at a given point in thermodynamic space will have two fundamental consequences. 1) While p, T, and x_i continue to be variables of state and thus to unambiguously determine the physical state of fully equilibrated matter, they merely act as boundary conditions describing metastable states that allow to calculate, for example, their free enthalpies. 2) As metastable states evolve with time passing, and eventually will have transformed to the respective ground states, life times need to be considered (and eventually to be added to graphical representations of phase diagrams that include metastable states).

The full scenario can be conclusively addressed in terms of ergodicity.[10–12] Thermodynamic equilibrium corresponds to a globally ergodic state, whereas metastable states can be associated with locally ergodic regions in the space of atom configurations that can be defined for a given temperature, pressure, and observation time.[10,12] Such a region is that part of the energy landscape of a chemical system, which at the given temperature and pressure, and for a given observation

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time, can be in local equilibrium. If the system is in local equilibrium for a sufficiently long time, while residing in the locally ergodic region, physical measurements on the system will yield reproducibly thermally averaged results on the observational time scale. For all practical purposes, this is the appropriate definition of calling the material at hand a metastable compound, and thus the locally ergodic regions on the landscape correspond to the compounds capable of existence for the given observational time scale and thermodynamic boundary conditions.

Recently, we have developed a general strategy to predict and compute equilibrium phase diagrams in the low-temperature regime including both crystalline and solid solution phases without recourse to any experimental information (Figure 1).[13–17] This approach employs a combination of global explorations of the energy landscape of the system[6,7,18] for many different compositions, using empirical potentials, and local optimizations of the structure candidates determined, on the ab initio level. By analyzing the set of local minima found using the CMPZ algorithm,[19] families of structurally related local minima can be identified, and we can deduce the existence—or non-existence—of thermodynamically stable and metastable solid solution-like phases[14] or ordered crystalline modifications[20] in the system. Next, the excess Gibbs energies are obtained by fitting the enthalpies of formation computed on the ab initio level for many different compositions, and by adding the configurational entropy in case of solid solution-like phases. As we perform extrapolations of the Gibbs energies from zero temperature, the contribution of the heat capacities to differences of the Gibbs free energies can commonly be neglected to first order.[14]

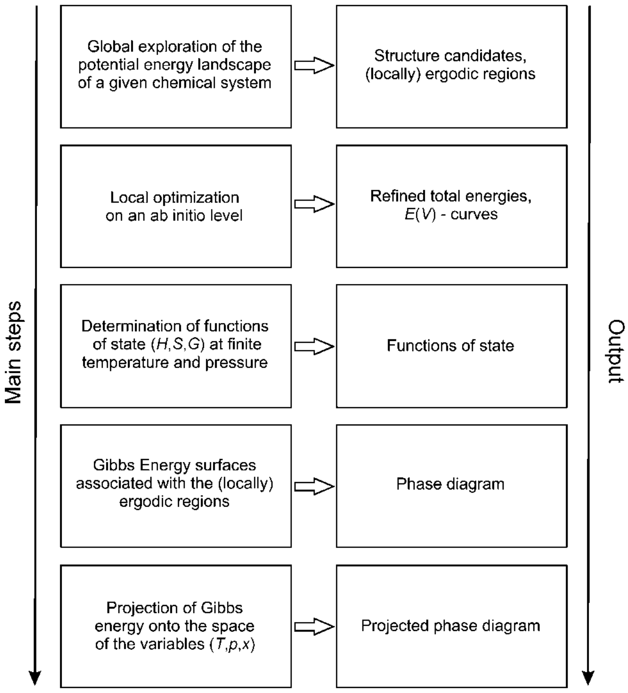

Figure 1. The general procedure: main steps and output.

Metastable materials cannot unambiguously be located in phase diagrams experimentally, because the transition temperatures and pressures would vary greatly depending on the experimental procedures applied. Since our approach for calculating equilibrium phase diagrams does not require any experimental pre-information, the same procedure as described above is also suitable to calculate free enthalpies for metastable states of matter, which can be included in the representation of $G_{eq}(p, T, x_i)$.

As an example to illustrate the construction of such an "extended phase diagram", we consider the low-temperature part of the phase diagram of the quasi-binary system LiBr–NaBr. Several hundred global optimization runs using simulated annealing were performed for a number of different cation compositions (3:1, 2:1, 1:1, 1:2, 1:3) with up to eight formula units each, at a pressure of 0 Pa. For each composition, the set of low-energy structures found could be divided into four sets of structure candidates that a) belonged to the same binary structure family, that is, the NaCl-, NiAs-, Wurtzite- and 5-5-type,[21] respectively, and b) showed very small energy differences between the candidates within each family (see Figure 2 for the $E(V)$ curves of these four families). This strongly indicates that for temperatures above approximately 1 K four (meta)stable solid solutions will be found.[27] To explore the energy landscape of all four phases in more detail, many additional structure candidates belonging to each structure family were generated by permutation of the cation positions followed by two local optimization runs: first with the empirical potential, and subsequently on ab initio level. As a next step, we calculated the enthalpy of formation for the four structure families j ($j = 1, 2, 3, 4$) for each composition x according to Equation (1):

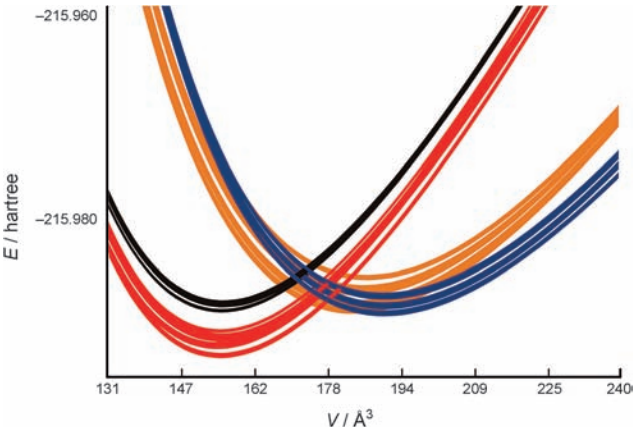

Figure 2. $E(V)$ curves for the LiBr–NaBr system, showing four families: red—NaCl, black—NiAs, blue—Wurtzite, and orange—5-5-type.

$$\Delta_f H^{(j)}(\mathrm{Li}_{1-x}\mathrm{Na}_x\mathrm{Br}) = \langle E^{(j)}(\mathrm{Li}_{1-x}\mathrm{Na}_x\mathrm{Br})\rangle - (1-x)E^{(j)}(\mathrm{LiBr}) - x\,E^{(j)}(\mathrm{NaBr}) \qquad (1)$$

Here, $\langle E^{(j)}(\mathrm{Li}_{1-x}\mathrm{Na}_x\mathrm{Br})\rangle$ is the average energy of the structure candidates belonging to the particular structure family j, $E^{(j)}(\mathrm{LiBr})$ and $E^{(j)}(\mathrm{NaBr})$ are the (calculated) energies of the boundary compounds LiBr and NaBr in the corresponding structure family, respectively, and x is the fraction of NaBr in the overall composition. Also, one should note, that at standard pressure, the contribution of the pV term is negligible. Based on the fit of $\Delta_f H(x)$ with a Redlich–Kister polynomial for all four structure families (for the coefficients, see Table I in the Supporting Information), we calculated Gibbs energies by including the ideal entropy of mixing of the solid phases, $S = -R[x \ln x + (1-x)\ln(1-x)]$.

The resulting $\Delta G_f(x)$ for the globally and three locally ergodic states of solid $Li_xNa_{1-x}Br$ are plotted in Figure 3b). At 300 K, the thermodynamically stable NaCl family as well as the metastable NiAs and Wurtzite families develop pronounced miscibility gaps, whereas for the 5-5-family complete miscibility is found (see Figure 3a). For the ground-state NaCl family the computational results can be validated by comparison with experimental data,[22] where the agreement between the location of the miscibility gap by experiment and interpolated by CALPHAD on the one hand, and the calculated one on the other is quite good[14] (see Table II in the Supporting Information), considering the typical error of about ±100 K for such calculations.

For the locally ergodic (metastable) states, their lifetimes, which depend on the temperature prevailing, need to be included. Using measurements of the probability flow on the energy landscape with the threshold algorithm,[23] one can estimate the temperature range, over which a particular metastable phase can exist for a given time t_{obs} (see the Supporting Information). This is shown in Figure 3c, where for an observation time $t_{obs} \approx 10^3$ s one finds an approximate stability range up to a temperature $T_{limit} \approx 300$ K, $T_{limit} \approx 30$ K, and $T_{limit} \approx 30$ K, for the NiAs-type, Wurtzite-type and 5-5-type phase, respectively. For shorter times, the regions where the three metastable phases are observable will extend to somewhat higher temperatures, whereas for longer times, for example, years, the regions will rapidly shrink towards lower temperatures. Of course, this can only be a very rough estimate, since a full numerical determination of this time scale involving very large MC- or MD-simulations with thousands of atoms is beyond the purview of this work. Our focus is the general issue of extending the classical equilibrium phase diagram description to a graphical representation of the complete set of phases that are (meta)stable on a given observation time scale.

Nevertheless, this kind of representation includes all metastable relevant phases, in principle, and thus encompasses the full richness of the phase-realm of a chemical system, where we stress again the supreme importance of the observational time scale. While the "extended phase diagram" is more difficult to visualize than a simple equilibrium phase diagram (which corresponds to the $t_{obs} \rightarrow \infty$ cross-section of the extended phase diagram, of course), we do not think that it is more complex than typical quaternary, or even higher component equilibrium phase diagrams, which also can only be visualized by more or less complicated two- or three-dimensional sections. But because of the inclusion of all

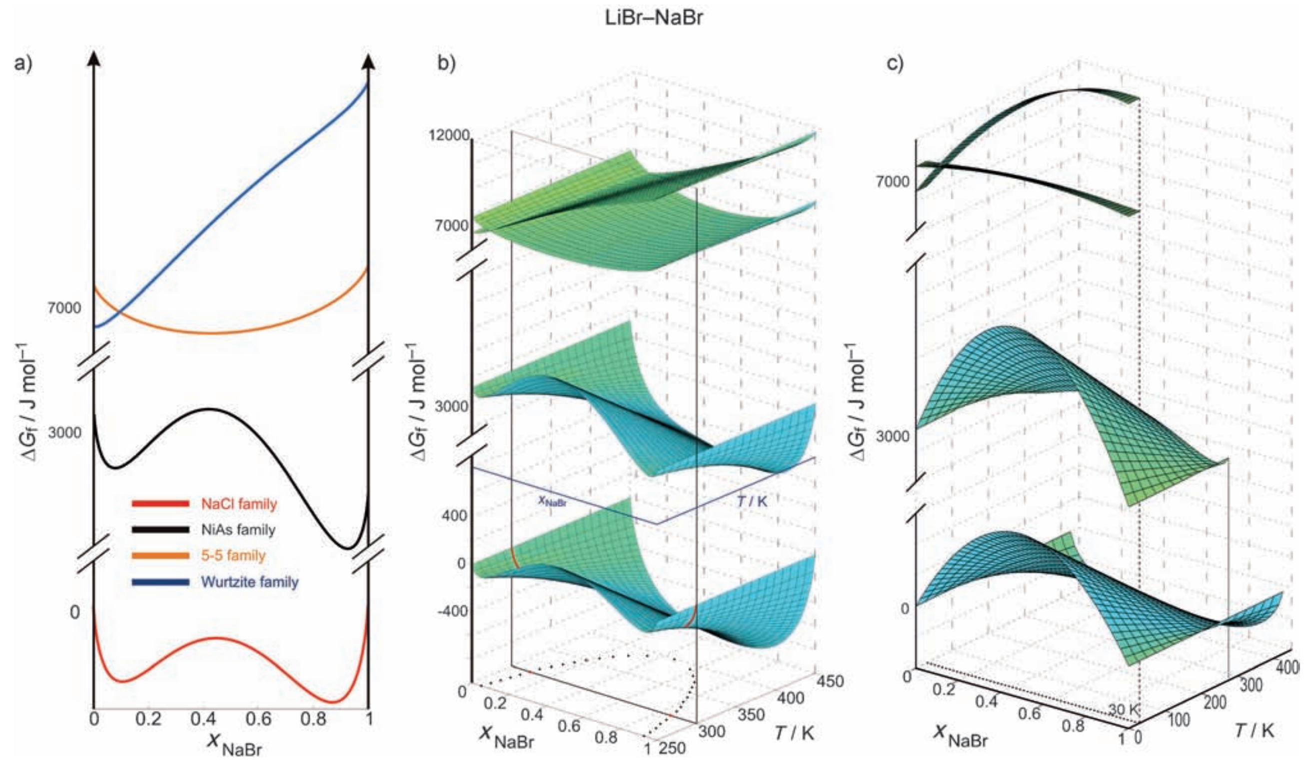

Figure 3. a) Section of Gibbs energy surfaces based on DFT-LDA-VBH data for the LiBr–NaBr system at 300 K. b) Gibbs energy surfaces based on DFT-LDA-VBH data for the LiBr–NaBr system, together with projection of the thermodynamically stable phase in the (T, x) plane (dotted curve). c) Gibbs energy surfaces restricted to the (T, x) ranges, for which the four solid solution phases are locally ergodic on a time scale of $O(10^3)$ s. The order of the energy surfaces is the same in (a–c).

metastable phases in a chemical system together with their lifetimes, the "extended phase diagram" can serve as a true guide to the materials chemistry of the chemical system. Of course, this construction can only be applied to chemical systems where locally ergodic regions dominate the landscape; for example, glassy systems which are marginally ergodic at best[10] and show aging phenomena, do not achieve thermodynamic equilibrium even locally and must be excluded from the extended phase diagram.

We have reported a general approach for addressing metastable states of matter by including them in an "extended equilibrium phase diagram". The in-principle feasibility has been shown at the example of the quasi-binary system LiBr–NaBr. All computational results agree with the—admittedly scarce—experimental knowledge available: LiBr has been shown to exist as a metastable Wurtzite-type polymorph,[24] and LiBr–LiI form a metastable Wurtzite-type solid solution with a large miscibility gap.[25,26] Interestingly, just including the dominant contribution to the entropy of formation, that is, the ideal entropy of mixing, has yielded quite pleasing results. Of course, the accuracy can be improved by appropriately taking into account all possible thermal excitations in the respective system under investigation.

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[27] Below 1 K, the free energy of the individual family members with the lowest energy can be competitive with the configurational entropy term, and the size of the locally ergodic region becomes too small on the time scale of observation to allow for enough potential energy minima to contribute to the configurational entropy of the solid solution.