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ENERGY LANDSCAPE CONCEPTS FOR CHEMICAL SYSTEMS UNDER EXTREME CONDITIONS

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Abstract:

Traditionally, energy landscape studies of chemical systems deal with an isolated system with no interaction with the environment except possibly non-zero pressure and temperature. This changes drastically, if we consider materials under extreme conditions, since now the interaction with the environment plays a central role. In this work, we present extensions and generalizations of the energy landscape paradigm to chemical systems that strongly interact with their environments. The focus is on the general concepts involved, where we discuss the way to incorporate general external fields, e.g., mechanical stresses, electric and magnetic fields, and fluxes, e.g., electric and thermal currents, and analyze the issue of time-dependent energy landscapes. Finally, possible applications of energy landscape concepts in a variety of chemical and physical systems in strong contact with the environment are discussed, and first examples of landscape studies of materials under extreme conditions are given.

Keywords: energy landscapes, extreme pressures, high temperature, structure prediction, stress, nanostructures, theoretical methods, electromagnetic radiation, corrosive environments

1. Introduction

Materials found in nature and developed for technological applications are usually observed and employed at so-called standard conditions: room temperature, the pressure of one atmosphere, etc. However, very often the processes needed for these materials to come into existence are quite extreme,[1] e.g., high pressures and/or high temperatures,[2-5] and similarly the materials might be exposed to extreme conditions during their applications, e.g., high magnetic or electric fields,[6-10] large currents,[11,12] aggressive chemical environments[13,14], high fluxes of radiation,[15,16] or high temperatures and pressures.[17,18] Such "extreme" conditions can occur not only in situations with exposure to highly energetic processes as mentioned above but also at the other end of the energy spectrum in cases of an (effective) reduction of a bulk material to lower dimensions such as monolayers,[19,20] quasi-one-dimensional systems[21,22] or sub-monolayer molecular structures on substrates,[23-25] not to mention three-dimensional materials with an extremely low density such as metal-organic frameworks.[26,27] Here, too, our standard intuition trained in the study of bulk materials can fail, and new concepts and methods - both experimental and theoretical ones - will be needed. However, we do not include the energy landscapes of such systems in this overview, since they will be discussed elsewhere.[28] Similarly, we are not discussing single molecules or clusters under extreme conditions,[29] such as the so-called Coulomb explosion [30], current flows through single molecules [31,32], or high-pressure studies of single molecules, [33] although the general concepts presented in this work will also be relevant for such systems.

Trying to resolve the details of the thermodynamic processes involved under extreme conditions, including the existence of thermodynamically stable and metastable materials and chemical compounds and their synthesis - in a controlled fashion if feasible -, or of the morphology and stability of the materials in equilibrium and non-equilibrium situations, and their physical and chemical properties in general, constitutes a great challenge. From a theoretical point of view, combinations of molecular dynamics and Monte Carlo simulations with finite element modeling,[34,35] analytical phenomenological models,[36,37] and empirical and ab initio computations of equilibrium properties,[38] have been employed to investigate specific features of systems and the processes taking place in a given phase and/or structure, at extreme conditions.[39-41] In recent decades, there has been added a more holistic point of view,[42-48] where one investigates the energy landscape of the chemical system on a global level in order to explore the full range of possible stable and metastable phases the system can exhibit for, e.g., a given pressure,[49-51] to analyze their stability against transformations as function of pressure and temperature,[52] and to study the system's reactions to perturbations and its relaxation to equilibrium. This approach has proven to be highly fruitful and has led to the prediction of new not-yet synthesized compounds and modifications[53-56] and high-pressure structures[57,58] up to the prediction of phase diagrams as function of temperature, pressure, and composition.[46,52,59-62]

Typically, such studies assumed that the system was isolated from the environment, apart from a given constant pressure and temperature. In the case of materials under extreme conditions, such isolation is no longer true - and usually not appropriate even for simple models -, unless the energy landscape were to include the atoms that make up the whole experimental apparatus. Instead, we have to add the environment of the material in some reasonably efficient fashion, where extreme conditions usually are only a special instance of the general type of environment added to the system of interest. The impact of the environment can make itself felt through applied external fields such as pressure, electromagnetic fields, mechanical stresses, etc., or in the presence of various kinds of currents, such as electric or thermal ones, moving through the material in a steady-state fashion. Other very important aspects of the interaction with the environment - both for strong and weak interactions - are the externally applied temperature, and furthermore the time variation or time evolution of the environment, and their effects on the material. Such interactions can result in new (meta)stable equilibrium phases and equilibrium properties of the material, a steady-state configuration of the material, and/or non-equilibrium behavior of the system. In principle, there can even be a coupling between the material and the environment in the sense that the change in the material can affect the properties of the environment in the zone near the material; an example might be the formation of protective surface layers of the material, which prevents or slows down further corrosion.

It is thus an interesting question, how and to what extent energy landscape concepts can also be applied to materials under extreme conditions. In this overview, we are going to address this issue, discussing both general concepts and first applications.

2. Energy landscape concepts

2.1 General cost functions and exploration methods

Energy landscapes in chemical systems are a special case of so-called cost functions, which are studied in a large number of fields ranging from mathematics,[63-65] physics,[66-68] chemistry,[43,44,69] over various fields of engineering,[65,70] to the social sciences and economics.[71-73]

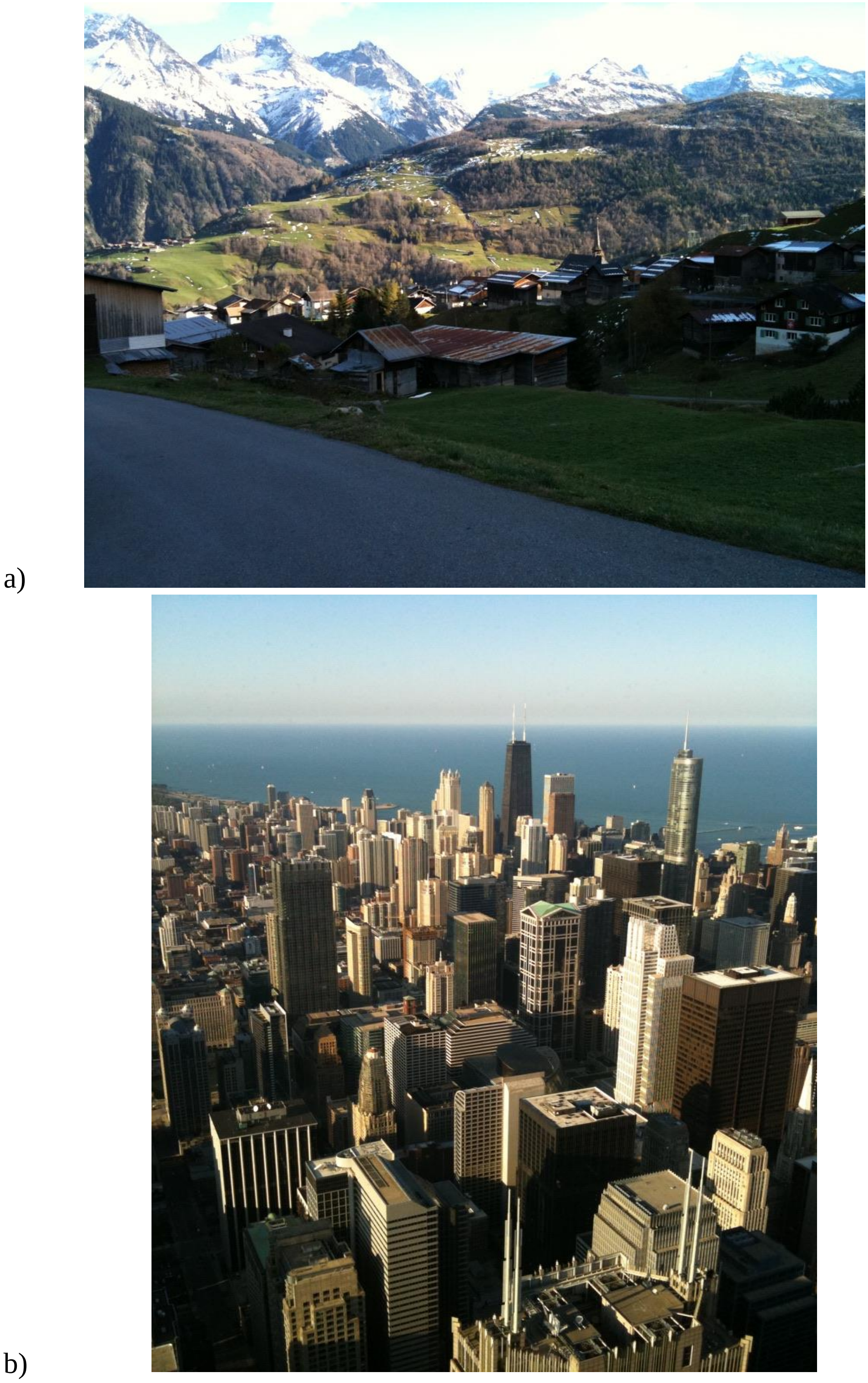

Figure 1: a) Potential energy landscape made by nature (near Disentis in Switzerland). Note that to reach the highest snow-capped mountains on the left, you need to cross the deep Rhine valley in-between. b) Potential energy landscape made by man (downtown Chicago). Note that this is like a fitness landscape for managers - the higher the office, the fitter the manager, in many ways.

Quite generally, a cost function $C: S \rightarrow R$ is a real function that maps configurations $\vec{X} \in S$ (also called (micro)states or solutions, depending on the field of application) to real numbers $C(\vec{X}) \in R$. In the case of a molecule consisting of N atoms, the configuration space S would be equal to R^{3N}, i.e., each possible arrangement of the atoms in the molecule would correspond to a point $\vec{X} = (\vec{x}_1, \dots, \vec{x}_N) \in R^{3N}$, where $\vec{x}_i$ are the position vectors of atoms i in R^3.[1] Similarly, if we want to study the behavior of a set of elementary magnets that each can only point up or down along, e.g., the z-axis, then each point in configuration space would correspond to a possible arrangement of orientations of the magnets $\vec{\sigma}_i$, $\vec{X} = (\vec{\sigma}_1, \dots, \vec{\sigma}_N) \in (Z_2)^N$, where $Z_2 = \{-1, +1\}$ is the set of possible orientations of a given spin. Clearly, the set of states S of the simple magnetic system is a discrete one, while, for the molecule, S is a continuous set of configurations. The cost function $C(\vec{X})$ can represent a real economic cost, the value of a combinatorial optimization problem,[63-65] the difference between computed and measured data,[69,74] or the potential energy of an arrangement of atoms, where the last two types of costs are of particular interest in materials.

In order for the cost function and the state space to become a landscape, we need to define a neighborhood relation between the states, such that we can associate a neighborhood to each state, $\vec{X} \rightarrow \mathbb{N}(\vec{X})$. In physical or chemical systems like a molecule or the magnet system mentioned above, this neighborhood tells us, which states are (infinitesimally) close to the current state, and thus how the system can evolve on a given time scale. If the set S is a subset of, e.g., R^n (as would be the case for the molecule), then we often employ the standard neighborhood relation in R^n, i.e., the neighbors of a configuration are all the atom arrangements that differ from the present configuration by only (infinitesimally) small shifts in the atom positions. Similarly, if S consists of, e.g., a finite number of discrete states, then a sensible definition of the neighbors should be consistent with the time evolution algorithm, i.e., the moveclass represents our model of the system's dynamics.[2] But if the cost function refers to, e.g., an optimization problem such as the traveling salesman problem (TSP) of finding the optimal route among a set of cities, then the neighborhood describes the way our search algorithm moves in the state space of the problem, and we usually call the neighborhood relation the moveclass of the algorithm.

Configuration space, moveclass and cost function together define the cost function landscape; for discrete spaces this is sometimes called a metagraph.[70]

Once the cost function landscape has been constructed, we are particularly interested in the evolution of the system, i.e., its movement in configuration space. Such an evolution can correspond to the changes that occur in a physical or chemical system as function of time according to the laws of physics; in chemical systems, the existence of stable states corresponding to distinct regions on the landscape dynamically separated from the rest of configuration space by barriers is of special interest. In general cost function problems, evolution usually refers to the progress of a given global exploration or optimization algorithm, but it can also refer to the time evolution, e.g., of the fitness of an organism, or to the populations dynamics on a socio-economic landscape.

In order to analyze and model such an evolution, the landscape is globally explored using various computational methods, c.f., e.g. [43,75] and references cited therein. This results in a "complete" description of the landscape in terms of static properties such as local

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[1] The configuration space is also called the state space, or sometimes the solution space if we consider the microstates as the feasible solutions of a cost function optimization problem.

[2] For example, a neighbor state of a current state in the magnet system might differ from the current state by only one or two magnets having flipped their orientation, as this would appear to be a good approximation of the true dynamics.

minima and maxima, saddle points, including their curvatures, characteristic regions[3], together with the probability flows between various regions of configuration space,[77-79] i.e., the probabilities $\wp_{AB}(t_{step})$ to reach a certain region $A \subset S$ from region $B \subset S$ during the time step t_{step}. Here, t_{step} corresponds to both the time between two measurements of the real system, and to the length of the exploratory simulations used to measure the transition probabilities between the two regions A and B. Of course, these flows are completely determined once the landscape and its dynamics, such as the (deterministic or stochastic) exploration / evolution algorithm we employ to study the landscape, have been given.[4]

Such regions of interest are often basins around local minima or locally ergodic regions (for a given observational time scale; see below) that are separated by generalized barriers on the landscape, which are extracted from the probability flows and incorporate entropic and kinetic features in addition to purely energetic aspects.[81] Based on this information, one can actually optimize the optimization search procedure or control the time evolution of the system, such that one will reach the global minimum or any other prescribed region of the landscape (perhaps corresponding to a desired metastable compound), in the most efficient fashion with the highest probability for a given (or randomly chosen) starting point on the landscape[82-84].[5]

We note that in this description, the landscape appears as the constant playing field on which the time evolution of the chemical system takes place; however, in many situations - both in physical/chemical systems and in general cost function problems -, the cost function, and also the set of states S, might vary as a function of time.[6] Clearly, this can have important effects on how we employ energy landscapes in practice, to address physical and chemical questions or typical cost function problems. This is discussed in more detail below in section 3.5.

2.2 Application to chemical systems isolated from the environment

In the case of a chemical system without any applied external fields or other contact with the environment, i.e., zero pressure $p = 0$, no magnetic or electric fields $\vec{B} = 0, \vec{E} = 0$, etc., the configuration space is usually given by all the possible arrangements of the N atoms of the system in space, such that each point corresponds to a vector $\vec{X} = (\vec{x}_1, \dots, \vec{x}_N)$ in R^{3N} with $\vec{x}_i \in R^3$ as the coordinates of atom i. As energy function serves the potential energy of

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[3] A characteristic region is defined as the set of all microstates, from which one reaches the same distribution of local minima when performing many stochastic quenches.[76] In particular, this allows us to assign microstates with energies higher than those of various saddle points to minima basin states (this can refer to one minimum or a group of structurally related minima) or transition states (two or more structurally distinct minima are reached by the quenches from the same microstate).

[4] One should also note that studies of the behavior of the phase space trajectories obtained by solving Newton's equations in the so-called phase space where the microstates are defined by the position and momentum vectors of the N atoms $(\vec{x}_1, \dots, \vec{x}_N; \vec{p}_1, \dots, \vec{p}_N) \in R^{6N}$, can result in valuable insights [80] beyond the standard molecular dynamics results, e.g., illuminating the importance of entropic and kinetic aspects of the generalized barriers on the landscape, in addition to the more standard energetic ones.

[5] From a mathematical point of view, this optimization of the time evolution of the system constitutes an optimal control problem, as one encounters in applications of finite-time thermodynamics to chemical systems, where one attempts to maximize the output of a chemical process or to minimize the entropy production, if the process has to be finished within a finite time span.[85-87]

[6] The variation of the cost function can easily be imagined as, e.g., building, repairing or blocking roads between cities in the TSP problem and thus increasing or decreasing the length of a route, or the time the route requires, throughout the day or over a year. But the set of states (= set of feasible routes) can also change by adding/removing/substituting cities along the route, or by permanently removing or adding roads between two cities. Note that the removal of a road between two cities can be effectively achieved by assigning such a road an infinite length - in that case, the route is still "feasible" but "infinitely" unfavorable.

the system $E_{pot}(\vec{X})$, which is either evaluated via some empirical potential or as the electronic ground state energy on ab initio level computed, e.g., using DFT or the Hartree-Fock approximation.[7] In the case of solids, where the number of particles is on the order of Avogadro's number N_{Av}, one usually ignores surface effects and reduces the number of degrees of freedom by assuming periodic boundary conditions (with variable size and shape of the periodic cell), such that the configuration is defined by $\vec{X} = (\vec{x}_1, \ldots, \vec{x}_{N_{cell}}; a, b, c, \alpha, \beta, \gamma)$, where N_{cell} is the number of atoms in the periodic cell, and $\vec{x}_i = (x_i, y_i, z_i)$ with $x_i, y_i, z_i \in [0,1]$ are the fractional coordinates of the atom i inside the cell, and $(a, b, c, \alpha, \beta, \gamma)$ are the variable cell parameters. Since $x_i = 1$ corresponds to $x_i = 0$ (and analogously for y_i, z_i) because of the periodic boundary conditions, and, furthermore, many choices of the cell parameters correspond to the same infinite crystal, the topology of this landscape is the one of a complicated high-dimensional torus.

If we want to describe the time evolution of the system or study the stability of metastable phases, it is important to keep in mind that a physical or chemical system has a "natural" or "inherent" time evolution based on the laws of physics, which depends on, and thus is prescribed by, the initial state, the (effective) interactions between the constituents of the systems (atoms, spins, ...), and the applied external forces and thermodynamic boundary conditions, where the external parameters can vary with time, of course. In such a case, we have a naturally defined set of states and neighborhoods, as function of evolution time, which cannot be modified, in principle. In order to ensure that the moveclass corresponds to the physical time evolution, we only allow very small changes in the atom positions or the cell parameters during each move, as mentioned above.[8] This requirement of physical realism also presents us with a natural set of properties and features of the system's landscape which we want to determine via various exploration algorithms. To identify these, we note that our physical measurements in the experiment always depend on the observational time scales t_{obs} over which the measurements are performed, on the values of the external parameters, and on the initial state of the system, unless we can assume that the system is in (local) equilibrium. Here, we remark upon the importance of keeping apart the features of the true landscape of the real physical system, and those aspects accessible in model systems when using simulation algorithms, as far as their time evolution is concerned.

On the other hand, for global optimizations in configuration spaces, e.g., if we want to find the local minima of the potential energy, or the atom configuration whose diffractogram agrees best with the measured data, we frequently include additional (unphysical) moves such as atom exchanges, local scrambling of atoms etc., which occur in real systems on much longer time scales but are very efficient for jumping among major basins of the energy landscape. Thus, the neighborhood of a configuration $\vec{X} = (\vec{x}_1, \ldots, \vec{x}_N)$ contains states $\vec{Y} = (\vec{y}_1, \ldots, \vec{y}_N)$ that are a (large) finite distance away from the current configuration if measured by a typical distance metric $D(\vec{X}, \vec{Y}) = \sum_{k=1}^{N} (\vec{x}_k - \vec{y}_k)^2$. Therefore, the topology of

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[7] In this notation, we are ignoring the spin degrees of freedom associated with the atoms/ions, which need to be included, of course, in the more general case, e.g., for non-vanishing magnetic fields. Furthermore, we assume that the Born-Oppenheimer approximation can be used, to separate the electronic from the nuclear degrees of freedom.

[8] Note that if we model the solid via a reduced set of coordinates with a small periodically repeated simulation cell, then we can only describe a very limited type of evolution. For example, typical nucleation and growth processes are only accessible if we use very large periodic cells, and, similarly, surface reactions or transformations cannot be modelled (unless we replace the 3D solid by a 2D slab).

the configuration space becomes highly complex when seen through the eyes of the global optimization algorithm.[9]

Having considered the basic concepts of a static landscape in isolation from the environment, in the following section we turn to the modifications needed and the effects generated by including the environment into the description and analysis of the landscape of a chemical system. Here, we note that one will always prefer a minimalistic approach when dealing with and accounting for the effects of the environment. Thus, instead of including the atoms of the device that generates, e.g., the high pressure or the electric field, or those that represent the interface through which a constant temperature inside the material is established, one modifies the cost function by adding simple terms to the energy that reflect the thermodynamic (boundary) conditions due to the environment. However, in many situations, it will be necessary to include the contact with the environment explicitly in the configuration space of the energy landscape, e.g., when heating a substrate while growing a film at a high deposition rate on its surface,[88] because otherwise important features of the time evolution of the system would be lost.

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[9] As a consequence, most global optimization algorithms employed in, e.g., structure prediction in chemistry, are unsuitable for obtaining information about the barriers that surround and stabilize the predicted metastable compounds.

3. Energy landscape of chemical systems in contact with the environment

3.1 Extensions of the potential energy landscape in the presence of external fields

When applying external fields or other related boundary conditions representing the environment, the energy landscape needs to be modified appropriately. Three different levels are to be distinguished: a) The additional quantities are constant in time with zero flux of any quantity, i.e., the system is in thermodynamic equilibrium with respect to the applied field. b) The fields are constant in time but induce non-vanishing stationary fluxes of some quantity, i.e., the material is in a steady-state as far as the flows induced by the externally imposed fields are concerned. c) The external fields are variable in time, usually implying time-varying fluxes of some quantity, and thus the system most likely is in a non-equilibrium state.[10] Note that in all the necessary extensions of the original potential energy landscape, we will be guided to a considerable extent by thermodynamic considerations. Due to its conceptual complexity, level c) will be discussed separately in section 3.5.

3.1.1 External stresses

The most straightforward case is the application of a constant (mechanical) pressure. In this case, the cost function of interest is the so-called "potential enthalpy", which is defined as $H_{pot}(\vec{X}) = E_{pot}(\vec{X}) + pV(\vec{X})$.[42,43] Here, we are inspired by the Legendre transformation of the energy to the enthalpy in thermodynamics, where the pressure $p = -\frac{\partial E}{\partial V}$ replaces the volume V as the independent thermodynamic variable, and the enthalpy $H = E + pV$ replaces the energy E as the thermodynamic potential.[91] Of course, in statistical mechanics and thermodynamics, E and V are now functions of pressure and we have performed the ensemble average over all microstates $\vec{X}$. But in the case of the energy landscape, the potential enthalpy function, like the potential energy before, is a function of $\vec{X}$, and p is just an external parameter. The local minima on this potential enthalpy landscape are those modifications of the chemical system, which are favored at a prescribed pressure p. Note that we can generate a whole family of potential enthalpy landscapes by modifying the pressure, and analyze how they slowly change as a function of pressure (c.f. Fig. 2).

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[10] In the non-equilibrium situations - both full non-equilibrium and steady state -, we also need to be concerned with how the field penetrates into the material. The frequently implicit assumption that the field is present everywhere with constant strength does not hold in general - just recall the screening of the electric field by a metal.[89] Another example would be the time scale on which a variation of an external temperature will establish itself throughout the material, or heat generated by, e.g., chemical reactions or phase transformations, will spread through the system. Other examples are, e.g., the heat release during the deposition of atoms on a cold surface with finite thermal conductivity, leading to a "hot" surface layer that allows some annealing at an effective temperature much higher than the one inside the substrate,[88], or the billions of years needed for the heat stored and generated inside the Earth to reach the surface (according to an estimate of the cooling rate of Earth of ca. 5 - 10 K/10^8 years) [90].

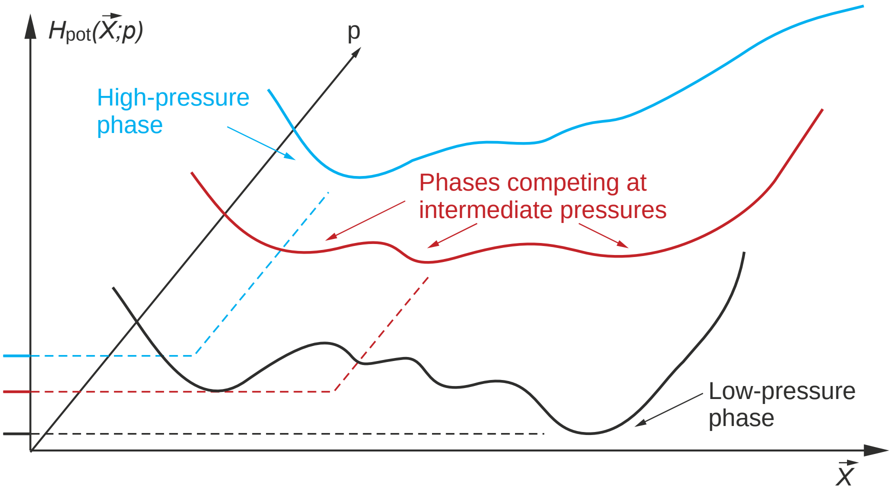

Figure 2: Schematic potential enthalpy landscapes $H_{pot}(\vec{X};p)$ as function of pressure p. Note how the potential enthalpy of the corresponding ground states increases with pressure, due to the presence of the pV term in the potential enthalpy, $H_{pot}(\vec{X};p) = E_{pot}(\vec{X}) + pV(\vec{X})$.

The constant pressure is a special instance of applying an external stress field $\overleftrightarrow{\sigma}$ to the chemical system. Viewed as a macroscopic solid, the system will adjust its macroscopic shape according to the applied stress, e.g., a shear force or an uni-axial pressure gradient, within and beyond the elastic approximation; especially for large stresses, plastic deformations will occur. While this effect is important in its own right, we can only model this within the energy landscape picture if we consider all $O(N_{Av})$ atoms in the solid, i.e., by treating a N_{Av}-atom configuration of the macroscopic solid as a point in $R^{3N_{Av}}$. As long as we employ the usual periodic cell model, we can only deal with the second effect of the applied stress, i.e., the deformation of the periodic cell[11] without additional changes in the macroscopic shape of the solid.[12] In this case, we introduce a local deformation term $\overleftrightarrow{\sigma}\overleftrightarrow{u}(\vec{X})$ to the generalized potential energy function, where $\overleftrightarrow{u}(\vec{X})$ is the macroscopic deformation tensor of the material translated into the deformation of the periodic cell.[92,93] In general, we might need to use the continuum approximation in the case of spatially varying stress fields and integrate the energy term $\overleftrightarrow{\sigma}(\vec{r})\overleftrightarrow{u}(\vec{r};\vec{X})$ over the whole macroscopic solid ($\vec{r}$ labels the material points in the continuum approximation [94]). We also note that when talking about external pressure (and stresses), one usually thinks of mechanical pressure p_{mech} applied at the surface of the material, but other sources of pressure are also common, e.g., due to electromagnetic fields or intense laser radiation.[13]

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[11] Note that the system could try to minimize the energy by massively deforming the simulation cell, thus mimicking the macroscopic deformation of the material. To avoid such spurious low-energy minima (which - due to the periodicity of the system - represent the same infinite crystal by being just different approximants of the same crystal), we would restrict the allowed anisotropy and flatness of the simulation cell.

[12] As far as elasticity theory is concerned, we are essentially staying in the "elastic" region without allowing for macroscopic plastic deformations, even though the applied stresses might go far beyond those for which the elastic approximation is appropriate. Here, the "elastic" behavior does not need to be linear, and can even involve a complete rearrangement of the atoms inside the periodic cell including a transformation to a different crystalline modification as far as the local minima are concerned. The importance is that the changes are restricted to the periodic cell containing only a small fixed number of atoms.

[13] In this context, we note that for systems with a finite number of atoms that are exposed to an external pressure, it is not always clear how the volume $V(\vec{X})$ at microstate $\vec{X}$ is supposed to be evaluated. If the atoms form a

3.1.2 External electric and magnetic fields

An analogous procedure yields extensions of the energy landscape for the case of magnetic and electric fields. Concerning the electric and magnetic fields, several cases need to be distinguished, depending on the level of model description we employ: i) direct interaction of the external fields with atom level degrees of freedom, specifically the charges of the nuclei or ions and of the electrons; ii) direct interaction of the fields with electric and magnetic dipole moments of the atoms/nuclei/ions/electrons, if such (permanent) degrees of freedom are present in the system - depending on the level on which we model the microstates of the system, this might also include permanent dipole moments of molecules; iii) dipole moments present on the molecular or material point level[14]; in particular, induced electric and magnetic moments, especially for strong electric and magnetic fields; and iv) the energy density of the applied electromagnetic field.

i) The fact that a chemical system is composed of N atoms i that each consists of a positively charged nucleus with charge $q_i = Z_i e$ ($e = |q_{el}| > 0$) and Z_i negatively charged electrons ($q_{el} = -e$), has, in principle, dramatic consequences in the presence of a constant electric field $\vec{E} = E_0 \vec{e}_x$ with $E_0 > 0$. The global minimum configuration of the nuclei+electrons system would involve a total separation of nuclei and electrons, with all the nuclei located at $x = +\infty$ and all the electrons at $x = -\infty$, regardless of the strength of the electric field (!), since for each nucleus i and electron j we need to add a term $-Z_i e\vec{E} \cdot \vec{R}_i$ and $e\vec{E} \cdot \vec{r}_j$ to the potential energy[15]. Here, we note that the microstates of the system would be given as $\vec{X} = \left(\vec{R}_1, \dots, \vec{R}_N; \vec{r}_1, \dots, \vec{r}_{N_{el}}\right)$ listing the "positions" $\vec{R}_i$ of the N nuclei and the "positions" $\vec{r}_j$ of the $N_{el} = \sum_{i=1}^{N} Z_i$ electrons, i.e., $E_{pot}\left(\vec{X}; \vec{E}\right) = E_{pot}\left(\vec{X}\right) + \sum_{i=1}^{N}\left(-Z_i e\vec{E} \cdot \vec{R}_i\right) + \sum_{j=1}^{N_{el}} e\vec{E} \cdot \vec{r}_j$.[16]

In practice, we usually do not have to deal with such an infinitely extended field. More commonly, we study a finite piece of material, such as a molecule or a crystal, that is placed inside a capacitor (with the plus-plate located at $x = 0$ and the minus-plate at $x = d$, with a voltage difference between the two plates of $V_c = E_0 d$, and a constant electric field between the two plates $\vec{E} = E_0 \vec{e}_x$ (and zero outside the capacitor). Now, as long as $eV_c < W$, where W is the work function of the material, i.e., the amount of energy needed to remove an electron from the material, the electrons will remain inside the material, and the electric field contribution to the total potential energy will not dominate the energy landscape of the material. At least for insulators, this often means that we can try to include the electric field directly into the quantum mechanical calculation of the energy of a given atom configuration, and thus return to microstates that only refer to the atom positions.

However, such a constant electric field will influence the electron distribution inside the material, of course. For insulators, this can lead to local induced dipoles, and in the case of a metal, it can result in a macroscopic change in the electron distribution - inducing a

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more or less cohesive cluster, for which an approximate surface can be defined via a convex-hull construction, then the volume enclosed by this surface can be identified with the volume of the system. If this is not possible, an alternative is to evaluate the term $pV\left(\vec{X}\right)$ via the application of an effective pressure-like force on the individual atoms, where this force is proportional to the applied pressure and is directed towards to center of mass of the finite set of atoms.

[14] In principle, we also need to consider higher moments such as quadrupole moments, etc.

[15] The zero of the potential energy connected to the electric field is located at the origin, $x = 0$, w.l.o.g.

[16] Of course, in principle, we need to deal with the electrons and nuclei on a quantum mechanical level, and thus find the solution of the Schrödinger equation for an electron/nucleus modeled as a point charge in an infinitely extended constant electric field. However, this would not change the discussion of the ground state of the system, i.e., we would again obtain a separation of positive and negative charges.

macroscopic electric dipole inside the material that shields the external field - or, alternatively, in a constant current through the material. The latter requires the presence of external contacts to the material such that both a source and a sink for the electric current are available. Usually, this has only indirect effects on the spatial arrangement of the atoms, but it can change the potential energy of the atom configurations such that high- and low-electric field phases and atom arrangements will exist, and thus structural distortions or phase transformations can occur; examples are piezo-electricity or ferro-electric phase transitions that involve structural re-arrangements.[95]

An important special case is the presence of mobile ions, where not only the electrons but also the atoms can be so easily moved even for moderate electric fields, that ion currents can be caused by the presence of the electric field. In model energy landscapes where we employ cations and anions as the basic entities instead of the atoms, such individual charges that directly interact with the electric field would appear, e.g., when one uses empirical energy functions that include ions instead of atoms, or allow charge transfer between the atoms. In that case, we need to distinguish two different situations.

Firstly, the chemical system consists of a finite set of atoms, such as a molecule or cluster of N atoms. In this case, we can write down a term $-q_i\vec{E}\cdot\vec{R}_i$ for every ion i with charge q_i in the energy function, where $\vec{R}_i$ is the distance of the ion from the center of mass of the cluster, analogous to the case of the nuclei and electrons, favoring the movement of every ion towards $x = \pm\infty$. Again, one would want to exclude this effect by restricting the size of the volume that can be occupied by the ions belonging to the cluster; e.g., the ions are only allowed inside a sphere with some maximal diameter $D_{max} \leq 2Nd_{ion}$, where d_{ion} is the diameter of an ion in the cluster.[17] As long as $\sum_i \left|q_i\vec{E}\right|D_{max}$ does not exceed the cohesive energy of the cluster without electric field applied, we can expect that the low-energy isomers with a diameter $d_{clust} < D_{max}$ will still be the relevant minima of the system. For fields where $\sum_i \left|q_i\vec{E}\right|d_{clust}$ is larger than the cluster energy, we would expect a break-up of the molecule to occur, similar to the case of a Coulomb explosion that takes place when too much charge is placed on a small molecule or cluster [30].

The second case is the one of an infinite ionic solid when we employ as description a variable unit cell containing only a small number N_{atom} of atoms, with periodic boundary conditions, as a periodic approximant to the true infinite solid.[18] Again, the electric field can couple directly to the charges of the ions (due to the use of an empirical model potential for the ion-ion interactions). Now, we can try to deal with the situation by assuming that the periodic cell and its content play the role of the cluster in the finite system case a) above. We again use the same approach of trying to estimate a maximal allowed cell size (with N_{atom} atoms), where we use the expression $-q_i\vec{E}\cdot\vec{R}_i$, where now $\vec{R}_i$ is the distance of ion i from the center of the periodic unit cell in Cartesian coordinates, as the interaction term of the ions with the electric field in the energy function.[19] Due to the periodicity of the system, the potential energy contribution of the electric field takes on a "saw-tooth"-like shape, since each repeated cell resets the zero of the potential. As a consequence, the effect of the electric field becomes larger if we go to larger simulation cells containing proportionally more atoms. Especially for large fields, this will make itself felt in the ranking of the energies of the

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[17] We encounter similar complications when studying a single molecule or cluster in a simulation cell of infinite size: except at $T = 0$, the statistically preferred state would consist of isolated atoms randomly spread out over the infinite available space. Again, one addresses this problem by restricting the atoms to be inside a sphere of finite diameter D_{max} when performing global explorations of the landscape.

[18] Analogous considerations would apply when modeling the solid as nuclei+electrons instead of cations+anions.

[19] In order to avoid the simulation cell to maximize the electrostatic energy by becoming extremely anisotropic and flat, one would need to enforce limits on the shape of the periodic simulation cell, similar to the case of an applied mechanical shear stress field.

equivalent minimum structures representing the same infinite crystal, when they are computed for different sizes of periodic simulation cells.

We note that one also needs to avoid double-counting the energy, e.g., if the electric or magnetic field contribution is already included in the *ab initio* energy calculation.[20] Furthermore, even if no ionic charges are present in the system and we only deal with atom centered dipole moments in an insulator, very large fields might remove the valence electrons from the atom, effectively destroying the localized dipole moments and creating an ion-electron plasma in the system, or, at least, switching the system from an insulating to a conducting state for the same configuration $\vec{X}$.

ii) In the next case, the presence of permanent atomic or molecular electric or magnetic dipoles, we first need to compute the (permanent) magnetization $\vec{M}(\vec{X}) = \vec{M}_{perm}(\vec{X})$ or electric polarization $\vec{P}(\vec{X}) = \vec{P}_{perm}(\vec{X})$ of the system associated with a microstate $\vec{X}$. In the most straightforward case, this can be done by computing or employing given atomic electric and magnetic dipole moments $\vec{p}_i$ and $\vec{m}_i$, respectively, such that $\vec{P}_{perm}(\vec{X}) = \sum_i \vec{p}_i$ and $\vec{M}_{perm}(\vec{X}) = \sum_i \vec{m}_i$.[21] Alternatively, (relativistic) spin-polarized energy calculations can provide a split of electronic bands via spin-orbit coupling for the given atom configuration, which again allows us to couple the magnetic field to the spin of the quasi-electrons occupying the bands for a given atom configuration $\vec{X}$. However, if we cannot associate the moments with individual atoms, and thus straightforwardly with a single microstate, i.e., atom arrangement, it may be necessary to compute the moments in the continuum approximation.[89] Analogously to the application of pressure, we are now guided by thermodynamics in adding terms $-\vec{M}(\vec{X})\vec{B}$ and $-\vec{P}(\vec{X})\vec{E}$ to the potential energy or enthalpy, resulting in a cost function $C(\vec{X}) = E_{pot}(\vec{X}) + pV(\vec{X}) - \vec{M}(\vec{X})\vec{B} - \vec{P}(\vec{X})\vec{E}$.[22]

iii) If such a coupling to permanent (atom level) dipoles is not present, this term linear in the electromagnetic field does not appear. However, if the applied field is large, it can induce a dipole moment for individual atoms, molecules or groups of atoms, which is a function of the applied field, e.g., $\vec{M}_{ind}(\vec{X};\vec{B})$ or $\vec{P}_{ind}(\vec{X};\vec{E})$. This induced polarization subsequently couples to the field, yielding non-linear terms (in the field), e.g., $-\vec{M}_{ind}(\vec{X};\vec{B})\vec{B}$, in the cost function. In general, we would have, e.g., for the magnetization in the presence of a magnetic field a term $\vec{M}(\vec{X}) = \vec{M}_{perm}(\vec{X}) + \vec{M}_{ind}(\vec{X};\vec{B})$. Such terms might become very relevant at extreme conditions. Here, we must note that the induced magnetizations and polarizations will often be many-body effects in the sense that the already re-oriented permanent dipoles together with induced dipoles of neighbor atoms or molecules, will have an effect on the size of the induced electric and/or magnetic dipole moment on a given atom or molecule, up to a transition to, e.g., a ferromagnetic phase. Thus, such induced dipoles, e.g., $\vec{M}(\vec{X};\vec{r})$, are often associated not only with individual atoms but with all the atoms contained inside a material point (labeled $\vec{r}$) in the continuum approximation[89], which can considerably complicate the evaluation of the energy contribution due to the

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[20] In some ab initio codes, such constant electric fields can be directly implemented when computing the ground state energy; external magnetic fields are more difficult, although there have been proposals how to address this issue.[96] Here, we are more concerned with the general principle for an ideal energy landscape.

[21] Note that the orientation of these magnetic and electric dipoles are additional degrees of freedom in the microstate description of the atom configuration. If we deal with the interaction on the electrons+nuclei level, then the individual nuclear spins and the individual electron spins would enter the definition of the microstates. Here, one must again be careful not to double-count the interactions with the electric and magnetic fields, e.g., if we include both individual electron spins and permanent dipoles of an atom or a molecule in our model.

[22] Clearly, if the electric or magnetic field becomes large enough, (crystalline) modifications with large polarization or magnetization, respectively, are the preferred ones, just like a high pressure favors high-density modifications.

interaction of the magnetic and electric field with the induced dipoles of the material, for a given microstate.[23]

iv) In addition to the terms that couple directly with the atoms via their dipole moments or charges, there is the term associated with the energy of the magnetic and/or the electric field itself, which generates an energy density $\frac{1}{8\pi}\mu(\vec{X})(\vec{B})^2$ and $\frac{1}{8\pi}\varepsilon(\vec{X})(\vec{E})^2$, respectively. This term is always present, regardless of whether the chemical system couples directly to the electromagnetic field or not.[24] This electromagnetic energy density contributes a pressure-like term to the cost function, resulting in the expression $C(\vec{X}) = E_{pot}(\vec{X}) + \left[p_{mech} + \frac{1}{8\pi}\mu(\vec{X})(\vec{B})^2 + \frac{1}{8\pi}\varepsilon(\vec{X})(\vec{E})^2\right]V(\vec{X}) - \vec{M}(\vec{X})\vec{B} - \vec{P}(\vec{X})\vec{E} + \sum_{i=1}^{N}(-q_i\vec{E}\cdot\vec{R}_i)$ - where the last term corresponds to the effect of the electric field on the ions in the system (if this term has not been already included in $E_{pot}(\vec{X})$) - for the generalized energy function, which again favors modifications that exhibit a high density analogously to the case of high pressures.[25]

3.2 Temperature and free energy landscapes

Pressure, mechanical stresses, and electromagnetic fields are quantities that can be taken into account via a straightforward generalization of the potential energy as a function of atom arrangement $\vec{X}$. In fact, the resulting cost function does not structurally differ from the original potential energy landscape insofar as we can still characterize the energy landscape in terms of its local minima and generalized barriers[77,81].

In contrast, introducing temperature into the system results in a major conceptual change in our treatment of the energy landscape. While the configuration space and the energy function of the system do not change, we can no longer expect to find the chemical system at a fixed position in configuration space, e.g., a local minimum, during a given observation time t_{obs}. Instead, the system will explore various regions of configuration space during this observation time, depending on where we start initially. In order to be able to perform statistical mechanical calculations of various properties of the system that are in agreement with observations (averaged over the observation time), we have to focus on regions of the energy landscape that are locally ergodic on the time scale of observation.[97,43] We call a region $\mathcal{R}$ locally ergodic on the time scale t_{obs}, if $t_{obs} \gg \tau_{eq}(\mathcal{R})$ while the observation time is much smaller than the time scale on which the system would leave the region, $t_{obs} \ll \tau_{esc}(\mathcal{R})$. Here, $\tau_{eq}(\mathcal{R}; O; a)$ is the shortest time for which the time average of an observable O for a typical trajectory inside the region $\mathcal{R}$ equals the ensemble average of the observable over the region $\mathcal{R}$ with an accuracy a, $\left\| \langle O\rangle_{ens;\mathcal{R}} - \langle O\rangle_{t_{obs};\mathcal{R}} \right\| < a$. Similarly, $\tau_{esc}(\mathcal{R})$ would depend on the amount of probability flow leaving the locally ergodic region $\mathcal{R}$, which one is willing to accept up to the escape time scale. Of

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[23] We also note that establishing such induced dipoles in response to the application of the field might require some time to occur τ_{ind}, such that adding the corresponding energy terms might only be appropriate if we study the system on sufficiently large observational time scales $t_{obs} \gg \tau_{ind}$.

[24] Even if the atoms in the system do not react to the applied field at all (we assume the field is not so strong that it "ionizes" the atoms in the material as discussed above), we still have $\mu(\vec{X}) = 1(\neq 0)$ and $\varepsilon(\vec{X}) = 1(\neq 0)$, and thus this energy density does not vanish.

[25] In principle, the magnetic and electric field can vary as function of position - thus requiring an integral $\frac{1}{V(\vec{X})}\int_{V(\vec{X})} \vec{M}(\vec{X};\vec{r})\vec{B}(\vec{r})dV$ instead of $\vec{M}(\vec{X})\vec{B}$, and an analogous expression for the electric field term -, but we will assume for now that they are constant as function of position.

course, both the equilibration time and the escape time for a region depend on the temperature of the system; as a consequence, the set of locally ergodic regions for a given observation time scale changes as a function of temperature. Those states that do not belong to these locally ergodic regions (LER) are assigned to transition regions between the LERs or to marginally ergodic regions [46] commonly observed in liquids and glasses.

One important consequence of local ergodicity is the existence of a well-defined local free energy $F(\mathcal{R}) = -k_B T ln Z(\mathcal{R}) \ = -k_B T ln\left[\sum_{i\in\mathcal{R}} e^{-E_i/k_B T}\right]$ for all the regions $\mathcal{R}$ that are locally ergodic on the time scale of observation.[26] These locally ergodic regions correspond to the (meta)stable modifications of the system that can be present on the given time scale of observation. Note that once the system is prepared inside a locally ergodic region $\mathcal{R}$, it is not "aware" that other locally ergodic regions might exist with lower local free energy for observation times $t_{obs} \ll \tau_{esc}(\mathcal{R})$.[27]

Clearly, this local ergodicity analysis can be applied to all generalized potential energy landscapes that include pressure, electric and magnetic fields, yielding a set of locally ergodic regions for a given time scale of observation at a given temperature and thermodynamic boundary conditions. We can visualize this effect by constructing a free energy landscape in a graph-like fashion consisting of discrete locally ergodic regions that are separated by generalized barriers (on a given time scale t_{prob}, and at a given temperature). These barriers incorporate both energetic and entropic aspects and are computed from the probability flows between the regions,[77,78] which are determined using global exploration algorithms such as, e.g., the threshold algorithm.[98,99,79] This time scale dependence of the free energy barriers can be seen in the changes in the free energy landscape as function of observation time.[100] Another way to visualize the observation time dependence of the phases in a chemical system is shown in Fig. 3, where for different temperatures and pressures, the free energies and the time range over which the phases are locally ergodic are shown.

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[26] As far as the microstates of the configuration space are concerned, they can either be assigned to non-overlapping locally ergodic regions or to transition regions between the locally ergodic regions. To what extent the transition regions contribute to the total free energy of the system depends on type of system, temperature, and observation time scale. In a crystalline material at low temperatures, only the locally ergodic regions are important, but for a liquid or glass, the transition regions can be thermodynamically relevant. Here, we note that a glass usually exhibits a sequence of nested locally ergodic regions, whose escape times approximately equal their equilibration times, leading to marginally ergodic behavior.[46] Finally, we remark that the microstates belonging to a locally equilibrated region remain in equilibrium on all time scales larger than $\tau_{eq}(\mathcal{R}; O; a)$, even if the observation time scale exceeds the escape time τ_{esc} from this region.

[27] This seems to contradict the approach of "minimizing the (local) free energy" when finding the preferred phase of a system. But this minimization can only be done, if we have allowed the system to equilibrate globally over a relaxation time $t_{relax} \gg \tau_{eq}^{global}$ before the measurement takes place, such that the probability $p(\mathcal{R}) = \frac{Z(\mathcal{R})}{Z_{total}} = exp(-F(\mathcal{R})/k_B T)/exp(-F_{total}/k_B T)$ to be found in region $\mathcal{R}$ during a subsequent measurement for an observation time t_{obs} is maximal for the minimal local free energy $F(\mathcal{R})$. Furthermore, this concept makes only sense, if $\sum_\alpha Z(\mathcal{R}_\alpha) \approx Z_{total}$ such that $\sum_\alpha p(\mathcal{R}_\alpha) \approx 1$, i.e., the locally ergodic regions dominate the relevant regions of configuration space at the given temperature.

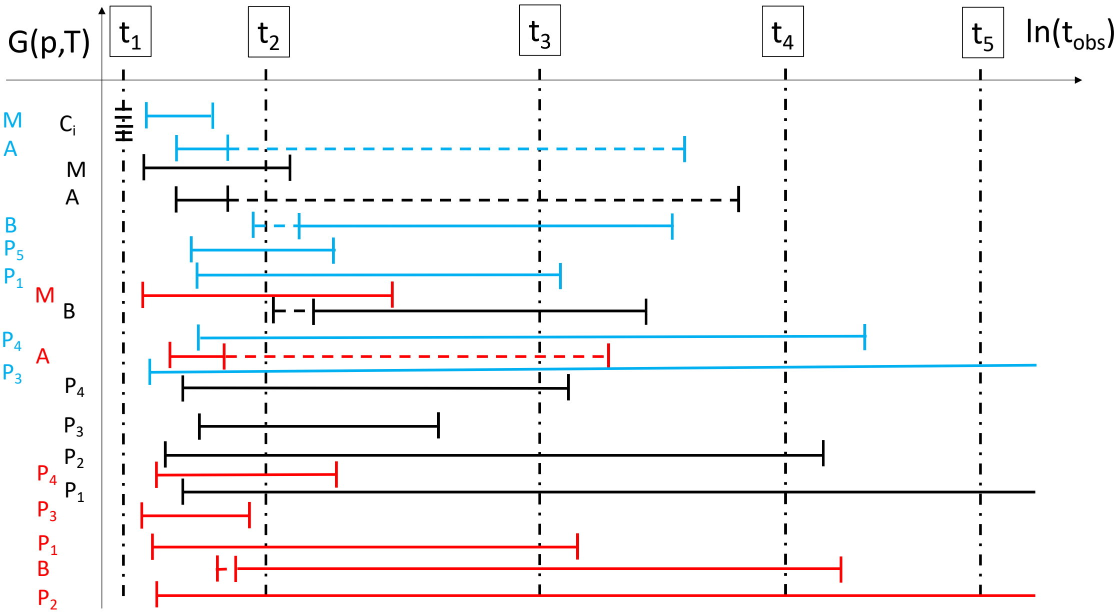

Figure 3: Qualitative sketch of Gibbs free energies of some typical locally ergodic regions found in a solid, for a given temperature and pressure. C corresponds to individual defect configurations, M is the super-cooled melt, B is a solid solution phase, A is a glassy phase, and P_1 - P_5 are (real, i.e., including all the local minima that correspond to equilibrium defect configurations) crystalline modifications. At temperature and pressure (T_1, p_1) - marked in black -, P_1 is the thermodynamically stable phase, P_2 - P_4 are metastable phases, and P_5 is not locally ergodic on any observational time scale. In contrast, at $(T_2 > T_1, p_1)$ - marked in red -, P_2 is the thermodynamically stable (high-temperature) phase, P_1, P_3 and P_4 are metastable phases, and P_5 is not present. Finally, at $(T_1, p_2 > p_1)$ - marked in blue -, P_3 is the stable (high-pressure) phase, and P_1, P_4 and P_5 are metastable phases, while P_2 is no longer locally ergodic on any time scale. Note that the Gibbs free energy of a given phase usually increases with increasing pressure - due to the $+pV$ term in the free energy -, while it usually decreases with increasing temperature - due to the $-TS$ term in the free energy -, respectively. The horizontal solid lines indicate the range of observation times for which these phases would be locally ergodic - the bar to the left would be the equilibration time, and the bar to the right the escape time, respectively. The horizontal dashed line to the right indicates the marginal ergodicity of the amorphous phase - at the end of this line, formation of crystalline modifications within the amorphous matrix would take place. The dashed line to the left of the solid solution phase B indicates the marginal ergodicity of this phase while it slowly moves towards full local ergodicity. The vertical lines denote various observation times; e.g., at time t_4, we have only two locally ergodic regions left: P_1 and P_2 for (T_1, p_1), P_2 and the solid solution phase B for (T_2, p_1), and P_3 and P_4 for (T_1, p_2). Remember that once we have prepared the system in one of the phases that are metastable for a given observation time, we would not know of the existence of competing phases with possibly lower local free energy. Note that we have assumed that $T_{1,2} < T_{melt}$, and thus only a super-cooled melt can be present (on relatively short observational time scales), and not the actual melt phase.

3.3 Steady-state energy landscapes

Next to the static external conditions such as applying a constant pressure or electric/magnetic field, we can expose the system to various fluxes that are constant in time, resulting in a stationary state or steady-state of the system. Examples are electric currents, thermal currents or diffusion currents, due to an applied electric field, a temperature gradient, or chemical potential gradient, respectively.[28] The effects on the system of such fluxes are threefold, in principle: i) a direct coupling to the (atomic) degrees of freedom, beyond the one discussed above for electric or magnetic fields, ii) an indirect effect through the build-up of, e.g., a large magnetic field inside the material carrying the electric current, which results in a pressure-like term as discussed above, and iii) the generation of heat in the system through dissipation of the electric current, leading to a non-zero temperature inside the system even in cases when the system is not connected to an external heat reservoir at some temperature T. Conversely, a temperature gradient can generate an electric field (the Seebeck-effect[91,101]). Quite generally, we must keep the Onsager relations[91] in mind, which couple the thermal, the diffusive and the electric currents. Again, we take our inspiration on how to proceed from thermodynamics, specifically non-equilibrium thermodynamics.[102-105]

A direct coupling of, e.g., an electric current to the atomistic degrees of freedom of the chemical system is not a common situation. An example may be the (supposedly non-thermal) effect of the electric current on phase transitions in orbital liquids,[106] but in this case, we are dealing with a primarily electronic effect. While this subsequently might induce some structural phase transition, this example would be less a "chemical" one and more a "physical" one. Usually, for a given configuration of the atoms $\vec{X}$, the current itself does not play a role; instead, it is the electric field driving the current, which exerts a force on the atoms, and thus leads to a contribution to the potential energy of the system, as discussed above. An instance where such a direct effect of the current on the energy of the configuration may be observed, might be ionic transport, since - on a given observational time scale - this would lead to an "averaged out" position of ions along various channels in the structure and thus influence the locally ergodic regions of the landscape.[29]

Of greater relevance is usually the generation of a contribution to the electric and magnetic field energy of the system. Here, we assume that we are applying a constant current $\vec{j}$ to the system. This implies a driving electric field $\vec{E} = \left(\sigma_{el}(\vec{X})\right)^{-1}\vec{j}$ that generates the current for the electric conductivity the system possesses in configuration $\vec{X}$.[30] Thus, if we want to enforce the value of the current to be $\vec{j}$, we generate an energy density contribution due to the electric field of magnitude $\frac{\varepsilon(\vec{X})}{8\pi}\left[\left(\sigma_{el}(\vec{X})\right)^{-1}\vec{j}\right]^2$. Similarly, due to the magnetic field associated with the electric current, there is a contribution to the magnetic energy density of $\frac{\mu(\vec{X})}{8\pi}[\vec{B}^2]$.[31] In both cases, we can modify the energy contribution (which is obtained by multiplying the electromagnetic energy densities with $V(\vec{X})$ as before), if we change to a

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[28] We note that for an applied voltage generated via a static electric field, a current can only flow if the material is also connected to a source and a drain for the electrons (or ions). For the case of the electric field discussed in section 3.1, it was assumed that the material was isolated and thus no current could flow - only a build-up of electric charge at the surface resulting in a (macroscopic) dipole moment, would have been possible for a finite size system. Similarly, a steady-state diffusion current also requires a source and a drain for the atom/molecule carriers, where the injection and removal of the carriers takes place, respectively. In contrast, in a thermal current, no exchange of material particles with the environment is required as heat can also be carried by lattice vibrations or radiation.

[29] One could also imagine that the collisions of these ions that are trying to move on average in a certain direction with the other (stationary) atoms can be represented by a pressure gradient leading to a deformation of the system.

[30] In general, the conductivities and permeabilities will be tensors.

[31] To compute the magnetic field $\vec{B}$ generated by the current I flowing through the material one would usually employ Biot-Savart's law;[89] note that the field will depend on the shape of the material, in general.

configuration $\vec{X}$ that exhibits a different magnetic permeability $\mu(\vec{X})$, electric permeability $\varepsilon(\vec{X})$ or electric conductivity $\sigma_{el}(\vec{X})$.[32] Fig. 4 shows a schematic representation of the extended energy landscape as function of electric current density, indicating the effect of electric conductivity and the pressure created by the electric and magnetic fields associated with the current density.

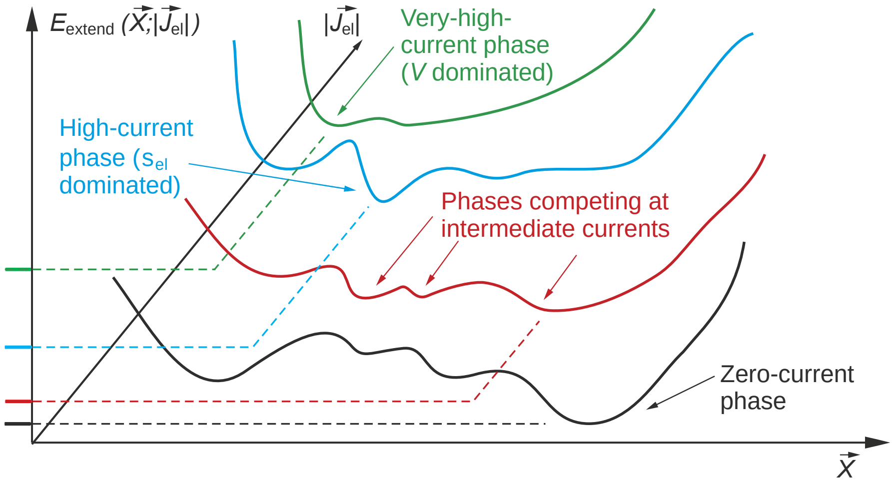

Figure 4: Schematic depiction of an extended energy landscape as function of constant current $|\vec{J}_{el}|$. At very high currents, and thus at very high electromagnetic pressure contributions, the global minimum of the extended energy landscape will favor a structure with minimal volume / atom. However, at intermediate currents, the phase with the largest (but finite) conductivity can dominate the low-energy region of the energy landscape, even if it does not exhibit a high density nor does it constitute a minimum of the regular potential energy.

Concerning a constant thermal current, we note that creating such a current requires establishing a thermal gradient in the material. As a consequence, the (macroscopic) solid would consist of a sequence of slices with different temperatures. Within each such slice, the temperature is approximately constant - as can be seen in, e.g., MD simulations[107] -, and we could treat the degrees of freedom associated with this slice as a subsystem that establishes its own local equilibrium at the temperature of the slice. Regarding the energy landscape as a whole, the locally ergodic regions associated with the whole solid would correspond to a union of atom arrangements restricted to each slice, which are individually in local thermal equilibrium, slightly modified by the interfaces, of course, in case the general structures of adjacent slices are different. In particular, we would see a competition between locally ergodic regions that correspond to a homogeneous phase of the whole solid with those

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[32] There is one general problem here: what does one do, if $\sigma_{el}(\vec{X}) = 0$ for configuration $\vec{X}$? Enforcing a current $\vec{J}$ then implies the application of an infinitely large electric field. Since this would result in an infinite energy contribution of the electric field density, such states would not (and should not) contribute to the physics/chemistry of the system. In particular, one would remove those configurations from the configuration space of the system, either directly or indirectly by assigning an infinite energy penalty. Of course, in reality such gigantic electric fields would destroy the constituent atoms of the chemical system by turning the solid into an electron-ion plasma, making an atom-based energy landscape description infeasible. However, since we are interested in extreme conditions, this possibility should be kept in mind; after all, once the electric field is so large that it can promote electrons from the valence to the conduction band, current can flow even in an insulator.

that correspond to, e.g., a low-temperature phase at the low-temperature end and a high-temperature phase at the high-temperature end, with some interface or even intermediary phases in-between. Note, that this description can only be realized in the context of the energy landscape picture if we are dealing with the complete landscape consisting of N_{Av} atoms. In the reduced picture, where we use a small periodically repeated cell, such a description is not possible, of course.[33]

We note, that, in contrast to the electric current, no term is added to the generalized potential energy function. In principle, we could try to introduce a "minimization-of-thermal-current" criterion to the system, i.e., we add a penalty term associated with the total amount of heat energy being fed into the system in the sense that we "prefer" those phases, which have the highest thermal conductivity and thus require the smallest thermal gradient to establish a given amount of heat current, i.e., $T_{high} - T_{low}$ is the smallest temperature difference possible that generates a given thermal current (per volume) for a given average external temperature $T_{ext} \approx \frac{T_{high}-T_{low}}{2}$. However, since this thermal energy does not, by itself, influence the generalized potential energy function, we will not include this term in our description of the energy landscape proper.[34]

The third type of current due to interaction with the environment would be the diffusion of some type of atoms or molecules through the material, with equal numbers entering and leaving the chemical system.[35] The driving force behind such a current are differences in the concentration of the species of interest at the two sides of the material, and thus in the differences in the associated chemical potentials that are related to the concentration of the species (frequently in an exponential fashion when the relevant atoms can be modeled as a gas-like entity).[91,101] Again, we need a source and drain, respectively, on the opposite sides of the material for a steady-state current; else, the chemical potential difference would just lead to an accumulation and depletion of the species on the two sides of the material.[36] Enforcing such a current requires the presence of an appropriate chemical potential difference that could be explicitly included in the extended cost function. However, one issue complicating the situation is the fact that one frequently incorporates the electric potential into the chemical potential, thus employing an "electrochemical potential" when dealing with diffusion of ions in both an electric field and concentration gradient.[101] In the present discussion, we try to keep these potentials separate, although the fact that the same carriers (ions) realize both currents establishes a connection automatically, which is formalized by the Onsager relations mentioned above.[91,101]

We note that, as in the case of the electric field derived from the imposed current, we would need to determine the diffusion constant $D(\vec{X};\vec{r})$ that enters Fick's law[91,93] connecting the current with the concentration gradient, by using simulations or models on the

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[33] As a compromise, one could study the reduced periodic system for a multitude of temperatures in-between the applied temperatures T_{low} and T_{high}, and construct an approximate landscape description by combining the locally ergodic regions for all the different temperatures, which might yield decent results as long as we can ignore the interfaces between the slices.

[34] If we consider the system on time scales t_{obs} large enough to establish local equilibrium, then we also need to keep in mind the thermal expansion associated with each modification for non-zero temperatures. As a consequence, each locally ergodic region would be associated with an average density that enters the cost function via the $pV(\vec{X})$ term. Of course, as long as we compute the energy / cost directly as function of $\vec{X}$, this term is included directly, but if we were to analyze the free energy landscape based only on the locally ergodic regions instead of the energy landscape, such a term should be included, similar to the induced magnetization or electric polarization for the contribution due to the magnetic and electric fields, respectively.

[35] Of course, there are other types of currents that could be established in a material, such as spin-polarized currents.[108] We are not discussing such currents, but an analysis analogous to the one we have given in this section could be performed, of course.

[36] This is similar to the case of ion conduction but driven by concentration differences instead of an electric field.

material point level, before we can compute the difference in the chemical potentials. However, there is no new energy density term associated with the chemical potential in this steady-state situation, in contrast to the energy of the magnetic field of the electric current.

As mentioned earlier, the material properties such as permeabilities, conductivities, etc. are usually defined and computed on the continuum level, i.e., entering them into the energy landscape is a non-trivial calculation by itself for a given atom arrangement $\vec{X}$, even if we employ the reduced periodic cell description of the energy landscape of a solid. Nevertheless, this contribution extends the potential energy landscape to steady-state situations with constant currents flowing through the system, or to the presence of static external elastic and electromagnetic fields. In practice, it is highly non-trivial to compute, from first principles, quantities like electric or thermal conductivity, the electric or magnetic permeability, or the elastic constants relating the stress tensor to the deformation tensor,[37] possibly as function of material point position $\vec{r}$ in the continuum approximation. It might require performing MD-simulation experiments of "macroscopic" (or at least mesoscopic) versions of the (solid) system, in order to deduce these quantities from the simulations.[38] Alternatively, one could use semi-classical[101] or - if feasible - linear response methods[109] to deduce, e.g., conductivities via integration over $(\omega;\vec{k})$-dependent quantities like the group velocity, relaxation time, specific heat, charge, etc., of the (quasi-particle) carriers involved. Usually, one would not invest the time and effort, but, in principle, such an analysis for a given configuration $\vec{X}$ is possible, and should be performed as part of the evaluation of the cost function $(\vec{X})$.

3.4 Systems with a variable number of atoms

A very important though subtle interaction of the chemical system with the environment concerns the addition or removal of atoms to or from the system, respectively. Again, this can take place in equilibrium, in a steady-state situation, or while the system is in a non-stationary state out of equilibrium. There are several approaches for including this interaction into the energy landscape picture, of different complexity.

Ideally, we include all the relevant atoms or degrees of freedom that describe the interface to the environment directly in the landscape. For non-equilibrium situations, this might often be the only solution that captures the important features of the dynamics of the system.

In contrast, the minimalistic extension represents the environment via a chemical potential-like term μ_i in the cost function, $\mu_i N_i(\vec{X})$, for species i, and configuration $\vec{X}$.[110,42] Here, μ_i can either be the "price-to-pay" for removing an atom of species *i* from its reservoir, before including it into the chemical system, or we can consider $\mu_i = \mu^{(i)} - \mu_i^{ref}$ as the difference between the chemical potential parameter inside the material $\mu^{(i)}$ and the chemical potential of the atom of type *i* in the appropriate reference reservoir.[39]

A major consequence of this approach is that the configuration space of the system must now accommodate atom arrangements with different numbers of atoms of the various

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[37] Actually, this latter case is not so relevant since we can often employ the directly computable deformation tensor.

[38] Such simulations might be needed especially in the extreme conditions we are considering here, since then the linear approximations and the formulas based on linear response theory would not really apply anymore.

[39] Note that if we allow a variation in the number of atoms while we set $\mu = 0$, then the system usually gains energy when adding an atom, although the energy / atom might not be favorable, if the interaction energy of the newly added atom lies below the average interaction energy of the other atoms. This can lead to phase separation in, e.g., multinary systems.

species in the chemical system. Thus, the locally ergodic regions no longer correspond to sets of atom arrangements for only a fixed number of atoms, but can include atom configurations with a spread in the composition. Furthermore, the moveclass will need to be modified to allow an efficient insertion and extraction of the atoms in the chemical system.[40]

In principle, we can introduce whole molecules or complex ions as species, each with its own chemical potential. By modifying the moveclass such that it becomes possible to, e.g., exchange one carbon atom plus two oxygen atoms (that are close together) by one CO_2 molecule, we now are constructing an energy landscape for the efficient realization of chemical reactions in a spatially distributed system on a time scale, where such reactions can be visualized as taking only "one-step" between configurations in the state space. Of course, the underlying time scale of this moveclass is much larger than the one on which the actual reaction of a carbon atom with two oxygen atoms takes place.[41]

We note, that we can, in principle, treat μ_i as a thermodynamic parameter we are free to vary, like the applied pressure, and, thus, we can analyze the extended energy landscape as a function of μ_i. Usually, μ_i would be fixed by the specific environment the system interacts with, but we often might have some freedom in adjusting the chemical potential by modifying the experimental set-up. However, determining such an energy price is a rather tricky issue, since one needs to decide whether one wants to use an atom in the gas phase, an atom in the element in its solid ground state, or in some other state such as in a molecule or in an educt (e.g., in some binary compound), as the reference energy. In addition, this chemical potential would change as a function of temperature, of course.

Of course, like in the case of the electric field or the temperature, the chemical potential can vary as a function of position $\vec{r}$ (and time). Thus, the term in the cost function would again require an integral over all material points, $\frac{1}{V(\vec{X})}\int_{V(\vec{X})} N_i(\vec{X};\vec{r})\mu_i(\vec{r})dV$. As a consequence, the LERs on the time scale of observation would consist of atom arrangements $\vec{X}$, where certain species are accumulated in some spatial regions of the material while being depleted in others. We note that a spatially varying chemical potential can be of interest even if we enforce the requirement that the overall number of atoms of a species $\frac{1}{V(\vec{X})}\int_{V(\vec{X})} N_i(\vec{X};\vec{r})dV$ is constant, i.e., if there is no exchange of atoms between the material and the environment. Then the LERs could, for a given set of atoms, correspond to unions of spatially distributed modifications that are each stable but for different values of the locally

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[40] For solids represented by a periodic simulation cell, we encounter a conceptual and practical problem: we need to add/remove the atoms "inside" the system, i.e., inside the periodic simulation cell, instead of through the surface as would happen in a real system, - clearly a non-physical process; an exception is the transmutation of atoms during radioactive decay (but in that case there is no back-mutation possible, of course). As a practical consequence, "empty space" needs to be created to accommodate the added atoms, because we encounter extremely high repulsive interaction terms due to the fact that we insert an atom "on top" of the (usually tightly packed) atoms already in the cell. But a fluctuation in the volume of the simulation cell sufficient to create a large enough empty space to accommodate an additional atom is extremely unlikely, and furthermore, we generate additional $p\Delta V$ terms, whenever we change the volume of the simulation cell. In practice, the insertion/removal of the atom would be combined with an enlargement/reduction of the periodic cell, possibly followed by a local optimization, such that the energy/atom does not vary by a large amount after performing this complex move. Clearly, such a move corresponds to a realistic time evolution of the system only on very large time scales, and thus it is usually only employed in the context of global optimization studies such as structure prediction or structure fits to experimental data, for variable compositions.[110,42]

[41] For the analysis of an individual chemical reaction, we would employ the usual moveclass that allows only tiny atom displacements, but we would add the excited states of the atoms as part of the configuration space description of the microstates. Alternatively, we could also introduce the excited state landscape(s) of the chemical system, i.e., for each atom arrangement, several possible energy levels of the system (on ab initio level) exist, and our moveclass allows us to move on either landscape, and to switch between the landscapes with a certain probability.

prescribed chemical potential, similar to the distribution of high- and low-temperature phases in a material in a temperature gradient.

Of course, such spatially distributed modifications that split the material into regions with high and low occurrences of various atom species will also be possible, if we allow the overall number of atoms of the various species to vary due to atom exchange with the environment, such that the average chemical potential will establish an overall composition of the chemical system.

There are certain situations, e.g., the study of defect compounds as a function of composition, where the use of a chemical potential can be very helpful. In such a case, we can assume that we are on time scales, for which the amounts of, e.g., hydrogen or oxygen atoms/ions inside the material are expected to be in thermodynamic equilibrium with a reservoir of gaseous hydrogen or oxygen molecules. Instead of dealing with the many additional degrees of freedom required by an atom level description of the reservoir, its presence is incorporated in the chemical potential. Another example is, e.g., the use of a chemical potential based on the partial pressure of, e.g., an oxygen atmosphere in equilibrium with a solid.[111] In this situation, the gaseous state of the oxygen atoms which are in equilibrium with the solid is properly accounted for by the (adjustable) chemical potential, since in this case the dependence of the chemical potential on, e.g., the temperature or the overall pressure, is well-established from experiments for many gas species.

We note that for the special case of a simple gradient of the chemical potential for a particular atom species, with corresponding source and drain, a diffusion flux will be established inside the system, and the material will be in a steady-state, where a sequence of modifications from high- to low-concentrations of the species appears when moving from the source to the drain region. This is the dual case to the enforced steady-state diffusion flux that implied a chemical potential difference, which we discussed in the previous section 3.3.

The third way to incorporate the environment into the energy landscape when the number of atoms in the chemical system is not constant, is to add an explicit reservoir to the energy landscape. Here, a large number of atoms are in equilibrium in a reservoir in form of the reference state, which might be an elemental gas, liquid, solid, or some simple binary or ternary compound at given thermodynamic boundary conditions such as the temperature. In that case, the chemical potential as a "price-to-pay" is automatically computed from the (free) energy loss of the reservoir when moving the atom into the chemical system.[42] In this way, we would be able to establish a grand canonical (equilibrium) energy function. This approach is particularly useful, if it is difficult to directly obtain the chemical potential as a function of, e.g., pressure or temperature.

This last approach again underlines the importance of time scales. Just like an externally applied pressure or temperature require time to establish themselves throughout the chemical system, the same holds true for an externally prescribed chemical potential. Now, we often can assume that the generation of a prescribed pressure distribution will take place, e.g., with a speed on the order of the speed of sound, and thus, the time needed can frequently be ignored in experiments, $t_{obs} \gg \tau_{eq}^{(p)}$, and, similarly, one can often assume that $t_{obs} \gg \tau_{eq}^{(T)}$, where $\tau_{eq}^{(p)}$ and $\tau_{eq}^{(T)}$ are the time scales on which applied stress or temperature are present

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[42] Here, we can either employ the instantaneous change in energy or a time-average of the (free) energy associated with the atom in the reservoir as the "price-to-pay". In both cases, we catch the fluctuations in the reservoir, as function of temperature, pressure, etc., when we average over many moves that correspond to a forward-and-backward transfer of an atom between the system and the reservoir. Such in-situ simulations of the chemical potential that also include efficient procedures to insert the atoms into the chemical system, are by now incorporated in a number of simulation packages.[112]

throughout the system, respectively.[43] However, the equilibration time scales for external parameters is often a problem in the case of the chemical potential, since the addition/removal of atoms usually takes place via a real interface (surface, grain boundary, etc.). Thus, equilibration with respect to the thermodynamic boundary condition in form of the prescribed chemical potential will be established on the time scale of the diffusion, which can be extremely slow when we are dealing with a solid.

We still can explore the extended cost function landscape of a chemical system for a given chemical potential, and thus determine, e.g., the set of metastable phases in the system as function of the chemical potentials μ_i. But we will often have to deal with non-equilibrium situations, because the processes we are interested in take place on much shorter time scales, i.e., $t_{obs} \ll \tau_{eq}^{(\mu)}$, where $\tau_{eq}^{(\mu)}$ is the time scale on which a chemical potential has been established throughout the material.

3.5 Time-dependent energy landscapes

In the context of materials under extreme conditions, and especially in the case of material-environment combinations, which exhibit strong non-equilibrium behavior, we often encounter energy landscapes that depend on time, $E(\vec{X};t)$. Since an energy landscape is defined via three elements - cost/energy function, moveclass and configuration space -, we must address possible time dependencies of all three elements. Of course, in general, all three elements together can, and often will, depend on time. In addition, derived features that control the dynamics on the landscape such as generalized barriers or locally ergodic regions will also depend on time, especially if the equilibration times are large compared to the time scale of variation of the landscape.

3.5.1. Time-dependent moveclass

In this case, neither the set of configurations nor the energy assigned to a given configuration changes with time; instead, it is the connectivity of the configuration space which is affected. This case is most relevant for optimization problems, although it can also occur in the case of physical or chemical systems, where the time evolution of the system is modified. Usually, the physics of a system does not allow for a change in the evolution laws without at the same time modifying, e.g., the energy function itself; exceptions are externally driven dynamics where, e.g., certain "flips" of spins are controlled and initiated by some (time-varying) external effective force. But here the issue is one of the time scales, because, on the physical time scale (femto seconds), our "control" does not apply unless it makes itself felt by a modification of the energy function to generate the driving force (but this was not supposed to happen!). In that case, we would be back to the situation of a physically defined moveclass with a time-varying energy function. As a consequence, variations of only the moveclass in a physical time evolution must reflect the behavior of the chemical or physical system on (moderately) long time scales exceeding the time scale of the elementary processes which would be involved in variations of the energy.

Since the moveclass implicitly defines what we call a local minimum, changes of the moveclass also change the locally ergodic regions on the landscape. Furthermore, moveclass changes modify not only the energetic but also the entropic and kinetic barriers, and thus the

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[43] Of course, there are many instances, such as shock waves, where we are interested in the way the system reacts to the sudden application of an external stress at some local region on the surface of the material, and thus the influence of the barrier landscape on the relaxation behavior of the (macroscopic) system would need to be studied.

generalized barriers and probability flows, and therefore alter the corresponding free energy landscape.[44]

3.5.2. Time-dependent changes in configuration space

Next, we turn to changes in configuration space as a function of time, where we modify the set of states S over which the energy function is defined. The most relevant such change in chemical systems is usually the addition or removal of atoms from the system.[45] Clearly, we can treat this as a switch between two configuration spaces, but we could also consider a giant state space (analogous to the Hilbert-Fock space in elementary particle physics), where creation and annihilation of atoms is part of the moveclass, and configurations can exhibit varying numbers and types of atoms or molecules. In a way, we would keep the "additional" atoms in "reserve" in some kind of a virtual reservoir. As mentioned earlier in the discussion of the chemical potential (c.f., section 3.4), it is not always clear, how to account for these atoms energetically, but we could imagine that this change in configuration space is enforced from the outside and does not constitute an equilibrium process (as our interpretation of the chemical potential as a "price-to-pay" implies).

In this context, we note that the locally ergodic regions change automatically when adding/removing an atom. If we have an order parameter, which classifies all (relevant) LERs,[97] then we might be able to group the LERs for different numbers of atoms - and even for some ranges of composition - together according to the order parameter value. This might work for LERs corresponding to real crystalline phases - i.e., the LER consists of a minimum representing the ideal crystal plus all minima associated with equilibrium defect configurations -, on relatively long observation times, which can be classified based on, e.g., (averaged) symmetries, cell parameters and atom positions inside the unit cell, which is possible for a slowly varying energy landscape. But this order parameter approach becomes essentially impossible for fast variations of the landscape that allow only stable regions on very short observation times, where single local minima corresponding to individual defect arrangements constitute the only LERs of the system.

3.5.3 Time-dependent energy function

Probably the most common and important time-dependence occurs when the energy function itself is modified. There are two different basic types of changes for chemical systems: i) changes of the interaction terms, leading to what is sometimes called "computational alchemy"[114-117] since we are essentially transforming one chemical system into another one, and ii) changes in the external forces and thermodynamic parameters, such as pressure, electric field, stresses, etc. Of course, any combination of these two basic types is likely to occur for some environments the material is in contact with.

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[44] From an algorithmic point of view, any adaptive exploration or global optimization algorithm changes the moveclass as function of its progression, perhaps based on information about the properties of the landscape studied so far.

[45] Other typical changes of the configuration space of chemical systems would be adding or removing restrictions on the allowed volume $V(\vec{X})$ that the simulation cell is allowed to have (both maximum and minimum bounds - e.g., for a MOF - on the volume are possible), or allowing the oxidation state of the ions to vary instead of keeping them fixed; the contribution to the energy is then accounted for in terms of the ionization energies and electron affinities of the ions.[113,42]

In both cases, the configuration space and the moveclass do not change, i.e., we are still dealing with the same set of atoms, where the state $\vec{X}$ is given by their coordinates (plus the unit cell parameters when we model a solid via a periodically repeated simulation cell), and, furthermore, the neighborhood of the states $\mathbb{N}(\vec{X})$ is unchanged, and only the energy or cost functions $E(\vec{X})$ or $C(\vec{X})$, respectively, are modified. Of course, changing the cost function can and will modify not only the size of the LERs, but will also lead to the creation and/or annihilation of LERs on a given observational time scale. This is obvious when one considers the fact that both minima and energy barriers (and also entropic barriers) will change their shape and size, and even vanish or appear as such. Clearly, this affects the probability flows in the system, and thus the equilibration and escape times of feasible LERs. As a consequence, the (thermodynamic) time evolution of the system changes, and we gain a measure of control over the system, which can be used to guide it to a certain modification, or compute the difference in free energies between two chemical systems in an efficient fashion.[118]

3.5.4 Slow variation of the energy landscape

Of particular interest is the comparison between the time scale of observation t_{obs} and the time scale of variation t_{var} on which a noticeable change of the moveclass, the energy function and/or the configuration space takes place. If $t_{var} \gg t_{obs}$, then we can picture the time-dependent landscape as a sequence of only slightly modified versions, where for each such time slice we can compute the locally ergodic regions, probability flows, and other properties of the system for small enough time scales of observation.

If now physically and chemically interesting locally ergodic regions exist on the time scale of interest t_{obs}, then there will be an adiabatic slow evolution of this set of LERs and other features of the landscape, and we can treat the landscape at each time as an essentially constant (time-independent) case, as far as features present on the time scale t_{obs} are concerned. Possibly critical is the case when, e.g., LERs vanish or come into existence starting at some time along with the time evolution of the landscape, corresponding to a singularity in the free energy landscape as a function of time. But since the size of the LER will decrease/increase only slowly and smoothly, this can be handled without major discontinuities.

3.5.5 Fast variation of the energy landscape

But what about fast variations of the landscape with time? Then, we will only be able to define LERs and "controlled" probability flows on very short observational times scales $t_{obs} \ll t_{var}$, which might correspond to having only a few local minima representing individual defect states as LERs on the landscape. In such a case, the system becomes strongly non-equilibrated, where we never reach local equilibrium - and, usually, also do not reach a steady-state - on the relevant time scale of observation. Thus, the results will not only strongly depend on the starting state, but we never establish any real control over the system. Still, if the fast variation with time is periodic (!) in time, we might again be able to establish some kind of equilibrium-like state, plus some resonances in the system. Similarly, the case of a fast variation around some average energy function but with only limited amplitude as far as the changes are concerned, might be amenable to treatment.

Fig. 5 shows the evolution of a schematic landscape where the energy function changes with time, at two different speeds (a: moderately slow; b: rather fast), together with the evolution of a probability distribution of a system that had originally been prepared in region B in configuration space in the first time slice. Here, it is assumed that the moderately slow change in the energy function results in an adiabatic transfer of the system into a target region E in the configuration space in the final time slice 5, even though region D is assumed to be the minimum of the free energy in this time slice. Here, we can imagine that region E is the result of a "merged" evolution of the former regions B and C, while region D is mostly the result of the evolution of region A. Thus, for a very slow change, such that the system is always in global equilibrium at each time slice, we would find some non-vanishing probability in every region for all time slices, and in the final slice, the maximum of the probability would be in region D. On the other hand, a rapid change in the energy function leads to a transfer of some probability into region D, when switching between slices 3 and 4. The reason is that the fast evolution of the energy function "left" some of the original probability from region B in the transition region between the former regions A and B at slice 3, and thus when regions B and C "morphed" into region E in slice 4, some of the probability in the transition region moved into the region D that incorporated the former region A.

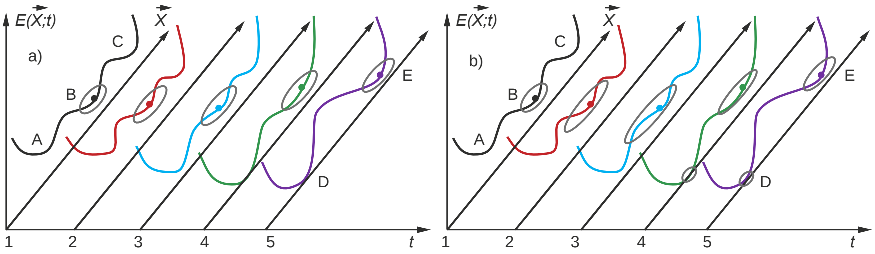

Figure 5: Schematic time-dependent energy landscapes, shown for five different time slices. The general change in the two landscapes is the same but the rate at which the change takes place is assumed to be slower in picture (a) than in picture (b), i.e., the actual times elapsed between the slices are considerably larger in the picture (a) than in picture (b). At the beginning (slice 1), the system is prepared in region B, with no probability in regions A and C, even though some probability would be in these regions in global equilibrium. At the last time slice, we show two valleys: the "target" region E, and a second region D, where D is actually assumed to be the thermodynamically stable phase at the last time slice. The moderately slow evolution shown in Fig. (a) allows the system prepared in the locally ergodic region B to adiabatically be transformed into occupying only one locally ergodic region, the target region E, at the end of the transformation of the landscape. In contrast, the fast evolution of the landscape in Fig. (b) leads to a split of the probability flow of the system when moving from slice 3 to slice 4. Thus, not only the target region E is occupied at the end of the process, but also a non-negligible amount of probability resides in region D.

Let us consider now some energy landscape aspects if the time variation of the energy function (or the moveclass or the configuration space) is very rapid:[46]

i) $t_{var} \approx t_{obs} \geq \tau_{eq}(\mathcal{R})$ such that the escape time shrinks to the order of t_{var}, $\tau_{esc}(\mathcal{R}) \approx \tau_{eq}(\mathcal{R}) \approx t_{var}$: In this case, the locally ergodic regions are reduced to being only marginally ergodic, but without the nesting property which had generated aging behavior in the case of, e.g., amorphous solids. Thus, we will not observe aging but a kaleidoscopic

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[46] Note that here we mainly think of time variation of the energy function; we assume that the moveclass and the configuration space are essentially unchanged. But the discussion would also apply if the moveclass and/or the configuration space varied in time.

procession or random walk through a gallery of LERs that are capable of existence on the time scale t_{obs}. However, the fraction of the landscape associated with transition regions is also very likely to grow compared to the fraction belonging to LERs, possibly quite substantially.

ii) The noticeable variation of the energy landscape with time is so fast and so large that we are greatly out of equilibrium, such that even local minimizations (via, e.g., a stochastic quench - both in physical experiments and in simulations with realistic moveclasses -) are no longer controllable. In this situation, we face serious problems, like a sailor in a boat with rapidly but also randomly appearing mountains and troughs in the water, and it is not clear, whether knowledge of the energy landscape as such will yield insights beyond its availability to compute, e.g., the (Newtonian) forces on the atoms at any given moment.

iii) However, we might want to consider fast variations of the energy function, which only show a small amplitude in the random fluctuations of the landscape parameters around some average values. Usually, this means that the LERs actually do not change by much, unless the small fluctuations reduce the generalized barriers stabilizing the LERs to such a degree that $\tau_{esc}(\mathcal{R}) \leq t_{obs}$. Such "noisy" landscapes are sometimes assigned a noise-temperature proportional to the (square root) of the size of the fluctuations in the energy of the system; as a consequence, simulations on the landscape represent the dynamics reasonably well at temperatures larger than the noise-temperature.[47] An application of such a noisy landscape is the optimization of the parameters in a neural network (NN) for machine learning applications.[119-121] The cost function landscape for such an optimization problem consists of varying training sets of examples to be solved by the network. Since the members of these training sets present slightly different tasks to the neural network, the cost function that measures the agreement between the correct assignment and the one produced by the neural network of the quantity of interest for a given set of NN parameters, changes with time as function of the training set currently being shown, thus acquiring a "noise" feature in the process.

iv) We next consider periodic variations, i.e., the landscape is periodic in time with period t_{var}: if we check the landscape on periodic time points, $t, t+T, t+2T, \ldots$, where $T = t_{var}$ is the period of the time variation of the landscape, we might expect to find various kinds of attractors, like in the theory of chaos. Quite likely, the system will reach some "steady-state" like behavior via a "spreading" of probability all over the landscape such that we get a stable distribution of probability over all the LERs in the system when observed in time steps of the period of the variation.[48] This kind of distribution might correspond to a limit cycle, but it might also show properties of a strange attractor,[122] depending on the type of energy function and its time variation.

To identify this set of stationary distributions of the occupation probability of the LERs, we need to simulate probability flows over many periods of the system, starting in various LERs, and see whether the flow becomes periodic in agreement with the driving force

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[47] From a mathematical point of view, we expect some kind of "quasi-periodic" and/or chaotic behavior for such a "noisy" landscape. But while the trajectories of the system in configuration space can rapidly diverge, this might not influence the existence of the LERs; it may well happen that the equilibration times are actually somewhat smaller (since the chaotic mixing of the trajectories can accelerate the establishment of local ergodicity), while the escape times are only weakly reduced, as long as the magnitude of the fluctuations is small.

[48] In the limit of very long observation times, we would expect to have a certain distribution at each location in time between two such measurement points, which evolves into the next "stable" distribution a short time afterwards, and always repeats after a time interval T has elapsed. Clearly, since we have a strongly varying though bounded variation of the energy landscape, at each point in time inside the time interval of the period of the system, there will be a different set of LERs present (only for very short observation times $t_{obs} \ll t_{var}$, of course), in principle, and thus the distribution over these LERs will change from time to time until one period has passed.

(= landscape variation), after some initialization phase. However, one should note that the probability distribution over the configuration space might not exhibit, or cannot be associated with locally ergodic regions at all, especially if the variation of the energy function is very large such that no consistent set of LERs can be identified as stable (or at least as approximately stable) between successive times of observation in the first place. As a consequence, we can only try to extract a periodic occupation probability over the whole configuration space from our simulations or explorations, which reflect or incorporate the time-dependence of the energy landscape (possibly, but not necessarily in an average fashion).

v) Even if there is no periodicity in the rapid and sizeable fluctuations of the energy landscape, i.e., we are dealing with a non-periodic or chaotic variation of the landscape with a large amplitude in contrast to the small amplitude in case iii) but not so wildly oscillating as in case ii), we might obtain some "averaged" occupation probability distribution over the configuration space as a whole as long as the amplitude of the variation is limited in size. But in this case, since we no longer have a real "reference" set of LERs (which could reappear periodically as in the case of periodic variation), we must extract such a "constant" distribution over "quasi-stationary" not-equilibrated regions from the outcome of many simulations starting from a large number of starting points on the landscape at the initial time $t_0(= 0)$. We note that this behavior of the probability flows on the energy landscape exhibits many analogies with the chaotic dynamics found in many classical mechanical systems, when viewed from a statistical point of view.[122,123]

vi) A special case would be a large variation of the energy function with time, where the "amount of change" with respect to the starting energy function increases in a monotonic fashion. We note that monotonicity lies in the eyes of the beholder considering the fact that we have a high-dimensional parameter space to perform the change in, e.g., by varying the many parameters in empirical potentials. Here, we assume that the change is monotonic in terms of the energies of the ground state and other low-energy local minima; our discussion also would apply to other criteria of monotonicity as long as we do not enter unphysical regimes.

In order to avoid a growth of the energy in the system beyond all bounds in either the negative or the positive direction (i.e., we demand that the energy of the system remains bounded from below and the ground state energy does not grow toward positive infinity either), this usually would require the change to cease after a finite total time (of the simulation or experiment). Alternatively, the change in the energy function of the system might rapidly slow down for times beyond some cut-off time, e.g., corresponding to an exponential cut-off. Of course, this would result in a "limit" landscape, which could be analyzed like any constant or nearly constant energy landscape. But on observational time scales shorter than this limit time, interesting phenomena may emerge. We note that such monotonic changes in the landscape are reminiscent of the adiabatic change of the landscape mentioned earlier in the context of chemical alchemy: again, we essentially switch the system from a starting to a final landscape. But in this more general case, the switch can take place in an arbitrary fashion, ranging from a single sudden jump over a multi-jump trajectory to a smooth movement like in the case of the adiabatic transition. As a consequence, we most likely will be able to split the analysis into studying separately the time-regimes, where the change is slow enough to allow the establishment of locally ergodic regions and well-defined probability flows between them, and those where the large sudden jumps occur, corresponding to the case discussed earlier under the heading of very fast landscape changes.

But as long as we deal with large but solitary jumps in the shape of the energy landscape that are separated by long time intervals, the dynamics resemble the relaxation processes of a quenched system, in the sense that the original equilibrium probability distribution over the microstates greatly differs and is highly inappropriate for the new landscape after the jump in the parameters of the energy function, yet there is enough time until the next jump in the shape of the landscape to extract important features of the relaxation behavior.

This seems to resemble the analysis of the relaxation processes in, e.g., a glass quenched from the melt. But an important difference to the dynamics of a quenched melt, is that the temperature of the system might still be high, because the new landscape is caused by the change in the energy function and not by a reduction in temperature. In contrast, when quenching from the melt, we only change the relevant accessible part of the complete (unchanged) landscape seen by the system: at high temperatures, the system moved in a zone of the landscape above the deep minima basins barely noticing the underlying energy barriers and deep minima, while at low temperatures, the system is forced to cross major energy barriers all the time by essentially hopping among the deep minima separated by large barriers, and thus possibly getting frozen into, e.g., amorphous atom arrangements.[49]

3.5.6 Bounds derived for smooth time variations

Beyond these more general considerations, let us consider, whether we can deduce any information from the change in time of the energy function $E(\vec{X},t)$, if this change takes place in a smooth fashion, such that its derivative is defined, $\frac{\partial E(\vec{X},t)}{\partial t}$, at state $\vec{X}$, i.e., can we make statements about the time evolution / equilibration / search algorithm performance if we know $\frac{\partial E(\vec{X},t)}{\partial t}$?

If $\frac{\partial E(\vec{X},t)}{\partial t}$ varies weakly enough such that $max_A\left[\frac{\partial E(\vec{X},t)}{\partial t}\right]t_{var} \ll E^A_{barrier}(t)$, inside some region A (which might be taken as a locally ergodic region at the initial time), then this region would (probably) be stable enough to preserve local ergodicity on time scales $t_{obs} \approx t_{var}$. We say "probably", because it is not clear what energy barriers we might have to deal with - just those that separate A from the rest of the landscape and thus mainly affect $\tau_{esc}(A)$, or also those barriers inside the region A, which would influence the equilibration time $\tau_{eq}(A)$, leading to a possible split of the region A into several smaller regions that are each locally ergodic on the time scale t_{var} .

Let us assume that we are dealing with a low-temperature case such that energetic barriers are most relevant in the system. Then, for a locally ergodic region $\mathcal{R}$, the ratio of the largest relevant energy barrier and the rate of change of the energy, $E^{\mathcal{R}}_{barrier}(t)/max_{\mathcal{R}}\left[\frac{\partial E(\vec{X},t)}{\partial t}\right] = t_{var}$ represents the time scale beyond which $\mathcal{R}$ is expected to be strongly affected by the change in $E(\vec{X},t)$ with time. As long as $t_{var} > \tau_{esc}(\mathcal{R})$, we can treat the local ergodicity property of $\mathcal{R}$ as being preserved on the time scale t_{var}. If this applies to all LER of $E(\vec{X},t)$ on the time scales t_{obs} of interest, then the LER structure of the system does not change by much. Thus, for $t_{obs} < t_{var}$, we essentially remain inside the phase $\mathcal{R}$ which is modified, of course, due to the time dependence of $E(\vec{X},t)$, but we do not leave the specific region(s) during, e.g., the experiment, which we are simulating.

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[49] Such a rapid change in the relevant landscape by slight changes in temperature has been proposed as the mechanism of the glass transition via so-called exponential trapping in the low-energy range of the landscape of glass formers that exhibit exponential growth in the local density of states of the low-energy range of the landscape, such as in lattice networks.[124]

If $t_{obs} > t_{var} > \tau_{esc}(\mathcal{R})$, then we need to be concerned about the effect of the changes in $E(\vec{X}, t)$ on the probability flows. If, on the other hand, $t_{var} \gg t_{obs} \approx \tau_{eq}(\mathcal{R})$, then we can expect that, at least to a certain extent, the probability flows between the LERs on the time scale of t_{obs}, are still similar to those at the starting time.

Clearly, this suggests that we might be able to use optimal control theory, analogously to finite-time thermodynamics, to guide the system to a certain region in configuration space, if we can control the change in the energy function. But can this be done even if we are not close to equilibrium ?[50]

In this case, we might have to deal with cost functions that are defined by a very complicated process but which still depends on the $(\vec{X}; t)$, of course.[51]

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[50] Sometimes, this is possible if the non-equilibrium probability flows are moving in the "right" direction, even without detailed control via quasi-equilibrium states.

[51] An example would be a TSP problem with N_C cities where the connections between the cities and their travel times evolve on an (exterior) time scale - called t_{ext}, and the goal is to finish the route in as short a time $T(\vec{X}; t_{ext})$. This task is straightforward, if the we can finish the route before the connections have changed as function of the exterior time. But we have problems, if the travel time $T(\vec{X}; t) = T(\vec{X}; t_{ext})$ needed to cover the route $\vec{X}$ changes as function of time while we are still driving, i.e., the speed v is so small that we cannot drive the whole route while the effective lengths (which change with time) of the individual distances between the cities are still approximately constant. In this case, we have a "quasi-external" parameter (the interior time), which controls the route scheduling. Assuming, we have a well-defined starting time for the route t_0, we must compute, for given speed, for each suggested route the total time expression (which corresponds to our cost function) $C(\vec{X}) = \sum_{i=1}^{N_C} T_i(t_i) = \frac{1}{v}\sum_{i=1}^{N_C} L_i(t_i)$, where T_i is the time it takes to drive piece i, and $t_i = \frac{1}{v}\sum_{j=1}^{i-1} L_j(t_j)$ $= \sum_{j=1}^{i-1} T_j(t_j)$ is the moment in time when the salesman starts segment i of the route. In this case, the cost function is a bit complicated, since it is "path-dependent", but, due to the straightforward relationship between the effective path lengths $L_i(t_i)$ and the "internal" time points t_i , each state $\vec{X}$ (= selected city route) of the system has a well-defined length (as long as we fix the point in time when we want to start the route). Thus, we can globally optimize the corresponding TSP-problem; ie., we have "incorporated" the time aspect into the state itself, because the state corresponds to the whole route. Only, if we were to compute the cost (= time) of the route for extremely high speeds such that in the expression $\frac{1}{v}\sum_{i=1}^{N_C} L_i(t_i)$ all the $L_i(t_i)$ have essentially the value $L_i(t_{ext})$ (and thus we can add them in arbitrary order without having to worry about their changing in the time needed to cover the whole route), would it make sense to consider a distinct sequence of cost functions $C(\vec{X}; t_{ext}) = T(\vec{X}; t_{ext})$ and their corresponding cost landscapes. But this approach only works on the level of an optimization problem, for which we know the $L_i(t)$ for every distance piece between any two cities at any time (of the day). Ideally, we would proceed in the same fashion for all processes with general time dependent energy functions - also for physical or chemical systems - , but this is usually much too complex and difficult to do, as it would correspond to solving the time-evolution on the time dependent energy landscape for each possible trajectory of the system. However, if simplified model descriptions of the chemical and physical processes are available, then such problems can be addresses with the tools of finite-time thermodynamics.

4. Systems under extreme conditions: Examples for possible energy landscape applications

The above extensions of the energy landscape picture that allow us to include pressure, external electric and magnetic fields, or currents, temperature, and chemical potentials, in a general fashion, can straightforwardly be employed when dealing with very large pressures, currents etc., as long as we do not destroy the constituents, i.e., the atoms, molecules, etc., of the system. Furthermore, these extensions of the energy landscape can also be employed in the study of molecules and clusters, or (quasi-)low-dimensional chemical systems, keeping in mind that for such small systems, the continuum approximation most likely will no longer be applicable, and therefore the influence of the electric and magnetic fields, etc., always needs to be accounted for on the atomic level as part of the Hamiltonian.

However, there are a number of extreme situations, where an energy landscape representation of the solid via a small periodic cell is not sensible. We have seen this in the case of large mechanical loads, where a major effect, in practice, will be the macroscopic deformation of the solid, which cannot be captured in the periodic cell model of the solid without moving to cells of macroscopic size. Furthermore, we realize that in such situations the system will often be out of equilibrium as far as temperature, stress, or field distribution, or composition are concerned. If possible, we would want to establish a steady-state situation, as we did in the case of currents, where the amount of, e.g., energy deposited inside the system is balanced by the outflow of, e.g., heat through the surface of the system. Once this kind of stationary state has been reached, we can treat the system as exhibiting a steady-state behavior, but possibly requiring a modeling of the energy landscape on the continuum level instead of only the atomic level, in order to incorporate the non-homogeneous ways energy or particles are inserted/injected into the system.

We also note, that for strong interactions with the environment, non-negligible changes in the composition will frequently occur. In certain situations, we can assume that the system is in equilibrium with the environment in form of a reservoir of atoms, which can be included in the cost function in terms of a chemical potential. However, in many instances, the chemical potential by itself is not sufficient for modeling the effect of the environment; thus, the actual interface needs to be included in the configuration space and the energy landscape.

In this section, we consider a couple of important cases of extreme conditions, and investigate, to what extent energy landscape concepts can still apply and be useful. Furthermore, we present a number of examples of energy landscape studies for bulk-like materials in extreme conditions. However, one should note, that only very few dedicated studies of such energy landscapes have been published. Thus, for most of the examples we only indicate how the concepts mentioned above would be applicable in practice, or that such systems might be suitable for analysis with the help of the extended energy landscapes presented above.

4.1. High-pressure structure prediction

The most clear-cut examples of energy landscapes for extreme conditions are the enthalpy landscapes in chemical systems at high pressures. Usually, these are investigated with the goal of identifying possible high-pressure modifications as might be found in a planetary interior or might be of interest for technological applications. Quite commonly, these landscape studies assist experimentalists in characterizing the structure of such newly synthesized modifications. The reason for the latter application is the fact that in many cases only powder diffractograms of moderate quality are available from the experiment, making it very difficult to deduce the crystal structure of the new polymorph only from experimental data. For that reason, one often calls this work structure solution in contrast to structure prediction, because some experimental information such as, e.g., cell parameters, or a number of formula units per periodic unit cell are known from the experiment - even just knowing that a compound with a certain composition and density exists tends to be of help in setting and tuning the parameters of the global exploration algorithm.[52]

Twenty years ago, examples of early successful structure predictions of high-pressure phases based on global enthalpy landscape explorations at a variety of pressures were the alkali metal sulfides M_2S (M = Li, Na, K, Rb, Cs). At the time, these theoretical explorations were performed in parallel with experimental high-pressure investigations of the compounds Li_2S, Na_2S and K_2S, where the theoretical[57,58] and experimental[125-127] results were published at essentially the same time. The experiments and the global searches found the same high-pressure structures in these systems, confirming the validity of the energy landscape approach in the prediction of high-pressure phases. Nearly ten years later, finally the experiments for Rb_2S [128] and Cs_2S [129] were successful, where also the originally predicted structures[58] were found.

At the same time, a similar confirmation of originally theoretically predicted high-pressure phases occurred in the sodium nitride (Na_3N) system. Here, theoretical predictions based on global energy landscape explorations had suggested that a metastable compound of this composition should be capable of existence, with several possible candidate structures being suggested in the M_3N family of compounds (M = alkali metals),[130,131,57] e.g., the Li_3P, Li_3N or the ReO_3 structure type. The reason for suggesting several feasible candidates was two-fold: For one, the fact that the expected compound would only be metastable against decomposition into sodium metal and nitrogen gas made it impossible to select one of the local minima as the thermodynamic "winner" since the modification obtained in the experiment would greatly depend on the synthesis route. Furthermore, the precise energy ranking of these structures depended on the choice of DFT functional where the lack of experimental information made it impossible to guarantee the "correct" choice of functional. However, the global searches combined with the *ab initio* calculations allowed us to predict a sequence of high-pressure phase transitions - independent of the choice of functional -, from the ReO_3-type over the Li_3N- and Li_3P types to the Li_3Bi type. Several years after the successful synthesis of Na_3N in the ReO_3 structure type,[132] these high-pressure structures were successfully obtained,[133] validating the earlier predictions.[53]

Since these early studies, high-pressure structure prediction and structure solution using global energy landscape exploration methods has grown into a veritable industry,[134-151] employing a variety of landscape exploration algorithms, with many reviews available [49-51]. However, only rarely one finds attempts to go beyond the search for local minima and to identify, e.g., enthalpy barriers on the landscape that separate the possible structure candidates represented by local minima, such as was done for several of the earth alkaline oxides.[53] An example for such studies of how the enthalpy landscape and its barrier structure, and also the free enthalpy landscape change with pressure / temperature are the investigations of SrO [53,52] for pressures ranging from -16 GPa to +160 GPa. Fig. 6 shows a free energy landscape for two different pressures by combining the Gibbs free energies with a tree graph depicting the energy barriers between the different locally ergodic regions.

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[52] However, since structure prediction sounds more exciting, and one often technically employs a structure prediction algorithm, some authors ignore the direct or indirect contributions of the experiment to the shaping of the global search they perform, and call their work "structure prediction" with the implication of an unbiased non-guided search in a completely unknown chemical system.

[53] In the experiment, an additional intermediary phase exhibiting the YF_3 structure type was observed.

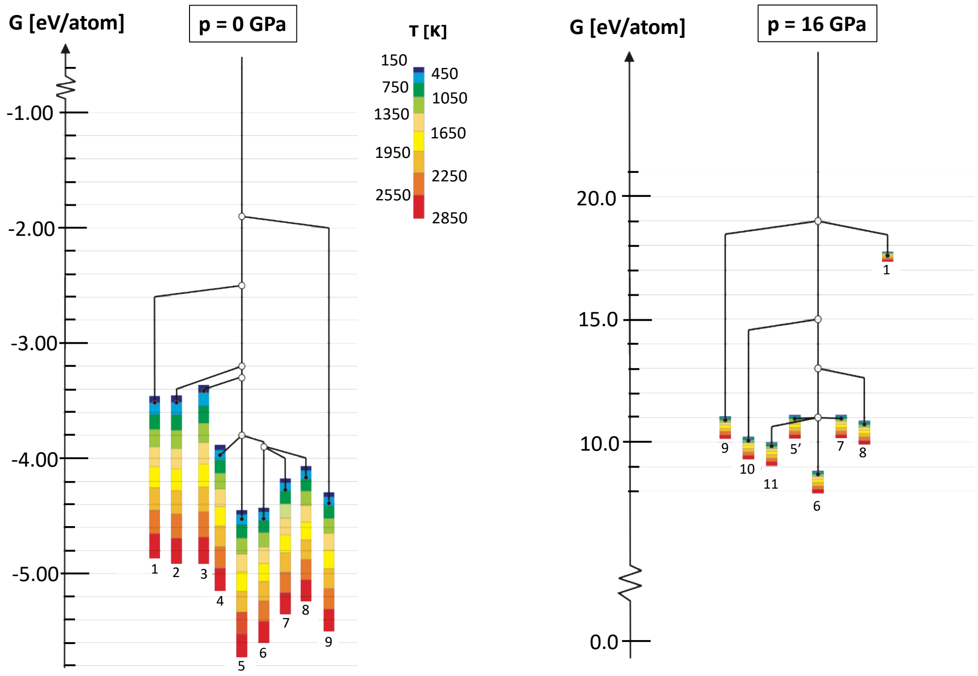

Figure 6: Free energy landscape of SrO for two different pressures and ten different temperatures (free energy in the harmonic approximation); note that only the potential energy barriers are shown (energy difference between black and white circles), and not the full generalized barriers, in order to avoid cluttering the picture.[52] Left: 0 GPa; Right: 16 GPa. Note that the NaCl- and the CsCl-type structures are the ground state for all temperatures at pressures of 0 GPa and 16 GPa, respectively. Modifications shown: 1 = sphalerite; 2 = β-BeO; 3 = wurtzite; 4 = 5-5-structure; 5 = NaCl; 5' = rhombohedrally distorted NaCl; 6 = CsCl; 7 = NiAs; 8 = NbS; 9 = TiP; 10 = II-SrO; 11 = I-SrO. Fig. adapted from ref. [52].

In this context, one should note that for multinary systems, studying only the enthalpy landscape of the compound of interest is not sufficient, because decomposition into, e.g., binary compounds can take place as a function of pressure. An interesting example is the case of the hypothetical alkali metal orthocarbonates $M_4(CO_4)$ - M = alkali metal -, whose possible modifications were studied as a function of pressure.[56] Several of the orthocarbonates were predicted to be stable at high pressures, but they are expected to decompose into the corresponding oxides M_2O and carbonates $M_2(CO_3)$ at standard pressure. To compute the transition pressures below which the decompositions will occur for the various orthocarbonates, or conversely, above which the orthocarbonate would be stable, required the analysis of the enthalpy landscapes of the alkaline oxides [60] and alkali metal carbonates [152].

4.2 Very high temperatures

As we have discussed in section 3.2, for non-zero temperatures, we need to switch from energy to free-energy landscapes, where we analyze the system on various time scales regarding the existence of locally ergodic regions, and the evolution to thermodynamic equilibrium. But at very high temperatures, we can sample pretty much the full configuration space of the landscape, including not only atom configurations associated with crystalline solids but also configurations belonging to the gaseous and the liquid phases. As a consequence, we need to use large periodic cells or very large clusters as approximations to the full macroscopic system with $O(N_{Av})$ atoms.[54]

Thus, the usual picture of a landscape dominated by many well-defined locally ergodic regions that are stable over a large range of observation times and/or at least marginally ergodic regions, might no longer be suitable. On time scales shorter than the global equilibration time, i.e., until the material has completely reached the liquid/gaseous state, the probability flows are dominated by entropic barriers and less so by energy barriers - unless we are dealing with situations where "ultra-high temperature" also includes temperatures below the evaporation, and even below the melting temperature.

We comment here on two special situations, starting with the case $T_{gas} > T > T_{melt}$. Here, a MC or MD simulation based exploration of the landscape would encounter only intermittently stable regions on the landscape.[153] This is somewhat analogous to a glass transition-like behavior but on much shorter time scales where local clustering of atoms, similar to the behavior of cage models of liquids,[154] is relevant on these very short time scales. Similar to glasses, only marginally ergodic regions are present instead of locally ergodic regions, until the global equilibrium of the melt phase has been reached. Quite generally, individual local minima become irrelevant, and even whole minima basins may not be very important on typical observational time scales. Energy landscapes of such systems have been studied for a long time.[155,156]

Similarly, energy landscapes are of great importance for the second case, $T < T_{melt}$. Here, glass formers are of particular interest, especially for temperatures near the glass transition temperature, $T \lesssim T_{glass} (\approx 2/3\, T_{melt})$. In this case, we are in a temperature range, where the onset of aging phenomena and a widespread marginal ergodicity of nested regions on the energy landscape are central to our understanding of the dynamics of the chemical system on the landscape.[46,157] For such systems, more or less random network structures or random atom packings dominate the landscape and crystalline modifications are difficult to reach. Just as with research in the liquid state, energy landscapes of amorphous and glassy materials have been common subjects of study,[158,159] and great efforts have been devoted to the analysis of the similarities and differences between liquids and glasses.

On the other hand, for predominantly crystalline systems that do not easily form amorphous phases, we frequently find transformations to high-temperature crystalline modifications associated with a single minimum, or directly a transition to the melt. In this case, standard crystal structure prediction via global exploration of the energy landscape will yield candidates for (metastable) high-temperature modifications.[42,43,45,48] Alternatively, the central elements on the energy landscape relevant at high temperatures are often multi-minima basins that include various defect structures, and multiple symmetry-related stable regions, etc., instead of individual crystal structure minima. As long as the energies of these minima are very similar, they can jointly contribute to the so-called configurational entropy that provides thermodynamic stability to high-temperature phases, such as glasses, high-temperature structures with partly mobile (rotations and/or translations) complex anions, solid solution phases, or combinations thereof. Studying such systems and predicting their phases is considerably more involved than the simple search for local minima representing standard crystalline modifications, however.[160,59]

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[54] For practical purposes, we might want to study ultrahigh temperatures only in the presence of high pressures to avoid evaporation of the material. Clearly, without high pressures, the liquid or even the gaseous state constitutes the dominant locally ergodic region, and since all the other regions are massively suppressed for most experimental times scales if they exist as locally ergodic regions at all (like a superheated solid, for example), this locally ergodic region essentially constitutes the only set of configurations that are of interest.

4.3 Spin-glass systems with magnetic fields

An important class of complex energy landscapes is encountered in the study of spin systems and, in particular, spin glasses.[161] Here, a more or less random interaction among neighboring spins leads to frustration and a multitude of local minima with nearly the same energy in contrast to the well-developed global minimum of a spin system with, e.g., ferromagnetic interactions. Such systems exhibit highly complex multi-minima landscapes with aging behavior already in zero external magnetic fields,[162] and their energy landscapes have been studied in great detail for a long time[66,67,163] using a variety of exploration algorithms. For example, it was found that the local densities of states, and also the local densities of local minima, exhibited approximately exponential growth in the low-energy region of the landscape, and tree graph representations of their equilibration as a function of time - so-called equilibration or free-energy trees[63] - were obtained.[67] We note, that for many physical and non-physical problems, spin glasses have served as prototypical complex systems and test-beds of both new algorithms and new concepts.

Thus, it is no surprise that the application of magnetic fields has been an important tool in learning more about the properties of such systems.[164-167] For example, using a three-dimensional Edwards-Anderson spin-glass model on a cubic lattice, the ground states of this system have been determined as a function of the magnetic field.[165] Not surprisingly, the high degeneracy of the ground state is eliminated already for small magnetic fields, and the spin-glass phase does not survive, and the system starts behaving like a paramagnet. However, if one employs an energy function of the mean-field type that can be represented by a highly dilute spin glass, there remain distinct large regions exhibiting spin-glass behavior even for finite non-zero magnetic field up to some maximum critical field.

4.4 Phase transitions in a temperature gradient

Concerning the study of energy landscapes for systems exhibiting a macroscopic temperature gradient, there do not appear to exist typical standard landscape explorations. However, MD simulations of such systems have been performed yielding well-developed temperature gradients in a steady state of constant heat flow through the system.[107,168] Furthermore, phase separation in thin films has been studied using the master-equation approach[169] on an Ising-spin model description of a binary mixture,[170] and phase-field simulations have been performed regarding the effect of a temperature gradient on the interface structure in diffusion couples.[171] Thus, global energy landscape studies should clearly be quite promising for systems with thermal gradients, especially considering the large number of experimental investigations, which have studied the effect of temperature gradients on phase transitions and phase separations. These range from phase equilibria such as in the UO_2-PuO_2 system,[172] phase separation in polymer solutions,[173,174] phase and morphological changes in, e.g., diamond films,[175] to phase transitions in, e.g., ferro-electric crystals.[176] Of course, here not only temperature gradients play a role, but also applied stresses, e.g., due to the substrates onto which the film is deposited, or external pressures for bulk materials can be important. We note that an inverse application of the phase transition due to thermal gradients, and the concurrent heat flows in the system, is the use of combinations of two phase change materials to block the flow of heat in one direction, thus creating a thermal rectifier, analogous to an electric diode.[177]

A well-known classic application of the combination of high pressure and temperature gradients is the formation of minerals inside the mantle of the Earth.[178,179] This has actually motivated a large part of the body of work mentioned above in the context of high-pressure structure prediction and structure solution via energy landscape methods mentioned in section 4.1, although no landscapes incorporating thermal flows appear to have been employed up to now.

4.5 Energy landscape with applied electric currents

An important class of steady-state energy landscapes is that, where we encounter phases, which are stabilized by the applied electric currents. While there do not appear to exist global investigations of such energy landscapes, instances observed in the experiment should serve as a motivation to perform such landscape studies in suitable systems where theoretical calculations are feasible. An example are the current-stabilized electronic phases in Ca_2RuO_4,[180] where the current induces a semi-metallic state without any significant heating because in the experiment a sufficient amount of cooling was provided.[106] Since the two phases - the equilibrium and the steady-state non-equilibrium one - exhibit slightly different crystal structures, the transition between the phases as a function of current would be present on the steady-state energy landscape of atom configurations. One should note that even without applied currents, Ca_2RuO_4 switches from an antiferromagnetic Mott insulator to a (2D) ferromagnetic metal,[181] and even becomes superconducting[182], under application of pressure, and, furthermore, it exhibits a metal-insulator transition[183] as a function of temperature.

Such phases based on the electronic degrees of freedom are not always easily treatable in an energy landscape picture, due to the difficulty in setting up a suitable state space and moveclass for the system. However, recent work on orbital ordering[184] shows that such electronic phase transitions can also exhibit nucleation-and-growth behavior typical for first-order phase transitions, suggesting that complex landscape models that exhibit a multi-basin structure and a hierarchy of time scales for the equilibration among the microstates of the system, should be useful for modeling the state space of this quantum system and analyzing its dynamics.

In the materials literature, there exist investigations of phase transitions in the presence of electric currents, where the transitions are associated with a rapid change in the electric conductivity.[105] These are concerned with the existence and growth of nuclei of the second phase, and thus the possible appearance of hysteresis, but fit nicely into the general formalism of steady-state energy landscapes. A related class of theoretical studies deals with the investigation of the use of electric currents in alloy processing,[103,104] which represents processes that occur on the steady-state energy landscape of alloy-forming systems in the presence of substantial electric currents.

4.6 High levels of particle and/or electromagnetic radiation

In the case of electromagnetic radiation, we deposit energy into the system, leading to two effects, in general: The first one is an overall heating of the system, once the deposited energy is transformed into vibrations and distributed throughout the material. The steady-state equilibrium state would correspond to the system being at a certain (high) average temperature, possibly with a more or less complex distribution of regions at different temperatures, depending on where the absorption happens, such that a thermal flow takes place on top of the average temperature of the system, e.g., from the inside to the surface that is at the temperature of the environment; in the case of a vacuum, we would lose the heat energy via emission of black body radiation. The second effect is the direct absorption of radiation via electronic excitation of the local atoms or ions. While this may well lead to interesting phenomena such as luminescence, etc., this is not really a classical energy landscape feature, since it does not deal with the arrangements of atoms in a molecule or a solid. An exception would be the breaking of bonds due to radiation - in this case, we can use the standard energy landscape of the (free) system, and implement the effect of the radiation as part of the moveclass, i.e., as a move corresponding to the breaking of the bond under discussion.[55]

Of course, we can always extend the energy landscape treatment to include energy landscapes describing electronically excited states of the atoms in the material, as is frequently done in the study of molecular reactions.[185,186] In this fashion, absorption of radiation can be modeled and the coupling of electronic and ionic degrees of freedom can be studied, and the influence of electronic excitations on transition probabilities and flows and the corresponding generalized barriers can be investigated. Quite generally, while we usually discuss the energy landscape only as a function of atomic or ionic coordinates, one should keep this option of adding excited state energy landscapes in mind since they might be relevant for materials in contact with extreme environments. However, in such a case, one should also investigate, whether the Born-Oppenheimer approximation is still valid as far as states of the system and the energy function are concerned.[56]

In the case of particle radiation, not only do we deposit energy into the system "via the surface", but also change the composition of the system if the particles are incorporated into the material.[57] As discussed earlier in section 3.4, a change in composition can be accommodated in the energy landscape picture, in principle, but requires the introduction of an appropriate chemical potential that assigns a "price in energy" analogous to a chemical potential accounting for the addition of an atom (or other constituent) to the system - essentially, we would be taking the atom from a reservoir (and removing it to a reservoir, in principle, e.g. when an atom decays radioactively) whenever we change the composition of the system.

In the way described above, we would be able to establish an extended energy function for a system in thermal equilibrium as far as its atom exchange with the environment is concerned. However, this would most likely not correspond to the physical/chemical situation of a piece of material being bombarded by energetic particles, since in that case there would be no "price to pay" because the environment, i.e., the ion beam, forces these molecules/atoms/ions into the material. Then, we can ignore this chemical potential (or set it to zero), and just assume that there exists a continuous stream of particles that are added to the system.[58] But in that case, there is no steady-state, and we are dealing with a non-equilibrium situation.

Note, that the time scales of the processes involved become of importance, depending on the features we want to investigate: Do we want to study the system on time scales where we can assume that a constant spatial distribution of foreign atoms in the material is established, and we are interested in short-term local equilibrium properties, or are we

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[55] Essentially, we are crossing a high-energy barrier along a (usually) very narrow path, which would not be easily reached via thermal excitations of the system; the effect of the high-energy radiation on the molecule corresponds to avoiding a large entropic barrier by a well-focused injection of energy into a narrow group of degrees of freedom, i.e., the ones that need to be activated in order to, e.g., split the molecule into two pieces.

[56] For example, the ground state energy landscape (as function of atom positions) might correspond to a superconducting state instead of the metal or insulator obtained as the ground state from the simple DFT or HF based calculation in the Born-Oppenheimer approximation.

[57] If we deposit (or have incorporated) radioactive material inside the system, we generate not only heat in the bulk of the material but also He-atoms from the α-particles produced during the decay.

[58] If we were to study the likelihood of the system to absorb these particles and later release them back into the environment, then the chemical potential controlling the emission of the molecules out of the material into the gas phase would become relevant. After a very long time, a steady-state process of the particle flow into and out of the material via an ongoing implantation and subsequent release of the particles might become established, with some constant (time) averaged distribution of the particles over the material.

interested in the time evolution of the system without it ever reaching some kind of local equilibrium? In the former case, we can deal with it in analogy to the temperature gradient situation, where we split the system into slices or regions of different compositions, and analyze the energy landscapes of each such slice individually. In the latter case, we need to modify the energy landscape approach with respect to the boundary conditions. We now deal with a fast evolving landscape compared to, e.g., the equilibration with respect to various thermodynamic boundary conditions, $t_{var} \ll \tau_{eq}^{(T)}, \tau_{eq}^{(\mu)}$, for which concepts like global - and even local - ergodicity and equilibration are most likely not applicable. Instead, we must define probability flows on a landscape that varies with time, such that we can address questions that are of relevance in such a situation: limits on stability of (formerly) locally ergodic regions under changing external conditions such as structural changes due to changing composition, size dependence of locally equilibrated regions, etc. Here, we need to employ the approaches discussed in section 3.5 for time-dependent energy landscapes.

4.7 Corrosive environments

In general, corrosion processes are a special case of chemical reactions occurring at the surface or interfaces such as grain boundaries of a material. We can surely study the mechanisms of various local reactions on the atomic level, e.g., oxidation of (individual) atoms belonging to a metal surface, using energy landscapes restricted to the few atoms and molecules involved in this reaction. As mentioned earlier, such energy landscape studies are rather common.

However, once we go beyond such individual local processes that essentially take place in equilibrium, we are confronted by a non-equilibrium situation, which is, furthermore, complicated by a spatially inhomogeneous evolution of the surface structure. Thus, this is an example of a system out of equilibrium on large time scales while exhibiting local equilibrium on the time scale of individual reaction processes. Unless we focus on small regions and short time scales only - where we can assume constant thermodynamic conditions and a constant overall atomic composition -, we are again dealing with a situation, where standard landscape ideas do not apply, and we have to look towards the approaches suggested for time-dependent energy landscapes.

For slow corrosion, we could probably use time-slices, i.e., consider the landscape spatially varying in composition and boundary conditions but constant in time otherwise, and analyze corresponding quasi-stable slices/regions, perhaps with a large (periodic) simulation cell, analogous to the case of nucleation and growth phenomena. Again, we would want to introduce either particle reservoirs or chemical potentials, in order to deal with the changing composition of the chemical system.

Of course, we can imagine that we continually remove, e.g., the few atom layers of rust once they have been formed, thus establishing a kind of steady-state for a sub-system of interest, i.e., at the interface between the material and the corroding environment. But quite generally, the interesting issues of corrosion and its mechanisms are usually the time-evolution, stability, and non-equilibrium aspects involved in these processes, and not a true steady-state situation.

4.8 Prediction and analysis of synthesis routes

Energy landscapes in the presence of external fields or currents, or an environment in general, would be expected to play an important role in describing the atomistic behavior of chemical systems during various processes involved in chemical synthesis. The reason is that the energy landscape of the "pure" system that contains only the atoms belonging to the final product, is often much too limited for representing the actual synthesis, for a number of reasons: For one, unless the synthesis takes place essentially spontaneously from the gas phase or by phase transformation, additional atoms, e.g., in the educts or in the solvent or in the substrate, must be present to facilitate the synthesis. Furthermore, in many cases, we need to steer the synthesis, e.g., by applying le Chatelier's law via pressure variation, and thus we clearly move within the family of enthalpy landscapes of the system at a variety of pressures. Similarly, the presence of external fields in some fashion represents our ability to, e.g., polarize molecules or individual bonds, which reduces or raises energy barriers on the landscape that favor the desired outcome of the synthesis.

A classic example of an implicit use of energy landscapes for guiding a synthesis is the so-called reverse synthesis in organic chemistry,[187,188] because the individual reaction steps can often be modeled and analyzed theoretically with the help of appropriate energy landscapes for the atoms and molecules involved in the step under consideration. This kind of kinetic control of the chemical reactions by the organic chemist is based on the "intuitive" yet systematic [189] visualization of these reaction step energy landscapes. In practice, most theoretical studies of such energy landscapes start with known chemical reactions, and devote their efforts to understanding in-depth the processes occurring during such a synthesis step or sequence of steps.[190,191] But conversely, one could as well analyze many hypothetical reactions via their corresponding energy landscapes, before turning to the experiment for validation and implementation. Analogous to the optimal control built into the study of thermodynamics in finite time, one could then envision the design of synthesis routes in an optimal fashion by combining a whole library of models for specific synthesis processes derived from detailed analyses of the corresponding energy landscapes.[192]

4.9 Computational alchemy and finite-time thermodynamics

Another important application of energy landscapes under extreme conditions is the computation of free energy differences between compounds via the smooth change of the energy function, sometimes called computational alchemy.[114-117] Here, the "extreme" aspect is the change in the underlying energy function of the system, while we use thermodynamic integration methods[193-196] to compute the free energy difference along the "path" connecting the two compounds of interest. This approach to compute free energy differences is based on the laws of thermodynamics, where the change in the energy function results in work being done on / by the system. If we can stay as close as possible to thermodynamic equilibrium along the path, the total amount of work corresponds to the free energy difference between the two compounds. In the case of a realization via simulations, this corresponds to running an ensemble of walkers that are equilibrated in a locally ergodic region while the underlying energy landscape slowly changes (c.f. Fig. 5a). Thus, the formal change in the Hamiltonian of the system can be visualized in analogy to a Hamiltonian that depends on time, resulting in a time-dependent energy landscape, with all the consequences for, e.g., the time scales involved in switching between the two different chemical systems.

Besides the question of optimally controlling the path between the two energy landscapes, i.e., how to distribute the amount of change per step, for a given number of allowed changes in the energy function[118,197] - a problem belonging to the realm of finite-time thermodynamics[87] -, a major complication is that we must perform this transformation of the energy landscapes fast enough such that the walkers still remain inside the given locally ergodic region all along the path. For simple systems, e.g., when moving from NaCl in the rocksalt structure to KCl in the rocksalt structure, via a smooth change in the ionic radius from r(Na) to r(K), this is most likely assured. But we clearly will face problems, if the transformation is supposed to be from MgO in the rocksalt structure to BaO in the cesium chloride structure, or if it involves metastable structures with short escape times: in that case, we either must confront the possibility that some of the walkers will leave the locally ergodic region during the process (c.f. Fig. 5b), or accept that the resulting free energy difference will most likely be rather inaccurate.

4.10 Time crystals

In analogy to the usual periodicity in space exhibited by crystalline compounds, it has been suggested[198,199] that one should define "time crystals", which exhibit periodicity in time as far as their structure is concerned. We note that this does not refer to individual vibrational excitations of the system, but to ground state analogues of a structural crystal with respect to periodicity in time. However, it has been proven that such a breaking of time-translation symmetry is not possible in a standard equilibrium system.[200] Nevertheless, such a time-crystalline state is possible, if the system is out of equilibrium, e.g., in a steady-state situation, where periodic forces are applied in some fashion, or periodically varying currents flow through the material. Clearly, this constitutes an example of a time-varying energy landscape. In particular, we are talking about the special case mentioned in subsection 3.6.5.iv), where we observe the system at periodic intervals, with a period that is an integer multiple of the time period of the driving force, $T_{system} = nT_{driving}$, $n > 1$. Usually, it is assumed that the induced periodicity is due to external fields or flows that add/extract energy to/from the chemical system with a certain period.

While we do not have our usual locally ergodic regions on the landscape, we can identify time-repeating configurations of the relevant degrees of freedom, which are stable for essentially infinite numbers of periods, and exhibit ground-state like properties such as no net-heating of the material (no entropy production) due to the periodically applied forces. Furthermore, to distinguish the "time crystals" from many phenomena observed in periodically driven systems,[201] one usually demands that the period of the time crystal be larger than the one of the driving force, i.e., $n > 1$. So far, example systems tend to be very small and focus on some spin degree of freedom in, e.g., 1D chains of trapped ions[202] or nitrogen vacancy centers[203], but more complex systems might be feasible where positional degrees of freedom exhibit non-trivial periodicity in time, creating a time-crystalline ground state.

4.11 Quark-Gluon Plasma

Finally, a perhaps a bit outlandish example of an energy landscape at extreme conditions would be the one associated with the phase diagram of quantum chromodynamics,[204,205] where a so-called quark-gluon plasma phase is expected. Here, the temperatures and pressures or densities are gigantic compared to anything we encounter in chemical systems. But even in this extreme case, we would expect an energy landscape approach to be feasible once we have decided on the proper state space and moveclass of the system. The landscape would be one that includes variation in the number of particles, i.e., we would need to introduce a chemical potential, and the state space would consist of quarks and gluon fields discretized on a four-dimensional (3 space and 1 time dimension) grid, and the Hamiltonian that provides the energy function would have to be replaced by the QCD Lagrangian.[206,207] This lattice field theory allows us to explore the energy landscape; however, the open question is the choice of moveclass, since for this we need a reasonable model for the time-evolution operation. Besides temperature and density, people have studied the effect of, e.g., magnetic fields,[204] yielding - in the limit of time-scales where the system is globally ergodic - a magnetic field-temperature-density phase diagram, which covers both the state of the early universe, neutron stars, and the "normal" world around us on Earth at the present time. But there are open questions regarding the existence of metastable phases in the quark-gluon plasma; such phases might be accessible when employing energy landscape exploration methods to this system.

5. Conclusions and outlook

In this essay, the energy landscapes of chemical systems in contact with the environment have been discussed, with a focus on extreme conditions. Ideally, the atoms or relevant degrees of freedom that constitute the interface between the devices representing the environment and the (bulk) material of interest would be included in an all-encompassing landscape. Since this is usually impossible for macroscopic systems, we introduce minimalistic extensions of the (potential) energy landscape of an isolated system by parametrizing the environment in terms of, possibly time-dependent, macroscopic fields and fluxes, such as mechanical stresses, electromagnetic fields, electric, particle and thermal currents, other thermodynamic parameters such as the temperature, or particle reservoirs and the associated chemical potentials.

Here, we are guided by the way such forces and fluxes are added to the potential energy in thermodynamics. A critical technical issue one confronts in this process is the computation of material properties - needed for the implementation of the desired (minimalistic) parametrization - that are usually defined on the continuum level, such as conductivities and permeabilities, which must nevertheless be associated with individual microstates of the configuration space of the chemical system. While complicating the matter, this is the price one often has to pay when representing the environment in the cost function by terms that involve only simple field variables. The appropriate choice of such representative variables will depend on the specific chemical system and the kind of extreme conditions it is exposed to, i.e., on the environment it interacts with. Since these external parameters will frequently show spatial and/or time dependences, it might often be necessary to explore the landscape for many small versions of the system - still perhaps containing thousands of atoms -, on small enough time scales such that the parameters can be taken as constant, to obtain information about the feasible (meta)stable states or phases of the system. These piecemeal landscapes can then be joined together to describe the macroscopic system and its time evolution. In particular, the characteristic time scales on which the energy landscape varies, are going to be in competition with the inherent time scales of each of the time-independent energy landscapes, such as the equilibration and escape times of locally ergodic regions and the time scales of the probability flows on the landscape, for given fixed values of the environment parameters.

However, this competition will allow us to control the dynamics of the chemical system, providing a way to obtain optimal synthesis routes for difficult to synthesize compounds or enable phase transformations in a given system in a controlled fashion. We also note that the "extreme conditions" are only special cases of the general interaction with the environment, as long as the forces we apply do not "destroy" the system, e.g., by turning it into a plasma. Similarly, extreme conditions can also be realized in the landscape of small or (quasi-)low-dimensional systems, such as molecules, clusters or nanotubes. However, in these instances, the use of continuum level parameters, such as conductivities or permeabilities, to simplify the extended energy landscape, will be problematic or impossible. Instead, we would need to include the fields explicitly in the Hamiltonian when solving the Schrödinger or Dirac equation of the system.

This points to one of the major open questions in the field of energy landscapes of chemical systems: the construction of an energy landscape for systems, whose state space is fully quantum mechanical in nature, e.g., when the Born-Oppenheimer approximation is no longer valid and thus the space of atom arrangements is no longer sufficient as the configuration space, or where the landscape of interest is primarily a function of the electronic degrees of freedom and only secondarily depends on the atom arrangement. While there are many phenomenological models described by quantum mechanical Hamiltonians for specific systems or properties, there does not always exist a natural choice of microstates for the state space of the landscape - after all, any linear combination of eigenstates of the Hamiltonian with the same energy, or even with different energies, can be employed as a quantum mechanical basis for the system. Similarly, the choice of moveclass is less obvious than in the case of classical atom arrangements, since the interaction with the environment can couple many microstates that seem to be far away or are very different, with a non-negligible probability. Furthermore, the interference of probability amplitudes describing the time evolution can lead to strange connectivities among the states of the landscape when defining the moveclass. This touches on the famous measurement problem in quantum mechanics, which we encounter, e.g., if we want to enforce a periodic reduction to a classical state, in order to recapture our familiar energy landscape picture.[208,209]

While some answers to these questions may be found in the field of quantum thermodynamics [210,211] and, in particular, in the use of quantum master equations [212-214] for the description of dynamics of coarse-grained models of the energy landscape at the quantum level, properly addressing these issues may require new energy landscape concepts, whose development might be driven by the study of systems under extreme conditions. But for the moment, there are enough chemical systems under extreme conditions, ranging from high pressures and temperatures over strong electric and magnetic fields and electric currents, to large thermal gradients and heat flows, all of which might vary with time, where the use of the generalized "classical" energy or cost functions discussed in this work can provide deep insights into the properties and dynamics of the materials.

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