Thermodynamic Tree: The Space of Admissible Paths[*]

Alexander N. Gorban[†]

Abstract. Is a spontaneous transition from a state x to a state y allowed by thermodynamics? Such a question arises often in chemical thermodynamics and kinetics. We ask the following more formal question: Is there a continuous path between these states, along which the conservation laws hold, the concentrations remain nonnegative, and the relevant thermodynamic potential G (Gibbs energy, for example) monotonically decreases? The obvious necessary condition, $G(x) \geq G(y)$, is not sufficient, and we construct the necessary and sufficient conditions. For example, it is impossible to overstep the equilibrium in 1-dimensional (1D) systems (with n components and $n-1$ conservation laws). The system cannot come from a state x to a state y if they are on the opposite sides of the equilibrium even if $G(x) > G(y)$. We find the general multidimensional analogue of this 1D rule and constructively solve the problem of the thermodynamically admissible transitions. We study dynamical systems, which are given in a positively invariant convex polyhedron D and have a convex Lyapunov function G. An admissible path is a continuous curve in D along which G does not increase. For $x, y \in D$, $x \succsim y$ (x precedes y) if there exists an admissible path from x to y and $x \sim y$ if $x \succsim y$ and $y \succsim x$. The tree of G in D is a quotient space $D/\sim$. We provide an algorithm for the construction of this tree. In this algorithm, the restriction of G onto the 1-skeleton of D (the union of edges) is used. The problem of existence of admissible paths between states is solved constructively. The regions attainable by the admissible paths are described.

1. Introduction.

1.1. Motivation, ideas, and a simple example. "Applied dynamical systems" are models of real systems. The available information about the real systems is incomplete, and uncertainties of various types are encountered in the modeling. Often, we view them as errors, such as errors in the model structure, errors in coefficients, and errors in the state observation among others. Nevertheless, there is an order in this world of errors: some information is more reliable, and we trust in some structures more and even respect them as laws. Some other data are less reliable. There is a hierarchy of reliability—our knowledge and beliefs (described, for example by R. Peierls [53] for model making in physics). Extracting as many consequences from the more reliable data either without or before use of the less reliable information is a task which arises naturally.

In our paper, we study dynamical systems with a strictly convex Lyapunov function G defined in a positively invariant convex polyhedron D. For them, we analyze the admissible

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[†]Department of Mathematics, University of Leicester, Leicester, United Kingdom (ag153@le.ac.uk).

paths, along which G decreases monotonically, and find the states that are attainable from the given initial state along the admissible paths. The main areas of applications of these systems are chemical kinetics and thermodynamics. The motivation of our research comes from the hierarchy of reliability of the information in these applications.

Let us discuss the motivation in more detail. In chemical kinetics, we can rank the information in the following way. First, the list of reagents and conservation laws should be known. Let the reagents be $A_1, A_2, \ldots, A_n$. The nonnegative real variable $N_i \geq 0$, the amount of A_i in the mixture, is defined for each reagent, and N is the vector of composition with coordinates N_i. The conservation laws are presented by the linear balance equations

$$(1) \qquad b_i(N) = \sum_{j=1}^{n} a_i^j N_j = \text{const} \quad (i = 1, \ldots, m).$$

We assume that the linear functions $b_i(N)$ $(i = 1, \ldots, m)$ are linearly independent.

The list of the components together with the balance conditions (1) is the first part of the information about the kinetic model. This determines the space of states, the polyhedron D defined by the balance equations (1), and the positivity inequalities $N_i \geq 0$. This is the background of kinetic models, and any further development is less reliable. The polyhedron D is assumed to be bounded. This means that there exist such coefficients λ_i that the linear combination $\sum_i \lambda_i b_i(N)$ has strictly positive coefficients: $\sum_i \lambda_i a_i^j > 0$ for all $j = 1, \ldots, n$.

The thermodynamic functions provide us with the second level of information about the kinetics. Thermodynamic potentials, such as the entropy, energy, and free energy, are known much better than the reaction rates, and, at the same time, they give us some information about the dynamics. For example, the entropy increases in isolated systems. The Gibbs free energy decreases in closed isothermal systems under constant pressure, and the Helmholtz free energy decreases under constant volume and temperature. Of course, knowledge of the Lyapunov functions gives us some inequalities for vector fields of the systems' velocity, but the values of these vector fields remain unknown. If there are some external fluxes of energy or nonequilibrium substances, then the thermodynamic potentials are not Lyapunov functions, and the systems do not relax to the thermodynamic equilibrium. Nevertheless, the inequality of positivity of the entropy production persists, and this gives us useful information even about the open systems. Some examples are given in [26, 28].

The next, third part of the information about kinetics is the reaction mechanism. It is presented in the form of the *stoichiometric equations* of the elementary reactions,

$$(2) \qquad \sum_i \alpha_{\rho i} A_i \rightarrow \sum_i \beta_{\rho i} A_i \,,$$

where $\rho = 1, \ldots, m$ is the reaction number and the *stoichiometric coefficients* $\alpha_{\rho i}, \beta_{\rho i}$ $(i = 1, \ldots, n)$ are nonnegative integers.

A *stoichiometric vector* γ_ρ of the reaction (2) is an n-dimensional vector with coordinates $\gamma_{\rho i} = \beta_{\rho i} - \alpha_{\rho i}$, that is, "gain minus loss" in the ρth elementary reaction.

The concentration of A_i is an intensive variable $c_i = N_i/V$, where $V > 0$ is the volume. The vector $c = N/V$ with coordinates c_i is the vector of concentrations. A nonnegative intensive

quantity, r_ρ, the reaction rate, corresponds to each reaction (2). The kinetic equations in the absence of external fluxes are

$$(3) \qquad \frac{\mathrm{d}N}{\mathrm{d}t} = V \sum_\rho r_\rho \gamma_\rho.$$

If the volume is not constant, then equations for concentrations include $\dot{V}$ and have a different form.

For perfect systems and not so fast reactions the reaction rates are functions of concentrations and temperature given by the *mass action law* and by the *generalized Arrhenius equation*. A special relation between the kinetic constants is given by the *principle of detailed balance*: For each value of temperature T there exists a positive equilibrium point where each reaction (2) is equilibrated with its reverse reaction. This principle was introduced for collisions by Boltzmann in 1872 [10]. Wegscheider introduced this principle for chemical kinetics in 1901 [67]. Einstein in 1916 used it in the background for his quantum theory of emission and absorption of radiation [17]. Later, it was used by Onsager in his famous work [51]. For a recent review see [30].

At the third level of reliability of information, we select the list of components and the balance conditions, find the thermodynamic potential, guess the reaction mechanism, accept the principle of detailed balance, and believe that we know the kinetic law of elementary reactions. However, we still do not know the reaction rate constants.

Finally, at the fourth level of available information, we find the reaction rate constants and can analyze and solve the kinetic equations (3) or their extended version with the inclusion of external fluxes.

Of course, this ranking of the available information is conventional, to a certain degree. For example, some reaction rate constants may be known even better than the list of intermediate reagents. Nevertheless, this hierarchy of the information availability—list of components, thermodynamic functions, reaction mechanism, reaction rate constants—reflects the real process of modeling and the stairs of available information about a reaction kinetic system.

It seems very attractive to study the consequences of the information of each level separately. These consequences can be also organized "stairwise." We have the hierarchy of questions: how do we find the consequences for the dynamics (i) from the list of components, (ii) from this list of components plus the thermodynamic functions of the mixture, and (iii) from the additional information about the reaction mechanism?

The answer to the first question is the description of the balance polyhedron D. The balance equations (1) together with the positivity conditions $N_i \geq 0$ should be supplemented by the description of all the faces. For each face, some $N_i = 0$, and we have to specify which N_i have zero value. The list of the corresponding indices i, for which $N_i = 0$ on the face, $I = \{i_1, \ldots, i_k\}$, fully characterizes the face. This problem of *double description* of the convex polyhedra [49, 14, 21] is well known in linear programming.

The list of vertices [6] and edges with the corresponding indices is necessary for the thermodynamic analysis. This is the 1-*skeleton* of D. Algorithms for the construction of the 1-skeletons of balance polyhedra as functions of the balance values were described in detail in 1980 [26]. The related problem of double description for convex cones is very important for the pathway analysis in systems biology [58, 22].

In this work, we use the 1-skeleton of D, but the main focus is on the second step, i.e., on the consequences of the given thermodynamic potentials. For closed systems under classical conditions, these potentials are the Lyapunov functions for the kinetic equations. For example, for perfect systems we assume the mass action law. If the equilibrium concentrations c^* are given, the system is closed, and both temperature and volume are constant, then the function

$$(4) \qquad G = \sum_i c_i(\ln(c_i/c_i^*) - 1)$$

is the Lyapunov function; it should not increase in time. The function G is proportional to the free energy $F = RTG + \text{const}$ (for detailed information about the Lyapunov functions for kinetic equations under classical conditions, see the textbook [68] or the recent paper [33]).

If we know the Lyapunov function G, then we have the necessary conditions for the possibility of transition from the vector of concentrations c to c' during the nonstationary reaction: $G(c) \geq G(c')$ because the inequality $G(c(t_0)) \geq G(c(t_0 + t))$ holds for any time $t \geq 0$.

The inequality $G(c) \geq G(c')$ is necessary if we are to reach c' from the initial state c by a thermodynamically admissible path, but it is not sufficient because in addition to this inequality there are some other necessary conditions. The simplest and most famous of them is the following: if D is 1-dimensional (1D) (a segment), then the equilibrium c^* divides this segment into two parts, and both $c(t_0)$ and $c(t_0 + t)$ $(t > 0)$ are always on the same side of the equilibrium.

In 1D systems the overstepping of the equilibrium is forbidden. It is impossible to overstep a point in dimension one, but it is possible to circumvent a point in higher dimensions. Nevertheless, in any dimension the inequality $G(c) \geq G(c')$ is not sufficient if we are to reach c' from the initial state c along an admissible path. Some additional restrictions remain in the general case as well. A two-dimensional example is presented in Figure 1. Let us consider the mixture of three components, $A_{1,2,3}$ with the only conservation law $c_1 + c_2 + c_3 = b$ (we take for illustration $b = 1$) and the equidistribution in equilibrium $c_1^* = c_2^* = c_3^* = 1/3$. The balance polyhedron is the triangle (Figure 1(a)). In Figure 1(b) the level sets of

$$G = \sum_{i=1}^{3} c_i(\ln(3c_i) - 1)$$

are presented. This function achieves its minimum at equilibrium, $G(c^*) = -1$. On the edges, the function G achieves its conditional minimum, g_0, in the middle points, and $g_0 = \ln(3/2) - 1$. G reaches its maximal value, $g_{\max} = \ln 3 - 1$, at the vertices.

If $G(c^*) < g \leq g_0$, then the level set $G(c) = g$ is connected. If $g_0 < g \leq g_{\max}$, then the corresponding level set $G(c) = g$ consists of three components (Figure 1(b)). The critical value is $g = g_0$. The critical level $G(c) = g_0$ consists of three arcs. Each arc connects two middle points of the edges and divides D into two sets. One of them is convex and includes two vertices, and the other includes the remaining vertex.

A thermodynamically admissible path is a continuous curve along which G does not increase. Therefore, such a path cannot intersect these arcs "from inside," i.e., from values $G(c) \leq g_0$ to bigger values $G(c) > g_0$. For example, if an admissible path starts from the
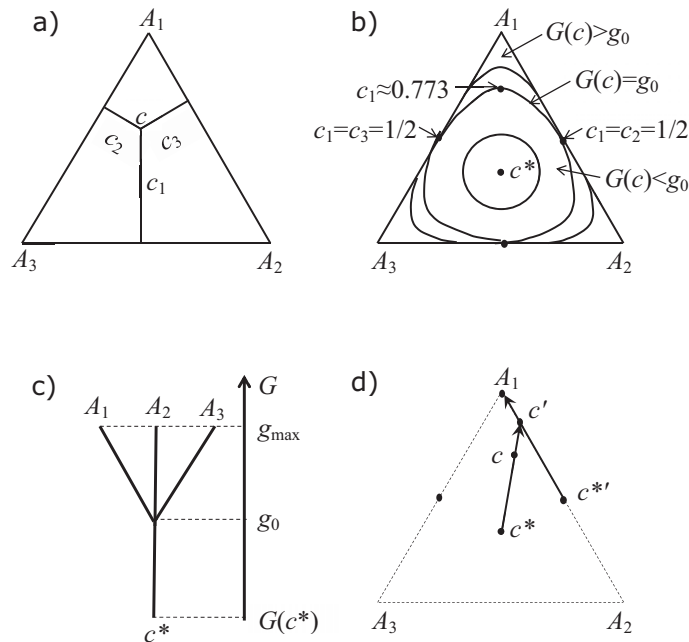
Figure 1. *The balance simplex* (a), *the levels of the Lyapunov function* (b), *and the thermodynamic tree* (c) *for the simple system of three components,* A_1, A_2, A_3. *Algorithm for finding a vertex* $v \succsim c$ (d).

state with 100% of A_2, then it cannot intersect the arc that separates the vertex with 100% A_1 from two other vertices. Therefore, no vertex can be reached from another one, and if we start from 100% of A_2, then the reaction cannot overcome the threshold $\sim 77.3\%$ of A_1, that is, the maximum of c_1 on the corresponding arc (Figure 1(b)). This is an example of the 2-dimensional (2D) analogue of the 1D prohibition of overstepping of equilibrium.

For $x, y \in D$, $x \succsim y$ (x precedes y) if there exists a thermodynamically admissible path from x to y, and $x \sim y$ if $x \succsim y$ and $y \succsim x$. The equivalence classes with respect to $x \sim y$ in D are the connected components of the level sets $G(c) = g$. The quotient space $\mathcal{T} = D/\sim$ is the space of these connected components. For the canonical projection we use the standard notation $\pi : D \to \mathcal{T}$. This is the *tree of the connected components of the level sets* of G. (Here "tree" stands for a 1D continuum, a sort of dendrite [13], and not for a tree in the sense of the graph theory.)

If $x \sim y$, then $G(x) = G(y)$. Therefore, we can define the function G on the tree: $G(\pi(c)) = G(c)$. It is convenient to draw this tree on the plane with the vertical coordinate $g = G(x)$ (Figure 1(c)). The equilibrium c^* corresponds to a root of this tree, $\pi(c^*)$. If $G(c^*) < g \leq g_0$, then the level set $G(c) = g$ corresponds to one point on the tree. The level $G(c) = g_0$ corresponds to the branching point, and each connected component of the level sets $G(c) = g$ with $g_0 < g \leq g_{\max}$ corresponds to a separate point on the tree. The terminal points ("leaves" with $g > g_0$) of the tree correspond to the vertices of D.

An *ordered segment* $[x, y]$ or $[y, x]$ ($x \succsim y$) on the tree $\mathcal{T}$ consists of points z such that $x \succsim z \succsim y$. A continuous curve $\varphi : [0, 1] \to D$ is an admissible path if and only if its

image $\pi \circ \varphi : [0, 1] \to \mathcal{T}$ is a path that goes monotonically down in the coordinate g. Such a monotonic path in $\mathcal{T}$ from a point x to the root is just a segment $[x, \pi(c^*)]$. On this segment, each point y is unambiguously characterized by $g = G(y)$. Therefore, if for $c \in D$ we know the value $G(c)$ and a vertex $v \succsim c$, then we can unambiguously describe the image of c on the tree: $\pi(c)$ is the point on the segment $[\pi(v), \pi(c^*)]$ with the given value of G, $g = G(c)$.

We can find a vertex $v \succsim c$ by a chain of central projections: the first step is the central projection of c onto the border of D with center c^*. The result is the point c' on a face (in Figure 1(d) this is the point c' on an edge). The second step is the central projection of the point c' onto the border of the face with the center at the partial equilibrium $c^{*\prime}$ (that is, the minimizer of G on the face) and so on (Figure 1(d)). If the projection on a face is the partial equilibrium, then for any vertices v of the face $v \succsim c$. In particular, if the face is a vertex v, then $v \succsim c$. For the simple example presented in Figure 1(d) this is the vertex A_1.

In this paper, we extend these ideas and observations to any dynamical system which is given in a positively invariant convex polyhedron and has there a strictly convex Lyapunov function. The class of chemical kinetic equations for closed systems provides us standard and practically important examples of the systems of this class.

1.2. A bit of history. It seems attractive to use an attainable region instead of the single trajectory in situations with incomplete information or with information with different levels of reliability. Such situations are typical in many areas of science and engineering. For example, the theory for the continuous-time Markov chain is presented in [2, 27] and that for the discrete-time Markov chains in [3].

Perhaps the first celebrated example of this approach was developed in biological kinetics. In 1936, Kolmogorov [40] studied the dynamics of interacting populations of prey (x) and predator (y) in the general form

$$\dot{x} = xS(x, y), \quad \dot{y} = yW(x, y)$$

under monotonicity conditions $\partial S(x, y)/\partial y < 0$, $\partial W(x, y)/\partial y < 0$. The zero isoclines, given by $S(x, y) = 0$ or $W(x, y) = 0$, are graphs of two functions $y(x)$. These isoclines divide the phase space into compartments with curvilinear borders. The geometry of the intersection of the zero isoclines, together with some monotonicity conditions, contain important information about the system dynamics that we can find [40] without exact knowledge of the kinetic equations. This approach to population dynamics was applied to various problems [45, 7]. The impact of this work on population dynamics was analyzed in the review [62].

In 1964, Horn proposed to analyze the attainable regions for chemical reactors [36]. This approach became popular in chemical engineering. It was applied to the optimization of steady flow reactors [23], to batch reactor optimization without knowledge of detailed kinetics [19], and to optimization of the reactor structure [34]. An analysis of attainable regions is recognized as a special geometric approach to reactor optimization [18] and as a crucially important part of the new paradigm of chemical engineering [35].

Many particular applications were developed, from polymerization [63] to particle breakage in a ball mill [47] and hydraulic systems [28]. Mathematical methods for the study of attainable regions vary from Pontryagin's maximum principle [46] to linear programming [38], the Shrink-Wrap algorithm [43], and convex analysis. In 1979 it was demonstrated how to utilize the

knowledge about partial equilibria of elementary processes to construct the attainable regions [24]. The attainable regions significantly depend on the reaction mechanism, and it is possible to use them for the discrimination of mechanisms [29].

Thermodynamic data are more robust than the reaction mechanism. Hence, there are two types of attainable regions. The first is the thermodynamic one, which uses the linear restrictions and the thermodynamic functions [25]. The second is generated by thermodynamics and stoichiometric equations of elementary steps (but without reaction rates) [24, 31]. Shinnar and other authors [61] rediscovered this approach. There was even an open discussion about priority [9].

Some particular classes of kinetic systems have rich families of the Lyapunov functions. Krambeck [41] studied attainable regions for linear systems and the l_1 Lyapunov norm instead of the entropy. Already simple examples demonstrate that the sets of distributions which are accessible from a given initial distribution by linear kinetic systems (Markov processes) with a given equilibrium are, in general, *nonconvex* polytopes [24, 27, 70]. The geometric approach to attainability was developed for all the thermodynamic potentials and for open systems as well [26]. Partial results for chemical kinetics and some other engineering systems are summarized in [68, 28].

The *tree of the level set components* for differentiable functions was introduced in the middle of the 20th century by Adelson-Velskii and Kronrod [1, 42] and Reeb [56]. Sometimes these trees are called the *Reeb trees* [20], but from the historical point of view it may be better to call them the Adelson-Velskii–Kronrod–Reeb (AKR) trees. These trees were essentially used by Kolmogorov and Arnold [4] in the solution of Hilbert's superposition problem (the ideas, their relations to dynamical systems, and role in Arnold's scientific life are discussed in his lecture [5]).

The general *Reeb graph* can be defined for any topological space X and real function f on it. It is the quotient space of X by the equivalence relation "$\sim$" defined by the following: $x \sim y$ holds if and only if $f(x) = f(y)$, and x, y are in the same connected component of $f^{-1}(f(x))$. Of course, this "graph" is again not a discrete object from graph theory but a topological space. It has applications in differential topology (Morse theory [48]), in topological shape analysis and visualization [20, 39], in data analysis [64], and in asymptotic analysis of fluid dynamics [44, 59]. The books [20, 39] include many illustrations of the Reeb graphs. The efficient mesh-based methods for the computation of the graphs of level set components are developed for general scalar fields on 2D and 3-dimensional (3D) manifolds [16].

Some time ago the tree of entropy in the balance polyhedra was rediscovered as an adequate tool for representation of the attainable regions in chemical thermodynamics [25, 26]. It was applied to analysis of various real systems [37, 69]. Nevertheless, some of the mathematical backgrounds of this approach were delayed in development and publication. Now, the thermodynamically attainable regions are in extensive use in chemical engineering and beyond [18, 19, 23, 28, 34, 35, 36, 37, 38, 41, 43, 46, 47, 60, 61, 63, 69]. In this paper we aim to provide the complete mathematical background for the analysis of the thermodynamically attainable regions. For this purpose, we construct the trees of strictly convex functions in a convex polyhedron. This problem allows a general meshless solution in higher dimensions because of topological and geometrical simplicity (the domain D is a convex polyhedron, and the function G is strictly convex in D). In this paper, we present this solution in detail.

1.3. The problem of attainability and its solution. Let us formulate precisely the problem of attainability and its solution before the exposition of all technical details and proofs. Our results are applicable to any dynamical system that obeys a continuous strictly convex Lyapunov function in a positively invariant convex polyhedron. The situations with uncertainty, when the specific dynamical system is not given with an appropriate accuracy but the Lyapunov function is known, give a natural area of application of these results.

Here and below, D is a convex polyhedron in $\mathbb{R}^n$, D_0 consists of the vertices of D, D_1 is the union of the closed edges of D, that is, the 1-*skeleton of D*, and $\widetilde{D_1}$ is the graph whose vertices correspond to the vertices of D and whose edges correspond to the edges (the *graph of the 1-skeleton*) of D. We use the same notation for vertices and edges of D and $\widetilde{D_1}$.

Let a real continuous function G be given in D. We assume that G is *strictly convex* in D [57]. Let x^* be the minimizer of G in D, and let $g^* = G(x^*)$ be the corresponding minimal value.

The *level set* $S_g = \{x \in D \,|\, G(x) = g\}$ is closed and the *sublevel set* $U_g = \{x \in D \,|\, G(x) < g\}$ is open in D (i.e., it is the intersection of an open subset of $\mathbb{R}^n$ with D).

Let us transform $\widetilde{D_1}$ into a labeled graph. Each vertex $v \in D_0$ is labeled by the value $\gamma_v = G(v)$ and each edge $e = [v, w] \subset D_1$ is labeled by the minimal value of G on the segment $[v, w] \subset D$, $g_e = \min_{[v,w]} G(x)$. The vertices and edges of $\widetilde{D_1}$ are labeled by the same numbers as the correspondent vertices and edges of D_1. By definition, the graph $\widetilde{D_1} \setminus U_g$ consists of the vertices and edges of $\widetilde{D_1}$, whose labels $\gamma \geq g$.

The graph $\widetilde{D_1} \setminus U_g$ depends on g, but this is a piecewise constant dependence. It changes only at $g = \gamma$, where γ are some of the labels of the graph $\widetilde{D_1}$. Therefore, it is not necessary to find this graph and to analyze connectivity in it for each value $G(y) = g$.

Definition 1.1. *A continuous path $\varphi[0,1] \to D$ is admissible if the function $G(\varphi(x))$ does not increase on $[0,1]$. For $x, y \in D$, $x \succsim y$ (x precedes y) if there exists an admissible path $\varphi[0,1] \to D$ with $\varphi(0) = x$ and $\varphi(1) = y$; $x \sim y$ if $x \succsim y$ and $y \succsim x$.*

The relation "$\succsim$" is transitive. It is a *preorder* on D. The relation "$\sim$" is an equivalence.

Definition 1.2. *The tree of G in D is the quotient space $\mathcal{T} = D/\sim$.*

The equivalence classes of $\sim$ are the path-connected components of the level sets S_g. For the natural projection of D on $\mathcal{T}$ we use the notation $\pi : D \to \mathcal{T}$. We denote by $\pi^{-1}(z) \subset D$ the set of preimages of $z \in \mathcal{T}$. The preorder "$\succsim$" on D transforms into a partial order on $\mathcal{T}$: $\pi(x) \succsim \pi(y)$ if and only if $x \succsim y$. We call $\mathcal{T}$ also the *thermodynamic tree*, keeping in mind the thermodynamic applications. The "tree" $\mathcal{T}$ is a 1D continuum. We have to distinguish this continuum from trees in the graph-theoretic sense, which have the same graphical representation but are discrete objects. In section 3.2 ("Coordinates on the thermodynamic tree") we describe the tree structure of this continuum. It includes the root, the edges, the branching points, and the leaves, but the edges are represented as the real line segments.

Definition 1.3. *Let $x, y \in \mathcal{T}$, $x \succsim y$. An ordered segment $[x, y]$ (or $[y, x]$) consists of points $z \in \mathcal{T}$ such that $x \succsim z \succsim y$.*

In section 3 we prove that any ordered segment $[x, y]$ ($x \neq y$) in $\mathcal{T}$ is homeomorphic to $[0,1]$. A continuous curve $\varphi : [0,1] \to D$ is an admissible path if and only if its image $\pi \circ \varphi : [0,1] \to \mathcal{T}$ is monotonic in the partial order on $\mathcal{T}$. Such a monotonic path in $\mathcal{T}$

from x to y ($x \succsim y$) is just a path along a segment $[x, y]$. Each point z on this segment is unambiguously characterized by the value of $G(z)$.

We also use the notation $[x, y]$ for the usual closed segments in $\mathbb{R}^n$ with ends x, y: $[x, y] = \{\lambda x + (1 - \lambda)y \,|\, \lambda \in [0, 1]\}$. The degenerated segment $[x, x]$ is just a point $\{x\}$. The segments without one end are $(x, y]$ and $[x, y)$, and (x, y) is the segment in $\mathbb{R}^n$ without both ends.

The attainability problem: Let $x, y \in D$ and $G(x) \geq G(y)$. Is y attainable from x by an admissible path?

The solution of the attainability problem can be found in several steps:

1. Find two vertices of D, v_x and v_y, that precede x and y, correspondingly. Such vertices always exist. There may be several such vertices in D. We can use any of them.
2. Construct the graph $\widetilde{D_1} \setminus U_{G(y)}$ by deleting from $\widetilde{D_1}$ all the elements with the labels $\gamma < G(y)$.
3. y is attainable from x by an admissible path if and only if v_x and v_y are connected in the graph $\widetilde{D_1} \setminus U_{G(y)}$.

So, to check the existence of an admissible path from x to y, we should check the inequality $G(x) \geq G(y)$ (the necessary condition) and then go up in G values and find the vertices, v_x and v_y, that precede x and y, correspondingly (such vertices always exist). Then we should go down in G values to $G(y)$ and check whether the vertices v_x and v_y are connected in the graph $\widetilde{D_1} \setminus U_{G(y)}$. The classical problem of determining whether two vertices in a graph are connected may be solved by many search algorithms [52, 50], for example, by the elementary breadth-first or depth-first search algorithm.

The procedure "find a vertex $v_x \in D_0$ that precedes $x \in D$" can be implemented as follows:

1. If $x = x^*$, then any vertex $v \in D_0$ precedes x.
2. If $x \neq x^*$, then consider the ray $r_x = \{x^* + \lambda(x - x^*) \,|\, \lambda \geq 0\}$. The intersection $r_x \cap D$ is a closed segment $[x^*, x']$. We call x' the central projection of x onto the border of D with the center x^*; $x' \succsim x$.
3. The central projection x' always belongs to an interior of a face D' of D, $0 \leq \dim D' < \dim D$. If $\dim D' > 0$, then set $x := x'$, $D := D'$, and $x^* := \operatorname{argmin}\{G(z) \,|\, z \in D'\}$, and go to step 1.
4. If $\dim D' = 0$, then it is a vertex $v \succsim x$ we are looking for.

The dimension of the face decreases at each step; hence, after not more than $\dim D - 1$ steps, we will definitely obtain the desired vertex. A simple example is presented in Figure 1(d).

The information about all connected components of $\widetilde{D_1} \setminus U_g$ for all values of g is summarized in the tree of G in D, $\mathcal{T}$ (Definition 1.2). The tree $\mathcal{T}$ can be described as follows (Theorem 3.3): it is the space of pairs (g, M), where $g \in [\min_D G(x), \max_D G(x)]$ and M is a connected component of $\widetilde{D_1} \setminus U_g$, with the partial order relation $(g, M) \succsim (g', M')$ if $g \geq g'$ and $M \subseteq M'$. For $x, y \in D$, $x \succsim y$ if and only if $\pi(x) \succsim \pi(y)$.

The tree $\mathcal{T}$ may be constructed gradually by descending from the maximal value of G, $g = g_{\max}$ (section 3.3). At $g = g_{\max}$, the graph $\widetilde{D_1} \setminus U_g$ consists of the isolated vertices with the labels $\gamma = g_{\max}$ (generically, this is one vertex). Going down in g, we add to $\widetilde{D_1} \setminus U_g$ the elements, vertices, and edges, in descending order of their labels. After adding each element we record the changes in the connected components of $\widetilde{D_1} \setminus U_g$.

For each point $z \in \mathcal{T}$, $z = (g, M)$, its preimage in D, $\pi^{-1}(g, M)$, may be described by the

equation $G(x) = g$ supplemented by a set of linear inequalities. Computationally, these linear inequalities can be produced by a *convex hull* operation from a finite set. This finite set is described explicitly in section 3.4.

For each point $z = (g, M)$ the set of all $z' = (g', M')$ attainable by admissible paths from z has a simple description, $g' \leq g$, $M' \supseteq M$.

The tree of G in D provides a workbench for the analysis of various questions about admissible paths. It allows us to reduce the n-dimensional problems in D to some auxiliary questions about such 1D or even discrete objects as the tree $\mathcal{T}$ and the labeled graph $\widetilde{D_1}$. For example, we use the thermodynamic tree to solve the following *problem of attainable sets*: For a given $x \in D$ describe the set of all $y \precsim x$ by a system of inequalities. For this purpose, we find the image of x in $\mathcal{T}$, $\pi(x)$, then define the set of all points attainable by admissible paths from $\pi(x)$ in $\mathcal{T}$, and finally describe the preimage of this set in D by the system of inequalities (section 3.4).

1.4. The structure of the paper. In section 2, we present several auxiliary propositions from convex geometry. We constructively describe the result of the cutting of a convex polyhedron D by a convex set U: The description of the connected components of $D \setminus U$ is reduced to the analysis of the 1D continuum $D_1 \setminus U$, where D_1 is the 1-skeleton of D.

In section 3, we construct the tree of level set components of a strictly convex function G in the convex polyhedron D and study the properties of this tree. The main result of this section is the algorithm for construction of this tree (section 3.3). This construction is applied to the description of the attainable sets in section 3.4. These sections include some practical recipes, and it is possible to read them independently, immediately after the introduction. Several examples of the thermodynamic trees for chemical systems are presented in section 4.

2. Cutting of a polyhedron D by a convex set U.

2.1. Connected components of $D \setminus U$ and of $D_1 \setminus U$. Let D be a convex polyhedron in $\mathbb{R}^n$. We use the following notation: $\mathrm{Aff}(D)$ is the minimal linear manifold that includes D; $d = \dim \mathrm{Aff}(D) = \dim D$ is the dimension of D; $ri(D)$ is the interior of D in $\mathrm{Aff}(D)$; $r\partial(D)$ is the border of D in $\mathrm{Aff}(D)$.

For $P, Q \subset \mathbb{R}^n$ the Minkowski sum is $P + Q = \{x + y \mid x \in P, y \in Q\}$. The convex hull (conv) and the conic hull (cone) of a set $V \subset \mathbb{R}^n$ are

$$\mathrm{conv}(V) = \left\{ \sum_{i=1}^{q} \lambda_i v_i \ \middle|\ q > 0,\ v_1, \ldots, v_q \in V,\ \lambda_1, \ldots, \lambda_q > 0,\ \sum_{i=1}^{q} \lambda_i = 1 \right\};$$

$$\mathrm{cone}(V) = \left\{ \sum_{i=1}^{q} \lambda_i v_i \ \middle|\ q \geq 0,\ v_1, \ldots, v_q \in V,\ \lambda_1, \ldots, \lambda_q > 0 \right\}.$$

For a set $D \subset \mathbb{R}^n$ the following two statements are equivalent (the *Minkowski–Weyl theorem*):
1. For some real (finite) matrix A and real vector b, $D = \{x \in \mathbb{R}^n \mid Ax \leq b\}$.
2. There are finite sets of vectors $\{v_1, \ldots, v_q\} \subset \mathbb{R}^n$ and $\{r_1, \ldots, r_p\} \subset \mathbb{R}^n$ such that

$$(5) \qquad\qquad D = \mathrm{conv}\{v_1, \ldots, v_q\} + \mathrm{cone}\{r_1, \ldots, r_p\}.$$

Every polyhedron has two representations, of types (1) and (2), known as (halfspace) H-representation and (vertex) V-representation, respectively. We systematically use both these representations. Most of the polyhedra in our paper are bounded; therefore, for them only the convex envelope of vertices is used in the V-representation (5).

The k-skeleton of D, D_k, is the union of the closed k-dimensional faces of D:

$$D_0 \subset D_1 \subset \cdots \subset D_d = D.$$

D_0 consists of the vertices of D, and D_1 is a 1D continuum embedded in $\mathbb{R}^n$. We use the notation $\widetilde{D_1}$ for the graph whose vertices correspond to the vertices of D and whose edges correspond to the edges of D, and we call this graph the *graph of the 1-skeleton* of D.

Let U be a convex subset of $\mathbb{R}^n$ (it may be a nonclosed set). We use U_0 for the set of vertices of D that belong to U, $U_0 = U \cap D_0$, and U_1 for the set of the edges of D that have nonempty intersection with U. By default, we consider the closed faces of D; hence, the intersection of an edge with U either includes some internal points of the edge or consists of one of its ends. We use the same notation U_1 for the set of the corresponding edges of $\widetilde{D_1}$.

A set $W \subset P \subset \mathbb{R}^n$ is a *path-connected component* of P if it is its maximal path-connected subset. In this section, we aim to describe the path-connected components of $D \setminus U$. In particular, we prove that these components include the same sets of vertices as the connected components of the graph $\widetilde{D_1} \setminus U$. This graph is produced from $\widetilde{D_1}$ by deletion of all the vertices that belong to U_0 and all the edges that belong to U_1.

Lemma 2.1. *Let $x \in D \setminus U$. Then there exists a vertex $v \in D_0$ such that the closed segment $[v, x]$ does not intersect U: $[v, x] \subset D \setminus U$.*

Proof. Let us assume the contrary: for every vertex $v \in D_0$ there exists $\lambda_v \in (0, 1]$ such that $x + \lambda_v(v - x) \in U$. The convex polyhedron D is the convex hull of its vertices. Therefore, $x = \sum_{v \in D_0} \kappa_v v$ for some numbers $\kappa_v \geq 0$, $v \in D_O$, $\sum_{v \in D_0} \kappa_v = 1$.

Let

$$\delta_v = \frac{\kappa_v}{\lambda_v \sum_{v' \in D_0} \frac{\kappa_{v'}}{\lambda_{v'}}}.$$

It is easy to check that $\sum_{v \in D_0} \delta_v = 1$ and

$$(6) \qquad x = \sum_{v \in D_0} \delta_v(x + \lambda_v(v - x)).$$

According to (6), x belongs to the convex hull of the finite set $\{x + \lambda_v(v - x) \mid v \in D_0\} \subset U$. U is convex; therefore, $x \in U$, but this contradicts the condition $x \notin U$. Therefore, our assumption is wrong, and there exists at least one $v \in D_0$ such that $[v, x] \cap U = \emptyset$. ∎

So, if a point from the convex polyhedron D does not belong to a convex set U, then it may be connected to at least one vertex of D by a segment that does not intersect U. Let us demonstrate now that if two vertices of D may be connected in D by a continuous path that does not intersect U, then these vertices can be connected in D_1 by a path that is a sequence of edges D, which do not intersect U.

Lemma 2.2. *Let $v, v' \in D_0$, $v, v' \notin U$. Suppose that $\varphi : [0, 1] \to (D \setminus U)$ is a continuous path, $\varphi(0) = v$, and $\varphi(1) = v'$. Then there exists a sequence of vertices $\{v_0, \ldots, v_l\} \subset (D \setminus U)$ such that any two successive vertices, v_i, v_{i+1}, are connected by an edge $e_{i,i+1} \subset (D_1 \setminus U)$.*

Proof. Let us first prove the following statement: *the vertices v, v' belong to one path-connected component of $D \setminus U$ if and only if they belong to one path-connected component of $D_1 \setminus U$.*

Let us iteratively transform the path φ. On the kth iteration we construct a path that connects v and v' in $D_{d-k} \setminus U$, where $d = \dim D$ and $k = 1, \ldots, d - 1$. We start from a transformation of the path in a face of D.

Let $S \subset D_j$ be a closed j-dimensional face of D, $j \geq 2$, and let $\psi : [0,1] \to (D_j \setminus U)$ be a continuous path, $\psi(0) = v$, $\psi(1) = v'$, and $\psi([0,1]) \cap U = \emptyset$. We will transform ψ into a continuous path $\psi_S : [0,1] \to (D_j \setminus U)$ with the following properties: (i) $\psi_S(0) = v$, $\psi_S(1) = v'$, (ii) $\psi_S([0,1]) \cap U = \emptyset$, (iii) $\psi_S([0,1]) \setminus S \subseteq \psi([0,1]) \setminus S$, and (iv) $\psi_S([0,1]) \cap ri(S) = \emptyset$. The properties (i) and (ii) are the same as for ψ, the property (iii) means that all the points of $\psi_S([0,1])$ outside S belong also to $\psi([0,1])$ (no new points appear outside S), and the property (iv) means that there are no points of $\psi_S([0,1])$ in $ri(S)$. To construct this ψ_S we consider two cases:

1. $U \cap ri(S) \neq \emptyset$; i.e., there exists $y^0 \in U \cap ri(S)$.
2. $U \cap ri(S) = \emptyset$.

In the first case, let us project any $\psi(\tau) \in ri(S)$ onto $r\partial(S)$ from the center y^0. Let $y \in S$, $y \neq y^0$. There exists a $\lambda(y) \geq 1$ such that $y^0 + \lambda(y)(y - y^0) \in r\partial(S)$. This function $\lambda(y)$ is continuous in $S \setminus \{y^0\}$. The function $\lambda(y)$ can be expressed through the Minkowski gauge functional [32] defined for a set K and a point x:

$$p_K(x) = \inf\{r > 0 \mid x \in rK\}; \quad \lambda(y) = \left(p_{(D - y_0)}(y - y_0)\right)^{-1}.$$

Let us define for any $y \in ri(S)$, $y \neq y^0$, a projection $\pi_S(y) = y^0 + \lambda(y)(y - y^0)$. This projection is continuous in $S \setminus \{y^0\}$, and $\pi_S(y) = y$ if $y \in r\partial(S)$. It can be extended as a continuous function onto the whole $D_j \setminus \{y^0\}$:

$$\pi_S(y) = \begin{cases} \pi_S(y) & \text{if } y \in S \setminus \{y^0\}, \\ y & \text{if } y \in D_j \setminus S. \end{cases}$$

The center $y^0 \in U$. Because of the convexity of U, if $y \notin U$, then $y^0 + \lambda(y - y^0) \notin U$ for any $\lambda \geq 1$. Therefore, the path $\psi_S(t) = \pi_S(\psi(t))$ does not intersect U and satisfies all the requirements (i)–(iv).

Let us consider the second case, $U \cap ri(S) = \emptyset$. There are the moments of the first entrance of $\psi(t)$ in S and the last exit of this path from S:

$$\tau_1 = \min\{\tau \mid \psi(\tau) \in S\}, \quad \tau_2 = \max\{\tau \mid \psi(\tau) \in S\},$$

$0 \leq \tau_1 \leq \tau_2 \leq 1$. Let $y^1 = \psi(\tau_1)$ and $y^2 = \psi(\tau_2)$. If $y^1 = y^2$, then we can just delete the loop between τ_1 and τ_2 from the path $\psi(\tau)$ and get the path that does not enter $ri(S)$. So, let $y^1 \neq y^2$.

These points belong to $r\partial(S)$. Let $y^S \in ri(S)$ be an arbitrary point in the relative interior of S which does not belong to the segment $[y^1, y^2]$ ($\dim S \geq 2$). The segments $[y^1, y^S]$ and $[y^2, y^S]$ do not intersect U for the following reasons: $U \cap S \subset r\partial(S)$ (may be empty), neither y^1 nor y^2 belong to U, and all other points of the 3-vertex polygonal chain $[y^1, y^S, y^2]$ belong to $ri(S)$.
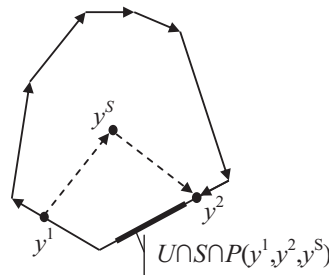
Figure 2. *Intersection of a face S with the plane $P(y^1, y^S, y^2)$ when $U \cap ri(S) = \emptyset$ (Lemma 2.2, case 2). In this intersection, $U \cap S \subset r\partial(S)$ belongs to one side of the polygon (the bold segment). The dashed lines with arrows represent the 3-vertex polygonal chain $[y^1, y^S, y^2]$. There exists a path from y^1 to y^2 along the boundary of the polygon. In Figure, this is the polygonal chain that follows the solid lines with arrows.*

Let $P(y^1, y^S, y^2)$ be a plane that includes the chain $[y^1, y^S, y^2]$. The intersection $S \cap P(y^1, y^S, y^2)$ is a convex polygon. The convex set $U \cap S \cap P(y^1, y^S, y^2)$ belongs to the border of this polygon. Therefore, it belongs to one side of it (Figure 2) (may be empty) because of the convexity of the polygon and of the set U. The couple of points y^1, y^2 cut the border of the polygon in two connected broken lines. At least one of them does not intersect U (Figure 2). Let us substitute ψ on the interval $[\tau_1, \tau_2]$ by this broken line. The new path does not intersect $ri(S)$. Let us use for this new path the notation $\psi_S(t)$. The path ψ_S does not intersect $ri(S)$ and U, and all the points on them outside S are the points on the path ψ for the same values of the argument τ.

So, for any closed face $S \subset D$ with $\dim S = j \geq 2$ and a continuous path $\psi : [0,1] \to (D_j \setminus U)$ that connects the vertices v, v' of D ($\psi(0) = v$, $\psi(1) = v'$) we construct a continuous path $\psi_S : [0,1] \to (D_j \setminus U)$ that connects the same vertices, does not intersect $ri(S)$, and takes no new values outside S, $\psi_S([0,1]) \setminus S \subseteq \psi([0,1]) \setminus S$.

Let us order the faces $S \subseteq D$ with $\dim S \geq 2$ in such a way that $\dim S_i \geq \dim S_j$ for $i < j$: $D = S_0, S_1, \ldots, S_\ell$. Let us start from a given path $\varphi : [0,1] \to D \setminus U$ that connects the vertices v and v', and let us apply sequentially the described procedure:

$$\theta = (\ldots (((\varphi_{S_0})_{S_1})_{S_2}) \ldots)_{S_\ell}.$$

By the construction, this path θ does not intersect any relative interior $ri(S_k)$ ($k = 0, 1, \ldots, \ell$). Therefore, the image of θ belongs to D_1, $\theta : [0,1] \to (D_1 \setminus U)$. It can be transformed into a simple path in $D_1 \setminus U$ by deletion of all loops (if they exist). This simple path (without self-intersections) is just the sequence of edges we are looking for. ∎

Lemmas 2.1 and 2.2 allow us to describe the connected components of the d-dimensional set $D \setminus U$ through the connected components of the 1D continuum $D_1 \setminus U$.

Proposition 2.3. Let $W_1, \ldots, W_q$ be all the path-connected components of $D \setminus U$. Then $W_i \cap D_0 \neq \emptyset$ for all $i = 1, \ldots, q$, the continuum $D_1 \setminus U$ has q path-connected components, and $W_i \cap D_1$ are these components.

Proof. Due to Lemma 2.1, each path-connected component of $D \setminus U$ includes at least one vertex of D. According to Lemma 2.2, if two vertices of D belong to one path-connected component of $D \setminus U$, then they belong to one path-connected component of $D_1 \setminus U$. The

reverse statement is obvious because $D_1 \subset D$ and a continuous path in D_1 is a continuous path in D. ∎

We can study connected components of a simpler, discrete object, the graph $\widetilde{D_1}$. The path-connected components of $D \setminus U$ correspond to the connected components of the graph $\widetilde{D_1} \setminus U$. (This graph is produced from $\widetilde{D_1}$ by deletion of all the vertices that belong to U_0 and all the edges that belong to U_1.)

Proposition 2.4. Let $W_1, \ldots, W_q$ be all the path-connected components of $D \setminus U$. Then the graph $\widetilde{D_1} \setminus U$ has exactly q connected components, and each set $W_i \cap D_0$ is the set of the vertices of D of one connected component of $\widetilde{D_1} \setminus U$.

Proof. Indeed, every path between vertices in D_1 includes a path that connects these vertices and is the sequence of edges. (To prove this statement we just have to delete all loops in a given path.) Therefore, the vertices v_1, v_2 belong to one connected component of $\widetilde{D_1} \setminus U$ if and only if they belong to one path-connected component of $D_1 \setminus U$. The rest of the proof follows from Proposition 2.3. ∎

We proved that the path-connected components of $D \setminus U$ are in one-to-one correspondence with the components of the graph $\widetilde{D_1} \setminus U$ (the correspondent components have the same sets of vertices). In applications, we will meet the following problem. Let a point $x \in D \setminus U$ be given. Find the path-connected component of $D \setminus U$ which includes this point. There are two basic ways to find this component. Assume that we know the connected components of $\widetilde{D_1} \setminus U$. First, we can examine the segments $[x, v]$ for all vertices v of D. At least one of them does not intersect U (Lemma 2.1). Let it be $[x, v_0]$. We can find the connected component $\widetilde{D_1} \setminus U$ that contains v_0. The point x belongs to the correspondent path-connected component of $D \setminus U$. This approach exploits the V-description of the polyhedron D. The work necessary for this method is proportional to the number of vertices of D.

Another method is based on projection on the faces of D. Let $x \in ri(D)$. We can take any point $y^0 \in D \setminus U$ and find the unique $\lambda_1 > 1$ such that $x^1 = y_0 + \lambda_1(x - y^0) \in r\partial(D)$. Let $x^1 \in ri(S_1)$, where S_1 is a face of D. If $S_1 \cap U = \emptyset$, then we can take any vertex $v_0 \in S_1$ and find the connected component $\widetilde{D_1} \setminus U$ that contains v_0. This component gives us the answer. If $S_1 \cap U \neq \emptyset$, then we can take any $y^1 \in S_1 \cap U$ and find the unique $\lambda_2 > 1$ such that $x^2 = y^1 + \lambda_2(x^1 - y^1) \in r\partial(S)$. This x^2 belongs to the relative boundary of the face S_1. If x^2 is not a vertex, then it belongs to the relative interior of some face S_2, $\dim S_2 > 0$, and we have to continue. At each iteration, the dimension of faces decreases. After $d = \dim D$ iterations at most we will get the vertex v we are looking for (see also Figure 1) and find the connected component of $\widetilde{D_1} \setminus U$ which gives us the answer. Here we exploit the H-description of D.

2.2. Description of the connected components of $D \setminus U$ by inequalities. Let $W_1, \ldots, W_q$ be the path-connected components of $D \setminus U$.

Proposition 2.5. For any set of indices $I \subset \{1, \ldots, q\}$ the set

$$K_I = U \bigcup \left(\bigcup_{i \in I} W_i \right)$$

is convex.

Proof. Let $y^1, y^2 \in K_I$. We have to prove that $[y^1, y^2] \subset K_I$. Five different situations are possible:

1. $y^1, y^2 \in U$;
2. $y^1 \in U$, $y^2 \in W_i$, $i \in I$;
3. $y^1, y^2 \in W_i$, $i \in I$, $[y^1, y^2] \cap U = \emptyset$;
4. $y^1, y^2 \in W_i$, $i \in I$, $[y^1, y^2] \cap U \neq \emptyset$;
5. $y^1 \in W_i$, $y^2 \in W_j$, $i, j \in I$, $i \neq j$.

We will systematically use two simple facts: (i) the convexity of U implies that its intersection with any segment is a segment, and (ii) if $x^1 \in W_i$ and $x^2 \in D \setminus W_i$, then the segment $[x^1, x^2]$ intersects U because W_i is a path-connected component of U.

In case 1, $[y^1, y^2] \subset U \subset K$ because of convexity U.

In case 2, there exists a point $y^3 \in (y^1, y^2)$ such that $[y^1, y^3] \subseteq U \cap [y^1, y^2] \subseteq [y^1, y^3]$. The segment $(y^3, y^2]$ cannot include any point $x \in D \setminus W_i$ because it does not include any point from U. Therefore, in this case $(y^3, y^2] \subset W_i \subset K$ and $y^3 \in K$ because it belongs either to U or to W_i.

In case 3, $[y^1, y^2] \subset W_i \subset K$ because W_i is a path-connected component of $D \setminus U$ and $[y^1, y^2] \cap U = \emptyset$.

In case 4, $[y^1, y^2] \cap U$ is a segment L with the ends x^1, x^2. It may be $[x^1, x^2]$ ($y^1 < x^1 \leq x^2 < y^2$), $(x^1, x^2]$ ($y^1 \leq x^1 < x^2 < y^2$), $[x^1, x^2)$ ($y^1 < x^1 < x^2 \leq y^2$), or (x^1, x^2) ($y^1 \leq x^1 < x^2 \leq y^2$). This segment cuts $[y^1, y^2]$ into three segments: $[y^1, y^2] = L_1 \cup L \cup L_2$; L_1 includes y^1, and L_2 includes y^2. Therefore, $L_1 \subset W_i$, $L \subset U$, and $L_2 \subset W_i$ because W_i is a path-connected component of $D \setminus U$ and U is convex. So, $[y^1, y^2] \subset K$.

In case 5, $[y^1, y^2] \cap U$ is also a segment L with the ends x^1, x^2. It may be $[x^1, x^2]$ ($y^1 < x^1 \leq x^2 < y^2$), $(x^1, x^2]$ ($y^1 \leq x^1 < x^2 < y^2$), $[x^1, x^2)$ ($y^1 < x^1 < x^2 \leq y^2$), or (x^1, x^2) ($y^1 \leq x^1 < x^2 \leq y^2$). This segment cuts $[y^1, y^2]$ into three segments: $[y^1, y^2] = L_1 \cup L \cup L_2$; L_1 includes y^1, and L_2 includes y^2. Therefore, $L_1 \subset W_i$, $L \subset U$, and $L_2 \subset W_j$ because $W_{i,j}$ are path-connected components of $D \setminus U$ and U is convex. So, $[y^1, y^2] \subset K$. ∎

Typically, the set U is represented by a set of inequalities, for example, $G(x) \leq g$. It may be useful to represent the path-connected components of $D \setminus U$ by inequalities. For this purpose, let us first construct a convex polyhedron $Q \subset U$ with the same number of path-connected components in $D \setminus Q$, $V_1, \ldots, V_q$ and with inclusions $W_i \subset V_i$. We will construct Q as a convex hull of a finite set. Let us select the edges e of D which intersect U, but the intersection $e \cap U$ does not include vertices of D. For every such edge we select one point $x_e \in e \cap U$. The set of these points is Q_1. By definition,

$$(7) \qquad Q = \operatorname{conv}(U_0 \cup Q_1).$$

Q is convex; hence, we can apply all the previous results about the components of $D \setminus U$ to the components of $D \setminus Q$.

Lemma 2.6. *The set $U_0 \cup Q_1$ is the set of vertices of Q.*

Proof. A point $x \in U_0 \cup Q_1$ is not a vertex of $Q = \operatorname{conv}(U_0 \cup Q_1)$ if and only if it is a convex combination of other points from this set: there exist $x_1, \ldots, x_k \in U_0 \cup Q_1$ and $\lambda_1, \ldots, \lambda_k > 0$

such that $x_i \neq x$ for all $i = 1, \ldots, k$ and

$$\sum_{i=1}^{k} \lambda_i = 1, \quad \sum_{i=1}^{k} \lambda_i x_i = x.$$

If $x \in U_0$, then this is impossible because x is a vertex of D and $U_0 \cup Q_1 \subset D$. If $x \in Q_1$, then it belongs to the relative interior of an edge of D and, hence, may be a convex combination of points D from this edge only. By construction, $U_0 \cup Q_1$ may include only one internal point from an edge and in this case does not include a vertex from this edge. Therefore, all the points from Q_1 are vertices of Q. ■

Lemma 2.7. *The set $D \setminus Q$ has q path-connected components $V_1, \ldots, V_q$ that may be enumerated in such a way that $W_i \subset V_i$ and $W_i = V_i \setminus U$.*

Proof. To prove this statement about the path-connected components, let us mention that Q and U include the same vertices of D and the set U_0 and cut the same edges of D. Graphs $\widetilde{D_1} \setminus Q$ and $\widetilde{D_1} \setminus U$ coincide. $Q \subset U$ because of the convexity of U and the definition of Q. To finalize the proof, we can apply Proposition 2.4. ■

Proposition 2.8. *Let I be any set of indices from $\{1, \ldots, q\}$:*

$$(8) \qquad Q \bigcup \left(\bigcup_{i \in I} V_i \right) = \mathrm{conv} \left(U_0 \bigcup Q_1 \bigcup \left(\bigcup_{i \in I} \left(D_0 \bigcap V_i \right) \right) \right).$$

Proof. On the left-hand side of (8) we see the union of Q with the connected components V_i $(i \in I)$. On the right-hand side there is a convex envelope of a finite set. This finite set consists of the vertices of Q $(U_0 \cup Q_1)$ and the vertices of D that belong to V_i $(i \in I)$. Let us denote by R_I the right-hand side of (8) and by L_I the left-hand side of (8).

L_I is convex due to Proposition 2.5 applied to Q and V_i. The inclusion $R_I \subseteq L_I$ is obvious because L_I is convex and R_I is defined as a convex hull of a subset of L_I. To prove the inverse inclusion, let us consider the path-connected components of $D \setminus R_I$. Sets V_j $(j \notin I)$ are the path-connected components of $D \setminus R_I$ because they are the path-connected components of $D \setminus Q$, $Q \subset R_I$, and $R_I \cap V_j = \emptyset$ for $j \notin I$. There exist no other path-connected components of $Q \subset R_I$ because all the vertices of V_i $(i \in I)$ belong to R_I by construction; hence, $D_0 \setminus R_I \subset \cup_{j \notin I} V_j$. Due to Lemma 2.1 every path-connected component of $D \subset R_I$ includes at least one vertex of D. Therefore, V_j $(j \notin I)$ are all the path-connected components of $D \setminus R_I$ and $D \setminus R_I = \cup_{j \notin I} V_j$. Finally, $R_I = D \setminus \cup_{j \notin I} V_j = Q \cup (\cup_{i \in I} V_i) = L_I$. ■

According to Lemma 2.6, each path-connected component $W_i \subset D \setminus U$ can be represented in the form $W_i = V_i \setminus U$, where V_i is a path-connected component of $D \setminus Q$. By construction, $Q \subset U$; hence

$$(9) \qquad\qquad\qquad W_i = (Q \cup V_i) \setminus U.$$

If U is given by a system of inequalities, then representations (8) and (9) give us the possibility of representing W_i by inequalities. Indeed, the convex envelope of a finite set in (8) may be represented by a system of linear inequalities. If the sets $Q \cup V_i$ and U in (9) are represented by inequalities, then the difference between them is also represented by the system of inequalities.

The description of the path-connected component of $D \setminus U$ may be constructed by the following steps:
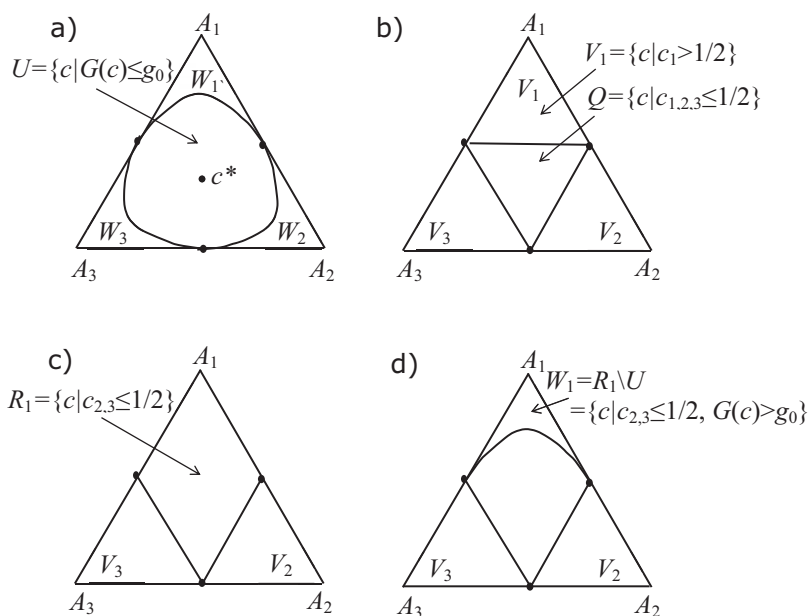
Figure 3. *Construction of the path-connected components W_i of $D \setminus U$ for the simple example. (a) The balance simplex D, the set U, and the path-connected components W_i. (b) The polyhedron $Q = \mathrm{conv}(U_0 \cup Q_1)$ (7) ($U_0 = \emptyset$; Q_1 consists of the middle points of the edges) and the connected components V_i of $D \setminus Q$: $V_i = \{c \in D \,|\, c_i > 1/2\}$. (c) The set $R_1 = \mathrm{conv}(U_0 \cup Q_1 \cup (D_0 \cap V_1))$. (d) The connected components W_1 described by the inequalities (as $R_1 \setminus U$ (8)).*

1. Construct the graph of the 1-skeleton of D; this is $\widetilde{D_1}$.
2. Find the vertices of D that belong to U; this is the set U_0.
3. Find the edges of D that intersect U; this is the set U_1.
4. Delete from $\widetilde{D_1}$ all the vertices from U_0 and the edges from U_1; this is the graph $\widetilde{D_1} \setminus U$.
5. Find all the connected components of $\widetilde{D_1} \setminus U$. Let the sets of vertices of these connected components be $V_{01}, \ldots, V_{0q}$.
6. Select the edges e of D which intersect U, but the intersection $e \cap U$ does not include vertices of D. For every such edge select one point $x_e \in e \cap U$. The set of these points is Q_1.
7. For every $i = 1, \ldots, q$ describe the polyhedron $R_i = \mathrm{conv}(U_0 \cup Q_1 \cup V_{0i})$.
8. There exist q path-connected components of $D \setminus U$: $W_i = R_i \setminus U$.

Every step can be performed by known algorithms, including algorithms for the solution of the double description problem [49, 14, 21] and the convex hull algorithms [55].

Let us use the simple system of three reagents, $A_{1,2,3}$ (Figure 1) to illustrate the main steps of the construction of the path-connected components. The polyhedron D is here the 2D simplex (Figure 1(a)). The plane $\mathrm{Aff}\,D$ is given by the balance equation $c_1 + c_2 + c_3 = 1$. We select $U = \{c \,|\, G(c) \le g_0\}$ as an example of a convex set (Figure 3(a)). It includes no vertices of D; hence, $U_0 = \emptyset$. U intersects each edge of D in the middle point; hence, U_1 includes all the edges of D. The graph $\widetilde{D_1} \setminus U$ consists of three isolated vertices. Its connected

components are these isolated vertices. Q_1 consists of three points, the middle points of the edges $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$, and $(0, 1/2, 1/2)$ (in this example, the choice of these points is unambiguous; see Figure 3(a)).

The polyhedron Q is a convex hull of these three points, that is, the triangle given in $\mathrm{Aff}(D)$ by the system of three inequalities $c_{1,2,3} \leq 1/2$ (Figure 3(b)). The connected components of $D \setminus Q$ are the triangles V_i given in D by the inequalities $c_i > 1/2$. In the whole $\mathbb{R}^3$, these sets are given by the systems of an equation and inequalities:

$$V_i = \{c \,|\, c_{1,2,3} \geq 0,\ c_1 + c_2 + c_3 = 1,\ c_i > 1/2\}.$$

The polyhedron R_i is the convex hull of four points, the middle points of the edges and the ith vertex (Figure 3(c)). In D, R_i is given by two linear inequalities, $c_j \leq 1/2$, $j \neq i$. In the whole $\mathbb{R}^3$, these inequalities should be supplemented by the equation and inequalities that describe D:

$$R_i = \{c \,|\, c_{1,2,3} \geq 0,\ c_1 + c_2 + c_3 = 1,\ c_j \leq 1/2 \,(j \neq i)\}.$$

The path-connected components of $D \setminus U$, W_i are described as $R_i \setminus U$ (see Figure 3(d)): in D we get $W_i = \{c \,|\, c_j \leq 1/2 \,(j \neq i),\ G(c) > g_0\}$. In the whole $\mathbb{R}^3$,

$$W_i = \{c \,|\, c_{1,2,3} \geq 0,\ c_1 + c_2 + c_3 = 1,\ c_j \leq 1/2 \,(j \neq i),\ G(c) > g_0\}.$$

V_i are convex sets in this simple example; therefore, it is possible to slightly simplify the description of the components W_i and to represent them as $V_i \setminus U$:

$$W_i = \{c \,|\, c_{1,2,3} \geq 0,\ c_1 + c_2 + c_3 = 1,\ c_i > 1/2,\ G(c) > g_0\}$$

(or $W_i = \{c \,|\, c_i > 1/2,\ G(c) > g_0\}$ in D).

In the general case (more components and balance conditions), the connected components V_i may be nonconvex; hence, description of these sets by the systems of linear equations and inequalities may be impossible. Nevertheless, there exists another version of the description of W_i where a smaller polyhedron is used instead of R_i.

Let V_{0i} be the set of vertices of a connected component of the graph $\widetilde{D_1} \setminus U$. Let $E_{\mathrm{out}}(V_{0i})$ be the set of the *outer edges* of V_{0i} in $\widetilde{D_1}$; i.e., this is the set of edges of $\widetilde{D_1}$ that connect vertices from V_{0i} with vertices from $D_0 \setminus V_{0i}$. For each $e \in E_{\mathrm{out}}(V_{0i})$ the corresponding edge $e \subset D_1$ intersects U because V_{0i} is the set of vertices of a connected component of the graph $\widetilde{D_1} \setminus U$.

Let us select a point $x_e \in U \cap e$ for each $e \in E_{\mathrm{out}}(V_{0i})$ (we use the same notation for the edges from $\widetilde{D_1}$ and the corresponding edges from D_1). Let us use the notation

$$Q_{0i} = \{x_e \,|\, e \in E_{\mathrm{out}}(V_{0i})\}.$$

Proposition 2.9. *The path-connected component W_i of $D \setminus U$ allows the following description:*

$$W_i = \mathrm{conv}(Q_{0i} \cup V_{0i}) \setminus U.$$

Proof. The set $Q_{0i} \subset U$ and V_{0i} is the set of vertices of a connected component of the graph $\widetilde{D_1} \setminus Q_{0i}$ by construction because Q_{0i} cuts all the outer edges of V_{0i} in D_1. The rest of the proof follows the proofs of Lemma 2.7 and Proposition 2.8. ∎

This proposition allows us to describe W_i by the system of inequalities. For this purpose, we have to use a convex hull algorithm and describe the convex hull $\mathrm{conv}(Q_{0i} \cup V_{0i})$ by the system of linear inequalities and then add the inequality that describes the set $\setminus U$.

In the simple system (Figure 3), the connected components of the graph $\widetilde{D_1} \setminus U$ are the isolated vertices. The set Q_{0i} for the vertex A_i consists of two middle points of its incident edges. In Figure 3(b), the set $\mathrm{conv}(Q_{0i} \cup V_{0i})$ for $V_{0i} = \{A_1\}$ is the triangle V_1.

3. Thermodynamic tree.

3.1. Problem statement. Let a real continuous function G be given in the convex bounded polyhedron $D \subset \mathbb{R}^n$. We assume that G is *strictly convex* in D, i.e., the set (the epigraph of G)

$$\mathrm{epi}(G) = \{(x, g) \mid x \in D, \, g \geq G(x)\} \subset D \times (-\infty, \infty)$$

is convex, and for any segment $[x, y] \subset D$ $(x \neq y)$, G is not constant on $[x, y]$. A strictly convex function on a bounded convex set has a unique minimizer. Let x^* be the minimizer of G in D, and let $g^* = G(x^*)$ be the corresponding minimal value. The level set $S_g = \{x \in D \mid G(x) = g\}$ is closed and the sublevel set $U_g = \{x \in D \mid G(x) < g\}$ is open in D. The sets S_g and $D \setminus U_g$ are compact, and $S_g \subset D \setminus U_g$.

Let $x, y \in D$. According to Corollary 3.4, proven in the next subsection, an admissible path from x to y in D exists if and only if $\pi(y)$ belongs to the ordered segment $[\pi(x^*), \pi(x)]$. Therefore, to constructively describe the relation $x \succsim y$ in D we have to solve the following problems:

1. How do we construct the thermodynamic tree $\mathcal{T}$?
2. How do we find an image $\pi(x)$ of a state $x \in D$ on the thermodynamic tree $\mathcal{T}$?
3. How do we describe by inequalities a preimage of an ordered segment of the thermodynamic tree, $\pi^{-1}([w, z]) \subset D$ $(w, z \in \mathcal{T}, z \succsim w)$?

3.2. Coordinates on the thermodynamic tree. We get the following lemma directly from Definition 1.1. Let $x, y \in D$.

Lemma 3.1. $x \sim y$ if and only if $G(x) = G(y)$ and x and y belong to the same path-connected component of S_g with $g = G(x)$.

The path-connected components of $D \setminus U_g$ can be enumerated by the connected components of the graph $\widetilde{D_1} \setminus U_g$. The following lemma allows us to apply this result to the path-connected components of S_g.

Lemma 3.2. Let $g > g^*$, $W_1, \ldots, W_q$ be the path-connected components of $D \setminus U_g$, and let $\sigma_1, \ldots, \sigma_p$ be the path-connected components of S_g. Then $q = p$ and σ_i may be enumerated in such a way that σ_i is the border of W_i in D.

Proof. G is continuous in D; hence, if $G(x) > g$, then there exists a vicinity of x in D where $G(x) > g$. Therefore, $G(y) = g$ for every boundary point y of $D \setminus U_g$ in D and S_g is the boundary of $D \setminus U_g$ in D.

Let us define a projection $\theta_g : D \setminus U_g \to S_g$ by the conditions $\theta_g(x) \in [x, x^*]$ and $G(\theta_g(x)) = g$. By definition, the inequality $G(x) \geq g$ holds in $D \setminus U_g$. The function $f_x(\lambda) = G((1-\lambda)x^* +$

$\lambda x)$ is a strictly increasing, continuous, and convex function of $\lambda \in [0, 1]$, $f_x(0) = g^* < g$, $f_x(1) = G(x) \geq g$. The function $f_x(\lambda)$ depends continuously on $x \in D \setminus U_g$ in the uniform metrics. Therefore, the solution λ_x to the equation $f_x(\lambda) = g$ on $[0, 1]$ exists (the intermediate value theorem), is unique, and continuously depends on $x \in D \setminus U_g$. The projection θ_g is defined as $\theta_g(x) = (1 - \lambda_x)x^* + \lambda_x x$.

The fixed points of the projection θ_g are elements of S_g. The image of each path-connected component W_i is a path-connected set. The preimage of every path-connected component σ_i is also a path-connected set. Indeed, let $\theta_g(x) \in \sigma_i$ and $\theta_g(y) \in \sigma_i$. There exists a continuous path from x to y in $D \setminus U_g$. It may be composed from three paths: (i) from x to $\theta_g(x)$ along the line segment $[x, \theta_g(x)] \subset [x, x^*]$, (ii) then a continuous path in σ_i between $\theta_g(x)$ and $\theta_g(y)$ (it exists because σ_i is a path-connected component of S_g and it belongs to $D \setminus U_g$ because $S_g \subset D \setminus U_g$) and, finally, (iii) from $\theta_g(y)$ to y along the line segment $[\theta_g(y), y] \subset [x^*, y]$. Therefore, the image of a path-connected component W_i is a path-connected component of S_g that may be enumerated by the same index i, σ_i. This σ_i is the border of W_i in D. $\blacksquare$

The equivalence class of $x \in D$ is defined as $[x] = \{y \in D \,|\, y \sim x\}$. Let $W(x)$ be a path-connected component of $D \setminus U_g$ ($g = G(x)$) for which $\theta_g(W(x)) = [x]$. Due to Lemma 3.2, such a component exists and

$$(10) \qquad W(x) = \{y \in D \,|\, y \succsim x\}.$$

Let us define a one-dimensional continuum $\mathcal{Y}$ that consists of the pairs (g, M), where $g^* \leq g \leq g_{\max}$ and M is a set of vertices of a connected component of $\widetilde{D_1} \setminus U_g$. For each (g, M) the fundamental system of neighborhoods consists of the sets V_ρ ($\rho > 0$):

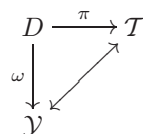$$(11) \qquad V_\rho = \{(g', M') \,|\, (g', M') \in \mathcal{Y}, \, |g - g'| < \rho, \, M' \subseteq M\}.$$

Let us define the partial order on $\mathcal{Y}$:

$$(g, M) \succsim (g', M') \text{ if } g \geq g' \text{ and } M \subseteq M'.$$

Let us introduce the mapping $\omega : D \to \mathcal{Y}$:

$$\omega(x) = (G(x), W(x) \cap D_0).$$

Theorem 3.3. *There exists a homeomorphism between $\mathcal{Y}$ and $\mathcal{T}$ that preserves the partial order and makes the following diagram commutative:*

$$
\begin{array}{ccc}
D & \xrightarrow{\pi} & \mathcal{T} \\
\omega \downarrow & \nearrow & \\
\mathcal{Y} & &
\end{array}
$$

Proof. According to Lemma 3.2, (10), and Proposition 2.4, ω maps the equivalent points x to the same pair (g, M) and the nonequivalent points to different pairs (g, M). For any $x, y \in D$, $x \succsim y$ if and only if $\omega(x) \succsim \omega(y)$.

The fundamental system of neighborhoods in Y may be defined using this partial order. Let us say that (g, M) is compatible to (g', M') if $(g', M') \succsim (g, M)$ or $(g, M) \succsim (g', M')$. Then for $\rho > 0$

$$V_\rho = \{(g', M') \in \mathcal{Y} \,|\, |\gamma - \gamma'| < \rho \text{ and } (g', M') \text{ is compatible to } (g, M)\}.$$

For sufficiently small ρ this definition coincides with (11).

So, by the definition of $\mathcal{T}$ as a quotient space $D/\sim$, $\mathcal{Y}$ has the same partial order and topology as $\mathcal{T}$. The isomorphism between $\mathcal{Y}$ and $\mathcal{T}$ establishes one-to-one correspondence between the π-image of the equivalence class $[x]$, $\pi([x])$, and the ω-image of the same class, $\omega([x])$. ∎

$\mathcal{Y}$ can be considered as a coordinate system on $\mathcal{T}$. Each point is presented as a pair (g, M), where $g^* \leq g \leq g_{\max}$ and M is a set of vertices of a connected component of $\widetilde{D_1} \setminus U_g$. The map ω is the coordinate representation of the canonical projection $\pi : D \to \mathcal{T}$. Now, let us use this coordinate system and the proof of Theorem 3.3 to obtain the following corollary.

Corollary 3.4. *An admissible path from x to y in D exists if and only if*

$$\pi(y) \in [\pi(x^*), \pi(x)].$$

Proof. Let there exist an admissible path from x to y in D, $\varphi : [0, 1] \to D$. Then $\pi(x) \succsim \pi(y)$ in $\mathcal{T}$. Let $\pi(x) = (G(x), M)$ in coordinates $\mathcal{Y}$. For any $v \in M$, $\pi(y) \in [\pi(x^*), \pi(v)]$ and $\pi(x) \in [\pi(x^*), \pi(v)]$.

Assume now that $\pi(y) \in [\pi(x^*), \pi(x)]$ and $\pi(x) = (G(x), M)$. Then the admissible path from x to y in D can be constructed as follows. Let $v \in M$ be a vertex of D. $G(v) \geq G(x)$ for each $v \in M$. The straight line segment $[x^*, v]$ includes a point x_1 with $G(x_1) = G(x)$ and y_1 with $G(y_1) = G(y)$. Coordinates of $\pi(x_1)$ and $\pi(x)$ in $\mathcal{Y}$ coincide as well as coordinates of $\pi(y_1)$ and $\pi(y)$. Therefore, $x \sim x_1$ and $y \sim y_1$. The admissible path from x to y in D can be constructed as a sequence of three paths: first, a continuous path from x to x_1 inside the path-connected component of $S_{G(x)}$ (Lemma 3.1), then from x_1 to y_1 along a straight line, and after that a continuous path from y_1 to y inside the path-connected component of $S_{G(y)}$. ∎

To describe the space $\mathcal{T}$ in coordinate representation $\mathcal{Y}$, it is necessary to find the connected components of the graph $\widetilde{D_1} \setminus U_g$ for each g. First, this function,

$$g \mapsto \text{ the set of connected components of } \widetilde{D_1} \setminus U_g,$$

is piecewise constant. Second, we do not need to solve at each point the computationally heavy problem of the construction of the connected components of the graph $\widetilde{D_1} \setminus U_g$ "from scratch." The problem of the parametric analysis of these components as functions of g appears to be much cheaper. Let us present a solution to this problem. At the same time, this is a method for the construction of the thermodynamic tree in coordinates (g, M).

The coordinate system $\mathcal{Y}$ allows us to describe the *tree structure* of the continuum $\mathcal{T}$. This structure includes a root, (g^*, D_0), edges, branching points, and leaves.

Let M be a connected component of $\widetilde{D_1} \setminus U_g$ for some g, $g^* < g < g_{\max}$. If $M \subsetneqq D_0$, then the set of all points $(g, M) \in \mathcal{T}$ has for a given M the form $(\underline{a}_M, \overline{a}_M] \times M$, $\underline{a}_M < \overline{a}_M$. We call this set an *edge* of $\mathcal{T}$.

If M includes all the vertices of D ($M = D_0$), then the set of all points $(g, M) \in \mathcal{T}$ has the form $[g^*, \overline{a}_{D_0}] \times D_0$. This may be either an edge (if $\overline{a}_{D_0} > g^*$) or just a *root*, $\{(g^*, D_0)\}$ (this is possible in 1D systems).

Let us define the numbers $\underline{a}_M = \inf\{g \,|\, (g, M) \in \mathcal{T}\}$. Let us introduce the set of outer edges of M in $\widetilde{D_1}$, $E_{\text{out}}(M)$. This is the set of edges of $\widetilde{D_1}$ that connect vertices from M with

vertices from $D_0 \setminus M$. We keep the same notation, $E_{out}(M)$, for the set of the corresponding edges of D:

$$(12) \qquad \underline{a}_M = \max_{e \in E_{out}(M)} \min\{G(x) \mid x \in e\}.$$

This number, $\underline{a}_M$, is the "cutting value" of G for M. It cuts M from the other vertices of $\widetilde{D}_1$ in the following sense: if we delete from $\widetilde{D}_1$ all the edges e with the label values $< \underline{a}_M$, then M will remain attached to some vertices from $D_0 \setminus M$. If we delete the edges with the label values $\leq \underline{a}_M$, then M becomes disconnected from $D_0 \setminus M$. There is the only connected component of $\widetilde{D}_1 \setminus U_{\underline{a}_M}$ that includes M, $M' \supsetneq M$. The pair $(\underline{a}_M, M') \in \mathcal{T}$ is a *branching point* of $\mathcal{T}$. The edge $(\underline{a}_M, \overline{a}_M] \times M$ connects two vertices, the upper vertex $(\overline{a}_M, M)$ and the lower vertex, $(\underline{a}_M, M')$.

If M consists of one vertex, $M = \{v\}$, then the point $(G(v), \{v\})$ is a *leaf* of $\mathcal{T}$.

3.3. Construction of the thermodynamic tree. To construct the tree of G in D we need the graph $\widetilde{D}_1$ of the 1-skeleton of the polyhedron D. Elements of $\widetilde{D}_1$ should be labeled by the values of G. Each vertex v is labeled by the value $\gamma_v = G(v)$, and each edge $e = [v, w]$ is labeled by the minimal value of G on the segment $[v, w] \subset D$, $g_e = \min_{[v,w]} G(x)$. We need also the minimal value $g^* = \min_D\{G(x)\}$ because the root of the tree is (g^*, D_0).

The strictly convex function G achieves its local maxima in D only in vertices. The vertex v is a (local) maximizer of g if $g_e < \gamma_v$ for each edge e that includes v. The leaves of the thermodynamic tree are pairs $(\gamma_v, \{v\})$ for the vertices that are the local maximizers of G.

As a preliminary step of the construction, we arrange and enumerate the labels of the elements of $\widetilde{D}_1$, the vertices and edges, in descending order. Let there exist l different label values: $g_{\max} = a_1 > a_2 > \cdots > a_l$. Each a_k is a value $\gamma_v = G(v)$ at a vertex $v \in D_0$ or the minimum of G on an edge $e \subset D_1$ (or both). Let A_i be the set of vertices $v \in D_0$ with $\gamma_v = a_i$, and let E_i be the set of edges of D_1 with $g_e = a_i$ $(i = 1, \ldots, l)$.

Let us construct the connected components of the graph $\widetilde{D}_1 \setminus U_g$ starting from $a_1 = g_{\max}$. The function G is strictly convex; hence, $a_1 = \gamma_v$ for a set of vertices $A_1 \subset D_0$, but it is impossible that $a_1 = g_e$ for an edge e; hence, $E_1 = \emptyset$.

The set of connected components of $\widetilde{D}_1 \setminus U_g$ is the same for all $g \in (a_{i+1}, a_i]$. For an interval $(a_2, a_1]$ the connected components of $\widetilde{D}_1 \setminus U_g$ are the one-element sets $\{v\}$ for $v \in A_1$.

For $g \in [g^*, a_l]$ the graph $\widetilde{D}_1 \setminus U_g$ includes all the vertices and edges of $\widetilde{D}_1$, and, hence, it is connected for this segment. Let us take, formally, $a_{l+1} = g^*$.

Let $\mathcal{L}_i = \{M_1^i, \ldots, M_{k_i}^i\}$ be the set of the connected components of $\widetilde{D}_1 \setminus U_g$ for $g \in (a_i, a_{i-1}]$ $(i = 1, \ldots, l)$. Each connected component is represented by the set of its vertices M_j^i. Let us describe the recursive procedure for the construction of $\mathcal{L}_i$:

1. Let us take formally $\mathcal{L}_0 = \emptyset$.
2. Assume that $\mathcal{L}_{i-1}$ is given and $i \leq l$. Let us find the set $\mathcal{L}_i$ of connected components of $\widetilde{D}_1 \setminus U_g$ for $g = a_i$ (and, therefore, for $g \in (a_{i+1}, a_i]$).
   - Add the one-element sets $\{v\}$ for all $v \in A_i$ to the set

$$\mathcal{L}_{i-1} = \{M_1^{i-1}, \ldots, M_{k_{i-1}}^{i-1}\}.$$

Denote this auxiliary set of sets as $\widetilde{L}_{i,0} = \{M_1, \ldots, M_q\}$, where $q = k_{i-1} + |A_i|$.

- Enumerate the edges from E_i in an arbitrary order: $e_1, \ldots, e_{|E_i|}$. For each $k = 0, \ldots, |E_i|$, create recursively an auxiliary set of sets $\widetilde{L}_{i,k}$ by the union of some of elements of $\widetilde{L}_{k-1}$: Let $\widetilde{L}_{i,k-1}$ be given, and let e_k connect the vertices v and v'. If v and v' belong to the same element of $\widetilde{L}_{i,k-1}$, then $\widetilde{L}_{i,k} = \widetilde{L}_{i,k-1}$. If v and v' belong to the different elements of $\widetilde{L}_{i,k-1}$, M and M', then $\widetilde{L}_{i,k}$ is produced from $\widetilde{L}_{i,k-1}$ by the union of M and M':

$$\widetilde{L}_{i,k} = (\widetilde{L}_{i,k-1} \setminus \{M\} \setminus \{M'\}) \cup \{M \cup M'\}$$

(we delete two elements, M and M', from $\widetilde{L}_{i,k-1}$ and add a new element $M \cup M'$).

The set $\mathcal{L}_i$ of connected components of $\widetilde{D_1} \setminus U_g$ for $g = a_i$ is $\mathcal{L}_i = \widetilde{L}_{i,|E_i|}$.

Generically, all the labels of the graph $\widetilde{D_1}$ vertices and edges are different, and the sets E_i and A_i include not more than one element. Moreover, for each i either E_i or A_i is generically empty, and the description of the recursive procedure may be simplified for the generic case:

1. Let us take formally $\mathcal{L}_0 = \emptyset$.
2. Assume that $\mathcal{L}_{i-1}$ is given and $i \leq l$.
   - If a_i is a label of a vertex v, $a_i = \gamma_v$, then add the one-element set $\{v\}$ to the set $\mathcal{L}_{i-1}$: $\mathcal{L}_i = \mathcal{L}_{i-1} \cup \{\{v\}\}$.
   - Let a_i be a label of an edge $e = [v, v']$. If v and v' belong to the same element of $\mathcal{L}_{i-1}$, then $\mathcal{L}_i = \mathcal{L}_{i-1}$. If v and v' belong to the different elements of $\mathcal{L}_{i-1}$, M and M', then $\mathcal{L}_i$ is produced from $\mathcal{L}_{i-1}$ by the union of M and M' (delete elements M and M', and add an element $M \cup M'$).

The described procedure gives us the sets of connected components of $\widetilde{D_1} \setminus U_g$ for all g, and, therefore, we get the tree $\mathcal{T}$. The descent from the higher values of G allows us to avoid the solution of the computationally more expensive problem of the calculation of the connected components of a graph at any level of G.

3.4. The problem of attainable sets. In this section, we demonstrate how to solve the problem of attainable sets. For given $x \in D$ (an initial state) we describe the *attainable set*

$$Att(x) = \{y \in D \mid x \succsim y\}$$

by a system of inequalities. Let the tree $\mathcal{T}$ of G in D be given, and let all the pairs $(g, M) \in \mathcal{T}$ be described. We also use the notation $Att(z)$ for sets attainable in $\mathcal{T}$ from $z \in \mathcal{T}$.

First, let us describe the *preimage of a point* $(g, M) \in \mathcal{T}$ *in* D. It can be described by the equation $G(x) = g$ and a set of linear inequalities. For each edge e we select a minimizer of G on e, $x_e = \arg\min\{G(x) \mid x \in e\}$ (we use the same notation for the elements of the graph $\widetilde{D_1}$ and of the continuum D_1). Let

$$Q_M = \{x_e \mid e \in E_{\text{out}}(M)\}.$$

In particular, $\underline{a}_M = \max\{G(x) \mid x \in Q_M\}$.

The following proposition is a direct consequence of Proposition 2.9.

Proposition 3.5. *The preimage of* (g, M) *in* D *is a set*

(13) $$\pi^{-1}(g, M) = \{x \in \text{conv}(Q_M \cup M) \mid G(x) = g\}.$$

The sets M and Q_M in (13) do not depend on the specific value of g. It is sufficient that the point $(g, M) \in \mathcal{T}$ exists.

Let us consider the second projection of $\mathcal{T}$, i.e., the set of all connected components of the graph $\widehat{D_1} \setminus U_g$ for all g. For a connected component M, the *lower chain* of connected components is a sequence $M = M_1 \subsetneq M_2 \subsetneq \cdots \subsetneq M_k$. ("Lower" here means the descent in the natural order in $\mathcal{T}, \gtrsim$.) For a given initial element $M = M_1$ the *maximal lower chain* of M is the lower chain of M that cannot be extended by adding new elements. By construction of connected components, the maximal lower chain of M is unique for each initial element M. In the maximal lower chain $\underline{a}_{M_i} = \overline{a}_{M_{i+1}}$.

For each set of values $H \subset (\underline{a}_M, \overline{a}_M]$ the preimage of the set $H \times M \subset \mathcal{T}$ is given by (13) as

$$(14) \qquad \pi^{-1}(H \times M) = \{x \in \operatorname{conv}(Q_M \cup M) \mid G(x) \in H\}.$$

We describe the set $Att(x)$ for $x \in D$ by the following procedures: (i) find the projection $\pi(x)$ of x onto $\mathcal{T}$, (ii) find the attainable set in $\mathcal{T}$ from $\pi(x)$, $Att(\pi(x))$, and (iii) find the preimage of this set in D:

$$(15) \qquad Att(x) = \pi^{-1}(Att(\pi(x))).$$

The attainable set $Att(g, M)$ in $\mathcal{T}$ from $(g, M) \in \mathcal{T}$ is constructed as a union of edges and its parts. Let $M = M_1 \subsetneq M_2 \subsetneq \cdots \subsetneq M_k = D_0$ be the maximal lower chain of M. Then

$$(16) \qquad \begin{aligned} Att(g, M) = &(\underline{a}_1, g] \times M_1 \cup (\underline{a}_2, \underline{a}_1] \times M_2 \cup \cdots \\ &\cup (\underline{a}_{k-1}, \underline{a}_{k-2}] \times M_{k-1} \cup [\underline{a}_k, \underline{a}_{k-1}] \times M_k, \end{aligned}$$

where $\underline{a}_i = \underline{a}_{M_i}$.

To find the preimage of $Att(g, M)$ in D we have to apply formula (14) to each term of (16). In section 1.3 we demonstrated how to find $\pi(x)$. Therefore, each step of the solution of the problem of attainable set (15) is presented.

4. Chemical thermodynamics: Examples.

4.1. Skeletons of the balance polyhedra.
In chemical thermodynamics and kinetics, the variable N_i is the amount of the ith component in the system. The balance polyhedron D is described by the positivity conditions $N_i \geq 0$ and the balance conditions (1) $b_i(N) = \operatorname{const}$ ($i = 1, \ldots, m$). Under the isochoric (the constant volume) conditions, the concentrations c_i also satisfy the balance conditions, and we can construct the balance polyhedron for concentrations. Sometimes, the balance polyhedron is called the *reaction simplex* with some abuse of language because it is not obligatorily a simplex when the number m of the independent balance conditions is greater than one.

The graph $\widehat{D_1}$ depends on the values of the balance functionals $b_i = b_i(N) = \sum_{j=1}^n a_i^j N_j$. For the positive vectors N, the vectors b with coordinates $b_i = b_i(N)$ form a convex polyhedral cone in $\mathbb{R}^m$. Let us denote this cone by Λ. $\widehat{D_1}(b)$ is a piecewise constant function on Λ. Sets with various constant values of this function are cones. They form a partition of Λ. Analysis of this partition and the corresponding values of $\widehat{D_1}$ can be done by the tools of linear programming [26]. Let us present several examples.
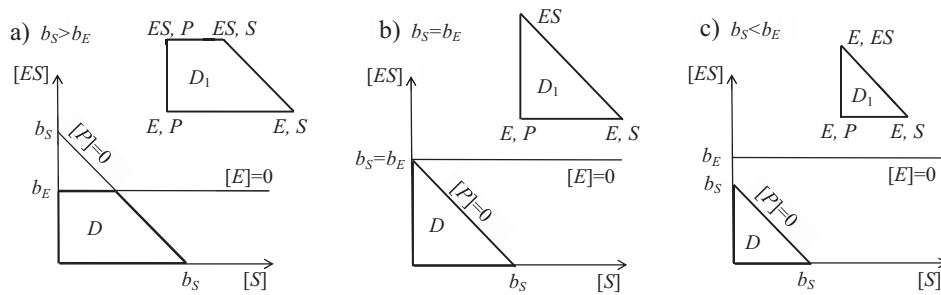
Figure 4. *The balance polygon D on the plane with coordinates $[S]$ and $[ES]$ for the four-component enzyme-substrate system S, E, ES, P with two balance conditions, $b_S = [S] + [ES] + [P] = \text{const}$ and $b_E = [E] + [ES] = \text{const}$.*

In the first example, the reaction system consists of four components: the substrate S, the enzyme E, the enzyme-substrate complex ES, and the product P. We consider the system under constant volume. We denote the concentrations by $[S]$, $[E]$, $[ES]$, and $[P]$. There are two balance conditions: $b_S = [S] + [ES] + [P] = \text{const}$ and $b_E = [E] + [ES] = \text{const}$.

For $b_S > b_E$ the polyhedron (here the polygon) D is a trapezium (Figure 4(a)). Each vertex corresponds to two components that have nonzero concentrations in this vertex. For $b_S > b_E$ there are four such pairs, (ES, P), (ES, S), (E, P), and (E, S). For two pairs there are no vertices: for (S, P) the value b_E is zero, and for (ES, E) it should be $b_S < b_E$. When $b_S = b_E$, two vertices, (ES, P) and (ES, S), transform into one vertex with one nonzero component, ES, and the polygon D becomes a triangle (Figure 4(b)). When $b_S < b_E$, then D is also a triangle, and a vertex ES transforms in this case into (ES, E) (Figure 4(c)).

For the second example, we select a system with six components and two balance conditions: H_2, O_2, H, O, H_2O, OH,

$$b_H = 2N_{H_2} + N_H + 2N_{H_2O} + N_{OH},$$
$$b_O = 2N_{O_2} + N_O + N_{H_2O} + N_{OH}.$$

The cone Λ is a positive quadrant on the plane with the coordinates b_H, b_O. The graph $\widetilde{D_1}(b)$ is constant in the following cones in Λ ($b_H, b_O > 0$): (a) $b_H > 2b_O$, (b) $b_H = 2b_O$, (c) $2b_O > b_H > b_O$, (d) $b_H = b_O$, and (e) $b_H < b_O$ (Figure 5).

The cases (a) $b_H > 2b_O$, (c) $2b_O > b_H > b_O$, and (e) $b_H < b_O$ (Figure 5) are regular: there are two independent balance conditions, and for each vertex there are exactly two components with nonzero concentration. In case (a) ($b_H > 2b_O$), if $b_H \to 2b_O$, then two regular vertices, H_2, H_2O and H, H_2O, join in one vertex (case (b)) with only one nonzero concentration, H_2O (Figure 6(a)). This vertex explodes in three vertices O, H_2O; O_2, H_2O; and H_2O, OH when b_H becomes smaller than $2b_O$ (case (c), $2b_O > b_H > b_O$) (Figure 6(a)). Analogously, in the transition from the regular case (c) to the regular case (e) through the singular case (d) ($b_H = b_O$) three vertices join in one, OH, which explodes in two (Figure 6(b)).

For the modeling of hydrogen combustion, the eight-component model is usually used: H_2, O_2, H, O, H_2O, OH, H_2O_2, HO_2. In Figure 7 the graph $\widetilde{D_1}$ is presented for one particular relation between b_H and $2b_O$, $b_H = 2b_O$. This is the so-called *stoichiometric mixture*, where
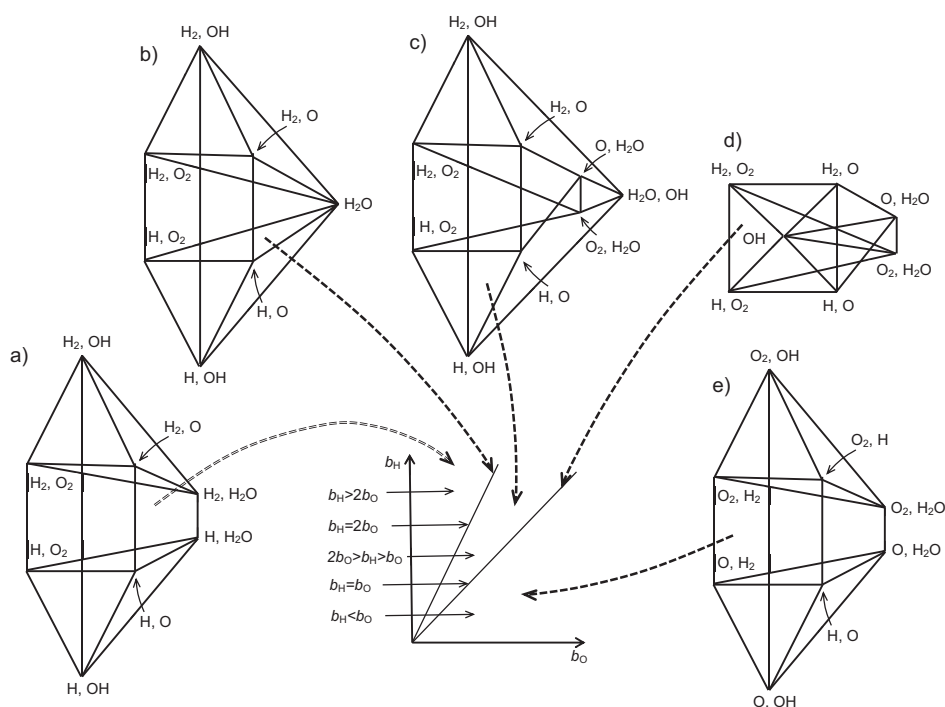
Figure 5. *The graph $\widetilde{D_1}(b)$ of the 1-skeleton of the balance polyhedron for the six-component system, H_2, O_2, H, O, H_2O, OH, as a piecewise constant function of $b = (b_H, b_O)$. For each vertex the components which have nonzero concentrations at this vertex are indicated.*

proportion between b_H and $2b_O$ is the same as in the "product," H_2O.

4.2. Examples of the thermodynamic tree. In this section, we present two examples of the thermodynamic tree. First, let us consider the trapezium (Figure 4(a)). Let us select the order of numbers γ_v and g_e according to Figure 8. The vertices and edges are enumerated in order of γ_v and g_e (starting from the greatest values). The tree is presented in Figure 8. On the right, the graphs $\widetilde{D_1} \setminus U_g$ are depicted for all intervals $(a_{i-1}, a_i]$. For $(\gamma_2, \gamma_1]$ it is just a vertex v_1. For $(g_1, \gamma_2]$ it consists of two disjoint vertices, v_1 and v_2. For $(\gamma_3, g_1]$ these two vertices are connected by an edge. On the interval $(g_2, \gamma_3]$ the graph $\widetilde{D_1} \setminus U_g$ is an edge (v_1, v_2) and an isolated vertex v_3. On $(\gamma_4, g_2]$ all three vertices v_1, v_2, and v_3 are connected by edges. For $(g_3, \gamma_4]$ the isolated vertex v_4 is added to the graph $\widetilde{D_1} \setminus U_g$. For $g \leq g_3$ the graph $\widetilde{D_1} \setminus U_g$ includes all the vertices and is connected.

For the second example (Figure 9) we selected the six-component system (Figure 5) with the stoichiometric hydrogen-oxygen ratio, $b_H = 2b_O$. The selected order of numbers γ_i, g_j is presented in Figure 9.

5. Conclusion. We studied dynamical systems that obey a continuous strictly convex Lyapunov function G in a positively invariant convex polyhedron D. Convexity allows us to transform n-dimensional problems about attainability and attainable sets into an analysis of 1D continua and discrete objects.
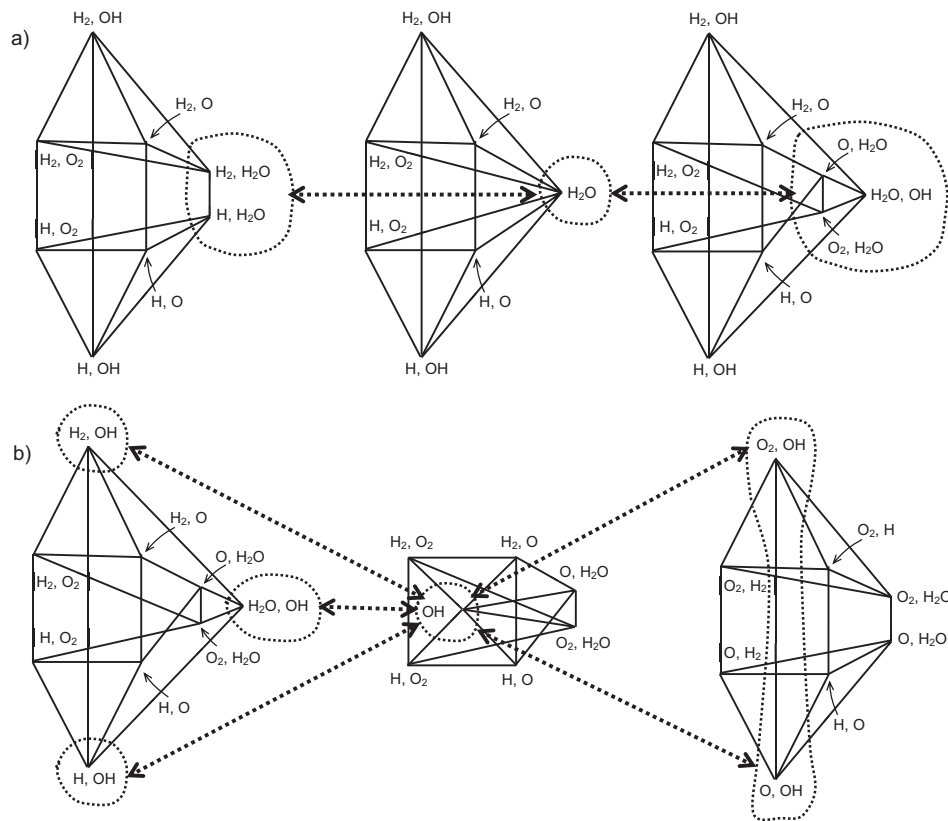
Figure 6. *Transformations of the graph $\widetilde{D}_1(b)$ with changes of the relation between b_H and b_O. (a) Transition from the regular case $b_H > 2b_O$ to the regular case $2b_O > b_H > b_O$ through the singular case $b_H = 2b_O$. (b) Transition from the regular case $2b_O > b_H > b_O$ to the regular case $b_H < b_O$ through the singular case $b_H = b_O$.*

We construct the tree (the Adelson-Velskii–Kronrod–Reeb (AKR) tree [1, 42, 56]) of the function G in D and call this 1D continuum the *thermodynamic tree.*

The thermodynamic tree is a tool to solve the "attainability problem": is there a continuous path between two states, x and y, along which the conservation laws hold, the concentrations remain nonnegative, and the relevant thermodynamic potential G (Gibbs energy, for example) monotonically decreases? This question arises often in nonequilibrium thermodynamics and kinetics. The analysis of the admissible paths can be considered as a dynamical analogue of the study of the steady states' feasibility in chemical and biochemical kinetics. In this recent study, the energy balance method, the stoichiometric network theory, the entropy production analysis, and the advanced algorithms of convex geometry of polyhedral cones are used [8, 54].

The obvious inequality, $G(x) \geq G(y)$, is a necessary but not a sufficient condition for existence of an admissible path from x to y. In 1D systems, the space of states is an interval, and the thermodynamic tree has two leaves (the ends of the interval) and one root (the equilibrium). In such a system, a spontaneous transition from a state x to a state y is allowed by thermodynamics if $G(x) \geq G(y)$ and x and y are on the same side of the equilibrium, i.e.,
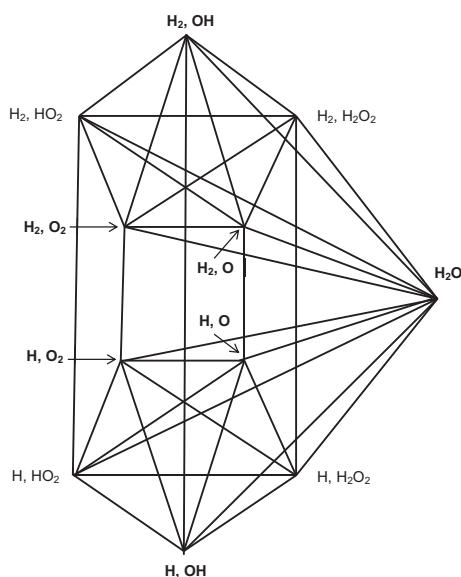
Figure 7. *The graph $\widetilde{D_1}$ for the eight-component system, H_2, O_2, H, O, H_2O, OH, H_2O_2, HO_2, for the stoichiometric mixture, $b_H = 2b_O$. The vertices that also correspond to the six-component mixture are distinguished by bold font.*

if they belong to the same branch of the thermodynamic tree. This is just a well-known rule: "it is impossible to overstep the equilibrium in 1D systems."

The construction of the thermodynamic tree gives us the multidimensional analogue of this rule. Let $\pi : D \to \mathcal{T}$ be the natural projection of the balance polyhedron D on the thermodynamic tree $\mathcal{T}$. A spontaneous transition from a state x to a state y is allowed by thermodynamics if and only if $\pi(y) \in [\pi(x), \pi(N^*)]$, where N^* is the equilibrium and $[\pi(x), \pi(N^*)]$ is the ordered segment.

In this paper, we developed methods for solving the following problems:

1. How do we construct the thermodynamic tree $\mathcal{T}$?
2. How do we solve the attainability problem?
3. How do we describe the set of all states attainable from a given initial state x?

For this purpose, we analyzed the cutting of a convex polyhedron by a convex set and developed the algorithm for construction of the tree of level set components of a convex function in a convex polyhedron. In this algorithm, the restriction of G onto the 1-skeleton of D is used. This finite family of convex functions of one variable includes all necessary information for analysis of the tree of the level set component of the convex function G of many variables.

In high dimensions, some steps of our analysis become computationally expensive. The most expensive operations are the convex hull (description of the convex hull of a finite set by linear inequalities) and the double description operations (description of the faces of a
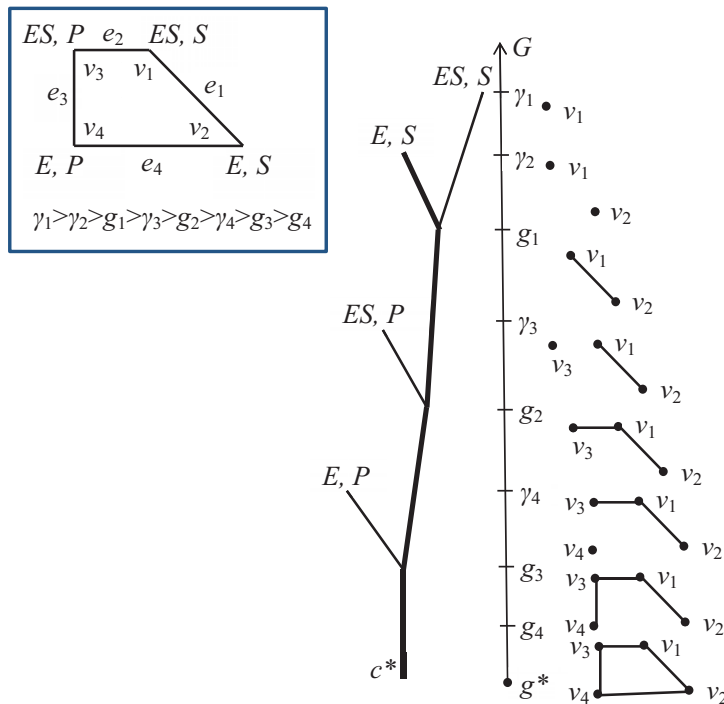
Figure 8. *The thermodynamic tree for the four-component enzyme-substrate system S, E, ES, P (Figure 4) with excess of substrate: $b_S > b_E$ (case (a)). The vertices and edges are enumerated in order of γ_v and g_e (starting from the greatest values). The order of these numbers is represented in the Figure. On the right, the graphs $\widetilde{D}_1 \setminus U_g$ are depicted. The solid bold line on the tree is the thermodynamically admissible path from the initial state E, S (enzyme plus substrate) to the equilibrium. There are leaves at all levels $g = \gamma_i$. There are branching points at $g = g_{1,2,3}$ and no vertices at $g = g_4$.*

polyhedron given by a set of linear inequalities). Therefore, in high dimensions some of the problem may be modified; for example, instead of the explicit description of the convex hull, it is possible to use the algorithm for solution of a problem: does a point belong to this convex hull [55]? The computational aspects of the discussed problems in higher dimensions deserve more attention, and the proper modifications of the problems should be elaborated. For example, the following two problems need to be solved efficiently:

- Find the maximal and the minimal values of any linear function f in a class of thermodynamic equivalence.
- Evaluate the maximum and the minimum of dG/dt in any class of thermodynamic equivalence: $-\overline{\sigma} \leq dG/dt \leq -\underline{\sigma} \leq 0$.

For any $w \in \mathcal{T}$, the solution of the first problem allows us to find an interval of values of any linear function of state in the corresponding class of thermodynamic equivalence. We can use the results of section 2.2 to reformulate this problem as the convex programming problem.

The second problem gives us the possibility of considering the dynamics of relaxation on $\mathcal{T}$. On each interval on $\mathcal{T}$ we can write

$$(17) \qquad\qquad -\overline{\sigma}(g) \leq dg/dt \leq -\underline{\sigma}(g) \leq 0,$$

$$\gamma_1 > \gamma_2 > \gamma_3 > g_1 > g_2 > \gamma_4 > \gamma_5 > g_3 > g_4 > \gamma_6 > g_5 > g_6 > g_7 > g_8 > \gamma_7 > g_9 > g_{10}$$
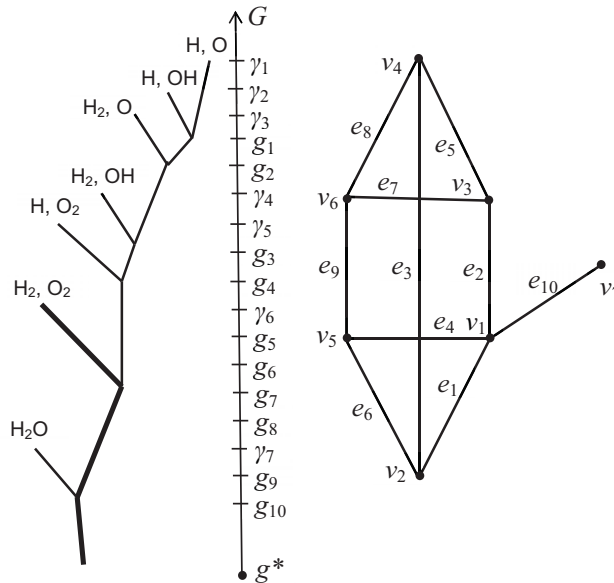
Figure 9. *The thermodynamic tree for the six-component* H_2–O_2 *system,* H_2, O_2, H, O, H_2O, OH, *with the stoichiometric hydrogen-oxygen ratio,* $b_H = 2b_O$ *(Figure* 5(b)*). The order of numbers* γ_i, g_j *is presented in the Figure. On the right, the graph* $\widetilde{D_1} \setminus U_g$ *is represented for* $g = g_{10}$. *For* $g \leq g_{10}$, *the graph* $\widetilde{D_1} \setminus U_g$ *includes all the vertices and is connected. The solid bold line on the tree is the thermodynamically admissible path from the initial state* H_2, O_2 *to the equilibrium. There are leaves at all levels* $g = \gamma_i$. *There are branching points at* $g = g_{1-4,7,10}$ *and no vertices at* $g = g_{5,6,8,9}$.

where the functions $\overline{\sigma}(g), \underline{\sigma}(g) \geq 0$ depend on the interval on $\mathcal{T}$.

This differential inequality (17) will be a tool for the study of the dynamics of relaxation and may be considered as a reduced kinetic model that substitutes dynamics on the d-dimensional balance polyhedron D by dynamics on the 1D dendrite. The problem of the construction of the reduced model (17) is closely related to the following problem [66]: "Can one establish a lower bound on the entropy production, in terms of how much the distribution function departs from thermodynamical equilibrium?" In 1982, Cercignani [12] proposed a simple linear estimate for $\underline{\sigma}(g)$ for the Boltzmann equation (Cercignani's conjecture). After that, these estimates were studied and improved by many authors [15, 11, 65, 66], and now the state of the art achieved for the Boltzmann equation gives us some hints as to how to create the relaxation model (17) on the thermodynamic tree for general kinetic systems. This may be the next step in the study of thermodynamic trees.

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