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Modeling liquidus hypersurfaces through simplicial complexes

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Abstract

This paper describes an operational pipeline that exploits computational geometry to derive useful knowledge about the crystallization behaviour of materials composed of varying amounts of pure components. Starting from existing knowledge related to the pure components, we compute the Gibbs free energy of all their possible compositions in a given range of temperatures, both in liquid and solid phases. Then, we exploit the convex hull method to derive the coexistence of solid and liquid phases, and model the resulting liquidus hypersurface as a simplicial complex. On such a complex, we propose novel tools to robustly compute descent lines describing the crystallization path induced by heat loss for any initial composition in the system.

Categories and Subject Descriptors (according to ACM CCS): I.3.5 [Computer Graphics]: Computational Geometry and Object Modeling

1. Introduction

Many interesting materials studied today are mixtures of several pure components. Typically, in Material Research the absolute amount of pure components constituting a complex material is not very important, while it is much more interesting to know their relative amount. For example, *pseudowollastonite* is always composed of 50% CaO and 50% SiO_2 in molar proportions independently of the bulk amount of the substance. In many cases, the characteristics of a mixture can be derived based on the characteristics of its components, their relative amount, and a number of other variables such as the temperature or pressure. It is often useful to know, for example, which is the minimum temperature at which a given material begins to melt. On the contrary, when lowering the temperature, it is useful to know at which point a molten substance begins to crystallize (e.g. at sea level, water becomes ice at zero degrees). Such a temperature of incipient crystallization depends on the crystallization temperature of the constituting pure components, but this dependence is not necessarily as easy as a linear combination.

Given N pure components representing a thermodynamic system, the domain of all their possible “relative amounts” in a mixture can be modelled as a simplex. Within such a *compositional* simplex, one may define a multivariate function called the *liquidus* which associates, to each possible composition, the crystallization temperature of the corresponding material. At the vertices of the simplex the value of the liquidus corresponds to the crystallization temperature of the corresponding pure components, whereas in the interior of the simplex it varies in a non-trivial manner. In general, the liquidus cannot be represented in closed analytical form, therefore the domain is typically sampled in a discrete manner.

Computational geometry proved to be extremely useful to model and analyze complex thermodynamic systems from many points of view. First, the graph of the liquidus is a hypersurface, and this paper shows that it is convenient to represent it through a simplicial complex. We show how to exploit the computation of convex hulls to derive the liquidus starting from known properties of the pure components, and suggest a novel approach to analyze the liquidus hypersurface in order to predict crystallization paths for any initial composition in the system. The study of such processes is fundamental to understand important phenomena that involve molten materials such as, for example, the evolution of magma bodies and volcanic eruptions.

2. Related work

This section reports some fundamentals of computational thermodynamics and useful notions of discrete differential geometry which are necessary to understand the contribution of the paper.

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Computational Thermodynamics - Material research and engineering try to understand the characteristics of complex materials by studying the interrelationship of composition, microstructure and process conditions represented in *phase diagrams* [8]. The calculation of phase diagrams (CALPHAD, for short) is one of the main objectives of computational thermodynamics. Roughly speaking, a mixture of pure *components* constitutes a thermodynamic system that may exist is different aggregation states (*phases*) depending on temperature (T), pressure (P) and composition (X). Depending on its initial configuration, a system may change dynamically in order to attain an equilibrium state. For example, ice tends to pass from solid to liquid at ambient P and T, when this last is slightly enhanced. A phase diagram is a chart describing how the various phases of a system depend on thermodynamic parameters such as T, P, and X. In 1870, J.W. Gibbs proposed the equality $\boldsymbol{f = c - p + 2}$ that relates the number of components $\boldsymbol{c}$ and the number of phases $\boldsymbol{p}$ with the number of degrees of freedom $\boldsymbol{f}$ of a system. Such an equality became famous as the *Gibbs' phase rule*.

Although it is not possible to establish *a priori* the typology of the various phases that may nucleate in a system we know that their number at given P,T conditions is constrained by the Gibbs' phase rule and their composition by the Gibbs free energy (G) minimization principle:

$$\mathrm{G_{total} = G_{min} = U + PV - TS = H - TS} \tag{1}$$

(where U, V, S and H are internal energy, volume, entropy and enthalpy respectively), when operating at constant P,T conditions or by the Helmholtz free energy minimization:

$$\mathrm{F_{total} = F_{min} = U - TS} \tag{2}$$

when operating at constant V,T conditions.

We also know that that the Gibbs free energy of the system ($\mathrm{G_{total}}$) is composed of all the Gibbs free energies of the various phases in the system itself, defined by the chemical potentials of their components (μ). Algebraically, this is expressed as

$$\mathrm{G_{total}} = \sum_{\mathrm{i}} \mu_{\mathrm{i}} \mathrm{n_i} \tag{3}$$

where $\mathrm{n_i}$ is the number of moles of the $\mathrm{i^{th}}$ component, μ_{i} is its chemical potential, and summation is extended to all components. For a system at constant T and P:

$$\left(\frac{\partial \mathrm{G_{total}}}{\partial \mathrm{n_i}}\right)_{\mathrm{P,T}} = \mu_{\mathrm{i}} \tag{4}$$

Chemical reactions proceed spontaneously in the direction of lowering of chemical potentials, and, based on eqs. 3,4 minimization of chemical potentials correspond to minimization of the Gibbs free energy of the system. The topology of phase diagrams (e.g. the Schreinemaker's projections of stable coexistence) is complicated by the fact that the chemical potential is a "*partial molar property*" i.e. a property whose "local" (partial) values, though referred to one mole of substance (molar) depends in a complex manner by the chemistry of the system. This is due to the fact that the various components interact among themselves in different ways according to the aggregation state (structure, local-, medium- or long-range ordering) of the regions (i.e. "phases") of the system, developing or absorbing heat according to their chemical affinity, eventually developing an excess volume, and so on. To offer a rationale in the interpretation of phase stability in complex systems it is common practice to represent the limiting regions that define the T-X condition of incipient crystallization (i.e. "*liquidus*") or incipient melting (i.e. "*solidus*"), and, eventually, their evolution with P. The use of piecewise linear manifold meshes [1] to model and analyze such hypersurfaces requires discrete versions of differential concepts.

Discrete Differential Geometry - *Normal vectors* can be estimated on non-differentiable surfaces such as triangle meshes. Clearly, internal points of a triangle are locally differentiable, hence their tangent plane is defined and its normal vector can be computed as the normalized cross product of two of the three edges. If necessary, the normal at a vertex can be estimated as a weighted average of the normal vectors at its incident triangles.

Roughly speaking, the *gradient* of a real function defined on a surface is the vector of its partial derivatives, and its magnitude can be interpreted as the "slope" of the function at that point. Hence, the gradient provides a support for the computation of steepest descent paths on surfaces. For the sake of simplicity we introduce the concept for surfaces in $\mathbf{R}^3$, however the gradient can be defined on manifolds of any dimension. Let M *in* $\mathbf{R}^n$ be a *(n-1)*-manifold and $f : M \rightarrow \mathbf{R}$ be a function of class C^k, $k \geq 1$; then, the *gradient* of f is defined as

$$\nabla f := (\partial_{x_1} f, \ldots, \partial_{x_n} f) \tag{5}$$

and its magnitude is the "slope" of f at each point of M.

As shown in [1], the gradient can be estimated on a triangle mesh as well. In this case, the function f is typically associated to the vertices of the mesh, whereas for points belonging to the interior of a higher-order simplex (triangle or edge) a linear combination of the function values at the simplex vertices is normally considered.

The gradient of a real function f defined on a triangle mesh M in R^3 at each vertex position can be estimated as shown in [9]. For the sake of computing steepest descent curves, however, we can calculate the gradient at points inside triangles instead of estimating it at vertices. Note that the interior of each triangle t is differentiable and therein the gradient $\nabla f\,|_t$ is defined everywhere, is constant, and its value can be computed as the solution of the following 3x3 linear system[11]:

$$\begin{pmatrix} \mathbf{p}_j - \mathbf{p}_i \\ \mathbf{p}_k - \mathbf{p}_j \\ \mathbf{N} \end{pmatrix} \nabla f\,|_t = \begin{pmatrix} f(\mathbf{p}_i) - f(\mathbf{p}_j) \\ f(\mathbf{p}_j) - f(\mathbf{p}_k) \\ 0 \end{pmatrix} \quad (6)$$

where t is a triangle made of vertices ($\mathbf{p}_i$, $\mathbf{p}_j$, $\mathbf{p}_k$) and whose normal vector is **N.** $\nabla f\,|_t$ lies on the plane of the triangle and points towards the direction of maximum decrease of f. The gradient estimation in meshes of higher dimensions is a mostly unstudied problem. We provide a general solution for our application in Section 3.

3. Liquidus derivation and analysis

Overview - The operational pipeline that we propose is based on known information about the pure components constituting the material under analysis. Generally speaking we may divide the phases that may form in a system as pertaining to three distinct classes: a) mechanical mixtures; b) mixtures with partial miscibility; c) mixtures with complete miscibility. The term "mixture" (IUPAC notation) stresses that we treat all components in mixture in the same manner (i.e. same standard state of pure component in pure phase at T,P of interest). Mechanical mixtures do not actually mix in any proportion, partial mixtures have only a limited solubility while mixtures with complete miscibility accept all component in any proportion. For the sake of simplicity we will illustrate the case of a ternary system (CaO-Al_2O_3-SiO_2; hereafter CAS system) where at first approximation we may treat all crystalline phases as mechanical mixtures and the liquid as a phase with complete miscibility (though with a discrete P-T dependent miscibility gap; see later). We will disregard for the moment the effect of the intensive variable P, hence we will not deal with the volume properties of the phases (cf. Eq. 1).

In our framework, the domain of all the possible compositions is modelled by a d-simplex, with d+1 being the number of pure components (e.g. d+1 = 3 for the CAS system). For each analysis, the Gibbs free energy is evaluated at a fixed number of uniformly spaced sample points spanning the whole simplex (See step 1 below). Once the Gibbs energy is known for each phase, and at discrete temperatures within the desired ranges, we proceed by applying the convex hull method to extract the compositions that, at any given temperature, coexist in different phases (Step 2). Since these compositions are just samples over the domain of all the possible compositions, we interpolate them using a Delaunay triangulation to reconstruct a piecewise linear approximation of the ideally continuous *liquidus* (Step 3). Within such a simplicial complex, the computation of descent lines may take advantage of a novel gradient-based approach (Step 4).

Note that Steps 2, 3 and 4 in our pipeline make a strong use of concepts from computational geometry. Step 1 does not, but it is described here for completeness of the exposition.

Step 1: Modelling the Gibbs energy for each phase

Aim of this first step is to derive the Gibbs free energy for each possible composition of the pure components at each temperature in a given range. Thus for each temperature T_i we compute the Gibbs free energy of all the possible solids (mechanical mixtures) that may exist at that temperature. Also, we sample the compositional simplex and, for each sample composition, we compute the Gibbs free energy of the liquid at the same temperature T_i.

The input to our process is represented by the *standard state properties* of both the pure components and all the possible solids being combinations of the pure components. In the practice, such input data is measured experimentally, and its total amount can be summarized in a rather small real-valued matrix (32x12 for the CAS system, see Tables A1,2 in Appendix I of [10]).

The Gibbs energy of mechanical mixtures - In mechanical mixtures the Gibbs free energy is simply defined in terms of their standard state properties and heat capacity integrals:

$$G_T = H^0_{f,Tref} + \int_{T_{ref}}^{T} C_P dT - T\left(S^0_{Tref} + \int_{Tref}^{T} \frac{C_P}{T} dT \right) \quad (7)$$

We must anticipate that though we know with sufficient precision the G(T,P) of a (compositionally invariant) mechanical mixture, we have no clues on the local values of the potentials of component in mixture unless we equilibrate the mechanical mixture with another phase in the system of interest. In fact, if two or more phases coexist stably in the system the potentials of a given component is equal in all phases stable at equilibrium. A single computation, based on equation (7) (when working at ambient pressure) and stemming from the standard state thermodynamic data will be generally sufficient for each mechanical mixture nucleating in the system of interest. In our example of the CAS system, the silicate liquid exhibits however complete miscibility at sufficiently high T, with miscibility gaps limited to the high-SiO_2-content regions (see later). We may depict its bulk Gibbs free energy as composed of two distinct terms: - the weighted molar summation (i.e. in terms of molar fractions) of the chemical potentials of the pure liquid components; - the Gibbs free energy of mixing (eventually but not necessarily split into ideal + excess contributions):

$$G_{liquid,T} = \sum_i \mu^0_{i,liquid} X_i + G_{mix,ideal} + G_{mix,excess} \quad (8)$$

The Gibbs energy of liquid mixtures - For the liquid we will use two distinct (but operationally similar) approaches: the Modified Quasi-Chemical Model (hereon MQC) and the Hybrid Polymeric Approach (HPA) whose details are given in [10]. MQC is a well tested model with important applications in Material Science, but it has the disadvantage of requiring high order interactions whose significance cannot be foreseen by the application of first principles. For example, if one wants to reproduce the topology of the liquidus in the CAS system, it is necessary to introduce two ternary parameters [5] to the binary interactions [10].

HPA is perhaps conceptually more complex but it has the advantage of avoiding high order interaction terms and of providing a conceptual rationale in the interpretation of the various forms of energy which concur to the overall stability of the amorphous substance. In the case of the CAS system it may be shown for instance that the previously mentioned ternary terms of the MQC model arise from entropic terms closely related to the Al-avoidance principle and known to hold in crystalline media [6]. Once HPA binary interactions among the various components have been established, there is no need of further "*ad hoc*" parameterization, and the model may be virtually extended to n dimensions with no compositional limit.

The various forms of energy are described in both models by continuous functions (see the relevant equations in [10], Appendix I), but, for computational purposes, it is convenient to select a sampling grid in the system spanning in a uniform way the simplex. The adopted compositional step will depend upon the geometrical complexity of the liquidus and on the degree of accuracy one want to achieve in terms of thermal assessment of bivariant, univariant and invariant points. In the case study we present here (the CaO-Al_2O_3-SiO_2 system; hereon CAS) we sampled the simplex along equally-spaced points differing at percentual level. The simple algorithm adopted is the following.

```
npoint=99
for i=1 to npoint {
  XSiO2=1.0-0.01*i
  tox=0.01*i
  ntimes=npoint*(1-xsio2)+1
  for iratio=0 to ntimes {
    xtimes=(iratio*1.0)/(ntimes*1.0)
    XAl2O3=tox*xtimes
    XCaO=tox-XAl2O3
  }
}
```

It may be conceived as a Toop's projection with the pivotal point represented by the network-former SiO_2. It may be eventually extended to higher compositional dimensions by addition of further nested loops.

Step 2: Deriving the liquidus samples

We recall that, at each point of its domain, the liquidus represents the temperature of incipient crystallization of a substance; in other words, at that temperature the solid coexists stably with the liquid mixture. This condition is verified if (1) the chemical potentials of the solid and the liquid are equal **and** (2) the Gibbs free energy is minimized. In a binary system (i.e. made of two pure components), for example, the compositions for which these two conditions are verified can be derived at a given temperature as follows: first, observe that the compositional domain is a 1-simplex which, in the Euclidean space, is a segment. Thus the Gibbs free energy of the liquid at a given temperature can be plotted as a curve in a 2D chart (see Figure 4, top row). In the same chart, we can add a point for each of the solids existing at that temperature. For each of these "solid" points, we consider the straight line passing through it and being tangent to the "liquid" curve. The tangency point represents a composition where the solid and the liquid coexist stably. For simplicity, in this example we assumed that there are no miscibility gaps. In a 2-dimensional compositional simplex, the straight line becomes a plane, and a liquid and two different solids may coexist stably. The approach can be extended to any dimension.

Common numerical methods to compute phase diagrams based on the minimization of the Gibbs free energy of the system and equality of the chemical potentials of phase components at equilibrium require an initial approximation that is not always simple to tune, and in some cases a wrong choice may significantly spoil the result, especially when splitting solutions are expected [12]. Thus, we employ a more robust approach based on the construction and analysis of convex hulls of the Gibbs energies. To the best of our knowledge, current solutions do not provide evidence of functionality on systems made of more than three components. For ternary systems, examples of use of the convex hull method can be found both in the literature (e.g. [12]) and in experimental software prototypes (e.g. http://matforge.org).

In our pipeline, the method of the convex hulls is dimension-independent and proceeds as follows. First, the Gibbs energies of all the phases at a given temperature T and pressure P computed in Step 1 are considered altogether, and all the sample points are put in a common reference system where the last coordinate identifies the Gibbs energy, whereas the other coordinates identify the composition. Formally, let the system have n components, so that each point x in the compositional domain can be represented using either n barycentric coordinates or $n-1$ Euclidean coordinates within the compositional simplex. Our sampling is defined as $S = \{s_i \in \Re^n : s_i = \langle e_1, e_2, \ldots, e_{n-1}, G_\gamma(\langle e_1, e_2, \ldots, e_{n-1}\rangle)\rangle, i \in [1,k], \gamma \in \text{set of phases}\}$, where k is the number of samples, e_i are the Euclidean coordinates of the composition, and $G_\gamma(x)$ is the Gibbs energy of the composition x in phase γ.

Then, the convex hull Ch(S) of the resulting point cloud S is computed and each non-triangular facet (if any) is triangulated. After this step, the lower hull Lh(S) is extracted by selecting all the facets of the convex hull whose normal points downwards (i.e. the triangles whose normal's last coordinate is negative). The projection D of the lower hull obtained by discarding its last coordinate is a Delaunay triangulation of the compositional domain. From now on, a vertex of D being the projection of a sample of the liquid energy will be called a "liquid" point, whereas a vertex being the projection of a sample of the energy of a solid phase will be called a "solid" point. Depending on the nature of its vertices, each triangle of D determines a region that, for temperature T and pressure P, can either belong to a single-phase, or represent a two- or three-phase equilibrium.

To derive a section of the liquidus at the given T and P, it is sufficient to find all the edges of the triangulation that connect a solid point with a liquid point. Specifically, the interface between solid and liquid phases is tracked by the liquid points of the triangulation which are connected to at least a solid point through an edge. The determination of coexisting liquids is a bit more tricky: in principle, an edge connecting two liquid points may indicate such a coexistence, but in practice we have used a finite sampling of the domain, and therefore an edge may be there simply because the two points are successive samples of the same portion of the energy hypersurface. In order to exclude such "fake" coexistences, besides computing the convex hull of the Gibbs energy samples, we also compute the Delaunay triangulation K of **all** the energy samples projected on the compositional domain, thus including both the vertices of the convex hull and the other "internal" energy points. Then, we declare that two liquids coexist only if their points are connected by an edge of D which is not in K.

In our implementation, the freely available qhull software is used to compute convex hulls [2].

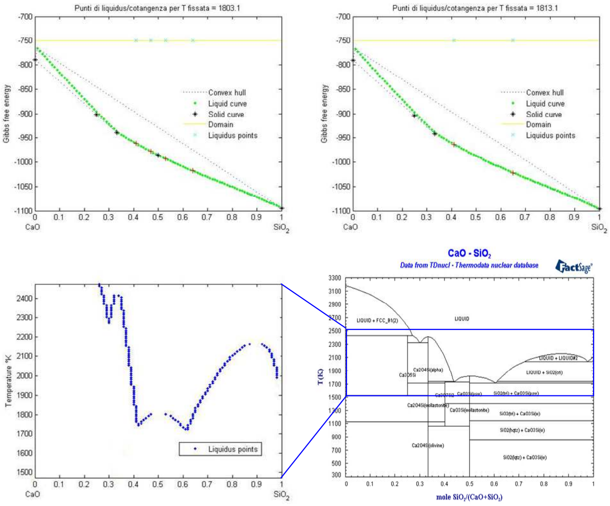

Figure 1: *Example of application of the convex hull method in a binary system. In the top row the convex hull is computed for the energy points of all the phases evaluated at 1803.1 K (left) and 1813.1 K (right). In both the cases the red dots indicate liquid points which are connected to solid points through an edge. By performing the same task at all the temperatures in the range 1500 K – 2500 K with a step of 10 K, our algorithm could track the liquidus curve (bottom-left). The result of the FactSage software is reported for comparison (bottom-right).*

Step 3: Interpolating the samples

After having repeated step 2 for each temperature and pressure within the range of interest, the resulting samples can be interpolated to define an explicit topology of the phase diagram. Once again, the Delaunay triangulation of the samples appears to be the best choice as it guarantees well-shaped simplexes for robust computation. As an example, we have interpolated the liquidus samples computed as described in step 2 for a CAS system in a range of temperatures from 1400 C to 2600 C and at constant pressure. The result is shown in Figure 2.

The CGAL library provides excellent implementations of Delaunay triangulation algorithms for any dimension (see [4] for details on the algorithms and their complexity).

Step 4: Gradient-based calculation of descent lines

Being able to correctly identify the direction of steepest descent on the liquidus is important, and in some cases it might also help in the determination of the crystallization path (e.g. on cotectic lines connecting primary phase surfaces in ternary systems). Thus, we derived a formal approach to compute such a direction.

At each point within the simplicial complex, the steepest descent direction is given by the inverse of the gradient vector. Since the function to be minimized is defined at a discrete set of sample points (i.e. the vertices of the simplicial complex), we need a procedure to estimate the gradient at all the other points of the domain. When the gradient in known, tracking the path reduces to computing a sequence of points of intersection of the path itself with non-maximal simplexes. Since deriving the gradient is a constant-time task, tracking the path costs O(n_p) operations, where n_p is the number of simplexes traversed by the path.

In order to estimate the gradient within simplexes of any dimension we assume that the function value within such simplexes is a linear interpolation of the value at its vertices. Having said that, the gradient can be assumed to be constant across all the inner points of any simplex, and can be derived as follows.

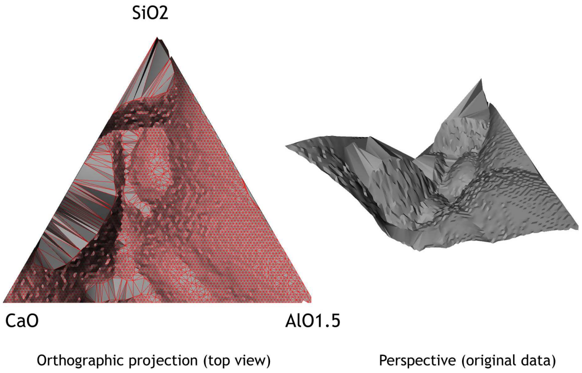

Figure 2: *Liquidus of a CAS system in a range of temperatures between 1400 C and 2600 C at constant pressure.*

Gradient Estimation within Euclidean simplexes

Our aim is to find the gradient vector of the piecewise linear function $f : \mathbb{R}^n \longrightarrow \mathbb{R}$ on a simplex defined by *n+1* vertices, let them be $\mathbf{p}^1 = (p_1^1, \ldots, p_n^1), \ldots, \mathbf{p}^{n+1} = (p_1^{n+1}, \ldots, p_n^{n+1})$.

With the following described method we are able to give the analytic form, inside a simplex, of the (linear) function f instead, and so the gradient vector is defined as:

$$\nabla f(\mathbf{x}) = (\frac{\partial f}{\partial x_1}, \frac{\partial f}{\partial x_2}, \ldots, \frac{\partial f}{\partial x_n}).$$

Step by step, a general idea of the gradient evaluation process is:

1. $f : \mathbb{R}^n \longrightarrow \mathbb{R}$ is explicitly defined just at mesh vertices;
2. linear interpolation is assumed for points internal to each simplex;
3. inside each simplex, the analytic form of *f* is computed;
4. finally, the *n* gradient vector coordinates are extrapolated (first *n* coefficients of analytic form).

When considered with its associated function *f*, an *n*-dimensional simplex in $\mathbf{R^n}$ can be embedded in an (*n+1*)-dimensional space where the additional coordinate represents the value of *f*. Within such a space, the hyperplane containing the simplex has the following analytical form:

$$\begin{vmatrix} x_1 & \cdots & x_n & f(x_1, \ldots, x_n) & 1 \\ p_1^1 & \cdots & p_n^1 & f(p_1^1, \ldots, p_n^1) & 1 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ p_1^{n+1} & \cdots & p_n^{n+1} & f(p_1^{n+1}, \ldots, p_n^{n+1}) & 1 \end{vmatrix} = 0.$$

By resolving the determinant, for example with respect to the first row, we obtain the following expression of the plane:

$$\lambda_1 x_1 + \ldots + \lambda_n x_n - \lambda_{n+1} f(x_1, \ldots, x_n) + \lambda_0 = 0,$$

where λ are real numbers. The above expression can be rewritten as:

$$f(x_1, \ldots, x_n) = \frac{\lambda_1}{\lambda_{n+1}} x_1 + \ldots + \frac{\lambda_n}{\lambda_{n+1}} x_n + \frac{\lambda_0}{\lambda_{n+1}},$$

which is the analytic form of the function *f* within the simplex. Thus, the gradient vector within the simplex can be estimated using the following expression:

$$\nabla f(\mathbf{x}) = (\frac{\partial f}{\partial x_1}, \ldots, \frac{\partial f}{\partial x_n}) = (\frac{\lambda_1}{\lambda_{n+1}}, \ldots, \frac{\lambda_n}{\lambda_{n+1}}).$$

Conclusions

Though the role of computational geometry in the study of phase diagrams is well established, we have shown that its potential impact might be more significant than expected. The exploitation of simplicial meshes to model the system proved to be useful in many aspects, starting from pure visualization issues, up to the development of robust algorithms to track lines of descent. Furthermore, the method of the convex hull employed to track isobaric-isothermal sections can be extended to systems of any dimension and, differently from standard approaches, does not require any initial approximation to be set and is less sensitive to numerical issues. Thus, simplicial meshes and the convex hull method are promising tools to be further investigated in the context of multi-dimensional systems.

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