Generic Aspects of Convexification
with Applications to Thermodynamic Equilibrium

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Abstract

This work presents a mathematical analysis of the process of convexification of a smooth function based on singularity theory. The theory developed is applied to the problem of thermodynamic phase equilibrium. The central notion introduced here is that of phase simplex, which we use to discuss phase equilibrium and phase transition in an abstract framework. One of the by-products of the results of this paper is a rigorous proof of Gibbs’ Phase Rule for multicomponent systems, in which a well-accepted mathematical notion of genericity is used to account for ostensible exceptions to the rule. Also, many other features known from theoretical or experimental thermodynamics can be rediscovered through purely mathematical arguments from the notions introduced here. Such features include, among other things, the existence of saturation pressures, the existence of multiple or critical points, and the existence of spontaneous or continuous changes in the composition of the phases at phase transitions.

1. Introduction

Given an extended real-valued function (a potential) \( E : \mathbb{R}^n \to (-\infty, \infty] \), the convex envelope (or convex hull) \( \text{conv} E \) of \( E \) is the largest convex function...
majorized by $E$ on $R^n$. It is one of the aims of this paper to analyze in some detail the mechanism of construction of $\text{conv } E$ in terms of $E$ under additional smoothness assumptions. After having established that this mechanism obeys very precise rules under appropriate assumptions on $E$ of a generic nature, we shall demonstrate that knowledge of these rules allows us to describe mathematically and to explain many phenomena intimately related to phase splitting at thermodynamic equilibrium, including phase transition. A rigorous proof of Gibbs's Phase Rule for multicomponent systems will also be obtained as a by-product.

The starting point of our analysis is the theorem of Carathéodory (cf., [22]) saying that, for $d \in R^n$, $(\text{conv } E)(d)$ can be computed through the formula

$$
(\text{conv } E)(d) = \inf \sum_{i=1}^{q} \lambda_i E(d^i),
$$

(1.1)

where the infimum is taken over all convex combinations $d = \sum_{i=1}^{q} \lambda_i d^i$ with $q \geq 1$, $0 < \lambda_i \leq 1$, $d^i \in R^n$ and $d^i \neq d^j$ for $i \neq j$. Carathéodory's Theorem also asserts that we may assume that $q \leq n + 1$ with no loss of generality.

Under general conditions frequently met in the applications, the infimum in (1.1) is always a minimum for $d \in \text{conv}(\text{dom}(E))$, the convex hull of $\text{dom}(E) = \{\delta \in R^n : E(\delta) < \infty\}$. For reasons that will be fully justified by our applications we shall call a stable phase splitting of $d$ any convex combination $d = \sum_{i=1}^{q} \lambda_i d^i$ for which the minimum in (1.1) is achieved. In this definition, we understand that $\lambda_i > 0$ and $d^i \neq d^j$ for $i \neq j$, but we do not require that $q \leq n + 1$.

In accord with the definition of a stable phase splitting, we may call $d^1, \ldots, d^q$ the phases of $d$. Doing so, we face the obvious ambiguity that such phases are not defined in a unique way, as elementary one-dimensional examples show. However, we shall see that uniqueness of a stable phase splitting is nevertheless valid for every $d \in \text{int}(\text{conv}(\text{dom}(E))) = \text{int}(\text{dom}(\text{conv } E))$ for a generic choice of $E$. Our precise notion of genericity is defined in Section 3.

Actually, the aforementioned uniqueness property is a corollary to the result fundamental to our analysis, which says that, for a generic choice of $E$, any stable phase splitting $d = \sum_{i=1}^{q} \lambda_i d^i$ is such that $\text{conv}\{d^1, \ldots, d^q\}$ is a $(q - 1)$-simplex, the phase simplex $\Sigma(d)$ of $d$. The proof of this assertion is based on Mather's multijet version of Thom's Transversality Theorem. As a result, no minimizer exists with $q > n + 1$ in the generic case. Thus, the inequality $q \leq n + 1$ not only may, but must hold.

The notion of a phase simplex along with the uniqueness of the phases (for a generic choice of $E$, as implicitly assumed in all subsequent comments) makes it possible to consider questions related to phase transitions, questions that we examine in an abstract framework. Indeed, since there is no ambiguity in defining $\phi(d)$ as the number of phases of $d \in \text{int}(\text{dom}(\text{conv } E))$, we may say that $d$ is a point of phase bifurcation if $\phi$ is not locally constant near $d$. Our choice of the terminology "phase bifurcation" over "phase transition" is only meant to emphasize some analogies with standard bifurcation phenomena, which should appear clearly later on.