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PRESSURE LAWS AND FAST LEGENDRE TRANSFORM

P. HELLUY, H. MATHIS

ABSTRACT. In this paper we investigate algorithms based on the Fast Legendre Transform (FLT) in order to compute tabulated equation of state for fluids with phase transition. The equation of state of a binary mixture is given by an energy minimization principle. According to the miscible or immiscible nature of the mixture, the energy of the system is either a convex envelope or an inf-convolution of the energies of the phases. Because these operations are closely linked to the Legendre transform, it is possible to construct $O(N)$ algorithms that compute efficiently these operations, where N is the number of points in the table. In addition, it appears that the natural mathematical tool for studying mixture thermodynamics in the Legendre space is the max-plus algebra theory.

INTRODUCTION

We are interested in the modelling of compressible fluids that can present phase transitions. The dynamical evolution of such fluids is described by the principles of conservation of mass, momentum and energy, that form the Euler system of conservation laws. This system has to be closed by an Equation Of State (EOS) able to depict the thermodynamical behaviour of the fluid. Physical principles of thermodynamics require the EOS to satisfy certain convexity constraints, that ensure, for instance, the hyperbolicity of the Euler system.

The standard van der Waals equation is a classical model for fluids with phase transition. However, this EOS is not convex in the whole state space. It causes the fluid equations to be a mixed hyperbolic/elliptic type [MP89]. An admissible pressure law is obtained by applying the Maxwell equal-area rule. It appears that this construction is equivalent to compute the convex hull of the van der Waals energy. The same problem may appear when one wants to mix several phases with different EOS. Standard approximation tools, such as polynomial interpolation, generally do not preserve convexity and may lead to unphysical behavior.

The main result of our work is that the good mathematical framework for constructing admissible EOS is the theory of the so-called max-plus algebra [Mas87], which is itself closely related to the Legendre-Fenchel transformation. This tool is classically applied to optimal control problems or in probability theory. Once this framework is set, natural numerical algorithms can be constructed in order to properly approximate real EOS.

The outlines of this paper are the following.

In the section 1, we recall the thermodynamics of a single fluid. The internal energy is a convex function of the entropy and the volume of the fluid, either in terms of extensive or intensive parameters. Then we investigate

the thermodynamics of mixtures. First we consider immiscible mixture of two phases of a same pure body as in [HS06]. According to the minimum energy principle, the mixture energy turns to be the inf-convolution of both energies, in extensive variables. In terms of intensive variables the mixture energy is the convex hull of the minimum of the two surfaces defined by the energies of both phases. This property is studied by Facanoni in her thesis [AF07]. A similar analysis is performed in the case of miscible mixture. The mixture energy comes down to be an inf-convolution operation both in terms of extensive and intensive parameters.

As it is noticed in [HS06] the equilibrium energy can be related to classical operations in convex analysis that are the inf-convolution and the Legendre transform. These two operations are closely linked: the inf-convolution is transformed into an addition by the Legendre transform. Moreover applying twice a Legendre transform to any function turns out to be the convex hull of the function. This operation has thus an interest in the computation of equilibrium state laws. Besides, as the Fourier transform, the Legendre transform can be computed by a fast linear-time algorithm (see [Br89], [Lu96], [Lu98]). In Section 2 general properties about the Legendre transform are recalled and an efficient algorithm is provided.

The Section 3 is devoted to the numerical application of the linear-time algorithm in the thermodynamical framework. First we point out that the FLT can be used to very easily and naturally perform many changes of variables. This fact is applied to the computation of isothermal curves. Then we compute the equilibrium of two phases satisfying the perfect gas law. The results are in agreement with those available in [JA01] or [HS06]. Our algorithm is also applied to the van der Waals EOS: applying twice the Legendre transform is equivalent to a convexification process. It is also equivalent to apply the equal-area rule in the Maxwell construction. Finally we propose a three-phase mixture example in order to illustrate the generality of our approach.

1. PHASE TRANSITION THERMODYNAMICS

1.1. Single fluid thermodynamics. We consider a pure body of mass $M \geq 0$, entropy $S \geq 0$, occupying a volume $V \geq 0$. We assume the system to be entirely described by its state vector:

$$W = (M, S, V) \in C.$$

The set C is the set of admissible states. It is a closed convex cone of \mathbb{R}^3 defined by

$$C = \{W = (M, S, V), M \geq 0, S \geq 0, V \geq 0\}.$$

Remark 1. *The positivity of the entropy S is ensured by the less known Nernst third law of thermodynamics (see [Ca85]).*

It is classical in thermodynamics to distinguish between extensive and intensive quantities.

Definition 1. *Let F be an application from C into \mathbb{R}^+ . The quantity F is said to be an extensive variable iff F is Positively Homogeneous of degree*

one (PH1 in short), i.e.

$$(1.1) \quad \forall \lambda \in \mathbb{R}^+, \forall W \in C, F(\lambda W) = \lambda F(W).$$

Definition 2. Let F be an application from C into \mathbb{R}^+ . The quantity F is said to be an intensive variable iff F is Positively Homogeneous of degree zero (PH0 in short), i.e.

$$(1.2) \quad \forall \lambda \in \mathbb{R}^+, \forall W \in C, F(\lambda W) = F(W).$$

By taking the ratio of two components of W , it is possible to construct several intensive variables, either molar or volumic ones:

- the specific volume: $\tau = \frac{V}{M}$,
- the specific entropy: $s = \frac{S}{M}$,
- the density: $\rho = 1/\tau = \frac{M}{V}$,
- the volumic entropy: $\sigma = \rho s = \frac{S}{V}$.

Although it is usual to consider the system through its entropy function [HS06], we decide here to describe it by its internal energy E . The thermodynamical behavior of the system is entirely described by the energy function

$$E : (M, S, V) \rightarrow E(M, S, V).$$

We enunciate here the main features of a fluid energy (for physical justifications, we refer to [Ca85]).

Postulat 1. The energy E satisfies the following properties:

- E is extensive (which implies that it is a positive quantity):

$$\forall \lambda > 0, \forall W \in C, E(\lambda W) = \lambda E(W).$$

- E is convex with respect to $W = (M, S, V)$.

Assuming that E is continuously differentiable we can define the temperature, the thermodynamical pressure and the chemical potential (or Gibbs potential) of the fluid:

$$(1.3) \quad T = \frac{\partial E}{\partial S},$$

$$(1.4) \quad p = -\frac{\partial E}{\partial V},$$

$$(1.5) \quad \mu = \frac{\partial E}{\partial M}.$$

We recover then the classical relation of thermodynamics in extensive variables:

$$(1.6) \quad dE = TdS - pdV + \mu dM.$$

As gradients of a PH1 function, these parameters are PH0 functions or so-called intensive variables. It is also possible to give an intensive form of the energy, either a molar form:

$$(1.7) \quad \epsilon(\tau, s) = E \left(1, \frac{S}{M}, \frac{V}{M} \right) = \frac{E}{M},$$

or a volumic form:

$$(1.8) \quad \varepsilon(\rho, \sigma) = \rho\epsilon = \frac{E}{V}.$$

The intensive formulation of the fundamental relation reads as follow:

$$(1.9) \quad d\epsilon = Tds - pd\tau.$$

From the definition, we have the following result

Proposition 1. *The equation of state $\epsilon = \epsilon(\tau, s)$ is a convex function of τ and s . Moreover the volumic internal energy $\varepsilon = \varepsilon(\rho, \sigma)$ is also a convex function of ρ and σ .*

We suppose ϵ and ε to be \mathcal{C}^2 strictly convex functions for a pure phase, liquid or vapour. That is not anymore true in the case of two phase mixture, see section 1.2.

1.2. Immiscible mixtures. We consider now two phases of the same pure body. Each phase is characterized by its own energy function E_i , $i = 1, 2$, depending on the state $W_i \in C$. The extensive variables for the whole system are:

$$(1.10) \quad M = M_1 + M_2,$$

$$(1.11) \quad S = S_1 + S_2.$$

If the two phases are immiscible, we have also:

$$(1.12) \quad V = V_1 + V_2.$$

In the thermodynamics framework it is common practice to enunciate the entropy maximum postulate or in a like manner the energy minimum principle:

Postulat 2. *Out of equilibrium, the energy of the system reads:*

$$E(W_1, W_2) = E_1(W_1) + E_2(W_2).$$

At equilibrium, the energy of the system tends to decrease down to a minimum value, i.e.

$$(1.13) \quad E(W) = \min_{(W_1, W_2) \in \Omega} E(W_1, W_2)$$

$$(1.14) \quad \text{with } (X_1, X_2) \in \Omega \iff \begin{cases} (M_1, S_1, V_1) \in C, \\ (M_2, S_2, V_2) \in C, \\ M_1 + M_2 = M, \\ S_1 + S_2 = S, \\ V_1 + V_2 = V. \end{cases}$$

Because the set of constraints Ω is a compact and the energy E is smooth, the convex optimization problem is well-posed. Existence of a global minimum is ensured for such convex function. The minimization problem can be summed up by:

$$(1.15) \quad E(W) = \min_{W_1 \in Q} E_1(W_1) + E_2(W - W_1)$$

$$(1.16) \quad \text{with } W_1 = (M_1, S_1, V_1) \in Q \iff \begin{cases} 0 \leq M_1 \leq M, \\ 0 \leq S_1 \leq S, \\ 0 \leq V_1 \leq V. \end{cases}$$

If we assume that outside the cone C the energies are extended by $+\infty$:

$$(1.17) \quad E_i(W) = \begin{cases} E_i(W) & \text{if } W \in C, \\ +\infty & \text{elsewhere.} \end{cases}$$

Then the equilibrium energy is defined by :

$$(1.18) \quad \mathcal{E}(W) = E_1 \square E_2 (W) = \min_{W_1 \in \mathbb{R}^3} (E_1(W_1) + E_2(W - W_1)),$$

where the symbol \square stands for the inf-convolution operation.

The inf-convolution operation possesses many properties. For instance :

- it ensures the existence and the convexity of the equilibrium energy E ,
- it is closely related to the Legendre-Fenchel operation.

Some basic definitions and properties about these two operations are developed in section 2.1. Moreover it exists fast algorithms to compute inf-convolution and Legendre-Fenchel operations. Such an algorithm is detailed in section 2.3 and is applied to approximate equilibrium pressure law when analytical expression cannot be found (see Section 3).

The optimization process can be written in terms of the intensive variables. Moreover it is possible to give a geometrical interpretation of the intensive mixture energy. To begin let us recall a definition of the convex hull of a function:

Definition 3. For a given function f , minorized by an affine map, the (closed) convex hull of f denoted by $co(f)$ is

$$co(f)(x) := \sup\{g(x), g \text{ affine}, g \leq f\}.$$

It is usual in convex analysis to link optimization problem to convexification process. The following result is introduced in [Ca85], [JA01] and noticeably detailed in [AF07].

Theorem 1. At equilibrium the surface of the mixture energy ϵ is the closed convex hull of the energies ϵ_1 and ϵ_2 , that is:

$$(1.19) \quad \epsilon = co(\min(\epsilon_1, \epsilon_2)).$$

Proof. We introduce the volume fraction α , the mass fraction φ and the entropy fraction ζ defined by:

$$(1.20) \quad 0 \leq \alpha = \frac{V_1}{V} \leq 1, \quad 0 \leq \varphi = \frac{M_1}{M} \leq 1, \quad 0 \leq \zeta = \frac{S_1}{S} \leq 1.$$

The specific volume and specific entropy of a phase i , $i = 1, 2$, reads thus:

$$\tau_i = \frac{V_i}{M_i}, \quad s_i = \frac{S_i}{M_i},$$

in other words:

$$(1.21) \quad \tau_1 = \frac{\alpha}{\varphi} \tau, \quad \tau_2 = \frac{1-\alpha}{1-\varphi} \tau,$$

$$(1.22) \quad s_1 = \frac{\zeta}{\varphi} s, \quad s_2 = \frac{1-\zeta}{1-\varphi} s.$$

By the way we can notice that $0 \leq \tau_i \leq \tau$ and $0 \leq s_i \leq s$. At equilibrium the mixture energy reads:

$$E(W) = \min_{W_1 \in Q} E_1(W_1) + E_2(W - W_1).$$

Because E and E_i are PH0 functions, we can divide by the total mass to obtain an intensive formulation.

We set:

$$\begin{aligned} \epsilon(\tau, s, \alpha, \varphi, \zeta) &= \frac{1}{M} (E_1(M_1, S_1, V_1) + E_2(M_2, S_2, V_2)) \\ (1.23) \quad &= \varphi \epsilon_1 \left(\frac{\alpha}{\varphi} \tau, \frac{\zeta}{\varphi} s \right) + (1 - \varphi) \epsilon_2 \left(\frac{1 - \alpha}{1 - \varphi} \tau, \frac{1 - \zeta}{1 - \varphi} s \right). \end{aligned}$$

The equilibrium specific energy is obtained after minimization with respect to $(\alpha, \varphi, \zeta) \in [0, 1]^3$. Let $(\alpha, \varphi, \zeta) \in [0, 1]^3$ be a triplet achieving the minimization, then we set

$$(1.24) \quad \epsilon_{eq}(\tau, s) = \epsilon(\tau, s, \alpha(\tau, s), \varphi(\tau, s), \zeta(\tau, s)).$$

Usually the minimum is reached on the boundary of the constraints $\alpha = \varphi = \zeta = 0$ or $\alpha = \varphi = \zeta = 1$, thus only one phase is stable. If the minimum is reached in the interior of the constraint set, *i.e.* alle the fractions satisfy $(\alpha, \varphi, \zeta) \in]0, 1[^3$, the gradient of ϵ must be zero, that is:

$$(1.25) \quad \epsilon_\alpha = \tau(-p_1 + p_2) = 0,$$

$$(1.26) \quad \epsilon_\zeta = s(T_1 - T_2) = 0,$$

$$(1.27) \quad \epsilon_\varphi = (\mu_1 - \mu_2) = 0.$$

The equilibrium corresponds then to the equality of the pressures, temperatures and Gibbs potentials of the two phases. Let us denote $\epsilon_1(\tau_1, s_1)$ the state for which $\alpha = \varphi = \zeta = 1$, and $\epsilon_2(\tau_2, s_2)$ the one for $\alpha = \varphi = \zeta = 0$. Let N_1 (resp. N_2) be a point belonging to the surface \mathcal{E}_1 (resp. \mathcal{E}_2) of equation $\epsilon_1(\tau_1, s_1)$ (resp. $\epsilon_2(\tau_2, s_2)$) and N a point in the mixture area given by the equation $\epsilon_{eq}(\tau, s)$. Then

$$\begin{aligned} &N_1(\tau_1, s_1, \epsilon_1(\tau_1, s_1)), \\ &N_2(\tau_2, s_2, \epsilon_2(\tau_2, s_2)), \\ &N(\tau, s, \epsilon_{eq}(\tau, s)). \end{aligned}$$

The points N_1 , N_2 and N are aligned, because:

$$(1.28) \quad \begin{cases} \tau = \varphi \tau_1 + (1 - \varphi) \tau_2, \\ s = \varphi s_1 + (1 - \varphi) s_2, \\ \epsilon_{eq}(\tau, s) = \varphi \epsilon_1(\tau, s) + (1 - \varphi) \epsilon_2(\tau, s). \end{cases}$$

It is easy to check that

$$\begin{aligned} \frac{\partial \epsilon_{eq}}{\partial \tau} &= p = p_1 = p_2, \\ \frac{\partial \epsilon_{eq}}{\partial s} &= T = T_1 = T_2 \end{aligned}$$

The segment defined by the set of points satisfying (1.28) is thus tangent to \mathcal{E}_1 at N_1 and tangent to \mathcal{E}_2 at N_2 (because of the relations (1.25)-(1.27)). Therefore each state $(\alpha, \varphi, \zeta) \in [0, 1]^3$ minimizing ϵ belongs to a bitangent plane tangent to \mathcal{E}_1 at N_1 and tangent to \mathcal{E}_2 at N_2 . The mixture energy is

thus the convex hull of $\min(\epsilon_1, \epsilon_2)$. We can notice that the function ϵ is not \mathcal{C}^2 but merely \mathcal{C}^1 (see [AF07]). \square

Remark 2. *In section 2 we provide a more general proof based on the properties of the inf-convolution and the Legendre transform.*

In the sequel we use the following notation:

Definition 4. *Considering two phases of energies ϵ_i , $i = 1, 2$, the immiscible mixture energy is denoted:*

$$(1.29) \quad \epsilon_1 | \epsilon_2 := \text{co}(\min(\epsilon_1, \epsilon_2)).$$

It would be convenient to deal with the convex change of variables:

$$\epsilon_i(\rho_i, \sigma_i) \rightarrow \epsilon_i(\tau_i, s_i), \quad i = 1, 2.$$

such that $\rho_i = \frac{1}{\tau_i}$, $\sigma_i = \rho_i s_i$. The theorem (1) enunciates in like manner:

Theorem 2. *At equilibrium the surface of the mixture energy ϵ is the closed convex hull of the surfaces ϵ_1 and ϵ_2 , that is:*

$$(1.30) \quad \epsilon = \text{co}(\min(\epsilon_1, \epsilon_2)).$$

Proof. Using the fractions introduced in proof 1.2, we set:

$$(1.31) \quad \begin{aligned} \epsilon(\rho, \sigma, \alpha, \varphi, \zeta) &= \frac{1}{V} (E_1(M_1, S_1, V_1) + E_2(M_2, S_2, V_2)) \\ &= \alpha \epsilon_1 \left(\frac{\varphi}{\alpha} \rho, \frac{\zeta}{\alpha} \sigma \right) (1 - \alpha) \epsilon_2 \left(\frac{1 - \varphi}{1 - \alpha} \rho, \frac{1 - \zeta}{1 - \alpha} \sigma \right). \end{aligned}$$

The equilibrium energy ϵ is obtained after minimization with respect to $(\alpha, \varphi, \zeta) \in [0, 1]^3$. Thanks to the arguments provided in the proof 1.2, the mixture energy ϵ is a convex hull of $\min(\epsilon_1, \epsilon_2)$. \square

1.3. Miscible mixtures. We consider now two phases of a same pure body, totally described by their energies E_i , $i = 1, 2$. As in the immiscible case each phase is characterized by its vector W_i of parameters: $W_i = (M_i, S_i, V_i) \in C$. Because the two fluids are perfectly miscible, they can occupy the whole volume. The set of constraints Ω is thus slightly changed:

$$(1.32) \quad (W_1, W_2) \in \Omega \iff \begin{cases} (M_1, V_1, S_1) \in C, \\ (M_2, V_2, S_2) \in C, \\ M_1 + M_2 = M, \\ S_1 + S_2 = S, \\ V_1 = V, \\ V_2 = V. \end{cases}$$

Eliminating W_2 , the mixture energy is again an inf-convolution of E_1 and E_2 :

Proposition 2. *Considering $Z_1 = (M_1, S_1) \in Q$ with*

$$Q = \{(M_i, S_i), 0 \leq M_i \leq M, 0 \leq S_i \leq S\},$$

we extend the energies E_i such that:

$$(1.33) \quad E_i(Z, V) = \begin{cases} E_i(Z, V) & \text{if } Z \geq 0, \\ +\infty & \text{elsewhere.} \end{cases}$$

Then the equilibrium energy reads:

$$(1.34) \quad \begin{aligned} E(Z, V) &= (E_1 \square E_2)(Z, V) \\ &= \min_{Z_1 \in Q} E_1(Z_1, V) + E_2(Z - Z_1, V). \end{aligned}$$

Using the fact that E_i are PH1 functions, we can define an intensive formulation:

Theorem 3. *The specific energy of a miscible mixture is given by an inf-convolution operation:*

$$(1.35) \quad \varepsilon(\rho, \sigma) = \varepsilon_1 \square \varepsilon_2(\rho, \sigma)$$

$$(1.36) \quad = \min_{(\rho_1, \sigma_1) \in D} \varepsilon_1(\rho_1, \sigma_1) + \varepsilon_2(\rho - \rho_1, \sigma - \sigma_1)$$

with, for $i = 1, 2$,

$$(1.37) \quad \begin{aligned} \sigma_i &= \rho_i s_i, \\ D &= \{(\rho_i, \sigma_i), 0 \leq \rho_i \leq \rho, 0 \leq \sigma_i \leq \sigma\}, \\ \varepsilon_i(\rho_i, \sigma_i) &= \varepsilon_i(\tau_i, s_i). \end{aligned}$$

Proof. We consider the mixture energy in extensive variables given by formula (1.34). Because it is a PH1 function, we can divide by the fixed volume V to get:

$$(1.38) \quad \begin{aligned} E\left(\frac{M}{V}, \frac{S}{V}, 1\right) &= \\ \min_{(M_1, S_1) \in Q} E_1\left(\frac{M_1}{V}, \frac{S_1}{V}, 1\right) &+ E_2\left(\frac{M - M_1}{V}, \frac{S - S_1}{V}, 1\right). \end{aligned}$$

Using the notations (1.37), the intensive formulation is straightforward. \square

We can notice the following proposition

Proposition 3. *If the mixture is perfectly miscible, then at equilibrium*

$$(1.39) \quad \mu_1 = \mu_2,$$

$$(1.40) \quad T_1 = T_2,$$

$$(1.41) \quad p = p_1 + p_2.$$

The last relation is called the Dalton law.

2. FAST LEGENDRE TRANSFORM

2.1. Basic definitions and properties. In this section Legendre transform (LT) is investigated and an efficient algorithm to compute Fast Legendre Transform (FLT) is provided. The Legendre transform is a well-known operation in the thermodynamical framework. Besides it takes place in physical process described in Section 1. Let us consider two fluids of energy ε_i , $i = 1, 2$, then,

- if the two phases are miscible, the mixture energy is the inf-convolution of the two energies:

$$\varepsilon = \varepsilon_1 \square \varepsilon_2,$$

- if the mixture is immiscible, the global energy is the convex hull of the minimum of the two energies:

$$\varepsilon = \varepsilon_1 \mid \varepsilon_2.$$

Applying twice the LT algorithm to any regular function turns out to give the convex hull of the function. To begin we sum up basic ideas and properties of Legendre transform. For more details we refer for instance to Hiriart-Urruty and Lemaréchal [HL01].

Definition 5. Let $f : \mathbb{R}^n \rightarrow \mathbb{R} \cup \{+\infty\}$ a (non necessarily convex) function such that

- $\exists x \in \mathbb{R}^n, f(x) \neq +\infty$ (then f is said to be a proper function),
- there exists an affine function minimizing f on \mathbb{R}^n ,

then f is said to be an admissible function.

It implies that $f(x) > -\infty, \forall x \in \mathbb{R}^n$, and in particular, if f is a convex function, there is always an affine function minimizing f .

Definition 6. Let $f : \mathbb{R}^n \rightarrow \mathbb{R} \cup \{+\infty\}$ be an admissible function. Its conjugate (or Legendre or Fenchel transform) f^* is given by:

$$(2.1) \quad f^* : s \in \mathbb{R}^n \rightarrow \mathbb{R}$$

$$(2.2) \quad s \mapsto \sup_{x \in \mathbb{R}^n} \{ \langle s, x \rangle - f(x) \}.$$

where $\langle \cdot, \cdot \rangle$ denotes the scalar product on \mathbb{R}^n .

We can notice that $\forall s \in \mathbb{R}^n, f^*(s) > -\infty$ and that f^* is an admissible function.

Proposition 4. Let f be an admissible function. Then the conjugate f^* is a lower semi-continuous everywhere (or closed) convex function.

Let us provide two examples using piecewise linear functions.

Example 1. We consider $\mathbb{I}_{[a,b]}$ the convex indicator function of the interval $[a, b] \subset \mathbb{R}$:

$$\mathbb{I}_{[a,b]}(x) = \begin{cases} 0 & \text{if } a \leq x \leq b, \\ +\infty, & \text{elsewhere.} \end{cases}$$

Then

$$(\mathbb{I}_{[a,b]})^*(\chi) = \sup_{x \in \mathbb{R}} (\chi x - \mathbb{I}_{[a,b]}(x)) = \sup_{x \in [a,b]} \chi x.$$

In other words:

$$(\mathbb{I}_{[a,b]})^*(\chi) = \begin{cases} 0, & \text{if } \chi = 0, \\ a\chi, & \text{if } \chi < 0, \\ b\chi, & \text{if } \chi > 0. \end{cases}$$

Example 2. Let us consider the absolute value function on a certain domain $[a, b]$ ($a < 0 < b$):

$$f(x) = \begin{cases} -x, & \text{if } a \leq x \leq 0, \\ x, & \text{if } 0 \leq x \leq b, \\ +\infty, & \text{elsewhere.} \end{cases}$$

Then f^* is the zero-function on $[-1, 1]$ i.e.:

$$f^*(s) = \begin{cases} as - 1, & \text{if } s \leq -1, \\ 0, & \text{if } -1 \leq s \leq 1, \\ bs - 1, & \text{if } s \geq 1. \end{cases}$$

Following the definition, some properties are straitforward:

Proposition 5. *Let f be an admissible function and let f^{**} the biconjugate of the function f :*

$$\forall x \in \mathbb{R}^n, f^{**}(x) = (f^*)^*(s) = \sup\{\langle s, x \rangle - f^*(s) \mid s \in \mathbb{R}^n\}.$$

*Then the biconjugate f^{**} is also the closed convex hull of f : $f^{**} = co(f)$.*

In order to compute the mixture energy in the immiscible case, the LT operation can thus be applied twice. According to the following result, the inf-convolution operation that defines the energy of a miscible mixture can be expressed in terms of Legendre transform too:

Proposition 6. *Let f_1 and f_2 be two admissible functions. Then their inf-convolution satisfies*

$$(f_1 \square f_2)^* = f_1^* + f_2^*,$$

and conversely:

Proposition 7. *Let f_1 and f_2 be two admissible functions. The conjugate of their sum is:*

$$(f_1 + f_2)^* = f_1^* \square f_2^*.$$

The Legendre transform being an involutive operation for convex lsc functions, it ensures that if f_1 and f_2 are convex lsc:

$$(2.3) \quad (f_1 \square f_2) = (f_1^* + f_2^*)^*.$$

Proposition 8. *Let f_1 and f_2 be two admissible functions. The conjugate of their min is the max of their conjugates, that is:*

$$(\min(f_1, f_2))^* = (co(\min(f_1, f_2)))^* = \max(f_1^*, f_2^*).$$

Thanks to these properties we provide another proof of theorem (1).

Proof of theorem 1. We consider an immiscible mixture of two phases described by their extensive energies E_i , $i = 1, 2$. Because the Legendre transform is an involutive operation, it satisfies:

$$E^{**} = (E_1^* + E_2^*)^*.$$

The Legendre transform of E_1 reads:

$$\begin{aligned} E_1^*(M', S', V') &= \sup_{M, S, V \geq 0} (MM' + SS' + VV' - E_1(M, S, V)) \\ &= \sup_{M, S, V \geq 0} V (\rho M' + \sigma S' + V' - \varepsilon_1(\rho, \sigma)) \\ &= \sup_{V \geq 0} V (V' + \varepsilon_1^*(M', S')). \end{aligned}$$

Defining the set $A := \{M', S', V', \varepsilon_1^*(M', S') \leq -V'\}$, we observe that E_1^* is the indicator function of A . In the same manner the Legendre transform E_2^* is the indicator function of $B := \{M', S', V', \varepsilon_2^*(M', S') \leq -V'\}$. As a consequence $E^* = \mathbb{I}_{A \cap B}$, where $A \cap B := \{M', S', V', \max(\varepsilon_1^*, \varepsilon_2^*)(M', S') \leq -V'\}$. According to Proposition 8, we deduce that ε is the convex hull of $\min(\varepsilon_1, \varepsilon_2)$. \square

Before clarifying the FLT algorithm, we emphasize that the computation of any regular function can be boiled down to the study of a boxed linear function. We provide simple benchmark examples and refer to convergence results given in [Lu96] [Lu98].

2.2. The Legendre transform of boxed piecewise linear functions.

In [Lu96], the author proposes a fast algorithm to compute Legendre transform and gives some results on theoretical convergence. However the approximation is good only on a certain part of the studied domain, even in one-dimensional case. The author recommends to take into account a larger domain to obtain convergence. To avoid this handling, we propose a better treatment of the boundaries of the studied domain.

Let f be a real-valued function given on a domain $[a, b] \subset \mathbb{R}$. We assume the function to be extended outside its domain as follow:

$$(2.4) \quad f(x) = \begin{cases} f(x), & \text{if } x \in [a, b], \\ +\infty, & \text{elsewhere.} \end{cases}$$

Such a function will be called a boxed function. The LT computation requires to discretize the function, that is to consider a boxed piecewise affine function. We define thus the following interpolation operator.

Definition 7. Let $\{x_0, x_1, \dots, x_N\}$ be a set of $N + 1$ distinct points. We note Πf the projection of f such that:

$$(2.5) \quad \forall x \in \mathbb{R}, \Pi f(x) = \begin{cases} \frac{f(x_{i+1}) - f(x_i)}{x_{i+1} - x_i}(x - x_i) + f(x_i), & \text{if } x_i \leq x \leq x_{i+1}, \\ +\infty, & \text{if } i \in \{0, \dots, N - 1\}, \\ & \text{elsewhere.} \end{cases}$$

According to Definition 6, the domain of the conjugate f^* is the set of all affine functions minimizing f . In other words the Legendre transform of a convex function f turns out to be the function f itself and in particular:

$$co(f)^* = f^*.$$

Thus it is necessary to come down to the discrete convex hull of Πf , that we denote $co(\Pi f)$. We propose a simple algorithm to build it, others can be found for instance in [Lu98].

Let P_i be the points of coordinates $(x_i, \Pi f(x_i))$, $i = 0, \dots, N$. The discrete convex hull $co(\Pi f)$ is the set of points P_k , $k = 0, \dots, N^*$ ($N^* \leq N$), such that the slopes of $co(\Pi f)$, between two consecutive points, form an increasing sequence. For instance, if f is a concave function, the convex hull $co(\Pi f)$ is the set $\{P_0, P_N\}$. Before enunciating our algorithm, let us fixe some notations.

We denote G the list $G := \{P_i \mid i = 0, \dots, N\}$ and $|G|$ its cardinal. The slope between two points P_i and P_k of G is:

$$S(P_i, P_k) = \frac{\Pi f(x_i) - \Pi f(x_k)}{x_i - x_k}.$$

The convexification algorithm is the following:

PROCEDURE: CO(G)

variable remove : boolean.

```

REPEAT
  remove=false
  DO  $i = 1, \dots, |G| - 1$ 
    IF  $S(P_{i-1}, P_i) < S(P_i, P_{i+1})$  THEN
       $G = G \setminus \{P_i\}$ ,
      remove=true.
    END IF
  END DO
  WHILE ( $|G| > 2$ ) AND (remove=true)
END PROCEDURE: CO

```

Remark 3. *This algorithm is obviously non optimal. Under slight modifications it is easy to obtain a $O(N)$ algorithm.*

As a result $co(\Pi f)$ is again a convex piecewise linear function, whose slopes

$$\xi_i = \frac{co(\Pi f)(x_i) - co(\Pi f)(x_{i-1})}{x_i - x_{i-1}}, \quad i = 1, \dots, N^*,$$

where N^* denotes the discretization of the dual domain of $co(\Pi f)$. The sequence of slopes satisfy:

$$(2.6) \quad \xi_1 \leq \xi_2 \leq \dots \leq \xi_{N^*}.$$

Remark 4. *In the sequel we set $N^* = N$ in order to avoid heavy notations. However the discretization of the dual domain can differ from the one of the real domain.*

The computation of the conjugate $(co(\Pi f))^*$ is the following (see figure 2.1):

- For any fixed $x \in]x_{i-1}, x_i[$, $i \in \{1, \dots, N\}$, let Δ_i be the linear line of slope ξ_i . By definition the value $(co(\Pi f))^*(\xi_i)$ equals the maximum distance δ between the segment $[P_{i-1}, P_i]$ and Δ_i .
- For any fixed $x < a$ (resp. $x > b$), we plot the affine line Δ_a of slope ξ_1 (resp. the affine line Δ_b of slope ξ_N). Because $co(\Pi f)$ is extended by $+\infty$ outside $[a, b]$, the maximum distance between Δ_a (resp. Δ_b) and $co(\Pi f)$ is reached in a (resp. b).

To sum up the conjugate function of π^* reads

$$(2.7) \quad (co(\Pi f))^*(\xi) = \begin{cases} a\xi - co(\Pi f)(a), & \text{if } \xi \leq \xi_1, \\ x_i\xi - co(\Pi f)(x_i), & \text{if } \xi_i \leq \xi \leq \xi_{i+1}, \quad i = 1, \dots, N-1, \\ b\xi - co(\Pi f)(b), & \text{if } \xi \geq \xi_N. \end{cases}$$

The function $(co(\Pi f))^*$ is a piecewise linear convex function defined on the dual domain $[\xi_1, \xi_N]$ and extended by lines of slopes a and b outside. In general the discretization points of $(co(\Pi f))^*$ are no more equally spaced. It is necessary, for implementing the 2D algorithm described below, to sample the conjugate once again and to consider $\Pi((co(\Pi f))^*)$. In order to avoid heavy notation, we denote f^* the sampled conjugate $\Pi((co(\Pi f))^*)$ and f^{**} the sampled biconjugate.

The same study can be performed to compute the biconjugate approximation f^{**} . According to proposition (4), f^* is a convex function. Its slopes,

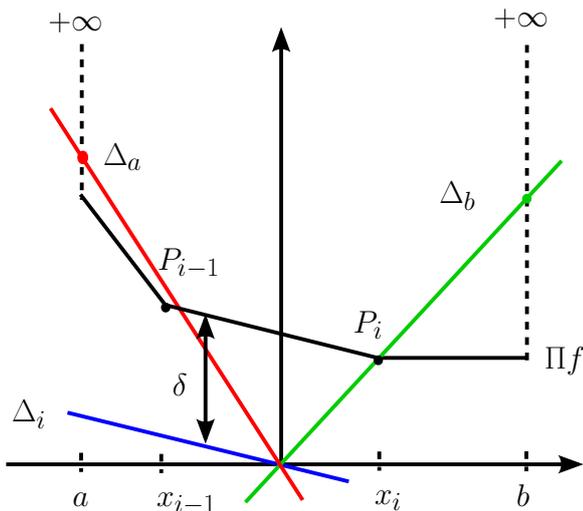


FIGURE 2.1. Legendre transform of a boxed piecewise linear function.

given by the formula 2.7, read:

$$a = x_0 \leq x_1 \leq \dots \leq x_{N-1} \leq x_N = b,$$

up to sampling. It is easy to check that the domain of f^{**} is the exact initial domain of study $[a, b]$. Before giving the Legendre transform algorithm, let us show the sampling effect on the previous examples.

Example 3. We consider the convex indicator $\mathbb{I}_{[-2,3]}$ (see Example 1). The computation of its conjugate and its biconjugate leads to the results of Figure 2.2. The computation regarding Example 2 are given in Figure 2.3.

Example 4. A discrete map $f(x) = x^2$ being given, the algorithm provides a discrete approximation of the biconjugate f^{**} . The Figure 2.4 shows the effect of the discretization.

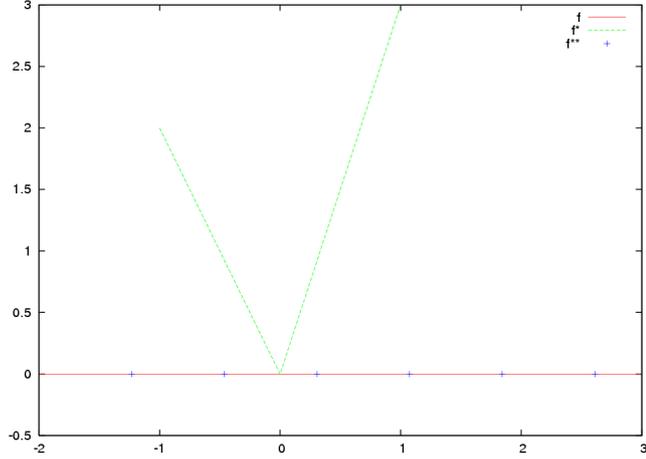


FIGURE 2.2. Conjugate and Biconjugate of $\mathbb{I}_{[-2,3]}$.

2.3. The Linear Legendre Transform algorithm. The Fast Legendre Transform algorithm (FLT) we propose is similar to the one given by [Br89] and [Lu98], except that we suppose real-valued functions to be extended by $+\infty$ outside their domain and conjugates are extended by affine maps.

Let us consider a function f defined on $[a, b] \subset \mathbb{R}$. We introduce

$$X = \{x_0, x_1, \dots, x_i, \dots, x_N\}$$

a regular discretisation of $[a, b]$ such that:

$$(2.8) \quad x_i = a + i \frac{b-a}{N}, \quad i = 0, \dots, N.$$

The discretization of f is given by the definition (7), that is:

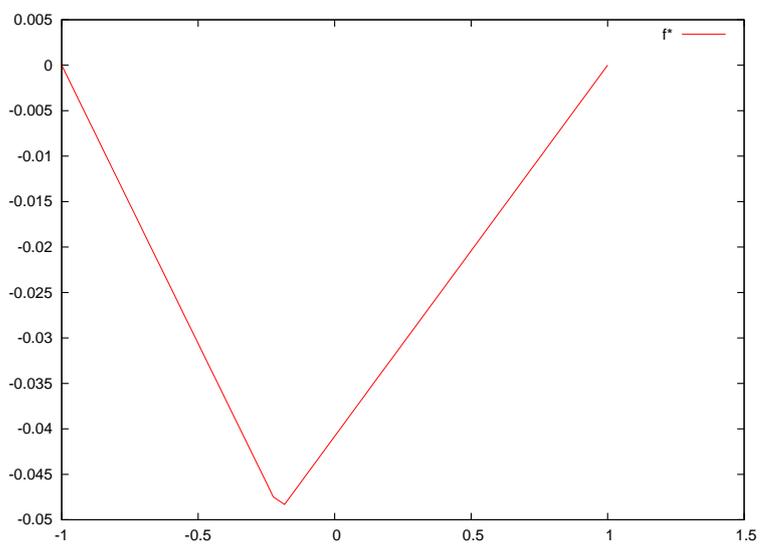
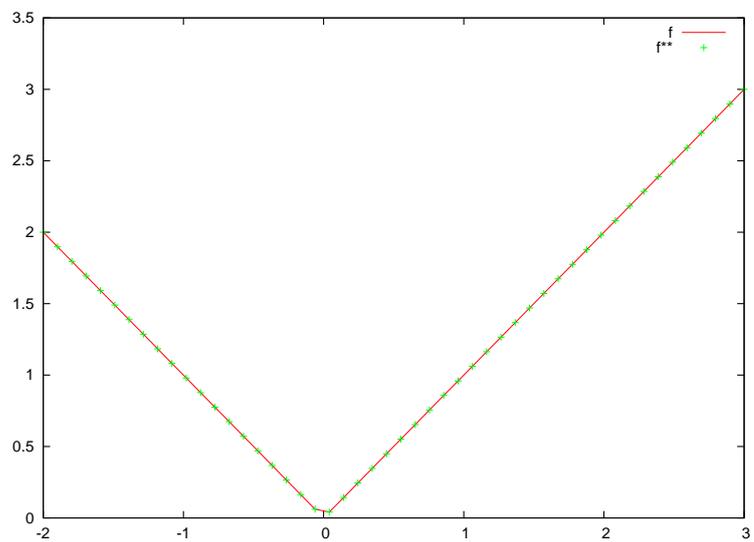
$$f \simeq \Pi f.$$

We are now able to give the discrete one-dimensional LT algorithm:

- Step 1:** Compute the convex hull $co(\Pi f)$.
- Step 2:** Compute the discrete dual set Γ of slopes of $co(\Pi f)$.
- Step 3:** Compute $(co(\Pi f))^*$, according to formula (2.7).
- Step 4:** Compute $f^* = \Pi((co(\Pi f))^*)$ using the linear interpolation operator (in order to recover N discrete values).
- Step 6:** Extend f^* by affine maps outside the dual domain Γ .

Although the two operations are identical, computationally speaking, let us detail the inverse Legendre transform algorithm.

- Step 1:** Compute the convex hull $co(\Pi f^*)$.
- Step 2:** Compute Δ , the discrete set of slopes of $co(\Pi f^*)$.
- Step 3:** Compute $(co(\Pi f^*))^*$, according to formula (2.7).

FIGURE 2.3. Conjugate and Biconjugate of the $f(x) = |x|$.

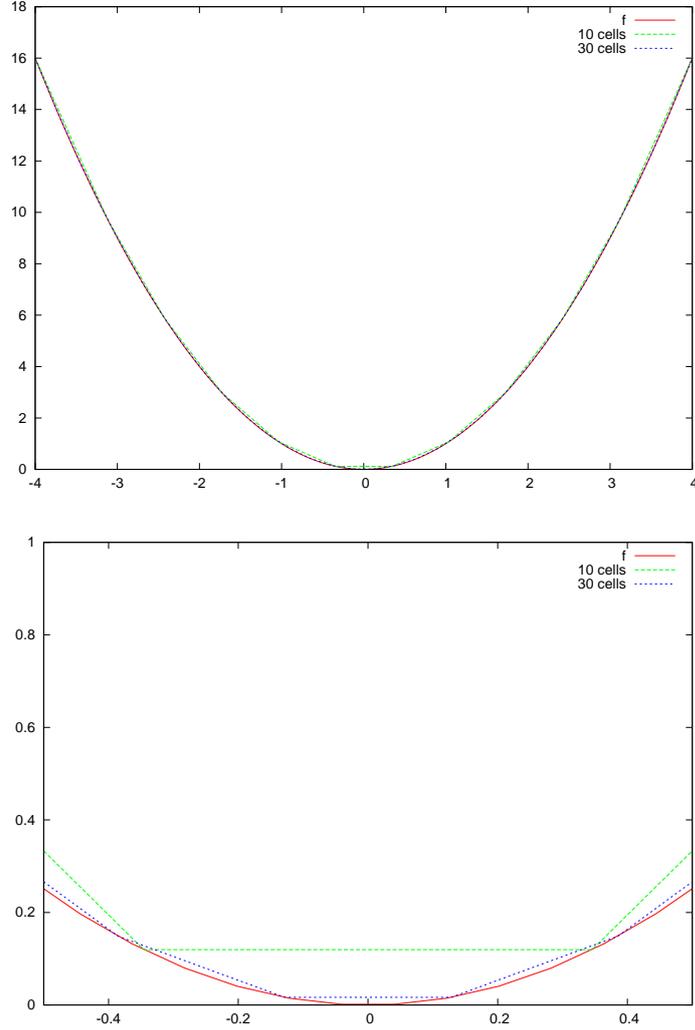


FIGURE 2.4. Conjugate and Biconjugate of the $f(x) = x^2$.

Step 5: Compute $f^{**} = \Pi((co(\Pi f^*))^*)$ using the linear interpolation operator (in order to recover N discrete values).

Step 6: Extend f^{**} by $+\infty$ outside the dual domain Δ .

By construction the set Δ turns to be the initial real domain X , up to sampling.

2.4. Extension to higher dimensions. While $O(N)$ convex hull algorithms exist in the planar case, it is no more true in \mathbb{R}^n , $n \geq 3$. Following the proposition (5), using the LT operation twice seems to be an efficient way to compute the convex hull. Indeed we can prove that the LT in \mathbb{R}^n may be factorized in n LT in \mathbb{R} . Moreover the planar algorithm has a $O(N)$ complexity.

For $f : \mathbb{R}^n \rightarrow \mathbb{R} \cup \{+\infty\}$, the definition (6) gives the expression of the conjugate f^* :

$$(2.9) \quad f^*(\xi) = \sup_{x_1 \in \mathbb{R}} \left[\xi_1 x_1 + \sup_{x_2 \in \mathbb{R}} \left[\xi_2 x_2 + \dots + \sup_{x_d \in \mathbb{R}} [\xi_d x_d - f(x)] \right] \right].$$

For more clearness and to go back to the thermodynamic context, we only detail the two-dimensional conjugate:

$$(2.10) \quad f^*(\xi_1, \xi_2) = \sup_{x_1 \in \mathbb{R}} \left[\xi_1 x_1 + \sup_{x_2 \in \mathbb{R}} [\xi_2 x_2 - f(x_1, x_2)] \right].$$

In the sequel we will denote $f^{*,1}$ (resp. $f^{*,2}$) the partial Legendre transform with respect to the variable x_1 (resp. x_2). Then it is easy to prove that

Proposition 9. *Only one-dimensional Legendre transforms are involved in the multidimensional problem, i.e.*

$$f^* = (-f^{*,2})^{*,1}.$$

This proposition can easily be applied in higher dimensions. Therefore convergence and complexity results enunciated in [Lu98] hold.

Remark 5. *If f is convex with respect to x_1 , then $f^{*,2}$ is a concave function of x_1 . It is necessary to consider $-f^{*,2}$ in order to recover a convex function.*

A bivariate function $f : [a, b] \times [c, d] \rightarrow \mathbb{R}$ being given, the two-dimensional algorithm proceeds as follow:

Step 1: discretization:

- (1) Compute the discrete sets X and Y such that:

$$(2.11) \quad X := \left\{ x_i = a + i \frac{b-a}{N}, \quad i = 0, \dots, N \right\},$$

$$(2.12) \quad Y := \left\{ y_j = c + j \frac{d-c}{M}, \quad j = 0, \dots, M \right\}.$$

Remark 6. *To avoid heavy notation and without loss of generality, we assume the discretization of the dual domain to be the same as the one of the real domain.*

Step 2: For $y_j \in Y, j \in \{1, \dots, M\}$:

- (1) Compute the piecewise affine function $\Pi f(x, y_j), x \in X$.
- (2) Compute the convex hull $co(\Pi f)(x, y_j)$.
- (3) Compute the set $\Xi = \{\xi_1, \dots, \xi_N\}$ of slopes of $co(\Pi f)(x, y_j)$.
- (4) Compute $f^{*,1} = \Pi \left((co(\Pi f))^{*,1} \right)$ using the one-dimensional LT algorithm.

Step 3: For $\xi_i \in \Gamma, i \in \{1, \dots, N\}$:

- (1) Compute the piecewise affine function $\Pi(-f^{*,x1})(\xi_i, y), y \in Y$.
- (2) Compute the convex hull $co(\Pi(-f^{*,x1}))(\xi_i, y)$.
- (3) Compute the set $\Gamma = \{\gamma_1, \dots, \gamma_M\}$ of slopes of $co(\Pi(-f^{*,x1}))(\xi_i, y)$.
- (4) Compute $f^* = \Pi \left((co(\Pi(-f^{*,x1})))^{*,2} \right)$ using the one-dimensional LT algorithm.

Applying this algorithm once again, we recover the closed convex hull of the initial surface on the exact initial domain $[a, b] \times [c, d]$, that is:

$$f^{**} \simeq \text{co}(f).$$

Remark 7. *Let us consider $f : \mathbb{R}^2 \rightarrow \mathbb{R}$. Its graph is said to be a ruled surface in the ξ direction if f can be written:*

$$f(\xi, \gamma) = g(\gamma) + h(\gamma)(\xi - \xi_0),$$

for given functions g and h , $(\xi, \gamma) \in \mathbb{R}^2$. According to this definition, for $\xi < \xi_1$ and $\xi > \xi_N$ (resp. for $\gamma < \gamma_1$ and $\gamma > \gamma_M$), the conjugate $f^{*,1}(\xi, \gamma)$ (resp. $f^{*,2}(\xi, \gamma)$) defines a ruled surface in the ξ direction (resp. γ direction). As a consequence the graph of f^* is locally a hyperplane in $\mathbb{R}^2 \setminus \{([a, b] \times \mathbb{R}) \cup (\mathbb{R} \times [c, d])\}$.

3. NUMERICAL APPLICATIONS TO THERMODYNAMICS

3.1. Numerical change of variables. In this section the multidimensional FLT algorithm is applied to very simple phase transition models in order to assess the validity of our algorithm. The considered models are the van der Waals model and a mixture of perfect gases model. Analytical expression of the mixture entropy are available in [JA01], [AF07] and [HS06]. It is classical to study the EOS through the isothermal curves in the (τ, p) plane. It appears that, using the Legendre transform algorithm, it is possible to construct the isothermal curves easily. We consider a fluid described by its energy $\epsilon(\tau, s)$. The Legendre transform of ϵ with respect to s , denoted F , is:

$$(3.1) \quad F(\tau, T) = \epsilon^{*,s}(\tau, T) = Ts - \epsilon(\tau, s),$$

where $T = \frac{\partial \epsilon}{\partial s}(\tau, s)$.

The function F is nothing else than the opposite of the Helmholtz free energy function in intensive variables. Because

$$(3.2) \quad dF = pd\tau + sdT,$$

the pressure can be computed as:

$$(3.3) \quad \frac{\partial F}{\partial \tau}(\tau, T) = p(\tau, T).$$

To sum up isothermal curves are constructed applying once a FLT algorithm in the s direction and computing the slopes in the τ direction.

3.2. Maxwell construction for a van der Waals gas. In the perfect gas model, the gas atoms are supposed to not interact and their volumes are negligible. For high densities, this model is no more adapted (the distance between particules is about the interaction distance). The van der Waals equation of state is an extension of the perfect gas law, which takes into account the attraction between atoms and the decrease of the free volume. The complete EOS is given by

$$(3.4) \quad \epsilon(\tau, s) = (\tau - b)^{-R/c_V} \exp\left(\frac{s}{c_V}\right) - \frac{a}{\tau}$$

Constants	Value
R	$8.314 J.K^{-1}.mol^{-1}$
c_V	$4186 J.Kg^{-1}.K^{-1}$
a	$0.544 Pa.m^{-6}$
b	$30.510^{-6} m^3$

TABLE 1. van der Waals constants for liquid water

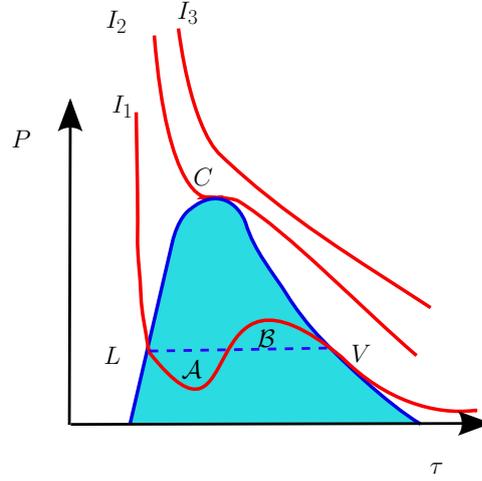


FIGURE 3.1. isothermal curves for the van der Waals EOS

(it is extended by $+\infty$ for $\tau \leq b$ or $s \leq 0$) where R is the perfect gas constant, c_V is the specific heat, a and b are positive constants. These constants are given in the table 3.2 in the case of liquid water. For other materials we refer to [Ca85] or [JA01].

This EOS can be applied to liquids as well as gases. But it is not physically correct in the phase transition area. In the mixture zone, liquid and gas are present by a continuous change of liquid fraction. While isothermal curves are monotone above the critical point C (see Figure 3.1), it is no more true in the mixture zone. We can observe two local extrema in this area, called spinodal points. The maximum corresponds to supersaturated vapour and the minimum to the overexpanded liquid. Between these two points $\frac{\partial p}{\partial \tau}(\tau, T) > 0$, which is physically excluded. In order to get an admissible

behaviour of phase transition in the mixture zone the equilibrium pressure must be calculated as a function of the temperature. This construction is called the Maxwell's principle. It consists in constructing the segment $[L, V]$ in such a way that the volume \mathcal{A} is equal to the volume \mathcal{B} . Along the segment $[L, V]$ (called Maxwell line) the two phases coexist at equilibrium. The main problem is that the positions of both points cannot be found analytically and requires a numerical resolution that can be CPU consuming when many EOS evaluations are needed. In fact the Maxwell construction is equivalent to set equality of Gibbs potentials, pressures and temperatures along the segment $[L, V]$. In other words it is equivalent to the construction of the bitangent plan between two stable sticks of the van der Waals law [AF07], *i.e.* to compute the convex hull of the energy surface by applying twice the FLT algorithm.

We consider a fluid described by the equation of state (3.4) for liquid water. At the critical point the pressure satisfy:

$$(3.5) \quad \frac{\partial p}{\partial \tau} = 0,$$

$$(3.6) \quad \frac{\partial^2 p}{\partial \tau^2} = 0.$$

The values of specific entropy and volume are thus known and we can characterize the isothermal curves around the critical point. Because the van der Waals model includes liquid-vapour phase transition, it is not necessary to distinguish energies of each phase. The saturation dome in the (τ, p) plane is merely obtained by computing:

$$\epsilon(\tau, s) - co(\epsilon(\tau, s)).$$

Where this quantity is > 0 corresponds to the saturation dome. It leads to the result of Figure 3.2. Using the change of variables introduced in previous section, the isothermal curves in the spinodal area are easily depicted before the convexification process (see Figure 3.3) and after (see Figure 3.4).

3.3. Immiscible mixture of two perfect gases. In this section we consider an immiscible mixture at equilibrium. The vapour and liquid phases (denoted respectively 1 and 2) are modelled by a perfect gas laws

$$(3.7) \quad \epsilon_1(s_1, \tau_1) = \exp(s_1) \tau_1^{1-\gamma_1},$$

$$(3.8) \quad \epsilon_2(s_2, \tau_2) = \exp(s_2) \tau_2^{1-\gamma_2},$$

with $\gamma_1 > \gamma_2$ (specific heats are supposed to be equal to 1). The optimization problem consists in fixing the Gibbs potentials, pressures and temperatures equilibrium. The equation of the coexistence curve in the (T, p) plane follows:

$$(3.9) \quad p = \exp(-1) \left(\frac{(\gamma_1 - 1)^{\gamma_1 - 1}}{(\gamma_2 - 1)^{\gamma_2 - 1}} \right)^{\frac{1}{\gamma_1 - \gamma_2}} T$$

For detailed calculus we refer to [AF07] and [JA01]. The equation of the phase transition curve in the (τ, p) and (τ, ϵ) is deduced from continuity of

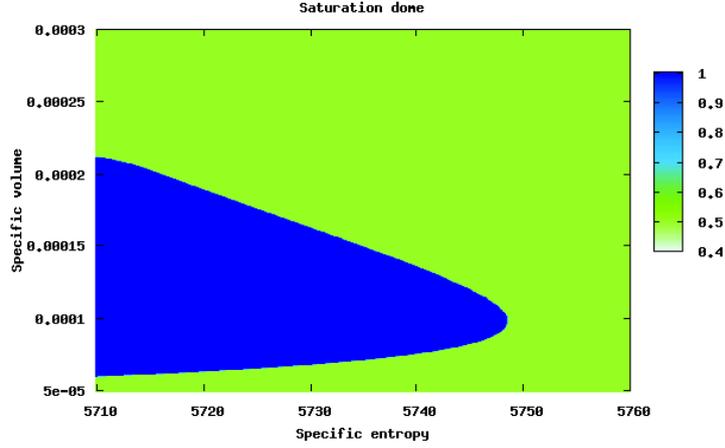


FIGURE 3.2. Saturation dome of the van der Waals model

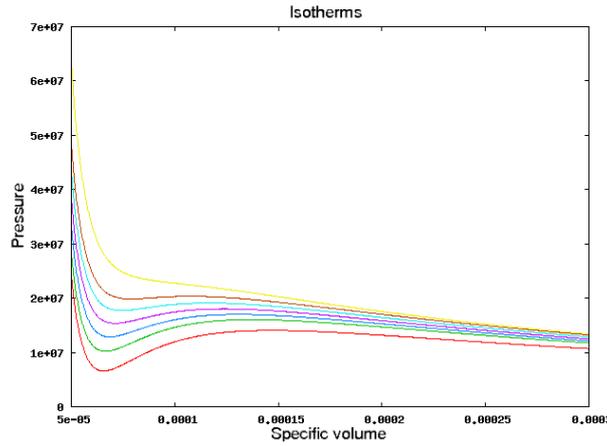


FIGURE 3.3. Isothermal curves of the van der Waals model

pressure and temperature between pure phases and mixture zone. Finally the global energy reads:

$$(3.10) \quad \epsilon(\tau, s) = \begin{cases} \exp(s)\tau^{(1-\gamma_1)}, & \text{if } \tau \leq \tau_2, \\ \exp\left(s - (1 - \gamma_1)\left(\frac{\tau}{\tau_1} - 1\right)\right)\tau_1^{1-\gamma_1}, & \text{if } \tau_2 \leq \tau \leq \tau_1, \\ \exp(s)\tau^{(1-\gamma_2)}, & \text{if } \tau \geq \tau_1. \end{cases}$$

Let A be a point of the coexistence curve in the (T, p) plane. It corresponds to a horizontal segment AB in the (τ, p) plane (see figure 3.5). Contrary to the van der Waals EOS, the liquid vapour phase transition does not model a critical behaviour. Such results can be obtained numerically.

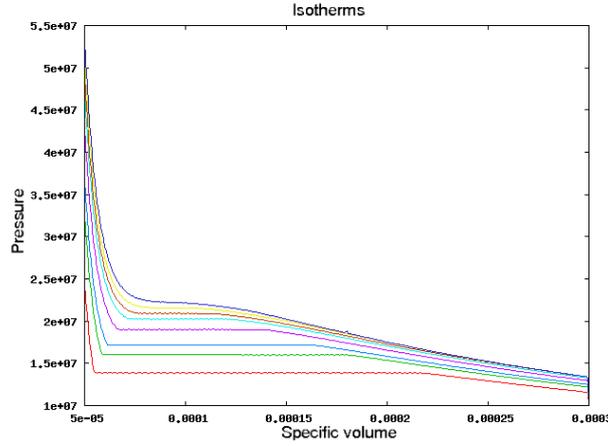


FIGURE 3.4. Isothermal curves of the van der Waals model

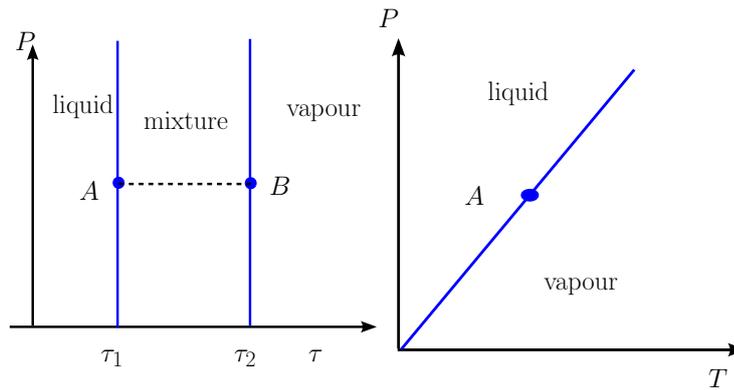


FIGURE 3.5. Isothermal curves for perfect gas mixture

Setting $\gamma_1 = 1.6$ and $\gamma_2 = 1.5$, we compute the saturation curve:

$$(\epsilon_1 | \epsilon_2) - \min(\epsilon_1, \epsilon_2).$$

We observe (see Figure 3.6) that the saturation dome does not present a critical point. Because the phase transition happens at constant pressure and temperature, isothermal curves are horizontal in the (τ, p) plane in the mixture zone. The isothermal curves present a kink at the saturation boundaries as shown of Figure 3.7.

3.4. Three-phase mixture. In Section 1 we depict an algebraic structure of thermodynamic mixtures on the set of the convex functions of \mathbb{R}^3 equipped

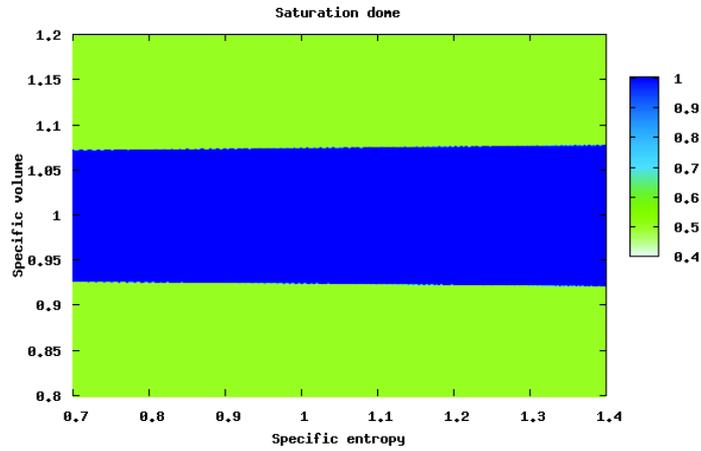


FIGURE 3.6. Saturation dome for perfect gas mixture.

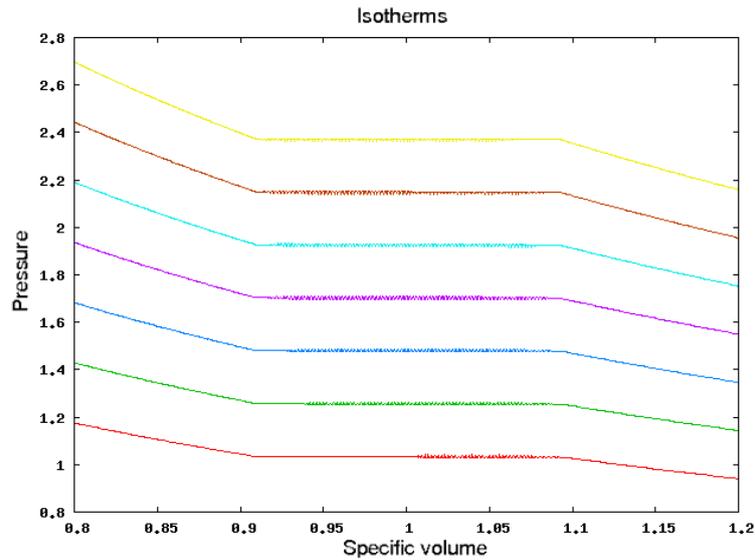
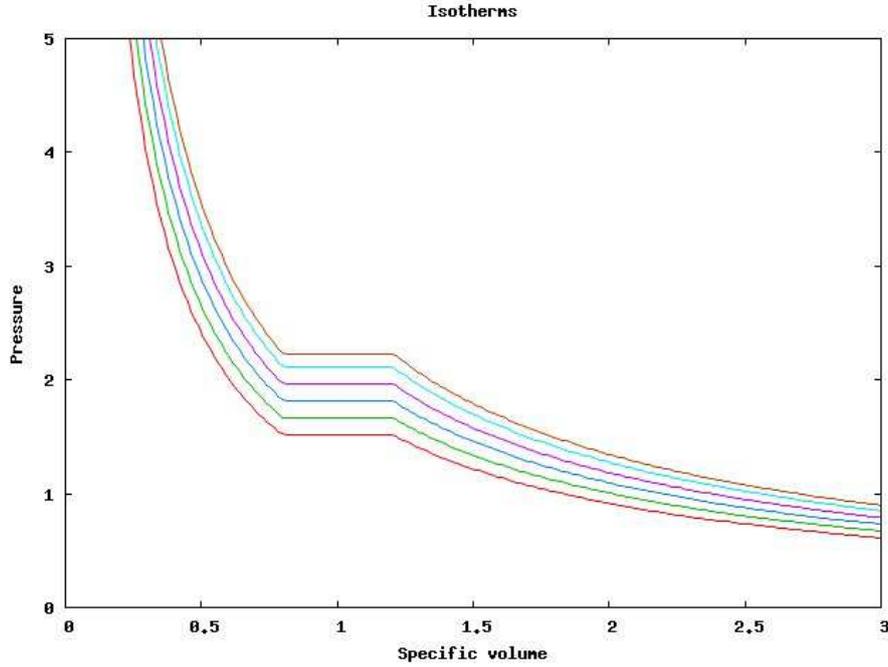


FIGURE 3.7. isothermal curves of perfect gas mixture

with the two binary operations $|$ and \square . According to the propositions (7) and (8), the dual structure is a $(\max, +)$ algebra on the Legendre space. In this section we consider a three phases mixture involving both operations. Each phase is described by a perfect gas law. The Gibbs potential is the Legendre transform of the energy that simultaneously replaces the entropy

FIGURE 3.8. Isothermal curves with $\alpha = \beta = 0.5$.

by the temperature and the volume by the pressure as independent variables:

$$(3.11) \quad \mu(T, p) = -\varepsilon^*(T, p)$$

$$(3.12) \quad = -\sup_{s, \tau} \left(\frac{\partial \varepsilon}{\partial \tau} \tau + \sup_{s, \tau} \left(\frac{\partial \varepsilon}{\partial s} s - \varepsilon(s, \tau) \right) \right)$$

$$(3.13) \quad = p\tau - Ts + \varepsilon.$$

In the case of a perfect gas, the Gibbs potential reads:

$$(3.14) \quad \mu(T, p) = T \left[\gamma - \ln T + (1 - \gamma) \ln \left(\frac{(\gamma - 1)T}{p} \right) \right].$$

We assume that the phases 1 and 2 are miscible and that the phase 3 is immiscible with the others. In other words, the mixture Gibbs potential μ_m satisfy:

$$(3.15) \quad \mu_m = \max((\mu_1 + \mu_2), \mu_3).$$

First we set $\alpha\mu_1 + \beta\mu_2 = \mu_3$ with $\alpha = \beta = 0.5$, $\gamma_1 = \gamma_2 = 1.6$ and $\gamma_3 = 1.4$. The global mixture boils down to be a perfect gas mixture. We recover similar results as in section 3.3 (see Figure 3.8). Then the miscible mixture is slightly changed assuming $\alpha = 0.5$ and $\beta = 0.4$. The isothermal curve profile still present a kink at the saturation boundaries. However the saturation curves are no more vertical strait lines in the (T, p) plane but appear to be affine lines. The pressure in the mixture area seems to be constant as shown in Figure 3.9.

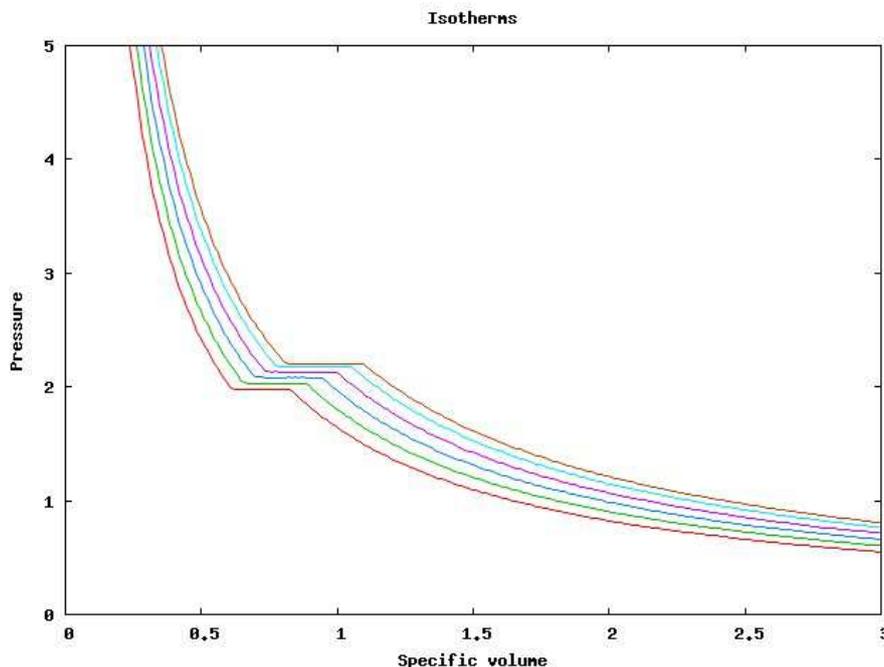


FIGURE 3.9. Isothermal curves with $\alpha = 0.5$ and $\beta = 0.4$.

4. CONCLUSION

In this work, we reviewed some results of thermodynamics of binary mixture. At equilibrium the energy of two phases is given by an optimization problem on a convex set of constraints on extensive variables. The equilibrium energy is the inf-convolution of the energies of the two phases. In intensive parameters we proved that:

- for an immiscible mixture, the mixture energy is the convex hull of the energies;
- for a miscible mixture, the equilibrium energy is the inf-convolution of the phases energies.

Both operations transform respectively into max and plus operations in the Legendre space. We have thus put in evidence that the natural mathematical tool for studying mixture EOS is the theory of max-plus algebra.

The link with the Fast Legendre Transform algorithm has been investigated. The $O(N)$ algorithm that we provide ensures a good treatment of the boundaries. The whole development is applied to mixture EOS. In the case of a perfect gas mixture, the algorithm allows us to recover the profil of isothermal curves. In a like manner the Maxwell area rule method for a van der Waals fluid is recovered by computing the convex hull using the LT algorithm. Finally we propose the computation of a three phase mixture in order to show that the whole approach can also be applied to more complex EOS.

This work can be extended in many directions. To our opinion, the main application would be the correct treatment of tabulated EOS incorporated in Computational Fluid Dynamics (CFD) softwares. Usually, these tabulated

EOS are approximated by polynomials. There is no mathematical reason that these polynomials preserve the convexity of the thermodynamical potentials. This is particularly critical in the mixture region, where the energy is convex but no more strictly convex. It can lead to loss of hyperbolicity and instabilities of the numerical model. Using the recently developed theory of max-plus algebra [Mas87, KM97] should lead to much more powerful and robust numerical techniques for approximating real EOS.

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