**THE TANGENT PLANE INTERCEPT: A NEW METHOD IN PHASE EQUILIBRIUM CALCULATIONS**

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A new method for describing the equilibrium behaviour of multicomponent systems, based on an earlier approach originating from geometric programming, is proposed. The new emerging function, called by the authors the tangent plane intercept function, exhibits an array of interesting properties, proving itself as a useful tool in some cases of non-trivial LLE calculations.

Keywords: multiphase equilibria, geometric programming, tangent plane distance function, tangent plane intercept

**INTRODUCTION**

In an array of papers, Geană\(^1\)-\(^4\) proposed a new approach in phase equilibrium calculations, based on the duality theorem, as stated in the theory of geometric programming. Although this approach is not widely used, due to technical problems in solving the primal problem associated with the minimum Gibbs free energy condition, the primal function proved useful by itself in describing a multiphase-system at equilibrium. This work lays down some properties of this new function, reiterating and developing some observations made by the same author\(^5\),\(^6\),\(^9\)

**MATHEMATICAL PROPERTIES**

**OBTAINING THE Y FUNCTION**

As stated before, the origins of the Y function reside in a new approach to the equilibrium problem, based on geometric programming. Starting with the classical condition for thermodynamic equilibrium:

\[
\sum_{\phi} n_{c}^{\phi} = n_{c}^{0} \quad \text{(closure conditions)}
\]

\[
n_{c}^{\phi} > 0 \quad \text{(minimum presence conditions)}
\]

where \(n_{c}^{\phi}\) is the mole number of component \(c\) in phase \(\phi\) and \(\mu_{c}^{\phi}\) is the chemical potential associated with component \(c\) in phase \(\phi\). For the chemical potential, a generic model can be used:

\[
\mu_{c}^{\phi} = \mu_{c}^{0}(T) + RT \ln \gamma_{c}^{\phi} + RT \ln \frac{n_{c}^{\phi}}{n_{\phi}}
\]

where \(\gamma_{c}^{\phi}\) is the activity coefficient of component \(c\) in phase \(\phi\), and \(n_{\phi}\) is the total amount of phase \(\phi\), in moles.

The classical problem stated above can be transformed in order to become compatible with the duality theorem from geometric programming (see e.g. Marușciac, 1978):

\[
\max \, v = \prod_{i=0}^{N} \left( \frac{c_{i}}{n_{i}} \right)^{n_{i}} \prod_{\phi=1}^{p} n_{\phi}^{n_{\phi}}
\]  \hspace{1cm} (1)
For the above relation to be complete, a index set and a family of constants $c_i$ have to be specified.

The index set can be constructed as follows:

Define the partial index sets $I_j$ such as

$$\forall c = 1, C \quad i \in I_1$$

$$n_1 = n_c^1$$

$$\forall c = 1, C \quad i \in I_2$$

$$n_1 = n_c^2$$

$$\vdots$$

$$n_1 = n_c^p$$

$$\forall c = 1, C \quad i \in I_p$$

Take the new index set as the reunion of these partial sets (non-overlapping, as it can be seen from their definitions):

$$I = (I_0 = \{0\}) \cup I_1 \cup \cdots \cup I_p = \bigcup_{j=0}^{p} I_p$$

The family of constants is defined such as:

$$\tilde{C} = \left\{ c \in 1, c_i = \frac{1}{\gamma_j}, \forall j \in I \setminus I_0 \right\}$$

With these definitions, problem (1) becomes the dual problem from geometric programming. The corresponding primal problem is obtained via the duality theorem, and is given by eq. (2)

$$\begin{align*}
\min p_0 &= c_0 \prod_{j=1}^{C} Z_j^{a_{nj}} \\
\sum_{i=1}^{p} c_i \prod_{j=1}^{C} Z_j^{a_j} &\leq 1 \\
Z_j &> 0, \quad \forall j = 1, C
\end{align*}$$

Matrix $a$ is defined as:

$$a^T = \begin{pmatrix} 1 & 0 & 0 & \cdots & 0 \\ -N_0 & id_c & id_c & \cdots & id_c \end{pmatrix}$$

where $N_0$ is the initial amount vector:

$$N_0 = \begin{pmatrix} n_1^0 \\ n_2^0 \\ \vdots \\ n_C^0 \end{pmatrix}$$

and $id_c$ is the $C \times C$ identity matrix:

$$id_c = \begin{pmatrix} 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & 0 \\ 0 & 0 & \cdots & 0 & 1 \end{pmatrix}$$

As eq. (2) shows, the C+F restrictions of the primal problem define a non-void acceptance region, making this problem super-consistent, so that the duality theorem can be applied.

On the basis of this theorem, variables $Z$ can be interpreted as activities $a$, phase-independent at equilibrium on the basis of the mass-transfer stationarity conditions. Indeed, according to the duality theorem, between the primal and dual solution the following relation exists:

$$\begin{align*}
n_i &= \begin{cases} 1 & \text{if } i \in I_0 \\ n_f u_i & \text{if } i \in I_f \end{cases} \\
\end{align*}$$

(3)

where $u_i$ is a restriction term such as:

$$u_f = c_f \prod_{j=1}^{C} Z_j^{a_{fj}}$$

According to the definition of the index system \( \{ j \mid \gamma_j \} \), the relation described by eq. (3) becomes:

$$\frac{n_c^f}{n_f} = c_c Z_c = \frac{Z_c}{\gamma_c}$$

Matrix $a$ is defined as:
thus, at equilibrium, \( Z_c \) really is the activity of the component \( c \).

Based on this treatment, a new function is introduced, given by:

\[
Y = - \sum_{c=1}^{C} n_c^0 \ln a_c
\]

(4)

which is the negative logarithm of the objective function in the primal problem (2). From the method used to construct it, one can observe that the \( Y \) function makes sense only for a system at equilibrium. On the other hand, the \( Y \) function has a geometric meaning, being the intercept of the tangent plane at point \( x \) to the Gibbs surface energy, on the line \( x = x_0 \), corresponding to the global composition. This interpretation is illustrated in fig. 1.

![Figure 1. Geometric meaning of the Y function](image)

**Computational properties**

The \( Y \) function, as defined by eq. (4) can be rewritten as

\[
Y = - \sum_{c=1}^{C} x_c^0 \mu_c^{am}
\]

(5)

according to the definition for the chemical potential of mixing, \( \mu_c^{am} \):

\[
\mu_c^{am} = \mu_c - \mu_c^0 = RT \ln a_c
\]

where \( a_c \) is the activity of the \( c^{th} \), phase-independent at equilibrium.

Due to the normalisation condition:

\[
\sum_{i=1}^{C} x_i = 1
\]

equation (5) becomes:

\[
Y = - \sum_{c=1}^{C-1} x_c^0 (\mu_c - \mu_C) + \mu_C
\]

(5')

Thus, the gradient of this function is:

\[
\nabla Y = \left( \frac{\partial Y}{\partial x_1}, \frac{\partial Y}{\partial x_2}, \ldots, \frac{\partial Y}{\partial x_{C-1}} \right)
\]

where the partial derivatives are given by:

\[
\frac{\partial Y}{\partial x_c} = - \sum_{j=1}^{C-1} x_c^0 \left( \frac{\partial \mu_c^{am}}{\partial x_c} - \frac{\partial \mu_c^{am}}{\partial x_j} - \frac{\partial \mu_c^{am}}{\partial x_c} \right)
\]

On the other hand, from the Gibbs-Duhem equation, we have:

\[
\sum_{i=1}^{C-1} x_i (d\mu_i^{am} - d\mu_c^{am}) - d\mu_c^{am} = 0
\]

which is equivalent to

\[
\sum_{j=1}^{C-1} \sum_{i=1}^{C-1} x_i \left( \frac{\partial \mu_i^{am}}{\partial x_j} - \frac{\partial \mu_c^{am}}{\partial x_j} + \frac{\partial \mu_c^{am}}{\partial x_j} \right) dx_j = 0
\]

This, in turn, is equivalent to the set of identities:

\[
\sum_{j=1}^{C-1} \sum_{i=1}^{C-1} x_i \left( \frac{\partial \mu_i^{am}}{\partial x_j} - \frac{\partial \mu_c^{am}}{\partial x_j} + \frac{\partial \mu_c^{am}}{\partial x_j} \right) = 0, \forall j \in \{1, C-1\}
\]

(6)
Differentiating again eq. (6) with respect to \( x_k \), eq. (7) can be obtained, after some algebraic transformations:

\[
\frac{\partial \mu^m_{am}}{\partial x_j} - \frac{\partial \mu^c_{am}}{\partial x_j} + \sum_{i=1}^{C-1} x_i \left( \frac{\partial^2 \mu^m_{am}}{\partial x_j \partial x_i} - \frac{\partial^2 \mu^c_{am}}{\partial x_j \partial x_i} \right) + \frac{\partial^2 \mu^c_{am}}{\partial x_j \partial x_k} = 0, \forall j, k = 1, C-1
\]

(7)

According to its definition, the \((i,j)\)th term of the hessian matrix associated with the Gibbs function can be expressed as:

\[
\left( H_{\Delta^G} \right)_{ij} = \frac{\partial^2 (\Delta^G)}{\partial x_i \partial x_j}
\]

\[
= \left( \frac{\partial \mu^m_{am}}{\partial x_j} - \frac{\partial \mu^c_{am}}{\partial x_j} \right) + \left( \frac{\partial \mu^m_{am}}{\partial x_i} - \frac{\partial \mu^c_{am}}{\partial x_i} \right) + \sum_{k=1}^{C-1} x_k \left( \frac{\partial^2 \mu^m_{am}}{\partial x_i \partial x_j} - \frac{\partial^2 \mu^c_{am}}{\partial x_i \partial x_j} \right) + \frac{\partial^2 \mu^c_{am}}{\partial x_i \partial x_j}
\]

(8)

Combining eqns. (7) and (8), we obtain:

\[
\left( H_{\Delta^G} \right)_{ij} = \frac{\partial \mu^m_{am}}{\partial x_j} - \frac{\partial \mu^c_{am}}{\partial x_j}, \forall i, j = 1, C-1
\]

(8')

Combining eq. (8) with the formula obtained above for \( \nabla Y \), the first important computational property of this function emerges:

\[
\nabla Y = -H_{\Delta^G} \otimes \left( x^0 - x \right)
\]

(9)

where \( x^0 \) and \( x \) are the initial (global), respectively actual, composition vectors, \( x^0, x \in \mathbb{R}^{C-1} \). This property shows that, if \( x \) is a stationary point of the \( Y \) function corresponding to the initial composition \( x_0 \) (i.e. equation (9) reduces to a linear homogenous system in the unknown \( x_0 \)) then there are two possibilities:

- \( x \) is not a spinodal point, \( |H_{\Delta^G}| \neq 0 \). In this case, the only solution of (9) is the trivial solution \( x = x_0 \) that is, the only \( Y \) function having a stationary point in \( x \) is the one corresponding to the feed \( x_0 \);

- \( x \) is a spinodal point, \( |H_{\Delta^G}| = 0 \). In this case, there are infinitely many \( Y \) functions having a stationarity in \( x \).

This shows that, if \( x \) is a stationary point for at least two different \( Y \) functions (corresponding to two different feed compositions, \( x_01 \) and \( x_02 \)), then this is a spinodal point for the system.

Differentiating relation (9) again with respect to the mole fraction, say, \( x_k \), and making appropriate use of the Gibbs-Duhem equation and its consequences, as stated above, an expression for \( H_Y \), the hessian matrix associated with \( Y \), may be obtained as:

\[
H_Y = A + H_{\Delta^G}
\]

(10)

where \( A \) is a new matrix given by:

\[
A_{ik} = -\sum_{j=1}^{C-1} (x^0_j - x^0_k) \left( \frac{\partial^2 \mu^m_{am}}{\partial x_j \partial x_k} - \frac{\partial^2 \mu^c_{am}}{\partial x_j \partial x_k} \right)
\]

Analyzing eqns (9) and (10), it can be stated that any stationary point of the \( Y \) function is either identical to the initial (global) composition, or lies on the spinodal curve.

At \( x_0 \), the initial (global) composition point, matrix \( A \) vanishes element-wise, so the \( Y \) surface and the Gibbs energy surface have the same convexity.

For a binary system, a third computational property can be obtained. Consider two initial points \( x^0_i \) and \( x^0_2 \). Requesting that the corresponding \( Y \) functions be equal, the following equation is obtained:

\[
Y_{x^0_i} = Y_{x^0_2} \iff \left( x^0_i - x^0_2 \right) \mu^m_{am} = \left( x^0_i - x^0_2 \right) \mu^c_{am} \iff \mu^m_{am} = \mu^c_{am}
\]

Equation (12) is invariant to any change in \( x_0 \), so it can be stated that all the , so it can be stated that all
the Y functions corresponding to a feasible global composition must pass through a number of fixed points.

These computational properties, expressed by eqns (9)+(11), may be used in describing the equilibrium state of a system, as illustrated below.

**Results and discussion**

Following are examples on using the Y function in liquid-liquid equilibrium calculations. The challenging aspect of this kind of calculations is the need for reliable initial approximations. Making appropriate use of the above stated properties of the Y function, such reliable approximations may be found. Especially property (9) is of interest, because the spinodal and the binodal curves are relatively close in the constitutive space.

Property (10) is used to assess the instability of a system, due to the well-known fact that at an unstable point, the Gibbs energy surface is non-convex. But, due to property (10), this is also the case with the Y function.

**Binary systems**

We start exploring the various possibilities in using the Y function with the example of a binary system (methanol+n-heptane, at 328 K and 1 bar; parameters taken from DEHEMA, 1980). First of all, figure 2 illustrates property (11), showing that five functions of the Y class, corresponding to five different initial compositions, pass through the same points.

![Figure 2. Common intersection points for multiple Y functions. Methanol+n-hexane, 328 K and 1 bar.](image)

Next, figure 3 illustrates the use of the Y function in solving the liquid-liquid equilibrium problem. The initial point is labelled “I”, the spinodal points (stationarities of the Y functions) are labelled “S” and the equilibrium compositions are labelled “B”. The interesting aspect of this example is the position of the initial point: even initialized near the spinodal curve, the method still succeeds, enabling the Rachford-Rice equation to find a solution. In fact, due to property (9), the method will succeed even initialized on the spinodal curve, since this is a solution to the equation $\nabla Y = 0$. It should be noted at this point that other, more general, methods, such as the homotopic or gradient line approach (Sun and Seider\cite{10} Wasilkiewicz et. al.\cite{11} will fail in such a situation, because of the singularity of the hessian matrix associated with the Gibbs energy function.

![Figure 3. Using the Y function for equilibrium calculations for the system methanol+n-hexane, at 328 K and 1 bar.](image)

Another interesting feature of the Y function is that any family of several (at least two) different Y functions can provide informations about the equilibrium behavior of the system over the whole composition range. This is illustrated in figures 4 and 5, depicting, respectively, the $\Delta^m G$ at 300 K and 1 bar and several Y curves at the same temperature and pressure, for the binary system n-buthyl-acetate+water. Activities were calculated with the NRTL model.
As figure 4 shows, this system exhibits two miscibility gaps and, therefore, will have two spinodal curves. At a fixed temperature and pressure, these curves will generate four spinodal points, each of which, according to property (9), being a stationary point for an infinity of $Y$ curves. By calculating a few of these curves (four are shown in figure 5) we see that all of them share the four stationary points corresponding to spinodal compositions. Moreover, one of the four stationarities is also an intersection points for the curves. According to property (11), this means that the first derivative of the Gibbs energy of mixing vanishes at this point. In other words we must find here a multiple root of the first derivative (an inflection point with horizontal tangent), which is confirmed by figure 4. This shows that a family of $Y$ curves is sufficient to fully describe the equilibrium behavior over the entire composition range, providing, at the same time, reliable initial guesses for accurate flash calculations.

**Ternary systems**

Before presenting any calculation concerning the ternary case, we introduce the following conjecture:

All the stationarities of the $Y$ function corresponding to the initial composition $x_0$ lies on the same line, namely one of the eigendirections of the hessian matrix associated with the Gibbs energy function, that passes through $x_0$. This eigendirection corresponds to the minimum eigenvalue of the hessian matrix, and represents a close approximation to the direction of the tie line passing through $x_0$.

Although this proposition is a conjecture, it proved very useful in calculating liquid-liquid equilibrium compositions, because it helps transforming the exploration of the feasible domain from a two-dimensional problem in a one-dimensional (far much easier) one. Based on this conjecture, the following algorithm may be outlined:

Calculate the eigensystem of the hessian matrix associated with the Gibbs energy surface at $x_0$.

Take the eigenline corresponding to the minimal eigenvalue; solve the non-linear system $\nabla Y = 0$ along this line. Based on the above conjecture, all stationarities of the $Y_{x_0}$ function are guaranteed to lie on this line.

Starting with the stationary points found above (and, of course, different from $x_0$), solve the Rachford-Rice equation, thus finding the equilibrium compositions corresponding to the global state $x_0$.

Figures 6 and 7 show the progress of this algorithm for the system methanol+n-hexane+n-heptane, at 328 K and 1 bar (parameters were taken from DECHEMA, 1980). In the case illustrated by figure 6, the procedure was started at an unstable point (inside the spinodal curve), so the eigenline of the hessian matrix exactly matches the tie line. A contour plot of the $Y$ surface and the profile of the $Y$ function along the eigenline are used to show that a one-dimensional search is sufficient in order to find the stable solution.
Figure 6. Geometry of the Y function surface and its profile along the proper eigenvalue of the $H_G$ matrix (methanol+n-nexane+n-heptane at 328 K and 1 atm)

Figure 7. Geometry of the Y function near the critical point (methanol+n-hexane+n-heptane at 328 K and 1 atm)

Figure 7 illustrates a somewhat more challenging case, namely that of an initial composition close to the critical point. Since the initial point is again in the unstable region, the eigenline matches again the tie line. And again, a one dimensional search is enough to find the equilibrium compositions, even close to the critical point.

**Conclusions**

A new function (the Y function) is introduced, based on an original approach to the phase equilibrium problem, using geometric programming. The new introduced function has some general properties which makes it very useful in describing the equilibrium state in binary and ternary systems. Moreover, due to a conjecture introduced by the authors, the new function allows the equilibrium problem for ternary systems to be reduced to a one-dimensional search, all stationary points of the Y function being guaranteed to lie on the same line. These points being fair approximations to the stable solution, the problem is basically reduced to a one-dimensional search for the solutions to the non-linear system $\nabla Y = 0$. The new solution procedure, based on this function, is illustrated with examples for the binary and ternary case.

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