



Test for the detection of the retrograde melting phenomenon in computed solid–fluid equilibria of binary asymmetric systems



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ABSTRACT

The phenomenon of retrograde melting at constant temperature takes place when a solid phase is melted, or made to disappear, upon compression. Analogously, retrograde melting at constant pressure happens when a solid phase is melted, or made to disappear, upon cooling. In this work, we propose a test that makes possible to establish for a calculated, already converged, binary solid–fluid equilibrium (SFE) point (of temperature T_{SFE} , pressure P_{SFE} , and fluid phase composition z_2), whether the behavior is regular or retrograde and, in case of retrograde behavior, whether the melting phenomenon is retrograde with respect to temperature, or to pressure, or to both. The test is based on evaluating, at T_{SFE} and P_{SFE} , the derivatives of the reduced tangent plane distance (*tpd*) with respect to temperature ($dtpd^*/dT|_{P,z_2}_{SFE}$) and pressure ($dtpd^*/dP|_{T,z_2}_{SFE}$), for a tested phase of composition z_2 , and a trial phase consisting of the pure heavy component in solid state at T_{SFE} and P_{SFE} . The distinguishing feature of the present test is that the derivatives ($dtpd^*/dT|_{P,z_2}_{SFE}$ and $dtpd^*/dP|_{T,z_2}_{SFE}$) are evaluated explicitly from the already converged SFE point, i.e., the present test does not require the computation of additional SFE points. Consequently, the test is fast and can be used for all points of a calculated SFE segment of an isopleth envelope. This leads to the eventual identification of points along the computed SFE segment where transitions from retrograde to regular behavior occur. We present results for a couple of highly asymmetric systems with the help of a model that uses an equation of state for describing the fluid phases, and a standard equation for describing the fugacity of the pure heavy component as a function of temperature and pressure.

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1. Introduction

Experimental solid–fluid equilibrium (SFE) information for binary asymmetric systems is often obtained through the synthetic method, in the form of isopleth envelopes, or part of them, and within relatively narrow ranges of temperature and pressure. Typically, such data are compared to modeling results only within the narrow ranges of conditions of the experiments. The computations therefore do not correspond to a complete isopleth envelope but just to a part of it. For binary asymmetric systems, a generally accepted assumption is that the solid phase is made of the pure heavy component. Frequently, as in Figs. 1 and 2, calculated segments of isopleth envelopes have a constant sign for the pressure versus temperature slope. The knowledge of the sign of the slope may not be enough to determine, for the model, whether the SFE behavior is regular or retrograde. Retrograde melting at constant temperature means “melting upon compression at constant

temperature”, while retrograde melting at constant pressure means “melting upon cooling at constant pressure”.

Retrograde behavior for solid phases in asymmetric nonpolar mixtures has been reported by Łuszczczyk and Radosz [1] and by Gregorowicz [2].

Łuszczczyk and Radosz [1] observed a temperature minimum in the solid–liquid equilibrium curve for a number of constant overall composition tetracontane + propane mixtures. Such minimum implies the appearance of a solid phase upon decompression (at constant temperature) of the initial fluid mixture. This phenomenon can be named “retrograde solidification” at constant temperature, i.e., the appearance of an incipient solid phase by decreasing the system pressure. Vice versa, the disappearance of an incipient solid phase upon compression is named “retrograde melting” at constant temperature.

Gregorowicz [2] presented additional experimental data for the propane + tetracontane system and claimed that a temperature minimum, on the solid–liquid boundary of a constant composition mixture (isopleth), is a necessary condition for the occurrence of the phenomenon of retrograde melting.

For binary systems of type B (e.g., propane + tetracontane [1]) and of type F (e.g., ethylene + n-eicosane [2]) [3,4], Gregorowicz

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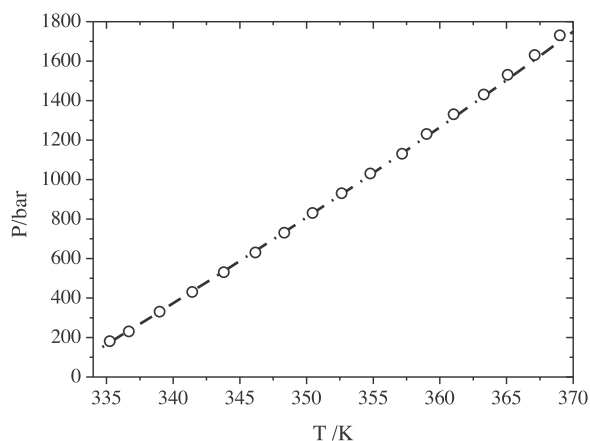


Fig. 1. Solid–fluid equilibrium isopleth segment for the system $\text{CH}_4 + n\text{-C}_{30}\text{H}_{62}$ at 0.5 $n\text{-C}_{30}\text{H}_{62}$ mole fraction. Experimental SFE data: \circ [12]. Calculated solid–fluid equilibrium: dashed-dotted line. Model: PR-EoS and Eq. (1) in Appendix A of Ref. [9]. Parameters: Tables 1a, 1b and 2.

[2] proposed to identify the occurrence of retrograde melting by looking, in an isopleth, at the sign of the slope of the solid–liquid equilibrium line, at the point where it meets the solid–liquid–vapor equilibrium curve. In this work, we show, among other things, that the sign of such slope is not, in general, a proper indicator of retrograde behavior.

As it was pointed out by Gregorowicz in Ref. [2], the appearance of a solid phase upon decompression has also been observed for other nonpolar asymmetric systems such as propane + acenaphthene [5], propane + tetratriacontane [6] and ethane + eicosane [7,8].

Moreover, this phenomenon was also detected in binary asymmetric systems containing pharmaceutical compounds and light solvents, within ranges of conditions including those where the solvents are near-critical or supercritical: CO_2 + mitotane [9], CO_2 + medroxyprogesterone acetate [10], CO_2 + progesterone [11] and n -butane + progesterone [11].

In Fig. 1 we present a solid–fluid equilibrium (SFE) isopleth envelope segment for the $\text{CH}_4 + n\text{-C}_{30}\text{H}_{62}$ system at 0.5 mole fraction of $n\text{-C}_{30}\text{H}_{62}$. The experimental data (circles) are from Ref. [12] and the dashed-dotted line corresponds to our calculation results. Analogous information is depicted in Fig. 2 for the SFE isopleth envelope segment of the CO_2 + progesterone system at 0.00014 mole fraction

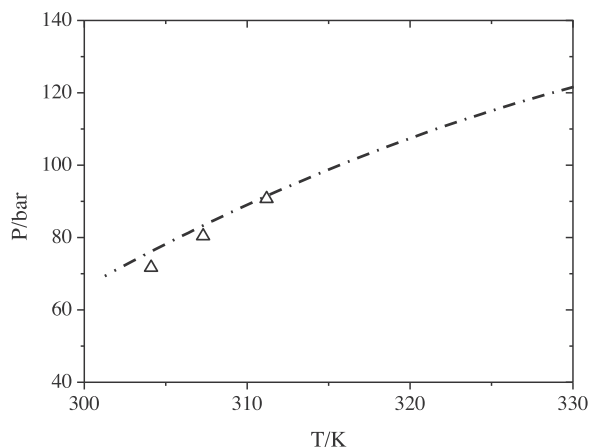


Fig. 2. Solid–fluid equilibrium isopleth segment for the system CO_2 + progesterone at 0.00014 progesterone mole fraction. Experimental SFE data: \triangle [11]. Calculated solid–fluid equilibrium: dashed-dotted line. Model: PR-EoS and Eq. (1) in Appendix A of Ref. [9]. Parameters: Tables 1a, 1b and 2.

of progesterone, where the experimental data (triangles) are from Ref. [11] and the dash-dotted line corresponds to our computations. Further details about the model and the parameters used to obtain the calculation results presented in Figs. 1 and 2 will be given later. Both figures show an acceptable description of the experimental data, at least in the range of the experimental SFE points. According to the experimental data and to the calculation results, the SFE isopleth envelope segment in Fig. 1 presents a positive slope but it is not possible to establish, just by looking at the plot, on which side of this SFE boundary the homogeneous and the heterogeneous states are located; in other words, whether the heterogeneous condition will be present at higher pressures or at lower pressures than those of the SFE boundary. If the heterogeneous region were located above the SFE boundary in Fig. 1, then, the system would present a regular behavior with respect to both, pressure and temperature. The opposite situation (heterogeneous region below the line in Fig. 1) corresponds to a retrograde solidification phenomenon with respect to pressure, which is characterized by the disappearance of a solid phase with the increase in pressure. Moreover, in this case, i.e., if the heterogeneous region laid below the SFE boundary, then, a retrograde behavior with respect to temperature would also be present because, at constant pressure, it would be possible, starting off at a point on the homogeneous region, to reach a SFE transition by increasing the temperature. This means also that a solid phase could be forced to melt by decreasing the temperature. Fig. 2 qualitatively looks just as Fig. 1, and the question on the location of the heterogeneous region relative to the solid–fluid boundary also applies to Fig. 2. It turns out that the behavior of the experimental data in Fig. 1 is regular and that of the experimental data in Fig. 2 is retrograde. The situation is the same for the calculated SFE boundaries. A given point of a SFE line is computed by solving iteratively the appropriate system of equations. To fully characterize the behavior of a given combination of SFE model and parameter values, it is desirable to define a local test, not requiring additional SFE calculations, that would tell, for a given converged SFE binary point, whether the behavior is, for the model, retrograde or regular. The purpose of this work is to propose and verify one such test. By using the word “local” we mean that the test should make possible to avoid the computation of a full isopleth envelope, or of a segment of the isopleth envelope, to determine the nature of the SFE behavior (regular versus retrograde). In other words a “local” test would be one relying only on the information of the already evaluated SFE point.

2. SFE model and SFE calculation

To illustrate how the SFE behavior test to be proposed works, we consider the systems methane + n -triacontane and carbon dioxide + progesterone, i.e., the systems of Figs 1 and 2. To obtain calculated SFE segments, as those of Figs 1 and 2, we solve the isofugacity condition for the heavy component in the fluid phase and in the solid phase, under conditions of uniform pressure and temperature throughout the heterogeneous system. For describing the fluid phase we adopted the Peng–Robinson equation of state (PR-EOS) [13]. Due to the high asymmetry of the binary systems studied in this work, we assume that a given solid phase is only made of the pure heavy component (i.e. n -triacontane in Fig. 1 and progesterone in Fig. 2). To represent the fugacity of the pure solid, which constitutes one of the phases at equilibrium, we adopted the expression described in Appendix A of Ref. [9]. The values for the pure compound parameters and for the binary interaction parameters (k_{ij} , l_{ij}) used within the PR-EOS are reported in Tables 1a and 1b, respectively, while the values for the constants of the pure heavy component solid fugacity expression are reported in Table 2. The parameters in Table 1b are such that a good agreement with

Table 1a
Pure compound properties.

Compound	$T_{\text{crit}}^{\text{a}}/\text{K}$	$P_{\text{crit}}^{\text{b}}/\text{bar}$	ω^{c}	Ref.
CH ₄	190.564	45.99	0.0115478	[21]
n-C ₃₀ H ₆₂	844	8.0	1.30718	[21]
CO ₂	304.1	73.8	0.239	[22]
Progesterone	932.3	19.2	0.52	[23]

^a Critical temperature.^b Critical pressure.^c Acentric factor.**Table 1b**
Binary interaction parameters for the PR-EOS [13].

System	k_{ij}	l_{ij}	Ref.
CH ₄ + n-C ₃₀ H ₆₂	0.0611	0.0206	[14]
CO ₂ + progesterone	0.0220	-0.0617	[11]

experimental data is found for the computed pressure–temperature projections of the isoplethic fluid–fluid equilibria shown later in this manuscript, i.e., in Figs. 6 and 7. Table 1b parameters for CH₄ + n-C₃₀H₆₂ were fitted in Ref. [14] from only fluid–fluid equilibrium data. For consistency, these parameters should be used for any other vapor–liquid, liquid–liquid or fluid–fluid equilibrium computation, since, due to the continuity between the vapor and liquid states, i.e., to the existence of fluid–fluid critical points, all fluid phases must have the same values for the interaction parameters. Table 1b parameters can be used to compute liquid–liquid equilibria at the conditions of Figs. 6 and 7. Such equilibria exist within the universe of the model, because the systems of both figures are highly asymmetric. We have verified this existence by using the algorithms reported in Ref. [15]. However, such equilibria were found to be metastable with respect to the equilibria shown in Figs. 6 and 7. No experimental data of equilibria involving solids have been used in obtaining the parameter values reported in Table 1b for Ref. [14]. Our approach has always been first to obtain the interaction parameters (which appear only in the fluid-state EOS) from experimental fluid–fluid equilibria only, and then to fit the (pure) solid phase parameters from experimental equilibrium information involving both a fluid phase and the solid phase. In conclusion, the interaction parameters such as those of Table 1b should be used for the fluid phase or fluid phases in any kind of equilibria involving at least one fluid phase (vapor–liquid, liquid–liquid, liquid–liquid–vapor, solid–liquid, solid–vapor, solid–liquid–vapor and etcetera). The goal of this paper is to present and evaluate a test related to solid–fluid equilibrium, and not to find models that would accurately reproduce experimental information over wide ranges of conditions. When looking for a good quantitative performance in the representation, for asymmetric systems, of equilibria involving fluid phases one should use mixing rules significantly more flexible than quadratic mixing rules, as, e.g., mixing rules cubic with respect to composition [16,17].

Table 2
Parameters for the solid fugacity expression.^a

System	CH ₄ + n-C ₃₀ H ₆₂ ^b	CO ₂ + progesterone ^c
$\Delta v^{\text{S-L}}/(\text{m}^3/\text{kmol})$	-0.0757501185	-0.156300841
C_1/bar	-13127.8951	-1995.3919
C_2/bar	13201.6315	-
C_3/bar	-41426.7181	-
T_{tp}/K	338.65	406.11
P_{tp}/bar	2.3321131×10^{-9}	$1.56246138 \times 10^{-4}$

^a Fugacity expression described in Appendix A of Ref. [9].^b Parameters from Ref. [14].^c Parameters from Ref. [4].

For further details on the model and the calculation algorithm used here for the computation of isopleths see Refs. [9,4].

3. A test for characterizing the nature of a calculated binary SFE point

We want to establish for an already converged binary SFE point, of temperature T , pressure P , and fluid phase composition z_2 , whether the behavior is regular or retrograde with respect to temperature and/or to pressure. For that, we consider the stability, at temperature T and pressure P , of a binary fluid phase of composition z_2 . This last variable is the mole fraction of the heavy component, i.e., the component labeled “2”, in the fluid phase. Whether the fluid phase is stable or not can be rigorously established by evaluating the tangent plane distance (TPD) function [18] at T and P , in the full range of variable w_2 . This variable is the mole fraction of component “2” in the trial phase. Strictly, all kinds of trial phases (fluid and/or solid) should be considered in the evaluation of the TPD function. If a trial phase of composition w_2 is found to have a negative TPD, then, the fluid phase of composition z_2 is globally unstable at the set T and P . The result is the same if instead of considering the TPD, we use the reduced tangent plane distance tpd , which is defined as $[tpd = \text{TPD}/(RT)]$, where R is the universal gas constant. In particular the TPD (or tpd) function is to be evaluated for a trial phase which is solid and it is made of the pure heavy component. It can be shown that such tpd , which we name tpd^* , is given by the natural logarithm of the ratio: fugacity of component “2” in pure solid state over fugacity of component “2” in the tested fluid phase (of composition z_2), being both fugacities evaluated at T and P . This conclusion can be reached from an equation analogous to Eq. (8) in Ref. [18] (p. 188) after some algebra, by considering that a differential amount of the heavy component is transferred, at constants T and P , from the binary fluid phase to the pure solid phase, thus taking the fluid phase as the tested phase and the pure heavy component solid phase as the trial phase. Also an equation analogous to Eq. (1) in p. 197 in Ref. [18] has to be considered. In the modeling approach of this work, the fugacities are not explicit functions of pressure. Therefore, tpd^* is calculated by solving the following system of equations:

$$F_1 = 0 \quad (1)$$

$$F_2 = 0 \quad (2)$$

$$F_3 = 0 \quad (3)$$

where the functions F_1 to F_3 are defined as follows:

$$F_1 = tpd^* - \ln \left[\frac{f_2^{\text{S}}(P, T, v_o)}{\hat{f}_2(T, z_2, v_z)} \right] \quad (4)$$

$$F_2 = P - h_{pVT}(T, z_2, v_z) \quad (5)$$

$$F_3 = P - h_{pVT}(T, 1, v_o) \quad (6)$$

In the above equations, $P = h_{pVT}(T, x_2, v)$ is the equation of state (EOS) relationship, for a binary system, at fluid state, between the absolute temperature (T), the molar volume of the fluid phase (v), the mole fraction of the heavy component, labeled “2” (x_2), and the absolute pressure (P), where the function h_{pVT} corresponds to the PR-EOS [13] in this work. $\hat{f}_2 = \hat{f}_2(T, z_2, v_z)$ is the fugacity of component 2 in the tested fluid phase and corresponds to the same EOS that defines the function h_{pVT} . Such fugacity is evaluated at the system temperature T , mole fraction of component 2, z_2 , and molar volume v_z , both of the tested fluid phase. tpd^* is the reduced tangent plane distance for a tested fluid phase at T , z_2 , and system pressure P , and a trial solid phase made of the pure heavy component “2” (the trial phase is at the same T and P than the tested phase). $f_2^{\text{S}}(P, T, v_o)$ is the fugacity of the pure heavy component

(labeled “2”) in solid state at system temperature T and pressure P . ν_o is the pure heavy component molar volume, in liquid state, at T and P . See Ref. [4].

To fix ideas, the tangent plane distance tpd^* could be calculated, at set T , P and z_2 , as follows. (a) Solve Eq. (2) for ν_z . (b) Solve Eq. (3) for ν_o . (c) Solve Eq. (1) for tpd^* . If the calculated tpd^* is such that $tpd^* > 0$, then, the tested (fluid) phase is stable with respect to a solid–fluid equilibrium. For $tpd^* < 0$, the tested phase is unstable with respect to a solid–fluid equilibrium. If it happens that the calculated tpd^* equals zero, then, the fluid phase is at equilibrium with the solid phase. Notice that at $tpd^* = 0$ Eq. (1) becomes the necessary condition of binary solid–fluid equilibrium, i.e., the isofugacity condition for the heavy component in the solid and fluid phases. Notice that the isofugacity condition for the light component (“1”) does not play a role under equilibrium conditions because such component is assumed not to be present in the solid phase.

As previously stated, if tpd^* is set equal to zero, then, Eqs. (4)–(6) become a SFE equilibrium system of equations. Although equilibrium among two or more phases implies that tpd equals zero for any pair of equilibrium phases (one taken as the tested phase, and the other as the trial phase), imposing a zero value for tpd generally does not imply equilibrium. This is true already for a binary two-phase equilibrium where none of the phases are made of a pure compound.

It should be clear that at, e.g., set T and z_2 , the set of Eqs. (1)–(3) implicitly define the variable tpd^* as a function of P . This is because the total number of variables is six (T , z_2 , P , ν_o , ν_z and tpd^*), and the number of equations is 3. This results in three degrees of freedom that can be considered to be the set T and z_2 , and P , which is considered to vary in a range. Eqs. (1)–(3) also define, implicitly, the derivative of tpd^* with respect to pressure P , at constant T and z_2 . This derivative could be computed numerically, e.g., through finite differences. This would require to solve Eqs. (1)–(3) at least twice, once at T , z_2 and P , and a second time at T , z_2 and $P + \Delta P$, having ΔP a suitable value that minimizes the error in the computed derivative. The numerical differentiation through finite differences can be avoided through implicit differentiation as explained below.

At set T and z_2 , the remaining variables in the set of Eqs. (1)–(3), are P , ν_o , ν_z and tpd^* , i.e., there is a degree of freedom. We add an equation to make the number of unknowns become equal to the number of equations, i.e.,

$$F_4 = 0 \quad (7)$$

where F_4 is defined as follows:

$$F_4 = P - P_{spec} \quad (8)$$

P_{spec} is a parameter that specifies the value of the pressure at which tpd^* is to be evaluated (by solving Eqs. (1)–(3) and (7)). For instance, to evaluate tpd^* at 35 bar P_{spec} has to be replaced by 35 in Eq. (7).

To evaluate the effect of pressure on tpd^* we need to compute the derivative of tpd^* with respect to pressure at set T and z_2 , i.e., $dtpd^*/dP|_{T,z_2}$, which we can obtain by implicitly differentiating the system of Eqs. (1)–(3) and (7). For that, we derive each of the four equations with respect to the only independent variable, i.e., P_{spec} , using the chain rule while recognizing that P , ν_o , ν_z and tpd^* become, each of them, exclusive functions of P_{spec} at set T and z_2 . In particular, P is always identical to P_{spec} , as stated by Eq. (7). The result of the implicit differentiation is the following equation:

$$J(\vec{F}) \left(\frac{d\vec{X}}{dP_{spec}} \right) + \left(\frac{\partial \vec{F}}{\partial P_{spec}} \right) = 0 \quad (9)$$

In Eq. (9), vectors \vec{X} , $d\vec{X}/dP_{spec}$, \vec{F} and $\partial \vec{F}/\partial P_{spec}$ are respectively the following:

$$\vec{X}^T = [tpd^* \quad P \quad \nu_z \quad \nu_o] \quad (10)$$

$$\left\{ \frac{d\vec{X}}{dP_{spec}} \right\}^T = \left[\frac{dtpd^*}{dP_{spec}} \quad \frac{dP}{dP_{spec}} \quad \frac{d\nu_z}{dP_{spec}} \quad \frac{d\nu_o}{dP_{spec}} \right] \quad (11)$$

$$\vec{F}^T = [F_1 \quad F_2 \quad F_3 \quad F_4] \quad (12)$$

$$\left\{ \frac{\partial \vec{F}}{\partial P_{spec}} \right\}^T = [0 \quad 0 \quad 0 \quad -1] \quad (13)$$

Notice that the system made of Eqs. (1)–(3) and (7) is written in a more compact way as follows:

$$\vec{F} = \vec{0} \quad (14)$$

where $\vec{0}$ is the null vector.

In Eq. (9), $J(\vec{F})$ is the Jacobian matrix of the vector function \vec{F} . $J(\vec{F})$ contains information on the partial derivatives of functions F_1 to F_4 with respect to the four variables in vector \vec{X} . The expressions for the partial derivatives which are the elements of $J(\vec{F})$ where obtained in this work by symbolic differentiation, i.e., we used an analytical Jacobian matrix.

The vector $d\vec{X}/dP_{spec}$ is the sensitivity vector whose first element is the derivative $dtpd^*/dP_{spec}|_{T,z_2}$ evaluated at a pressure value equal to P_{spec} . Vector $d\vec{X}/dP_{spec}$ is obtained by solving Eq. (9) which is actually a linear system of equations.

To again fix ideas, if, a set T and z_2 and P_{spec} , tpd^* has been calculated, then, all components of vector \vec{X} (Eq. (10)) are known and $J(\vec{F})$ can be evaluated. Next, Eq. (9) can be solved for the sensitivity vector, which provides a numerical value for $dtpd^*/dP_{spec}|_{T,z_2}$ at P_{spec} . Since Cramer’s rule provides an analytical expression for each of the variables that satisfy a linear system of equations, it is possible to obtain an analytical expression for the derivative $dtpd^*/dP_{spec}|_{T,z_2}$ at P_{spec} , that sets it as an explicit function of the variables of the system (14). In such a case the computation of $dtpd^*/dP_{spec}|_{T,z_2}$ at P_{spec} is non-iterative for an already calculated tpd^* . The calculation procedure for obtaining $dtpd^*/dP_{spec}|_{T,z_2}$ at P_{spec} works, both, when the tested fluid phase and the solid phase are not at equilibrium, and when they are. In other words, the procedure for computing $dtpd^*/dP_{spec}|_{T,z_2}$ is applicable both, when $tpd^* \neq 0$ (no SFE) and when $tpd^* = 0$ (SFE). Notice that the derivative $dtpd^*/dP_{spec}|_{T,z_2}$ is the same than the derivative $dtpd^*/dP|_{T,z_2}$, in virtue of Eq. (7). Notice that the derivative $dtpd^*/dP_{spec}|_{T,z_2}$ considers that the system (14) remains satisfied during the derivation process.

Suppose that we want to establish whether a calculated binary solid–fluid equilibrium point is regular or retrograde with respect to pressure at constant temperature and constant fluid phase composition. For such SFE, tpd^* equals zero, and the values for all variables in vector \vec{X} are known. With such information the derivative $dtpd^*/dP|_{T,z_2}$ can be computed as previously explained. If $dtpd^*/dP|_{T,z_2} > 0$, then, a differential increase in pressure ($dP > 0$) takes the value of tpd^* from zero to a positive value (since $dtpd^* > 0$). This indicates a transition from a SFE to a situation where the fluid phase is more stable than the SFE, i.e., a transition from a SFE to a homogeneous fluid state upon a pressure increase. This is a retrograde behavior with respect to pressure. If $dtpd^*/dP|_{T,z_2} > 0$, then, a differential decrease in pressure ($dP < 0$) makes tpd^* go from zero to a positive value (since again $dtpd^* > 0$): this is a transition from a SFE to a homogeneous fluid state upon a pressure decrease, i.e., this is a regular behavior with respect to pressure. In summary, if the derivative $dtpd^*/dP|_{T,z_2}$ evaluated under SFE conditions is positive, then, the behavior is retrograde with respect to pressure. Otherwise (negative sign), it is regular. Notice that this test can be applied to an isolated calculated SFE, i.e., the knowledge of a calculated segment of the isopleth envelope is not needed to apply the test. In other words, this test tells us what the nature is of a calculated SFE, when the pressure is changed at constant temperature and constant fluid phase composition, on the basis of solely the information of the

Table 3
Nature of the computed Solid–Fluid equilibrium behavior for binary systems.^{a,b,c}

Mathematical condition	Meaning
$(dtpd^*/dP _{T,z_2})_{SFE} > 0$	Retrograde SFE behavior with respect to pressure
$(dtpd^*/dP _{T,z_2})_{SFE} < 0$	Regular SFE behavior with respect to pressure
$(dtpd^*/dT _{P,z_2})_{SFE} < 0$	Retrograde SFE behavior with respect to temperature
$(dtpd^*/dT _{P,z_2})_{SFE} > 0$	Regular SFE behavior with respect to temperature

^a The solid phase is considered to be made of the pure heavy component.

^b The subscript “SFE” means that the derivative is evaluated under conditions of solid–fluid equilibrium ($tpd^* = 0$). Notice, however, that the SFE condition is NOT kept during the differentiation process.

^c Criteria applicable at the boundary between a homogeneous fluid region and a solid–fluid equilibrium region.

considered SFE point. Indeed, the present test can be applied to all points of a calculated segment of an isopleth envelope. A numerical example of the application of the present test is presented in Appendix A of this work.

An analogous analysis can be performed that would lead to a test to establish whether a SFE point, computed at set pressure and fluid phase composition, is retrograde with respect to temperature. In such a case, it is necessary to calculate the derivative of the tpd^* with respect to temperature at constant pressure, i.e., $dtpd^*/dT|_{P,z_2}$. The condition for retrograde behavior with respect to temperature is $dtpd^*/dT|_{P,z_2} < 0$, and for regular behavior is $dtpd^*/dT|_{P,z_2} > 0$. In this last case the solid is melted when the temperature is increased. The mentioned analogous analysis would require to redefine function F_4 as $F_4 = T - T_{spec}$, and to perform the implicit differentiation with respect to T_{spec} . Table 3 summarizes the test here proposed for detecting the nature of computed solid–fluid equilibria.

Notice that the criteria summarized in Table 3 apply at the boundary between a homogeneous fluid region and a heterogeneous solid–fluid region. It does not apply at a boundary between a (strictly) solid region and a solid–fluid region. This is because the present criteria imply the evaluation of the stability of a fluid phase with respect to a solid–fluid equilibrium, rather than the stability of a homogeneous solid phase with respect to a solid–fluid equilibrium.

4. Results

In Fig. 3 we present the results of the computation of $(dtpd^*/dP|_{T,z_2})_{SFE}$ for all points of the calculated solid–fluid

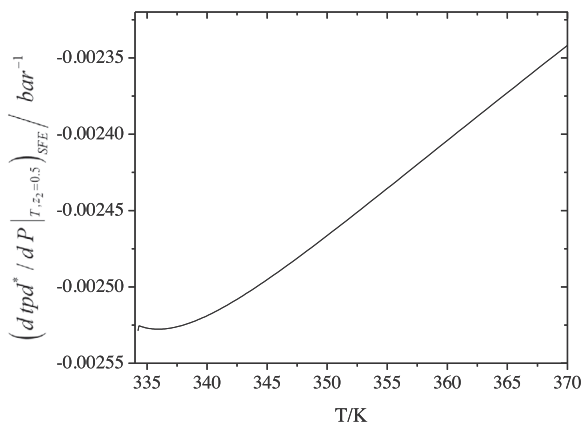


Fig. 3. The $(dtpd^*/dP|_{T,z_2=0.5})_{SFE}$ vs. temperature for the calculated solid–fluid equilibrium isopleth segment shown in Fig. 1. System: $\text{CH}_4(1) + n\text{-C}_{30}\text{H}_{62}(2)$. Isopleth composition: 0.5 mole fraction of $n\text{-C}_{30}\text{H}_{62}$ ($z_2 = 0.5$). The subscript “SFE” means that the derivative has been evaluated at solid–fluid equilibrium conditions $tpd^* = 0$.

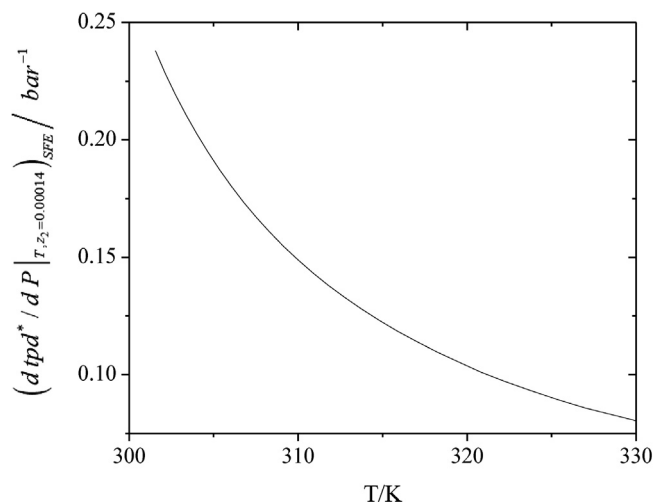


Fig. 4. The $(dtpd^*/dP|_{T,z_2=0.00014})_{SFE}$ vs. temperature for the calculated solid–fluid equilibrium isopleth segment shown in Fig. 2. System $\text{CO}_2(1) + \text{progesterone}(2)$. Isopleth composition: 0.00014 mole fraction of progesterone ($z_2 = 0.00014$). The subscript “SFE” means that the derivative has been evaluated at solid–fluid equilibrium conditions $tpd^* = 0$.

equilibrium isopleth segment (shown in Fig. 1) of $\text{CH}_4 + n\text{-C}_{30}\text{H}_{62}$ system at 0.5 mole fraction of $n\text{-C}_{30}\text{H}_{62}$. For the whole temperature range of Fig. 3 the derivative $(dtpd^*/dP|_{T,z_2})_{SFE}$ is less than zero, i.e., the test tells (Table 3) that, for the model, the SFE behavior is regular with respect to pressure, for the studied system, under the conditions in Fig. 1, i.e., the solid–fluid region lies, for the model, above the line in Fig. 1. This result agrees with the experimental behavior reported in Ref. [12]: the authors declare [12] that for obtaining the solid–fluid equilibrium data points (shown in Fig. 1) the experiment is started in the solid + fluid region and, keeping the pressure constant, the temperature is slowly increased until a homogeneous state is reached. Therefore, the heterogeneous condition is found at pressures higher than those of the experimental data in Fig. 1, in agreement with the results of our test.

Fig. 4 shows the calculated $(dtpd^*/dP|_{T,z_2=0.00014})_{SFE}$ for all points of the calculated solid–fluid equilibrium isopleth segment (shown in Fig. 2) of the $\text{CO}_2 + \text{progesterone}$ system at 0.00014 mole fraction of progesterone. Throughout the temperature range of this figure, the derivative $(dtpd^*/dP|_{T,z_2=0.00014})_{SFE}$ is positive. Hence, the present test tells (Table 3) that the model predicts a retrograde SFE behavior with respect to pressure. These results are in agreement with experimental observations by Favareto and coworkers [11] who obtained the SFE transitions from a homogeneous condition by diminishing pressure at constant temperature. Then, the homogeneous condition is found above each experimental point in Fig. 2, i.e., a retrograde behavior with respect to pressure was experimentally detected; and the results of our test imply that the model agrees with these observations (see Fig. 4).

For the SFE isopleth segment of 0.00014 in mole fraction of progesterone (considered in Figs. 2 and 4) we have also tested whether the phase behavior is, for the model, regular or retrograde, now with respect to temperature. The results shown in Fig. 5 confirm a retrograde behavior with respect to temperature, for the model, because the derivative $(dtpd^*/dT|_{P,z_2=0.00014})_{SFE}$ is negative (Table 3) throughout the temperature range of Fig. 5. This result indicates that the model is again in agreement with the experimental observations [11].

For gaining a deeper understanding of the predicted phase behavior of both systems here studied, we present their complete calculated isopleths in Figs. 6 and 7. In these figures, we show the experimental data from the literature and the lines that correspond to our calculation results (further details are available in

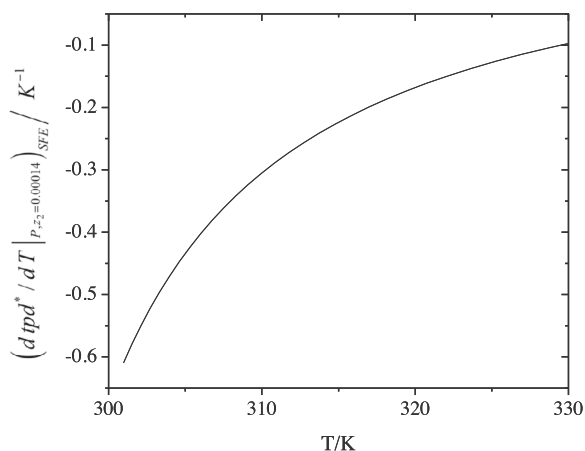


Fig. 5. The $(dtpd^*/dT)|_{P,z_2=0.00014}_{SFE}$ vs. temperature for the calculated solid–fluid equilibrium isopleth segment shown in Fig. 2. System $\text{CO}_2(1) + \text{progesterone}(2)$. Isopleth composition: 0.00014 mole fraction of Progesterone ($z_2 = 0.00014$). The subscript “SFE” means that the derivative has been evaluated at solid–fluid equilibrium conditions $tpd^* = 0$.

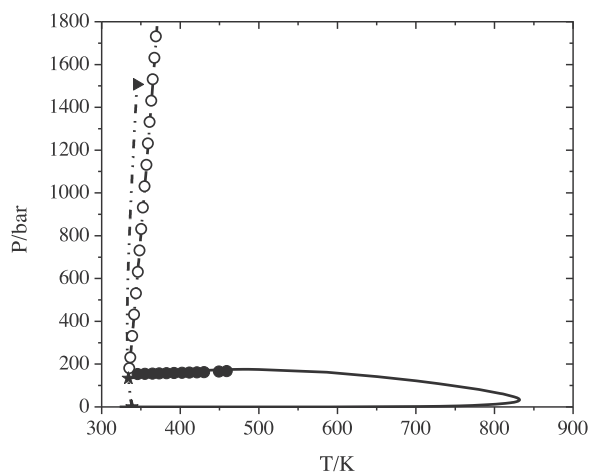


Fig. 6. Isopleth for the $\text{CH}_4 + n\text{-C}_{30}\text{H}_{62}$ system at 0.5 $n\text{-C}_{30}\text{H}_{62}$ mole fraction. Experimental data [12]: ● LVE, ○ SFE. Calculated phase equilibrium: solid line: LVE; dashed line: SFE; dashed-dotted line: SLV equilibrium; stars: SLV equilibrium points that belong to the calculated isopleth phase envelope; triangle: calculated second critical end point. Model: PR-EoS and Eq. (1) in Appendix A of Ref. [9]. Parameters: Tables 1a, 1b and 2.

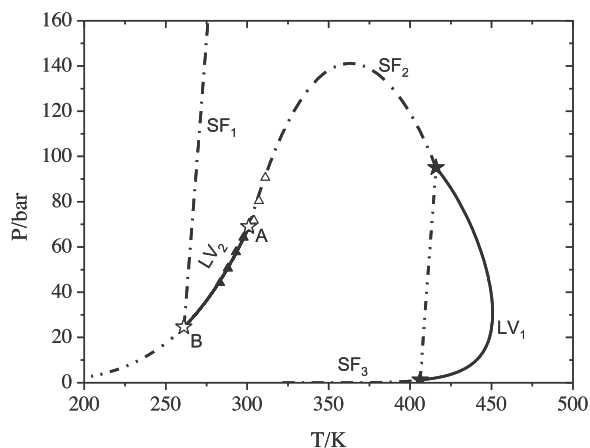


Fig. 7. Isopleth for the $\text{CO}_2 + \text{progesterone}$ system at 0.00014 progesterone mole fraction. Experimental data [11]: full triangles: LVE; empty triangles: SFE. Calculated phase equilibrium: solid lines: LVE; dashed-dotted lines: SFE; dashed-double dotted lines: SLV equilibrium; empty and full stars: calculated SLV equilibrium points that belong to the calculated isopleth phase envelope. Model: PR-EoS and Eq. (1) in Appendix A of Ref. [9]. Parameters: Tables 1a, 1b and 2.

the corresponding captions, where LVE stands for “liquid–vapor–equilibrium” and SLV means “solid–liquid–vapor”).

Fig. 6 shows the isopleth of 0.5 in mole fraction of $n\text{-C}_{30}\text{H}_{62}$ for the $\text{CH}_4 + n\text{-C}_{30}\text{H}_{62}$ system. This isopleth has a low pressure SFE segment (not clearly observed because of the linear scale of the pressure axis) which goes to higher pressures until it meets a SLV equilibrium point. There, a LVE segment arises and goes to higher pressures passing through a maximum in temperature (at about 835 K). Then this LVE line returns to low temperatures and meets a second SLV equilibrium point (star) at 334.23 K and 133.17 bar. Finally, a SFE segment originates at such SLV equilibrium point, and extends to higher pressures. The latter SFE segment is the one shown in Fig. 1, and it has a solid–liquid nature. The triangle in Fig. 6 is sometimes named “second critical end point (2nd CEP)”. It is a point of a binary SLV curve where the fluid phases have become critical. Such point is the termination of the SLV curve. This last curve originates at the triple point of the pure heavy component. At a 2nd CEP a binary critical phase is at equilibrium with a solid phase. In the model used in this work, such solid phase is made of only the pure heavy component of the binary mixture. At a 2nd CEP a binary critical line and a binary fluid–fluid–solid line meet. See Ref. [4] for further details.

Fig. 7 shows the full calculated isopleth of 0.00014 in mole fraction of progesterone. The isopleth envelope has four SLV equilibrium points. At low pressure there is a solid–vapor equilibrium (SVE) segment (SF3, not clearly observed because of the linear scale of the pressure axis) that meets a SLV point (low pressure black star). There, a LVE segment (LV1) originates and passes through a maximum in temperature (at about 450 K). Then, it meets another SLV point at higher pressure (high pressure black star). From this three-phase point, a SFE segment (SF2) arises and goes to lower temperature passing through a maximum in pressure (at about 140 bar) and meets a third SLV point (high pressure empty star). Notice that part of this SFE segment has been shown in Fig. 2. From the third SLV point a new LVE segment (LV2) originates and ends at the fourth SLV point of the isopleth envelope, at lower temperature (lowest temperature empty star). Finally a SFE equilibrium segment (SF1) originates at such three-phase point and goes to higher pressures.

In Figs. 6 and 7, we also show the segments, relevant to the set isopleth composition, of the calculated three-phase curves of these systems. Such information together with all the calculated segments of the isopleth phase envelope, make possible to have a more complete phase behavior description at any temperature and pressure condition. Each three-phase line is properly indicated in the figures. Notice that part of the low temperature SLV segment in Fig. 7 cannot be clearly seen because it is very close, in the isopleth pressure–temperature projection, to the low temperature LVE segment (LV2). In Fig. 8, we show the mass density of the fluid phases involved in the isopleth envelope segments of Fig. 7, vs. temperature. Notice that the density of the fluid phase (δ_F) in the SFE segment that has a local maximum in pressure (SF2) has a continuous change from vapor-like values at high temperature, to liquid-like values at low temperature. Analogous information can be seen in Fig. 9, where the mass density of the fluid phases of the isopleth segments of Fig. 7, is shown as a function of pressure.

When plots such as Figs. 6 and 7 are available, the trained eye can easily identify, for a given point belonging to a calculated solid–fluid equilibrium segment of the isopleth envelope, whether the behavior is regular or retrograde, both, with respect to pressure and with respect to temperature. The test here defined (Table 3), does the same, but solely based on the information of the corresponding converged (isolated) SFE point, and without resorting to additional SFE calculations.

From Figs. 7–9, it should be clear that the SFE segment SF1 is of the solid–liquid type, and the SFE segment SF2 is of the solid–liquid

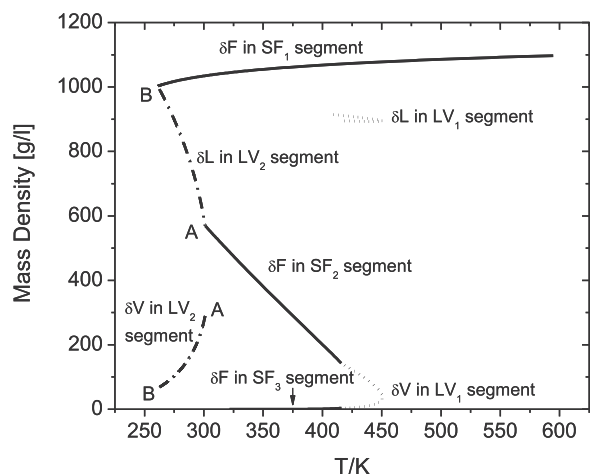


Fig. 8. Calculated mass density of the (fluid) phases at fluid–fluid equilibrium, and of the fluid phase at solid–fluid equilibrium, vs. temperature, for the calculated isopleth shown in Fig. 7. System CO_2 + progesterone at 0.00014 progesterone mole fraction. Phase equilibrium calculated using the PR-EoS and Eq. (1) in Appendix A of Ref. [9] and parameters in Tables 1a, 1b and 2. F = fluid, V = vapor, L = liquid. SF₁: low temperature solid–fluid equilibrium segment in Fig. 7. SF₂: solid–fluid equilibrium segment with a maximum in pressure in Fig. 7. SF₃: low pressure solid–fluid equilibrium segment in Fig. 7. LV₁: high temperature liquid–vapor equilibrium segment in Fig. 7. LV₂: low temperature liquid–vapor equilibrium segment in Fig. 7.

type at temperatures close enough to that of the three-phase point labeled “A” in Figs. 7–9. So, at the SFF point “A”, a positive-slope solid–liquid isopleth segment originates, i.e., segment SF₂. An analogous behavior is seen for segment SF₁, which originates at the SFF point B. However the behavior of segment SF₁ is regular, while that of segment SF₂ is retrograde. In conclusion, the sign of the slope of a solid–liquid segment of an isopleth envelope that originates at a SFF point is not an indicator, of general applicability, for the nature of the SFE behavior (either regular or retrograde). This conclusion improves on the work by Gregorowicz [2] where it was claimed that the sign of the slope of the solid–liquid equilibrium line emerging from the triphasic equilibrium curve, at the point of emergence, is what dictates whether the SF behavior is retrograde or not.

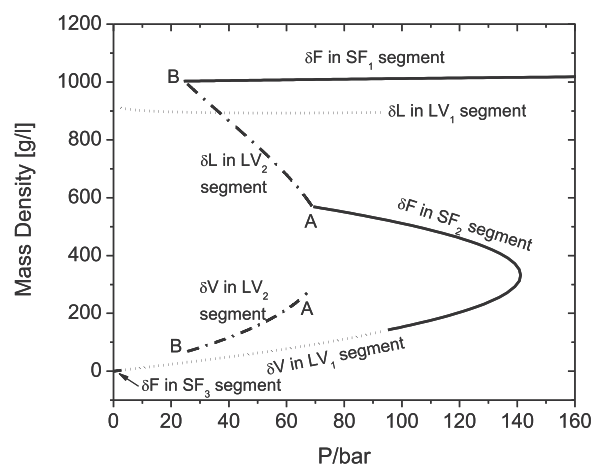


Fig. 9. Calculated mass density of the (fluid) phases at fluid–fluid equilibrium, and of the fluid phase at solid–fluid equilibrium, vs. pressure, for the calculated isopleth shown in Fig. 7. System CO_2 + progesterone at 0.00014 progesterone mole fraction. Phase equilibrium calculated using the PR-EoS and Eq. (1) in Appendix A of Ref. [9] and parameters in Tables 1a, 1b and 2. F = fluid, V = vapor, L = liquid. SF₁: low temperature solid–fluid equilibrium segment in Fig. 7. SF₂: solid–fluid equilibrium segment with a maximum in pressure in Fig. 7. SF₃: low pressure solid–fluid equilibrium segment in Fig. 7. LV₁: high temperature liquid–vapor equilibrium segment in Fig. 7. LV₂: low temperature liquid–vapor equilibrium segment in Fig. 7.

It is known that liquid densities computed using the PR-EoS have a limited quantitative agreement with experimental liquid densities [19]. Thus, a qualitative nature should be ascribed to the density values shown in Figs. 8 and 9.

The test proposed here can be used to quickly establish the presence or absence of retrograde phenomena with respect to pressure and/or temperature, for computed binary SVE and/or solid–liquid equilibrium (SLE) conditions. The test is applicable to all types of behaviors for the univariant lines of the binary system under consideration (i.e., types A to F in the classification of Ref. [4]).

5. Remarks and conclusions

The occurrence of a temperature minimum, in the pressure–temperature (P – T) plane, for a solid–liquid phase boundary of a constant composition mixture (isopleth), is recognized by Gregorowicz [2] as the phenomenon of retrograde melting (melting upon compression). According to Gregorowicz [2], a negative slope of the solid–liquid line emerging from a solid–fluid–fluid (SFF) equilibrium curve is the necessary condition for the retrograde phenomenon to occur. We have shown in this work that such criterion may lead, in some cases, to wrong conclusions.

As discussed in this work, actually, two types of retrograde behaviors can be considered: the retrograde behavior detected through pressure changes at constant temperature, and the retrograde behavior under temperature changes at constant pressure. Besides, along and isopleth envelope, the behavior can change from retrograde to regular or vice versa (e.g., in Fig. 7). Such changes may happen more than once along an isopleth envelope, i.e., retrograde behavior is a local phenomenon: to establish its existence a SFE isopleth phase envelope has to be evaluated point by point.

In this work, we have proposed a test (Table 3) to establish, for a given model + parameter values combination, the nature (retrograde or regular, either with respect to temperature or to pressure), within the universe of the model, of a given computed binary solid–fluid equilibrium (SFE) point. The test can indeed be applied to all points of a computed SFE segment of an isopleth phase envelope. After a converged SFE is obtained, the test is applied by explicitly evaluating a couple of derivatives of certain tangent plane distance. This test could be used when fitting the parameters of the model, for reproducing available SFE experimental information. This would be done by imposing that the evaluated derivatives have the proper sign (inequality restrictions) during the optimization course.

Notice that the present test is based on the relative stability between a homogeneous fluid condition and a solid–fluid equilibrium condition where the solid phase is made of the pure heavy component, i.e., only two points of the tangent plane distance function are considered in the definition of the test.

By applying this test, it is also possible to determine whether an isolated computed binary SFE point is a point of the isopleth envelope where the temperature or the pressure are local extrema. In such a case, one of the derivatives (Table 3) of the tangent plane distance must equal zero.

The present test could be extended in a straightforward way to the case where a multicomponent fluid mixture is at equilibrium with a solid solution, in a point of a SFE envelope segment of an isopleth of composition equal to that of the fluid mixture. In such case, the solution of the linear system of equations, that provides the value of the derivative of the tangent plane distance, might have to be iterative. Notice that the test is related to boundaries

between a homogeneous fluid region and a SFE region. The test is not designed for boundaries separating a (strictly) solid region from a SFE region.

Although we have discussed the present test in the context of computed isopleths, since the test is local, it can also be applied in the context of computed isotherms or isobars.

The present test is applied at phase equilibrium points which lie on the boundary between homogeneity and solid–fluid equilibrium, and the test is applicable to solid–liquid equilibrium, solid–vapor equilibrium and solid–fluid equilibrium where the fluid phase cannot clearly be labeled as “liquid” or “vapor”. Because, on one hand, in the solid–fluid transitions here considered the solid phase is the incipient (not the saturated) phase, and, on the other hand, the nature of the fluid phase is not restricted to the “liquid” case, the reader may find that the present test could be more properly named as a test to detect the phenomenon of “retrograde solidification” rather than of “retrograde melting”. Since in this work we only consider equilibrium situations, and equilibrium does not depend on the path through which it is approached, we have used the words “retrograde melting” as a synonym of “retrograde solidification”.

Notice that the situation where the system has a single solid phase with presence of both components of a binary system is not available to the model used in this work. This is because the solid phase is assumed to be made only of the pure heavy compound.

Notice that the equations presented in this work assume that the fluid phase pressure and fluid component fugacities are explicit functions of temperature, composition and molar volume. This is the case for the Peng–Robinson EOS, and also the case for a great number of other EOS, e.g., the various versions of the SAFT-EOS, for which the present test can be straightforwardly implemented.

Acknowledgements

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Appendix A.

A.1. Numerical example on the application of the present retrograde melting detection test

In this work, the actual calculations were performed using logarithmically scaled variables. To rewrite the system (14) we proceed as follows. Consider for instance the pressure P . We define the scaled pressure P^* as follows:

$$P^* = \ln(P) \quad (\text{A.1})$$

In the system (14), variable P has to be replaced by its expression in terms of P^* , as prescribed by the following equation, derived from Eq. (A.1):

$$P = \exp(P^*) \quad (\text{A.2})$$

Then, the system (14) becomes written in terms of the variables tpd^* , z_2^* , T^* , P^* , v_z^* , v_o^* and P_{spec}^* .

We designate the functions F_1 to F_4 , after having been re-written in terms of the previous scaled variables, as F_1^* , F_2^* , F_3^* and F_4^* , i.e.,

$$\vec{F}^{*T} = [F_1^* \quad F_2^* \quad F_3^* \quad F_4^*] \quad (\text{A.3})$$

Also:

$$\vec{X}^{*T} = [tpd^* \quad P^* \quad v_z^* \quad v_o^*] \quad (\text{A.4})$$

Then, system (14) is now re-written as:

$$\vec{F}^* = \vec{0} \quad (\text{A.5})$$

Notice that variable, tpd^* , has not been scaled in this work because it could have negative values or be equal to zero.

Logarithmically scaled variables have a much narrower range of variation than non-scaled variables when the non-scaled variables cover several orders of magnitude. This acquires practical importance, from the computational standpoint, when, for example, a binary solid–fluid equilibrium point at set temperature and pressure is being calculated and it happens that the mole fraction of one of the components tends to zero [20].

Moreover, Eq. (9) must be rewritten in terms of the scaled variables, i.e.,

$$J(\vec{F}^*) \left(\frac{d\vec{X}^*}{dP_{spec}^*} \right) + \left(\frac{\partial \vec{F}^*}{\partial P_{spec}^*} \right) = 0 \quad (\text{A.6})$$

where

$$\left\{ \frac{d\vec{X}^*}{dP_{spec}^*} \right\}^T = \left[\frac{dtpd^*}{dP_{spec}^*} \quad \frac{dP^*}{dP_{spec}^*} \quad \frac{dv_z^*}{dP_{spec}^*} \quad \frac{dv_o^*}{dP_{spec}^*} \right] \quad (\text{A.7})$$

Actually, rather than applying the recipe (A.2) directly on Eq. (8), it is better to define F_4^* as follows, as we did in this work:

$$F_4^* = P^* - P_{spec}^* \quad (\text{A.8a})$$

In this way, we avoid an unnecessary increase in the degree of non-linearity when going from system (14) to system (A.5). The same criterion is applied to Eqs. (5) and (6) which are conveniently replaced by the following equations:

$$F_2^* = P^* - \ln\{h_{pVT}[\exp(T^*), \exp(z_2^*), \exp(v_z^*)]\} \quad (\text{A.8b})$$

$$F_3^* = P^* - \ln\{h_{pVT}[\exp(T^*), 1, \exp(v_o^*)]\} \quad (\text{A.8c})$$

For the sake of completeness we show the expression for F_1^* , i.e.,

$$F_1^* = tpd^* - \ln \left\{ \frac{f_2^S[\exp(P^*), \exp(T^*), \exp(v_o^*)]}{\hat{f}_2[\exp(T^*), \exp(z_2^*), \exp(v_z^*)]} \right\} \quad (\text{A.8d})$$

Using the definition (A.8a) for F_4^* , we have:

$$\left\{ \frac{\partial \vec{F}^*}{\partial P_{spec}^*} \right\}^T = [0 \quad 0 \quad 0 \quad -1] \quad (\text{A.9})$$

Notice that the Jacobian $J(\vec{F}^*)$ is made of partial derivatives with respect to the variables of vector \vec{X} : three of them are scaled (P^* , v_z^* , v_o^*) and the remaining one, i.e., tpd^* , is not.

Now, consider a converged solid–fluid equilibrium point ($tpd^* = 0$) for the CO₂ + progesterone system belonging such point to the isopleth of 0.00014 mole fraction of progesterone (see model parameters in Tables 1a, 1b and 2). The fluid phase composition, temperature, pressure and molar volume values of such a converged point are listed in Table 4. We want to establish whether the melting behavior of this binary solid–fluid equilibrium point is regular or retrograde with respect to pressure at set temperature ($T = 415.9295999$ K) and set fluid phase composition ($z_2 = 0.00014$). Then, for such a point, the values for all the variables in vector \vec{X}^* (Eq. (A.4)); i.e., the vector of scaled variables, are known (see Table 4). With such information, $J(\vec{F}^*)$ can be evaluated (Table 5), and Eq. (A.6) can be solved for the sensitivity vector $d\vec{X}^*/dP_{spec}^*$ (Table 6). One of the components of the sensitivity vector is the derivative $dtpd^*/dP_{spec}^*$. Since $[(dtpd^*/dP_{spec}^*)/(dP^*/dP_{spec}^*)] = (dtpd^*/dP^*)$, we have that $(dtpd^*/dP^*) = 2.432654$ for the case of Table 6, i.e., $dtpd^*/dP^*|_{T,z_2} > 0$. Since the logarithm operator is a

Table 4
A calculated solid–fluid equilibrium point for the system CO₂(1) + progesterone(2).

Vector \vec{X}^* (system of Eq. (A.5) ^b)		Vector \vec{X} (system of Eq. (14))	
Variable (scaled, except for tpd^*)	Value	Variable (non-scaled)	Value
tpd^*	0 ^a	tpd^*	0 ^a
z_2^*	−8.873868135	z_2	0.00014
T^*	6.030516015	T/K	415.9295999
P^*	4.555916915	P/bar	95.19400004
P_{spec}^*	4.555916915	P_{spec}	95.19400004
u_z^*	−1.175765469	$u_z/(\text{m}^3/\text{kmol})$	0.308582679
u_o^*	−1.073126816	$u_o/(\text{m}^3/\text{kmol})$	0.341937668

^a Since $tpd^* = 0$ the solution given in this table corresponds to a converged SFE point.

^b System (A.5) used with prescriptions (A.8a)–(A.8d).

Table 5
Jacobian matrix $J(\vec{F}^*)$ at the converged SFE point of Table 4.^a

	tpd^*	P^*	u_z^*	u_o^*
F_1^*	1	0.430246	1.676554	128.8967
F_2^*	0	1	0.872453	0
F_3^*	0	1	0	136.943
F_4^*	0	1	0	0

^a z_2^* and T^* set at the values given in Table 4.

Table 6
Sensitivity vector components for the converged SFE point of Table 4.

$dtpd^*/dP_{spec}^*$	2.432654
dP^*/dP_{spec}^*	1
du_z^*/dP_{spec}^*	−1.14619
du_o^*/dP_{spec}^*	−7.30231E−03

monotonically increasing function of its argument, in view of Eq. (A.1) we conclude that the validity of inequation $dtpd^*/dP^*|_{T,z_2} > 0$ implies the validity of inequation $dtpd^*/dP|_{T,z_2} > 0$. Thus, from Table 3, we have retrograde behavior with respect to pressure. In other words, the SFE point of Table 4 is such that an increase of pressure, at constant temperature and constant fluid phase composition induces the melting of the incipient solid phase. This is a retrograde behavior with respect to pressure.

Notice that for evaluating the existence of retrograde behavior at constant pressure, for the converged SFE point of Table 4, we would first need to replace Eq. (A.8a) by the following equation:

$$F_4^* = T^* - T_{spec}^* \quad (\text{A.10})$$

Next, we would have to replace P_{spec}^* by T_{spec}^* in Eqs. (A.6), (A.7) and (A.9), and P^* by T^* in Eqs. (A.4) and (A.7). Besides, the Jacobian $J(\vec{F}^*)$ of Table 5 will have its P^* column changed by a T^* column, and indeed the values of a number of elements of the new $J(\vec{F}^*)$ will in principle differ from those reported in Table 5.

The analysis of the behavior (regular or retrograde) of the converged point of Table 4 does not depend on how the calculation of such point was specified. For instance, such point could have been calculated specifying z_2^* and tpd^* at the values of Table 4, and setting $T_{spec}^* = 6.030516015$; or specifying z_2^* , tpd^* and P_{spec}^* at the values of Table 4. The present test for retrograde melting at constant temperature would not have changed at all in such a case.

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