

Component-wise and unconditionally energy-stable VT flash calculation

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Abstract. Flash calculations of the hydrocarbon mixture are essential for determining how the mixture phase behaves, which will ultimately affect subsurface flow and transport. In this paper, a novel numerical scheme is proposed for calculating the two-phase equilibrium of Peng-Robinson (PR) fluid at constant volume, temperature, and moles, namely the volume-temperature (VT) flash framework based on the dynamic model. Since the dynamic model is based on the energy dissipation law and the Onsager's reciprocal principle, we proposed a linear energy-stable scheme with the help of the convex-concave splitting technique, the energy factorization approach, and the component-wise iteration framework. The scheme eventually results in a fully explicit algorithm, and it avoids the challenges of solving non-linear systems and other difficulties in the traditional flash calculation methods. This scheme inherits the original energy stability and significantly reduces the implementation burden. It also achieves convergence unconditionally, even with a huge time step. Numerical experiments are carried out to illustrate its accuracy.

Keywords: Energy-stable scheme · Component-wise framework · Peng-Robinson fluid · Dynamic modeling · Volume-temperature (VT) flash.

1 Introduction

A number of interrelated physical processes, including the multi-phases, the multi-components, and the phase equilibrium, widely exist in the subsurface reservoir, making it a complicated system [2,10,1]. Under different natural conditions and working circumstances, the characteristics of the fluid mixtures have a significant effect on the flow and compositions transfer. The flash calculation based on the equation of state (EoS) is the foundation for measuring the properties of the mixture. The Peng-Robinson (PR) EoS is widely acknowledged as

the most trustworthy and precise one to describe the characteristics of hydrocarbons.

More people and organizations have recently turned their attention to unconventional energy sources like shale gas or methane hydrate due to the exhaustion of traditional energy sources and the advancement of petroleum industry techniques [8,9,10]. In the tight formations, the capillary effect is more important for flash calculations and modeling than it is in a traditional reservoir. Also, modeling unconventional reservoirs does not want the main variables, such as pressure, to be as sensitive as they are in the PT flash framework. When it comes to the phase equilibrium problems for associating fluids, like H_2O , the VT flash process, which is based on Helmholtz free energy, is more preferred because the association contribution resulting from hydrogen bonding interactions was initially defined in terms of this kind of energy.

Even though the VT flash calculation and the PT flash calculation have different structures, they both follow the principle of energy minimization. The Helmholtz free energy is minimized in the VT flash calculation, while the Gibbs free energy is minimized in the PT flash calculation [6]. Both types of flash calculations generate a set of nonlinear equations and constraints based on mass conservation and phase equilibrium relations. Previous research on the PT or VT flash calculation typically involved introducing intermediate variables, such as the fugacity coefficient or the volume function coefficient. However, the dynamic model circumvents these intermediate variables by transforming the nonlinear system into a dynamic system, where the energy is minimized through an evolutionary process over time. Nevertheless, the dynamic model is still unable to avoid the high degree of nonlinearity.

Our study is based on the described dynamic model. The progress we make is to develop an unconditionally energy-stable method that employs a component-wise framework and results in a fully explicit algorithm. This method not only guarantees numerical convergence and efficiency but also makes implementation more convenient. To design an energy-stable linear scheme, we have utilized several techniques, including the convex-concave splitting approach [2], modified energy, and energy factorization method [5]. As a result, the molar fraction of each component and the phase volume can be easily calculated using simple arithmetic formulas, one by one.

The subsequent sections of this paper are organized in the following manner: Section 2 details the physical problem and defines the Helmholtz free energy. It also presents a physical and mathematical description of phase equilibrium and the dynamic model. Section 3 introduces a component-wise and unconditionally energy-stable method, along with some essential elements of its proof for energy stability. In Section 4, the stability and accuracy of this method are illustrated through a numerical example.

2 Mathematical model

2.1 Physical problem

Consider a mixture comprising q components, with a fixed temperature T and overall volume V^{tol} , the moles of each component are represented by \mathbf{N}^{tol} and their density by \mathbf{n} . The Helmholtz free energy is denoted by F and $f(\mathbf{n})$ is the energy density. The gas and liquid phases are denoted by G and L , with volumes V^G and V^L and moles $\mathbf{N}^G = [N_1^G, N_2^G, \dots, N_q^G]^T$ and $\mathbf{N}^L = [N_1^L, N_2^L, \dots, N_q^L]^T$. The pressure is p and the chemical potential of a component is μ_i . The volume and mole constraints are

$$\mathbf{N}^G + \mathbf{N}^L = \mathbf{N}^{tol}; \quad V^G + V^L = V^{tol}. \quad (1)$$

The general mathematical definition of Helmholtz free energy is

$$F = -pV + \sum_{i=1}^q \mu_i N_i. \quad (2)$$

Thus, for a two-phase system, if use \mathbf{N}^G and V^G as primary variables, we obtain:

$$F = f(\mathbf{n}^G) V^G + f(\mathbf{n}^L) V^L = f\left(\frac{\mathbf{N}^G}{V^G}\right) V^G + f\left(\frac{\mathbf{N}^{tol} - \mathbf{N}^G}{V^{tol} - V^G}\right) (V^{tol} - V^G), \quad (3)$$

where $\mathbf{n}^G = \frac{\mathbf{N}^G}{V^G}$, $\mathbf{n}^L = \frac{\mathbf{N}^L}{V^L}$. The Helmholtz free energy density of real fluid $f(\mathbf{n})$ is composed by three parts

$$f(\mathbf{n}) = f^{id}(\mathbf{n}) + f^{rep}(\mathbf{n}) + f^{att}(\mathbf{n}). \quad (4)$$

The mathematical formulas of the three components comprising the Helmholtz free energy density of a uniform PR fluid are listed:

$$f^{id}(\mathbf{n}) = RT \sum_{i=1}^q n_i (\ln n_i - 1); \quad (5)$$

$$f^{rep}(\mathbf{n}) = -nRT \ln(1 - bn); \quad (6)$$

$$f^{att}(\mathbf{n}) = \frac{a(T)n}{2\sqrt{2}b} \ln \left(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn} \right), \quad (7)$$

where n_i is the molar density of each component in \mathbf{n} . n is the sum of n_i for each phase. a and b are EoS parameters for repulsion and attraction terms [5].

2.2 Dynamic model

The system reaches equilibrium when Helmholtz free energy is minimized. This yields chemical potential and pressure balance equations. Time derivative of free energy can be expanded using the chain rule:

$$\frac{dF}{dt} = \frac{\partial F}{\partial V^G} \frac{\partial V^G}{\partial t} + \sum_{i=1}^q \frac{\partial F}{\partial N_i^G} \frac{\partial N_i^G}{\partial t}. \quad (8)$$

Onsager's reciprocal principle governs how components and phase volumes change. The second law of thermodynamics dictates the dissipation of Helmholtz free energy in a closed system over time. There is a symmetric full matrix $\Phi = (\phi_{i,j})_{i,j=1}^{q+1}$ that is negative-definite, and satisfies:

$$\frac{\partial N_i^G}{\partial t} = \sum_{j=1}^q \phi_{i,j} \left(\frac{\partial F}{\partial N_j^G} \right) + \phi_{i,q+1} \left(\frac{\partial F}{\partial V^G} \right); \quad (9)$$

$$\frac{\partial V^G}{\partial t} = \sum_{j=1}^q \phi_{q+1,j} \left(\frac{\partial F}{\partial N_j^G} \right) + \phi_{q+1,q+1} \left(\frac{\partial F}{\partial V^G} \right). \quad (10)$$

To simplify, only the negative definite matrix Φ 's diagonal is used as coefficients in the non-linear system, decoupling the system. This simplification improves computation efficiency and convergence, resulting in the dynamic model:

$$\frac{\partial N_i^G}{\partial t} = -K_{\mu_i} \frac{\partial F}{\partial N_i^G}, \quad i = 1, 2, \dots, q; \quad (11)$$

$$\frac{\partial V^G}{\partial t} = -K_p \frac{\partial F}{\partial V^G}. \quad (12)$$

Choose K_{μ_i} and K_p based on reference paper [4]. The dynamic model aims to quickly reach equilibrium, without focusing on non-equilibrium to equilibrium details. Using the definition of total Helmholtz free energy for the two-phase case and relations $\mu_i = \frac{\partial F}{\partial N_i}$ and $-p = \frac{\partial F}{\partial V}$, the dynamic model is expressed by

$$\frac{\partial N_i^G}{\partial t} = -K_{\mu_i} (\mu_i^G(\mathbf{n}^G) - \mu_i^L(\mathbf{n}^L)), \quad i = 1, 2, \dots, q; \quad (13)$$

$$\frac{\partial V^G}{\partial t} = -K_p ((-p^G) - (-p^L)). \quad (14)$$

When the system reaches a state of equilibrium, the resulting equations can be expressed as:

$$\mu_i^G(\mathbf{n}^G) - \mu_i^L(\mathbf{n}^L) = 0, \quad i = 1, 2, \dots, q; \quad p^G - p^L = 0. \quad (15)$$

Therefore, the energy dissipation law holds at a continuous level as follows:

$$\frac{dF}{dt} = - \sum_{i=1}^q K_{\mu_i} \left| \frac{\partial F}{\partial N_i^G} \right|^2 - K_p \left| \frac{\partial F}{\partial V^G} \right|^2 \leq 0. \quad (16)$$

2.3 Prerequisites and modified energy

To use the convex-concave splitting method for a mixture of multiple components, the paper [3] introduces an energy parameter $\eta > 0$, allowing the free energy density to be rewritten as

$$f^{\text{convex}}(\mathbf{n}) = (1 + \eta) f^{\text{id}}(\mathbf{n}) + f^{\text{rep}}(\mathbf{n}); \quad (17)$$

$$f^{\text{concave}}(\mathbf{n}) = f^{\text{att}}(\mathbf{n}) - \eta f^{\text{id}}(\mathbf{n}); \quad (18)$$

$$f(\mathbf{n}) = f^{\text{convex}}(\mathbf{n}) + f^{\text{concave}}(\mathbf{n}). \quad (19)$$

Subsequently, the modified combination of the Helmholtz free energy can be subjected to the convex-concave approach to sustain the unconditionally energy-stable feature without affecting the overall energy quantity or the convergent outcomes. In the case of a component-wise framework, we have discovered that

$$\frac{\partial^2 f^{\text{id}}}{\partial n_i^2} = RT \frac{1}{n_i} > 0; \quad \frac{\partial^2 f^{\text{rep}}}{\partial n_i^2} = RT \left(\frac{2b_i}{1-bn} + \frac{b_i^2 n}{(1-bn)^2} \right) > 0. \quad (20)$$

The attraction term may not be concave (namely $\partial^2 f^{\text{att}}/\partial n_i^2 < 0$) even in the component-wise framework. See [1] for details. Component-wise expressions are introduced before numerical scheme design.

$$\begin{cases} f(n_i^{k+1}) = f(n_1^{k+1}, n_2^{k+1}, \dots, n_{i-1}^{k+1}, n_i^{k+1}, n_{i+1}^k, \dots, n_q^k) \\ f(n_i^k) = f(n_1^{k+1}, n_2^{k+1}, \dots, n_{i-1}^{k+1}, n_i^k, n_{i+1}^k, \dots, n_q^k) \end{cases} \quad i = 1, 2, \dots, q. \quad (21)$$

$f(n_i^{k+1})$ is determined by using $n_j^k (j > i)$ and $n_j^{k+1} (j \leq i)$. The value of $f(n_i^k)$ is decided by $n_j^k (j \geq i)$ and $n_j^{k+1} (j < i)$. To keep mathematical expressions brief and concise, this notation is consistently utilized. Based on the modified energy, the discrete linear energy-stable scheme is designed by employing the convex-concave splitting approach and energy factorization method:

$$\frac{N_i^{G,k+1} - N_i^{G,k}}{\Delta t} = -K_{\mu_i} \left(\tilde{\mu}_i^G - \tilde{\mu}_i^L \right) \quad i = 1, 2, \dots, q; \quad (22)$$

$$\frac{V^{G,k+1} - V^{G,k}}{\Delta t} = -K_p (-\tilde{p}). \quad (23)$$

This equation uses $\tilde{\mu}_i^G$ and $\tilde{\mu}_i^L$ as linear approximations of the gas-phase chemical potential with respect to $N_i^{G,k+1}$ and the liquid-phase chemical potential with respect to $N_i^{L,k+1}$, respectively. \tilde{p} is also linear approximations of the pressure difference with respect to $V^{G,k+1}$.

3 Numerical scheme and proof

3.1 Ideal term

In this part, we demonstrate an energy inequality involving the ideal term of free energy.

$$f^{\text{id}} = RT \sum_{i=1}^q n_i (\ln n_i - 1) = RT \sum_{i=1}^q n_i \ln n_i - RT \sum_{i=1}^q n_i. \quad (24)$$

A linear scheme denoted by $\tilde{\mu}_i^{\text{id}}$ is proposed for the ideal term. The next steps describe the procedure for designing and validating of this linear scheme.

Lemma 1. *Suppose that the chemical potential associated with the ideal term within the semi-implicit linear scheme is defined as*

$$\tilde{\mu}_i^{\text{id}} = RT \left(\ln n_i^k + \frac{n_i^{k+1}}{n_i^k} - 1 \right). \quad (25)$$

Then, we have the inequality:

$$f^{\text{id}}(n_i^{k+1}) - f^{\text{id}}(n_i^k) \leq \tilde{\mu}_i^{\text{id}}(n_i^{k+1} - n_i^k). \quad (26)$$

Proof. Because of $\ln n_i$ is concave with respect to n_i , we obtain

$$\ln n_i^{k+1} - \ln n_i^k \leq \frac{1}{n_i^k} (n_i^{k+1} - n_i^k). \quad (27)$$

As $n_i^k > 0$ and $n_i^{k+1} > 0$, using (27), we have

$$\begin{aligned} n_i^{k+1} \ln n_i^{k+1} - n_i^k \ln n_i^k &= \ln n_i^k (n_i^{k+1} - n_i^k) + n_i^{k+1} (\ln n_i^{k+1} - \ln n_i^k) \\ &\leq \left(\ln n_i^k + \frac{n_i^{k+1}}{n_i^k} \right) (n_i^{k+1} - n_i^k). \end{aligned} \quad (28)$$

Through equations (21), (24) and (28), the change in energy density contributed by ideal term is obtained

$$\begin{aligned} f^{\text{id}}(n_i^{k+1}) - f^{\text{id}}(n_i^k) &= RT (n_i^{k+1} \ln n_i^{k+1} - n_i^k \ln n_i^k) - RT (n_i^{k+1} - n_i^k) \\ &\leq RT \left(\ln(n_i^k) + \frac{n_i^{k+1}}{n_i^k} - 1 \right) (n_i^{k+1} - n_i^k). \end{aligned} \quad (29)$$

If we define $\tilde{\mu}_i^{\text{id}}$ using (25), then it's obvious that the inequality (26) is satisfied

3.2 Repulsion term

In this part, we will establish and demonstrate a comparable inequality to (26) that pertains to the repulsion component of the Helmholtz free energy density, denoted as f^{rep} and defined in (6). The formula can be rephrased as follows:

$$f^{\text{rep}} = -nRT \ln(1 - bn) = - \sum_{i=1}^q n_i RT \ln \left(1 - \sum_{i=1}^q b_i n_i \right). \quad (30)$$

Before stating the lemma and its proof, these auxiliary variables W , w and ϵ are defined for the purpose of mathematical simplification.

$$w = \sum_{j \neq i}^q n_j; \quad W = 1 - \sum_{j \neq i}^q b_j n_j; \quad \epsilon = 1 - bn = 1 - \sum_{j \neq i}^q b_j n_j - b_i n_i = W - b_i n_i. \quad (31)$$

Regarding ϵ , w , and W , It is evident that they are all positive real numbers. We can rephrase the repulsion term of the energy density at the continuous level as:

$$f^{\text{rep}} = - \left(w + \frac{W - \epsilon}{b_i} \right) RT \ln \epsilon. \quad (32)$$

Moreover, we can define $\epsilon_i^k = 1 - \sum_{j < i}^q b_j n_j^{k+1} - b_i n_i^k - \sum_{j > i}^q b_j n_j^k$ and $\epsilon_i^{k+1} = 1 - \sum_{j < i}^q b_j n_j^{k+1} - b_i n_i^{k+1} - \sum_{j > i}^q b_j n_j^k$. Also, $w_i^k = \sum_{j < i}^q n_j^{k+1} + \sum_{j > i}^q n_j^k$ and $W_i^k = 1 - \sum_{j < i}^q b_j n_j^{k+1} - \sum_{j > i}^q b_j n_j^k$ can be defined based on the component-wise framework's Helmholtz free energy density in (21). Here we notice again that ϵ_i^k , ϵ_i^{k+1} , w_i^k and W_i^k are all positive real numbers.

Lemma 2. *The linear scheme of the chemical potential contributed by the repulsion term can be denoted as $\tilde{\mu}_i^{\text{rep}}$, and its definition is provided below:*

For any $\epsilon_i^{k+1}/\epsilon_i^k > 0$, select a coefficient $h_i = \min \{ \alpha, \epsilon_i^{k+1}/\epsilon_i^k \}$, so that there exists a corresponding coefficient $\beta_i = \frac{\frac{1}{h_i} - 1}{(1-\alpha)^2}$. Then the linear scheme is

$$\begin{aligned} \tilde{\mu}_i^{\text{rep}} = & RT \left(\frac{b_i}{W_i^k - b_i n_i^k} n_i^{k+1} - \frac{W_i^k}{W_i^k - b_i n_i^k} - \ln (W_i^k - b_i n_i^k) \right) \\ & + RT (W_i^k + w_i^k b_i) \left(\frac{\beta_i b_i}{(W_i^k - b_i n_i^k)^2} n_i^{k+1} + \frac{W_i^k - (1 + \beta_i) b_i n_i^k}{(W_i^k - b_i n_i^k)^2} \right). \end{aligned} \quad (33)$$

In particular, when the ratio of ϵ_i^{k+1} to ϵ_i^k is greater than or equal to a certain value, denoted by α (which is approximately equal to 0.31617), we can simplify the linear scheme form by setting β_i to 1. Then, the discrete energy dissipation law holds unconditionally.

$$f^{\text{rep}} (n_i^{k+1}) - f^{\text{rep}} (n_i^k) \leq \tilde{\mu}_i^{\text{rep}} (n_i^{k+1} - n_i^k). \quad (34)$$

Proof. By splitting the repulsion term into two parts:

$$f_1^{\text{rep}} = \frac{RT}{b_i} \epsilon \ln \epsilon; \quad f_2^{\text{rep}} = - \frac{RT}{b_i} (W + w b_i) \ln \epsilon. \quad (W + w b_i > 0) \quad (35)$$

Since the first part has the similar form with ideal part, it will yield that

$$\begin{aligned} f_1^{\text{rep}} (n_i^{k+1}) - f_1^{\text{rep}} (n_i^k) &= f_1^{\text{rep}} (\epsilon_i^{k+1}) - f_1^{\text{rep}} (\epsilon_i^k) \\ &\leq \frac{RT}{b_i} \left(\ln \epsilon_i^k + \frac{\epsilon_i^{k+1}}{\epsilon_i^k} \right) (\epsilon_i^{k+1} - \epsilon_i^k) \\ &= RT \left(\frac{b_i}{W_i^k - b_i n_i^k} n_i^{k+1} - \frac{W_i^k}{W_i^k - b_i n_i^k} - \ln (W_i^k - b_i n_i^k) \right) (n_i^{k+1} - n_i^k). \end{aligned}$$

So, by defining the chemical potential $\tilde{\mu}_{1,i}^{\text{rep}}$ as the right-hand side, we have the desired inequality for f_1^{rep} as

$$f_1^{\text{rep}} (n_i^{k+1}) - f_1^{\text{rep}} (n_i^k) \leq \tilde{\mu}_{1,i}^{\text{rep}} (n_i^{k+1} - n_i^k). \quad (36)$$

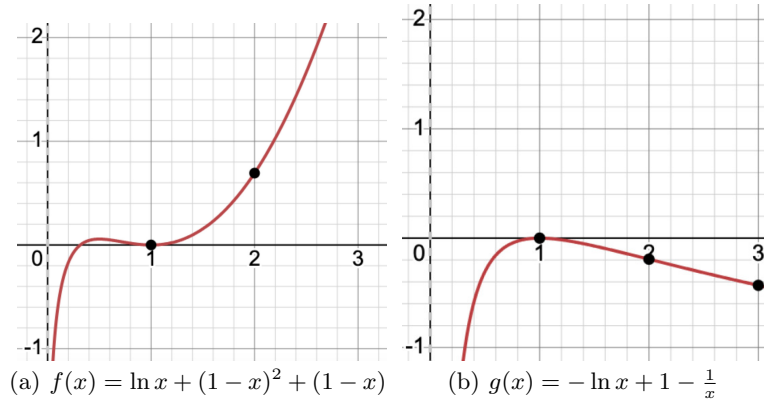


Fig. 1. The curves of auxiliary functions

Moving on to the second part, denoted as $f_2^{\text{rep}} = -\frac{RT}{b_i}(W + wb_i) \ln \epsilon$, where $W + wb_i > 0$, assume that $x = \epsilon_i^{k+1}/\epsilon_i^k$, where $\epsilon_i^{k+1} > 0$ and $\epsilon_i^k > 0$. We can make use of the properties of the following functions: (1) $g(x) = -\ln x + 1 - \frac{1}{x} \leq 0$; and (2) $f(x) = \ln x + (x-1)^2 + (1-x)$, which has two zeros at $x = 1$ and $x = \alpha \approx 0.31617$. We can conclude that $-\ln x \leq \frac{1}{x} - 1$ for any $x > 0$. Also, for any $x \geq \alpha$, we have:

$$-\ln x \leq (1-x) + (1-x)^2. \quad (37)$$

For any $h_i = x < \alpha$, we have the following inequality holds as

$$-\ln x \leq \frac{1}{x} - 1 = \frac{1}{h_i} - 1 < \frac{\left(\frac{1}{h_i} - 1\right)(1-x)^2}{(1-\alpha)^2} = \beta_i(1-x)^2 \leq (1-x) + \beta_i(1-x)^2. \quad (38)$$

Then for $\epsilon_i^{k+1}/\epsilon_i^k \geq \alpha$, the above inequality still holds because $\beta_i = 1$ obviously.

$$-\ln x \leq (1-x) + (x-1)^2 \leq (1-x) + \beta_i(1-x)^2. \quad (39)$$

The conclusion also means that for any $\epsilon_i^{k+1}/\epsilon_i^k > 0$, if choosing $h_i = \min\left\{\alpha, \frac{\epsilon_i^{k+1}}{\epsilon_i^k}\right\}$,

there is always a coefficient $\beta_i = \frac{\frac{1}{h_i} - 1}{(1-\alpha)^2}$ to ensure

$$(-\ln \epsilon_i^{k+1}) - (-\ln \epsilon_i^k) \leq \left(-\frac{1}{\epsilon_i^k} + \frac{\beta_i(\epsilon_i^{k+1} - \epsilon_i^k)}{(\epsilon_i^k)^2}\right)(\epsilon_i^{k+1} - \epsilon_i^k). \quad (40)$$

By defining $\tilde{\mu}_{2,i}^{\text{rep}}$ as

$$\tilde{\mu}_{2,i}^{\text{rep}} = RT(W_i^k + w_i^k b_i) \left(\frac{\beta_i b_i}{(W_i^k - b_i n_i^k)^2} n_i^{k+1} + \frac{W_i^k - (1 + \beta_i) b_i n_i^k}{(W_i^k - b_i n_i^k)^2} \right), \quad (41)$$

we have

$$\begin{aligned}
 & f_2^{\text{rep}}(n_i^{k+1}) - f_2^{\text{rep}}(n_i^k) = f_2^{\text{rep}}(\epsilon_i^{k+1}) - f_2^{\text{rep}}(\epsilon_i^k) \\
 &= \frac{RT}{b_i} (W_i^k + w_i^k b_i) (-\ln(\epsilon_i^{k+1}) - (\ln(\epsilon_i^k))) \\
 &\leq \frac{RT}{b_i} (W_i^k + w_i^k b_i) \left(-\frac{1}{\epsilon_i^k} + \frac{\beta_i (\epsilon_i^{k+1} - \epsilon_i^k)}{(\epsilon_i^k)^2} \right) (\epsilon_i^{k+1} - \epsilon_i^k) \\
 &= RT (W_i^k + w_i^k b_i) \left(\frac{\beta_i b_i}{(W_i^k - b_i n_i^k)^2} n_i^{k+1} + \frac{W_i^k - (1 + \beta_i) b_i n_i^k}{(W_i^k - b_i n_i^k)^2} \right) (n_i^{k+1} - n_i^k).
 \end{aligned}$$

When $\epsilon_i^{k+1}/\epsilon_i^k \geq \alpha$, we can use $\beta_i = 1$ directly.

There are a few key points that need to be emphasized. Upon the completion of updating the mole numbers, it is necessary to verify the linear scheme expression using a reverting process because it is unclear whether $\epsilon_i^{k+1}/\epsilon_i^k < \alpha$ or $\epsilon_i^{k+1}/\epsilon_i^k \geq \alpha$. Numerical results indicate that most computations satisfy the condition $\epsilon_i^{k+1}/\epsilon_i^k \geq \alpha$, and in such cases, β_i is set to 1 for faster convergence. However, if $\epsilon_i^{k+1}/\epsilon_i^k < \alpha$, A method for adaptively selecting the value of β_i is given. This involves starting with $h_i = \frac{1}{2}\alpha$ and gradually decreasing h_i until the condition is satisfied. In our simulations, this process only happens in the states near the phase boundary, a good initial guess can ensure the reverting process is under 10 times.

3.3 attraction term

Despite the fact that the attraction term of free energy density is not a concave function even under the component-wise framework, by introducing the modified energy like the one shown in equations (19), (17) and (18), if η is sufficiently large, the strict convex-concave splitting for the Helmholtz free energy density of a multicomponent mixture can be attained. We view the function $f^{\text{concave}}(\mathbf{n}) = f^{\text{att}}(\mathbf{n}) - \eta f^{\text{id}}(\mathbf{n})$ as a single entity in order to ensure energy stability. By taking a derivative with respect to n_i , we can directly derive the formulation of the chemical potential μ_i^{att} from the attraction term.

$$\begin{aligned}
 \tilde{\mu}_i^{\text{concave}} &= \frac{2 \sum_{j=1}^q a_{ij} n_j^k b n^k - b_i a (n^k)^2}{2\sqrt{2}(b n^k)^2} \ln \left(\frac{1 + (1 - \sqrt{2}) b n^k}{1 + (1 + \sqrt{2}) b n^k} \right) \\
 &+ \frac{a n^k}{2\sqrt{2}b} \left(\frac{(1 - \sqrt{2}) b_i}{1 + (1 - \sqrt{2}) b n^k} - \frac{(1 + \sqrt{2}) b_i}{1 + (1 + \sqrt{2}) b n^k} \right) - \eta RT \ln n_i^k.
 \end{aligned} \tag{42}$$

By integrating the schemes for all three types of terms, this linear scheme ensures the stability of the discrete free energy.

$$f(n_i^{k+1}) - f(n_i^k) \leq \tilde{\mu}_i(n_i^{k+1} - n_i^k). \tag{43}$$

3.4 Linear scheme for updating volume

After updating the moles of each composition in the dynamic model, A vital step of flash calculation is to utilize the provided formula to calculate the volume of each phase,

$$\frac{V^{G,k+1} - V^{G,k}}{\Delta t} = -K_p (-\tilde{p}^G - (-\tilde{p}^L)).$$

The formula for phase volume is complicated because it involves a complex non-linearity (the volume is the denominator of molar density). This makes it challenging to design a linear method. To address this issue, inspired by Kou's idea [4] on the convex-concave properties of energy with respect to volume and the relation of (2), We can conclude that the pressure terms arising from the convex part of the energy need to be handled in an implicit manner, while the concave part requires an explicit treatment to ensure energy stability. The pressure formula can be derived by taking the derivative of free energy and using the energy density of PR fluid.

$$\frac{\partial F}{\partial V} = -p = -\frac{RT}{v-b} + \frac{a(T)}{v^2 + 2bv - b^2}. \quad (44)$$

where $v = V/N$. Then, the semi-implicit scheme is

$$\frac{V^{G,k+1} - V^{G,k}}{\Delta t} = -K_p \left\{ \left[-\frac{N^G RT}{V^{G,k+1} - N^G b^G} + \frac{a(T)(N^G)^2}{(V^{G,k})^2 + 2b^G N^G V^{G,k} - (b^G)^2 (N^G)^2} \right] - \left[-\frac{N^L RT}{V^{L,k+1} - N^L b^L} + \frac{a(T)(N^L)^2}{(V^{L,k})^2 + 2b^L N^L V^{L,k} - (b^L)^2 (N^L)^2} \right] \right\}. \quad (45)$$

This makes the energy stability property to hold discretely. The following lemma is here to claim the existence of the linear scheme for $\tilde{p}(V^{G,k+1})$ only.

Lemma 3. *One can express the pressure term using a linear semi-implicit scheme as shown by*

$$-\tilde{p} = \bar{A}V^{G,k+1} + \bar{B}, \quad (46)$$

where the coefficient $\bar{A}(\mathbf{N}^{G,k+1}, V^{G,k})$ and $\bar{B}(\mathbf{N}^{G,k+1}, V^{G,k})$ only involve explicit variables. It is possible to maintain the energy-stability property of the discrete system with respect to phase volume V^G by using the linear scheme for the pressure term $-\tilde{p}$, namely

$$f(V^{G,k+1}) - f(V^{G,k}) \leq -\tilde{p}(V^{G,k+1} - V^{G,k}). \quad (47)$$

Proof. When combined with the volume constraints given by equation (1), the equation used to update the volume of the gas phase can be converted to

$$\frac{V^{G,k+1} - V^{G,k}}{\Delta t} = -K_p \left\{ \left[-\frac{N^G RT}{V^{G,k+1} - N^G b^G} + \frac{a(T)(N^G)^2}{(V^{G,k})^2 + 2b^G N^G V^{G,k} - (b^G)^2 (N^G)^2} \right] - \left[-\frac{N^L RT}{V^{L,k+1} - N^L b^L} + \frac{a(T)(N^L)^2}{(V^{L,k})^2 + 2b^L N^L V^{L,k} - (b^L)^2 (N^L)^2} \right] \right\}. \quad (48)$$

After updating the moles of all components as $N^G = \sum N_i^{G,k+1}$ and $N^L = \sum N_i^{L,k+1}$, the concave terms that are explicitly represented by notations $CA^{G,k}$ and $CA^{L,k}$ are used to simplify the mathematical expressions. Thus, the equation can be expressed as:

$$\frac{V^{G,k+1} - V^{G,k}}{\Delta t} = -K_p \left[\left(-\frac{N^G RT}{V^{G,k+1} - N^G b^G} + CA^{G,k} \right) - \left(-\frac{N^L RT}{V^{tol} - V^{G,k+1} - N^L b^L} + CA^{L,k} \right) \right]. \quad (49)$$

With some further relaxations on the time step to keep this energy dissipation property and the mathematical properties on the coefficients of linear terms. The relaxed time step will not influence the convergence of scheme. It finally reaches the following inequality:

$$f(V^{G,k+1}) - f(V^{G,k}) \leq [-N^G RT - (CA^{L,k} - CA^{G,k})(V^{G,k} - N^G b^G) - \frac{N^L RT (V^{G,k} - N^G b^G)}{V^{G,k+1} + N^L b^L - V^{tol}}] (V^{G,k+1} - V^{G,k}). \quad (50)$$

It also implies that if the scheme of $-\tilde{p}$ is defined as

$$-\tilde{p} = \bar{A}V^{G,k+1} + \bar{B}, \quad (51)$$

then the discrete energy law with respect to V^G still holds as

$$f(V^{G,k+1}) - f(V^{G,k}) \leq -\tilde{p}(V^{G,k+1} - V^{G,k}).$$

Thus, the coefficients $\bar{A} = N^G RT + (CA^{L,k} - CA^{G,k})(V^{G,k} - N^G b^G)$ and $\bar{B} = [N^G RT + (CA^{L,k} - CA^{G,k})(V^{G,k} - N^G b^G)](N^L b^L - V^{tol}) + \dots - N^L RT (V^{G,k} - N^G b^G)$, respectively. The final relaxed time step $\bar{\Delta t}$ is

$$\bar{\Delta t} = \frac{\Delta t}{(V^{G,k+1} - N^G b^G)(V^{tol} - V^{G,k+1} - N^L b^L)}. \quad (52)$$

In conclusion, the linear scheme $-\tilde{p} = \bar{A}V^{G,k+1} + \bar{B}$ is able to maintain the energy-stability property at a discrete level, as shown in Lemma (47). It is important to note that the relaxed time step will not affect the convergence or energy-stability property.

4 Numerical experiments

This section presents several numerical experiments conducted on a mixture to show the efficiency, accuracy and stability of this fully explicit and unconditionally energy-stable method for solving the Peng-Robinson VT flash problem. The obtained results are then compared to the data reported in Jiri's papers [7],

which are commonly used as a reference for comparison. The constant total volume of $V^{\text{total}} = 1\text{m}^3$ is established. To obtain a physically meaningful outcome, an initial guess is acquired using the Wilson correlation and the Rachford-Rice equation. For the dynamic model, the modified energy parameter is set to $\eta = 10$, and the time step is $dt = 10^8$. The values of dynamic model coefficients K_{μ_i} and K_p can typically be determined using the methods described in Kou's paper [4]. Set diffusion coefficient $D_i = 1$ for each component

$$K_{\mu_i} = \frac{D_i N_i}{RT}; \quad K_p = \frac{C_V^G C_V^L V^{\text{tol}}}{C_V^L p_G^k + C_V^G p_L^k}.$$

where the coefficients $C_V^G = C_V^L = 1$. The phase pressure p_G^k and p_L^k is the phase pressure in the last time step. The convergence criterion for the time loops is based on the relative errors in the moles of each component in the gas phase N_i^G and the gas phase volume V^G between two adjacent time steps. These relative errors are considered as the criteria, and convergence is achieved when they are both less than 10^{-6} .

$$\|\Delta N_i^G\|_{rel} = \frac{\|N_i^{G,k} - N_i^{G,k+1}\|}{\|N_i^{G,k}\|}; \quad \|\Delta V^G\|_{rel} = \frac{\|V^{G,k} - V^{G,k+1}\|}{\|V^{G,k}\|}.$$

4.1 Binary mixture of methane (C_1) and n -pentane (nC_5)

Initially, a binary mixture of methane (C_1) and n -pentane (nC_5) is used as a case study for a two-phase flash calculation. The mixture has a total molar density of $n = 6135.3 \text{ mol/m}^3$ with mole fractions of $z_{C_1} = 0.489575$ and $z_{nC_5} = 0.510425$ at a temperature of $T = 310.95 \text{ K}$. Additional parameters regarding the mixture are shown in Table 1.

Table 1. Properties of the constituents in the binary $C_1 - nC_5$ mixture

Component	$\omega_i [-]$	$T_{\text{crit}} [\text{K}]$	$P_{\text{crit}} [\text{MPa}]$	$M_w [\text{g/mol}]$
C_1	0.011	190.56	4.599	16
nC_5	0.251	469.70	3.37	72.2

The $C_1 - nC_5$ binary interaction coefficient $\delta_{C_1 - nC_5} = 0.041$.

Table 2 shows the equilibrium results, with the resulting equilibrium pressure being $p = 10.4651 \text{ MPa}$. These results show excellent agreement with the reference data from Jiri and Abbas' study [7]. The energy dissipation property can also be observed from Figure 2, where there is an apparent decay of energy at the initial stage. To provide a better visualization of the energy trend, a zoom window of the 150th – 200th time steps is included in the plot. Convergence is reached after 224 time steps, and the resulting properties are considered to be the equilibrium properties of the mixture.

Table 2. The resulting constitution and overall physical parameters of $C_1 - nC_5$ calculated by this novel scheme.

Property	Unit	Overall mixture	Phase Liquid	Phase Gas
molar density	mol/m^3	6135.30	10106.03	3177.74
C_1 mole fraction		0.489575	0.293459	0.954132
nC_5 mole fraction		0.510425	0.706541	0.045868
phase volume fraction			0.426881	0.573119

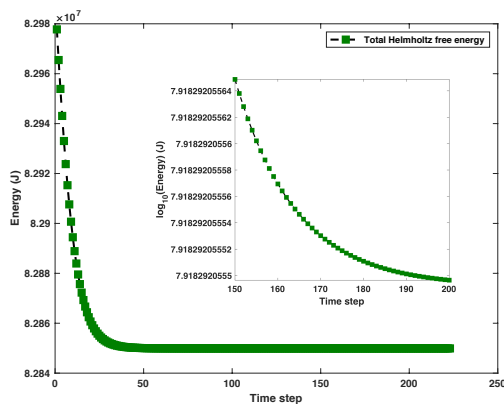


Fig. 2. Profile of total Helmholtz free energy of mixture with time step $\Delta t = 10^8$ for the binary mixture ($C_1 - nC_5$) case

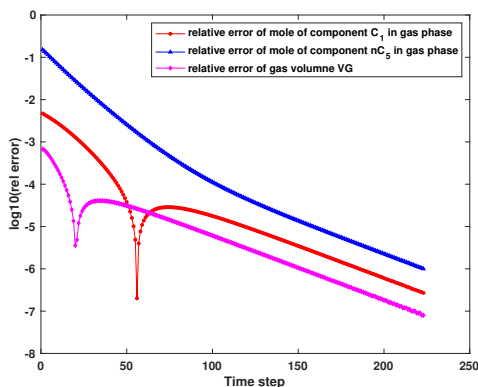


Fig. 3. Profile of relative error on moles of each component in the gas phase and gas volume with time steps for the binary mixture ($C_1 - nC_5$) case

Figure 3 illustrates the variability in the accuracy of the calculation process. The general trend is a decrease in the relative error. However, there is a sag in

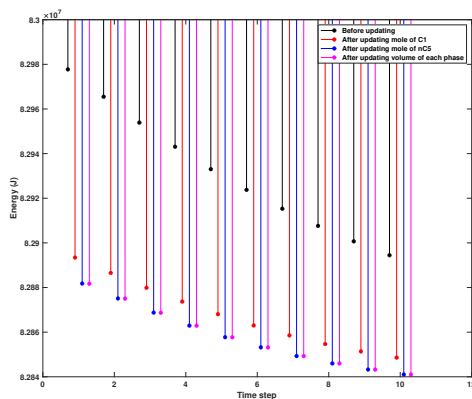


Fig. 4. Stem plot of the relative error change on moles of each component and phase volume with time steps for the binary mixture ($C_1 - nC_5$) case

the relative error for C_1 and gas volume at the initial stage, which could be attributed to the imprecise initial estimate and the non-synchronous nature of the component-wise iteration process. As the relative error only indicates a relative difference between two consecutive time steps, possibly, a numerical adjustment process occurred to overcome the asynchrony. Fortunately, the variability in relative error for moles and phase volume in the subsequent process exhibits a similar and unanimous trend of decreasing slope.

A stem plot is depicted in Figure 4, illustrating the energy fluctuations during the initial 10 time steps. The energy decreases as each component and then the volume are updated, which is which is in line with the proof and derivation. The energy continues to decrease within each time step, and it is observed that the energy before updating (the black stem) is higher than the energy after updating the volume of the previous time step (the magenta stem) when transitioning to a new time step. This phenomenon is caused by modifications to the PR EoS parameters a and b of the mixture at each finished time step. However, it is evident that the energy before updating (the black stem) consistently decreases throughout the entire dynamic process as expected.

5 Conclusion

This work proposes a numerical method for calculating two-phase equilibrium under constant volume, temperature, and moles, using the dynamic model for VT flash that upholds Onsager's reciprocal principle and the energy dissipation law. With a designed linear semi-implicit scheme, the moles of each component and phase volume can be updated while preserving the energy dissipation feature. The convex-concave splitting technique, energy factorization approach and

component-wise iteration framework are then employed for the mixture, resulting in a fully explicit algorithm. This method avoids solving complicated linear or nonlinear systems, making it easier to implement and apply in engineering contexts. Moreover, one component-wise and unconditionally energy-stable method is proposed for the first time for the multi-component flash calculation problem.

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