Advances in Applied Mathematics and Mechanics
Adv. Appl. Math. Mech., Vol. **9**, No. 5, pp. 1162-1188

DOI: 10.4208/aamm.OA-2016-0024
October 2017

A Convex-Splitting Scheme for a Diffuse Interface Model with Peng-Robinson Equation of State

Qiujin Peng*

Institute for Mathematical Sciences, Renmin University of China, No. 59 Zhongguancun Street, Haidian District, Beijing 100872, China

Received 3 June 2016; Accepted (in revised version) 5 December 2016

Abstract. We present a convex-splitting scheme for the fourth order parabolic equation derived from a diffuse interface model with Peng-Robinson equation of state for pure substance. The semi-implicit scheme is proven to be uniquely solvable, mass conservative, unconditionally energy stable and L^∞ convergent with the order of $\mathcal{O}(\Delta t + h^2)$. The numerical results verify the effectiveness of the proposed algorithm and also show good agreement of the numerical solution with laboratory experimental results.

AMS subject classifications: 65M06, 65M12, 65G99

Key words: Diffuse interface model, fourth order parabolic equation, convex-splitting scheme, convergence.

1 Introduction

Modeling and simulation of the multi-phase hydrocarbon systems involved in the oil-exploitation process are have been popular research topics in engineering practice recently [8]. The anisotropic force at the surface or an interface between two different phases at a pore scale yields the interfacial tension and consequently impacts the shape of liquid-gas interface. Moreover, the capillary effect caused by the surface tension in the Darcy-scale is usually the leading mechanism of oil recovery in fractured oil reservoirs [14]. Therefore, it is critical to simulate the interface between different phases of oil mixture and calculate the surface tension in appropriate scale.

The diffuse interface model is applied to evaluate the surface tension since it could provide more detailed description of the interface than the sharp interface model and more computational efficient than the numerical simulation conducted on the molecular scale. This theory was originally founded by van der Waals [29] to study the interface based on thermodynamic principles [1], and extended by Cahn and Hilliard [3–5]. In the

*Corresponding author.
Email: pengqiujin@ruc.edu.cn (Q. J. Peng)

 ©2017 Global Science Press

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

popularly studied Allen-Cahn equation and Cahn-Hilliard equation, the total free energy with double-well potential type homogeneous density is usually employed to qualitatively predict the interface behaviors of various multi-phase fluids. However, the free energy based on a realistic equation of state is really necessary to quantitatively describe the concerning behaviors of the crude oil mixture. The Peng-Robinson equation of state is well-known for its reliability on predicting volumetric and phase behaviors of complex hydrocarbon system [20,25]. The total free energy provided by this equation of state have been applied successfully to determine the evolution process or steady state of realistic hydrocarbon species in oil-gas systems within the framework of diffuse interface model, such as the work on simulations of the surface tension of single or multi-component mixtures [12–14, 23].

The equations derived from Peng-Robinson equation of state involve high nonlinearity. It is rather challenging to design numerical scheme involve such strong nonlinearity. In addition, the energy stability is quite desirable due to its physical background. Up to now, there are two basic approaches to guarantee energy stability. The first one is called the stabilized method, where stabilized terms are added to both sides of the equations. Energy stability has been proved either under a Lipschitz assumption on the nonlinearity [27], or under a L^∞ bound assumption on the numerical solution [34]. Recently, these technical restrictions have been removed in [16, 17]. The second approach is the convex-splitting scheme which was developed by Eyer in 1998 for the Cahn-Hilliard equation [7]. By using this method, the original total energy is divided into convex part and concave part. The derivative of the convex part in the equation is treated implicitly and the derivative of the concave part is treated explicitly. This scheme is uniquely solvable due to the convexity of the modified energy expression which is also stable during the whole evolution process. So far, there are many achievements have been obtained based on this method, see e.g., [2, 6, 9–11, 26, 30–33], and the references therein.

In this paper, we investigate the fourth-order parabolic equation derived from total free energy with the Peng-Robinson equation of state [13] of particular pure substances. As mentioned in the work of Qiao et al. [23], the homogeneous energy density is almost linear, and its nonconvexity can only be detected after subtracting a linear function from its original formula. Here, a first order convex-splitting scheme is proposed to solve this fourth order equation. The theoretical analysis manifests the mass conservation, unconditional stability and L^∞ convergence of this scheme. The unboundness of the homogeneous chemical potential is the main difficulty to obtain the convergence of this scheme. To overcome this barrier, we assume the unique existence of the original fourth order parabolic equation on a close subset of of its reasonable region $(0, \frac{1}{b})$, and apply a mathematical induction method to derive the bound of the new step solution.

This paper is organized as follows. The fourth order parabolic equation and its semi-discrete convex-splitting form are presented in next section. And then some auxiliary lemmas are provided based on appropriate spaces in the third section. After that, the fully discrete version of the convex-splitting scheme for the fourth-order parabolic equation and its unique solvability, energy stability and the convergence are proved in the

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

fourth section. Numerical results presented in the fifth section demonstrate the good properties of this scheme. Some concluding remarks are provided in the last section.

2 The fourth order parabolic equation

According to Peng-Robinson EOS, the total Helmholtz free energy of pure substance related in oil recovery process can be expressed as [12]

$$F(n(\mathbf{x},t))=\int_\Omega\Big[f_0(n(\mathbf{x},t))+\frac{c}{2}|\nabla n(\mathbf{x},t)|^2\Big]d\mathbf{x}, \tag{2.1}$$

where the homogeneous Helmholtz free energy of a single component fluid $f_0(n)$ is expressed as

$$\begin{aligned}
&f_0(n)=f_0^{\text{ideal}}(n)+f_0^{\text{excess}}(n)=f_0^{\text{ideal}}(n)+f_{01}^{\text{excess}}(n)+f_{02}^{\text{excess}}(n),\\
&f_0^{\text{ideal}}(n)=RTn\Big(\ln n-1\Big),\\
&f_{01}^{\text{excess}}(n)=-nRT\ln\Big(1-bn\Big),\\
&f_{02}^{\text{excess}}(n)=\frac{a(T)n}{2\sqrt{2}b}\ln\Big(\frac{1+(1-\sqrt{2})bn}{1+(1+\sqrt{2})bn}\Big).
\end{aligned}$$

Here, T is the notation of substance temperature, R is the universal gas constant and approximates 8.31432JK^{-1}mol^{-1}. The parameters $a=a(T)$ and b are provided in Appendix A.

The fourth-order equations derived from this model is described as follows,

$$\frac{\partial n(\mathbf{x},t)}{\partial t}=\nabla\cdot\nabla\frac{\delta F}{\delta n}(n)=-c\Delta^2 n(\mathbf{x},t)+\Delta\mu_0(n(\mathbf{x},t)) \tag{2.2}$$

with the initial condition

$$n(\mathbf{x},0)=n_0(\mathbf{x}). \tag{2.3}$$

Here, $\mu_0(n(\mathbf{x},t))$ is the first order variational derivative of the total homogeneous energy $\int_\Omega f_0(n(\mathbf{x},t))d\mathbf{x}$ with respect to the molar density $n(\mathbf{x},t)$, and could be interpreted as the homogeneous chemical potential of the substance. It is of the following form,

$$\mu_0(n)=RT\ln\Big(\frac{n}{1-bn}\Big)+\frac{RTbn}{1-bn}+\frac{a(T)}{2\sqrt{2}b}\ln\Big(\frac{1+(1-\sqrt{2})bn}{1+(1+\sqrt{2})bn}\Big)-\frac{a(T)n}{1+2bn-b^2n^2}. \tag{2.4}$$

The mass conservation and the energy stability of the fourth order equation (2.2) have already been proven in our previous work [21], so we skip their statements and take them for granted.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

For the gradient part of the total free energy

$$F_\nabla = \int_\Omega \frac{c}{2}|\nabla n(\mathbf{x},t)|^2 d\mathbf{x},$$

we have

$$\mu_\nabla = \frac{\delta F_\nabla}{\delta n} = -c\Delta n(\mathbf{x},t). \tag{2.5}$$

For the homogeneous part of the total free energy, if we set

$$f_{01}(n) = f_0^{\text{ideal}}(n) + f_{01}^{\text{excess}}(n) = RTn\Big(\ln n - 1\Big) - nRT\ln\Big(1-bn\Big),$$
$$f_{02}(n) = -f_{02}^{\text{excess}}(n) = -\frac{a(T)n}{2\sqrt{2}b}\ln\Big(\frac{1+(1-\sqrt{2})bn}{1+(1+\sqrt{2})bn}\Big),$$

then we have $f_0 = f_{01} - f_{02}$, and

$$\mu_{01}(n) = \mu_0^{\text{ideal}}(n) + \mu_{01}^{\text{excess}}(n) = RT\ln n - RT\ln\Big(1-bn\Big) + RT\frac{bn}{1-bn}, \tag{2.6a}$$
$$\mu_{02}(n) = -\mu_{02}^{\text{excess}}(n) = -\frac{a(T)}{2\sqrt{2}b}\ln\Big(\frac{1+(1-\sqrt{2})bn}{1+(1+\sqrt{2})bn}\Big) + \frac{a(T)n}{1+bn+bn(1-bn)}. \tag{2.6b}$$

Therefore,

$$\frac{\partial^2 f_{01}(n)}{\partial n^2} = \frac{\partial \mu_{01}(n)}{\partial n} = \frac{RT}{n(1-bn)^2} > 0, \tag{2.7a}$$
$$\frac{\partial^2 f_{02}(n)}{\partial n^2} = \frac{\partial \mu_{02}(n)}{\partial n} = \frac{2a(T)\Big(1+bn\Big)}{(1+2bn-b^2n^2)^2} > 0. \tag{2.7b}$$

So $f_0(n)$ can be convexly split with $f_0(n) = f_{01}(n) - f_{02}(n)$. The convex splitting of total energy described in (2.1) is $F = F_c - F_e$, where

$$\begin{aligned} F_c &= \int_\Omega \Big[\frac{c}{2}|\nabla n(\mathbf{x},t)|^2 + f_{01}(n)\Big] d\mathbf{x} \\ &= \int_\Omega \Big[\frac{c}{2}|\nabla n(\mathbf{x},t)|^2 + RTn\Big(\ln n - 1\Big) - nRT\ln\Big(1-bn\Big)\Big] d\mathbf{x}, \end{aligned} \tag{2.8a}$$
$$F_e = \int_\Omega f_{02} dx = -\int_\Omega \frac{a(T)n}{2\sqrt{2}b}\ln\Big(\frac{1+(1-\sqrt{2})bn}{1+(1+\sqrt{2})bn}\Big) d\mathbf{x}. \tag{2.8b}$$

Denote

$$\mu(n) = \frac{\delta F}{\delta n}(n) = \mu_c - \mu_e,$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

then $\mu(n)=\mu_\nabla+\mu_0$, and

$$\mu_c=\frac{\delta F_c}{\delta n}(n)=\mu_\nabla+\mu_{01}=-c\Delta n(\mathbf{x},t)+RT\ln n-RT\ln\Big(1-bn\Big)+RT\frac{bn}{1-bn}, \tag{2.9a}$$

$$\mu_e=\frac{\delta F_e}{\delta n}(n)=\mu_{02}=-\frac{a(T)}{2\sqrt{2}b}\ln\Big(\frac{1+(1-\sqrt{2})bn}{1+(1+\sqrt{2})bn}\Big)+\frac{a(T)n}{1+bn+bn(1-bn)}. \tag{2.9b}$$

We propose the semi-implicit scheme

$$n^{k+1}-n^k-\Delta t\Delta\tilde{\mu}=0,\quad \frac{\partial\tilde{\mu}^{k+1}}{\partial\nu}\Big|_{\partial\Omega}=0, \tag{2.10a}$$

$$\tilde{\mu}(n^{k+1},n^k)=\frac{\delta F_c}{\delta n}(n^{k+1})-\frac{\delta F_e}{\delta n}(n^k)=-c\Delta n^{k+1}+\mu_{01}(n^{k+1})-\mu_{02}(n^k),\quad \frac{\partial n^{k+1}}{\partial\nu}\Big|_{\partial\Omega}=0. \tag{2.10b}$$

Then

$$\begin{aligned}F(n^{k+1})-F(n^k)&\le\Big(\frac{\delta F_c}{\delta n}(n^{k+1})-\frac{\delta F_e}{\delta n}(n^k),n^{k+1}-n^k\Big)_{L^2}\\&=\Big(\tilde{\mu}(n^{k+1},n^k),\Delta t\Delta\tilde{\mu}(n^{k+1},n^k)\Big)\\&=-\Delta t\Big\|\nabla\tilde{\mu}(n^{k+1},n^k)\Big\|^2\le 0.\end{aligned}$$

3 Some auxiliary lemmas

We investigate the solution of the fourth order equations (2.2)-(2.3) at the time interval $[0,T_m]$ on the domain $\Omega=[0,L_x]\times[0,L_y]$. Here, T_m denotes the final time. Let $h_1=L_x/M_1$, $h_2=L_y/M_2$, $\Delta t=T_m/K$, $x_i=ih_1$, $y_j=jh_2$, $t_k=k\Delta t$. Denote the spaces for the discrete grid points on Ω and temporal interval $[0,T_m]$ as follows,

$$\begin{aligned}\Omega_h&=\Big\{\Big(x_i,y_j\Big)\Big|0\le i\le M_1,\,0\le j\le M_2\Big\},\\\Omega_\tau&=\Big\{t_k\,|\,0\le k\le K\Big\}.\end{aligned}$$

The space for the discrete periodic functional on Ω_h is denoted by

$$\mathcal{V}_h=\Big\{n|n=\{n_{ij}\},\,n_{i+M_1,j}=n_{ij},\,n_{i,j+M_2}=n_{ij}\Big\}.$$

Define the function space on Ω_τ as

$$\mathcal{W}_\tau=\Big\{w|w=\Big(w^0,w^1,\cdots,w^{K-1},w^K\Big)\Big\}.$$

The discrete difference on the space $\mathcal{V}_h$ and Sobolev norms on the space $\mathcal{W}_\tau$ are presented in Appendix B for brevity.

To demonstrate the solvability and the convergence of our proposed numerical schemes, we will frequently use the following lemmas.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

Lemma 3.1. *For any grid function $u, v \in \mathcal{V}_h$, it holds that*

$$\langle \Delta_h u, v\rangle = \langle u, \Delta_h v\rangle = -\langle \nabla_h u \cdot \nabla_h v, 1\rangle. \tag{3.1}$$

Lemma 3.2 (see [15,19,22])**.** *For any grid function $u \in \mathcal{V}_h$, it holds that*

$$\|\nabla_h u\|^2 \le \|u\|\|\Delta_h u\|, \quad \|u\|_\infty^2 \le k_0\|u\|(\|\Delta_h u\| + \|u\|),$$

where k_0 is independent of the grid size h and the function u.

Lemma 3.3 (Gronwall lemma, see [24,28])**.** *Let ξ be positive, and v, a_k, $(k = 0,1,2,3,\cdots)$ be nonnegative and satisfy*

$$a_k \le (1+\xi\tau)a_{k-1} + \nu\tau, \quad k = 1,2,3,\cdots,$$

then

$$a_k \le \exp(\xi k\tau)(a_0 + \nu/\xi), \quad k = 1,2,3,\cdots.$$

Referencing to the Lemma 4.2 given by [15], we can obtain the following similar results.

Lemma 3.4. *For any $u, v \in \mathcal{W}_\tau$ and $k \ge 1$, we have the following identities*

$$\sum_{l=0}^{k} u^{l+1}\delta_t v^{l+\frac{1}{2}} = \frac{1}{\Delta t}\left(u^{k+1}v^{k+1} - u^1 v^0\right) - \sum_{l=1}^{k} v^l \frac{u^{l+1}-u^l}{\Delta t},$$
$$\sum_{l=0}^{k} u^{l}\delta_t v^{l+\frac{1}{2}} = \frac{1}{\Delta t}\left(u^{k}v^{k+1} - u^0 v^0\right) - \sum_{l=1}^{k} v^l \frac{u^{l}-u^{l-1}}{\Delta t}.$$

Proof. We have

$$\begin{aligned}
\sum_{l=0}^{k} u^{l+1}\delta_t v^{l+\frac{1}{2}} &= \sum_{l=0}^{k} u^{l+1}\frac{v^{l+1}-v^l}{\Delta t} = \frac{1}{\Delta t}\sum_{l=1}^{k+1} u^l\left(v^l - v^{l-1}\right) = \frac{1}{\Delta t}\left[\sum_{l=1}^{k+1} u^l v^l - \sum_{l=0}^{k} u^{l+1}v^l\right] \\
&= \frac{1}{\Delta t}\left[\sum_{l=1}^{k}\left(u^l - u^{l+1}\right)v^l + u^{k+1}v^{k+1} - u^1 v^0\right] \\
&= \frac{1}{\Delta t}\left(u^{k+1}v^{k+1} - u^1 v^0\right) - \sum_{l=1}^{k}\frac{u^{l+1}-u^l}{\Delta t}v^l, \\
\sum_{l=0}^{k} u^{l}\delta_t v^{l+\frac{1}{2}} &= \sum_{l=0}^{k} u^{l}\frac{v^{l+1}-v^l}{\Delta t} = \frac{1}{\Delta t}\sum_{l=0}^{k} u^l\left(v^{l+1} - v^l\right) \\
&= \frac{1}{\Delta t}\left[\sum_{l=0}^{k} u^l v^{l+1} - \sum_{l=0}^{k} u^l v^l\right] = \frac{1}{\Delta t}\left[\sum_{l=1}^{k+1} u^{l-1} v^l - \sum_{l=0}^{k} u^l v^l\right] \\
&= \frac{1}{\Delta t}\left[u^k v^{k+1} - u^0 v^0 + \sum_{l=1}^{k}\left(u^{l-1} - u^l\right)v^l\right] \\
&= \frac{1}{\Delta t}\left(u^k v^{k+1} - u^0 v^0\right) - \sum_{l=1}^{k} v^l \frac{u^l - u^{l-1}}{\Delta t}.
\end{aligned}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

This completes the proof. □

Lemma 3.5. *Suppose the function $\Phi(u)$ has continuous second-order derivative on any connected subset of R. For $u=(u^0,u^1,\cdots,u^K)$, $\bar{u}=(\bar{u}^0,\bar{u}^1,\cdots,\bar{u}^K)\in\mathcal{W}_\tau$ and $k\in\{1,2,\cdots,K-1\}$, there exist $\rho\in(0,1)$, $\alpha_1=\rho u^{k+1}+(1-\rho)u^k$, $\alpha_2=\rho\bar{u}^{k+1}+(1-\rho)\bar{u}^k$, and $\xi\in(\min\{\alpha_1,\alpha_2\},\max\{\alpha_1,\alpha_2\})$ dependent on k such that*

$$\begin{aligned}
&\delta_t\left[\Phi\left(\bar{u}^{k+\frac{1}{2}}\right)-\Phi\left(u^{k+\frac{1}{2}}\right)\right]\\
=&\Phi'\left(\rho u^{k+1}+(1-\rho)u^k\right)\delta_t\left(\bar{u}^{k+\frac{1}{2}}-u^{k+\frac{1}{2}}\right)\\
&+\Phi''\left(\xi\right)\left(\rho\left(\bar{u}^{k+1}-u^{k+1}\right)+(1-\rho)\left(\bar{u}^k-u^k\right)\right)\delta_t\bar{u}^{k+\frac{1}{2}}.
\end{aligned}$$

Proof. We have

$$\begin{aligned}
&\delta_t\left[\Phi\left(\bar{u}^{k+\frac{1}{2}}\right)-\Phi\left(u^{k+\frac{1}{2}}\right)\right]\\
=&\frac{1}{\Delta t}\left\{\left[\Phi\left(\bar{u}^{k+1}\right)-\Phi\left(\bar{u}^k\right)\right]-\left[\Phi\left(u^{k+1}\right)-\Phi\left(u^k\right)\right]\right\}\\
=&\frac{1}{\Delta t}\left\{\left[\Phi\left(\bar{u}^k+\Delta t\delta_t\bar{u}^{k+\frac{1}{2}}\right)-\Phi\left(\bar{u}^k\right)\right]-\left[\Phi\left(u^k+\Delta t\delta_t u^{k+\frac{1}{2}}\right)-\Phi\left(u^k\right)\right]\right\}\\
=&\Phi'\left(\bar{u}^k+\rho\Delta t\delta_t\bar{u}^{k+\frac{1}{2}}\right)\delta_t\bar{u}^{k+\frac{1}{2}}-\Phi'\left(u^k+\rho\Delta t\delta_t u^{k+\frac{1}{2}}\right)\delta_t u^{k+\frac{1}{2}}\\
=&\Phi'\left(\rho\bar{u}^{k+1}+(1-\rho)\bar{u}^k\right)\delta_t\bar{u}^{k+\frac{1}{2}}-\Phi'\left(\rho u^{k+1}+(1-\rho)u^k\right)\delta_t u^{k+\frac{1}{2}}\\
=&\left[\Phi'\left(\rho\bar{u}^{k+1}+(1-\rho)\bar{u}^k\right)-\Phi'\left(\rho u^{k+1}+(1-\rho)u^k\right)\right]\delta_t\bar{u}^{k+\frac{1}{2}}\\
&+\Phi'\left(\rho u^{k+1}+(1-\rho)u^k\right)\delta_t\left(\bar{u}^{k+\frac{1}{2}}-u^{k+\frac{1}{2}}\right)\\
=&\Phi''\left(\xi\right)\left(\rho\left(\bar{u}^{k+1}-u^{k+1}\right)+(1-\rho)\left(\bar{u}^k-u^k\right)\right)\delta_t\bar{u}^{k+\frac{1}{2}}\\
&+\Phi'\left(\rho u^{k+1}+(1-\rho)u^k\right)\delta_t\left(\bar{u}^{k+\frac{1}{2}}-u^{k+\frac{1}{2}}\right).
\end{aligned}\tag{3.2}$$

In the derivation of (3.2), we treat $\Phi(\bar{u}^k+\Delta t\rho\delta_t\bar{u}^{k+\frac{1}{2}})-\Phi(u^k+\Delta t\rho\delta_t u^{k+\frac{1}{2}})$ as a function of $\rho\in[0,1]$ and then use the differential mean value theorem. This completes the proof. □

4 A convex-splitting scheme for the fourth-order parabolic equation

In this section, we provide the fully discrete version of the first order convex-splitting scheme for the fourth-order parabolic equation of pure substance (2.2) and investigate its unconditional stability, unique solvability and L^∞ convergence.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

4.1 The discrete convex-splitting scheme

Define the total discrete energy F_h to be

$$F_h(n)=\frac{c}{2}\left\|\nabla_h n\right\|^2+\left\langle f_{01}(n),1\right\rangle-\left\langle f_{02}(n),1\right\rangle. \tag{4.1}$$

Lemma 4.1 (Existence of a convex-splitting of the discrete total free energy)**.** *Suppose both n and $\Delta_h n$ are periodic. Define the energies*

$$F_h^c(n)=\frac{c}{2}\left\|\nabla_h n\right\|^2+\left\langle f_{01}(n),1\right\rangle,\quad F_h^e(n)=\left\langle f_{02}(n),1\right\rangle. \tag{4.2}$$

Then variational derivatives are

$$\frac{\delta F_h^c}{\delta n}=-c\Delta_h n+\mu_{01}(n)\quad \text{and}\quad \frac{\delta F_h^e}{\delta n}=\mu_{02}(n),$$

respectively. Both F_h^c and F_h^e are convex, admitting the convex splitting $F_h=F_h^c-F_h^e$.

Proof. As for any $\tilde{n}\in\mathcal{V}_h$, calculating the (discrete) variation of F_h^c and using summation-by-parts provide

$$\frac{dF_h^c}{d\varepsilon}(n+\varepsilon\tilde{n})|_{\varepsilon=0}=\langle -c\Delta_h n,\tilde{n}\rangle+\langle\mu_{01}(n),\tilde{n}\rangle.$$

The second variation reveals

$$\frac{d^2F_h^c}{d\varepsilon^2}(n+\varepsilon\tilde{n})|_{\varepsilon=0}=c\|\nabla_h\tilde{n}\|^2+\langle\mu_{01}'(n),\tilde{n}^2\rangle\geq 0.$$

For F_h^e, we have

$$\frac{dF_h^e}{d\varepsilon}(n+\varepsilon\tilde{n})|_{\varepsilon=0}=\langle\mu_{02}(n),\tilde{n}\rangle,$$
$$\frac{d^2F_h^e}{d\varepsilon^2}(n+\varepsilon\tilde{n})|_{\varepsilon=0}=\langle\mu_{02}'(n),\tilde{n}^2\rangle\geq 0.$$

These verify the convexity of the discrete functionals F_h^c and F_h^e. Since it is obvious that $F_h=F_h^c-F_h^e$, the proof is completed. □

We now describe the fully discrete scheme in detail. Define the discrete chemical potential $\tilde{\mu}$ to be

$$\tilde{\mu}(n^{k+1},n^k)=\frac{\delta F_h^c}{\delta n}(n^{k+1})-\frac{\delta F_h^e}{\delta n}(n^k)=-c\Delta_h n^{k+1}+\mu_{01}\left(n^{k+1}\right)-\mu_{02}\left(n^k\right). \tag{4.3}$$

The total discrete scheme for the original fourth order equation is the following: given n_{ij}^k, find periodic n_{ij}^{k+1} such that

$$\frac{n_{ij}^{k+1}-n_{ij}^k}{\Delta t}=\Delta_h\tilde{\mu}=-c\Delta_h^2 n_{ij}^{k+1}+\Delta_h\mu_{01}\left(n_{ij}^{k+1}\right)-\Delta_h\mu_{02}\left(n_{ij}^k\right), \tag{4.4}$$

with the initial condition

$$n^0(x_{ij})=n_0(x_{ij}). \tag{4.5}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

4.2 Mass conservation and unconditional energy stability

Lemma 4.2. *The solution of the discrete equation* (4.4) *satisfies the mass conservation, which means, for any* $0\le k\le K-1$,

$$h_1h_2\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}n_{ij}^{k+1}=h_1h_2\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}n_{ij}^{k}.$$

Proof. Denote $\tilde{\mu}_{ij}^{k+\frac{1}{2}}=\tilde{\mu}(n_{ij}^{k+1},n_{ij}^{k})$. Multiplying $h_1h_2\Delta t$ to both sides of (4.4) and summing for $i=1,\cdots,M_1$, $j=1,\cdots,M_2$, with the periodic boundary condition, we obtain

$$\begin{aligned}
&h_1h_2\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}\left(n_{ij}^{k+1}-n_{ij}^{k}\right)\\
=&-h_1h_2\Delta t\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}\Delta_h\tilde{\mu}\left(n_{ij}^{k+1},n_{ij}^{k}\right)-h_1h_2\Delta t\sum_{j=1}^{M_2}\frac{1}{h_1^2}\sum_{i=1}^{M_1}\left[\left(\tilde{\mu}_{i+1,j}^{k+\frac{1}{2}}-\tilde{\mu}_{ij}^{k+\frac{1}{2}}\right)-\left(\tilde{\mu}_{ij}^{k+\frac{1}{2}}-\tilde{\mu}_{i-1,j}^{k+\frac{1}{2}}\right)\right]\\
&-h_1h_2\Delta t\sum_{i=1}^{M_1}\frac{1}{h_2^2}\sum_{j=1}^{M_2}\left[\left(\tilde{\mu}_{i,j+1}^{k+\frac{1}{2}}-\tilde{\mu}_{ij}^{k+\frac{1}{2}}\right)-\left(\tilde{\mu}_{ij}^{k+\frac{1}{2}}-\tilde{\mu}_{i,j-1}^{k+\frac{1}{2}}\right)\right]\\
=&0.
\end{aligned}$$

This completes the proof. □

Theorem 4.1 (Energy stability)**.** *The scheme* (4.4) *for the fourth order equation* (2.2) *is unconditionally energy stable, which means that*

$$F_h(n^{k+1})\le F_h(n^{k}) \tag{4.6}$$

holds for any time step $\Delta t>0$.

Proof. From the convexity of the discrete energy $F_h^c(n)$ and $F_h^e(n)$, we can obtain

$$\begin{aligned}
F_h^c(n^{k+1})-F_h^c(n^{k})&\le\left\langle\delta_nF_h^c(n^{k+1}),n^{k+1}-n^{k}\right\rangle,\\
F_h^e(n^{k})-F_h^e(n^{k+1})&\le\left\langle\delta_nF_h^e(n^{k}),n^{k}-n^{k+1}\right\rangle.
\end{aligned}$$

Therefore,

$$\begin{aligned}
F_h(n^{k+1})-F_h(n^{k})&=\left(F_h^c(n^{k+1})-F_h^e(n^{k+1})\right)-\left(F_h^c(n^{k})-F_h^e(n^{k})\right)\\
&=F_h^c(n^{k+1})-F_h^c(n^{k})+F_h^e(n^{k})-F_h^e(n^{k+1})\\
&\le\left\langle\delta_nF_h^c(n^{k+1}),n^{k+1}-n^{k}\right\rangle+\left\langle\delta_nF_h^e(n^{k}),n^{k}-n^{k+1}\right\rangle\\
&\le\left\langle\delta_nF_h^c(n^{k+1})-\delta_nF_h^e(n^{k}),n^{k+1}-n^{k}\right\rangle
\end{aligned}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

$$
\begin{aligned}
&=\left\langle \tilde{\mu}(n^{k+1},n^k),\Delta t\Delta_h\tilde{\mu}(n^{k+1},n^k)\right\rangle\\
&=-\Delta t\left\|\nabla_h\tilde{\mu}(n^{k+1},n^k)\right\|^2\\
&\leq 0.
\end{aligned}
$$

This completes the proof. □

4.3 Unconditional unique solvability

Define $\mathcal{M}_0$ to be all the functions in $\mathcal{V}_h$ with zero average as follows,

$$\mathcal{M}_0=\left\{n\in\mathcal{V}_h\middle|\frac{1}{M_1M_2}\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}n_{i,j}=0\right\}.$$

The symmetry and positive definite property of the discrete operator under the periodic condition yields the following lemma.

Lemma 4.3 (see [33]). *For any $n_0\in\mathcal{M}_0$, there exists a unique periodic solution $\check{n}_0\in\mathcal{M}_0$ such that $-\Delta_h\check{n}_0=n_0$.*

Note that, the requirement of $\check{n}_0,n_0\in\mathcal{M}_0$ attributes to the zero average of the functions in $\mathcal{V}_h$ manipulated by Δ_h. From this lemma, we define the inverse of operator L_0, L_0^{-1}, as $\check{n}_0=L_0^{-1}n_0$. Obviously, L_0^{-1} is also symmetrical and positive definite.

Theorem 4.2 (Unique solvability). *The difference scheme* (4.4)-(4.5) *is uniquely solvable for any time step $\Delta t>0$.*

Proof. Define $L=\Delta tL_0=-\Delta t\Delta_h$. It is obvious that, both the operator L and its inverse L^{-1} are symmetrical and positive definite. For $n\in\mathcal{V}_h$, denote

$$\tilde{n}_{ij}=n_{ij}-\frac{1}{M_1M_2}\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}n_{ij},$$

then we have $\tilde{n}\in\mathcal{M}_0$. As for $k=0,1,\cdots,K-1$, define a functional on $\mathcal{V}_h$ as follows,

$$G(n)=\frac{1}{2}\langle L^{-1}(\tilde{n}),\tilde{n}\rangle-\langle L^{-1}(\tilde{n}),\tilde{n}^k\rangle+F_h^c(n)-\langle n,\delta_nF_h^e(n^k)\rangle. \tag{4.7}$$

For any $n_0\in\mathcal{M}_0$,

$$
\begin{aligned}
G(n+\lambda n_0)=&\frac{1}{2}\langle L^{-1}(\tilde{n}+\lambda n_0),\tilde{n}+\lambda n_0\rangle-\langle L^{-1}(\tilde{n}+\lambda n_0),\tilde{n}^k\rangle\\
&+F_h^c(n+\lambda n_0)-\langle n+\lambda n_0,\delta_nF_h^e(n^k)\rangle.
\end{aligned}
$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

So we have

$$\begin{aligned}&\frac{dG(n+\lambda n_0)}{d\lambda}\Big|_{\lambda=0}\\&=\langle L^{-1}(\tilde{n}+\lambda n_0-\tilde{n}^k),n_0\rangle+\langle\delta_n F_h^c(n+\lambda n_0),n_0\rangle-\langle\delta_n F_h^e(n^k),n_0\rangle\,|_{\lambda=0}\\&=\langle L^{-1}(\tilde{n}-\tilde{n}^k),n_0\rangle+\langle\delta_n F_h^c(n),n_0\rangle-\langle\delta_n F_h^e(n^k),n_0\rangle,\end{aligned}$$

it follows that

$$\delta_n G(n)=L^{-1}(\tilde{n}-\tilde{n}^k)+\delta_n F_h^c(n)-\delta_n F_h^e(n^k)$$

and

$$\frac{d^2G(n+\lambda n_0)}{d\lambda^2}\Big|_{\lambda=0}=\langle L^{-1}(n_0),n_0\rangle+\langle\delta_n^2 F_h^c(n),n_0^2\rangle.$$

The convexity of F_h^c and the positive definiteness of L^{-1} guarantee the convexity of $G(n)$ on $\mathcal{V}_h$. Supposing n^{k+1} solves (4.3)-(4.4), we can obtain

$$n^{k+1}-n^k+L\Big(\frac{\delta F_h^e}{\delta n}(n^{k+1})-\frac{\delta F_h^e}{\delta n}(n^k)\Big)=0. \tag{4.8}$$

The mass conservation of the solution of discrete equations (4.3)-(4.4) yields

$$\begin{aligned}\delta_n G(n^{k+1})&=L^{-1}(\tilde{n}^{k+1}-\tilde{n}^k)+\Big(\frac{\delta F_h^e}{\delta n}(n^{k+1})-\frac{\delta F_h^e}{\delta n}(n^k)\Big)\\&=L^{-1}(n^{k+1}-n^k)+\Big(\frac{\delta F_h^e}{\delta n}(n^{k+1})-\frac{\delta F_h^e}{\delta n}(n^k)\Big)\\&=0.\end{aligned}$$

Therefore, n^{k+1} solves (4.3)-(4.4) if and only if $\delta_n G(n^{k+1})=0$. The convexity of the functional $G(n)$ implies that it is uniquely minimized by n^{k+1}. □

It has to be noted that, Theorem 4.2 can only guarantee the unique existence of the real value of the solution $\mathbf{n}^{k+1}$ for the discrete system (4.4)-(4.5). However, the reasonable value of each component of the vector $\mathbf{n}^{k+1}$ has to be in the open subset $(0,1/b)$. This requirement for the solution from the physical background could not be guaranteed by Theorem 4.2. Here, the author would like to leave it as an open problem for further efforts. Fortunately, this requirement could be guaranteed during the numerical implementation process by selecting appropriate temporal steps since the program can only run ahead only if all the components of the vector $\mathbf{n}^{k+1}$ are in the region $(0,1/b)$. Furthermore, all the components of the numerical solution $\mathbf{n}^{k+1}$ are in a close subset of the reasonable $(0,1/b)$ due to the finiteness of their total number, which could be written as $[\epsilon,1/b-\epsilon]$, where $\epsilon\in(0,1/2b)$ is a really small value.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

4.4 Convergence

Denote

$$\alpha_{11}=\max\Big\{|\mu'_{01}(n)|:\ n\in\Big[\epsilon,\frac{1}{b}-\epsilon\Big]\Big\},\quad \alpha_{12}=\max\Big\{|\mu''_{01}(n)|:\ n\in\Big[\epsilon,\frac{1}{b}-\epsilon\Big]\Big\},$$

$$\alpha_{21}=\max\Big\{|\mu'_{02}(n)|:\ n\in\Big[\epsilon,\frac{1}{b}-\epsilon\Big]\Big\}=\max\Big\{\Big|\frac{2a(T)(1+bn)}{(1+2bn-b^2n^2)^2}\Big|:\ n\in\Big[\epsilon,\frac{1}{b}-\epsilon\Big]\Big\}\le 2a(T),$$

$$\alpha_{22}=\max\Big\{|\mu''_{02}(n)|:\ n\in\Big[\epsilon,\frac{1}{b}-\epsilon\Big]\Big\},\quad \alpha_{15}=\frac{\alpha_{11}^2+\alpha_{21}^2}{c^2},\quad \alpha_{13}=\frac{c+\alpha_{11}^2+a(T)^2}{c},$$

$$\alpha_{14}=\max\Big\{|\partial_t\bar{n}|:\ (x,t)\in\bar{\Omega}_T\Big\},\quad \alpha_{17}=\frac{\alpha_{12}\alpha_{14}+\alpha_{22}\alpha_{14}}{c},$$

$$\alpha_{16}=\frac{\alpha_{11}^2+\alpha_{21}^2+\alpha_{12}\alpha_{14}+\alpha_{22}\alpha_{14}}{c},\quad \alpha_{18}=16\alpha_{15}+\frac{2}{c}+4,$$

$$\alpha_{19}=\max\Big\{4\alpha_{13}\Big(4\alpha_{15}+1\Big)+4\alpha_{17},4\alpha_{16}\Big\},\quad C_{11}=\sqrt{\frac{|\Omega|}{\alpha_{13}}}m_1\exp\Big(\alpha_{13}T_m\Big),$$

$$C_{12}=\sqrt[4]{\frac{2\alpha_{18}}{\alpha_{13}\alpha_{19}}k_0^2|\Omega|^2}\exp\Big(\Big(\frac{\alpha_{13}}{2}+\frac{\alpha_{19}}{4}\Big)(k+1)\Delta t\Big)m_1.$$

Theorem 4.3 (Error estimate)**.** *Suppose a physically reasonable, smooth and periodic solution to the original fourth order equation* (2.2) *is given by* $\bar{n}(x,y,t)$ *on* $\bar{\Omega}$ *for* $0<t\le T_m$ *for some* $T_m<\infty$ *with initial data* $\bar{n}(x,y,0)$*. As for* $k=0,1,\cdots,K-1$*, define*

$$\bar{n}_{i,j}^k:=\bar{n}(x_i,y_j,k\Delta t),\tag{4.9}$$

and $e_{i,j}^k=\bar{n}_{i,j}^k-n_{i,j}^k$*, where* $n_{i,j}^k$ *is the k-th periodic solution of* (4.3)-(4.4) *with* $n_{i,j}^0=\bar{n}_{i,j}^0$*. Then if* $\Delta t<\frac{c}{2(\alpha_{11}^2+c)}$*, we have*

$$\Big\|e^K\Big\|\le C_{11}(h_1^2+h_2^2+\Delta t).$$

If $\Delta t<\min\{\frac{c}{2(\alpha_{11}^2+c)},\frac{c}{2\alpha_{12}\alpha_{14}}\}$*, the* L^∞ *error estimation could be given as*

$$\Big\|e^K\Big\|_\infty\le C_{12}(h_1^2+h_2^2+\Delta t).$$

Proof. The continuous function $\bar{n}$ solves the discrete equations

$$\frac{\bar{n}_{ij}^{k+1}-\bar{n}_{ij}^k}{\Delta t}=\Delta_h\tilde{\mu}(\bar{n}_{ij}^{k+1},\bar{n}_{ij}^k)+R_{ij}^{k+1},\tag{4.10}$$

where R_{ij}^{k+1} is the local truncation error, which satisfies

$$|R_{ij}^{k+1}|\le m_1(h_1^2+h_2^2+\Delta t),\tag{4.11}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

for all i, j, and k for some $m_1 \geq 0$ that depends on T_m, L_x, L_y and the $C^2([0,T_m];C^6(\bar{n}))$ norm of the function $\bar{n}(\mathbf{x},t)$.

Subtracting (4.4) from (4.10), we have

$$\frac{e_{ij}^{k+1}-e_{ij}^{k}}{\Delta t}=\Delta_h\tilde{\mu}\left(\bar{n}_{ij}^{k+1},\bar{n}_{ij}^{k}\right)-\Delta_h\tilde{\mu}\left(n_{ij}^{k+1},n_{ij}^{k}\right)+R_{ij}^{k+1},$$
$$1\leq i\leq M_1,\quad 1\leq j\leq M_2,\quad 0\leq k\leq K-1. \tag{4.12a}$$
$$e_{ij}^{0}=0,\quad 1\leq i\leq M_1,\quad 1\leq j\leq M_2. \tag{4.12b}$$

Taking inner product of (4.12a) with $2\Delta t e^{k+1}$ yields

$$\begin{aligned}&\left\|e^{k+1}\right\|^2-\left\|e^{k}\right\|^2+\left\|e^{k+1}-e^{k}\right\|^2\\&=2\Delta t\left\langle\Delta_h\tilde{\mu}\left(\bar{n}^{k+1},\bar{n}^{k}\right)-\Delta_h\tilde{\mu}\left(n^{k+1},n^{k}\right),e^{k+1}\right\rangle+2\Delta t\left\langle R^{k+1},e^{k+1}\right\rangle.\end{aligned} \tag{4.13}$$

According to Lemma 3.1, we have

$$\begin{aligned}&2\Delta t\left\langle\Delta_h\tilde{\mu}\left(\bar{n}^{k+1},\bar{n}^{k}\right)-\Delta_h\tilde{\mu}\left(n^{k+1},n^{k}\right),e^{k+1}\right\rangle\\&=-2\Delta t\left\langle-c\Delta_h^2e^{k+1}+\Delta_h\mu_{01}\left(\bar{n}^{k+1}\right)-\Delta_h\mu_{01}\left(n^{k+1}\right)-\left[\Delta_h\mu_{02}\left(\bar{n}^{k}\right)-\Delta_h\mu_{02}\left(n^{k}\right)\right],e^{k+1}\right\rangle\\&=-2c\Delta t\left\|\Delta_he^{k+1}\right\|^2+2\Delta t\left\langle\mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\Delta_he^{k+1}\right\rangle\\&\quad-2\Delta t\left\langle\mu_{02}\left(\bar{n}^{k}\right)-\mu_{02}\left(n^{k}\right),\Delta_he^{k+1}\right\rangle\\&=-2c\Delta t\left\|\Delta_he^{k+1}\right\|^2+2\Delta t\left\langle\mu_{01}'(\xi_1^{k+1})e^{k+1},\Delta_he^{k+1}\right\rangle-2\Delta t\left\langle\mu_{02}'(\xi_2^{k})e^{k},\Delta_he^{k+1}\right\rangle\\&\leq-2c\Delta t\left\|\Delta_he^{k+1}\right\|^2+2\alpha_{11}\Delta t\left\|e^{k+1}\right\|\left\|\Delta_he^{k+1}\right\|+2\alpha_{21}\Delta t\left\|e^{k}\right\|\left\|\Delta_he^{k+1}\right\|\\&\leq-2c\Delta t\left\|\Delta_he^{k+1}\right\|^2+\frac{\alpha_{11}^2\Delta t}{c}\left\|e^{k+1}\right\|^2+c\Delta t\left\|\Delta_he^{k+1}\right\|^2+\frac{\alpha_{21}^2\Delta t}{c}\left\|e^{k}\right\|^2+c\Delta t\left\|\Delta_he^{k+1}\right\|^2\\&\leq\frac{\alpha_{11}^2\Delta t}{c}\left\|e^{k+1}\right\|^2+\frac{a(T)^2\Delta t}{c}\left\|e^{k}\right\|^2,\end{aligned}$$

and

$$2\Delta t\left\langle R^{k+1},e^{k+1}\right\rangle\leq m_1^2|\Omega|\Delta t(h_1^2+h_2^2+\Delta t)^2+\Delta t\left\|e^{k+1}\right\|^2.$$

Combining all the above results and ignoring the nonnegative term $\|e^{k+1}-e^{k}\|^2$ in (4.13), we obtain

$$\left\|e^{k+1}\right\|^2-\left\|e^{k}\right\|^2\leq\left(\frac{\alpha_{11}^2}{c}+1\right)\Delta t\left\|e^{k+1}\right\|^2+\frac{a(T)^2\Delta t}{c}\left\|e^{k}\right\|^2+m_1^2|\Omega|\Delta t(h_1^2+h_2^2+\Delta t)^2. \tag{4.14}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

Replacing k in the inequality (4.14) by l and summing l from 0 to k, we obtain

$$\begin{aligned}\left\|e^{k+1}\right\|^2&=\sum_{l=0}^{k}\left(\left\|e^{l+1}\right\|^2-\left\|e^{l}\right\|^2\right)\\&\leq\left(\frac{\alpha_{11}^2}{c}+1\right)\Delta t\sum_{l=0}^{k}\left\|e^{l+1}\right\|^2+\frac{a(T)^2\Delta t}{c}\sum_{l=0}^{k}\left\|e^{l}\right\|^2+m_1^2|\Omega|(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t\\&\leq\left(\frac{\alpha_{11}^2}{c}+1\right)\Delta t\left\|e^{k+1}\right\|^2+\left(\frac{\alpha_{11}^2}{c}+1+\frac{a(T)^2}{c}\right)\Delta t\sum_{l=0}^{k}\left\|e^{l}\right\|^2+m_1^2|\Omega|(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t.\end{aligned}$$

Therefore,

$$\left[1-\left(\frac{\alpha_{11}^2}{c}+1\right)\Delta t\right]\left\|e^{k+1}\right\|^2\leq\left(\frac{\alpha_{11}^2}{c}+1+\frac{a(T)^2}{c}\right)\Delta t\sum_{l=0}^{k}\left\|e^{l}\right\|^2+4m_1^2|\Omega|(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t,$$

$$\left\|e^{k+1}\right\|^2\leq\frac{\frac{\alpha_{11}^2}{c}+1+\frac{a(T)^2}{c}}{1-(\frac{\alpha_{11}^2}{c}+1)\Delta t}\Delta t\sum_{l=0}^{k}\left\|e^{l}\right\|^2+\frac{m_1^2|\Omega|}{1-(\frac{\alpha_{11}^2}{c}+1)\Delta t}(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t.$$

If

$$\left(\frac{\alpha_{11}^2}{c}+1\right)\Delta t\leq\frac{1}{2},$$

we have

$$\begin{aligned}\left\|e^{k+1}\right\|^2&\leq\left(\frac{2\alpha_{11}^2}{c}+2+\frac{2a(T)^2}{c}\right)\Delta t\sum_{l=0}^{k}\left\|e^{l}\right\|^2+2m_1^2|\Omega|(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t\\&=2\alpha_{13}\Delta t\sum_{l=0}^{k}\left\|e^{l}\right\|^2+2m_1^2|\Omega|(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t.\end{aligned}\tag{4.15}$$

The Gronwall inequality yields

$$\left\|e^{k+1}\right\|^2\leq\frac{m_1^2|\Omega|}{\alpha_{13}}\exp\left(2\alpha_{13}T_m\right)\left(h_1^2+h_2^2+\Delta t\right)^2,\tag{4.16a}$$

$$\left\|e^{k+1}\right\|\leq\sqrt{\frac{|\Omega|}{\alpha_{13}}}m_1\exp\left(\alpha_{13}T_m\right)\left(h_1^2+h_2^2+\Delta t\right)=C_{11}\left(h_1^2+h_2^2+\Delta t\right).\tag{4.16b}$$

To derive the estimation of $\|\Delta_h e^{k+1}\|$, the Eq. (4.12a) is taken inner product with $\delta_t e^{k+\frac{1}{2}}=\frac{e^{k+1}-e^k}{\Delta t}$,

$$\left\|\frac{e^{k+1}-e^k}{\Delta t}\right\|^2=\left\langle\Delta_h\tilde{\mu}\left(\bar{n}^{k+1},\bar{n}^k\right)-\Delta_h\tilde{\mu}\left(n^{k+1},n^k\right),\delta_t e^{k+\frac{1}{2}}\right\rangle+\left\langle R^{k+1},\frac{e^{k+1}-e^k}{\Delta t}\right\rangle.\tag{4.17}$$

The last term of the above equation satisfies

$$\left\langle R^{k+1},\frac{e^{k+1}-e^k}{\Delta t}\right\rangle\leq\frac{m_1^2|\Omega|}{2}(h_1^2+h_2^2+\Delta t)^2+\frac{1}{2}\left\|\frac{e^{k+1}-e^k}{\Delta t}\right\|^2.\tag{4.18}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

And for the first term of the right hand side of (4.17), we have

$$\begin{aligned}
&\left\langle \Delta_h\tilde{\mu}\left(\bar{n}^{k+1},\bar{n}^k\right)-\Delta_h\tilde{\mu}\left(n^{k+1},n^k\right),\delta_t e^{k+\frac{1}{2}}\right\rangle\\
=&\left\langle -c\Delta_h^2 e^{k+1}+\Delta_h\mu_{01}\left(\bar{n}^{k+1}\right)-\Delta_h\mu_{01}\left(n^{k+1}\right)-\left[\Delta_h\mu_{02}\left(\bar{n}^k\right)-\Delta_h\mu_{02}\left(n^k\right)\right],\delta_t e^{k+\frac{1}{2}}\right\rangle\\
=&\frac{1}{\Delta t}\left\langle -c\Delta_h e^{k+1},\Delta_h e^{k+1}-\Delta_h e^k\right\rangle+\left\langle \mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle\\
&-\left\langle \mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle\\
=&-\frac{c}{2\Delta t}\left(\left\|\Delta_h e^{k+1}\right\|^2-\left\|\Delta_h e^k\right\|^2+\left\|\Delta_h e^{k+1}-\Delta_h e^k\right\|^2\right)\\
&+\left\langle \mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle-\left\langle \mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle\\
\le&-\frac{c}{2\Delta t}\left(\left\|\Delta_h e^{k+1}\right\|^2-\left\|\Delta_h e^k\right\|^2\right)+\left\langle \mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle\\
&-\left\langle \mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle. \qquad (4.19)
\end{aligned}$$

Combining of (4.17), (4.18) and (4.19) leads to

$$\begin{aligned}
\left\|\frac{e^{k+1}-e^k}{\Delta t}\right\|^2\le&\frac{m_1^2|\Omega|}{2}(h_1^2+h_2^2+\Delta t)^2+\frac{1}{2}\left\|\frac{e^{k+1}-e^k}{\Delta t}\right\|^2-\frac{c}{2\Delta t}\left(\left\|\Delta_h e^{k+1}\right\|^2-\left\|\Delta_h e^k\right\|^2\right)\\
&+\left\langle \mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle-\left\langle \mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle,
\end{aligned}$$

from which, we have

$$\begin{aligned}
&\frac{c}{2\Delta t}\left(\left\|\Delta_h e^{k+1}\right\|^2-\left\|\Delta_h e^k\right\|^2\right)\\
\le&\left\langle \mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle-\left\langle \mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle\\
&-\frac{1}{2}\left\|\frac{e^{k+1}-e^k}{\Delta t}\right\|^2+\frac{m_1^2|\Omega|}{2}(h_1^2+h_2^2+\Delta t)^2.
\end{aligned}$$

Accordingly,

$$\begin{aligned}
&\left\|\Delta_h e^{k+1}\right\|^2-\left\|\Delta_h e^k\right\|^2\\
\le&\frac{2\Delta t}{c}\left\langle \mu_{01}\left(\bar{n}^{k+1}\right)-\mu_{01}\left(n^{k+1}\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle-\frac{2\Delta t}{c}\left\langle \mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{k+\frac{1}{2}}\right\rangle\\
&-\frac{\Delta t}{c}\left\|\frac{e^{k+1}-e^k}{\Delta t}\right\|^2+\frac{m_1^2|\Omega|}{c}\Delta t(h_1^2+h_2^2+\Delta t)^2.
\end{aligned}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

Replacing k in the last inequality above by l and summing l from 0 to k, we can get

$$\begin{aligned}
&\left\|\Delta_h e^{k+1}\right\|^2=\sum_{l=0}^{k}\left(\left\|\Delta_h e^{l+1}\right\|^2-\left\|\Delta_h e^{l}\right\|^2\right)\\
\leq&-\frac{2\Delta t}{c}\sum_{l=0}^{k}\left\langle\mu_{02}\left(\bar{n}^l\right)-\mu_{02}\left(n^l\right),\delta_t\Delta_h e^{l+\frac{1}{2}}\right\rangle+\frac{m_1^2|\Omega|}{c}(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2\\
&+\frac{2\Delta t}{c}\sum_{l=0}^{k}\left\langle\mu_{01}\left(\bar{n}^{l+1}\right)-\mu_{01}\left(n^{l+1}\right),\delta_t\Delta_h e^{l+\frac{1}{2}}\right\rangle-\frac{\Delta t}{c}\sum_{l=0}^{k}\left\|\frac{e^{l+1}-e^l}{\Delta t}\right\|^2. \qquad (4.20)
\end{aligned}$$

Using Lemma 3.4 and Lemma 3.5, we have

$$\begin{aligned}
&\frac{2\Delta t}{c}\sum_{l=0}^{k}\left\langle\mu_{01}\left(\bar{n}^{l+1}\right)-\mu_{01}\left(n^{l+1}\right),\delta_t\Delta_h e^{l+\frac{1}{2}}\right\rangle\\
=&\frac{2}{c}\left\langle\mu'_{01}\left(\xi_{11}^{k+1}\right)e^{k+1},\Delta_h e^{k+1}\right\rangle-\frac{2\Delta t}{c}\sum_{l=1}^{k}\left\langle\delta_t\left[\mu_{01}\left(\bar{n}^{l+\frac{1}{2}}\right)-\mu_{01}\left(n^{l+\frac{1}{2}}\right)\right],\Delta_h e^l\right\rangle\\
\leq&-\frac{2\Delta t}{c}\sum_{l=1}^{k}\left\langle\mu'_{01}\left(\rho_{11}^{l+\frac{1}{2}}n^{l+1}+(1-\rho_{11}^{l+\frac{1}{2}})n^l\right)\delta_t\left(\bar{n}^{l+\frac{1}{2}}-n^{l+\frac{1}{2}}\right),\Delta_h e^l\right\rangle+\frac{2\alpha_{11}}{c}\left\|e^{k+1}\right\|\left\|\Delta_h e^{k+1}\right\|\\
&-\frac{2\Delta t}{c}\sum_{l=1}^{k}\left\langle\mu''_{01}\left(\xi_{12}^{l+\frac{1}{2}}\right)\left(\rho_{11}^{l+\frac{1}{2}}\left(\bar{n}^{l+1}-n^{l+1}\right)+(1-\rho_{11}^{l+\frac{1}{2}})\left(\bar{n}^l-n^l\right)\right)\delta_t\bar{n}^{l+\frac{1}{2}},\Delta_h e^l\right\rangle\\
\leq&\frac{1}{4}\left\|\Delta_h e^{k+1}\right\|^2+\frac{4\alpha_{11}^2}{c^2}\left\|e^{k+1}\right\|^2+\frac{\Delta t}{2c}\sum_{l=1}^{k}\left\|\delta_t e^{l+\frac{1}{2}}\right\|^2+\frac{2\alpha_{11}^2\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2\\
&+\frac{\alpha_{12}\alpha_{14}\Delta t}{c}\left\|e^{k+1}\right\|^2+\frac{2\alpha_{12}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|e^l\right\|^2+\frac{2\alpha_{12}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2. \qquad (4.21)
\end{aligned}$$

And

$$\begin{aligned}
&-\frac{2\Delta t}{c}\sum_{l=0}^{k}\left\langle\mu_{02}\left(\bar{n}^k\right)-\mu_{02}\left(n^k\right),\delta_t\Delta_h e^{l+\frac{1}{2}}\right\rangle\\
=&-\frac{2}{c}\left\langle\mu'_{02}\left(\xi_{21}^k\right)e^k,\Delta_h e^{k+1}\right\rangle+\frac{2\Delta t}{c}\sum_{l=1}^{k}\left\langle\delta_t\left[\mu_{02}\left(\bar{n}^{l-\frac{1}{2}}\right)-\mu_{02}\left(n^{l-\frac{1}{2}}\right)\right],\Delta_h e^l\right\rangle\\
\leq&\frac{2\Delta t}{c}\sum_{l=1}^{k}\left\langle\mu'_{02}\left(\rho_{12}^{l-\frac{1}{2}}n^l+(1-\rho_{12}^{l-\frac{1}{2}})n^l\right)\delta_t\left(\bar{n}^{l-\frac{1}{2}}-n^{l-\frac{1}{2}}\right),\Delta_h e^l\right\rangle+\frac{2\alpha_{21}}{c}\left\|e^k\right\|\left\|\Delta_h e^{k+1}\right\|\\
&+\frac{2\Delta t}{c}\sum_{l=1}^{k}\left\langle\mu''_{02}\left(\xi_{22}^{l-\frac{1}{2}}\right)\left(\rho_{12}^{l-\frac{1}{2}}\left(\bar{n}^l-n^l\right)+(1-\rho_{12}^{l-\frac{1}{2}})\left(\bar{n}^{l-1}-n^{l-1}\right)\right)\delta_t\bar{n}^{l-\frac{1}{2}},\Delta_h e^l\right\rangle\\
\leq&\frac{1}{4}\left\|\Delta_h e^{k+1}\right\|^2+\frac{4\alpha_{21}^2}{c^2}\left\|e^{k+1}\right\|^2+\frac{\Delta t}{2c}\sum_{l=1}^{k}\left\|\delta_t e^{l-\frac{1}{2}}\right\|^2+\frac{2\alpha_{21}^2\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2
\end{aligned}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

$$+\frac{2\alpha_{22}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|e^l\right\|^2+\frac{2\alpha_{22}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2. \tag{4.22}$$

Combining (4.20), (4.21) with (4.22), we can obtain

$$\begin{aligned}
&\left\|\Delta_h e^{k+1}\right\|^2\\
\le&\frac{1}{4}\left\|\Delta_h e^{k+1}\right\|^2+\frac{4\alpha_{11}^2}{c^2}\left\|e^{k+1}\right\|^2+\frac{\Delta t}{2c}\sum_{l=1}^{k}\left\|\delta_t e^{l+\frac{1}{2}}\right\|^2+\frac{2\alpha_{11}^2\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2\\
&+\frac{\alpha_{12}\alpha_{14}\Delta t}{c}\left\|e^{k+1}\right\|^2+\frac{2\alpha_{12}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|e^l\right\|^2+\frac{2\alpha_{12}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2+\frac{1}{4}\left\|\Delta_h e^{k+1}\right\|^2\\
&+\frac{4\alpha_{21}^2}{c^2}\left\|e^{k+1}\right\|^2+\frac{\Delta t}{2c}\sum_{l=1}^{k}\left\|\delta_t e^{l-\frac{1}{2}}\right\|^2+\frac{2\alpha_{21}^2\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2+\frac{2\alpha_{22}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|e^l\right\|^2\\
&+\frac{2\alpha_{22}\alpha_{14}\Delta t}{c}\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2-\frac{\Delta t}{c}\sum_{l=0}^{k}\left\|\frac{e^{l+1}-e^l}{\Delta t}\right\|^2+\frac{m_1^2|\Omega|}{c}(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2\\
\le&\frac{1}{2}\left\|\Delta_h e^{k+1}\right\|^2+4\alpha_{15}\left\|e^{k+1}\right\|^2+2\alpha_{16}\Delta t\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2+\frac{\alpha_{12}\alpha_{14}\Delta t}{c}\left\|e^{k+1}\right\|^2\\
&+2\alpha_{17}\Delta t\sum_{l=1}^{k}\left\|e^l\right\|^2+\frac{m_1^2|\Omega|}{c}(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2.
\end{aligned}\tag{4.23}$$

Using the inequality (4.15) under the condition

$$\left(\frac{\alpha_{11}^2}{c}+1\right)\Delta t\le\frac{1}{2},$$

we have

$$\begin{aligned}
&\frac{1}{2}\left\|\Delta_h e^{k+1}\right\|^2+\left\|e^{k+1}\right\|^2\\
\le&\left(4\alpha_{15}+1\right)\left[2\alpha_{13}\Delta t\sum_{l=0}^{k}\left\|e^l\right\|^2+2m_1^2|\Omega|(h_1^2+h_2^2+\Delta t)^2(k+1)\Delta t\right]+\frac{\alpha_{12}\alpha_{14}\Delta t}{c}\left\|e^{k+1}\right\|^2\\
&+2\alpha_{16}\Delta t\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2+2\alpha_{17}\Delta t\sum_{l=1}^{k}\left\|e^l\right\|^2+\frac{2m_1^2|\Omega|}{c}(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2\\
=&\left[2\alpha_{13}\left(4\alpha_{15}+1\right)+2\alpha_{17}\right]\Delta t\sum_{l=0}^{k}\left\|e^l\right\|^2+\frac{\alpha_{12}\alpha_{14}\Delta t}{c}\left\|e^{k+1}\right\|^2+2\alpha_{16}\Delta t\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2\\
&+\left(8\alpha_{15}+2+\frac{1}{c}\right)m_1^2|\Omega|(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2.
\end{aligned}\tag{4.24}$$

If

$$\frac{\alpha_{12}\alpha_{14}\Delta t}{c}\le\frac{1}{2},$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

then

$$\frac{1}{2}\left\|\Delta_h e^{k+1}\right\|^2+\frac{1}{2}\left\|e^{k+1}\right\|^2\leq\left[2\alpha_{13}\left(4\alpha_{15}+1\right)+2\alpha_{17}\right]\Delta t\sum_{l=0}^{k}\left\|e^l\right\|^2+2\alpha_{16}\Delta t\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2$$
$$+\left(8\alpha_{15}+\frac{1}{c}+2\right)m_1^2|\Omega|(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2. \tag{4.25}$$

Therefore,

$$\begin{aligned}&\left\|\Delta_h e^{k+1}\right\|^2+\left\|e^{k+1}\right\|^2\\&\leq\left[4\alpha_{13}\left(4\alpha_{15}+1\right)+4\alpha_{17}\right]\Delta t\sum_{l=0}^{k}\left\|e^l\right\|^2+4\alpha_{16}\Delta t\sum_{l=1}^{k}\left\|\Delta_h e^l\right\|^2\\&\quad+\left(16\alpha_{15}+\frac{2}{c}+4\right)m_1^2|\Omega|(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2\\&\leq\alpha_{19}\Delta t\sum_{l=0}^{k}\left(\left\|e^l\right\|^2+\left\|\Delta_h e^l\right\|^2\right)+\alpha_{18}m_1^2|\Omega|(k+1)\Delta t(h_1^2+h_2^2+\Delta t)^2.\end{aligned} \tag{4.26}$$

Gronwall inequality yields

$$\left\|e^{k+1}\right\|^2+\left\|\Delta_h e^{k+1}\right\|^2\leq\frac{\alpha_{18}}{\alpha_{19}}\exp\left(\alpha_{19}(k+1)\Delta t\right)\cdot\left|\Omega\right|\left[m_1\left(h_1^2+h_2^2+\Delta t\right)\right]^2, \tag{4.27}$$

where $k=0,1,\cdots,K-1$. Combining (4.16) and (4.27) and using Lemma 3.2, we obtain

$$\begin{aligned}\left\|e^{k+1}\right\|_\infty^2&\leq k_0\left\|e^{k+1}\right\|\left(\left\|\Delta_h e^{k+1}\right\|+\left\|e^{k+1}\right\|\right)\\&\leq k_0\sqrt{2\left\|e^{k+1}\right\|^2\left(\left\|e^{k+1}\right\|^2+\left\|\Delta_h e^{k+1}\right\|^2\right)}\\&\leq k_0\sqrt{\frac{2\alpha_{18}}{\alpha_{13}\alpha_{19}}}\exp\left(\left(\alpha_{13}+\frac{\alpha_{19}}{2}\right)(k+1)\Delta t\right)m_1^2\left|\Omega\right|\left(h_1^2+h_2^2+\Delta t\right)^2.\end{aligned}$$

Therefore,

$$\begin{aligned}\left\|e^{k+1}\right\|_\infty&\leq\sqrt[4]{\frac{2\alpha_{18}}{\alpha_{13}\alpha_{19}}k_0^2\left|\Omega\right|^2}\exp\left(\left(\frac{\alpha_{13}}{2}+\frac{\alpha_{19}}{4}\right)(k+1)\Delta t\right)m_1\left(h_1^2+h_2^2+\Delta t\right)\\&\leq C_{12}\left(h_1^2+h_2^2+\Delta t\right).\end{aligned}$$

This completes the proof. □

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

5 Numerical examples

In this section, we use the convex-splitting scheme (4.4)-(4.5) to obtain the steady state of the fourth order equations (2.2)-(2.3) on the two-dimensional domain $\Omega=[0,L]^2$ with $L=2\times10^{-8}$ meters. The whole domain Ω is divided into 200×200 rectangular meshes. The substance of isobutane (nC_4) is also selected to be simulated for comparing with the results of second order parabolic equation provided in [23]. The parameters are set as $a=1.6977$, $b=7.2442e-5$, $c=2.08869e-3$. The critical properties and the normal boiling point of isobutane (nC_4) are provided in Table 1. The absolute temperature T is set as a invariable value $350K$ on the whole domain Ω except in the the third subsection. The initial condition for the first three subsections are set as: the molar density equals the liquid isobutane (nC_4) under a saturated pressure in the region $[0.3L,0.7L]$, the rest of the domain is filled with a saturated nC_4 gas. The periodic boundary condition is imposed. Newton iterative method has been used to obtain the solution at every temporal step, and the resultant linear systems are solved by an algebraic multigrid (AMG) solver. The tolerances for the Newton iteration and AMG solver are set to be 10^{-5} and 10^{-6}, respectively.

5.1 Numerical accuracy check

In this subsection, we check the convergence rate in time of the convex-splitting scheme (4.4). Here, the exact solution is defined by the molar density at final time $T_m=0.0005$ obtained from $\Delta t=1.25e-8$ on a 200×200 meshes on the domain $[0,2.0e-8]\times[0,2.0e-8]$. The different norms of three kinds of error and their convergence rate of this scheme is provided by Table 2. We can see that, this scheme has about one order accuracy in time.

Table 1: Critical properties (Data from the Table 3.1 on Page 141 of the book by Firoozabadi [8]), ω and m (our computed results) of isobutane (nC_4).

symbol	T_c, K	P_c	ω	m
nC_4	425.18	3.797 MPa	0.1990	0.6709

Table 2: Error estimation at $t=5e-4$. The exact solution is defined as the solution obtained based on $\Delta t=1.25e-8$ with mesh size $hx=hy=1.0e-10$.

Δt	L^2 error	rate of L^2 error	L^1 error	rate	L^∞ error	rate
2.5e-8	1.016312	1.5594	2.9682625	1.5598	2.105e-4	1.5573
5.0e-8	0.0480765	1.1907	8.751	1.1912	6.195e-4	1.1881
1.0e-7	0.1097385	1.0631	19.892	1.0637	1.4115e-3	1.0713
2.0e-7	0.2292965	1.0087	41.768	1.0093	2.966e-3	1.0395
4.0e-7	0.4613745	0.9835	84.075	0.9839	6.0965e-3	1.0128
8.0e-7	0.9122275	0.9746	166.28	0.9750	0.0123015	1.0022
1.0e-6	1.133846	-	206.695	-	0.0153845	-

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

5.2 Spatial distribution of molar density and other chemical properties

In this part, three of physically interested variables at steady state are obtained based on their relationships with molar density. These desirable variables are the homogeneous contribution of chemical potential μ_0, the surface tension contribution to the Helmholtz free energy density $f_{intfTens}$ and the thermodynamic pressure p_0. μ_0 is defined by (2.4). The interfacial Helmholtz free energy density $f_{intfTens}$ is in the form of [23]

$$f_{intfTens}=2f_{\nabla}(n)=c\nabla n\cdot\nabla n. \tag{5.1}$$

And the thermodynamic pressure p_0 is calculated by [23]

$$p_0=n\Big(\frac{\partial f_0}{\partial n}\Big)-f_0=n\mu_0-f_0=\frac{nRT}{1-bn}-\frac{n^2a(T)}{1+2bn-b^2n^2}=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+b(v-b)}. \tag{5.2}$$

Here and the following subsections, the time step is set as $\Delta t=10^{-5}$, and the steady state is defined by the condition that the relative error between two neighboring time step is less than 10^{-8}. The corresponding results are depicted in Fig. 1. The left column of Fig. 1 presents the molar density of isobutane (nC_4) at initial state (a1), $t=0.005$ (b2) and the final state $t=0.139265$ (c1). The right column of Fig. 1 depicts the interfacial Helmholtz free energy density (a2), homogeneous chemical potential (b1) and the thermodynamic pressure (c2) at steady state obtained from the first order convex-splitting scheme. We can see that, the convex-splitting scheme of the fourth order parabolic equation provides similar molar density evolution history and final state with the convex-splitting scheme of the second order parabolic equation proposed in [23]. In addition, the clear dissipative trend of the total Helmholtz free energy during the whole evolution history is shown in Figs. 1(d1), (d2), which verifies the energy stability of the proposed convex-splitting scheme.

5.3 Calculation of interface tension and verification against Young-Laplace equation

In this part, the numerical scheme (4.4) is used to calculate the surface tension σ and the capillary pressure p_c at the interface between the liquid phase and the gas phase at steady state under several different temperature range from $250K$ to $350K$. Here the interface tension σ is calculated by the formula [8,23]

$$\sigma=\frac{\partial F}{\partial A}=\frac{F(n)-F_0(n_{init})}{A}$$

with a unit of J/m^2 or N/m under the assumption that σ is spatially constant within the interface for the investigated system. And the capillary pressure P_c is computed by the well-known Young-Laplace equation as [8,23]

$$P_c=P_{liquid}-P_{gas}=\frac{\sigma}{r}. \tag{5.3}$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

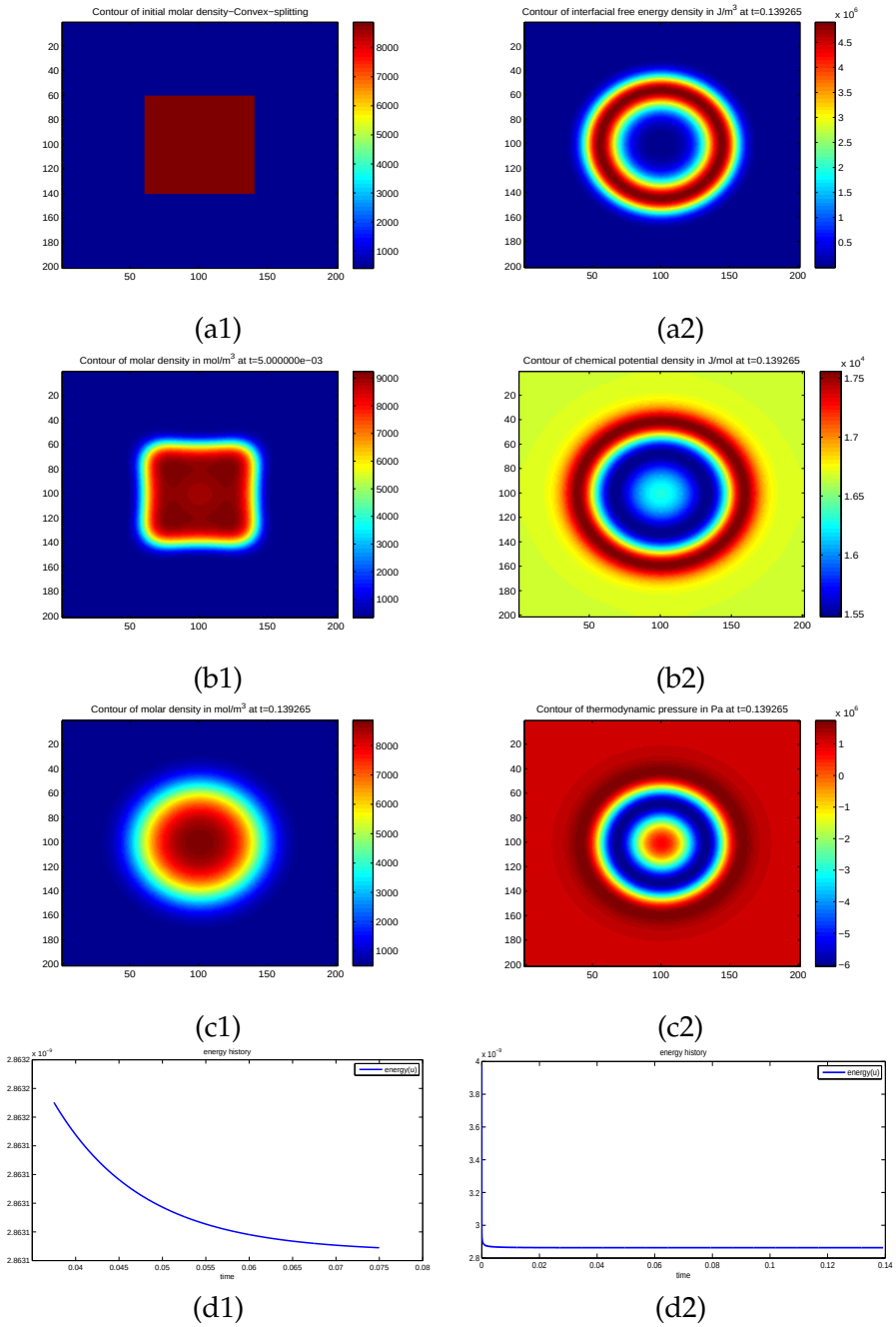
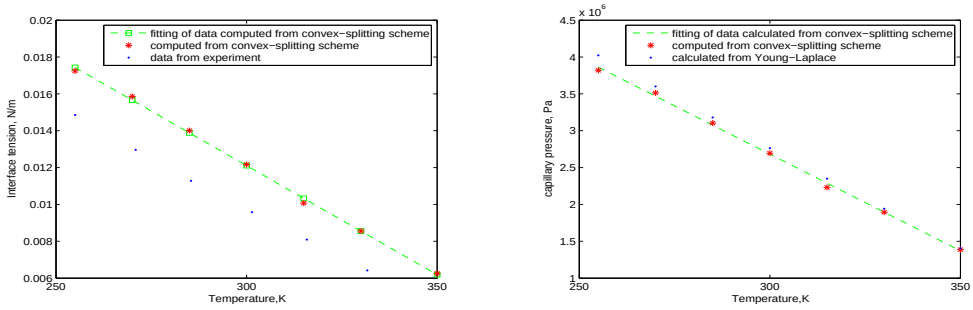


Figure 1: Numerical results given by the convex-splitting scheme. Molar density distribution at (a1) initial time, (b1) $t=5.0e-3$, (c1) final state. The final density distribution of (a2) interfacial Helmholtz free energy, (b2) chemical potential, (c2) thermodynamic pressure. (d1) energy evolution history during the evolution process, (d2) the total energy evolution history.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press



(a) (b)

Figure 2: Comparison between numerical predictions given by the Convex-splitting scheme and laboratory data: (a) surface tension (N/m); (b) capillary pressure.

In our simulation, the contribution of the interface tension to the total free energy at equilibrium state is defined as $\Delta F = F(n) - F_0(n_{init})$ based on the assumption that the steady state has a perfect circular shape. The radius of the droplet is also $r = 2\times10^{-8}\times(0.16/\pi)^{1/2} = 4.514\times10^{-9}$. The length of the circle $A = 2\pi\times4{,}514\times10^{-9}$ meters. For example, at temperature $T = 350K$, $F(n) - F_0(n_{init}) \cong 1.774\times10^{-10}J$, the surface tension is derived by $\sigma = 1.774\times10^{-10}/A = 6.2578\times10^{-3}J/m^2$. The surface tension at other temperatures are calculated in the same way. The results are plotted in Fig. 2 and compared with the laboratory results provided in Table 2 of [18]. We can see that, the difference between the surface tension trend calculated by our numerical scheme and the experimental data is small from the engineering point of view.

Based on this verification of the values of the interface tension at the interface, the capillary pressure is easily obtained based on their relationships provided by the Eq. (5.3). On the other hand, the capillary pressure is also defined as the difference between the thermodynamic pressure at the liquid phase and the gas part. Here, the pressure of the liquid drop P_{liquid} is picked from its center, at the grid point $(101,101)$; and the pressure in the bulk gas region is P_{gas} is picked from point $(51,51)$. Fig. 2(b) presents the comparison between these two methods. It could be viewed that, the capillary pressure obtained from these two different methods are in nice agreement. This guarantees the reliability of the fourth-order equation and the proposed convex-splitting scheme.

5.4 An additional example

In this part, the convex-splitting scheme is applied to predict the solution evolution history under a specific initial condition. The molar density distribution at several different points of time and the energy evolution history during the whole process are depicted by Fig. 3. The initial data is set by putting four commensurate square bubbles around the center of the domain symmetrically. From this group of pictures, we can see that, a gas-liquid interface is formed around every single bubble during initial time as

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

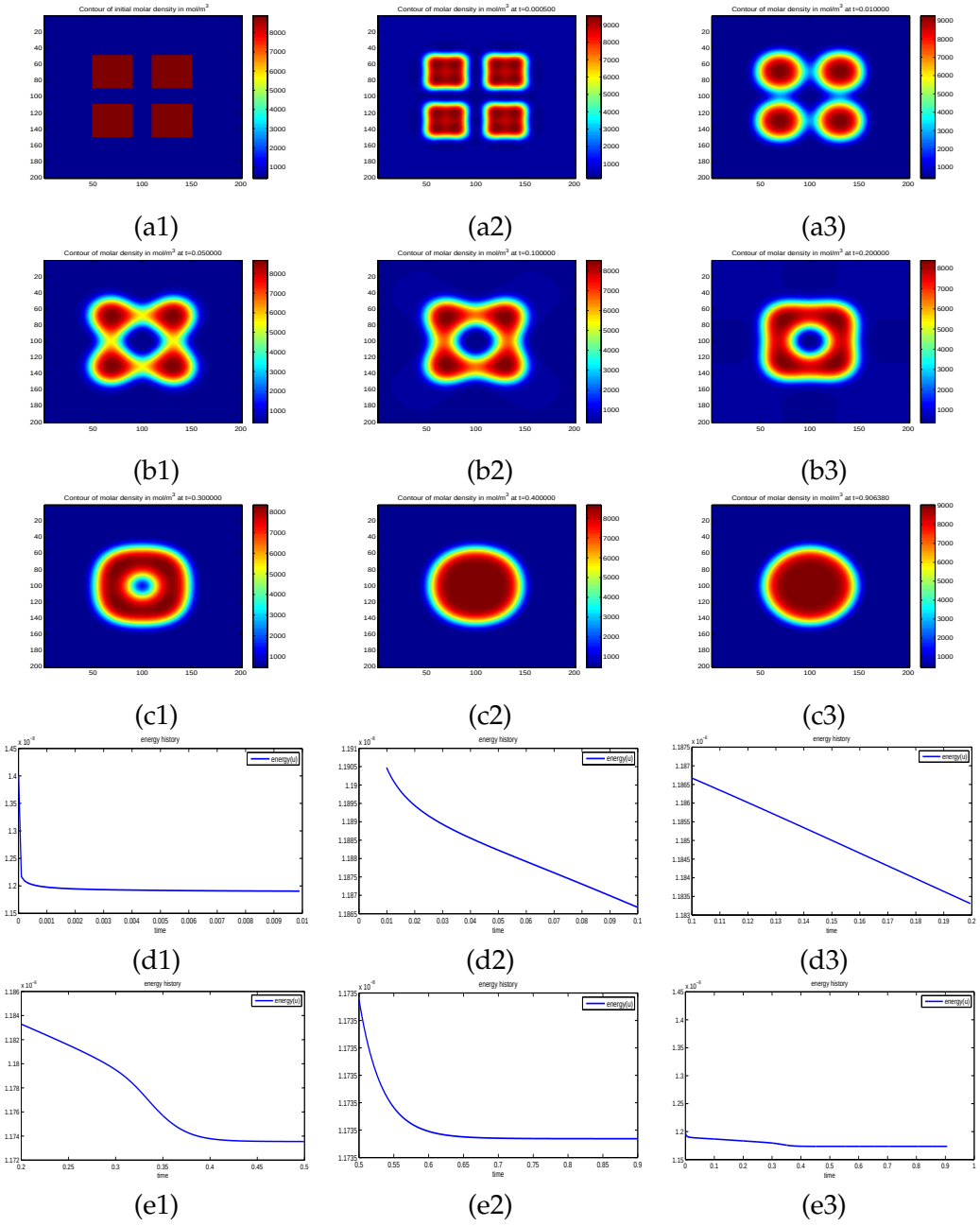


Figure 3: Evolution history of solution of the fourth-order parabolic equation and total energy under a specific initial condition. Subfigures (a1)-(c3) depict the molar density distribution at different points of time during the whole evolution history. Subfigures (d1)-(e2) depict the energy decreasing process during the time slots $[0.0,0.01]$, $[0.01,0.1]$, $[0.1,0.2]$, $[0.2,0.5]$ and $[0.5,0.9]$, separatively. And the subfigure (e3) describes the whole total Helmoltz energy evolution history.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

showed in Fig. 3(a2). These bubbles get rounded separately at early stage during time slot $[0.0005,0.01]$. At time $0.01s$, these nearly circular bubbles touch their neighboring bubbles. After that stage, the contact areas between contiguous droplets increase gradually, then, the bubbles become a unit ring. Finally, this single ring becomes a circular droplet at the center of the domain at time $T_m=0.90638$. The total energy is decreasing all the time and decays rapidly when the shape of the liquid bubble changes dramatically as shown by subfigures (d1)-(d3).

6 Conclusions

In this paper, a first order convex-splitting scheme has been proposed to solve the fourth order parabolic equation derived from the diffuse interface model with Peng-Robinson equation of state. The scheme is proved to satisfy mass conservation, be unconditional energy stable and L^∞ convergence under a unique existence of the continuous equation on a subset of the reasonable region of the molar density $(0,\frac{1}{b})$.

Appendix

A Parameters related to Peng-Robinson EOS

The parameter $a=a(T)$ and $b=b(T)$ can be derived from the critical properties of the particular species as follows,

$$a(T)=0.45724\frac{R^2T_c^2}{P_c}\left(1+m\left(1-\sqrt{\frac{T}{T_c}}\right)\right)^2,$$
$$b(T)=0.07780\frac{RT_c}{P_c}.$$

Here, T_c and P_c represent the critical temperature and the critical pressure of this substance, respectively. The parameter m has the following relations with the accentric parameter ω:

$$m=0.37464+1.54226\omega-0.26992\omega^2, \qquad \omega\le 0.49,$$
$$m=0.379642+1.485030\omega-0.164423\omega^2+0.016666\omega^3, \qquad \omega>0.49.$$

And the coefficient c in (2.1) is the influence parameter of pure substance and has the following relation with a and b:

$$c=ab^{2/3}\left(m_1^c\left(1-\frac{T}{T_c}\right)+m_2^c\right).$$

Here, m_1^c and m_2^c denote the coefficients which can be related to the accentric factor ω by

$$m_1^c=-\frac{10^{-16}}{1.2326+1.3757\omega}, \quad m_2^c=\frac{10^{-16}}{0.9051+1.5410\omega}.$$

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

B Discrete difference operators and Sobolev norms

For $n\in\mathcal{V}_h$, denote

$$\delta_x n_{i+\frac{1}{2},j}=\frac{1}{h_1}\Big(n_{i+1,j}-n_{i,j}\Big),\qquad \delta_y n_{i,j+\frac{1}{2}}=\frac{1}{h_2}\Big(n_{i,j+1}-n_{i,j}\Big),$$
$$\delta_x^2 n_{ij}=\frac{1}{h_1^2}\Big(n_{i+1,j}-2n_{ij}+n_{i-1,j}\Big),\qquad \delta_y^2 n_{ij}=\frac{1}{h_2^2}\Big(n_{i,j+1}-2n_{ij}+n_{i,j-1}\Big),$$
$$\nabla_h n_{i+\frac{1}{2},j+\frac{1}{2}}=\Big(\delta_x n_{i+\frac{1}{2},j},\delta_y n_{i,j+\frac{1}{2}}\Big)^T,\qquad \Delta_h n_{ij}=\Big(\delta_x^2+\delta_y^2\Big)n_{ij}.$$

For a grid function $w=(w^0,w^1,\cdots,w^{K-1},w^K)$ on Ω_τ, define

$$w^{n+\frac{1}{2}}=\frac{1}{2}\Big(w^n+w^{n+1}\Big),\quad \delta_t w^{n+\frac{1}{2}}=\frac{1}{\Delta t}\Big(w^{n+1}-w^n\Big),\quad 0\le k\le K-1.$$

For $u,v\in\mathcal{V}_h$, their inner product is defined as

$$\Big\langle u,v\Big\rangle=h_1h_2\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}u_{ij}v_{ij},$$

and Sobolev norms are defined as

$$\Big\|u\Big\|=\sqrt{\Big\langle u,u\Big\rangle},\qquad \Big\|u\Big\|_\infty=\max_{0\le i\le M_1,0\le j\le M_2}\Big|u_{ij}\Big|,$$
$$\Big\|\nabla_h u\Big\|=\sqrt{h_1h_2\sum_{i=0}^{M_1}\sum_{j=0}^{M_2}\Big|\nabla_h u_{i+\frac{1}{2},j+\frac{1}{2}}\Big|^2},\qquad \Big\|\Delta_h u\Big\|=\sqrt{h_1h_2\sum_{i=1}^{M_1}\sum_{j=1}^{M_2}\Big|\Delta_h u_{ij}\Big|^2}.$$

Acknowledgments

The author is grateful to Prof. Shuyu Sun of Division of Physical Sciences and Engineering (PSE), King Abdullah University of Science and Technology (KAUST) for his unreserved supply this meaningful model to investigate and sufficient explanation of the application background, Dr. Zhonghua Qiao of Department of Applied Mathematics, Hong Kong Polytechnic University, Prof. Zhizhong Sun of Department of Mathematics, Southeast University and Hehu Xie of Institute of Computational Mathematics Academy of Mathematics and Systems Sciences Chinese Academy of Sciences for providing useful suggestions and many helpful discussions.

References

[1] D. ANDERSON, G. B. MCFADDEN AND A. WHEELER, *Diffuse-interface methods in fluid mechanics,* Ann. Rev. Fluid Mech., 30 (1998), pp. 139–165.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

[2] A. BASKARAN, J. S. LOWENGRUB, C. WANG AND S. M. WISE, *Convergence analysis of a second order convex splitting scheme for the modified phase field crystal equation,* SIAM J. Numer. Anal., 51 (2013), pp. 2851–2873.
[3] J. W. CAHN AND J. E. HILLIARD, *Free energy of a nonuniform system I. Interfacial free energy,* J. Chem. Phys., 28 (1958), pp. 258–267.
[4] J. W. CAHN, *Free energy of a nonuniform system II. Thermodynamic basis,* J. Chem. Phys., 30 (1959), pp. 1121–1124.
[5] J. W. CAHN, *On spinodal decomposition,* Acta Metallurgica, 9 (1961), pp. 795–801.
[6] W. CHEN, S. CONDE, C. WANG, X. WANG AND S. WISE, *A linear energy stable scheme for a thin film model without slope selection,* J. Sci. Comput., 52 (2012), pp. 546–562.
[7] D. J. EYRE, *Unconditionally gradient stable time marching the Cahn–Hilliard equation,* in J. W. Bullard, R. Kalia, M. Stoneham and L. Q. Chen, (eds.) Computational and Mathematical Models of Microstructural Evolution, 53 (1998), pp. 1686–1712.
[8] A. FIROOZABADI, Thermodynamics of Hydrocarbon Reservoirs, McGraw-Hill, New York, 1999.
[9] S. GU, H. ZHANG AND Z. ZHANG, *An energy-stable finite-difference scheme for the binary fluid-surfactant system,* J. Comput. Phys., 270 (2014), pp. 416–431.
[10] J. GUO, C. WANG, S. M. WISE AND X. YUE, *An H^2 convergence of a second-order convex-splitting, finite difference scheme for the three-dimensional Cahn-Hilliard equation,* Commun. Math. Sci., 14(2) (2016), pp. 489–515.
[11] Z. HU, S. M. WISE, C. WANG AND J. S. LOWENGRUB, *Stable and efficient finite-difference nonlinear-multigrid schemes for the phase field crystal equation,* J. Comput. Phys., 228 (2009), pp. 5323–5339.
[12] J. KOU AND S. SUN, *An adaptive finite element method for simulating surface tension with the gradient theory of fluid interfaces,* J. Comput. Appl. Math., 255 (2014), pp. 593–604.
[13] J. KOU AND S. SUN, *Unconditionally stable methods for simulating multi-component two-phase interface models with Peng-Robinson equation of state and various boundary conditions,* J. Comput. Appl. Math., (2015).
[14] J. KOU, S. SUN AND X. WANG, *Efficient numerical methods for simulating surface tension of multi-component mixtures with the gradient theory of fluid interfaces,* Comput. Methods Appl. Mech. Eng., 292 (2015), pp. 92–106.
[15] J. LI, Z. Z. SUN AND X. ZHAO, *A three level linearized compact difference scheme for the Cahn-Hilliard equation,* Sci. China Math., 55(4) (2012), pp. 805–826.
[16] D. LI AND Z. QIAO, *On second order semi-implicit Fourier spectral methods for 2D Cahn-Hilliard equations,* J. Sci. Comput., (2016), DOI: 10.1007/s10915-016-0251-4.
[17] D. LI, Z. QIAO AND T. TANG, *Characterizing the stabilization size for semi-implicit Fourier-Spetral method to phase field equations,* SIAM J. Numer. Anal., 54 (2016), pp. 1653–1681.
[18] H. LIN AND Y. DUAN, *Surface tension measurements of propane $(r-290)$ and isobutane $(r-600a)$ from (253 to 333)K,* J. Chem. Eng. Data, 48 (2003), pp. 1360–1363.
[19] H. LIAO AND Z. SUN, *Maximum norm error bounds of ADI and compact ADI methods for solving parabolic equations,* Numer. Methods Partial Differential Equations, 26 (2010), pp. 37–60.
[20] D. Y. PENG AND D. B. ROBINSON, *A new two-constant equation of state,* Industrial and Engineering Chemistry Fundamentals, 15(1) (1976), pp. 59–64.
[21] Q. PENG, Z. QIAO AND S. SUN, *Stability and convergence analysis of second-order schemes for a diffuse interface model with Peng-Robinson equation of state*, J. Comput. Math., doi:10.4208/jcm.1611-m2016-0623.
[22] Z. QIAO, Z. SUN AND Z. ZHANG, *The stability and convergence of two linearized finite difference*

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press

schemes for the nonlinear epitaxial growth model, Numer. Methods Partial Differential Equations, 28(6) (2012), pp. 1893–1915.

[23] Z. QIAO AND S. SUN, *Two-phase fluid simulation using a diffuse interface model with Peng–Robinson equation of state,* SIAM J. Sci. Comput., 36(4) (2014), pp. B708–B728.

[24] Z. QIAO, Z. SUN AND Z. ZHANG, *Stability and convergence of second-order schemes for the nonlinear epitaxial growth model without slope selection.* Math. Comput., 84 (2015), pp. 653–674.

[25] D. B. ROBINSON, D. PENG AND S. Y. CHUNG, *The development of the Peng-Robinson equation and its application to phase equilibrium in a system containing methanol,* Fluid Phase Equilibria, 24 (1985), pp. 25–41.

[26] J. SHEN, C. WANG, X. WANG AND S. M. WISE, *Second–order convex splitting schemes for gradient flows with Ehrlich-Schwoebel type energy: application to thin film epitaxy,* SIAM J. Numer. Anal., 50 (2012), pp. 105–125.

[27] J. SHEN AND X. YANG, *Numerical approximations of Allen–Cahn and Cahn–Hilliard equations,* Discrete Contin. Dyn. Syst. Ser. A, 28 (2010), pp. 1669–1691.

[28] Z. SUN, *A second–order accurate linearized difference scheme for the two–dimensional Cahn–Hilliard equation,* Math. Comput., 64(212) (1995), pp. 1463–1471.

[29] J. D. VAN DER WAALS, "verhandel. konink. akad. weten. amsterdam" vol. 1 no. 8 (dutch) 1893, translation of J. D. van der Waals (*The thermodynamic theory of capillarity under the hypothesis of a continuous density variation*), J. Stat. Phys., 1979.

[30] P. VIGNAL, L. DALCIN, D. L. BROWN, N. COLLIER AND V. M. CALO, *An energy-stable convex splitting for the phase-field crystal equation,* Comput. Struct., 158 (2015), pp. 355–368.

[31] C. WANG, X. WANG AND S. M. WISE, *Unconditionally stable schemes for equations of thin film epitaxy,* Discrete Contin. Dyn. Syst. Ser. A, 28 (2010), pp. 405–423.

[32] C. WANG AND S. M WISE, *An energy stable and convergent finite-difference scheme for the modified phase field crystal equation,* SIAM J. Numer. Anal., 49 (2011), pp. 945–969.

[33] S. M. WISE, C. WANG AND J. S. LOWENGRUB, *An energy-stable and convergent finite-difference scheme for the phase field crystal equation,* SIAM J. Numer. Anal., 47 (2009), pp. 2269–2288.

[34] C. XU AND T. TANG, *Stability analysis of large time-stepping methods for epitaxial growth models,* SIAM J. Numer. Anal., 44 (2006), pp. 1759–1779.

https://doi.org/10.4208/aamm.OA-2016-0024 Published online by Cambridge University Press