ENERGY INEQUALITIES IN COMPOSITIONAL SIMULATION[*]

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Abstract. We investigate the single-phase flow of a mixture composed of n components in a porous medium under the influence of pressure gradients, viscosity, and gravity. For the case of the single-phase flow (i.e. assuming that under given conditions the phase splitting will not occur), we derive an energy inequality for the continuous problem. Then, we propose the fully implicit discretization of the transport problem which uses a combination of the mixed-hybrid finite element method for the velocity approximation and the finite volume method for the discretization of the transport equations. We prove that the proposed numerical scheme fulfills a discrete version of the energy inequality. A numerical experiment reveals exponential decay of the Helmholtz free energy when a system approaches the equilibrium state.

Key words. compositional simulation, transport in porous media, energy inequalities, single-phase stability, Helmholtz free energy

AMS subject classifications. 35M33, 65M08, 65M12, 65M55, 76S05

1. Introduction. Mathematical models of transport of mixtures consisting of several chemical components in porous media are important in many disciplines with many industrial applications including energy industry, reservoir engineering, nuclear waste storage, and CO_2 sequestration. We focus on the models describing transport of n components in porous media ($n \geq 2$) which are usually referred to as the compositional models. In the literature models of different degrees of complexity have been formulated [1, 4, 5, 22]. Depending on the thermodynamic conditions, the components of the mixture can remain in a single phase or split among two or possibly more fluid phases; therefore, we can distinguish among the single-phase, two-phase, or general multi-phase models. In compositional modeling the phases are assumed to be compressible and the phase behavior is usually described using conventional equations of state (EOS). Different models can be derived depending on what processes (like diffusion or capillarity) are taken into account. Industrial applications motivated development of many numerical methods for the solution of these models. Although many papers have been treating the numerical solution of the compositional models in past 40 years, it seems that a rigorous mathematical/numerical analysis of these models and numerical schemes is still missing. Therefore, we present here a basic formulation of a single-phase compositional model for which we derive an energy inequality. This energy inequality has a direct physical interpretation which is basically the balance of the Helmholtz free energy of the system. Then, we propose a fully implicit numerical scheme in which the spatial discretization is performed using the finite-volume method for the transport equations together with the mixed-hybrid finite-element method for the velocity. We show that the numerical solution obeys a discrete version of the energy inequality. A numerical experiment is presented to

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show exponential decay of the Helmholtz free energy in a closed system approaching the steady state.

2. Model formulation. We will investigate the flow of n chemical components ($n \geq 2$) in a porous domain $\Omega \subset \mathbb{R}^d$ with porosity ϕ and permeability $\mathbf{k}$. Transport of mixture components is described by the following transport equations [2]

$$(2.1) \qquad \frac{\partial(\phi c_i)}{\partial t} + \nabla \cdot (c_i \mathbf{v}) = F_i, \qquad i \in \{1, 2, \ldots, n\},$$

where c_i denotes the molar concentration of component i, $\mathbf{v}$ is the velocity, and F_i describes the sources and sinks. The velocity is given by Darcy's law [6, 2]

$$(2.2) \qquad \mathbf{v} = -\frac{\mathbf{k}}{\eta}(\nabla p - \rho \mathbf{g}),$$

where η denotes the mixture dynamic viscosity, p is the pressure, $\rho = \sum_{i=1}^{n} c_i M_i$ is the mass density of the mixture, M_i is the molar weight of component i, and $\mathbf{g}$ is the vector of gravity acceleration. We assume that $\mathbf{k} \in L^{\infty}(\Omega)^{d \times d}$ is a symmetric second-order tensor satisfying the condition of uniform ellipticity, i.e. there exists a constant $k_{min} > 0$ such that for all vectors $\xi \in \mathbb{R}^d$ and for all $\mathbf{x} \in \Omega$ we have

$$(2.3) \qquad \sum_{i=1}^{d} \sum_{j=1}^{d} \mathbf{k}_{ij}(\mathbf{x}) \xi_i \xi_j \geq k_{min} \sum_{i=1}^{d} \xi_i^2.$$

Constitutive equations for mixture viscosity and pressure are given in the following form

$$(2.4) \qquad \eta = \eta(T, c_1, \ldots, c_n), \qquad p = p(T, c_1, \ldots, c_n).$$

In this work, we assume that the problem is isothermal, i.e. temperature is a known constant. The exact form of these equations is not important for the discussion here but for definiteness, one can assume that we are using the Peng-Robinson equation state [19] to describe pressure, and LBC-model [12, 20] for the viscosities. We assume that the mixture has limited compressibility, i.e. pressure is defined on the set of admissible concentrations $\mathcal{C}$ defined as

$$(2.5) \qquad \mathcal{C} = \{[c_1, \ldots, c_n] \in \mathbb{R}^n : \forall i \in \{1, 2, \ldots, n\} \ c_i \geq 0, \ \text{and} \ \sum_{i=1}^{n} c_i b_i < 1\},$$

where b_i are positive constants for $i \in \{1, 2, \ldots, n\}$. For $\sum_{i=1}^{n} c_i b_i \to 1-$, the pressure tends to $+\infty$. The viscosity η is bounded from above and below by some positive constants, i.e. there exist constants $\eta_{min} > 0$ and $\eta_{max} > 0$ such that

$$(2.6) \qquad \forall[c_1, \ldots, c_n] \in \mathcal{C} : \qquad \eta_{min} \leq \eta(T, c_1, \ldots, c_n) \leq \eta_{max}.$$

The only restrictive condition is that the flow remains in a single phase, i.e. under the simulated conditions no phase-splitting occurs. The system has to be completed by suitable initial and boundary conditions. The initial conditions read as

$$(2.7) \qquad c_i(x, 0) = c_i^0(x), \qquad \forall x \in \Omega, \qquad \forall i \in \{1, 2, \ldots, n\}.$$

To avoid technicalities, we assume that the reservoir boundary is impermeable, and thus

$$(2.8) \qquad \mathbf{v} \cdot \mathbf{n}|_{\partial \Omega} = 0,$$

where $\mathbf{n}$ denotes the unit vector of outer normal on $\partial \Omega$.

3. Single-phase stability criterion. As stated above, the principal assumption of this work is that no phase splitting occurs. In the opposite case, the model would have to be reformulated to account for multiple phases. In other words, for every set of concentrations $c_1, \ldots, c_n$ that may occur in Ω, the single phase has to be stable. Phase stability testing is a basic problem in chemical engineering literature. The commonly used formulation is based on the Gibbs criterion of phase stability in which one tests whether splitting a trial phase of some unknown composition from the initial phase at given temperature and pressure may decrease the total Gibbs free energy of the system [7, 14, 15, 16]. This formulation does not fit to our context because in compositional simulation pressure is not known a-priori. For our purposes, we use the formulation of phase stability in a system with prescribed temperature, volume, and moles (or equivalently with prescribed temperature and concentrations). Unlike the Gibbs formulation, the formulation of stability and phase equilibria for systems described by the VTN-variables is relatively new [17, 18, 9, 10]. Therefore, we summarize the basic formulation of phase stability criterion here.

It is well known from equilibrium thermodynamics that for a system with prescribed volume V, temperature T, and mole numbers $N_1, \ldots, N_n$, Helmholtz free energy A is a natural thermodynamic potential. Using the fact that for a given temperature T, A is a homogeneous function of degree one in V and $N_1, \ldots, N_n$, it is natural to define the Helmholtz free energy density $a = A/V$ as a function of the molar concentrations $c_i = N_i/V$. For a system in a single phase, the Helmholtz free energy density a^I reads as

$$(3.1) \qquad a^I = a(T, c_1, \ldots, c_n) = \sum_{i=1}^{n} c_i \mu_i(T, c_1, \ldots, c_n) - p(T, c_1, \ldots, c_n),$$

where μ_i denotes the chemical potential of component i. For physically reasonable pressure equations of state p, functions a and μ_i can always be found such that (3.1) and the following conditions hold

$$(3.2) \qquad\qquad\qquad\qquad \frac{\partial a}{\partial c_i} = \mu_i,$$

and

$$(3.3) \qquad\qquad \sum_{i=1}^{n} c_i \nabla \mu_i = \nabla p \qquad \text{(Gibbs-Duhem relation)}.$$

If a system is split into Π phases with volume fractions $S_\alpha \in (0, 1)$, and molar concentrations $c_{\alpha,i}$, where $\alpha \in \{1, 2, \ldots, \Pi\}$, and $i = 1, 2, \ldots, n$, the Helmholtz free energy density reads as

$$(3.4) \qquad\qquad a^\Pi = \sum_{\alpha=1}^{\Pi} S_\alpha a(T, c_{\alpha,1}, \ldots, c_{\alpha,n})$$

with obvious volume and mole-balance constraints

$$(3.5) \qquad\qquad\qquad\qquad \sum_{\alpha=1}^{\Pi} S_\alpha = 1,$$

$$(3.6) \qquad\qquad \sum_{\alpha=1}^{\Pi} c_{\alpha,i} S_\alpha = c_i, \qquad i \in \{1, 2, \ldots, n\}.$$

These conditions imply that the overall composition is a convex combination of phase molar concentrations. The single-phase is stable if for any non-trivial phase-split satisfying the constraints (3.5), $a^{II} > a^{I}$. In other words, for the given temperature T, a has to be a strictly convex function of $c_1, \ldots, c_n$. If this is the case, then splitting a small amount of a trial phase with concentrations $c_1', \ldots, c_n'$ from the initial phase with concentrations $c_1, \ldots, c_n$ cannot decrease the value of the Helmholtz energy density. The phase with concentrations $c_1, \ldots, c_n$ is thus stable if and only if for any $[c_1', \ldots, c_n'] \in \mathcal{C}$ the following inequality holds

$$\sum_{i=1}^{n} c_i'[\mu_i(T, c_1', \ldots, c_n') - \mu_i(T, c_1, \ldots, c_n)]$$

(3.7)
$$- [p(T, c_1', \ldots, c_n') - p(T, c_1, \ldots, c_n)] \geq 0.$$

This is a Helmholtzian version of the Gibbs tangent plane distance criterion for single-phase stability testing. We refer the reader to [18] for detailed derivation of this criterion.

4. Energy inequality for the continuous problem. By multiplying each equation in (2.1) by μ_i, summing over i, integrating over Ω, and using Green's theorem, we derive the following equality

$$(4.1) \qquad \frac{\mathrm{d}}{\mathrm{d}t} \int_{\Omega} \phi a(T, c_1, \ldots, c_n) - \int_{\Omega} \nabla p \cdot \mathbf{v} = \sum_{i=1}^{n} \int_{\Omega} F_i \mu_i.$$

In the derivation of the above equations, we have used (3.2) to treat the time-derivative term, (3.3) in the other term on the left side, and the boundary conditions (2.8).

There are several ways to rewrite the second term on the left side of (4.1). In the first version, we combine (2.2) with (4.1). Using (2.3) and (2.6), it is possible to derive the following energy inequality

$$(4.2) \qquad \frac{\mathrm{d}}{\mathrm{d}t} \int_{\Omega} \phi a(T, c_1, \ldots, c_n) + C_1 \|\nabla p - \rho \mathbf{g}\|_{L^2(\Omega)^d}^2 \leq \sum_{i=1}^{n} \int_{\Omega} F_i \mu_i + \int_{\Omega} \rho \mathbf{g} \cdot \mathbf{v},$$

where $C_1 = k_{min}/\eta_{max}$. This is the balance law for the total Helmholtz free energy $A = \int_{\Omega} \phi a(c_1, \ldots, c_n)$ of the system. For a closed system without sources and sinks and without gravity, A will decrease in time until the pressure gradients vanish, which is in line with the second law of thermodynamics. The other possibility is to rewrite Darcy's law (2.2) equivalently as

$$(4.3) \qquad \eta \mathbf{k}^{-1} \mathbf{v} + \nabla p = \rho \mathbf{g}$$

and derive

$$(4.4) \qquad -\int_{\Omega} \nabla p \cdot \mathbf{v} = \int_{\Omega} \eta \mathbf{v} \cdot \mathbf{k}^{-1} \mathbf{v} - \int_{\Omega} \rho \mathbf{g} \cdot \mathbf{v}$$

The resulting energy equality is now

$$(4.5) \qquad \frac{\mathrm{d}}{\mathrm{d}t} \int_{\Omega} \phi a(T, c_1, \ldots, c_n) + \|\sqrt{\eta} \mathbf{k}^{-1/2} \mathbf{v}\|_{L^2(\Omega)^d}^2 = \sum_{i=1}^{n} \int_{\Omega} F_i \mu_i + \int_{\Omega} \rho \mathbf{g} \cdot \mathbf{v}.$$

Using (2.3) and (2.6), we get the following energy inequality

$$(4.6) \qquad \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega \phi a(T, c_1, \ldots, c_n) + C_2 \|\mathbf{v}\|^2_{L^2(\Omega)^d} \leq \sum_{i=1}^n \int_\Omega F_i \mu_i + \int_\Omega \rho \mathbf{g} \cdot \mathbf{v},$$

where $C_2 = \eta_{min}/\|\mathbf{k}\|_{L^\infty(\Omega)^{d \times d}}$. This inequality is well suited for using mixed finite element to approximate $\mathbf{v}$.

5. Numerical scheme. We assume that the domain Ω is polygonal so that it can be covered by a conforming triangulation. Integrating the transport equations (2.1) over an arbitrary element K of the triangulation, approximating the concentrations by piecewise constant functions over the elements, and using the fully implicit time discretization, we derive the following fully-implicit finite volume scheme [21]

$$(5.1) \qquad \phi_K \frac{c_{i,K}^{k+1} - c_{i,K}^k}{\tau_k} |K| + \sum_{E \subset \partial K} c_{i,E}^{k+1} v_{K,E}^{k+1} = F_{i,K}^{k+1} |K|.$$

In this scheme, the subscript K denotes averages over the element K, while E denotes the values assigned at an element face, k is the time step index, τ_k is the time step in step k. The value $c_{i,E}^{k+1}$ is evaluated using the upwind value with respect to $v_{K,E}^{k+1}$, i.e.

$$(5.2) \qquad c_{i,E}^{k+1} = \begin{cases} c_{i,K}^{k+1} & \text{if } v_{K,E}^{k+1} \geq 0 \\ c_{i,K'}^{k+1} & \text{if } v_{K,E}^{k+1} < 0 \end{cases} \qquad \text{for } E = \partial K \cap \partial K'.$$

The velocity $\mathbf{v}$ on each element is approximated in the lowest-order Raviart-Thomas space $RT_0(K)$, i.e.

$$(5.3) \qquad \mathbf{v}|_K(\mathbf{x}, t^{k+1}) \approx \mathbf{v}_h|_K(\mathbf{x}, t^{k+1}) := \sum_{E \subset \partial K} v_{K,E}^{k+1} \mathbf{w}_{K,E}(\mathbf{x}),$$

where $\mathbf{w}_{K,E}$ denote the basis functions of the $RT_0(K)$ space. These functions can be chosen such that (see [8, 13])

$$(5.4) \qquad \nabla \cdot \mathbf{w}_{K,E} = \frac{1}{|K|}, \qquad \text{and} \qquad \int_F \mathbf{w}_{K,E} \cdot \mathbf{n}_{K,F} = \delta_{E,F},$$

where E and F are faces of an element K, $\mathbf{n}_{K,F}$ is the unit vector of outer normal with respect to element K on face F, and $\delta_{E,F}$ is the Kronecker symbol. The weak form of Darcy's law can be derived by multiplying (4.3) by a vector test function $\mathbf{w}$, integrating over an element K, and using Green's theorem. As a result, we get

$$(5.5) \qquad \int_K \mathbf{w} \cdot \eta \mathbf{k}^{-1} \mathbf{v} + \int_{\partial K} p \mathbf{w} \cdot \mathbf{n} - \int_K p \nabla \cdot \mathbf{w} = \int_K \rho \mathbf{w} \cdot \mathbf{g}.$$

Approximating $\mathbf{v}$ by (5.3), requiring (5.5) to hold for all test functions from the $RT_0(K)$ space, and using (5.4), we derive the following mixed-hybrid finite-element discretization of Darcy's law for each element K and an arbitrary face $E \subset \partial K$

$$(5.6) \qquad \sum_{F \subset \partial K} \mathbb{A}_{K,E,F}^{k+1} v_{K,F}^{k+1} + \widehat{p}_E^{k+1} - p_K^{k+1} = \mathbb{B}_{K,E}^{k+1},$$

where $\widehat{p}_F^{k+1}$ denotes the pressure trace (average pressure) on face F, p_K^{k+1} is the average pressure over the element K, both at time t^{k+1}, and

$$(5.7) \qquad \mathbb{A}_{K,E,F}^{k+1} = \eta_K^{k+1} \int_K \mathbf{w}_{K,E} \cdot \mathbf{k}^{-1} \mathbf{w}_{K,F}, \qquad \mathbb{B}_{K,E}^{k+1} = \rho_K^{k+1} \int_K \mathbf{w}_{K,E} \cdot \mathbf{g}.$$

The mixed-hybrid finite-element formulation is completed by the conditions

$$(5.8) \qquad \sum_{K:E \subset \partial K} v_{K,E}^{k+1} = 0,$$

which is written for each face of the triangulation. For internal faces, this prescribes continuity of the normal component of velocity. On boundary faces, the last equation reduces to the condition of impermeability, which is in line with condition (2.8). The viscosity, density, and pressure are approximated by element-wise constant functions η_h, ρ_h, and p_h defined for each $\mathbf{x} \in \Omega$ and $t \in (t^k, t^{k+1}\rangle$ as

$$(5.9)$$
$$\eta_h(\mathbf{x},t) = \sum_K \eta_K^{k+1} \chi_K(\mathbf{x}), \quad \rho_h(\mathbf{x},t) = \sum_K \rho_K^{k+1} \chi_K(\mathbf{x}), \quad p_h(\mathbf{x},t) = \sum_K p_K^{k+1} \chi_K(\mathbf{x}),$$

where χ_K is the indicator function of element K, and

$$(5.10)$$
$$\eta_K^{k+1} = \eta(T, c_{1,K}^{k+1}, \ldots, c_{n,K}^{k+1}), \quad \rho_K^{k+1} = \sum_{i=1}^n c_{i,K}^{k+1} M_i, \quad p_K^{k+1} = p(T, c_{1,K}^{k+1}, \ldots, c_{n,K}^{k+1}).$$

The system of equations (5.1), (5.2), (5.6), (5.8), and (5.10) represents a system of non-linear algebraic equations for unknown concentrations $c_{i,K}^{k+1}$ of all components on all elements, and traces of pressure $\widehat{p}_F^{k+1}$ on all element faces at the time level $k+1$ that can be solved when the concentrations $c_{i,K}^k$ at the old time level are specified. For $k = 0$, we use the initial conditions (2.7)

$$(5.11) \qquad c_{i,K}^0 = \frac{1}{|K|} \int_K c_i^0(\mathbf{x}) \, \mathrm{d}\mathbf{x}.$$

The system can be solved by the Newton method with line search. As the solution of this system is a special case of a two-phase compositional simulation that is described in detail in [21], we refer the reader to that paper.

6. Energy inequality for the discretized problem. The main goal of this paper is to show that the fully implicit scheme presented above fulfills a discrete version of the energy inequality (4.6). To this end, we multiply (5.1) by $\mu_{i,K}^{k+1} :=$ $\mu_i(T, c_{1,K}^{k+1}, \ldots, c_{n,K}^{k+1})$, and sum the result over all components $i \in \{1, 2, \ldots, n\}$ and all elements K in the triangulation.

First, we adjust the time-difference term by adding and subtracting suitable terms to get a balance for the Helmholtz free energy of the system, i.e.

$$\frac{1}{\tau_k}\sum_{i=1}^{n}\sum_{K}\phi_K|K|\mu_{i,K}^{k+1}(c_{i,K}^{k+1}-c_{i,K}^{k})=$$

$$\frac{1}{\tau_k}\sum_{K}\phi_K|K|\left[\underbrace{\left(\sum_{i=1}^{n}\mu_{i,K}^{k+1}c_{i,K}^{k+1}-p_K^{k+1}\right)}_{a_K^{k+1}:=a(T,c_{1,K}^{k+1},\ldots,c_{n,K}^{k+1})}-\underbrace{\left(\sum_{i=1}^{n}\mu_{i,K}^{k}c_{i,K}^{k}-p_K^{k}\right)}_{a_K^{k}:=a(T,c_{1,K}^{k},\ldots,c_{n,K}^{k})}\right.$$

$$(6.1)\qquad\left.+\underbrace{\sum_{i=1}^{n}c_{i,K}^{k}(\mu_{i,K}^{k}-\mu_{i,K}^{k+1})-(p_K^{k}-p_K^{k+1})}_{\geq 0}\right]\geq\frac{1}{\tau_k}\sum_{K}\phi_K|K|(a_K^{k+1}-a_K^{k}).$$

The third term in the square bracket is non-negative due to the phase stability criterion (3.7) applied to the set of concentrations $c_{1,K}^{k+1},\ldots,c_{n,K}^{k+1}$. In the final estimate, this term will be neglected.

Next, we rewrite the transport term as

$$\sum_{K}\sum_{E\subset\partial K}\sum_{i=1}^{n}c_{i,E}^{k+1}\mu_{i,K}^{k+1}v_{K,E}^{k+1}=\sum_{E}\sum_{K:E\subset\partial K}\sum_{i=1}^{n}c_{i,E}^{k+1}\mu_{i,K}^{k+1}v_{K,E}^{k+1}=$$

$$=\sum_{E\in\mathcal{E}_{int}}\sum_{K:E\subset\partial K}\sum_{i=1}^{n}c_{i,E_{up}}^{k+1}(\mu_{i,E_{up}}^{k+1}-\mu_{i,E_{down}}^{k+1})|v_{K,E}^{k+1}|=$$

$$=\sum_{E\in\mathcal{E}_{int}}\sum_{K:E\subset\partial K}\left[\underbrace{\sum_{i=1}^{n}c_{i,E_{up}}^{k+1}(\mu_{i,E_{up}}^{k+1}-\mu_{i,E_{down}}^{k+1})-(p_{E_{up}}^{k+1}-p_{E_{down}}^{k+1})}_{\geq 0}\right]|v_{K,E}^{k+1}|+$$

$$+\sum_{E\in\mathcal{E}_{int}}\sum_{K:E\subset\partial K}(p_{E_{up}}^{k+1}-p_{E_{down}}^{k+1})|v_{K,E}^{k+1}|$$

$$\geq\sum_{E\in\mathcal{E}_{int}}\sum_{K:E\subset\partial K}(p_{E_{up}}^{k+1}-p_{E_{down}}^{k+1})|v_{K,E}^{k+1}|=\sum_{K}\sum_{E\subset\partial K}(p_K^{k+1}-\hat{p}_E^{k+1})v_{K,E}^{k+1}$$

$$=\sum_{K}\sum_{E\subset\partial K}\sum_{F\subset\partial K}\mathbb{A}_{K,E,F}v_{K,E}^{k+1}v_{K,F}^{k+1}-\sum_{K}\sum_{E\subset\partial K}\mathbb{B}_{K,E}^{k+1}v_{K,E}^{k+1}$$

$$(6.2)\qquad=\int_{\Omega}\mathbf{v}_h\eta_h\mathbf{k}^{-1}\mathbf{v}_h-\int_{\Omega}\rho_h\mathbf{v}_h\cdot\mathbf{g}=\|\sqrt{\eta_h}\mathbf{k}^{-1/2}\mathbf{v}_h\|_{L^2(\Omega)^d}^2-\int_{\Omega}\rho_h\mathbf{v}_h\cdot\mathbf{g}.$$

In the derivation of this inequality, we have first interchanged the order of summation. Then we have used the fact that each internal face E is surrounded by exactly two neighboring elements, the one in the upwind direction with respect to $v_{K,E}^{k+1}$ is denoted E_{up}, while the other one is denoted E_{down}. Due to the zero Neumann boundary conditions, it is sufficient to consider only summation over the internal faces. Then, suitable pressure terms are added and subtracted. The indicated term is non-negative due to the phase-stability criterion (3.7). In the next development, this term is neglected. Introducing pressure traces into the remaining term allows us to change the order of summation once again and using (5.6), we get the desired result.
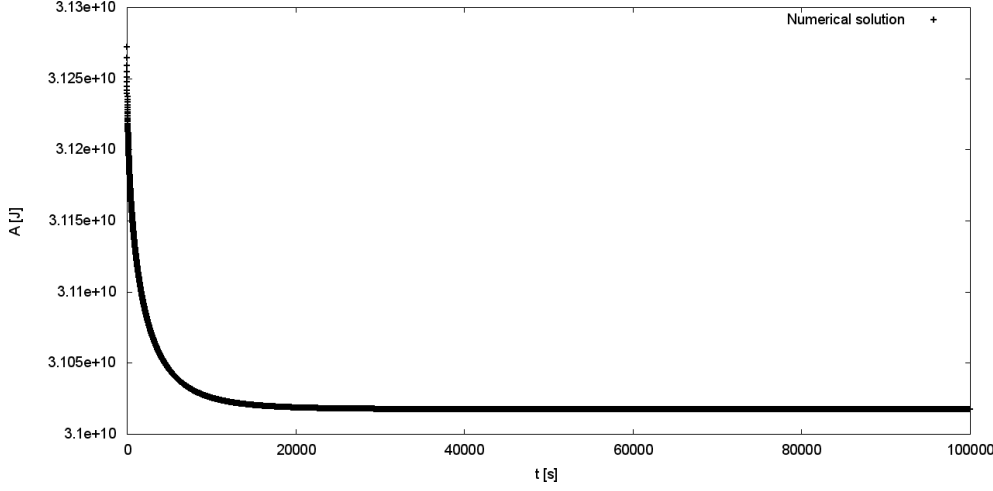
FIG. 7.1. *The Helmholtz free energy dependent on time.*

The last term in equation (5.1) is treated in a straightforward manner. Combining all the estimates, we get the following discrete energy inequality

(6.3)
$$\frac{1}{\tau_k} \sum_K \phi_K |K|(a_K^{k+1} - a_K^k) + C_2 \|\mathbf{v}_h\|_{L^2(\Omega)^d}^2 \leq \sum_K \sum_{i=1}^n F_{i,K}^{k+1} |K| \mu_{i,K}^{k+1} + \int_\Omega \rho_h \mathbf{v}_h \cdot \mathbf{g},$$

which is a discrete version of (4.6).

7. Long-time behavior of the Helmholtz free energy. In this part, we observe behavior of the Helmholtz free energy in a closed system consisting of a 2-component mixture of methane ($i = 1$) and propane ($i = 2$) without gravity and sources or sinks at temperature $397\,\text{K}$. The reservoir of $50 \times 50\,\text{m}^2$ has porosity $\phi = 0.2$ and isotropic permeability $\mathbf{k} = k\mathbf{I}$, where $k = 9.87 \cdot 10^{-15}\,\text{m}^2$. The Peng-Robinson equation of state [19] and the LBC-model for viscosity [12] are used with parameters given in Table 1 of [21]. The initial concentrations are

(7.1) $c_1^0(x) = 1600$ for $x \in \langle 15, 35 \rangle \times \langle 15, 35 \rangle$,

(7.2) $c_1^0(x) = 0$ for $x \in \langle 0, 50 \rangle \times \langle 0, 50 \rangle \setminus \langle 15, 35 \rangle \times \langle 15, 35 \rangle$,

(7.3) $c_2^0(x) = 2700$ for $x \in \langle 15, 35 \rangle \times \langle 15, 35 \rangle$,

(7.4) $c_2^0(x) = 2735.42$ for $x \in \langle 0, 50 \rangle \times \langle 0, 50 \rangle \setminus \langle 15, 35 \rangle \times \langle 15, 35 \rangle$,

where the concentrations are in $\text{mol}\,\text{m}^{-3}$ and the intervals in meters. The Helmholtz free energy computed for a simulation on a triangular mesh of $2 \cdot 40 \times 40$ triangles at different times and constant time step $5\,\text{s}$ is depicted in Fig. 7.1. As can be seen, the Helmholtz free energy decreases as the simulation evolves in time and since $40000\,\text{s}$ is almost constant.

To investigate the decrease of A trend in Fig. 7.1, we are inspired by [3], where the large-time asymptotic analysis of solutions of degenerate scalar parabolic convection-diffusion equations and certain systems of parabolic equations is carried out. For the scalar parabolic equation an exponential time decay of the solution to a steady state
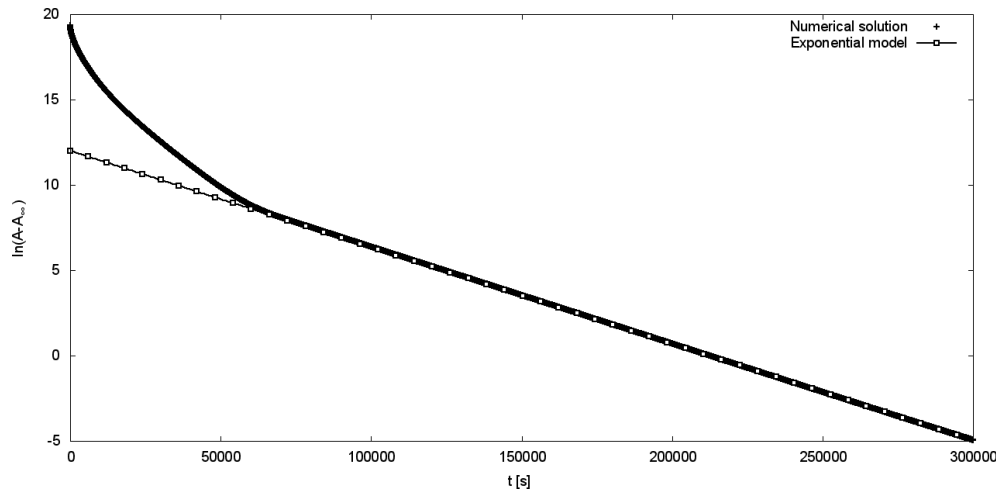
FIG. 7.2. *Comparison of the numerical solution with exponential model* (7.5).

is derived, while for the parabolic systems the decay is only algebraic. Our system of equations is not parabolic; therefore, it does not satisfy assumptions of paper [3]. Nevertheless, we have tried to fit both models to the numerical results and have found out that the exponential model can describe the decrease of A for larger times. Considering a general exponential model of the following form

$$(7.5) \qquad\qquad A(t) = A_\infty + \alpha e^{-\lambda t},$$

the parameters α and λ can be adjusted and A_∞ is the energy at some large-enough time. To specify the parameters, we can compute the natural logarithm of $A - A_\infty$ and rewrite (7.5) as

$$(7.6) \qquad\qquad \ln(A(t) - A_\infty) = \ln \alpha - \lambda t.$$

The numerical results and exponential model (7.6) with $\alpha = 162755$, $\lambda = 5.65 \cdot 10^{-5}$, and A_∞ taken from the numerical data at $t = 555000\,\mathrm{s}$ are plotted in Fig. 7.2. We can see an obvious linear decrease of the numerical solution starting at about $t = 70000\,\mathrm{s}$ and matching with the model. The linear decrease of the logarithm of $A - A_\infty$ indicates that A decreases exponentially according to (7.5) for larger times.

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