

Subcritical to Supercritical Transition of Fuel Mixtures in High Temperature and Pressure Environment

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1 Introduction

Supercritical evaporation exists in liquid rockets, diesel engines, and other practical engines that operate at high temperature and pressure conditions. Important insights on supercritical behaviors, as well as limitations of current theoretical modeling and numerical simulations are reviewed in [1-3]. Although there exists a good knowledge for the classical two-phase atomization regime and the supercritical one-phase mixing regime, the transition from the former to the latter is less understood, especially for fuel mixtures. Under what conditions the evaporation and mixing processes are subcritical in nature and under what conditions they become supercritical is one of the key questions for a multi-component fuel.

There are inconsistent answers to this question between experiments and modeling/simulations in the literature. One of the possible reasons is that when the mixture at the interface is approaching its critical mixing state, the thermodynamic and transport properties become very sensitive to small perturbations and are hard to model. In this work, Molecular dynamics (MD) simulation has been chosen to understand when and how a transition from classical evaporation to supercritical mixing takes place, when a cold liquid fuel is placed in a hot high-pressure environment. The biggest advantage of MD simulations is that no assumptions are made about the processes or physics to be investigated. The only input is a potential model that describes intermolecular interaction. For example, Equation of State (EOS), mixing rules, models for thermodynamic and transport properties are not required by MD, which have large uncertainties at high pressures, especially for complex mixtures near the critical state [4]. Thermodynamic and transport properties are results of MD simulations, rather than assumptions. Equilibrium at interface is not assumed.

The present paper investigates evaporation of binary hydrocarbon mixtures into nitrogen environment under various ambient pressures and temperatures via MD simulations. The emphasis is to understand at what conditions, when and how a transition from subcritical to supercritical takes place. After introducing the method of molecular dynamics simulations, the paper describes the main features of subcritical evaporation, supercritical evaporation for the fuel mixtures.

2 MD Models and Simulation Configuration

The united-atom (UA) model has been used to model the hydrocarbons, as it offers better computational efficiency by treating each CH_3 and CH_2 as one site. In particular, the SKS model by Smit et al. [5] has been used for the alkanes. The two-center L-J model Rivera 2002 [6] is used for modeling of nitrogen, which is the ambient in most of the test cases.

Figure 1 shows the rectangular simulation box with period boundary conditions at all sides. The box has a fixed area of cross section and the center of the box is filled with fuel mixture, which is surrounded by ambient gas on two sides. The liquid has an initial temperature of 363 K. The ambient temperature and pressure of nitrogen are varied to understand their effects on evaporation. NVT ensembles – constant atom number (N), constant volume (V), and constant temperature (T) – is used for the ambient gas nitrogen.

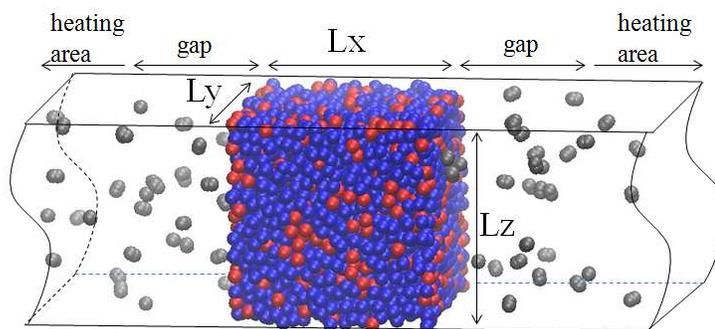


Figure 1. Configuration of the simulation box. Atoms: red (CH_3), blue (CH_2), grey (ambient)

The number of ambient gas molecules in the simulation box must be large enough so that the pressure increase due to the addition of vaporized fuel molecules into the ambient is negligible. Therefore, constant pressure of the ambient gas can be assumed during the evaporation. An atom ratio (ambient to fuel) of 5 is chosen for all simulations [7]. The final length of the simulation box becomes a function of the ambient temperature, pressure and the number of molecules. The ambient gas remains at a constant temperature and pressure during a simulation. It provides heat to the liquid for vaporization and because of that, the velocities of the molecules in this region are rescaled constantly to ensure a constant temperature. A gap between the heating area with a size of about 50σ (σ is nitrogen molecule diameter) is required to minimize the effect of the heating boundary on the liquid-surface dynamics, as illustrated in Fig. 1. Before modeling evaporation, the initial configurations for the liquid and the ambient gas are equilibrated separately and then combined by placing the equilibrated liquid in an equilibrated environment of nitrogen. The equilibrated liquid is prepared by equilibrium with its own vapor at the initial liquid temperature using NVT ensemble.

3 Results and Discussion

3.1 Subcritical Evaporation

The main purpose of looking into subcritical evaporation is to provide a baseline for understanding supercritical behaviors. For the example discussed below, the fuel mixture comprises of 360 n-heptane and 360 n-dodecane molecules. Ambient temperature and pressure are 550 K and 1 MPa, respectively. Note that the critical temperature of n-heptane and n-dodecane are 540 and 658 K, critical pressure are 2.736 and 1.817 MPa, respectively. The liquid fuel has an initial temperature of 363 K.

Fig. 2(a) shows the time history of number of molecules in a fixed boundary of $X = [-6.8, 6.8]$ nm and counting the flux of alkane molecules across that boundary. The choice of ± 6.8 nm is for convenience because it corresponds to the initial location of the interface right after heat-up, but before steady-state evaporation. The number of n-heptane molecules decreases faster than n-dodecane. Fig. 2(b) shows the surface tension development. The surface tension decreases during the heat-up stage because the temperature of the liquid core increases. Surface tension exists for the whole evaporation process.

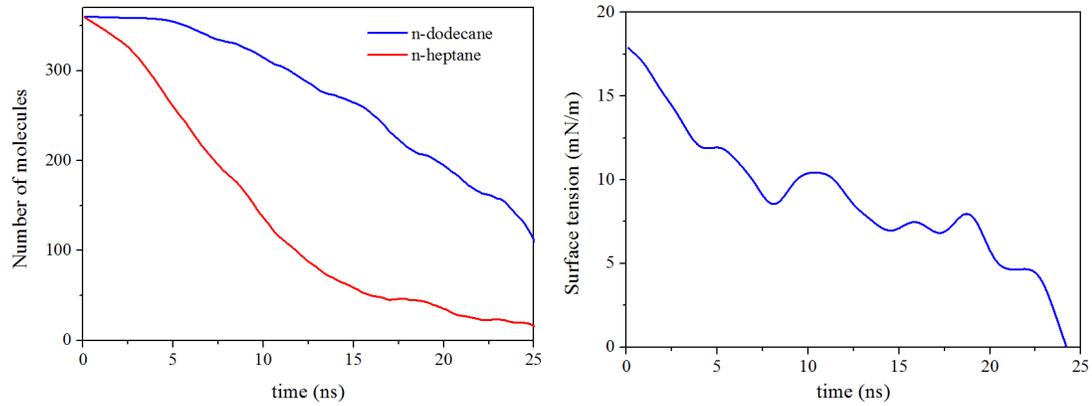


Figure 2. Left: (a) time history of number of fuel molecules in liquid core; right: (b) time history of surface tension

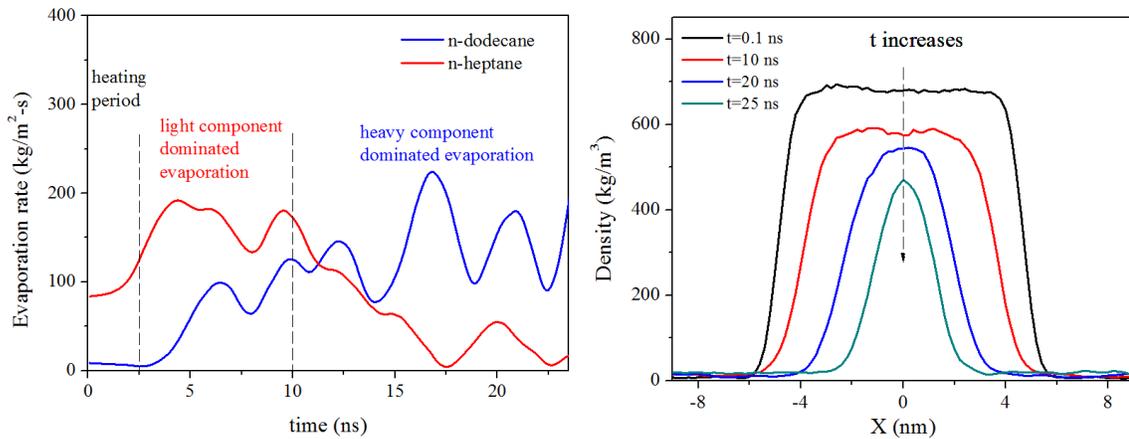


Figure 3. Left: (a) fuel evaporation rate; right: (b) time history of fuel density in the liquid core

Fig. 3(a) shows evaporation rate. After the heat-up period, the evaporation is dominated by n-heptane, and then move to n-dodecane. The majority of lighter species evaporates first, and then heavier species. This is consistent with the numerical simulation observations at subcritical conditions [8]. Fig. 3(b) shows the mixture density profiles along X directions. The density in the liquid core decreases gradually because the liquid fuel is being heated up by the ambient. However, the liquid always exists during the whole

evaporation process. The interface between liquid core and ambient is always distinguishable as liquid core regresses.

3.2 Supercritical Evaporation

In this case, n-heptane and n-dodecane (molecule ratio: 360:360) is vaporizing into nitrogen with an ambient temperature of 1316 K and pressure of 20 MPa. When the liquid fuel is exposed to an ambient temperature and pressure greater than the critical point of the liquid fuel, the liquid first undergoes subcritical evaporation and then passes a transition point to reach supercritical evaporation where surface tension vanishes and the interface disappears and the evaporation becomes a diffusion-controlled one-phase mixing.

Fig. 4(a) shows that the number of both n-heptane and n-dodecane molecules decreases rapidly while n-heptane is slightly faster than n-dodecane. Fig. 4(b) indicates that the surface tension decreases rapidly and eventually disappears at $t = 1$ ns. This means that the evaporation transits from subcritical to supercritical at this point. Fig. 5(a) shows the evaporation rates for both components. The evaporation rate of n-heptane always decreases from the beginning. However for n-dodecane, the rate first increases and then decreases while reaching the maximum at the transition point. In the supercritical stage, the evaporation rate decreases, mainly because the density gradient between the liquid core and the ambient decreases over time. When evaporation enters a diffusion-dominated regime, the rate of mixing would depend on the diffusion coefficient, mass fraction gradient, and temperature gradient. In this situation, temperature gradient vanishes more quickly than concentration gradient will, so thermal diffusion effect is less prominent. Fig. 5(b) shows the density spatial distribution in the liquid center decreases rapidly which is different from subcritical case. This means that the liquid core disappears very fast and the evaporation enters diffusion controlled evaporation.

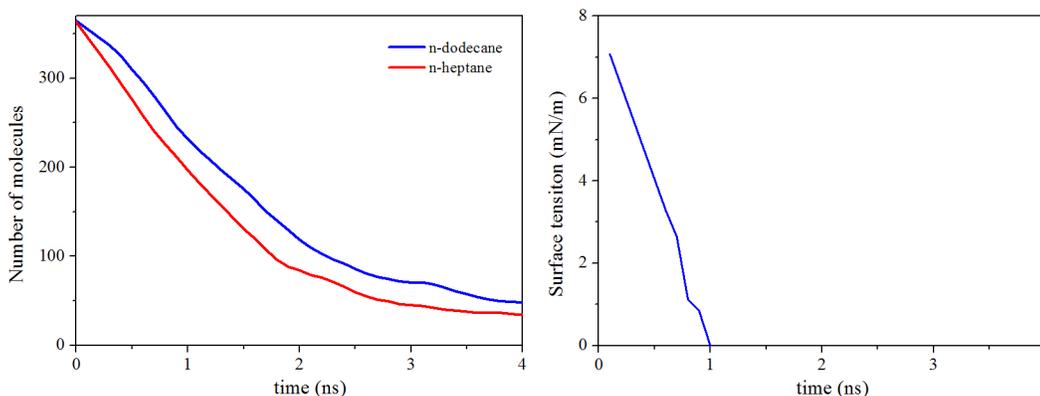


Figure 4. Left: (a) time history of number of fuel molecules in liquid core; right: (b) time history of surface tension

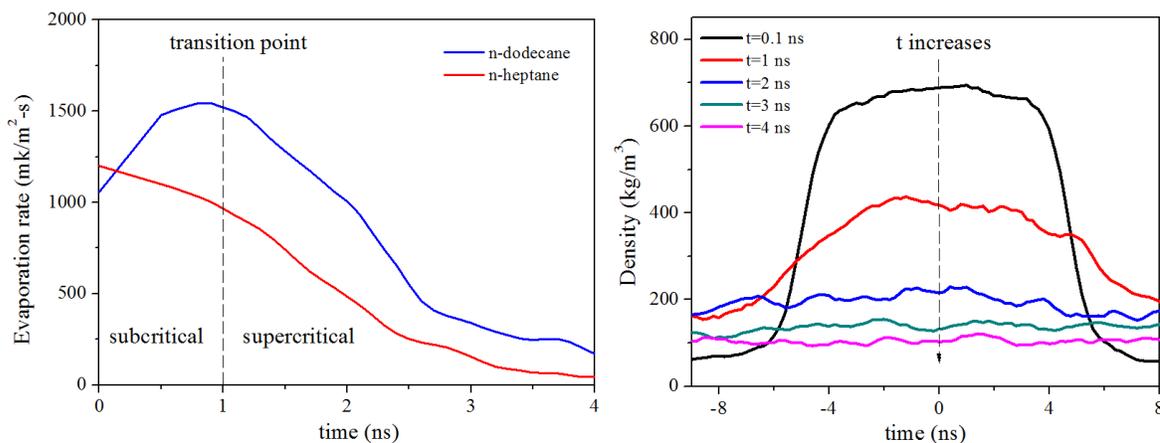


Figure 5. Left: (a) fuel evaporation rate; right: (b) time history of fuel density in the liquid core

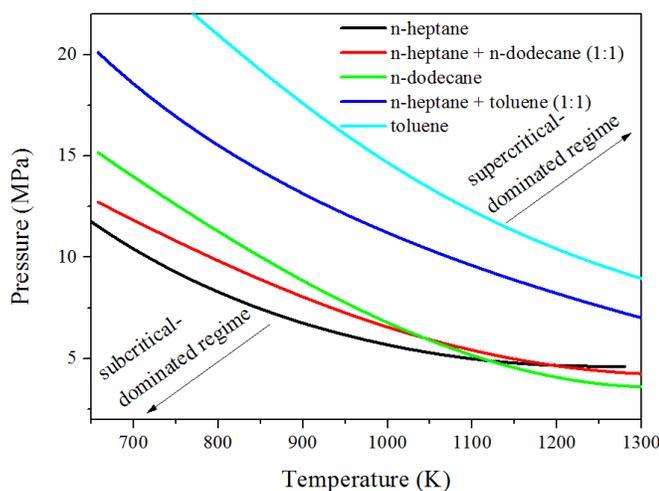


Figure 6. Comparison of transition regimes of various single and multi-component fuels

4 Conclusion

MD simulations have been conducted in this study to understand subcritical and supercritical evaporations of alkane mixtures and also the transition from subcritical to supercritical. At subcritical conditions, a distinctive interface always exists that separates the liquid core and the ambient gas. During the heat-up period, the liquid core swells slightly and then regresses. For fuel mixtures, the lighter component dominates the evaporation first and then heavier component control the evaporation process. On the contrary, under supercritical conditions the mole fraction of n-dodecane in the liquid core decreases rapidly due to significant nitrogen dissolution. At some point the interface disappears and surface tension vanishes, indicating a transition from classical subcritical two-phase evaporation to diffusion-controlled one-phase supercritical mixing. The temperature of n-dodecane and nitrogen mixture continues to increase and eventually exceeds the critical mixing temperature. The evaporation rate of lighter component decreases while heavier component increases and then decrease.

References

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