Abstract: For a multi-component hydrocarbon mixture under supercritical conditions, the mechanism and
criterion for the transition of the dominant mixing mode from evaporation to diffusion are not well
established. In this paper, phase transition processes of three-component hydrocarbon fuel (5.3 wt%
isoctane, 25.8 wt% n-dodecane and 68.9 wt% n-hexadecane) droplets in sub- and supercritical nitrogen
environments were studied using molecular dynamics, in comparison with those of single-component n-
hexadecane droplets. The initial diameters of the droplets were 25.5 nm (three-component) and 26.5 nm
(single-component), respectively. Based on the quantitative Voronoi tessellation, a new criterion, which
was a combination of two dimensionless critical values of $H_c = 0.85$ and $W_c = 0.35$, was proposed to
determine the transition of the dominant mixing mode from evaporation to diffusion during fuel-ambient
gas mixing. The droplet evaporation lifetime, initial heat-up time and evaporation rate constant were
analyzed for all simulation cases. Effects of ambient temperature and ambient pressure on the dominant
mixing mode transition were discussed. Results indicated that when the ambient pressure ranged from 2
MPa to 10 MPa and the ambient temperature ranged from 750 K to 1200 K, the density difference between
the vapor phase and the liquid phase decreased gradually with increasing ambient pressure or decreasing
ambient temperature. In the meantime, the dominant mixing mode gradually transitioned from evaporation
to diffusion. A new parameter, the vapor-liquid equal probability time $t_{pv} = pl$, was proposed to evaluate the phase transition speed of hydrocarbon fuels. Increasing the ambient pressure did not necessarily promote the occurrence of phase transition, while increasing ambient temperature accelerated the phase transition monotonically. The dominant mixing mode maps on the P-T diagram for evaporation systems of pure n-hexadecane droplets and three-component fuel droplets were presented. The addition of light components increased the minimum pressure of the mixing zone dominated by diffusion. A major finding was that under a certain ambient pressure, the ambient temperature where the fuel could undergo supercritical transition in ambient gas had not only a minimum but also a maximum.

Keywords: multi-component fuels; droplet evaporation; supercritical conditions; mixing transition criterion; phase transition; molecular dynamics

1. Introduction

With the current energy system for the world economy, fossil fuels, such as hydrocarbons, are widely used [1]. The large amounts of emissions of greenhouse gases, such as CO$_2$ [2-4] and nitrogen oxides [5], have made the problem of global warming more and more severe [6-10], and the issue of saving energy has also attracted people's attention [9, 11]. To solve the energy crisis, improving the utilization efficiency of fossil fuels is essential [12], in addition to exploring alternative and renewable energies [5, 13-17]. Achieving combustion of hydrocarbon fuels under high-pressure and high-temperature conditions is an important measure to improve the efficiency and reduce emissions of power devices such as internal combustion engines (ICEs) [18]. The actual hydrocarbon fuel used by engines is a complex mixture containing hundreds of components [19, 20]. The evaporation process is a necessary step before the fuel
is burned, and has a significant impact on the combustion and emission formation processes [21-24].

Under low-pressure conditions, a sharp interface exists between ambient gases and liquid fuels because of the surface tension, where the classic two-phase evaporation dominates the fuel-ambient gas mixing process [25]. However, when the ambient condition in the combustion chamber exceeds the critical point of the injected fuel, the fuel droplet surface will undergo a transition from the liquid state to a supercritical state [18, 26]. Under this circumstance, the surface tension gradually decreases, resulting in the disappearance of the vapor-liquid interface [27-29]. Dahms et al. [25] have reported that the one-phase diffusion would dominate the process of fuel-ambient gas mixing instead of the classical two-phase evaporation, due to the lack of intermolecular forces.

Different aspects of the evaporation of droplets under supercritical conditions have been reviewed [30-33]. Nonetheless, a reliable criterion to decide the dominant mixing mode in the mixing process of fuel-ambient gas, which is a fundamental question, has not been well established. Several theories and methods used to determine whether the transition occurs or not have been proposed [34]. Among these, the Knudsen number criterion [27] and the critical trajectory theory [35] are the most popular ones. The first is based on the comparison between the mean free path of the molecules and the thickness of the vapor-liquid interface. However, the theoretical analyses based on the Knudsen number are made under the assumption of steady-state, which cannot accurately depict the dynamic transition process [36]. In the critical trajectory theory, the transition process is evaluated through comparison between the apex of vapor-liquid equilibrium (VLE) curves of the binary system and temperature-fuel fraction profiles of the evaporation system. This method is applicable only if the critical point of the mixture is known, which itself is another difficult unsolved problem, especially for multi-component fuels [37-40]. Falgout et al. [38] concluded that the critical property of a mixture might be completely different from that of its individual component, so it was almost impossible to estimate the VLE curves of nitrogen and the mixed
fuel accurately in their study. It is reasonable to draw the conclusion that any scheme based on calculation of the critical point is not applicable for mixtures of multi-component fuels and ambient gases.

Remarkable differences are present between the evaporation process of a droplet in subcritical conditions and that in supercritical conditions [41]. It is inappropriate to apply the traditional droplet evaporation theory to supercritical conditions [26]. In addition, due to the inherent deficiency of CFD [33, 36], it is difficult to accurately calculate the critical properties of mixtures during the transition process.

In terms of experiments, the droplet evaporation process is usually studied by a droplet hanging test [22, 42-44]. However, due to the limitations of current experimental means, only macroscopic physical quantities can be obtained through experiments, whose macroscopic nature leads to its failure to analyze the supercritical transition behavior of the droplet in detail [26]. Molecular dynamics (MD) has been increasingly applied to the study of droplet evaporation, avoiding the problems encountered in CFD simulations and experiments [26, 45-47]. In MD simulations, no assumptions are required about the physical processes to be simulated except potential models of intermolecular forces, and all thermophysical properties are obtained by statistical methods. Consequently, the correct formulation and application of force potential functions is crucial [48]. MD simulations can be performed to study the detailed physical process under high pressures and/or high temperatures at atomic scales, thus resolving the vapor-liquid interface thickness [47]. As a result, some researchers have studied the scale effect on fuel evaporation using MD simulations [26, 36]. On the other hand, such simulations are computationally very expensive and require supercomputing resources.

Most of the existing MD simulations of droplet evaporation are focused on subcritical conditions [49-56] while studies under supercritical conditions are few and far inbetween [26, 57, 58], especially for complex hydrocarbon molecules [26]. This is because in the early days, it was difficult to simulate large molecular systems due to the lack of force potential functions suitable for complex molecules and the lack of sufficient computing power. Long et al. [56] studied the evaporation processes of argon droplets in
subcritical autogenous vapours, which did not involve supercritical cases. Kaltz et al. [58] found that when oxygen droplets evaporated in hydrogen or helium environments, the critical pressure for transition was much higher than that of pure oxygen. With the development of force potential functions and improvement in computing power, it is now feasible to simulate the supercritical transition of complex hydrocarbon fuels. MD simulations of the evaporation process of single-component hydrocarbon fuels under supercritical conditions have been performed in recent years [26, 47]. Mo et al. [36] studied the evaporation process of three types of single-component n-alkane liquid films in sub- and supercritical nitrogen environments. They concluded that the transition occurred earlier with increasing ambient temperature or ambient pressure. Xiao et al. [26] investigated the evaporation processes of n-dodecane droplets in sub- and supercritical nitrogen environments, and obtained a regime diagram for sub- and supercritical evaporation. However, these studies were focused on single-component fuels, leaving questions unanswered about realistic fuels for engines.

So far, there have been very limited MD simulations of the evaporation process of multi-component fuels due to the complexities in modeling and analysis. Chakraborty et al. [34] investigated supercritical transitions of two-component fuel liquid films and discussed the changes in surface tension. Zhang et al. [59] studied the evaporation process of a two-component n-alkane fuel film under sub- and supercritical conditions and focused on the non-VLE effects under supercritical conditions. On the other hand, surrogate fuels with multi-components (>2) have been shown to have a better match for the actual fuel [60]. The evaporation process of multi-component droplets is much more complex when supercritical transition is involved [61]. Establishing the MD approach for multi-component fuel evaporation to study the VLE and supercritical transition process has important theoretical and practical significances [62, 63].

As has been reported [64], to have evaporation behaviors similar to those of real fuels, a surrogate fuel should have at least three components. In this paper, the evaporation processes of a three-component fuel droplet and a single-component (n-hexadecane) droplet under sub- and supercritical conditions were
investigated using MD simulations. The three-component fuel was composed of iso-octane (5.3 wt%), n-dodecane (25.8 wt%) and n-hexadecane (68.9 wt%). This fuel was very close to Fuel C which consisted of iso-octane (10 wt%), n-dodecane (30 wt%) and n-hexadecane (60 wt%) [65]. Fuel C had a similar distillation curve to Phillips #2 reference diesel fuel (DF2), as has been reported by Myong et al. [65]. The distillation curves of Fuel C and DF2 are shown in Fig. 1. Therefore, it was expected to have similar evaporation characteristics to those of commercial diesel fuels [65]. The n-hexadecane, the most representative single-component surrogate fuel for diesel [66], was also studied to provide comparisons.

In recent years, researchers have found that the supercritical fluid region can still be divided into the gas-like phase region and the liquid-like phase region [67, 68], demonstrated in recent experiments [69]. In this paper, the local density distribution of the hydrocarbon fuel in evaporation systems was obtained from the Voronoi tessellation [70]. The objective of this paper is to investigate phase transition of multi-component hydrocarbon fuel droplets using MD simulations. A new criterion was proposed to determine whether the transition of the dominant mixing mode occurred or not for multi-component hydrocarbon fuels in supercritical conditions. A new parameter was proposed to estimate the phase transition speed of a hydrocarbon fuel. Effects of ambient temperature and ambient pressure on the mode transition were discussed. Moreover, effects of ambient conditions on phase transition speeds of different components were investigated. The dominant mixing mode maps on the P-T diagram for evaporation systems of pure n-hexadecane droplets and three-component fuel droplets were presented. Atomic-level insights into the differences between the mixing modes were obtained via the molecular distributions of both single-component and three-component fuel droplets.
2. Research methods

2.1. Interatomic potentials

The MD simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [71], an open source MD code. In MD simulations, the molecular motion is calculated based on Newton's laws of motion. The calculation of intermolecular interaction forces is based on the potential model, whose choice is crucial [26]. Among the potential models for complex long-chain alkanes like n-dodecane, the United Atom Model (UAM) has been widely used because of its good balance between computational efficiency and precision [47]. The C-H bonds in complex alkanes are much longer and more powerful than the C-C bonds, which becomes the basis of the UAM [47]. An atom group, such as methyl (CH$_3$) or methylene (CH$_2$), is treated as a pseudo-atom [72]. As a result, alkane molecules are simplified into straight or branched molecules consisting of several associated atoms, as shown in Fig. 2.
Fig. 2. The schematic diagram of the United Atom Model: (a) Isooctane, (b) n-Dodecane and (c) n-Hexadecane.

The Transferable Potentials for Phase Equilibria United Atom (TraPPE-UA) Model [73-75], which were shown to accurately produce fluid phase data of alkanes, were used to describe the interactions of fuel molecules. The non-bonded interaction between pseudo-atoms that are separated by more than three bonds or belong to two different molecules is described by the 12-6 Lennard-Jones potential:

\[ U_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]  

where \( \sigma_{ij} \) is the size parameter, \( \varepsilon_{ij} \) is the energy parameter, and \( r_{ij} \) is the distance between the two interacting pseudo-atoms. The LJ parameters for identical pseudo-atoms are listed in Table 1 [74], where \( k_B \) is the Boltzmann constant. The LJ parameters for all unlike atoms are determined by the standard Lorentz-Berthelot combining rules [76], \( \varepsilon_{ij} = \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}} \) and \( \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \).

<table>
<thead>
<tr>
<th>pseudo-atom</th>
<th>( \varepsilon/k_B ) [K]</th>
<th>( \sigma ) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>98</td>
<td>3.75</td>
</tr>
<tr>
<td>CH₂</td>
<td>46</td>
<td>3.95</td>
</tr>
<tr>
<td>CH</td>
<td>10</td>
<td>4.68</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>6.4</td>
</tr>
</tbody>
</table>
In the classical TraPPE-UA model, bond lengths between two connected pseudo-atoms are fixed. However, LAMMPS does not provide an algorithm for fixing the bond length of a long-chain molecule like n-dodecane or n-hexadecane. Therefore, the bond-stretching interaction is described by a harmonic potential with a large force constant:

\[ U_s(r) = \frac{1}{2} k_b (r - r_0)^2 \]  

(2)

where \( r_0 = 1.54 \, \text{Å} \), and \( k_b/k_B = 96508 \, K \cdot \text{Å}^{-2} \), which are taken from the NERD model [77]. Previous study has shown that this modification would not induce any difference in the simulation results of alkanes [36]. Bond angle bending is also described by a harmonic potential:

\[ U_b(\theta) = \frac{1}{2} k_{\theta} (\theta - \theta_0)^2 \]  

(3)

The motion of a dihedral angle, which is the interaction between two pseudo-atoms separated by three bonds, is described by the OPLS (optimized potentials for liquid simulations) torsion potential [78]:

\[ U_t(\phi) = c_0 + c_1 [1 + \cos \phi] + c_2 [1 - \cos 2\phi] + c_3 [1 + \cos 3\phi] \]  

(4)

The bond bending and torsion parameters for alkanes are listed in Table 2 [74].

<table>
<thead>
<tr>
<th>Bond bending</th>
<th>( \theta_0 ) [°]</th>
<th>( k_{\theta}/k_B ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_x)-(CH(_2))-CH(_y)</td>
<td>114</td>
<td>62500</td>
</tr>
<tr>
<td>CH(_x)-(CH)-CH(_y)</td>
<td>112</td>
<td>62500</td>
</tr>
<tr>
<td>CH(_x)-(C)-CH(_y)</td>
<td>109.47</td>
<td>62500</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond torsion</th>
<th>( c_0/k_B ) [K]</th>
<th>( c_1/k_B ) [K]</th>
<th>( c_2/k_B ) [K]</th>
<th>( c_3/k_B ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_x)-(CH(_2))-CH(_y) (n-Alkanes)</td>
<td>0</td>
<td>335.03</td>
<td>-68.19</td>
<td>791.32</td>
</tr>
<tr>
<td>CH(_x)-(CH(_2))-CH(_y) (branched alkanes)</td>
<td>-251.06</td>
<td>428.73</td>
<td>-111.85</td>
<td>441.27</td>
</tr>
<tr>
<td>CH(_x)-(CH(_2))-C-CH(_y) (branched alkanes)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>461.29</td>
</tr>
</tbody>
</table>

To simplify calculations, each nitrogen molecule is regarded as two atoms connected by a fixed bond length according to the SHAKE algorithm [79]. The interactions between the non-
bonded atoms are described by the potential function of 12-6 Lennard Jones. The size parameter and the energy parameter are as follows: \( \sigma_N = 0.332 \text{ nm} \) and \( \varepsilon_N = 0.3026 \text{ kJ/mol} \).

The bond length is fixed at 0.1106 nm.

2.2. Properties of fuels

Unlike lighter n-alkanes, n-hexadecane is prone to pyrolysis under high temperatures. Only a few VLE data of n-hexadecane under the conditions of high-temperature were published. Lin et al. [80] obtained the VLE data of the N₂-n-hexadecane (n-C₁₆H₃₄) system by the flow method. To estimate the VLE data of the N₂–n-C₁₆H₃₄ binary system, theoretical calculations based on the combination of a real-fluid equation of state (EoS) and the VLE theory are widely used [38, 81-84], and the experimental results obtained by Lin et al. [80] are usually used to validate the theoretical model. Totally 26 data points were published by Lin et al. [80], with the temperature range of 463-703 K and the pressure range of 2-25.5 MPa. In this work, the Peng-Robinson (PR) EoS [85] along with the classical mixing rules [86] was chosen to establish a model for estimating the fluid properties of the system over the range of pressures and temperatures of interest. This EoS is selected since it is computationally efficient and can give reasonably accurate estimations of the VLE for non-polar mixtures [86]. Then, the model was used in combination with the VLE theory to obtain the properties of the vapor state and the liquid state at given ambient conditions (pressure and temperature).

The PR EoS can be written as

\[
P = \frac{RT}{v-b} - \frac{a}{v(v+b)-(v-b)}
\]  

where \( P \) is pressure, \( T \) is temperature, and \( v \) is molar volume. \( R \) is the universal gas constant (8.314 J/mol \cdot K\(^{-1}\)). \( a \) is the attraction force and \( b \) is the volume parameter. For an individual component:

\[
a = 0.457235 \frac{RT_c^2}{P_c^2} \cdot \alpha(T)
\]  

\[
b = 0.077796 \frac{RT_c}{P_c}
\]
where $T_c$ is the critical temperature, and $P_c$ is the critical pressure of a component. $\kappa$ can be determined by
\[
\kappa = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3
\]  
where $\omega$ is the acentric factor of a component. In the case of a mixture, the classical van der Waals mixing rule is used to calculate these parameters:

\[
a = \sum_i \sum_j x_i x_j a_{ij}
\]
\[
b = \sum_i x_i b_i
\]
\[
a_{ij} = (1 - \delta_{ij}) \sqrt{a_i a_j}
\]
where $x_i$ and $x_j$ are the mole fractions of components $i$ and $j$ in the mixture, respectively. $\delta_{ij}$ is the binary interaction parameter. For the N$_2$-n-C$_{16}$H$_{34}$ system, as discussed by García-Sánchez et al. [87], $\delta_{ij} = 0.1816$ can give good prediction results.

VLE conditions can be expressed as
\[
T^V = T^L
\]
\[
P^V = P^L
\]
\[
f_i^V = f_i^L
\]
where superscript $V$ denotes the vapor phase, $L$ denotes the liquid phase.

$f_i$ is the fugacity of component $i$, which can be determined by
\[
f_i^V = y_i \phi_i^V
\]
\[
f_i^L = x_i \phi_i^L
\]
where $\phi_i$ is fugacity coefficient. Using the PR EoS, the analytical solutions of fugacity coefficients can be expressed as
\[
\ln \varphi_i^L = \frac{b_i}{b_i^L R T} (p v^L - R T) - \ln \left[ \frac{p}{RT} (v^L - b^L) \right] - \frac{a^L}{\sqrt{u^2 - 4w b^L R T}} \left[ \frac{2 \sum \gamma_j a_j}{a^L} - \frac{b_i}{b^L} \right] \times \ln \left[ \frac{2 u + (u + \sqrt{u^2 - 4w b^L})}{2 u + (u - \sqrt{u^2 - 4w b^L})} \right]
\]

(15)

\[
\ln \varphi_i^V = \frac{b_i}{b_i^V R T} (p v^V - R T) - \ln \left[ \frac{p}{RT} (v^V - b^V) \right] - \frac{a^V}{\sqrt{u^2 - 4w b^V R T}} \left[ \frac{2 \sum \gamma_j a_j}{a^V} - \frac{b_i}{b^V} \right] \times \ln \left[ \frac{2 u + (u + \sqrt{u^2 - 4w b^V})}{2 u + (u - \sqrt{u^2 - 4w b^V})} \right]
\]

Fig. 3. VLE diagram of the nitrogen–n-hexadecane binary system. The experimental data are from [80].

The VLE curves obtained by theoretical calculations (EoS) under various pressures are shown in Fig. 2 in the form of a temperature-composition (T-x) phase diagram, along with experimental data taken from Lin et al. [80]. The VLE calculations by MD simulations were also performed, and the obtained data were plotted in Fig. 1. We can see from the figure that results from theoretical calculations are basically consistent with those from experiments under all conditions. Calculation results obtained by MD simulation can also give a fairly good prediction for the critical point of the binary mixture.

The characteristics of supercritical transition of a fuel rely heavily on its critical point. A theoretical method based on empirical equations [88, 89] was used to estimate the critical point of the three-component fuel. The estimation equation of the critical temperature of a simple mixture was given by Li et al. [88], which can be expressed as
\[ T_{c,m} = \sum_{i=1}^{n} \theta_i T_{c,i} \]  
(16)

where \( T_{c,i} \) and \( \theta_i \) are the critical temperature and the volumetric fraction of the \( i \)th component, respectively. The later can be expressed as \( \theta_i = (x_i V_{c,i}) / (\sum_{i=1}^{n} x_i V_{c,i}) \), where \( x_i \) and \( V_{c,i} \) are the mole fraction and critical molar volume of the \( i \)th component, respectively. The estimation equation of critical pressure of a mixture was proposed by Kreglewski et al. [89], which can be expressed as

\[ P_{c,m} = P_{pc} \left[ 1 + (5.808 + 4.93 \omega_m) \frac{T_{c,m} - T_{pc}}{T_{pc}} \right] \]  
(17)

where \( T_{pc} \) is the pseudo critical temperature, \( P_{pc} \) is the pseudo critical temperature and the pseudo critical pressure of a mixture, and \( \omega_m \) is the mean acentric factor. They can be expressed as the molar averages of all individual components:

\[ T_{pc} = \sum_{i=1}^{n} x_i T_{c,i}, \quad P_{pc} = \sum_{i=1}^{n} x_i P_{c,i} \quad \text{and} \quad \omega_m = \sum_{i=1}^{n} x_i \omega_i. \]

The estimated critical properties (including critical temperature \( T_c \) and critical pressure \( P_c \)) of the three-component fuel, as well as that of its individual component, are shown in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>( T_c ) [K]</th>
<th>( P_c ) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>isooctane</td>
<td>544</td>
<td>2.57</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>658</td>
<td>1.81</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>722</td>
<td>1.4</td>
</tr>
<tr>
<td>3-component fuel</td>
<td>697</td>
<td>1.89</td>
</tr>
</tbody>
</table>

2.2. Simulation configurations

The evaporation of a single suspended fuel droplet surrounded by nitrogen ambient was considered in the present study. The initial configuration of the system is shown in Fig. 3. Before the simulations of evaporation of droplets in nitrogen, simulations of the fuel droplet and the nitrogen ambient were performed separately using the canonical ensemble (NVT, which means constant atom number N,
constant volume $V$, and constant temperature $T$) [36]. As both the fuel and the ambient gas reached their own thermodynamic equilibrium state, they were combined together, with the nitrogen molecules in the center region of the simulation box deleted to avoid the overlap of molecules. The initial temperature of the fuel was set to 363 K, close to that of the fuel in real engines before injection.

The size of the simulation box was 120 nm $\times$ 120 nm $\times$ 120 nm, and periodic boundary conditions were used in all three dimensions. The simulations were performed using the micro-canonical ensemble (NVE, which means constant atom number $N$, constant volume $V$, and constant energy $E$) [47]. The region outside of the sphere with a radius of 40 nm was named “thermostat region”, in which velocities of the molecules were rescaled every time step using a speed reset method [47]. The translational velocities of the molecules located in this region were rescaled every time step according to

$$v_i^{\text{new}} = v_i^{\text{old}} \sqrt{\frac{3k_B T N_i}{2E_k}}$$

(18)

where $E_k$ indicates the total kinetic energy of the $N_i$ atoms in the thermostat region, and $T$ indicates the target ambient temperature. $k_B$ is the Boltzmann constant. As a result, the temperature of this region could be kept at a constant target value. The initial ambient pressure was determined by a combination of the initial ambient temperature and the initial number of nitrogen molecules in the simulation box. Different from the ambient temperature, in NVE simulations, the ambient pressure could not be automatically kept by the simulator, which can be solved well by choosing the suitable initial number of nitrogen molecules in the system [47]. The number ranges of nitrogen molecules are shown in Table 4. Moreover, a molecule was removed as one of its atoms entered the thermostat region, so that the influences of vapor phase fuel molecules on the droplet evaporation process were eliminated [26]. In this case, the evaporation of the droplet can be thought of as taking place in an infinite space [26]. It is worth mentioning that the ambient pressure, together with the gradients of temperature and fuel molar fractions, may
decrease due to the ongoing evaporation of the droplet. However, the droplet accounts for less than 1% of the volume of the simulation box, so these changes are negligible.

Fig. 4. Initial configurations: (a) A single-component fuel droplet, (b) A three-component fuel droplet. Purple particles indicate n-hexadecane molecules, green particles indicate n-dodecane molecules and red particles indicate isooctane molecules.

Initially, the single-component droplet and the three-component droplet contained 19,999 and 19,815 fuel molecules, forming initial diameters of 26.5 nm and 25.5 nm, respectively. Other details are summarized in Table 4. In order to consider both subcritical and supercritical conditions [47], the target ambient temperature and the target ambient pressure of simulations for two types of fuel droplets were both 750-1200 K and 2-10 MPa, respectively. Considering typical operating conditions for a supercharged diesel engine near the end of the compression stroke [47], the maximum ambient temperature (1200 K) and the maximum ambient pressure (10 MPa) were chosen in this study. To take into account the traditional evaporation behavior, the minimum ambient temperature (750K) and the minimum ambient pressure (2 MPa) were selected in this study. The reduced ambient temperature $T_r$ and the reduced ambient pressure $P_r$ are both calculated by dividing ambient values by critical values of fuel. The integral of the
equation of motion was carried out by the velocity-Verlet algorithm [90]. In all cases, the time step is 2.0 femtosecond. The total time steps for each simulation case varied with the droplet evaporation lifetime.

Table 4. Simulation details of single-component fuel droplets and three-component fuel droplets.

<table>
<thead>
<tr>
<th></th>
<th>Single-component droplet</th>
<th>Three-component droplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial number of fuel molecules</td>
<td>19,999 (n-hexadecane)</td>
<td>1830 (isooctane, 5.3 wt%)</td>
</tr>
<tr>
<td>in the droplet</td>
<td></td>
<td>5987 (n-dodecane, 25.8 wt%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11998 (n-hexadecane, 68.9 wt%)</td>
</tr>
<tr>
<td>Initial droplet diameter, nm</td>
<td>26.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Initial number of nitrogen molecules</td>
<td>205505 - 1585024</td>
<td>205709 - 1585230</td>
</tr>
<tr>
<td>Reduced ambient pressure</td>
<td>1.43 - 7.14</td>
<td>1.06 - 5.29</td>
</tr>
<tr>
<td>Reduced ambient temperature</td>
<td>1.04 - 1.6</td>
<td>1.08 - 1.72</td>
</tr>
</tbody>
</table>

The initial configuration mentioned above was validated by performing MD simulations of the evaporation of a two-component fuel droplet, as shown in Fig. 5. Figure 6 shows the droplet evaporation histories obtained by MD simulations, which is compared with the experimental results of Ghassemi et al. [91]. The squared droplet diameter $d^2$ was normalized here by the squared initial droplet diameter $d_0^2$, and time was also divided by $d_0^2$, to enable direct comparisons of the evaporation histories for different droplets. In their experiments [91], the evaporation process of a two-component droplet composed of 50 vol.% n-heptane and 50 vol.% n-hexadecane was recorded by a high-speed camera, and the temporal variations of the squared droplet diameter ($d^2$) were obtained. The evaporation histories of fuel droplets under the ambient pressure of 1.0 MPa and ambient temperatures ranging from 673 K to 973 K could be divided into two stages, which is induced by the obviously different evaporation characteristics of the two components of the droplet [91]. In our simulations, initially the two-component droplet included 12218 n-heptane molecules (52 vol.%) and 5697 n-hexadecane molecules (48 vol.%), with an initial diameter of
22 nm. The temporal variations of $d^2$ during the evaporation process under the ambient pressure of 1.0 MPa and ambient temperatures of 673 K and 973 K are also shown in Fig. 6. It is evident that the $d^2$ curve at 673 K shows an obvious two-stage phenomenon. At the higher ambient temperature (973 K), this two-stage phenomenon is not so noticeable, which is caused by the faster temperature increase of the droplet. The same trend was also observed in the studies of Ghassemi et al. [91], as shown in Fig. 6. It is worth mentioning that the difference in the droplet evaporation lifetime obtained in two studies at the higher temperature (973 K) is greater. As discussed in [92], in the experiment, the diameter of the droplet was obtained from the photograph by image processing, whose accuracy was limited. Moreover, the measurement of droplet diameter at the higher temperature (973 K) had a large error due to the influence of fuel vapor [92]. Therefore, MD simulations were proved to be able to capture the general behaviors of an evaporating multi-component droplet, despite the large gap between the scales investigated by these two methods.

**Fig. 5.** Initial configuration of the two-component system. Purple particles indicate n-hexadecane molecules and red particles indicate n-heptane molecules.
Fig. 6. Temporal variations of dimensionless square diameter \((d/d_0)^2\) of two-component droplets. The experiment data are from [91].

2.3. Voronoi tessellation

A certain space is divided into Voronoi cells according to the definition of the Voronoi tessellation. For a set of given points in a spatial domain, points in each Voronoi cell are closer to the given point in the Voronoi cell than any other points in the spatial domain [93]. Each cell could be regarded as a measure of volume of each particle [28]. To provide a clearer explanation, Fig. 7 shows a schematic diagram of Voronoi tessellation for particles on a plane. For a molecule system, the reciprocal of the Voronoi cell volume can be regarded as the local density of molecules, indicating the instantaneous local distributions of a certain molecule [28, 70, 94]. In fact, the Voronoi tessellation has been widely used in the density analyses of particle systems, and the inspections of local neighborhood relationships in the domains of physics and materials science [93].
Fig. 7. The Voronoi tessellation for particles in a plane. The blue points indicate the given data.

3. Results and discussion

3.1. The macroscopic evaporation characteristics of multi-component droplets

The definitions of evaluation parameters for droplets are from [26]. The boundary of the droplet is defined as the contour surface where the density is equal to the average of the maximum density and the minimum density of the system. The diameter of the droplet is defined as that of a sphere of the same volume as the droplet. Figure 8 shows temporal variations of dimensionless square diameter \( (d/d_0)^2 \) of droplet, and time is also divided by \( d_0^2 \). The data points located in the range of 0.862 \( d_0^2 \) to 0.215 \( d_0^2 \) (corresponding to the initial droplet volume of 80% to 10%) are fitted by the method of least squares linear fitting, and the slope of the fitting straight line is regarded as the evaporation rate constant \( k \). The time corresponding to the intersection point of the fitting line and the straight linear \( d^2 = d_0^2 \) is defined as the initial heat-up time \( t_h \). And the time corresponding to the intersection point of the fitting line and the straight linear \( d^2 = 0 \) is defined as the droplet evaporation lifetime \( t_L \). The relationship among them is as follows:

\[
t_L = t_h + \frac{d_0^2}{k}
\]  

(18)
Fig. 8. The temporal variation of dimensionless square diameter \((d/d_0)^2\) of n-hexadecane droplet.

Figure 9 shows the temporal variations of \((d/d_0)^2\) of the single-component droplet and the three-component droplet, and time is also divided by \(d_0^2\). The droplet size increases at the beginning of the evaporation, as shown in Fig. 9. This phenomenon has been attributed to the slow evaporation and the thermal expansion, revealed in previous studies [42]. The simulation results here suggest that the adsorption and dissolution of nitrogen molecules on the droplet may be additional reasons for it. Moreover, the normalized lifetimes of single-component droplets are longer than those of three-component droplets, especially under lower ambient pressures. The reason for this phenomenon will be discussed in the analysis of Fig. 10.
Fig. 9. Comparison of temporal variations of the dimensionless square diameters: (a) Single-component fuel droplets, (b) Three-component fuel droplets.

Figure 10 shows the change of the droplet evaporation lifetime $t_L$, initial heat-up time $t_h$ and evaporation rate constant $k$ as a function of ambient pressure, where the droplet evaporation lifetime and the initial heat-up time are normalized by $d_0^2$. With increasing ambient temperature, the temperature difference between fuel and ambient gas becomes larger, so the heat transfer is accelerated. Meanwhile, the gas phase diffusion coefficient also increases [26]. As seen from Fig. 10a, with increasing ambient temperature, the droplet evaporation lifetime decreases monotonously. Moreover, under the ambient temperatures investigated here, the droplet evaporation lifetime decreases monotonously with increasing ambient pressure. According to previous studies, including experiments [95, 96] and simulations [97], the droplet evaporation lifetime decreased monotonously under high temperatures (near $T_c$ or exceed $T_c$) with increasing ambient pressure. The effect of decreasing latent heat of vaporization exceeded the combined effects of decreasing mass diffusivity and increasing boiling point of the fuel, leading to the decrease of droplet evaporation lifetime [26]. The temperatures studied in this paper are very high ($T > T_c$), so the present conclusion is consistent with existing ones [63, 95-98]. However, when the ambient pressure is
higher (P > 6 MPa), the effect of the decreasing latent heat of evaporation with increasing ambient pressure is offset by the combined effect of the decreasing mass diffusivity, decreasing thermal conductivity, and increasing boiling point of the fuel [26]. As a result, the droplet evaporation lifetime hardly changes. The trend of the initial heat-up time $t_h$ (Fig. 10b) with the ambient temperature and/or the ambient pressure is basically consistent with that of the droplet evaporation lifetime $t_L$ (Fig. 10a), which is also consistent with the previous experimental results [42, 63]. The evaporation rate constant $k$ increases with increasing ambient temperature. However, $k$ first increases and then decreases with increasing ambient pressure. The trends are consistent with those obtained by experiments [42, 96]. The quantitative results are compared below. Since no published similar results (including experimental results and simulation results) are available to provide comparisons with those of the three-component droplet selected in this paper, only the calculation results of n-hexadecane droplets are discussed here. The experiments that the authors could find closest to the calculation cases of this paper come from Nomura et al. [42]. The ambient pressures studied by them ranged from 1 MPa to 3 MPa, and the minimum ambient pressure studied in this paper was 2 MPa. Therefore, the values of physical parameters at 2 MPa were selected for comparison. The selected ambient condition of Nomura et al. [42] was 2 MPa and 773 K. The ambient condition of 2 MPa and 750 K was selected for comparison in this paper. The fuel droplets were both n-hexadecane, and the ambient gas was both nitrogen. Since the initial size of the droplet is different (the experimental droplet diameter is 0.39 mm, and the simulated droplet diameter is 26.5 nm), all physical quantities are divided by the square of the initial diameter of the droplet for convenience of comparison. In the experiment of Nomura et al. [42], under the ambient condition of 2 MPa and 773 K, the droplet evaporation rate constant $k$ was 0.28 mm$^2$/s, the normalized droplet evaporation life $t_L/d_0^2$ was 8.2 s/mm$^2$, and the normalized droplet initial heating time $t_h/d_0^2$ was 5.2 s/mm$^2$. In the present simulation, under the ambient condition of 2 MPa and 750 K, the droplet evaporation rate constant $k$ was 0.27 mm$^2$/s, the normalized droplet evaporation life $t_L/d_0^2$ was 7.5 s/mm$^2$, and the normalized initial heating time of the
droplet \( t_h/d_0^2 \) was 3.8 s/mm². It should be noted that the ambient temperature used in the simulation was slightly lower than that used in the experiment. For \( k \) and \( t_L/d_0^2 \), the results of simulation and experiment agree well. As for \( t_h/d_0^2 \), the results of the two are not quite consistent. This is because the data of \( d^2 \) obtained by the experiment fluctuates greatly, and the ranges of \( d^2 \) adopted for fitting \( k \) are different in the simulation (using 0.862\( d_0^2 \)-0.215\( d_0^2 \)) and experiment (using 0.5\( d_0^2 \)-0.15\( d_0^2 \)), which will directly decide the value of \( t_h/d_0^2 \). There is another interesting point worth discussing. As mentioned before, the normalized lifetimes of single-component droplets are longer than those of three-component droplets, especially under lower ambient pressures (\( P \leq 6 \) MPa, Fig. 10a). The difference in the initial heat-up time \( t_h \) between a single-component droplet and a three-component droplet is always greater than that in the droplet evaporation lifetime \( t_L \) between the two droplets under lower pressures (\( P \leq 6 \) MPa). Meanwhile, the evaporation rate constant \( k \) of the three-component droplet is smaller than that of the single-component droplet under almost all conditions. Equation (18) can be transformed as follows for an individual droplet:

\[
\frac{t_L}{d_0^2} = \frac{t_h}{d_0^2} + \frac{1}{k}
\]  

Corresponding to equation (19), the \( 1/k \) term of the three-component droplet is larger than that of the single-component droplet (Fig. 10c), but the \( t_L/d_0^2 \) term of the former is smaller under lower pressures (\( P \leq 6 \) MPa) (Fig. 10a), indicating that the shorter evaporation lifetime of the three-component droplet is caused by \( t_h/d_0^2 \) term. In other words, the shorter evaporation lifetime of the three-component droplet, compared with that of the single-component droplet, is caused by shorter initial heat-up time (Fig. 10b). In the initial heat-up period, light components (isooctane and n-dodecane) of three-component droplets evaporate first and take away the absorbed heat. As a result, the three-component droplet has a shorter initial heat-up time, and a smaller size-increase as well, as shown in Fig. 9.
Fig. 10. Comparisons of evaporation evaluation parameters of two droplets: (a) Normalized evaporation lifetime, (b) Normalized initial heat-up time and (c) Evaporation rate constant.

3.2. The phase transition and the dominant mixing mode transition of multi-component fuel droplets

In this section, the Voronoi tessellation method was used to calculate the local density distributions of the two droplet evaporation systems. A new criterion was proposed to evaluate whether single-component and multi-component fuels had realized the transition of the dominant mixing mode from evaporation to diffusion in the mixing process of fuel-ambient gas. A new parameter was proposed to evaluate the phase transition speed of the hydrocarbon fuel. The dominant mixing mode maps on the P-T diagram for the evaporation systems of pure n-hexadecane droplets and three-component hydrocarbon fuel droplets were presented.

3.2.1. The criterion for the transition of the dominant mixing mode

Figure 11 shows the local density distribution of n-hexadecane in the single-component droplet evaporation system. The left and right peaks of the probability profile represent the vapor phase density
probability peak and the liquid phase density probability peak of n-hexadecane, respectively. The local
density distribution was fitted by the non-parametric fitting method with MATLAB. Four parameters \(w_1, w_2, h_1\) and \(h_2\) are defined, as shown in Fig. 11. \(w_1\) represents the density difference corresponding to two
peak values when the two peak values of the probability profile are equal. \(w_2\) represents the maximum
density difference of the n-hexadecane in the evaporation system. \(W\), equal to \(w_1/w_2\), represents the
dimensionless transition density. \(h_1\) represents the probability value corresponding to the trough of the
probability profile. \(h_2\) represents the probability value when the two peak values of the probability profile
are equal. \(H\), equal to \(h_1/h_2\), represents the dimensionless transition probability. Yoon et al. [70] obtained
the local density distribution of the supercritical \(\text{CO}_2\) by the Voronoi tessellation, and proposed the
Inverse Gamma-Normal mixture model to fit it. Figure 12 shows the local density distribution of
\(\text{CO}_2\) at \(\text{Tr} = 0.99\). Based on a quantitative analysis of the local density distribution and the Inverse
Gamma-Normal mixture model of the \(\text{CO}_2\) in supercritical state, and combined with the above analyses
in this paper, two critical values of \(H_c = 0.85\) and \(W_c = 0.35\) are adopted here. When diffusion instead of
evaporation becomes the dominant mode in the mixing process, the fuel and ambient gas both diffuse into
each other dramatically due to the large difference in density at the initial interface between them. After
that, the volume of Voronoi cell changes smoothly [28], and there is no longer a well-defined gas-liquid
interface. As a result, the transition between the two peaks of the probability profile will be smoother.
Besides, the two probability peaks will move close to each other [70], so the difference in the local
densities corresponding to the two peaks will decrease. In this case, for these two dimensionless
parameters, \(H\) will increase and \(W\) will decrease. For single-component fuels, when \(W \leq W_c\) and \(H \geq H_c\), the dominant mode in the mixing process of fuel-ambient gas is diffusion, otherwise it is evaporation.
For multi-component fuels, the weighted average method is used to calculate the two parameters, and the
criterion to decide the dominant mixing mode in the mixing process of fuel-ambient gas is the same as
that of single-component fuels.
**Fig. 11.** The local density distribution of the n-hexadecane in the single-component droplet evaporation system.

**Fig. 12.** The local density distribution of CO$_2$. Redrawn based on [70].
3.2.2. The mechanism for the transition of the dominant mixing mode

Figures 13-16 show the changes of W and H parameters of n-hexadecane in single-component droplets and individual component (n-hexadecane, n-dodecane, and isooctane) in three-component droplets with ambient conditions, respectively. As shown in Figs. 13, W decreases and H increases with increasing ambient pressure. However, W increases and H decreases slightly with increasing ambient temperature. Variations of W and H of individual components of the three-component droplet (Figs. 14-16) with ambient conditions are basically consistent with those of the single-component n-hexadecane droplet (Fig. 13). The following conclusions can be drawn. With increasing ambient pressure, the density differences between the vapor phase and the liquid phase decrease, and the dominant mode in the mixing process of fuel-ambient gas may experience a transition from evaporation to diffusion. However, with increasing ambient temperature, the density differences between the vapor phase and the liquid phase increase, and evaporation gradually becomes the dominant mixing mode in the mixing process of fuel-ambient gas.

The latest research from Banuti et al. [99] has provided the modified phase diagram of pure substances, as shown in Fig. 17. The supercritical fluid region includes the whole regions of the liquid-like phase and the gas-like phase, and part of the region of the ideal gas phase. Widom line, a finite length line segment above the critical point, divides the supercritical phase into liquid-like one and gas-like one [67]. Moreover, according to the previous study [100], similar to the pure fluid, a mutually miscible binary mixture experiences a transition between liquid-like phase and gas-like phase in the region of supercritical phase across a single Widom line. However, phase separation appears when transition occurs in the region of supercritical phase for the immiscible binary mixture, and two Widom lines are present.

The following explanation is given in this paper. As isooctane, n-dodecane and n-hexadecane can be miscible together, the ternary mixture could be treated as a pure fluid with a single Widom line in case of transition in the supercritical region. Although nitrogen cannot be miscible with hydrocarbon fuel, it is
able to affect the phase transition of hydrogen fuel under supercritical conditions, that is, the length, shape and position of the Widom line could be changed. The mixture of hydrocarbon fuel and nitrogen belongs to type III [101], whose characteristic is that the critical pressure of the mixture system is getting higher and the critical temperature is getting lower with increasing content of nitrogen. All ambient temperatures investigated here \( (T \geq 750 \text{ K}) \) are higher than critical temperatures of the two types of fuel (three-component fuel: 697 K; single-component fuel: 722 K). Meanwhile, the critical temperature of the mixture system, including the fuel droplet and nitrogen, is lower than that of the fuel itself because of the addition of nitrogen.

Based on analyses above, there is no doubt that all ambient temperatures investigated here are higher than the critical temperature of the two types of mixture systems. Several possible thermodynamic pathways for phase transition of fuel are described below. The fuel is initially liquid. When the ambient pressure is relatively higher and the ambient temperature is relatively lower, the final state of fuel will be located in the region of the gas-like phase state or even the liquid-like phase state. Under this circumstance, the thermodynamic path experienced by fuel is from the liquid phase to the supercritical gas-like phase or the supercritical liquid-like phase. The density difference before and after phase transition is small (the density of supercritical phase is slightly smaller than that of liquid phase, but much larger than that of gas phase), and diffusion becomes the dominant mode in the mixing process of fuel-ambient gas. Thermodynamic paths experienced by fuel are shown by the red dotted line with arrows in Fig. 17. When the ambient temperature is relatively higher and the ambient pressure is relatively lower, the final state of the fuel will be located in the region of the gas phase or even the ideal gas phase. When the thermodynamic path experienced by fuel is from the liquid phase to the gas phase or the ideal gas phase, the density difference between the initial phase state and the final phase state is larger, and evaporation will become the dominant mode in the mixing process of fuel-ambient gas. Thermodynamic paths experienced by fuel are shown by the orange solid line with arrows in Fig. 17.
Fig. 13. Dimensionless transition density (W) and probability (H) diagrams of n-hexadecane in single-component droplets: (a) W, (b) H. The blue points indicate the primary data.

Fig. 14. Dimensionless transition density (W) and probability (H) diagrams of n-hexadecane in three-component droplets: (a) W, (b) H. The blue points indicate the primary data.
Fig. 15. Dimensionless transition density ($W$) and probability ($H$) diagrams of $n$-dodecane in three-component droplets: (a) $W$, (b) $H$. The blue points indicate the primary data.

Fig. 16. Dimensionless transition density ($W$) and probability ($H$) diagrams of isooctane in three-component droplets: (a) $W$, (b) $H$. The blue points indicate the primary data.
3.2.3. Effects of ambient conditions on phase transition speeds of different components

The following definition is adopted in this paper. In the diagram of the local density distribution, the time when the two peak values of the probability profile are equal is defined as the vapor-liquid equal probability time $t_{pv} = p_l$. Figures 18a-18d show the vapor-liquid equal probability time diagram of n-hexadecane of the single-component droplet and individual component (n-hexadecane, n-dodecane, and isooctane) of the three-component droplet, respectively. The magnitude of $t_{pv} = p_l$ can be used to represent the phase transition speed. Under the same ambient pressure, $t_{pv} = p_l$ gradually decreases with increasing ambient temperature, which means that the phase transition process is accelerated, consistent with previous studies [102]. However, the effect of pressure on the speed of phase transition is different from that of temperature. As shown in Figs. 18a-18c, when the ambient temperature remains constant, $t_{pv} = p_l$ of n-hexadecane and n-dodecane decreases with increasing ambient pressure until 4 MPa. When the ambient pressure exceeds 4 MPa, $t_{pv} = p_l$ of the fuel is basically unchanged with increasing ambient pressure. This means that the speed of phase transition remains constant, which is consistent with earlier conclusions.

**Fig. 17.** Thermodynamic paths for liquid fuels. Redrawn based on [99].
[26, 42]. However, the effect of pressure on the evaporation of isooctane (Fig. 18d) is different from that of n-dodecane or n-hexadecane. For isooctane, $t_{pv} = pl$ increases monotonically with increasing ambient pressure. This suggests that increasing ambient pressure might not be a good choice for speeding up the mixing process of light component fuel (isooctane) and ambient gas. This finding agrees with the previous study on n-heptane [103]. In their study, this was attributed to the decreasing mass diffusivity [103].

![Fig. 18. Vapor-liquid equal probability time diagrams: (a) Single-component n-hexadecane droplets, (b) n-Hexadecane in three-component droplets, (c) n-Dodecane in three-component droplets and (d) Isooctane in three-component droplets. The blue points indicate the primary data.](image-url)
3.2.4. The dominant mixing mode maps

According to the criterion proposed in Section 3.2.1, the dominant mixing mode maps on the P-T diagram of pure n-hexadecane droplets, n-hexadecane in three-component fuel droplets and three-component fuel droplets were obtained, as shown in Figs. 19a-19c respectively. According to the comparison of Figs. 19a and 19b, the following conclusion can be drawn. For n-hexadecane in the three-component fuel droplet, the maximum ambient temperature of the mixing zone dominated by diffusion is higher under the same ambient pressure, compared with that of pure n-hexadecane droplet. For the three-component fuel droplet, the minimum ambient pressure of the mixing zone dominated by diffusion is higher than that of its individual component n-hexadecane, as shown in Figs. 19a and 19c. This is because lighter components (isooctane and n-dodecane) have higher critical pressures compared with those of heavy ones (n-hexadecane), increasing the overall critical pressure of the mixture.

Investigating the molecular distribution of supercritical fluid by Voronoi tessellation has been tried before [28, 70]. The method of distinguishing the two dominant mixing modes based on the quantitative Voronoi tessellation analysis was proposed in this paper, which is different from the two criterion mentioned above [27, 35]. In previous reports [26, 27, 36], the minimum ambient temperature required for fuel to undergo supercritical transition in ambient gas, that is, the critical mixing temperature, increases with decreasing ambient pressure. Moreover, under a certain ambient pressure, as long as the ambient temperature is not less than the critical mixing temperature, the supercritical transition always occurs. In this study, it was found that the relationship between the critical mixing temperature and the ambient pressure was more complicated when the supercritical transition of fuel occurred in ambient gas. Under a certain ambient pressure, the ambient temperature where the fuel could undergo supercritical transition in ambient gas had not only a minimum (the critical mixing temperature), but also a maximum. With decreasing ambient pressure, the maximum value of the ambient temperature where the supercritical
transition could occur also decreased. So, this study provided a new insight into the process of supercritical transition of fuel.

**Fig. 19.** The dominant mixing mode maps: (a) Pure n-hexadecane droplets, (b) n-Hexadecane in three-component fuel droplets and (c) Three-component fuel droplets.
Fig. 20. Molecular distributions in the mixing process of single-component fuel droplets and three-component fuel droplets. Purple particles indicate n-hexadecane molecules, green particles indicate n-dodecane molecules and red particles indicate iso-octane molecules.

According to the classification of Fig. 19, Fig. 20 shows molecular distributions in the mixing process of single-component fuel droplets and three-component fuel droplets in different dominant modes. In order to show the fuel phase transition process more clearly, only fuel molecules are included in the figure here, and nitrogen molecules are not shown. Figures 20a and 20b show the cases of single-component fuel
droplets in evaporation mode and diffusion mode, respectively, while Figs. 20c and 20d show the cases of three-component fuel droplets in evaporation mode and diffusion mode, respectively. The moment of the snapshot is determined according to the vapor-liquid equal probability time $t_{pv} = t_{pl}$ proposed in Section 3.2.3. The weighted average method is used to calculate the vapor-liquid equal probability time of the three-component droplet. From the analysis in Section 3.2.2, when evaporation dominates the mixing process of fuel droplets, the fuel transitions from the liquid phase to the gas phase or the ideal gas phase, and the density of the fuel varies greatly before and after the phase transition. As shown in Figures 20a and 20c, either droplet maintains a spherical shape, and the droplet boundary is sharp and clear. In the interface between the liquid fuel and the ambient gas, the density gradient of the fuel is large. When diffusion dominates the mixing process of fuel droplets, the fuel transitions from the liquid phase to the supercritical gas-like phase or the supercritical liquid-like phase, and the density difference of the fuel before and after the phase transition is small. As shown in Figures 20b and 20d, the contour of any droplet is difficult to identify. Compared with the phase transition shown in Figs. 20a and 20c, the fuel after the phase transition is denser and the thickness of the phase transition zone increases significantly, which causes the density gradient of the fuel in this region to smaller (Figs. 20b and 20d). As a result, the phase interface cannot be identified.

4. Conclusions

The evaporation process of the three-component hydrocarbon fuel (5.3 wt% isoctane, 25.8 wt% n-dodecane and 68.9 wt% n-hexadecane) droplet in a nitrogen environment was studied using MD simulations. As a comparison, the pure n-hexadecane droplet was also studied. Ambient conditions from subcritical to supercritical were considered. The ambient pressure ranged from 2 MPa to 10 MPa and the ambient temperature ranged from 750 K to 1200 K. Significant results of this study include:

1) Macroscopic droplet evaporation characteristics, such as the droplet evaporation lifetime, initial heat-up time, and evaporation rate constant, were analyzed. The evaporation lifetime of the multi-component
droplet decreases with increasing ambient pressure and/or temperature. The change trend of droplet initial
heat-up time with ambient temperature and/or ambient pressure is basically consistent with that of the
droplet evaporation lifetime. The shorter evaporation lifetime of the three-component droplet is caused by
the shorter initial heat-up time, compared with that of the single-component droplet.

2) The new criterion suitable for both the single-component fuel and the multi-component fuel is one of
the main contributions of this paper. Based on the quantitative Voronoi tessellation analysis, a new
criterion, which is a combination of two dimensionless critical values of $H_c = 0.85$ and $W_c = 0.35$, was
proposed for the first time to determine the dominant mode in the mixing process of fuel-ambient gas. The
thermodynamic paths of the phase transition of fuel in the ambient gas were for the first time analyzed on
the revised phase diagram. Effects of ambient temperature and ambient pressure on the transition of the
dominant mixing mode were analyzed. When increasing ambient pressure or decreasing ambient
temperature, the density difference between the vapor and the liquid decreases, and the dominant mixing
mode gradually transitions from evaporation to diffusion. When the fuel experiences the phase transition
from the liquid phase to the supercritical liquid-like phase or the supercritical gas-like phase, the mixing
process of fuel-ambient gas is dominated by diffusion. However, when the fuel experiences the phase
transition from the liquid phase to the gas phase or the ideal gas phase, the mixing process of fuel-ambient
gas is dominated by evaporation.

3) A new parameter, namely the vapor-liquid equal probability time $t_{pv} = t_{pl}$, was proposed to evaluate the
phase transition speed of hydrocarbon fuels. The phase transition speed of each component of the three-
component fuel is accelerated with increasing ambient temperature. With increasing ambient pressure, the
phase transition speed of isooctane slows down, while that of n-dodecane or n-hexadecane increases. In
other words, increasing ambient pressure does not necessarily accelerate the phase transition, while
increasing ambient temperature increases the phase transition speed monotonically.
4) The dominant mixing mode maps on the P-T diagram for the evaporation systems of pure n-hexadecane droplets and three-component hydrocarbon fuel droplets were presented. A major finding was that under a certain ambient pressure, the ambient temperature where fuel could undergo supercritical transition in the ambient gas had not only a minimum but also a maximum. With decreasing ambient pressure, the maximum value of the ambient temperature where the supercritical transition could occur also decreased. The addition of light components significantly increases the minimum pressure of the mixing zone dominated by diffusion. In evaporation mode, the droplet boundary is sharp and clear. In the interface between the liquid fuel and the ambient gas, the density gradient of the fuel is large. In diffusion mode, the contour of the droplet is difficult to identify. The fuel after the phase transition is denser and the thickness of the phase transition zone increases significantly, which causes the density gradient of the fuel in this region to smaller. Future work could be to explore the relationship between the critical temperature and the critical pressure of a multi-component fuel system under wider ambient conditions.

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References


