Development of a New Kinetic Model for the Analysis of Heating and Evaporation Processes in Complex Hydrocarbon Fuel Droplets

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Declaration

I hereby certify that this thesis is the original work of the author except where otherwise indicated. I have identified my sources of information, and in particularly have put in quotation marks and identified the origins of any passages that have been quoted word for word. This thesis has not been previously submitted to this or any other university for a degree, and does not incorporate any materials already submitted for a degree.

Signed:

Date:
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Abstract

This work is concerned with the development of a new quantitative kinetic model for the analysis of hydrocarbon fuel droplet heating and evaporation, suitable for practical engineering applications. The work mainly focuses on the following two areas. Firstly, a new molecular dynamics (MD) algorithm for the simulation of complex hydrocarbon molecules, with emphasis on the evaporation/condensation process of liquid n-dodecane ($C_{12}H_{26}$), which is used as an approximation for Diesel fuel, has been developed. The analysis of n-dodecane molecules has been reduced to the analysis of simplified molecules, consisting of pseudoatoms, each representing the methyl ($CH_3$) or methylene ($CH_2$) groups. This analysis allows us to understand the underlying physics of the evaporation/condensation process of n-dodecane molecules and to estimate the values of its evaporation/condensation coefficients for a wide range of temperatures related to Diesel engines. Nobody, to the best of our knowledge, has considered MD simulation of molecules at this level of complexity.

Secondly, a new numerical algorithm for the solution of the Boltzmann equation, taking into account inelastic collisions between complex molecules, has been developed. In this algorithm, additional dimensions referring to inelastic collisions have been taken into account alongside three dimensions describing the translational motion of molecules as a whole. The conservation of the total energy before and after collisions has been considered. A discrete number of combinations of the values of energy corresponding to translational and internal motions of molecules after collisions have been allowed and the probabilities of the realisation of these combinations have been assumed to be equal.
This kinetic model, with the values of the evaporation coefficient estimated based on MD simulations, has been applied to the modelling of the heating and evaporation processes of n-dodecane droplets in Diesel engine-like conditions. In the previously developed kinetic models, applied to this modelling, all collisions were assumed to be elastic and the evaporation coefficient was assumed equal to 1. It is shown that the effects of inelastic collisions lead to stronger increase in the predicted droplet evaporation time relative to the hydrodynamic model, compared with the similar increase predicted by the kinetic model considering only elastic collisions. The effects of a non-unity evaporation coefficient are shown to be weak at gas temperatures around or less than 1,000 K but noticeable for gas temperatures 1,500 K. The application of the rigorous kinetic model, taking into account the effects of inelastic collisions and a non-unity evaporation coefficient, and the model considering the temperature gradient inside droplets is recommended when accurate predictions of the values of droplet surface temperature and evaporation time in Diesel engine-like conditions are essential.
Contents

1 Introduction

1.1 Background ................................................. 1
1.2 Motivation and Objectives ................................. 7
1.3 Thesis Structure ............................................. 9

2 Molecular Dynamics Study on Evaporation and Condensation 10

2.1 Introduction to Chapter 2 ............................... 10
2.2 Model and Simulation ..................................... 13
   2.2.1 Intermolecular potential .......................... 13
   2.2.2 Equilibrium simulation of a liquid-vapour system ... 15
2.3 Simulation Results and Discussions ......................... 18
   2.3.1 Liquid-vapour phase quasi-equilibrium at the interface .. 18
   2.3.2 Chain orientation at the interface ................... 23
   2.3.3 Molecular mechanism of evaporation and condensation .... 24
   2.3.4 Typical evaporation and condensation behaviours ....... 30

\v
2.4 Conclusions to Chapter 2 ................................................. 34

3 Kinetic Boundary Conditions .............................................. 36
  3.1 Introduction to Chapter 3 .............................................. 36
  3.2 Problem Formulation .................................................. 38
  3.3 Evaporation/Condensation Coefficient .............................. 40
  3.4 Velocity Distribution Function ..................................... 43
  3.5 Revised Boundary Conditions ...................................... 49
  3.6 Conclusions to Chapter 3 ............................................. 51

4 Kinetic Theory of Evaporation and Condensation .................. 53
  4.1 Introduction to Chapter 4 ............................................. 53
  4.2 A model for inelastic collisions ................................... 56
  4.3 An algorithm for the solution of the Boltzmann equation ...... 63
  4.4 Applications ............................................................. 67
    4.4.1 Shock wave structure ......................................... 67
    4.4.2 Heat flux between two parallel plates ....................... 70
    4.4.3 Evaporation of n-dodecane into nitrogen ................... 74
  4.5 Conclusions to Chapter 4 ............................................. 77

5 Droplet Heating and Evaporation:
  Effects of Inelastic Collisions and a Non-unity Evaporation Coeffi-
  cient ................................................................. 80
  5.1 Introduction to Chapter 5 ............................................. 80
  5.2 Physical Models ....................................................... 82
    5.2.1 Liquid phase region ......................................... 84
    5.2.2 Kinetic region .................................................. 89
    5.2.3 Hydrodynamic region ..................................... 90
List of Figures

1.1 A schematic presentation of different regions related to the hydrodynamic approach, kinetic modelling and molecular dynamics simulations. \( \delta_{Tr} \) and \( \delta_{Kn} \) are the thickness of the transition layer and kinetic region, respectively. ................................................................. 2

2.1 Schematic presentation of an n-dodecane (C\(_{12}\)H\(_{26}\)) molecular (a) and its presentation using united atom model (b). The bending angles between neighbouring bonds (\( \sim 114^\circ \)) (zigzag structure of the molecule) are taken into account. ................................................................. 13

2.2 Schematic presentation of the bonds and the interactions between atoms for a portion of the n-dodecane chain, consisting of four united atoms. ................................................................. 14

2.3 Snapshots of the simulation box 64.24\( \sigma \times 16.48\sigma \times 16.48\sigma \) for 720 n-dodecane molecules: initial state (a) and liquid-vapour quasi-equilibrium state at 400 K (b), 450 K (c), 500 K (d) and 550 K (e), respectively. ................................................................. 16

2.4 Density profiles for temperatures 400 K, 450 K, 500 K, and 550 K. ................................................................. 19

2.5 Liquid and vapour densities versus temperatures at phase equilibria. ................................................................. 19
2.6 The thickness of the liquid-vapour interface versus reduced liquid temperature, as predicted by the present MD simulations for n-dodecane, and inferred from the published results for argon, water, and methanol. The reduced temperature is defined as the ratio of the liquid temperature to the critical temperature.

2.7 Local translational and rotational kinetic energies (normalised by $\varepsilon_{CH_2}$ given in Table 2.1) of n-dodecane versus their positions along $x$ axis at 500 K for simulation boxes $51.39\sigma \times 13.73\sigma \times 13.73\sigma$ (a) and $137.04\sigma \times 13.73\sigma \times 13.73\sigma$ (b).

2.8 Local orientation parameter $S(x)$ of n-dodecane molecules versus their positions along $x$ axis at 500 K.

2.9 A typical time history of a spontaneously evaporating n-dodecane molecule at 500 K: (a) trajectory of the molecules in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).

2.10 A typical time history of a spontaneous condensing n-dodecane molecule at 500 K: (a) trajectory of the molecule in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).

2.11 A typical time history of a reflection condensation n-dodecane molecule in the liquid phase at 500 K: (a) trajectory of the molecule in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).
2.12 A typical time history of a reflection evaporation n-dodecane molecule in the vapour phase at 500 K: (a) trajectory of the molecule in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{\text{CH}_2}$ given in Table 2.1). 29

2.13 Schematic presentation of typical evaporation and condensation behaviours of simple molecules (a) and n-dodecane chains (b). 31

2.14 Typical trajectories of the mass centres of n-dodecane molecules during spontaneous evaporation (a), reflection evaporation (b), spontaneous condensation (c), reflection condensation (d) and trapping-desorption evaporation/condensation (e). 33

3.1 Schematic presentation of molecular mass fluxes of evaporation and condensation. 40

3.2 The condensation coefficient of n-dodecane versus reduced temperature, as predicted by MD simulations and the transition state theory; the values of this coefficient for argon, water, and methanol, obtained by other researchers, using MD simulations. The reduced temperature is defined as the ratio of the liquid temperature to the critical temperature. 42

3.3 The velocity distribution of molecules with respect to velocity components tangential to the interface $v_y$ (a) and $v_z$ (b) in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 500 K. The solid curve shows a one-dimensional normalised Maxwellian distribution at 500 K. 45
3.4 The velocity distribution of molecules with respect to velocity components tangential to the interface $v_y$ (a) and $v_z$ (b) in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 550 K. The solid curve shows a one-dimensional normalised Maxwellian distribution at 550 K. 

3.5 The velocity distribution of molecules with respect to velocity component normal to the interface $v_x$ in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 500 K. The solid and dotted curves show one-dimensional normalised Maxwellian distributions at 500 K and 627 K.

3.6 The velocity distribution of molecules with respect to velocity component normal to the interface $v_x$ in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 550 K. The solid and dotted curves show one-dimensional normalised Maxwellian distributions at 550 K and 681 K.

3.7 Normalised velocity distribution of evaporated and reflected molecules from the vapour-liquid interface and that of all molecules leaving this surface for liquid temperature equal to 500 K.

3.8 Evaporation coefficient $\sigma_e$ as a function of translational energy $E_x/k_B$ for liquid temperature equal to 500 K.

4.1 Schematic presentation of the rotation of vector $\mathbf{X}$ in a three-dimensional space ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$).

4.2 The energies of the individual degrees of freedom ($E_i$) versus $N_i$ at initial state and after steps 1, 2 and 3.
4.3 A projection of the surface of an $N$-dimensional sphere, describing the energies referring to translational and internal degrees of freedom of two colliding molecules, into a two-dimensional space referring to two translational degrees of freedom. $p$ and $p^*$ show the locations of the molecular momenta before the collision. The dashed circle shows possible locations of molecular momenta after the collision if the contribution of internal degrees of freedom is ignored. The thin solid circle shows possible locations of molecular momenta after the collision if molecular internal energy increases during the collision. The thick solid circle shows possible locations of molecular momenta after the collision if molecular internal energy decreases during the collision. $p'$ and $p''$ show the allowed locations of the molecular momenta after the collision if molecular internal energy decreases during the collision.

4.4 Plots of $n = (n_n - n_-)/(n_+ - n_-)$, where $n_n$ is the current number density of nitrogen, versus the distance $x$ normalised by mean free path $\ell = (\sqrt{2\pi\sigma_{N_2}^2}n_-)^{-1}$, where $\sigma_{N_2}$ is the diameter of $N_2$ molecules. $x = 0$ shows the location of the shock wave.

4.5 Plots of $n = (n_n - n_-)/(n_+ - n_-)$ versus the distance $x$ normalised by mean free path $\ell$ of $N_2$ molecules show the results of our calculations when the contributions of various number of internal degrees of freedom $N_{int}$ are taken into account.

4.6 A schematic presentation of the heat flux transfer between two parallel plates, separated by the distance $L$ along the $x$ axis and kept at temperatures $T_{w1}$ and $T_{w2}$. $n_d$ and $n_n$ are number densities of n-dodecane and nitrogen molecules. $T \equiv T(x)$ is the temperature between the two plates.
4.7 Plots of \( n_d \) (a) and \( n_n \) (b) versus the distance \( x \) normalised by the mean free path \( \ell \) for three values of \( N_{\text{int}} \) for the setup shown in Figure 4.6.  

4.8 Plots of \( T_d \) (a) and \( T_n \) (b) versus the distance \( x \) normalised by the mean free path \( \ell \) for three values of \( N_{\text{int}} \) for the setup shown in Figure 4.6. 

4.9 Plots of normalised heat flux \( q \) versus \( N_{\text{int}} \) for pure n-dodecane and the mixture of n-dodecane and nitrogen for the setup shown in Figure 4.6. 

4.10 A schematic presentation of the evaporation of n-dodecane into nitrogen. n-dodecane is evaporated from the left plate with temperature kept at \( T_{w1} \) and is fully condensed on the right plate with temperature kept at \( T_{w2} \). \( L \) is the distance between two plates; \( n_d \) and \( n_n \) are number densities of n-dodecane and nitrogen molecules; \( T \equiv T(x) \) is the temperature between the two plates. 

4.11 Plots of \( n_d \) (a) and \( n_n \) (b) versus the distance \( x \) normalised by the mean free path \( \ell \) for four values of \( N_{\text{int}} \) for the setup shown in Figure 4.10. 

4.12 Plots of normalised mass flux of n-dodecane \( j \) versus \( N_{\text{int}} \) for the setup shown in Figure 4.10. 

5.1 Liquid phase, kinetic and hydrodynamic regions in the vicinity of droplet surface. \( T_s \) is the surface temperature of droplet, \( \rho_s \) is the vapour density in the immediate vicinity of the droplet surface, \( T_{Rd} \) and \( \rho_{Rd} \) are the temperature and density of vapour at the outer boundary of kinetic region. \( \delta_{Rd} \) indicates the thickness of kinetic region, \( j_v \) and \( q \) show the directions of vapour mass and heat fluxes, respectively. 

5.2 Plots of normalised heat flux \( \tilde{q}_{k} = q_k/(p_0\sqrt{R_vT_0}) \) in the kinetic region versus normalised temperature \( \tilde{T}_{Rd} = T_{Rd}/T_s \) for various numbers of internal degrees of freedom \( N_{\text{int}} \), assuming that \( T_s = T_0 = 600 \text{ K} \). \( \rho_{Rd} \) is taken equal to 0.9\( \rho_s \).
5.3 Plots of normalised heat flux $\tilde{q}_k$ in the kinetic region versus normalised density $\tilde{\rho}_{Rd} = \rho_{Rd}/\rho_s$ for $N_{int} = 20$ and $\tilde{T}_{Rd} = 1.1$ and 1.2.  

5.4 Plots of $\tilde{q}_k$ versus $\tilde{T}_{Rd}$ for $N_{int} = 0$ and 20, and the plot of $\tilde{q}_h = q_h/(\rho_0 \sqrt{R_v T_0})$ versus $\tilde{T}_{Rd}$ for $T_0 = T_s = 600$ K, $T_g = 1,000$ K, $R_{d0} = 5$ $\mu$m and $\tilde{\rho}_{Rd} = 1$. The intersections between the plots of $\tilde{q}_k$ and $\tilde{q}_h$ give the required values of $\tilde{T}_{Rd}$.  

5.5 Plots of $\tilde{j}_k = j_k/(\rho_0 \sqrt{R_v T_0})$ versus $\tilde{\rho}_{Rd}$ for $N_{int} = 0$ and 20, and the plot of $\tilde{j}_h = j_h/(\rho_0 \sqrt{R_v T_0})$ versus $\tilde{\rho}_{Rd}$ for $T_0 = T_s = 600$ K, $T_g = 1,000$ K, $R_{d0} = 5$ $\mu$m and $\tilde{T}_{Rd} = 1.026$. The intersections between the plots of $\tilde{j}_k$ and $\tilde{j}_h$ give the required values of $\tilde{T}_{Rd}$.  

5.6 Plots of $\tilde{j}_k$ versus $\tilde{\rho}_{Rd}$ for $N_{int} = 20$ and $\sigma_c = 1$ and 0.36 versus $\tilde{\rho}_{Rd}$ for $T_0 = T_s = 600$ K, $T_g = 1,000$ K, $R_{d0} = 5$ $\mu$m and $\tilde{T}_{Rd} = 1.026$.  

5.7 Plots of $R_d$ versus time $t$ for an n-dodecane droplet, predicted by hydrodynamic ITC model (curve 1), kinetic ITC model ignoring the effects of inelastic collisions (curve 2), the kinetic ITC model taking into account the effects of inelastic collisions (curve 3), hydrodynamic ETC model (curve 4), kinetic ETC model ignoring the effects of inelastic collisions (curve 5), kinetic ETC model taking into account the effects of inelastic collisions (curve 6) (a). Zoomed part of (a) shows the plots at the final stage of evaporation processes (b). All plots are shown for $T_g = 750$ K, $T_{d0} = 300$ K and $R_{d0} = 5$ $\mu$m.  

5.8 The same as Figure 5.7 but for $T_s$.  

5.9 The same as Figure 5.7 but for $T_g = 1,000$ K.  

5.10 The same as Figure 5.8 but for $T_g = 1,000$ K.
5.11 Plots of $R_d$ and $T_s$ versus time $t$ for an n-dodecane droplet, predicted by hydrodynamic ITC model (curve 1), kinetic ITC model ignoring the effects of inelastic collisions and non-unity of $\sigma_e$ (curve 2), the kinetic ITC model taking into account the effects of inelastic collisions but ignoring the non-unity of $\sigma_e$ (curve 3), the kinetic ITC model taking into account the effects of inelastic collisions and non-unity of $\sigma_e$ which is calculated based on Eq. (5.27) (curve 4) (a). Zoomed part of (a) shows the values of $R_d$ and $T_s$ at the final stage of the evaporation processes (b). Plot (a) is shown for $T_g = 1,000$ K, $T_{d0} = 300$ K and $R_{d0} = 5$ $\mu$m. 107

5.12 The same as Figure 5.11 but for $T_g = 1,500$ K. 108
List of Tables

2.1 Values of normalised parameters used in the MD simulations. . . . . . . 17

2.2 The results of liquid-vapour equilibrium simulations for n-dodecane (C_{12}H_{26}).

\( T_l \) is the liquid temperature, \( \rho_v \) is the saturated vapour density, \( \rho_l \) is the
liquid density, \( p_v \) is the vapour pressure, \( \delta \) is the thickness of the inter-
face, \( j_c \) is the mass flux density of condensed molecules, \( j_m \) is the
maximum mass flux density of molecules evaporated from the liquid
surface. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 18

2.3 Fractions of various condensation behaviours at \( T_l = 500 \) K. The values
in parentheses of \( \langle J_{\text{sp}} \rangle \), \( \langle J_{\text{tr}} \rangle \) and \( \langle J_{\text{ref}} \rangle \) columns are the fractions
of mass flux of spontaneous, trapping-desorption and reflection conden-
sations, respectively. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34

5.1 Condensation/evaporation coefficient as a function of the liquid temper-
ature. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 106
Nomenclature

Roman Symbols

\( a \) parameter introduced in Eq.(3.5)

\( A_0 \) parameter introduced in Eq.(5.25)

\( A_1 \) parameter introduced in Eq.(5.25)

\( a_{ij} \) elements of matrix \( A \)

\( A \) rotation matrix

\( b \) parameter introduced in Eq.(3.5)

\( B_1 \) parameter introduced in Eq.(5.25)

\( b_{ij} \) elements of source term introduced in Eq.(4.9)

\( B_M \) Spalding mass transfer number

\( B_T \) Spalding heat transfer number

\( c \) specific heat capacity

\( c_i \) torsion coefficient

\( C_F \) friction drag coefficient estimated by Eq.(5.15)
$D_{va}$ binary diffusion coefficient

$\mathbf{E}$ unit matrix

$\Delta E_0$ activation energy

$E$ energy

$\mathbf{e}$ unit vector

$f, F$ velocity distribution functions

$h$ convection heat transfer coefficient

$h_0$ parameter defined by Eq.(5.10)

$j$ mass flux

$J_{\alpha\beta}$ collision integrals

$k$ thermal conductivity

$k_\theta$ bending coefficient

$k_B$ Boltzmann constant

$L$ distance between two plates

$Le$ Lewis number

$La$ Latent heat of evaporation

$M$ molar mass

$m$ molecular mass

$N$ sample number
$n$ number density

$N_{int}$ number of internal degrees of freedom

$p$ momenta or pressure

$Pe$ droplet Peclet number

$Pr$ Prandtl number

$q$ heat flux

$q_n$ parameter defined by Eq.(5.11)

$r$ vector in the physical space

$\dot{R}_d$ the rate of change of droplet radius

$R$ distance form droplet centre

$r$ radius of the energy sphere

$R_{C_{12}H_{26}}$ gas constant of n-dodecane

$r_{ij}$ distance between atoms

$Re$ Reynolds number

$\Delta S$ entropy difference of a molecule between its liquid and gas states

$S$ orientation order parameter

$T$ temperature

$t$ time

$u$ potential between atoms
v velocity

v speed

$V^g$ specific volumes of gas

$V^l$ specific volumes of liquid

X energy vector

X molar fraction

$Y_{v,Rd}$ mass fraction of vapour at the interface between kinetic and hydrodynamic regions

**Greek Symbols**

$\chi$ parameter defined by Eq.(5.13)

$\kappa$ thermal diffusivity

$\ell$ molecular mean free path

$\lambda_n$ positive solutions to Eq.(5.9)

$\mu$ dynamic viscosity

$\mu_0$ parameter defined by Eq.(5.7)

$\Phi$ torsion angle

$\Phi_{ij}$ parameter introduced in the definition of $k_{mix}$

$\rho$ mass density

$\sigma$ diameter parameter of an atom or evaporation/condensation coefficient
\( \tau \)  time step

\( \theta_0 \)  equilibrium bending angle

\( \theta \)  bending angle

\( \Theta_n \)  function defined by Eq.(5.6)

\( \varepsilon \)  energy parameter of an atom

\( \varphi \)  angle between the direction of bonds and the plane normal to the \( x \)-axis or parameter defined by Eq.(5.24)

\( \xi \)  \( R/R_d \)

**Superscripts**

–  average

\( bend \)  bending potential

\( e \)  evaporation

\( LJ \)  Lennard-Jones potential

\( \sim \)  normalised

\( out \)  leaving the liquid-vapour interface from the liquid phase

\( + \)  summation

\( r \)  reflection

\( T \)  transpose

\( tors \)  torsion potential
Subscripts

\[ a \] air
\[ cr \] critical
\[ d \] droplet
\[ g \] gas
\[ h \] hydrodynamic region
\[ k \] kinetic region
\[ l \] liquid
\[ mix \] mixture
\[ r \] reference
\[ Rd \] interface between kinetic and hydrodynamic regions
\[ s \] droplet surface
\[ v \] vapour
\[ x \] velocity component in the \( x \) direction
\[ y \] velocity component in the \( y \) direction
\[ z \] velocity component in the \( z \) direction

Acronyms

AAM  All Atoms Model

CFD  Computational Fluid Dynamics
ETC  Effective Thermal Conductivity

GAFF  General Amber Force Field

IHS  Inelastic Hard Sphere

ITC  Infinity Thermal Conductivity

KBC  Kinetic Boundary Condition

MD  Molecular Dynamics

OPLS  Optimised Potential for Liquid Simulation

TST  Transition State Theory

UAM  United Atom Model
Chapter 1

Introduction

1.1 Background

The importance of accurate and computer efficient modelling of droplet heating and evaporation in engineering applications is widely accepted by research and industrial communities (Alexander et al. [2005]; Sazhin [2006]). Unless rarefied gases are considered, the conventional approach to this modelling has been based on the assumption that vapour in the vicinity of the droplet surface is always saturated. In this case, the rate of evaporation is essentially controlled by vapour diffusion from the vicinity of the droplet surface to the ambient gas (Sazhin [2006]). This hydrodynamic approach is almost universally used in the modelling of evaporation of liquid fuels in engineering applications (Diesel engines) and is incorporated into relevant computational fluid dynamics (CFD) codes. However, preliminary comparisons between the predictions of the simplified kinetic model and the hydrodynamic approach for typical fuel droplet evaporation in realistic Diesel engine-like conditions (gas pressure 30 bar) showed that the hydrodynamic approach can under-predict the droplet lifetime by about 5–10% (Kryukov et al. [2004]). This error is expected to lead to a corresponding error in
predicting the ignition delay in these engines and hence the combustion phasing (Crua [2002]; Lefebvre [1989]). This is likely to compromise the applicability of currently available CFD codes as predictive tools. Although the kinetic model introduced by Kryukov et al. [2004] correctly describes the general processes which take place during the evaporation, it is based on a number of simplified assumptions, which enabled the authors to formulate it in terms of the conservation equations at the outer boundary of the kinetic region and to describe the processes inside this layer using rather simplistic models. Hence, the results of the comparison between kinetic and hydrodynamic models reported by Kryukov et al. [2004] can be considered as preliminary. A schematic presentation of droplets heating and evaporation in the presence of the kinetic effects is shown in Figure 1.1.

![Diagram of different regions](image)

Figure 1.1: A schematic presentation of different regions related to the hydrodynamic approach, kinetic modelling and molecular dynamics simulations. \( \delta_{Tr} \) and \( \delta_{Kn} \) are the thickness of the transition layer and kinetic region, respectively.

In the mathematical modelling of the evaporation process, as shown in Figure 1.1, the hydrodynamic approach can provide a correct description of the bulk of the liquid and vapour phase regions. However, the exchange of the mass and energy between the two phases take place at the liquid-vapour interface and in the Knudsen layer,
across which the macroscopic quantities can be fully understood only on the basis of a microscopic theory, i.e., the kinetic theory (Frezzotti [2011]). The theory of evaporation and condensation has its foundations in the kinetic theory since the pioneering work of Hertz [1882] and Knudsen [1915] on the evaporation of liquid mercury into vacuum. The widely used formula for the net mass flux at the interface was derived by Hertz and Knudsen (Schrage [1953]). When deriving this formula, the collisions between molecules near the interface were ignored. These effects, however, may be significant and result in the inverse temperature gradient (Cercignani et al. [1985]; Koffman et al. [1984]; Pao [1971a,b]). The Knudsen layer structure, in the case of a dilute vapour phase, can be obtained by the well developed theoretical and numerical methods of the kinetic theory (Frezzotti [2007]; Frezzotti and Ytrehus [2006]; Ytrehus and Ostmo [1996]).

Further work in this direction was performed by Shishkova and Sazhin (EPSRC Grant EP/C527089/1). During their work, a new kinetic model for droplet evaporation into a high pressure background gas, approximated by air, was developed. The kinetic effects predicted by the new model turned out to be negligible when the contribution of air in the kinetic region is ignored. These effects, however, appeared to be noticeable and larger than those predicted by the approximate analysis, if the contribution of air in the kinetic region was taken into account (Sazhin et al. [2007]; Shishkova and Sazhin [2006]).

Despite considerable progress in the development of numerical kinetic models of evaporation, these models still had to be based on a number of assumptions and their applicability to Diesel engines is not at first evident. For example, it was assumed that the temperature of the outer boundary of the kinetic region is equal to the droplet surface temperature and heat transfer processes inside this layer can be ignored. This issue was addressed in the second EPSRC project (Grant EP/E02243X/1), in which
a new numerical algorithm for the solution of the Boltzmann equation, taking into account both mass and heat transfer processes in the kinetic region, was developed. The new algorithm was applied to the calculations of heating and evaporation of fuel droplets in Diesel engine-like conditions. It was demonstrated that in the case of droplet heating in a hot gas ($T_g = 1,000 - 1,500$ K), the effect of non-zero heat flux in the kinetic region is important. For droplets with initial radii $5 \mu$m the predicted evaporation time in the presence of the heat flux in the kinetic region proved to be about 14% longer than that predicted by the hydrodynamic model. The increase of this time in the case where the heat flux in the kinetic region is ignored would only be about 8%. The application of the rigorous kinetic model, taking into account the heat and mass fluxes in the kinetic region, was recommended when accurate predictions of the droplet surface temperature and evaporation time are essential (Sazhin and Shishkova [2009]). More detailed analysis of the Boltzmann equation and its applications are given by Bird [1994]; Cercignani [1988]; Chapman and Cowling [1970].

The main limitations of the models described above are that the evaporation coefficient for n-dodecane (C$_{12}$H$_{26}$, approximation of Diesel fuel) was assumed equal to 0.04, 0.5 or 1 at the liquid-vapour interface for the solution of the Boltzmann equation, and the contribution of inelastic collisions was ignored. Kryukov et al. [2004] considered two values of this coefficient, 0.04 and 0.5 (minimal and average values of this coefficient for water), while Shishkova and Sazhin [2006] and Sazhin et al. [2007] assumed that this coefficient is equal to 1. None of these values can be rigorously justified (see review of measurements and estimations of this coefficient for water by Marek and Straub [2001]). Thus, the results of the work on previous EPSRC projects enable us to illustrate the kinetic effects on the evaporation processes in Diesel fuel, but we still are not able to use our model as a predictive tool for engineering applications. Note that the evaporation and condensation processes in Diesel engines can be assumed to
be in equilibrium at the molecular level. Hence, the corresponding evaporation and condensation coefficients can be assumed to be equal. The condensation coefficient is defined as the ratio of the mass flux of incident molecules upon the liquid-vapour interface which are condensed in the liquid phase to the total mass flux of the incident molecules (Tsuruta et al. [1999]).

In the traditional kinetic theory, the liquid-vapour interface is described as a surface of zero thickness, i.e., the interface structure is not resolved. However, the interface between the liquid and vapour phases, as shown in Figure 1.1, is typically a couple of molecular diameters thick. The mathematical modelling of the liquid-vapour interface is difficult and a comprehensive theory of dense fluids has not been developed (Frezzotti [2011]; Frezzotti and Gibelli [2003]; Meland and Ytehus [2001]). In this case, molecular dynamics (MD) simulations can be used to study the liquid-vapour interface (Cao [2008]; Cao et al. [2005, 2006]; Cao and Guo [2007], see also Shishkova and Sazhin [2006] for a review of earlier results in this field). The simulation techniques developed so far have been applied either to monoatomic molecules or relatively simple polyatomic molecules, such as water (Tsuruta and Nagayama [2004]), methanol (Ishiyama et al. [2004a]; Nagayama et al. [2006]) and n-octane (Simon et al. [2006, 2004]). Also, a number of models have been developed to describe the dynamics of complex hydrocarbon molecules such as n-dodecane. These will be described in Chapter 2.

An alternative approach to this problem is based on the transition state theory (TST), or theory of the absolute reaction rates. In this approach, the free volume and free angle ratio were introduced to calculate the condensation coefficient by Kincaid and Eyring [1938]. Moreover, Mortensen and Eyring [1960] obtained the value of condensation coefficient by approximating the rotational partition function of activated state in the transition state to that in the liquid state. Maerefat et al. [1990] improved this method using statistical mechanics and derived the following expression for the
condensation coefficient

\[
\sigma_c = \frac{V^g}{V^l} \exp \left( -\frac{\Delta S}{k_B} \right),
\]  

(1.1)

where \(V^l\) and \(V^g\) are the specific volumes of liquid and gas respectively, \(\Delta S\) is the entropy difference between liquid and gas states of the molecule, and \(k_B\) is the Boltzmann constant. The values of the condensation coefficient obtained by Eq. (1.1) were shown to be in a good agreement with the experimental data for water and other polyatomic molecules. The value of unity, however, was predicted by Eq. (1.1) for all monatomic molecules. According to MD simulations, this coefficient for monatomic molecules is smaller than unity, and it decreases when the liquid temperature increases.

To further investigate the condensation process, Nagayama and Tsuruta [2003] considered the condensation process at the liquid-vapour interface as a kind of chemical reaction. The general theory of rate processes (Gladstone et al. [1941]) was applied. In this case, the molecules with sufficient energies can get into the activated state and are condensed in the liquid phase after passing through the energy barrier. The condensation coefficient, taking into account the partition function, can be expressed as

\[
\sigma_c = \left[ 1 - \left( \frac{V^l}{V^g} \right)^{1/3} \right] \exp \left( -\frac{E_0}{k_B T_l} \right),
\]  

(1.2)

where \(\Delta E_0\) is the activation energy and \(T_l\) is the liquid temperature. \(\Delta E_0\) can be obtained using the MD simulations:

\[
E_0 = \frac{1}{2} \frac{1}{\sqrt[3]{V^g/V^l} - 1} k_B T_l
\]
Therefore, the condensation coefficient can be presented as

\[
\sigma_c = \left[1 - \left(\frac{V^l}{V^g}\right)^{1/3}\right] \exp\left[-\frac{1}{2} \left(\frac{V^g}{V^l}\right)^{1/3} - 1\right].
\] (1.3)

The values of \(\sigma_c\), predicted by Eq. (1.3), depend on the surface temperature. They are close to 1 at the triple point due to \(V^l \ll V^g\) and decrease to 0 at the critical point due to \(V^l \approx V^g\).

On the other hand, the contribution of inelastic collisions to the processes in gases has been considered in numerous papers. However, to the best of our knowledge, all these papers were focused either on the analysis of collisions between inelastic spheres (Biben et al. [2002]; Santos [2003]) or simple diatomic or triatomic molecules (Kondo et al. [2004]; Koura [1998]). The generalisation of these models to complex hydrocarbon molecules is not feasible at the moment.

### 1.2 Motivation and Objectives

The main purpose of this thesis is to investigate the heating and evaporation of fuel droplets in Diesel engine-like conditions. When dealing with the small droplets in a high gas temperature, the kinetic effects are noticeable in the vicinity of the droplet surface (see Figure 1.1). Theoretical predictions of the evaporation/condensation coefficient, obtained based on the transition state theory, were shown to be in good agreement with the results of molecular dynamics simulations for argon (Nagayama and Tsuruta [2003]; Tsuruta et al. [1999]), water (Tsuruta and Nagayama [2004]) and methanol (Ishiyama et al. [2004a]; Nagayama et al. [2006]). It is not clear, however, whether this approach can be applied to complex molecules such as n-dodecane (C_{12}H_{26}) with long chain structures. The transition state theory does not consider detailed structures and motions in chain-like molecules and complex evaporation/condensation behaviours.
The application of Eq. (1.3) to n-dodecane needs more rigorous justification, based on molecular dynamics simulations. Thus, the evaporation/condensation coefficient will be investigated at the liquid-vapour interface using the molecular dynamics simulations (see Figure 1.1).

Although the analysis of the dynamics of n-dodecane molecules is simplified by considering the united atom model (Cao et al. [2011]), the number of internal degrees of freedom of this molecule is expected to exceed one hundred. There seems to be no justification for ignoring their contribution. Therefore, the thesis will also focus on the development of a new numerical algorithm for the solution of the Boltzmann equation, taking into account the contribution of inelastic collisions between molecules in the kinetic region (see Figure 1.1).

The main objectives in this thesis are the following:

1) To develop a molecular dynamics algorithm for complex hydrocarbon molecules of n-dodecane.

2) To estimate the evaporation/condensation coefficient of n-dodecane for a wide range of parameters relevant to Diesel engine-like conditions.

3) To develop a new numerical algorithm for the solution of the Boltzmann equation, taking into account the effects of inelastic collisions between complex hydrocarbon molecules.

4) To perform the kinetic modelling of heating and evaporation of n-dodecane droplets in Diesel engine-like conditions, taking into account the effects of inelastic collisions in the kinetic region, a non-unity evaporation coefficient, and temperature gradient inside the droplet.

It is anticipated that meeting these objectives will lead to the development of a new quantitative kinetic model for complex hydrocarbon fuel droplet heating and evaporation in Diesel engine-like conditions.
1.3 Thesis Structure

At first the focus of the thesis will be on the development of a molecular dynamics simulation technique for the evaporation and condensation of complex hydrocarbon molecules of n-dodecane (C_{12}H_{26}) in terms of the united atom model (Chapter 2). Then the focus will shift to the application of this technique to determination of the evaporation/condensation coefficient of n-dodecane and investigation of the velocity distribution functions in the vicinity of the vapour-liquid interface, in order to provide boundary conditions for the kinetic equations (Chapter 3). Then a new numerical algorithm for the Boltzmann equation taking into account the inelastic collisions between complex hydrocarbon molecules is described (Chapter 4). This algorithm is applied to modelling of the heating and evaporation of complex hydrocarbon fuel droplets in Diesel engine-like conditions (Chapter 5). Finally, the main conclusions are drawn and future work is suggested (Chapter 6). The results of this thesis have been reported in a number of journal articles (Cao et al. [2011]; Sazhin et al. [2013]; Shishkova et al. [2013]; Xie et al. [2011c, 2012a]) and refereed conference proceedings (Sazhin et al. [2012a,b, 2011a, 2012c]; Xie et al. [2011a,b, 2012b]).
Chapter 2

Molecular Dynamics Study on Evaporation and Condensation

2.1 Introduction to Chapter 2

As mentioned in the general introduction, rigorous estimation of the evaporation and condensation coefficients requires the application of molecular dynamics technique (Cao [2008]; Cao et al. [2005, 2006]; Cao and Guo [2007]). Perhaps one of the most advanced molecular dynamics investigations of these coefficients for water was reported by Tsuruta and Nagayama [2004]. In that paper, two models for intermolecular potential were used: the Carravetta and Clementi model (Carravetta and Clementi [1984]) and the extended simple point charge model (Berendsen et al. [1987]). In both models, the intermolecular interactions were treated as a combination of the short-range pairwise potential of atoms and the long-range Coulombic interaction. The predictions of the extended simple point charge model were shown to be in better agreement with the experimental data than those of the Carravetta and Clementi model. It was pointed out that translational motion is of primary importance for the evaporation/condensation
process, whereas the effects of rotational motion are insignificant.

The results of molecular dynamic simulations for argon and water were shown to be in good agreement with the prediction of the evaporation/condensation coefficient by the transition state theory, developed by Penner [1948a,b]. This theory was further improved by Nagayama and Tsuruta [2003]. In the latter paper, condensation/evaporation processes at the liquid-vapour interface were considered as a kind of chemical reaction and the general theory of rate processes was applied (Gladstone et al. [1941]) (see Eq. (1.3) of Chapter 1). As for n-dodecane (C₁₂H₂₆) molecules, they have chain-like structures and complex evaporation/condensation behaviours. The application of Eq. (1.3) to n-dodecane needs to be validated based on molecular dynamics simulations.

A number of models have been developed to describe the dynamics of complex hydrocarbon molecules such as n-dodecane (C₁₂H₂₆), including the OPLS (Optimised Potential for Liquid Simulation) originally introduced by Jorgensen et al. [1984], the de Pablo et al. [1993], Toxvaerd [1990] and Padilla and Toxvaerd [1991] models. These models are reviewed by Smit et al. [1995] and they also suggested their new model. This new model is based on the OPLS potentials and is claimed to be more accurate than the previous models. All these models are based on the observation that the C-H bond in complex hydrocarbon molecules is much shorter and much stronger than the C-C bond, and also stronger than the van der Waals forces between molecules. Thus the methyl (CH₃) or methylene (CH₂) groups can be regarded as separate atom-like structures in a relatively simple united atom model (Simon et al. [2004]). The underlying physics of all these models is essentially the same, but they differ from the energy parameters and diameters of CH₃ and CH₂ groups, and bond bending and torsion potentials. Smit et al. [1995] applied all the above mentioned models to complex hydrocarbons to determine their vapour-liquid coexistence curves using the Gibbs-ensemble technique and
the configuration-bias Monte Carlo method. All models gave nearly identical results at standard conditions but predicted critical temperatures which could differ by up to 100 K. It was claimed that the new model developed by Smit et al. [1995] gave a good description of the phase behaviour of this curve over a large temperature range. Besides, Simon et al. [2004] applied the Toxvaerd model (Toxvaerd [1990], Padilla and Toxvaerd [1991]) to the molecular dynamic simulation of n-octane. Previous molecular dynamics simulations of n-alkane liquid-vapour interfaces focused on interfacial properties, such as phase equilibria, interface tension and thermodynamic parameters (Amat and Rutledge [2010]; Harris [1992]; Ibergay et al. [2007]; Simon et al. [2006]; Zahn [2008]). However, none of these studies focused on the molecular dynamics analysis of the vapour-liquid equilibria of n-dodecane (C\textsubscript{12}H\textsubscript{26}) (the closest approximation to Diesel fuel) and the estimation of the evaporation/condensation coefficient for this substance.

Alternatively, the molecular dynamics simulation of n-dodecane (C\textsubscript{12}H\textsubscript{26}) in an equilibrium system has been also performed using AMBER version 10.0 (a package of molecular simulation programmes) (Mizuguchi et al. [2010]). In that paper, the general Amber force field (GAFF) has been applied and the potential energy has been presented as a sum of bending, torsion, van der Waals and Coulomb energies. As this molecular simulation package takes the hydrogen atoms explicitly into account, it can be called the all atoms model (AAM). Due to the increased number of interactions taken into account, this all atoms model is much more time-consuming compared with the united atom model (UAM). Hence, the attractiveness of the UAM model for practical engineering applications is easily seen. Moreover, the UAM has been successfully used for modelling the phase behaviour of a large number of n-alkanes ranging from pentane (C\textsubscript{5}H\textsubscript{12}) to octatetracontane (C\textsubscript{48}H\textsubscript{98}) (Smit et al. [1995]).

In this chapter, the OPLS potential is applied to study the n-dodecane (C\textsubscript{12}H\textsubscript{26})
liquid-vapour interface and the phase transition phenomena. In Section 2.2, the details for the model and simulation method are introduced. In Section 2.3, the model and method are applied to identify the density profile, interfacial thickness, chain orientation and typical evaporation/condensation behaviours at the n-dodecane liquid-vapour interface. The main results are summarised in Section 2.4.

2.2 Model and Simulation

2.2.1 Intermolecular potential

Our simulation is based on the UAM and we refer to united atoms as atoms and to molecules as chains. The essence of the united atom model, applied to an n-dodecane molecule, is schematically illustrated in Figure 2.1.

![Figure 2.1: Schematic presentation of an n-dodecane (C_{12}H_{26}) molecular (a) and its presentation using united atom model (b). The bending angles between neighbouring bonds (~114°) (zigzag structure of the molecule) are taken into account.](image)

The non-bonded interactions between atoms, which belong to either different chains or the same chain but more than four atoms apart (there should be at least 3 atoms between the interacting atoms, see Figure 2.2), are characterised by the truncated
Lennard-Jones (L-J) 12-6 potential (Allen and Tildesley [1987]; Rapaport [1995]),

\[ u^{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]. \] (2.1)

The energy parameters of CH$_2$ and CH$_3$ groups are $\varepsilon_{CH_2}/k_B = 47$ K and $\varepsilon_{CH_3}/k_B = 114$ K, respectively. According to the geometric rule, the energy parameter between CH$_2$ and CH$_3$ groups is estimated as $\varepsilon_{CH_2-CH_3}/k_B = \sqrt{\varepsilon_{CH_2}\varepsilon_{CH_3}/k_B} = 73.2$ K. The diameters of CH$_2$ and CH$_3$ groups are assumed to be equal and estimated as $\sigma_{ij} = \sigma = 3.93 \times 10^{-10}$ m. The L-J 12-6 interaction is truncated at $13.8 \times 10^{-10}$ m in our simulations.

The interactions within the chains include bond bending and torsion with the bond length constrained at $1.53 \times 10^{-10}$ m. The bending can take place between any three neighbouring atoms and the potential introduced by van der Ploeg and Berendsen [1982] is used:

\[ u^{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2, \] (2.2)
where the bending coefficient is estimated as \( k_\theta/k_B = 62.500 \text{ K/rad}^2 \), and the equilibrium angle is \( \theta_0 = 114^\circ \) (see Figure 2.1). The torsion can take place between four neighbouring atoms and the torsion potential introduced by Jorgensen et al. [1984] is applied:

\[
u^{\text{tors}}(\Phi) = c_0 + 0.5c_1 (1 + \cos \Phi) + 0.5c_2 (1 - \cos 2\Phi) + 0.5c_3 (1 + \cos 3\Phi), \quad (2.3)
\]

where \( c_0/k_B = 0 \text{ K}, c_1/k_B = 355 \text{ K}, c_2/k_B = -68.19 \text{ K}, c_3/k_B = 791.3 \text{ K} \) and \( \Phi \) is the torsion dihedral angle. Its equilibrium value is \( 180^\circ \). The details of calculations of forces and potentials can be found in Appendix A.

### 2.2.2 Equilibrium simulation of a liquid-vapour system

Systems consisting of 400 (Cao et al. [2011]) and 720 (Xie et al. [2011c]) n-dodecane (\( \text{C}_{12}\text{H}_{26} \)) molecules have been considered. In the case of 720 molecules (8640 CH\(_3\) and CH\(_2\) groups) a three-dimensional rectangular simulation box of \( L_x \times L_y \times L_z = 64.24\sigma \times 16.48\sigma \times 16.48\sigma \) (\( \sigma \) is the rescaled length given in Table 2.1, and \( L_x, L_y \) and \( L_z \) are the lengths of the simulation box in the \( x, y \) and \( z \) directions) was used for liquid temperatures 400 K, 450 K, 500 K and 550 K (Xie et al. [2011c]). The size of this box corresponds to \( 25.25 \text{ nm} \times 6.48 \text{ nm} \times 6.48 \text{ nm} \). These molecules were initially oriented along the \( x \) axis and placed in the middle of the simulation box (see Figure 2.3(a)). They had zigzag configurations (see Figure 2.1), and the numbers of molecules in the \( x, y \) and \( z \) directions were taken to be 5, 12 and 12, respectively.

The equations of motion of the atoms were integrated using the Verlet leapfrog method (Allen and Tildesley [1987]; Rapaport [1995]). For n-dodecane chains, the bond length constraints refer only to the near-neighbour atoms, and the bond lengths are
Figure 2.3: Snapshots of the simulation box $64.24\sigma \times 16.48\sigma \times 16.48\sigma$ for 720 n-dodecane molecules: initial state (a) and liquid-vapour quasi-equilibrium state at 400 K (b), 450 K (c), 500 K (d) and 550 K (e), respectively.
Table 2.1: Values of normalised parameters used in the MD simulations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass ($m^*$)</td>
<td>$m_{CH_2} = 2.3252 \times 10^{-26}$ kg</td>
</tr>
<tr>
<td>Energy ($\varepsilon^*$)</td>
<td>$\varepsilon_{CH_2} = 0.6486 \times 10^{-21}$ J</td>
</tr>
<tr>
<td>Length ($l^*$)</td>
<td>$\sigma = 3.93 \times 10^{-10}$ m</td>
</tr>
<tr>
<td>Temperature ($T^*$)</td>
<td>$\varepsilon_{CH_2}/k_B = 47$ K</td>
</tr>
<tr>
<td>Density ($\rho^*$)</td>
<td>$m_{CH_2}/\sigma^3$ kg/m$^3$</td>
</tr>
<tr>
<td>Time ($t^*$)</td>
<td>$\tau = \sigma \sqrt{m_{CH_2}/\varepsilon_{CH_2}}$ s</td>
</tr>
<tr>
<td>Velocity ($v^*$)</td>
<td>$\sigma/\tau = 167$ m/s</td>
</tr>
</tbody>
</table>

constrained by the SHAKE scheme adjusting the atom coordinates one by one cyclically to satisfy a given tolerance (Allen and Tildesley [1987]; Rapaport [1995]; Ryckaert et al. [1977]). The time step in all simulations was taken equal to 0.002 $\tau$, which corresponds to 5 fs ($1$ femtosecond $= 10^{-15}$ second). Periodic boundary conditions were applied in all directions. To achieve higher calculation efficiency, reduced units were used for physical parameters as indicated by the superscript * in Table 2.1 (other thermodynamic parameters are reported by Cao [2008]). The system was relaxed with a constraint of fixed homogeneous and isotropic temperature. The molecules began to relocate within the liquid phase and to evaporate gradually. We monitored the system temperature, pressure, density, molecular configuration and interface locations to determine whether or not the system had reached quasi-equilibrium state. Typically this required 15,000 ps. The term quasi-equilibrium is used by following Tsuruta and Nagayama [2004] to indicate a state reasonably close to equilibrium, although we are not able to quantify the closeness of this state to the perfect equilibrium state. At the quasi-equilibrium state, the liquid film was sandwiched between the layers of the vapour phases (see Figure 2.3(b)-(e) for temperatures 400 K, 450 K, 500 K and 550 K). The densities in the liquid and vapour zones gradually approached to those of actual liquid and vapour. Then we started sampling data for another 10,000 ps. The positions of the two liquid-vapour interfaces were identified by the density profiles. The interface
Table 2.2: The results of liquid-vapour equilibrium simulations for n-dodecane (C\textsubscript{12}H\textsubscript{26}). T\textsubscript{l} is the liquid temperature, \( \rho_v \) is the saturated vapour density, \( \rho_l \) is the liquid density, \( p_v \) is the vapour pressure, \( \delta \) is the thickness of the interface, \( j_c \) is the mass flux density of condensed molecules, \( j_m \) is the maximum mass flux density of molecules evaporated from the liquid surface.

<table>
<thead>
<tr>
<th>( T_l ) [K]</th>
<th>( \rho_v ) [kg/m\textsuperscript{3}]</th>
<th>( \rho_l ) [kg/m\textsuperscript{3}]</th>
<th>( p_v ) [atm]</th>
<th>( \delta ) [10\textsuperscript{-9}m]</th>
<th>( j_c ) [kg/(m\textsuperscript{2}s)]</th>
<th>( j_m ) [kg/(m\textsuperscript{2}s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2.832</td>
<td>668.3</td>
<td>0.544</td>
<td>2.27</td>
<td>141.63</td>
<td>157.37</td>
</tr>
<tr>
<td>450</td>
<td>5.647</td>
<td>628.3</td>
<td>1.224</td>
<td>2.78</td>
<td>230.38</td>
<td>333.88</td>
</tr>
<tr>
<td>500</td>
<td>9.737</td>
<td>588.3</td>
<td>2.345</td>
<td>3.28</td>
<td>358.04</td>
<td>606.85</td>
</tr>
<tr>
<td>550</td>
<td>12.376</td>
<td>548.3</td>
<td>3.279</td>
<td>3.53</td>
<td>364.04</td>
<td>808.97</td>
</tr>
</tbody>
</table>

parameters, such as density and evaporation/condensation coefficient, were obtained by averaging them over these 10,000 ps. The effects of hydrodynamic turbulence have not been taken into account in our analysis.

The system consisting of 720 molecules enabled us to perform the molecular dynamics simulations using a standard PC (2.83 GHz CPU, 4 GB RAM work station) over a reasonable time period (just over one week per simulation).

2.3 Simulation Results and Discussions

2.3.1 Liquid-vapour phase quasi-equilibrium at the interface

Quasi-equilibrium density profiles at temperatures 400 K, 450 K, 500 K and 550 K are shown in Figure 2.4 for the simulations using 720 molecules. These profiles are time-averaged over 5,000 ps during a steady state period. The densities of liquid phase are lower at higher liquid temperatures in this figure. The liquid-vapour coexistence curve is shown in Figure 2.5 and the densities of vapour and liquid phases are presented in Table 2.2. As follows from this figure, our results agree reasonably well with experimental data (Maxwell [1955]) and the results of the Monte Carlo simulations (Smit et al. [1995]).
Figure 2.4: Density profiles for temperatures 400 K, 450 K, 500 K, and 550 K.

Figure 2.5: Liquid and vapour densities versus temperatures at phase equilibria.
Figure 2.6: The thickness of the liquid-vapour interface versus reduced liquid temperature, as predicted by the present MD simulations for n-dodecane, and inferred from the published results for argon, water, and methanol. The reduced temperature is defined as the ratio of the liquid temperature to the critical temperature.

The thickness of the transition layer at the liquid-vapour interface (interface thickness) is defined as the thickness of the region where the bulk vapour phase changes to the bulk liquid phase. In Figure 2.4, this refers to the thickness over which the density of n-dodecane changes from $0.95\rho_l$ to $(\rho_v + 0.01\rho_l)$, where $\rho_l$ and $\rho_v$ are densities of liquid and vapour, respectively (Tsuruta and Nagayama [2004]). The calculated values of the interface thickness of n-dodecane are presented in Table 2.2 and are also plotted in Figure 2.6. In the same figure, the interface thickness for argon, water and methanol, reported by Ishiyama et al. [2004a]; Tsuruta and Nagayama [2004], are also presented. As one can see in Figure 2.6, the thickness of the transition layer of n-dodecane increases from about 2.3 to 3.5 nm when the reduced temperature increases from about 0.60 to about 0.85, which corresponds to temperatures increased from 400 to 550 K. The reduced temperature is defined as the ratio of the liquid temperature to the critical temperature. These values are noticeably larger than those of argon (Tsuruta and Nagayama [2004]), water (Tsuruta and Nagayama [2004]) and methanol (Ishiyama et al.
(note that critical temperatures for argon, water and methanol are 150.86 K, 647.13 K and 403.73 K, respectively). The greater thickness of the transition layer at high temperatures may reduce the evaporation/condensation probability of n-dodecane molecules at the liquid surface. For chain-like n-dodecane molecules, the large thickness of the transition layer would act as a barrier to the condensation of vapour molecules or the evaporation of molecules leaving the liquid surface. Hence, it is expected that the increased thickness of the transition layer at high temperatures would result in smaller evaporation/condensation coefficients. This is confirmed by our estimates of the evaporation/condensation coefficient discussed later in Chapter 3.

The effects of non-homogeneous local temperatures have been discussed by Consolini et al. [2003]; Matsumoto [1998]; Matsumoto et al. [1995]; Tsuruta and Nagayama [2004]; Wang et al. [2001]. These effects are linked with the deviation from a thermo-static equilibrium of molecules near the interfaces. The translational and rotational energies of molecules are averaged separately and the results for 400 molecules are shown in Figure 2.7. As follows from Figure 2.7(a), both translational and rotational energies are rather low and almost equal to each other in the liquid phase. The translational energies of vapour chains near the interface, however, are generally larger than their rotational energy, although considerable fluctuations of these energies are clearly seen (especially in the case of translational energies). This is consistent with the results reported in the literature and can be related to the fact that vapour in the Knudsen layer adjacent to the liquid-vapour interface is in a non-equilibrium state (Aoki et al. [1990]; Labuntsov and Krykov [1979]; Sone and Onishi [1978]; Tsuruta and Nagayama [2004]). The Knudsen number is estimated to be in the range of 1-10 for temperatures under consideration. For a larger simulation box shown in Figure 2.7(b), the results are similar to those shown in Figure 2.7(a). As follows from Figure 2.7(b), there is a clearly recognised trend for translational and rotational energies to approach each other when
Figure 2.7: Local translational and rotational kinetic energies (normalised by $\epsilon_{\text{CH}_2}$ given in Table 2.1) of n-dodecane versus their positions along $x$ axis at 500 K for simulation boxes $51.39\sigma \times 13.73\sigma \times 13.73\sigma$ (a) and $137.04\sigma \times 13.73\sigma \times 13.73\sigma$ (b).
the distance from the liquid surface increased. This means that the system approaches
the quasi-equilibrium state in the gas phase away from this surface, according to the
equipartition of energy.

2.3.2 Chain orientation at the interface

The degree of the molecular ordering at the interface is quantified by the orientation
order parameter \( S(x) \) based on the second order Legendre polynomial (Maxwell [1955]):

\[
S(x) = \frac{1}{2} \langle 3\sin^2 \varphi - 1 \rangle,
\]

where \( \varphi \) is the angle between the direction of the bonds and the plane perpendicular
to the \( x \) axis (this plane is parallel to the interface); the averaging was performed over
all bonds within a specified slab in the \( x \) direction. The range of this parameter is
\([-0.5, 1]\). Its positive values indicate the preferential alignment normal to the interface
plane (i.e. parallel to the \( x \) axis). Negative values indicate the preferential alignment
parallel to the interface (i.e. normal to the \( x \) axis). Values near zero show the random
alignment. Note that the orientation refers to the backbone of the chains.

Typical values of the orientation parameter \( S(x) \) based on the simulation of 400
molecules at 500 K are shown in Figure 2.8. As can be seen from this figure, the
chain orientation parameter fluctuates greatly, which implies that the directions of the
chains are not completely random in most cases. At the interface region, the orientation
parameter tends to be negative (up to \(-0.05\)). Thus, the chains lie preferentially (but
not completely, which would have been achieved for \( S(x) = -0.5 \)) parallel to the
interface, which is consistent with the results obtained for other polymer or n-alkane
chains (Harris [1992]; Kawamata and Yamamoto [1997]; Pierce et al. [2008]; Tsige and
This orientation of the chains tends to increase their bonding with the interface and contributes to its stability. Also, this orientation restricts the rotation of molecules in the immediate vicinity of the interface, which is consistent with the earlier mentioned observation that the translation of the chains contributes more to evaporation, than does their rotation.

### 2.3.3 Molecular mechanism of evaporation and condensation

The mechanism of evaporation and condensation of n-dodecane has been studied in detail by recording the trajectories and translational energies of molecules (Xie et al. [2011c]). Examples, based on the simulations of 720 molecules, are shown in Figures 2.9-2.12. As follows from Figure 2.9, a molecule escapes from the bulk of the liquid and is evaporated (see Figure 2.9(a)) when its translational energy abruptly increases (see Figure 2.9(b)). In the case shown in Figure 2.10, the condensation of a molecule is accompanied by the reduction of its translational energy (see Figure 2.10(b)). This
energy in the liquid phase remains close to the mean kinetic energy of the system. In the case shown in Figure 2.11, a molecule gathers large translational energy and moves outward from the bulk of the liquid towards the interface; during this process, it collides with other molecules and loses most of its translational energy before it reaches the interface (see Figure 2.11(b)). As a result, the molecule returns to the liquid phase (see Figure 2.11(a)). In the case shown in Figure 2.12, the molecule with large translational energy in the vapour phase enters the interface and then it returns to the vapour phase (see Figure 2.12(a)) due to colliding with other molecules at the interface and losing most of its translational energy (see Figure 2.12(b)). The evaporation and condensation behaviours shown in Figures 2.9-2.12 allow us to conclude that the translational energy plays an important role in the evaporation and condensation processes. Note that Figures 2.9-2.12 are complementary to Figure 2.14 discussed in subsection 2.3.4, where a number of trajectories of molecules are presented although without accompanying the translational energies (Cao et al. [2011]).

The effect of the translational energy on the evaporation and condensation processes of n-dodecane is similar to its effect on the monatomic molecule of argon (Tsuruta et al. [1999]) and polyatomic molecules of water and methanol (Nagayama and Tsuruta [2003]). This supports the idea of activation energy in the liquid-vapour transition, which follows from the transition state theory (Nagayama and Tsuruta [2003]). The transition layer builds a three-dimensional structure at the liquid-vapour interface with a kind of interfacial resistance, as discussed in subsection 2.3.1. The fact that the molecules in the transition layer preferentially lie parallel to the interface is expected to contribute to the blocking of molecular evaporation and condensation.
Figure 2.9: A typical time history of a spontaneously evaporating n-dodecane molecule at 500 K: (a) trajectory of the molecules in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).
Figure 2.10: A typical time history of a spontaneous condensing n-dodecane molecule at 500 K: (a) trajectory of the molecule in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).
Figure 2.11: A typical time history of a reflection condensation n-dodecane molecule in the liquid phase at 500 K: (a) trajectory of the molecule in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).
Figure 2.12: A typical time history of a reflection evaporation n-dodecane molecule in the vapour phase at 500 K: (a) trajectory of the molecule in the physical space; (b) time evolution of its translational energy (normalised by $\varepsilon_{CH_2}$ given in Table 2.1).
2.3.4 Typical evaporation and condensation behaviours

Several evaporation and condensation behaviours of simple molecules, such as argon, methanol, and water, have been discussed in literatures (Matsumoto [1998]; Matsumoto et al. [1995]; Wang et al. [2001]) and are summarised in Figure 2.13(a). As follows from our analysis, the behaviour of chain molecules can be more complex and it is schematically presented in Figure 2.13(b). The evaporation and condensation behaviours of simple molecules normally include spontaneous evaporation/condensation, reflection evaporation and molecular exchange, as shown in Figure 2.13(a). The behaviours of chains include spontaneous evaporation/condensation (Cases 1 and 3 in Figure 2.13(b)), reflection evaporation/condensation (Cases 2 and 4 in Figure 2.13(b)), and trapping-desorption evaporation/condensation (Cases 5 and 6 in Figure 2.13(b)). Comparing Figures 2.13(a) with (b) one can see that Cases 1, 2 and 3 (spontaneous evaporation/condensation and reflective evaporation) are the same for simple and chain molecules. We have not, however, observed any cases of molecular exchange (Case 4 in Figure 2.13(a)) for chain molecules. This can be related to the fact that chain molecules collide with several molecules in the liquid phase simultaneously and the energy transferred to individual molecules appears to be insufficient to remove new molecules from liquid phase. To the best of our knowledge, reflection condensation (Case 4 in Figure 2.13(b)) has never been reported for simple molecules. This can be related to the fact that the collision cross-sections of chain molecules in the interface region are larger, compared with simple molecules. Hence the likelihood of chain molecules leaving the liquid phase to return to it from the interface is higher, compared with simple molecules. Note that even for chain molecules, this case is rarely observed. Also, trapping-desorption evaporation/condensation (Cases 5 and 6 in 2.13(b)) have never been reported for simple molecules. In these cases, the chains can be trapped inside the liquid-vapour interface for a long time and lose their original memory: vapour
or liquid.

Figure 2.13: Schematic presentation of typical evaporation and condensation behaviours of simple molecules (a) and n-dodecane chains (b).

All six cases for chain molecules, schematically shown in Figure 2.13(b), are illustrated in Figure 2.14, based on the analysis of trajectories (positions along x axis) of the mass centres of 400 individual n-dodecane molecules. A classic example of the spontaneous evaporation process (Case 1 in Figure 2.13(b)) is illustrated in Figure 2.14(a). As can be seen in this figure, the trajectory of the molecule in the liquid phase is rather complex, but its penetration time through the interface is very short. An example of reflection evaporation (Case 2 in Figure 2.13(b)) is illustrated in Figure 2.14(b). As can be seen in this figure, the trajectory of the molecule in the vapour phase is rather complex and it stays for a relatively short time at the interface (although longer than in the case of spontaneous evaporation, as shown in Figure 2.14(a)). The cases of spontaneous and reflection condensations, shown in Figures 2.14(c) and (d), are almost mirror images of the cases of spontaneous and reflection evaporations shown in Figures 2.14(a) and (b). For spontaneous condensation, the trajectory of the molecule in the vapour phase is rather complex, but the penetration time through the interface
is relatively short (although longer than for spontaneous evaporation). With regard to reflection condensation, the trajectory of the molecule is also complex. It leaves the liquid phase and returns to it four times during the period, as shown in Figure 2.14(d). The cases of trapping-desorption evaporation/condensation (Cases 5 and 6 in Figure 2.13(b)) are illustrated in Figure 2.14(e). The main difference between these cases and the ones considered earlier is that the molecules spend much more time at the interface, compared with the cases shown in Figures 2.14(a)-(d). During this stay at the interface, the molecules effectively lose their original memory, as mentioned earlier. The trapping-desorption evaporation process is illustrated on the left hand side of Figure 2.14(e). The evaporated molecule reaches the computational boundary at large positive $x$ axis. Since the periodic boundary condition is imposed at this boundary, the molecule re-emerges at another periodic boundary at negative $x$ axis. Eventually, it re-enters the liquid phase after spending considerable time at the interface (trapping-desorption condensation).

Note that the above mentioned Cases 1-6 in Figure 2.14 make different contributions to evaporation and condensation processes. As shown in Table 2.3, for the case of 400 molecules the molecular mass fluxes of spontaneous condensation $\langle J_{\text{sp} cond} \rangle$, trapping-desorption condensation $\langle J_{\text{trap} cond} \rangle$ and reflection condensation $\langle J_{\text{refl} cond} \rangle$ are 62.2 kg/(m$^2$s), 270 kg/(m$^2$s) and 290.8 kg/(m$^2$s), which correspond to 10%, 43.3% and 46.7%, respectively. This indicates that the trapping-desorption condensation contributes more than the spontaneous condensation does. Also, we can see from Table 2.3 that for the system with 720 molecules the same trends are observed. The molecular mass fluxes of spontaneous condensation, trapping-desorption condensation and reflection condensation are 83 kg/(m$^2$s), 332 kg/(m$^2$s) and 270 kg/(m$^2$s), which correspond to 12.1%, 48.4% and 39.5%, respectively. This trend is attributed to the ordering of the n-dodecane molecules inside the liquid-vapour interface. A molecule cannot easily get through a
Figure 2.14: Typical trajectories of the mass centres of n-dodecane molecules during spontaneous evaporation (a), reflection evaporation (b), spontaneous condensation (c), reflection condensation (d) and trapping-desorption evaporation/condensation (e).
Table 2.3: Fractions of various condensation behaviours at $T_l = 500$ K. The values in parentheses of $\langle J_{\text{spon}}^{\text{cond}} \rangle$, $\langle J_{\text{trap}}^{\text{cond}} \rangle$ and $\langle J_{\text{refl}}^{\text{cond}} \rangle$ columns are the fractions of mass flux of spontaneous, trapping-desorption and reflection condensations, respectively.

<table>
<thead>
<tr>
<th>Molecules (Atoms)</th>
<th>$\langle J_{\text{spon}}^{\text{cond}} \rangle$ [kg/m$^2$s]</th>
<th>$\langle J_{\text{trap}}^{\text{cond}} \rangle$ [kg/m$^2$s]</th>
<th>$\langle J_{\text{refl}}^{\text{cond}} \rangle$ [kg/m$^2$s]</th>
<th>$J_{\text{out}} = \rho_v \sqrt{RT_l/(2\pi)}$ [kg/m$^2$s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 (4800)</td>
<td>62.2 (10.0%)</td>
<td>270.0 (43.3%)</td>
<td>290.8 (46.7%)</td>
<td>623.0</td>
</tr>
<tr>
<td>720 (8640)</td>
<td>83.0 (12.1%)</td>
<td>332.0 (48.4%)</td>
<td>270.0 (39.5%)</td>
<td>685.0</td>
</tr>
</tbody>
</table>

stable array of chain layers. Hence, the molecular behaviour should be taken into account when studying the evaporation and condensation of n-dodecane, and probably other n-alkanes.

Note that there is some ambiguity regarding the physical nature of the “reflection condensation”. In fact, we could say that in this case the liquid molecule does not evaporate and condense. We still refer to it as condensation, keeping in mind the above mentioned comment. The main difference between “trapping-desorption evaporation/condensation” and “spontaneous evaporation/condensation” is the length of time molecule stays in the interface region. We appreciate that it would be difficult to take into account reflection condensation and trapping-desorption evaporation/condensation in kinetic modelling and experimental measurements.

2.4 Conclusions to Chapter 2

Evaporation and condensation for n-dodecane ($C_{12}H_{26}$) at liquid temperatures 400–600 K have been studied based on molecular dynamics simulations, using 400 (Cao et al. [2011]) and 720 (Xie et al. [2011c]) molecules. A modified OPLS model, taking into account the Lennard-Jones, bond bending and torsion potentials with the bond length constrained, have been used to simulate the processes at the n-dodecane liquid-vapour equilibrium interface. The thickness of this interface is predicted to be 2.3–3.5 nm. It
is pointed out that the molecular chains lie preferentially parallel to the liquid-vapour interface in the immediate vicinity of this interface. It is shown that molecules at the liquid surface need to obtain relatively large translational energy to evaporate. The vapour molecules with large translational energy can easily penetrate deeply into the transition layer and condense in the liquid phase. Typical molecular behaviours in the evaporation and condensation processes have been identified. It is pointed out that molecular exchange condensation, typical for simple molecules, has never been observed for n-dodecane molecular chains.
Chapter 3

Kinetic Boundary Conditions

3.1 Introduction to Chapter 3

As discussed in Chapter 1, the practical application of the combined or kinetic modelling requires the specification of boundary conditions at the droplet surface and at the interface between the kinetic and hydrodynamic regions. These boundary conditions include the evaporation/condensation coefficient at the droplet surface and the specification of the distribution functions of molecules leaving the droplet surface or entering the kinetic region from the hydrodynamic one. Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006] implicitly or explicitly assumed that this distribution function is isotropic Maxwellian in both cases. The values of the evaporation/condensation coefficients had been considered equal to 0.04 and 0.5 (the minimal and average value of this parameter for water) by Kryukov et al. [2004] or 1 by Sazhin and Shishkova [2009]; Sazhin et al. [2007]; Shishkova and Sazhin [2006]; Tsige and Patnaik [2008]. None of these assumptions could be rigorously justified. The only practical way to perform this justification is to base it on the molecular dynamic simulation at the interface region.
The interface between the gas and its condensed phase (liquid) is typically a couple of molecular diameters wide (Cao et al. [2011]). Hence, molecular dynamics (MD) simulation is ideally suited to probe the molecular mechanism of phase change. Tsuruta et al. [1999] have used molecular dynamics to simulate the stationary evaporation and condensation between two liquid slabs kept at different temperatures and calculated the evaporation and condensation coefficients for an argon-like fluid. Both coefficients are equal under equilibrium conditions. Anisimov et al. [1999] have simulated evaporation into vacuum by removing all molecules that left the gas region of the simulation cell. They have considered a completely absorbing wall and found the evaporation/condensation coefficient for simple liquids in a wide range of temperatures. Nagayama and Tsuruta [2003] and Nagayama et al. [2006] have studied the condensation coefficients of argon and water in terms of the transition state theory and molecular dynamics simulations. They found that the condensation coefficients of argon and water decreased when liquid temperatures increased.

The main aim of this Chapter is to further investigate the evaporation and condensation processes of n-dodecane with particular emphasis on the determination of evaporation/condensation coefficient and the analysis of the molecular distribution functions in various locations relative to the gas-liquid interface. In Section 3.2, the kinetic boundary condition (KBC) is discussed. Section 3.3 focuses on the estimation of the evaporation/condensation coefficient. The velocity distribution functions are presented in Section 3.4. The revised kinetic boundary conditions are introduced in Section 3.5. The conclusions to this chapter are drawn in Section 3.6.
3.2 Problem Formulation

In the kinetic theory, the interface is modelled as a surface of zero thickness (Kryukov et al. [2004]; Shishkova and Sazhin [2006]) and molecules hitting it from the vapour phase can be captured (condensed) or reflected. Using molecular dynamics simulations for relatively simple molecules, it has been found that the condensation probability does not depend on the incoming velocity (Tsuruta and Nagayama [2004]; Tsuruta et al. [1999]). Also, the incident angle of the molecules has no noticeable effect on the condensation coefficient (Tsuruta and Nagayama [2004]).

The distribution function of molecules leaving the interface from the liquid phase $f_{out}$ is usually presented as a sum of the distribution functions of the evaporated part $\sigma f^e$ and reflected part $(1 - \sigma) f^r$ (Cercignani [1988]),

$$f_{out} = \sigma f^e + (1 - \sigma) f^r, (v_x > 0)$$  \hspace{1cm} (3.1)

where $\sigma$ is the evaporation/condensation coefficient (both coefficients are equal in the equilibrium state), $f^e$ is the distribution function of vapour molecules at the temperature of condensed phase (liquid) and $v_x$ is the velocity component normal to the interface. For evaporated molecules, it is typically assumed that their distribution function is isotropic Maxwellian, with the temperature equal to that of the liquid phase, without drift velocity (Meland [2002]). The isotropic Maxwellian distributions with drift velocities have been reported in Refs. (Meland and Ytehus [2001]; Tsuruta et al. [1999]).

In kinetic modelling, Eq. (3.1) can be considered as the kinetic boundary condition (KBC) (Sazhin et al. [2007]; Shishkova and Sazhin [2006]). Alternative formulations of the kinetic boundary conditions have been discussed by Frezzotti [2011]; Ishiyama
et al. [2005]; Meland and Ytehus [2001]; Tsuruta et al. [1999]. When analysing heating and evaporation of n-dodecane (C\textsubscript{12}H\textsubscript{26}) in Diesel engine-like conditions, we used the kinetic boundary condition (KBC) in the form of Eq. (3.1) with the evaporation/condensation coefficient set to unity and assuming that the molecular distribution function is isotropic Maxwellian (Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006]). Some authors used Eq. (3.1) for monatomic molecules of argon (Ishiyama et al. [2004b]) and polyatomic molecules of water and methanol (Ishiyama et al. [2004a]) in their molecular dynamics simulations.

The maximum mass flux density of the molecules evaporated from the liquid surface, assuming that \( f^e \) is isotropic Maxwellian, is given by the Hertz formula (Landau and Lifshitz [1980]):

\[
j_m = \rho_v \sqrt{\frac{k_B T_l}{2\pi m}},
\]

(3.2)

where \( \rho_v \) is the density of saturated vapour in equilibrium state at the liquid temperature \( T_l \), \( m \) is the molecular mass and \( k_B \) is the Boltzmann constant. The ratio of the actual mass flux density of the evaporated molecules \( j_e \) to its maximum value \( j_m \) is defined as the evaporation coefficient \( \sigma_e \). The condensation coefficient is defined as the ratio of the actual mass flux of condensed molecules \( j_c \) to \( j_m \). Under the equilibrium condition, the condensed mass flux should be equal to the evaporated mass flux, i.e., \( j_c = j_e \), which implies that \( \sigma_e = \sigma = \sigma_c \). The condensed mass flux \( j_c \) and the evaporated mass flux \( j_e \) have been calculated by counting the number of molecules crossing a unit area per unit time at the interface zone.

As discussed in Chapter 2, the molecules of n-dodecane lie preferentially parallel to the interface in the liquid-vapour transition region, instead of being random. Also, it has been found that the translational energies are typically marginally larger than the rotational energies in the region close to the interface. Hence the distribution
function of evaporating molecules is expected to deviate from the isotropic Maxwellian distribution. This will be discussed in detail in Section 3.4.

3.3 Evaporation/Condensation Coefficient

The molecular evaporation and condensation at the vapour-liquid interface are shown in Figure 3.1. Assuming that the distribution function of molecules at the interface is isotropic Maxwellian which will be confirmed later by our MD simulations, the estimation of the maximum flux defined by Eq. (3.2) can be justified. Hence, in our calculations the evaporation and condensation coefficients have been estimated as the ratios of evaporated and condensed mass fluxes to the maximum flux given by Eq. (3.2). The equality of evaporation and condensation coefficients in equilibrium allows us to focus our analysis on one of the two coefficients and the condensation coefficient was chosen. The results will be compared with the predictions of the transition state theory discussed in Chapter 1. In this theory the condensation coefficient is estimated from Eq. (1.3).

The condensation coefficient of n-dodecane was calculated for liquid temperatures
$T_l = 400 \text{ K}, 450 \text{ K}, 500 \text{ K} \text{ and } 550 \text{ K}$. The plots of $\sigma_c$ versus the reduced temperature for n-dodecane (critical temperature 657.2 K), obtained for the system of 720 molecules, are shown in Figure 3.2 (open circles). As follows from this figure, the condensation coefficient decreases from about 0.93 at 400 K to about 0.45 at 550 K. The condensation coefficients of n-dodecane reported by Cao et al. [2011] using MD simulations in the system with 400 molecules are also shown in Figure 3.2 (filled circles). The values of the condensation coefficient predicted by the transition state theory (Eq. (1.3)) have been obtained using the densities of the liquid and vapour phases obtained in our MD simulations (dotted line). As follows from this figure, there is a general agreement between the present results, the predictions of the transition state theory and the prediction of Mizuguchi et al. [2010]. The condensation coefficients of other substances using MD simulations reported by other researchers are also shown in Figure 3.2 (filled (Tsuruta et al. [1999]) and open (Ishiyama et al. [2004b]) squares for argon, filled (Ishiyama et al. [2004a]) and open (Tsuruta and Nagayama [2004]) triangles for water and filled diamonds for methanol (Ishiyama et al. [2004a])).

In all cases it is found that the condensation coefficient decreases when the liquid temperature increases. This is consistent with the results for the interface thickness shown in Figure 2.6. As mentioned earlier in Chapter 2, the thicker interfaces at higher temperatures are expected to reduce the values of the evaporation/condensation coefficients.

The condensation coefficient for complex polyatomic molecules, such as n-dodecane, would be expected to be lower than for simpler molecules due to the constraint imposed by the rotational motion of molecules in the liquid phase (Sazhin et al. [1993]). However, in our MD simulations, it has been found that the rotational energy has no noticeable effect on this coefficient and its value is mainly controlled by the translational energy in agreement with the previously reported results (Cao et al. [2011]).
Figure 3.2: The condensation coefficient of n-dodecane versus reduced temperature, as predicted by MD simulations and the transition state theory; the values of this coefficient for argon, water, and methanol, obtained by other researchers, using MD simulations. The reduced temperature is defined as the ratio of the liquid temperature to the critical temperature.

Tsuruta and Nagayama [2004]). On the other hand, based on the transition state theory, we can expect that this coefficient is close to unity at low temperatures when \((\frac{V_g}{V_l})^{1/3}\) is large, and decreases with increasing temperature due to the decrease of the ratio \((\frac{V_g}{V_l})^{1/3}\). This trend is consistent with the prediction of our MD simulations.

The evaporation/condensation coefficient predicted by our MD simulations will be used in the formulation of the boundary conditions in kinetic modelling, instead of the previously used assumptions that this coefficient is equal to unity (Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006]) or rather arbitrary values 0.04 or 0.5 (Kryukov et al. [2004]). Also, the difficulties in obtaining the evaporation/condensation coefficients and some estimates of the uncertainties involved are discussed below. Firstly, the liquid-vapour interface moved around during the evaporation and condensation (see Figure 2.3). This resulted in the error in determination of molecular positions: vapour molecules, interface molecules or liquid
molecules. This led to errors in estimates of mass fluxes of molecules. Secondly, this value was less reliable at the low liquid temperatures due to small number of evaporation/condensation molecules. In order to overcome this problem, the system with large number of molecules needs to be considered in MD simulations. The maximum mass flux of vapour molecules was chosen in the saturated vapour phase (see Eq. 3.2) when obtaining the values of the evaporation/condensation coefficient. This estimate was valid when the vapour phase was in equilibrium. This led to additional errors in the estimate of evaporation/condensation coefficients in our MD simulations.

3.4 Velocity Distribution Function

As mentioned in Section 3.2, it is generally assumed that the distribution functions of the evaporated molecules and the molecules entering the kinetic region from the hydrodynamic one are isotropic Maxwellian. In what follows the range of applicability of this assumption is based on the calculations of distribution function using our MD simulations. Our analysis focuses on the investigation of this function inside the liquid phase, at the interface and in the vapour phase.

The distribution function of translational velocities of the mass centres of molecules can be calculated as (Ishiyama et al. [2004a]):

$$f_j = \frac{1}{\rho N_s \Xi_p \Xi_o} \sum_{N_s} \sum_{i \in (\Xi_p \cap \Xi_v)} m_i, \quad (3.3)$$

where $f_j$ is the distribution of the $j$ component of the translational velocity ($f_j = f_{x,y,z}$), $\Xi_p$ is a volume element in the physical space, $\Xi_o^j$ is a one-dimensional volume element in the $j$ direction in the three-dimensional molecular velocity space, $\Xi_p \cap \Xi_u^j$ denotes a four-dimensional volume element in the six-dimensional physical/velocity
space, and $m_i$ are masses of individual molecules that are assumed to be the same.

The distribution function $f_j$ is normalised by the density $\rho$ calculated in the volume

element $\Xi_p$ and sampled by $N_s = 20,000$. $N_s$ indicates the summation over $N_s$ samples.

The summation of $f_j$, defined by Eq. (3.3), over $\Xi_p$ gives 1 (this function is normalised

by unity).

The velocity distribution function was found by sampling the velocities of molecules

in the control volumes of thickness $0.642\sigma = L_x/100$ in the $x$ direction, in three regions:

inside the liquid phase, at the interface and in the vapour phase. Alternatively, the

velocity distribution function could be found by transforming the differential fluxes

(Tsuruta et al. [1999]), but this approach has various numerical problems (Meland and

Ytehus [2001]). It has not been used in our analysis.

Figures 3.3 and 3.4 show the distributions of molecules for $y$- and $z$-velocity com-

ponents $v_y$ and $v_z$ (parallel to the interface) in the above mentioned three regions at

temperatures 500 K and 550 K. The corresponding Maxwellian distributions for the

same temperatures are shown in these figures by solid curves. As one can see from

both figures, despite a considerable scatter of data in the vapour phase, for both tem-

peratures and in all three regions the distributions of tangential velocity components

are close to isotropic Maxwellian. Figures 3.5 and 3.6 show the distributions of evapo-

rated molecules for the $x$-velocity component $v_x$ (normal to the interface) for the same

temperatures as in Figures 3.3 and 3.4. The corresponding Maxwellian distributions

for the same temperatures as in the case shown in Figures 3.3 and 3.4 are shown in

both figures by solid curves. As can be seen from both figures, in the liquid phase and

at the interface, the predicted distribution functions are close to isotropic Maxwellian,

corresponding to temperatures 500 K and 550 K, as in the cases shown in Figures 3.3

and 3.4. The velocity distributions in vapour phase, however, turn out to be rather
different from the above mentioned Maxwellian distributions. These distributions are
Figure 3.3: The velocity distribution of molecules with respect to velocity components tangential to the interface $v_y$ (a) and $v_z$ (b) in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 500 K. The solid curve shows a one-dimensional normalised Maxwellian distribution at 500 K.
Figure 3.4: The velocity distribution of molecules with respect to velocity components tangential to the interface $v_y$ (a) and $v_z$ (b) in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 550 K. The solid curve shows a one-dimensional normalised Maxwellian distribution at 550 K.
close to Maxwellian, but with temperatures higher than those in the liquid phase and the interface. The latter are shown in Figures 3.5 and 3.6 by dotted curves for temperatures of 627 K and 681 K, respectively. These temperatures are shown to provide the best fit to the predicted distribution of molecules. Thus, the distribution of molecules in the vapour phase is expected to be close to bi-Maxwellian with different temperature in the direction normal to the interface. This means that the evaporated molecules have larger average translational energies in the direction normal to the interface than the corresponding energies in the direction parallel to the interface. Note that these distributions are typical for the outer space plasma (Sazhin [1993]).

Figure 3.5: The velocity distribution of molecules with respect to velocity component normal to the interface $v_x$ in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 500 K. The solid and dotted curves show one-dimensional normalised Maxwellian distributions at 500 K and 627 K.

The bi-Maxwellian distribution of molecules in the gas phase indicates that gas in this region is not in an equilibrium state. This does not contradict the analysis presented by Fujikawa et al. [2011], where the region in the gas phase close to the interface is explicitly called the “nonequilibrium region”. We should admit, however, that further studies of the problem, using larger numbers of molecules, are required to
Figure 3.6: The velocity distribution of molecules with respect to velocity component normal to the interface $v_x$ in the liquid phase, interface and the vapour phase as predicted by MD simulations for liquid temperature equal to 550 K. The solid and dotted curves show one-dimensional normalised Maxwellian distributions at 550 K and 681 K. These results are consistent with the results reported earlier in Section 3.2. The same phenomenon has also been observed in MD simulations of argon (Meland and Ytehus [2001]; Tsuruta et al. [1999]). Although we appreciate that this result needs to be confirmed by MD simulations with much larger numbers of molecules, we believe that the traditional approach to the formulation of the boundary conditions in kinetic modelling, when the distribution function of the evaporated molecules is assumed to be isotropic Maxwellian with the same temperatures for all velocity components, needs to be investigated more carefully. Schematic diagram of the kinetic boundary condition is shown in Figure 1.1.
3.5 Revised Boundary Conditions

Based on the velocity distributions introduced in Section 3.4, we further investigate the velocity distributions of molecules leaving the vapour-liquid interface, including the evaporated and reflected molecules. The normalised distribution function of molecules leaving the droplet surface in the direction normal to this surface $F^M_x$ is linked with the normalised distribution functions of evaporated $F^e_x$ and reflected $F^r_x$ molecules by the following equation

$$\rho^+ F^M_x = \rho^e F^e_x + \rho^r F^r_x,$$

(3.4)

where $\rho^+ = \rho^e + \rho^r$ is the total density of molecules leaving the droplet surface, $\rho^e$ is the density of evaporated molecules, and $\rho^r$ is the density of reflected molecules. The plots of $F^M_x$, $F^e_x$ and $F^r_x$ versus $v_x$ are shown in Figure 3.7.

![Figure 3.7: Normalised velocity distribution of evaporated and reflected molecules from the vapour-liquid interface and that of all molecules leaving this surface for liquid temperature equal to 500 K.](image)

As can be seen from Figure 3.7, for the velocity component normal to the interface
$v_x$, the distribution function for all molecules leaving the surface is close to isotropic Maxwellian, but these distributions for evaporated and reflected molecules noticeably deviate from the Maxwellian one. The distribution function of evaporated molecules is less than that of the Maxwellian for small velocities but greater than that of the Maxwellian for high velocities. The distribution function of reflected molecules, however, is greater than that of the Maxwellian for small velocities but less than that of the Maxwellian for high velocities. Thus, the main contribution to the molecules leaving the droplet surface at small velocities comes from the reflected molecules, while the main contribution to these molecules leaving the droplet surface at high velocities comes from the evaporated molecules.

Figure 3.8: Evaporation coefficient $\sigma_e$ as a function of translational energy $E_x/k_B$ for liquid temperature equal to 500 K.

Also, the ratios of the evaporated molecules to all molecules leaving the interface (evaporation coefficient) have been investigated for various velocities. The results are shown in Figure 3.8 by open circles. Following Tsuruta et al. [1999], these results are
approximated by the following formulae

\[ \sigma_e = a \left( 1 - b \exp \left( -\frac{E_x}{k_B T_i} \right) \right), \]  
\( (3.5) \)

where \( E_x = \frac{1}{2} m v_x^2 \) is the translational energy of molecules in the direction normal to the interface, and \( a \) and \( b \) are fitting constants which are determined by the liquid temperature; they are estimated as \( a = 0.71 \) and \( b = 0.296 \). Assuming that the distribution function of the molecules leaving the interface is Maxwellian

\[ F_{x}^{M} = \left( \frac{m}{2\pi k_B T_i} \right)^{1/2} \exp \left( -\frac{E_x}{k_B T_i} \right), \]  
\( (3.6) \)

we can estimate the average value of evaporation coefficient as

\[ \bar{\sigma}_e = \frac{1}{(k_B T_i/2\pi m)^{1/2}} \int_{0}^{\infty} \sigma_e F_{x}^{M} dv_x = a \left( 1 - \frac{b}{2} \right). \]  
\( (3.7) \)

The normalised velocity distribution functions of evaporated and reflected molecules, \( F_{x}^{e} \) and \( F_{x}^{r} \), can be obtained from the following relations (Tsuruta et al. [1999])

\[ F_{x}^{e} = \frac{\sigma_e}{\bar{\sigma}_e} F_{x}^{M} = \frac{1 - \beta \exp (-E_x/2k_B T_i)}{1 - \beta/2} \left( \frac{m}{2\pi k_B T_i} \right)^{1/2} \exp \left( -\frac{E_x}{k_B T_i} \right), \]  
\( (3.8) \)

\[ F_{x}^{r} = \frac{1 - \sigma_e}{1 - \bar{\sigma}_e} F_{x}^{M} = \frac{1 - \alpha + \alpha \beta \exp (-E_x/2k_B T_i)}{1 - \alpha + \alpha \beta/2} \left( \frac{m}{2\pi k_B T_i} \right)^{1/2} \exp \left( -\frac{E_x}{k_B T_i} \right). \]  
\( (3.9) \)

### 3.6 Conclusions to Chapter 3

The evaporation/condensation coefficient at various liquid temperatures has been estimated. It has been demonstrated that this coefficient decreases with the temperature
increasing, in agreement with the prediction of the transition state theory. The molecular velocity distribution functions in the liquid phase and the interface have been shown to be close to isotropic Maxwellian with temperatures equal to that of the liquid phase. These functions in the vapour phase, however, have been shown to deviate from the classical isotropic Maxwellian distributions. They can be approximated as bi-Maxwellian with temperatures in the direction normal to the interface larger than those in the directions parallel to the interface. The traditional approach to the formulation of the boundary conditions in kinetic modelling, when the distribution function of the evaporated molecules is assumed to be isotropic Maxwellian with the same temperatures for all velocity components, has been revised.
Chapter 4

Kinetic Theory of Evaporation and Condensation

4.1 Introduction to Chapter 4

The kinetic analysis of gas dynamics needs to be based on the solution of the Boltzmann equation, taking into account the collision processes. Note that the Boltzmann equation itself is an approximation of the more general chain of Bogolubov-Born-Green-Kirkwood-Yvon (BBGKY) chain of equations (Akhiezer et al. [1974]; Shishkova and Sazhin [2006]).

A number of approximate methods of the solution for the Boltzmann equation have been suggested. One of these methods is based on the replacement of this equation by the system of equations for the moments of the distribution function (Grad [1949]). Although this method is important from the point of view of theoretical developments, its practical applications to non-stationary and multi-dimensional problems are limited. An alternative approximate method is widely known as the method of the model kinetic equations. In this method, the actual collision integral is not calculated.
but modelled. One of the most widely used variations of this method was suggested by Bhatnagar et al. [1954] and is known as Bhatnagar-Gross-Krook (BGK) method (Igoshin and Kurochkin [1984]; Sazhin [1978]). More advanced versions of the method of the model kinetic equations were suggested by Shakhov [1974]. These methods are computationally economical but their accuracy becomes poor when the distribution of gas molecules (ions/electrons) deviates considerably from the equilibrium distribution. A more detailed analysis of these approximate methods and the results of their applications are reviewed in a number of monographs and papers including Kryukov et al. [2004]; Lifshitz and Pitaevski [1979]; Rose [1998]. Although these solutions have proven to be useful in qualitative analysis of phenomena and understanding of the underlying physics, their limitations for the quantitative analysis are well known.

It seems that the only way to perform the quantitative analysis of gas dynamics in the general case can be based on direct numerical methods (Tcheremissine [2006], Yen [1984]). For non-ionised gases such methods were developed by Bird [1994] and Aristov and Tcheremissine [1992]. Bird based his approach on direct statistical analyses of the dynamics of individual atoms while Aristov and Tcheremissine developed a new method of the direct numerical solution of the Boltzmann equation. These methods were further developed and applied to the analysis of gas dynamics, including evaporation and condensation problems in numerous papers including Aoki et al. [1998]; Aristov et al. [1991, 1997]; Aristov and Tcheremissine [1992]; Aristov et al. [1992]; Kosuge et al. [2001]; Kryukov et al. [2005]; Kryukov and Yastrebov [2003]; Raines [2002]; Taguchi et al. [2003, 2004]; Tcheremissine [1998, 2000]. Attempts to apply these methods to binary mixtures were reported by Aoki et al. [1998]; Kosuge et al. [2001]; Kryukov et al. [2005]; Raines [2002]; Taguchi et al. [2003, 2004]. Numerical difficulties in the analysis of these mixtures, however, led to imposing a number of restrictions on the properties of molecules. Molecules considered by Aoki et al. [1998]; Raines [2002];
Taguchi et al. [2004] were assumed to be mechanically identical. Kosuge et al. [2001]; Raines [2002] took into account the difference in the masses of molecules, but their diameters were assumed to be the same. These assumptions can hardly be justified in many practical engineering applications, where molecules in binary mixtures have very different diameters, such as the problem of evaporation of heavy hydrocarbons into air.

The models developed in above-mentioned papers are based on a number of assumptions, the most serious of which is that the contribution of inelastic collisions has been ignored. This assumption could have been justified in the case of monoatomic molecules, but appears to be highly questionable in the case of such complex molecules as n-dodecane (C$_{12}$H$_{26}$) considered in the above-mentioned papers. Even if the analysis of the dynamics of these molecules is simplified in terms of the UAM introduced in Chapter 2, the number of internal degrees of freedom of this molecule is expected to exceed one hundred. There seems to be no justification for ignoring their contribution.

Perhaps the first phenomenological model for binary collisions in a gas mixture having continuous internal energy was developed by Borgnakke and Larsen [1975]. This model was applied to Monte Carlo simulation of rarefied gas flows. Since the publication of this pioneering paper, a substantial number of papers have been published, in which various models of inelastic collision have been introduced. Without making any attempt to present an extensive list of these papers we mention Banasiak and Groppi [2003]; Benedetto and Caglioti [1999]; Biben et al. [2002]; Ferrari and Carbognani [1998]; Fournier and Mischler [2005]; Furioli et al. [2010]; Kondo et al. [2004]; Kremer et al. [2010]; Lambiotte et al. [2007]; Santos [2006]; Sizhuk and Yezhov [2006]; Tilinin [1996]. Based on the Wang-Chang and Uhlenbeck results for polyatomic gases (Wang-Chang and Uhlenbeck [1951]), Mores [1964] introduced the kinetic model for gases with internal degrees of freedom, which is, as in the case of the BGK model, related to the Boltzmann collision integral. Moreover, Cheremisin [2002] proposed another solution.
of the Wang-Chang-Uhlenbeck master equation to deal with the nonequilibrium processes in a gas with internal degree of freedom and generalised the Boltzmann equation. Also, Frezzotti and Ytrehus [2006] used the Borgnakke-Larsen collision model to deal with steady condensation of a polyatomic gas, and a simpler BGK-type collision model proposed by Holway [1966] for steady evaporation (Frezzotti [2007]).

This chapter focuses on the solution of the full Boltzmann equation taking into account inelastic collision. In Section 4.2, a new model of inelastic collisions between two molecules is introduced and the numerical algorithm is presented in Section 4.3. The applications of the new model to several engineering problems are presented and discussed in Section 4.4. The main conclusions of this chapter are drawn in Section 4.5.

### 4.2 A model for inelastic collisions

The model described in this section is different from those suggested earlier, although it is based on some widely used assumptions. Although this model has been tested for some rather specific problems, its nature is rather general and it can be applied to any molecules with arbitrary large numbers of internal degrees of freedom. This model is expected to be effective for the analysis of such complex molecules as n-dodecane. Following Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], we assume that the molecules can be approximated as hard spheres and only the effects of binary collisions are taken into account. This is justified by the fact that the Boltzmann equation is solved in a very thin layer, the thickness of which is typically about 10 mean free paths of the molecules. In contrast to these papers, however, we take into account the inelastic effects during the collisions of these spheres using a well known inelastic hard spheres (IHS) model (see Sizhuk and Yezhov [2006]).
Let us consider two colliding molecules. Regardless of the nature of the collision between them, their centre of mass is not affected by this collision. The state of the molecules after the collision is described in a reference system linked with this centre of mass. In this system, each molecule has three translational and a certain number of internal degrees of freedom and the total number of degrees of freedom of both molecules is equal to $N$. During the collisions, the energies of each molecule are redistributed between the degrees of freedom, but the total number of degrees of freedom remains the same. Let us assume that none of these degrees of freedom has any preference over the others. This allows us to consider the redistribution of energy between these degrees of freedom during the collision process as random. For each of these degrees of freedom we allocate one dimension in an $N$-dimensional space describing all degrees of freedom. Once we have done this, we consider a sphere in this space with its centre at the origin (where energies of all degrees of freedom are equal to zero) and radius given by the following expression:

$$r = \sqrt{\sum_{i=1}^{i=N} E_i},$$

(4.1)

where $E_i$ is the energy of the $i$th degree of freedom (translational or internal). Since $r^2$ gives the total energy of the system $E$, Eq. (4.1) can be considered as an equation of the conservation of energy at the surface of the sphere in the centre of mass system of reference.

Introducing the new coordinates $x_i = \pm \sqrt{E_i}$, we can consider an $N$-dimensional vector

$$\mathbf{X} = (x_1, x_2, \ldots, x_N)$$
with the basis \((e_1, e_2, \ldots, e_N)\) and the norm \(||X|| = r = \sqrt{E_f}||. The norms of all vectors \(e_i\) are equal to one and these vectors are mutually perpendicular.

![Figure 4.1: Schematic presentation of the rotation of vector \(X\) in a three-dimensional space \((e_1, e_2, e_3)\).](image)

The redistribution of energy between the degrees of freedom during the collision process can be described in terms of the rotation of vector \(X\) in the \(N\)-dimensional space. For \(N = 3\) this is schematically shown in Figure 4.1. If none of the degrees of freedom has any preference over the others, then this rotation of the vector \(X\) can be considered as random with uniform probability distribution. It can be described by the following equation:

\[
X' = AX, \tag{4.2}
\]
where $X'$ is the new position of vector $X$ after rotation, $A$ is the rotation matrix:

$$
A = \begin{bmatrix}
  a_{11} & a_{12} & \ldots & a_{1N} \\
  a_{21} & a_{22} & \ldots & a_{2N} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{N1} & a_{N2} & \ldots & a_{NN}
\end{bmatrix}
$$

The conservation of the total energy during the collision process implies that vector $X'$ remains at the surface of the sphere with radius $r$. This is possible if and only if

$$
A^T A = E,
$$

where $A^T$ is the transpose of the matrix $A$ and $E$ is the unit matrix

$$
E = \begin{bmatrix}
  1 & 0 & \ldots & 0 \\
  0 & 1 & \ldots & 0 \\
  \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & \ldots & 1
\end{bmatrix}
$$

Eq. (4.3) can be presented in a more explicit form as the combination of the following systems of equations

$$
\begin{aligned}
a_{11}^2 + a_{21}^2 + \ldots + a_{N1}^2 &= 1 \\
a_{12}^2 + a_{22}^2 + \ldots + a_{N2}^2 &= 1 \\
\vdots & \vdots & \ddots & \vdots \\
a_{1N}^2 + a_{2N}^2 + \ldots + a_{NN}^2 &= 1
\end{aligned}
$$

(4.4)
\[
\begin{align*}
\begin{cases}
a_{11}a_{12} + a_{21}a_{22} + \ldots + a_{N1}a_{N2} = 0 \\
a_{11}a_{13} + a_{21}a_{23} + \ldots + a_{N1}a_{N3} = 0 \\
\vdots \quad \vdots \quad \vdots \quad \vdots \\
a_{11}a_{1N} + a_{21}a_{2N} + \ldots + a_{N1}a_{NN} = 0
\end{cases}
\end{align*}
\]
\(\text{(4.5)}\)

\[
\begin{align*}
\begin{cases}
a_{12}a_{13} + a_{22}a_{23} + \ldots + a_{N2}a_{N3} = 0 \\
a_{12}a_{14} + a_{22}a_{24} + \ldots + a_{N2}a_{N4} = 0 \\
\vdots \quad \vdots \quad \vdots \quad \vdots \\
a_{12}a_{1N} + a_{22}a_{2N} + \ldots + a_{N2}a_{NN} = 0
\end{cases}
\end{align*}
\]
\(\text{(4.6)}\)

\[
a_{1(N-1)}a_{1N} + a_{2(N-1)}a_{2N} + \ldots + a_{N(N-1)}a_{NN} = 0
\]
\(\text{(4.7)}\)

When writing Eqs. (4.5)-(4.7) identical equations have been excluded. The total number of Eqs. (4.5)-(4.7) is

\[
(N - 1) + (N - 2) + (N - 3) + \ldots + 1 = \frac{N}{2}(N - 1)
\]

for \(N^2\) unknown coefficients \(a_{ij}\). This allows us to take randomly \(N^2 - \frac{N}{2}(N - 1) = \frac{N}{2}(N + 1)\) of these coefficients with an additional restriction imposed by Eq. (4.4) (normalisation condition).

The following algorithm for the construction of the matrix \(A\) is suggested.

1. The coefficients \(a_{11}, a_{21}, \ldots, a_{N1}\) are arbitrarily chosen but normalised based on
the first equation in System (4.4).

2. The coefficients $a_{12}, a_{22}, \ldots, a_{(N-1)2}$ are arbitrarily chosen, while the coefficient $a_{N2}$ is found from the first equation of System (4.5):

$$a_{N2} = -\frac{1}{a_{N1}} \left( a_{11}a_{12} + a_{21}a_{22} + \ldots + a_{(N-1)1}a_{(N-1)2} \right). \quad (4.8)$$

Then all coefficients are normalised based on the second equation in System (4.4).

3. The coefficients $a_{13}, a_{23}, \ldots, a_{(N-2)3}$ are arbitrarily chosen, while the coefficients $a_{(N-1)3}$ and $a_{N3}$ are found from the solution of the second equation in System (4.5) and the first equation in System (4.6). These equations can be rearranged as:

$$\begin{align*}
a_{(N-1)1}a_{(N-1)3} + a_{N1}a_{N3} &= b_{13} \\
a_{(N-1)2}a_{(N-1)3} + a_{N2}a_{N3} &= b_{23}
\end{align*} \quad (4.9)$$

where

$$b_{13} = - \left( a_{11}a_{13} + a_{21}a_{23} + \ldots + a_{(N-2)1}a_{(N-2)3} \right),$$

$$b_{23} = - \left( a_{12}a_{13} + a_{22}a_{23} + \ldots + a_{(N-2)2}a_{(N-2)3} \right).$$

Then all coefficients are normalised based on the third equation in System (4.4).

Following the same procedure all other components of matrix $A$ are found, and this allows us to calculate $X'$ based on Eq. (4.2). An example of the temporal evolution of the system with 100 degrees of freedom is shown in Figure 4.2. The ordinate axis in this figure shows the energies $E_i$ referring to individual degrees of freedom $N_i$ ($i \in [1, 100]$). Initially all degrees of freedom have energies equal to 1 ($E_i = 1$). This is shown in the top part of this figure (Initial state). After the first step energies $E_i$ acquire random values in the range from zero to 5, but the sum of all $E_i$ remains the same as at the initial state ($\sum_{i=1}^{100} E_i = 100$). The nature of the distribution of $E_i$ remains random.
Figure 4.2: The energies of the individual degrees of freedom ($E_i$) versus $N_i$ at initial state and after steps 1, 2 and 3.
after steps 2 and 3 although with different values of individual energies.

The model described above could be generalised to the case when the probabilities of excitation of various degrees of freedom are not equal. This could be achieved by introduction of the weighting function, and/or limiting the range of degrees of freedom to be activated. We cannot, however, specify this weighting function in the case of such complex molecules as n-dodecane, for which our model has been primarily developed, or even justify the need to introduce this function in this case.

4.3 An algorithm for the solution of the Boltzmann equation

Following Aristov and Tcheremissine [1992], the numerical solution of the Boltzmann equation (for one or several components) is performed in two steps. Firstly, molecular displacements are calculated without the effect of collisions. Secondly, the collisional relaxation is calculated under the assumption of spatial homogeneity.

Ignoring the effects of collisions, the discretised form of the Boltzmann equation describing molecular displacements for each component can be presented as

\[
\frac{\Delta f}{\Delta t} + \mathbf{v} \frac{\Delta f}{\Delta \mathbf{r}} = 0,
\]

(4.10)

where \( f \equiv f(\mathbf{v}, \mathbf{r}, t) \) is the distribution function of velocity \( \mathbf{v} \) in physical space \( \mathbf{r} \).

In this case, the total internal energy in each velocity range should be conserved, which implies that

\[
\frac{\Delta (E_{\text{int}}f)}{\Delta t} + \mathbf{v} \frac{\Delta (E_{\text{int}}f)}{\Delta \mathbf{r}} = 0,
\]

(4.11)
where $E_{\text{int}} = E_{\text{int}}(v, r, t)$ are internal energies of molecules with $v$ and $r$ at time $t$. Further details of the numerical solution of the Boltzmann equation are described in Appendix B.

A model for inelastic collisions, described in the previous section, allows us to obtain the energies of all degrees of freedom after individual collisions as illustrated in Figure 4.2. However, we are interested only in the net change of the kinetic energy of each molecule during collisions in the centre of mass reference system. This change of the kinetic energy can be described in terms of the change of the radius of the three-dimensional sphere, which is the projection of the $N$-dimensional sphere. This three-dimensional space describes the kinetic energies of both colliding molecules in three directions. This is schematically illustrated in Figure 4.3 for the case of the projection of the $N$-dimensional sphere on the two-dimensional plane. Following Shishkova and Sazhin [2006], this space is presented in terms of the components of momenta $p_x$ and $p_y$ of both colliding molecules. Points $p$ and $p^*$ show the positions of molecules before the collision. If the collisions were elastic, then the values of momenta after collisions would lie on the dashed circle shown in Figure 4.3, being separated by 180°. Possible values of these momenta after the collisions are shown as empty circles.

As mentioned by Shishkova and Sazhin [2006], randomly chosen directions of molecular momenta after collision are likely to lead to the values of these momenta lying between the values in the nodes of the discretised momenta space. This eventually can lead to non-conservation of momenta and energies during the collision process. To overcome this problem, following Shishkova and Sazhin [2006], the momenta are discretised not only during the description of molecular motion but also in the analysis of the collision process. Namely, we assume that the momenta after the collisions belong to an $a$ priori chosen set of momenta, which are nodes in the momenta space shown in Figure 4.3. This is achieved by moving the actual point on the surface of the sphere to
Figure 4.3: A projection of the surface of an \(N\)-dimensional sphere, describing the energies referring to translational and internal degrees of freedom of two colliding molecules, into a two-dimensional space referring to two translational degrees of freedom. \(p\) and \(p^*\) show the locations of the molecular momenta before the collision. The dashed circle shows possible locations of molecular momenta after the collision if the contribution of internal degrees of freedom is ignored. The thin solid circle shows possible locations of molecular momenta after the collision if molecular internal energy increases during the collision. The thick solid circle shows possible locations of molecular momenta after the collision if molecular internal energy decreases during the collision. \(p'\) and \(p'^*\) show the allowed locations of the molecular momenta after the collision if molecular internal energy decreases during the collision.
the nearest node. Since the nodes are not uniformly distributed on the surface of the sphere in the general case, this leads to partial loss of randomness of the distribution of momenta after collisions. This is the one of the weaknesses of the present model, but seems not to lead serious limitations of the range of its applicabilities as demonstrated in Section 4.4.

In the case shown in Figure 4.3, in the absence of inelastic collisions, there are 4 such points corresponding to 4 combinations of momenta of molecules after collision. The maximal number of these combinations in the plane is 8. In the three dimensional case, the circumferences shown in Figure 4.3 turn into the surfaces of spheres and the maximal number of possible intersection points increases to 24. This corresponds to the maximal total number of combinations of momenta after collision. This approach provides the consistency in discretisation processes used for the description of molecular dynamics and collision processes. It has been tested on numerous problems, some of which are discussed by Shishkova and Sazhin [2006].

If during the collision the net internal energy of molecules increases, this has to be compensated by the decrease in the kinetic energies of molecules and the radius of the corresponding circle in Figure 4.3 is decreased. In the opposite case, when the net internal energy of molecules decreases, this has to be compensated by the increase in the kinetic energies of molecules and the radius of the corresponding circle in Figure 4.3 is increased. Both cases are shown in Figure 4.3. In the case of increased net kinetic energy of molecules, possible values of the momenta of both molecules after the collision are shown as the grey circles. These include points \( p' \) and \( p'^* \). The changes of radii of the circles after collision have been calculated based on Korobov sequences (Korobov [1989]; Popov and Tcheremissine [1999]), enhanced by the randomisation of individual points (see Ferbel [1991] for more details). As in the case of elastic collisions, the points \( p' \) and \( p'^* \) are chosen to coincide with the nodes of the discretised momenta.
4.4 Applications

The model described in the previous section has been tested using three simple one-dimensional examples: shock wave structure in nitrogen, heat flux between two parallel plates in a mixture of n-dodecane and nitrogen and one-dimensional evaporation of n-dodecane into nitrogen.

4.4.1 Shock wave structure

The first test is focused on the prediction of the shock wave structure observed experimentally (Alsmeyer [1976]). In this experiment, the density distributions of argon and nitrogen in shock waves were accurately measured. These measurements were performed in a shock tube for Mach numbers ranging from 1.55 to 9 (argon) and from 1.55 to 10 (nitrogen) by the absorption of an electron beam. Our focus will be on the results referring to nitrogen with Mach number equal to 2 for the parameters before the shock wave. Using the Rankine-Hugoniot relationships, this leads to the following ratios of number densities \( n_\pm \), static temperatures \( T_\pm \) and velocities \( v_\pm \) after and before the shock wave at large distances from it (indicated by subscripts \(+\) and \(-\)) (Raines [2002]):

\[
\frac{n_+}{n_-} = 2.2857; \quad \frac{T_+}{T_-} = 2.0781; \quad \frac{v_+}{v_-} = 0.4375;
\]

Rotational relaxation in nitrogen is found to be very fast for all Mach numbers (Alsmeyer [1976]). Consequently the coupling between rotational and translational relaxation is expected to be very strong. Since the vibrational degrees of freedom could be ignored for the conditions of the experiment, we consider only two internal
degrees of freedom referring to the rotational motion \( (N_{\text{int}} = 2) \).

Figure 4.4: Plots of \( n = (n_n - n_-)/(n_+ - n_-) \), where \( n_n \) is the current number density of nitrogen, versus the distance \( x \) normalised by mean free path \( \ell = (\sqrt{2\pi\sigma_{N_2}^2 n_-})^{-1} \), where \( \sigma_{N_2} \) is the diameter of \( N_2 \) molecules. \( x = 0 \) shows the location of the shock wave.

The calculations have been performed for the normalised density \( n = (n_n - n_-)/(n_+ - n_-) \), where \( n_n \) is the current number density of nitrogen, taking into account and ignoring the two internal degrees of freedom. The results are shown in Figure 4.4. In the same figure, the experimental data obtained by Alsmeyer [1976] and the modelling results reported by Tcheremissine [2006] are also shown. Note that the approach used in Tcheremissine [2006] is different from the one described earlier in this chapter, although it also takes into account the contribution of inelastic collisions. As follows from this figure, although the curves referring to the cases with and without taking into account the internal degrees of freedom show similar trends, the number densities predicted by both approaches are visibly different. Thus, ignoring the contribution of the internal degrees of freedom, an approach widely used by the researchers in this area, including Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], can be a too crude method for many engineering applications. Also, the results of our calculations, taking into account the contribution of the internal degrees
of freedom, appear to be very close to experimental data and the modelling results reported by Tcheremissine [2006]. This gives us confidence in our approach to modelling this phenomenon.

In Figure 4.5, we have presented the results of calculations of a hypothetical case when nitrogen is allowed to have less or more than two internal degrees of freedom ($N_{int}$). The cases of $N_{int} = 0, 2, 6$ and 10 have been considered. As follows from this figure, the increase in the number of internal degrees of freedom from 0 to 2 and from 2 to 6 visibly affects the solution. However, further increase in this number from 6 to 10 produces only a relatively minor effect. This potentially opens the way for modelling systems with large numbers of internal degrees of freedom, by considering the contribution of a relatively small number of these degrees of freedom. This idea is supported by the tests in the next two subsections.
4.4.2 Heat flux between two parallel plates

Let us consider two parallel plates at normalised temperatures $T_{w1} = 1.5$ and $T_{w2} = 1.0$; the space between two plates is filled with a mixture of n-dodecane (C$_{12}$H$_{26}$) and nitrogen (N$_2$) at the initial normalised temperature $T = 1$. The normalised number densities of both components are assumed initially equal to 1 ($n_d \equiv n_{C_{12}H_{26}} = n_n \equiv n_{N_2} = 1$). The distance between the plates is $L = 5\ell$, where $\ell$ is the mean free path at $n_{C_{12}H_{26}} = n_{N_2} = 1$ and $T = 1$. The problem setup is schematically presented in Figure 4.6. Both components are calculated using two Boltzmann equations described by Shishkova and Sazhin [2006]. The calculations have been performed assuming that nitrogen has no internal degrees of freedom while the number of internal degrees of freedom of n-dodecane has been assumed to be in the range $N_{\text{int}} = 0$ to $N_{\text{int}} = 50$.

The distributions of number densities of n-dodecane ($n_d \equiv n_{C_{12}H_{26}}$) and nitrogen ($n_n \equiv n_{N_2}$), when the system has reached the steady state, are shown in Figure 4.7. Three values of the number of internal degrees of freedom of n-dodecane ($N_{\text{int}} = 0$, 3 and 7) have been considered. As one can see from this figure, the distributions of both n-dodecane and nitrogen number densities visibly change when $N_{\text{int}}$ increases from 0 to 3. These changes, however, become much smaller when $N_{\text{int}}$ increases further from 3 to 7.

The distributions of normalised temperatures of n-dodecane and nitrogen, when the system reached the steady state, are shown in Figure 4.8. As in the case of Figure 4.7, three values of the number of internal degrees of freedom of n-dodecane (0, 3 and 7) have been considered. As one can see from this figure, the distributions of both n-dodecane and nitrogen noticeably change when $N_{\text{int}}$ increases from 0 to 3. As in the case of Figure 4.7, these changes become much less significant when $N_{\text{int}}$ increases further from 3 to 7. The conclusions inferred from Figures 4.7 and 4.8 are consistent with those inferred from Figure 4.5 for a very different physical problem. The difference...
between the values of gas temperature near the walls and the wall temperatures can be clearly seen in Figure 4.8. This is a well known temperature jump in rarefied gases (Sazhin and Serikov [1997]).

The plots of the normalised heat flux \( q \) between the plates versus \( N_{\text{int}} \) are shown in Figure 4.9. We have used the normalisation factor

\[
\rho_{\text{C}_{12}\text{H}_{26}} \left( R_{\text{C}_{12}\text{H}_{26}} T_0 \right)^{3/2},
\]

where \( \rho_{\text{C}_{12}\text{H}_{26}} \) and \( R_{\text{C}_{12}\text{H}_{26}} \) are the density and gas constant of n-dodecane respectively, and \( T_0 \) is the initial temperature.

The cases of the above mentioned mixture of n-dodecane and nitrogen and pure n-dodecane have been considered. As follows from this figure, the changes of \( q \) at \( N_{\text{int}} \geq 15 \) are much smaller compared with the changes at \( N_{\text{int}} < 15 \). At \( N_{\text{int}} > 25 \), the values of \( q \) remain practically constant and do not depend on \( N_{\text{int}} \).
Figure 4.7: Plots of $n_d$ (a) and $n_n$ (b) versus the distance $x$ normalised by the mean free path $\ell$ for three values of $N_{\text{int}}$ for the setup shown in Figure 4.6.
Figure 4.8: Plots of $T_d$ (a) and $T_n$ (b) versus the distance $x$ normalised by the mean free path $\ell$ for three values of $N_{int}$ for the setup shown in Figure 4.6.
4.4.3 Evaporation of n-dodecane into nitrogen

Let us consider two parallel plates, similar to those studied in the previous section, but at normalised temperatures $T_{w1} = T_{w2} = 1.0$; initially the space between these plates is filled with nitrogen at the normalised temperature $T = 1.0$ and number density $n_n \equiv n_{N_2} = 1.0$. The total amount of nitrogen in the system is assumed to be constant. As in the previous problem, the distance between the plates is taken equal to $L = 5\ell$. n-dodecane is evaporated from the left plate in such a way that its normalised number density at the surface of this plate remains constant and equal to 1.5. Once n-dodecane reaches the right plate it fully condenses so that its number density at the surface of this plate remains equal to 0. This setup is schematically shown in Figure 4.10.

As in the previous problem, the calculations have been performed assuming that nitrogen has no internal degrees of freedom while the number of internal degrees of freedom of n-dodecane are assumed to be in the range $N_{int} = 0$ to $N_{int} = 50$.

The distributions of number densities of n-dodecane and nitrogen, when the system
Figure 4.10: A schematic presentation of the evaporation of n-dodecane into nitrogen. n-dodecane is evaporated from the left plate with temperature kept at $T_{w1}$ and is fully condensed on the right plate with temperature kept at $T_{w2}$. $L$ is the distance between two plates; $n_d$ and $n_n$ are number densities of n-dodecane and nitrogen molecules; $T \equiv T(x)$ is the temperature between the two plates.

reached the steady state, are shown in Figure 4.11. Four values of the number of internal degrees of freedom of n-dodecane ($N_{\text{int}} = 0, 3, 7$ and 10) have been considered. As one can see from this figure, the distributions of both n-dodecane and nitrogen number densities visibly change when $N_{\text{int}}$ increases from 0 to 3. These changes, however, become smaller when $N_{\text{int}}$ increases further from 3 to 7, and can be practically ignored when $N_{\text{int}}$ increases from 7 to 10.

The plots of normalised mass flux $j$ between the two plates versus $N_{\text{int}}$ are shown in Figure 4.12. We have used the normalisation factor

$$
\rho_{C_{12}H_{26}} \sqrt{R_{C_{12}H_{26}}T_0},
$$

where the notations are the same as the previous subsection.

As follows from this figure, the changes of $j$ at $N_{\text{int}} \geq 15$ are much smaller compared with the changes at $N_{\text{int}} < 15$, as in the previous problem. At $N_{\text{int}} > 25$, the values of $j$ remain practically constant and do not depend on $N_{\text{int}}$. 

75
Figure 4.11: Plots of $n_d$ (a) and $n_n$ (b) versus the distance $x$ normalised by the mean free path $\ell$ for four values of $N_{int}$ for the setup shown in Figure 4.10.
The results presented in this subsection open the way for applying the new method to systems with arbitrarily large numbers of internal degrees of freedom by considering systems with relatively small numbers of these degrees of freedom. The number of internal degrees of freedom to be chosen would depend on the required accuracy of the solution.

4.5 Conclusions to Chapter 4

When dealing with the evaporation/condensation process, a new approach to the solution of the Boltzmann equation, taking into account the effect of inelastic collisions, is suggested. This approach is based on the presentation of the collisions as the random (with uniform probability distribution) movement along the surface of an $N$-dimensional sphere, the squared radius of which is equal to the total energy of colliding molecules in reference system of centre of mass. The projection of a point on the surface of this sphere in each of $N$ directions gives the root square of the kinetic
energy in one of three directions in physical space, or internal energy referring to one
degree of freedom, of each colliding molecule. The kinetic energies of both colliding
molecules in three directions are described by the first six dimensions of the system
and the remaining \((N - 6)\) dimensions describe the internal energies. In contrast to the
case of elastic collisions, the radius of the three-dimensional sphere in the momentum
or velocity space describing the kinetic energies of both molecules changes after each
collision. The probabilities of changes of all energies (kinetic and internal) after the
collision are assumed to be equal. If during the collision the net internal energy of
molecules increases (decreases), this has to be compensated by the decrease (increase)
of the kinetic energies of molecules and the radius of the corresponding sphere in the
three-dimensional kinetic space decreases (increases). Following Shishkova and Sazhin
[2006], we assume that the momenta of molecules after the collisions belong to an \(a
priori\) chosen set of momenta, which are nodes in the discretised momenta space. The
changes of radii of the spheres in the kinetic energy space after collisions are calculated
based on Korobov’s sequences, enhanced by the randomisation of individual points.

The above mentioned new approach has been applied to three test problems: shock
wave structure in nitrogen, one-dimensional heat transfer through a mixture of n-
dodecane and nitrogen and one-dimensional evaporation of n-dodecane into nitrogen.
In the first problem, the predictions of the model, taking into account the contribution
of the rotational degrees of freedom, are shown to be close to experimental data and the
predictions of the earlier developed inelastic collision model. This problem has been
generalised to a hypothetical case when the number of internal degrees of freedom of
nitrogen \((N_{\text{int}})\) has been assumed to be in the range 0 to 10. It has been shown that
the results visibly change when \(N_{\text{int}}\) is increased from 0 to 2, but remain practically
unchanged at \(N_{\text{int}} \geq 6\).

The predicted heat flux for the second problem has been shown not to depend on
the number of internal degrees of freedom of the mixture $N_{\text{int}}$ when this number exceeds about 15. In the third problem, the predicted mass flux of n-dodecane also remained almost unchanged at $N_{\text{int}} \geq 15$. These results open the way for considering systems with arbitrarily large numbers of internal degrees of freedom by reducing the analysis of these systems to the analysis of systems with relatively small numbers of internal degrees of freedom.
Chapter 5

Droplet Heating and Evaporation: Effects of Inelastic Collisions and a Non-unity Evaporation Coefficient

5.1 Introduction to Chapter 5

As discussed in Chapter 1, in the case of droplet heating and evaporation into a high-pressure gas (Diesel engine-like conditions), the kinetic effects may not be negligible, and two regions of gas above the surface of the evaporating droplet were considered: the kinetic and hydrodynamic regions. In the most comprehensive model, described by Sazhin and Shishkova [2009], it was assumed that gas consisted of two components, fuel vapour and background gas (air), and both mass and heat transfer processes in kinetic region were taken into account. The analysis of the processes in this region was based on the numerical solution of the Boltzmann equations for fuel vapour and background gas with the relevant boundary conditions.
Sazhin et al. [2010b] suggested simple approximate formulae to describe the temporal evolution of Diesel fuel droplet radii and temperatures predicted by the kinetic model. These formulae are valid in the range of gas temperatures relevant to Diesel engine-like conditions and fixed values of initial droplet radii, or in the range of initial droplet radii relevant to Diesel engine-like conditions and fixed values of gas temperature. The new approximations were shown to be reasonably accurate for predicting the temporal evolution of droplet radii and droplet evaporation times. The predictions of droplet temperatures turned out to be less accurate than those of droplet radii, but this accuracy was believed to be sufficient for many practical applications. The application of these formulae is expected to reduce dramatically the CPU requirements of kinetic modelling, which can potentially open the way to the implementation of the kinetic models into computational fluid dynamics (CFD) codes designed to model droplet heating and evaporation in a realistic engineering environment, including that of Diesel engines (Flynn et al. [1999]; Stiesch [2003]).

Despite of considerable progress in the development of kinetic models of droplet heating and evaporation, all these models were based on a number of restrictive assumptions. Firstly, in all these models it was assumed that there is no temperature gradient inside droplets. The limitations of this assumption have been widely discussed in the literatures using the conventional hydrodynamic approach (Bertoli and Migliaccio [1999]; Kristyadi et al. [2010]; Maqua et al. [2008]; Sazhin [2006]). However, nobody has considered this effect in conjunction with kinetic modelling. Secondly, the kinetic models, described in Refs. (Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006]), were based on the assumption that all collisions between molecules are elastic. This assumption could be justified in the case of monoatomic molecules such as argon, but in the case of complex molecules, such as n-dodecane ($C_{12}H_{26}$, the closest approximation to Diesel fuel), this assumption
becomes highly doubtful. A new approach to the solution of the Boltzmann equation in the presence of inelastic collisions is introduced in Chapter 4. Thirdly, the models described by Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], assumed that the evaporation coefficient is equal to 1, which could not be rigorously justified. Moreover, in Chapter 3 it was shown that this coefficient can be well below 1 (close to 0.5) especially when the temperature is close to critical one (Cao et al. [2011]; Xie et al. [2011c, 2012a]).

The aim of this chapter is to develop further the kinetic model described by Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], in which these assumptions are relaxed. We will restrict our analysis to stationary droplets and ignore the effects of the moving boundary (see Mitchell et al. [2011]; Sazhin et al. [2010a] for the analysis of this effect), the formation of the thermal boundary layer around droplets (see Sazhin et al. [2011c] for details) and the effects of thermal radiation (Sazhin et al. [2011b]).

In Section 5.2 the physical models used in various regions inside and around droplets are described. The algorithm used for calculations is described in Section 5.3. The droplet temperatures and radii predicted by various models, but assuming that the evaporation coefficient is equal to 1, are compared in Section 5.4. The modifications of these results in the case when the evaporation coefficient is not equal to 1 are presented and discussed in Section 5.5. The main conclusions of this chapter are drawn in Section 5.6.

### 5.2 Physical Models

As discussed by Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], two regions of gas above the surface of
 evaporating fuel droplet are considered: the kinetic and hydrodynamic regions. In contrast to Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], we relax the assumption that the liquid thermal conductivity is infinitely large and consider the processes in the liquid phase region as well. All three regions are schematically shown in Figure 5.1. Following Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], we assume that gas consists of two components, fuel vapour and background air, both in kinetic and hydrodynamic regions. It is assumed that the contribution of chemical reactions of fuel vapour and oxygen can be ignored. Fuel vapour and air dynamics in the kinetic region are described by the Boltzmann equations, while the conventional hydrodynamic analysis is applied in the hydrodynamic region. The models used in all three regions and the conditions at the interface between the regions are discussed in the following three subsections.

Figure 5.1: Liquid phase, kinetic and hydrodynamic regions in the vicinity of droplet surface. $T_s$ is the surface temperature of droplet, $\rho_s$ is the vapour density in the immediate vicinity of the droplet surface, $T_{Rd}$ and $\rho_{Rd}$ are the temperature and density of vapour at the outer boundary of kinetic region. $\delta_{Rd}$ indicates the thickness of kinetic region, $j_v$ and $q$ show the directions of vapour mass and heat fluxes, respectively.
5.2.1 Liquid phase region

The models for droplet heating used by Maqua et al. [2008] and Kristyadi et al. [2010] were implicitly based on the assumptions that the evaporation rate of droplets is small and the droplet radius $R_d$ does not change during any time step (although this radius changes from one step to another). This means that the effect of a moving boundary on droplet heating was ignored. This is a well known approach used in all available CFD codes. Two approaches were developed to take into account the changes in droplet radius $R_d$ during the time steps. Firstly, it was assumed that $R_d$ is a linear function of time. Secondly, the evolution of droplet temperature was calculated for an a priori fixed function $R_d(t)$ (Sazhin et al. [2010a, 2011c]). These effects, however, will not be taken into account in present analysis.

Assuming that the droplet heating process is spherically symmetric, the droplet temperature ($T \equiv T(t, R)$) can be found from the solution to the equation for $T$ in the form (Carslaw and Jaeger [1986]; Kartashov [2001]):

$$\frac{\partial T}{\partial t} = \kappa \left( \frac{\partial^2 T}{\partial R^2} + \frac{2}{R} \frac{\partial T}{\partial R} \right)$$

(5.1)

for $0 \leq t < t_e$, $0 \leq R < R_d(t)$, where $\kappa$ is the liquid thermal diffusivity ($\kappa = k_l/(c_l \rho_l)$), $k_l$ is the thermal conductivity, $c_l$ is the specific heat capacity, $\rho_l$ is the density, $R$ is the distance from the droplet centre and $t_e$ is the evaporating time.

Remembering the physical background to the problem, we look for the solution to this equation in the form of a twice continuously differentiable function $T \equiv T(t, R)$ for $0 \leq t < t_e$, $0 \leq R < R_d(t)$. This solution should satisfy the boundary condition
(Sazhin et al. [2004]):

\[
\left( k_l \frac{\partial T}{\partial R} + hT \right) \bigg|_{R=R_d(t)} = hT_g + \rho_l L \dot{R}_{de}(t),
\]

Eq. (5.2) is the energy balance condition at \( R = R_d(t) \). The initial condition is taken in the form:

\[
T(t = 0) = T_0(R),
\]

where \( 0 \leq R \leq R_{d0} = R_d(t = 0) \). In conventional hydrodynamic models, the value of \( R_d(t) \) is controlled by vapour diffusion from the droplet surface and droplet thermal swelling. In our model, it is controlled by vapour diffusion from the interface between the kinetic and hydrodynamic regions (see Figure 5.1) and swelling, and can be found from the equation (Sazhin [2006]):

\[
\dot{R}_d \equiv \dot{R}_{de} + \dot{R}_{ds} = -\frac{k_g \ln (1 + B_M)}{\rho c_{pg} R_d} + \frac{R_{d0}}{\Delta t} \left[ \left( \frac{\rho(T_0)}{\rho(T_1)} \right)^{1/3} - 1 \right],
\]

where \( \dot{R}_{ds} \) is the rate of change of droplet radius due to swelling (or contraction), \( B_M = Y_{vR} / (1 - Y_{vR}) \) is the Spalding mass transfer number (assuming that there is no vapour in the ambient gas), \( Y_{vR} \) is the mass fraction of vapour at the interface between the kinetic and hydrodynamic regions, which is ultimately controlled by gas temperature \( T_{Rd} \) in this region (Sazhin [2006]), \( T_0 \) and \( T_1 \) are average droplet temperatures at the beginning and the end of the time step \( \Delta t \), \( k_g \) is the thermal conductivity of gas, \( c_{pg} \) is the specific heat capacity of gas and \( \rho \) are the corresponding densities. When
deriving Eq. (5.4) we ignored the difference between \( R_d \) and \( R_d + \delta_{Rd} \). The validity of this assumption was checked by a direct comparison of the results, taking and not taking into account the effects of the sphericity of droplets for the thickness of the kinetic region equal to ten mean molecular paths, calculated for pressure equal to 30 bars (Diesel engine-like conditions) and temperatures equal to fuel droplet surface temperatures (Sazhin et al. [2007]).

Assuming that \( R_d \) is fixed during the time step, the analytical solution to Eq. (5.1) subject to the above boundary and initial conditions was obtained in the form (Sazhin et al. [2004])

\[
T(R) = \frac{1}{R \sqrt{R_d}} \left[ \sum_{n=1}^{\infty} \Theta_n(t) \sin \left( \lambda_n \frac{R}{R_d} \right) + \frac{\mu_0(t)}{1 + h_0 R_d} \right],
\]

where

\[
\Theta_n(t) = \Theta_n(0) \exp \left[ -\frac{\kappa \lambda_n^2 t}{R_{d0}^2} \right] + f_n \int_0^t \frac{d\mu_0(\tau)}{d\tau} \exp \left[ -\frac{\kappa \lambda_n^2 (t - \tau)}{R_{d0}^2} \right] d\tau,
\]

\[
\mu_0(t) \equiv R_d^{5/2} \frac{h}{k_i} T_g,
\]

\[
f_n = -\frac{\sin \lambda_n}{||v_n||^2 \lambda_n^2}, \quad v_n(\xi) = \sin \lambda_n \xi \quad (n = 1, 2, ...).
\]

\[
|| v_n ||^2 = \frac{1}{2} \left( 1 - \frac{\sin 2\lambda_n}{2\lambda_n} \right) = \frac{1}{2} \left( 1 + \frac{h_0}{h_0^2 + \lambda_n^2} \right).
\]

\( \xi = R/R_d \), \( \lambda_n \) are positive solutions to the equation

\[
\lambda \cos \lambda + h_0 \sin \lambda = 0
\]
presented in ascending order,

\[ h_0 = \frac{h}{k_l} R_d - 1 \quad (5.10) \]

is assumed to be constant during the time step,

\[ \Theta_n(0) = q_n + \mu_0(0) f_n, \]

\[ q_n = \frac{1}{||v_n||^2} \int_0^1 R_{d0}^{3/2} \xi T_0(\xi R_{d0}) v_n(\xi) d\xi. \quad (5.11) \]

The effect of recirculation inside droplets was taken into account based on the effective thermal conductivity (ETC) model (Abramzon and Sirignano [1989]), in which the liquid thermal conductivity \( k_l \) is replaced by the effective thermal conductivity

\[ k_{\text{eff}} = \chi k_l, \quad (5.12) \]

where the coefficient \( \chi \) is defined as

\[ \chi = 1.86 + 0.86 \tanh \left[ 2.245 \log_{10} \left( \text{Pe}_{d(l)} / 30 \right) \right], \quad (5.13) \]

\( \text{Pe}_{d(l)} = \text{Re}_{d(l)} \text{Pr}_{(l)} \) is the droplet Peclet number, in which liquid transport properties and the maximum surface velocity inside droplets were used. The latter velocity was calculated by Abramzon and Sirignano [1989]:

\[ U_s = \frac{1}{32} \Delta U \left( \frac{\mu_g}{\mu_l} \right) \text{Re}_d C_F, \quad (5.14) \]

where \( \Delta U \equiv |U_g - U_d| \) is the relative velocity between ambient gas and droplets, \( \mu_{g(l)} \)
is the dynamic viscosity of gas (liquid), $Re_d$ is the droplet Reynolds number based on the droplet diameter, and $C_F$ is the friction drag coefficient estimated as (Abramzon and Sirignano [1989]):

$$C_F = \frac{12.69}{Re_d^{2/3}(1 + B_M)}.$$  \hspace{2cm} (5.15)

It can be shown that in the limit $k_l \to \infty$, Solution (5.5) reduces to (Sazhin and Krutitskii [2003]):

$$T_d = T_g + (T_{d0} - T_g) \exp \left( -\frac{3ht}{c_l \rho_l R_d} \right),$$  \hspace{2cm} (5.16)

where $T_d$ does not depend on $R$.

Eq. (5.16) was used in previously reported kinetic models of droplet heating and evaporation (Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006]). The model presented in this chapter is based on Eq. (5.5). The results predicted by the models based on both equations will be compared where appropriate.

The following approximations for n-dodecane are used, following Abramzon and Sazhin [2006]:

$$La = 37440 \cdot (T_{cr} - T_s)^{0.38} \quad \text{J/kg},$$

$$\rho_l = 744.11 - 0.771 \cdot (T - 300) \quad \text{kg/m}^3,$$

$$c_l = 2180 + 4.1 \cdot (T - 300) \quad \text{J/(kg \cdot K)},$$

where $T_{cr} = 659$ K is the critical temperature of n-dodecane. When calculating average liquid density and specific heat capacity, $T$ in the last two expressions is replaced with the average temperature $\overline{T}$. 

88
5.2.2 Kinetic region

Following Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], the evolution of molecular velocity distribution functions of air $f_a \equiv f_a(r,t,v)$ and vapour $f_v \equiv f_v(r,t,v)$ in the kinetic region is controlled by the corresponding Boltzmann equations:

$$\begin{align}
\frac{\partial f_a}{\partial t} + v_a \frac{\partial f_a}{\partial r} &= J_{aa} + J_{av} \\
\frac{\partial f_v}{\partial t} + v_v \frac{\partial f_v}{\partial r} &= J_{va} + J_{vv}
\end{align}$$

(5.17)

where $J_{\alpha\beta}$ ($\alpha = a,v; \beta = a,v$) are collision integrals, taking into account the contribution of the collisions between molecules. The general numerical scheme used for the solution of these equations is described in Appendix B. The model, taking into account the effects of inelastic collisions, was discussed in Section 4.2.

Eqs. (5.17) are solved subject to the boundary conditions at the interface between the kinetic and liquid phase regions and at the interface between the kinetic and hydrodynamic regions. The first boundary condition for fuel vapour can be presented as:

$$f_v^{\text{(out)}} = \sigma f_{vs} + (1 - \sigma) f_{vr},$$

(5.18)

where $f_{vs}$ is the distribution function of molecules leaving the liquid surface assuming that $\sigma = 1$, $f_{vr}$ is the distribution function of reflected molecules. Both $f_{vs}$ and $f_{vr}$ are assumed to be isotropic Maxwellian. Eq. (5.18) is identical to Eq. (3.1). The temperature for $f_{vs}$ is assumed to be equal to $T_s$, while the temperature for $f_{vr}$ is assumed to be equal to $T_{Rd}$. This is justified by the fact that the thickness of the kinetic region is small and the gas temperature just above the droplet surface is close
to $T_{Rd}$ (Fuchs [1959]). As introduced in Chapter 3, a more accurate approximation for $f_{vr}$ would have been a bi-Maxwellian distribution, but this effect is not taken into account in this chapter.

At the boundary between the kinetic and hydrodynamic regions the distribution function of both fuel vapour and air molecules entering the kinetic region is assumed to be Maxwellian, controlled by $\rho_{Rd}$ and $T_{Rd}$. Further details of the boundary conditions used for kinetic calculations are discussed by Sazhin et al. [2007].

The contributions of both mass and heat transfer in the kinetic region are taken into account following the approach described by Sazhin and Shishkova [2009]. At first, as discussed by Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006], it is assumed that the evaporation coefficient $\sigma_e$ is equal to 1. Then the effects of realistic $\sigma_e$ on droplet heating and evaporation will be investigated.

### 5.2.3 Hydrodynamic region

Kryukov et al. [2004]; Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006] assumed that the mass fluxes leaving the kinetic region and the corresponding diffusion fluxes in the hydrodynamic region are matched. This condition is presented in the form:

$$
\frac{M_v}{N_A} \int_{-\infty}^{+\infty} dv_y \int_{-\infty}^{+\infty} dv_z \int_{0}^{+\infty} dv_x v_x f_v(r, t, v) = \frac{\rho_{\text{mix}} D_{va}}{R_d} \ln (1 + B_M) \equiv j_h = j_v,
$$

(5.19)

where $\rho_{\text{mix}}$ is the density of the mixture of air and vapour at the inner boundary of the hydrodynamic region ($\rho_{\text{mix}} = \rho_{vRd} / Y_{vRd}$), $D_{va}$ is the binary diffusion coefficient (diffusion of vapour through air), $M_v$ is the molar mass of vapour, $N_A$ is the Avogadro number and $j_h$ is the mass flux of evaporated fuel. $B_M$ takes into account the effect of
the finite mass fraction of fuel vapour in the evaporation process. The binary diffusion coefficient is calculated from the following expression (Bird et al. [2002]):

\[ D_{va} = 1.8583 \times 10^{-7} \sqrt{\frac{T^3}{p \sigma_{va}^2 \Omega_{D,va}}} \] (5.20)

where \( D_{va} \) is in m\(^2\)/s, \( p \) is in atm (1 atm \( \approx 1.01 \times 10^5 \) Pa), \( \sigma_{va} = 0.5(\sigma_v + \sigma_a) \) is the average diameter of molecules of vapour and air, \( \Omega_{D,va} \) is the function of \( T^\ast \equiv k_B T_r / \varepsilon_{va} \), \( \varepsilon_{va} = \sqrt{\varepsilon_v \varepsilon_a} \), \( \varepsilon_v \) and \( \varepsilon_a \) are Lennard-Jones parameters of fuel vapour and air (Abramzon and Sirignano [1989]), \( k_B \) is the Boltzmann constant, \( T_r = T_s + \frac{1}{3}(T_g - T_s) \) is the reference temperature, \( T_s \) is the droplet surface temperature, \( M_a \) is the molar mass of air, and \( T_g \) is the ambient gas temperature.

Following Bird et al. [2002], the following approximation for \( \Omega_{D,va} \) is used:

\[ \Omega_{D,va} = \frac{1.06036}{T^{0.15610}} + \frac{0.19300}{\exp(0.47635T^\ast)} + \frac{1.03587}{\exp(1.52996T^\ast)} + \frac{1.76474}{\exp(3.89411T^\ast)}. \]

Following Sazhin and Shishkova [2009], the following values of parameters are used for most of our analysis: \( \sigma_v = 9.373 \times 10^{-10} \) m, \( \sigma_a = 3.667 \times 10^{-10} \) m, \( \varepsilon_v/k_B = 351.0 \) K and \( \varepsilon_a/k_B = 97.0 \) K (Abramzon and Sirignano [1989]).

The heat flux supplied to the droplet is estimated as:

\[ q_s = h(T_g - T_{Ra}), \] (5.21)

where the convection heat transfer coefficient \( h \) is obtained from the equation:

\[ h = \frac{k_{mix}}{R_d} \frac{\ln (1 + B_T)}{B_T}, \] (5.22)
$k_{\text{mix}}$ is the thermal conductivity of the mixture of vapour and air, $B_T$ is the Spalding heat transfer number calculated as (Sazhin [2006]):

$$B_T = (1 + B_M)^\varphi - 1,$$  \hfill (5.23)

$$\varphi = \left( \frac{c_{pv}}{c_{pg}} \right) \frac{1}{Le} = \frac{c_{pv} \rho_{\text{mix}} D_{va}}{k_{\text{mix}}},$$  \hfill (5.24)

$Le = k_{\text{mix}}/(c_{pg} \rho_{\text{mix}} D_{va})$ is the Lewis number, $c_{pv}$ and $c_{pg}$ are the specific heat capacities of fuel vapour and ambient gas (air), respectively. Note that $\varphi$ does not depend on $c_{pg}$. Eq. (5.24) is only valid for stationary droplets (Abramzon and Sirignano [1989]). However, the average droplet temperatures calculated using this formula are almost indistinguishable from the ones predicted by the models considering the non-zero droplet velocities (Elwardany et al. [2011]).

Following Sazhin and Shishkova [2009], the following approximations for $c_{pv}$, $k_v$ and $k_a$ are used

$$c_{pv} = 1594.60 + 1.15\tilde{T} - 100.567\tilde{T}^2 - 28.56\tilde{T}^3 + 5.07\tilde{T}^4 - 0.25\tilde{T}^5 \quad \text{J/(kg} \cdot \text{K),}$$

$$k_v = 0.02667 \cdot (T_r/300)) - 0.02087 \quad \text{W/(m} \cdot \text{K),}$$

$$k_a = 3.227 \times 10^{-3} + 8.3894 \times 10^{-5}T_r - 1.9858 \times 10^{-8}T_r^2 \quad \text{W/(m} \cdot \text{K),}$$

where $\tilde{T} = (T_r - 300)/300$.

The thermal conductivity of the mixture of fuel vapour and air is estimated as

$$k_{\text{mix}} = \sum_{i=1}^{2} \frac{X_i k_i}{\sum_{j=1}^{2} X_j \Phi_{ij}} \quad \text{W/(m} \cdot \text{K),}$$
where $i$ and $j$ stand for fuel vapour or air, and $X_{i,j}$ are molar fractions of the species,

$$
\Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{k_i}{k_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2,
$$

$M_{i,j}$ are molar masses of the corresponding species ($M_v = 170.3$ kg/kmol, $M_a = 28.97$ kg/kmol) (Abramzon and Sirignano [1989]).

Following Sazhin and Shishkova [2009], the values of the saturated fuel vapour pressure are estimated as:

$$p_{v\text{(sat)}} = A_1 \cdot \exp \left( \frac{T_s - A_0}{B_1} \right) \text{ Pa}, \quad (5.25)$$

where

$$
\begin{align*}
A_0 &= 300.17542 \\
A_1 &= 70.44441 \quad \text{when } T_s < 440 \text{ K} \\
B_1 &= 22.36885 \\
A_0 &= 449.87125 \quad \text{when } T_s \geq 440 \text{ K.} \\
A_1 &= 46204.48272 \\
B_1 &= 56.97142
\end{align*}
$$

Eq. (5.25) is an alternative presentation of the Clausius-Clapeyron equation (Atkins and de Paula [2002]).

The processes in the kinetic and hydrodynamic regions are linked by the matching conditions of conservation of mass flux (see Eq. (5.19)) and heat flux

$$q_k = q_h, \quad (5.26)$$
at the interface. Subscripts \( k \) and \( h \) refer to kinetic and hydrodynamic regions, respectively.

Note that Figures 7-13 of Sazhin and Shishkova [2009] were based on a simplified version of the above model for the hydrodynamic region. Namely, it was assumed that \( \Omega_{D,\text{eq}} = T^* \), \( \varphi = 1 \), \( La = 250,000 \) J/kg, \( \rho_l = 586 \) kg/m\(^3\), \( c_l = 2,900 \) J/(kg K), and \( k_{\text{mix}} = 0.035 \) J/(m K). These simplifications were justified by the fact that Sazhin and Shishkova [2009] focused on the comparison of the predictions of hydrodynamic and kinetic models rather than on the most accurate predictions of droplet radii and temperature during the heating and evaporation processes. In the present work, a considerably improved model is used as described above. The properties of n-dodecane (C\(_{12}\)H\(_{26}\)) can be found in Appendix C.

5.3 Solution Algorithm

The idea of the solution algorithm used in the analysis is similar to the one described by Sazhin and Shishkova [2009]. The first step in the solution of Eqs. (5.17) is to perform an investigation of mass and heat transfer processes in the kinetic region for a set of values of \( \rho_{Rd} \) and \( T_{Rd} \). Remembering that we consider the problem of heating and evaporation of droplets in a hot gas, these parameters are assumed to be in the ranges: \( \rho_{Rd} < \rho_s \) and \( T_{Rd} > T_s \). During the droplet heating process the temperature decreases away from the droplet; the evaporation process is possible when the fuel vapour density decreases away from the droplet surface. Once the values of \( \rho_{Rd} \) and \( T_{Rd} \) have been found, the solution of the Boltzmann Eqs. (5.17) in the kinetic region allows us to calculate the normalised mass and heat fluxes at the outer boundary of
\[ \tilde{j}_k = j_k / (\rho_0 \sqrt{R_v T_0}), \quad \tilde{q}_k = q_k / (p_0 \sqrt{R_v T_0}), \]

where \( R_v \) is the gas constant of fuel vapour, \( T_0 \) is the reference temperature chosen equal to 600 K, \( p_0 \) and \( \rho_0 \) are the saturated fuel vapour pressure and density corresponding to \( T_0 \), and \( \rho_0 \) is calculated from the ideal gas law.

We assume that \( \rho_{Rd} = 0.9 \rho_s \) and \( T_s = T_0 = 600 \) K. The values of \( \tilde{q}_k \) were calculated for the numbers of internal degrees of freedom \( N_{int} \) from 0 to 50 and \( \tilde{T}_{Rd} = T_{Rd} / T_s \) from 1 to 1.4. The results are shown in Figure 5.2. As follows from this figure, for all values of \( N_{int} \) the dependence of \( \tilde{q}_k \) on \( \tilde{T}_{Rd} \) is well described by a linear function, in agreement with the case reported by Sazhin and Shishkova [2009]. For any given \( \tilde{T}_{Rd} \) the values of \( \tilde{q}_k \) decrease with increasing \( N_{int} \). The rate of this decrease, however, becomes small at \( N_{int} > 10 \) and negligible at \( N_{int} > 20 \). This allows us to restrict our analysis to the case of \( N_{int} = 20 \), in agreement with the conclusion drawn in Chapter 4.

The plots of \( \tilde{q}_k \) versus \( \tilde{\rho}_{Rd} \equiv \rho_{Rd} / \rho_s \) for \( \tilde{T}_{Rd} = 1.1 \) and \( 1.2 \) and \( N_{int} = 20 \) are shown in Figure 5.3. As one can see in this figure, the plots for these values of \( \tilde{T}_{Rd} \) are the lines almost parallel to the \( \tilde{\rho}_{Rd} \) axis. This allows us to ignore the dependence of \( \tilde{q}_k \) on \( \tilde{\rho}_{Rd} \) in agreement with the similar result obtained by Sazhin and Shishkova [2009] for \( N_{int} = 0 \).

The plots of \( \tilde{q}_k \) versus \( \tilde{T}_{Rd} \) for \( \tilde{\rho}_{Rd} = 1, \; N_{int} = 0 \) and 20, and \( \tilde{q}_h = q_h / (p_0 \sqrt{R_v T_0}) \) versus \( \tilde{T}_{Rd} \) (horizontal line) are shown in Figure 5.4. The following values of parameters were used: \( T_g = 1,000 \) K, \( T_s = 600 \) K, \( R_d = 5 \) \( \mu \)m. The intersections between the horizontal and inclined lines give the required values of \( \tilde{T}_{Rd} \). For the case of only elastic collisions (\( N_{int} = 0 \)), \( \tilde{T}_{Rd} = 1.014 \); for the case when the contribution of inelastic collisions with \( N_{int} = 20 \) is taken into account, \( \tilde{T}_{Rd} = 1.026 \). This result indicates that
Figure 5.2: Plots of normalised heat flux $\tilde{q}_k = q_k/(p_0\sqrt{R_v}T_0)$ in the kinetic region versus normalised temperature $\tilde{T}_{Rd} = T_{Rd}/T_s$ for various numbers of internal degrees of freedom $N_{\text{int}}$, assuming that $T_s = T_0 = 600$ K. $\rho_{Rd}$ is taken equal to $0.9\rho_s$.

Figure 5.3: Plots of normalised heat flux $\tilde{q}_k$ in the kinetic region versus normalised density $\tilde{\rho}_{Rd} = \rho_{Rd}/\rho_s$ for $N_{\text{int}} = 20$ and $\tilde{T}_{Rd} = 1.1$ and 1.2.
the contribution of internal degrees of freedom leads to an increase in $\tilde{T}_{Rd}$.

The plots of $\tilde{j}_k$ versus $\tilde{\rho}_{Rd}$ for $T_{Rd} = 1.026$, $N_{int} = 0$ and 20, and $\tilde{j}_h = j_h/(p_0 \sqrt{R_v T_0})$ versus $\tilde{\rho}_{Rd}$ (horizontal line) are shown in Figure 5.5. This figure is presented for the same parameters as Figure 5.4. Following Sazhin and Shishkova [2009], it was assumed that $\rho_{Rd}$ in Eq. (5.19) can be replaced with $\rho_s$. The intersections between the horizontal and inclined lines give the required values of $\tilde{\rho}_{Rd}$. For the case of only elastic collisions ($N_{int} = 0$), $\tilde{\rho}_{Rd} = 0.968$; for the case when the contribution of inelastic collisions with $N_{int} = 20$ is taken into account, $\tilde{\rho}_{Rd} = 0.926$. This result indicates that the contribution of internal degrees of freedom leads to a decrease in $\tilde{\rho}_{Rd}$.

![Figure 5.4](image)

**Figure 5.4:** Plots of $\tilde{q}_k$ versus $T_{Rd}$ for $N_{int} = 0$ and 20, and the plot of $\tilde{q}_h = q_h/(p_0 \sqrt{R_v T_0})$ versus $T_{Rd}$ for $T_0 = T_s = 600$ K, $T_g = 1,000$ K, $R_{d0} = 5 \mu$m and $\tilde{\rho}_{Rd} = 1$. The intersections between the plots of $\tilde{q}_k$ and $\tilde{q}_h$ give the required values of $\tilde{T}_{Rd}$.

Similar values of $\tilde{T}_{Rd}$ and $\tilde{\rho}_{Rd}$ were obtained for other values of $T_g$ and $R_d$ relevant for Diesel engine conditions ($T_g = 750$ K and $R_d = 20 \mu$m) and the values of $T_s$ in the range from 300 K to the critical temperature. The corresponding values of $\tilde{T}_{Rd}$ and $\tilde{\rho}_{Rd}$ were used for the analysis of heating and evaporation of n-dodecane droplets in realistic Diesel engine-like conditions. The results will be presented in Section 5.4.
Figure 5.5: Plots of $\tilde{j}_k = j_k/(\rho_0\sqrt{R_vT_0})$ versus $\tilde{\rho}_{Rd}$ for $N_{int} = 0$ and 20, and the plot of $\tilde{j}_h = j_h/(\rho_0\sqrt{R_vT_0})$ versus $\tilde{\rho}_{Rd}$ for $T_0 = T_s = 600$ K, $T_g = 1,000$ K, $R_{d0} = 5$ µm and $\tilde{T}_{Rd} = 1.026$. The intersections between the plots of $\tilde{j}_k$ and $\tilde{j}_h$ give the required values of $\tilde{\rho}_{Rd}$.

Figure 5.6: Plots of $\tilde{j}_k$ versus $\tilde{\rho}_{Rd}$ for $N_{int} = 20$ and $\sigma_e = 1$ and 0.36 versus $\tilde{\rho}_{Rd}$ for $T_0 = T_s = 600$ K, $T_g = 1,000$ K, $R_{d0} = 5$ µm and $\tilde{T}_{Rd} = 1.026$. 

98
For realistic $\sigma_e < 1$ the values of $\tilde{q}_k$ were practically indistinguishable from those predicted by the model with $\sigma_e = 1$. The plots of $\tilde{j}_k$ versus $\tilde{\rho}_{Rd}$ for $\tilde{T}_{Rd} = 1.026$, $N_{int} = 20$ and $\sigma_e = 1$ and 0.36 are shown in Figure 5.6. The plot for $\sigma_e = 1$ is identical to the one shown in Figure 5.5, but presented in a wider range of $\tilde{\rho}_{Rd}$. The value of $\sigma_e = 0.36$ is close to the one predicted for $T_s = 600$ K. This will be discussed in Section 5.5. As follows from Figure 5.6, the linear dependence of $\tilde{j}_k$ on $\tilde{\rho}_{Rd}$ is maintained for $\sigma_e = 0.36$, but the values of $\tilde{j}_k$ predicted by the model with $\sigma_e = 0.36$ are lower than those predicted by the model with $\sigma_e = 1$. We follow the same procedure of calculating $\tilde{\rho}_{Rd}$ as described earlier for $\sigma_e = 1$ and shown in Figure 5.5. As one can see from Figure 5.6, this leads to the prediction of lower values of $\tilde{\rho}_{Rd}$ for $\sigma_e = 0.36$ than for $\sigma_e = 1$. Thus the reduction of $\sigma_e$ is expected to lead to the enhancement of the kinetic effects.

### 5.4 Results ($\sigma_e = 1$)

The algorithm described above was applied to the computation of heating and evaporation of Diesel fuel droplets in a hot gas at two temperatures (750 K and 1,000 K). The initial droplet temperature and gas pressure in all cases were assumed equal to 300 K and 30 bar respectively. The initial droplet radii were assumed to be equal to 5 $\mu$m. Droplets were assumed to be stationary, but the effect of swelling was taken into account. The calculations were performed using the Infinite Thermal Conductivity (ITC) and Effective Thermal Conductivity (ETC) models for the liquid phase, conventional hydrodynamic model, described in Section 5.2, and kinetic models taking and not taking into account the effects of inelastic collisions. The value of the evaporation coefficient was assumed equal to 1 in all cases.

The results of calculation of the radii and surface temperatures of droplets immersed into gas with temperature 750 K are shown in Figure 5.7 and 5.8 respectively. As follows
from Figure 5.8, at the initial stage of droplet heating and evaporation, the kinetic effects on temperature are negligible, but the difference in temperatures, predicted by the hydrodynamic models taking and not taking into account the effects of liquid finite thermal conductivity, is quite noticeable. This is consistent with the results earlier reported by Sazhin et al. [2006]. Initially, the droplet surface temperature predicted by the ETC model is larger than the one predicted by the ITC model. This larger droplet surface temperature predicted by the ETC model leads to the reduction of heat flux supplied to the droplet, which eventually leads to the situation when the droplet surface temperature predicted by the ETC model becomes smaller than the one predicted by the ITC model. This happens at times close to 0.4 ms. Smaller temperatures, predicted by the ETC model at this stage, lead to slightly slower evaporation rate and longer evaporation time of droplets as shown in Figure 5.7.

As follows from Figure 5.7, the kinetic models, taking and not taking into account inelastic collisions, predict longer evaporation times compared with the hydrodynamic ETC and ITC models, in agreement with the prediction of the model described by Sazhin and Shishkova [2009]. The kinetic model, taking into account inelastic collisions, predicts longer evaporation times compared with the model ignoring this effect, in agreement with the prediction of Figure 5.5. Similar enhancement of the kinetic effects due to the contribution of inelastic collisions can be observed from the temperature curves shown in Figure 5.8.

The results of calculation of the radii and surface temperatures of droplets immersed into gas with temperature 1,000 K are shown in Figure 5.9 and 5.10 respectively. As in the case shown in Figure 5.8, it follows from Figure 5.10 that at the initial stage of droplet heating and evaporation, the kinetic effects on temperature are negligible, but the difference in temperatures, predicted by the hydrodynamic models taking and not taking into account the effects of liquid finite thermal conductivity, is noticeable.
Figure 5.7: Plots of $R_d$ versus time $t$ for an n-dodecane droplet, predicted by hydrodynamic ITC model (curve 1), kinetic ITC model ignoring the effects of inelastic collisions (curve 2), the kinetic ITC model taking into account the effects of inelastic collisions (curve 3), hydrodynamic ETC model (curve 4), kinetic ETC model ignoring the effects of inelastic collisions (curve 5), kinetic ETC model taking into account the effects of inelastic collisions (curve 6) (a). Zoomed part of (a) shows the plots at the final stage of evaporation processes (b). All plots are shown for $T_g = 750$ K, $T_{d0} = 300$ K and $R_{d0} = 5 \mu m$. 
Figure 5.8: The same as Figure 5.7 but for $T_s$. 
Figure 5.9: The same as Figure 5.7 but for $T_g = 1,000$ K.
Figure 5.10: The same as Figure 5.8 but for $T_g = 1,000$ K.
Initially, the droplet surface temperature predicted by the ETC model is larger than the one predicted by the ITC model, but at times larger than about 0.25 ms the surface temperature predicted by the ETC model becomes smaller than the one predicted by the ITC model. In contrast to the case shown in Figure 5.7, in the case shown in Figure 5.9 the net effects of the increase of the temperature predicted by the ETC model before 0.25 ms and its decrease at times after 0.25 ms lead to shorter evaporation time predicted by the ETC model compared with the ITC model.

As in the cases shown in Figures 5.7 and 5.8, for gas temperature equal to 1,000 K, the kinetic models with and without inelastic collisions, predict longer evaporation times and higher temperatures at the final stage of droplet evaporation, compared with the hydrodynamic ETC and ITC models. Also, as in the cases shown in Figures 5.7 and 5.8, the kinetic models considering the inelastic collisions predict longer evaporation times and higher temperatures at the final stage of droplet evaporation, compared with the model ignoring this effect. These kinetic effects are stronger in the cases shown in Figures 5.9 and 5.10 than the cases shown in Figures 5.7 and 5.8.

5.5 Results ($\sigma_e < 1$)

As mentioned earlier, in previously described kinetic models it was assumed that $\sigma_e = 1$ (Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006]). This was justified by the fact that no reliable experimental data or theoretical predictions of $\sigma_e$ were available at that time. The situation changed after the publication of papers (Cao et al. [2011]; Xie et al. [2011c]), where a new model for molecular dynamic simulations of n-dodecane was suggested. Using this model, Cao et al. [2011] and Xie et al. [2011c] obtained the values of $\sigma_e$ at various surface temperatures relevant to Diesel engine conditions. These values are shown in Table 5.1, based on the most
Table 5.1: Condensation/evaporation coefficient as a function of the liquid temperature.

<table>
<thead>
<tr>
<th>$T_s$ (K)</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_e$</td>
<td>0.93</td>
<td>0.72</td>
<td>0.59</td>
<td>0.45</td>
</tr>
</tbody>
</table>

comprehensive calculations presented by Xie et al. [2011c].

The temperature dependence of $\sigma_e$ inferred from Table 5.1 can be approximated as:

$$\sigma_e(T_s) = 7.0 \times 10^{-6} T_s^2 - 9.8 \times 10^{-3} T_s + 3.7215. \quad (5.27)$$

For $T_s = 600$ K, Eq. (5.27) predicts $\sigma_e = 0.36$. This value of $\sigma_e$ was used for the plot presented in Figure 5.6.

In what follows the effects of $\sigma_e < 1$ on n-dodecane droplet heating and evaporation will be presented for the ITC model only. These effects for the ETC model are similar to those for the ITC model.

The results of calculation of the radii and surface temperatures of droplets with initial radii equal to 5 $\mu$m immersed into gas with temperature 1,000 K using the ITC model with $\sigma_e = 1$ and $\sigma_e$ predicted by Eq. (5.27) are shown in Figure 5.11. The plots for $\sigma_e = 1$ are the same as shown in Figures 5.9 and 5.10. As one can see from this figure, the effect of $\sigma_e < 1$ on droplet radius and temperature in this case is small and can be safely ignored in most practical applications. For gas temperature equal to 750 K, this effect is even smaller than in the case of gas temperature equal to 1,000 K. This means that the results of the analysis for $\sigma_e = 1$ presented in Section 5.4 and by Sazhin and Shishkova [2009]; Sazhin et al. [2010b, 2007]; Shishkova and Sazhin [2006] are applicable for the realistic case $\sigma_e < 1$.

Let us now consider a hypothetical case when a droplet with initial radius equal to 5 $\mu$m is immersed into gas with temperature 1,500 K. The results of calculation of
Figure 5.11: Plots of $R_d$ and $T_s$ versus time $t$ for an n-dodecane droplet, predicted by hydrodynamic ITC model (curve 1), kinetic ITC model ignoring the effects of inelastic collisions and non-unity of $\sigma_e$ (curve 2), the kinetic ITC model taking into account the effects of inelastic collisions but ignoring the non-unity of $\sigma_e$ (curve 3), the kinetic ITC model taking into account the effects of inelastic collisions and non-unity of $\sigma_e$ which is calculated based on Eq. (5.27) (curve 4) (a). Zoomed part of (a) shows the values of $R_d$ and $T_s$ at the final stage of the evaporation processes (b). Plot (a) is shown for $T_g = 1,000$ K, $T_{d0} = 300$ K and $R_{d0} = 5 \mu m$. 
Figure 5.12: The same as Figure 5.11 but for $T_p = 1,500$ K.
the radii and surface temperatures of droplets in this case are shown in Figure 5.12. As one can see from this figure, in this case the effect of $\sigma_e < 1$ is much more visible than the case shown in Figure 5.11. In the case shown by curve 4 the evaporation time is about 3% longer than that shown by curve 3. This effect leads to increased droplet evaporation time, thus enhancing the kinetic corrections to the prediction of the hydrodynamic model.

5.6 Conclusions to Chapter 5

The previously developed kinetic model for droplet heating and evaporation into a high pressure background gas (air) has been generalised to take into account the combined effects of inelastic collisions in the kinetic region, a non-unity evaporation coefficient and temperature gradient inside droplets. The Infinite Thermal Conductivity (ITC) and Effective Thermal Conductivity (ETC) liquid phase models have been used in the analysis. The effects of inelastic collisions have been investigated based on the model introduced in Chapter 4. Both heat and mass transfer in the kinetic region have been taken into account. The boundary conditions at the outer boundary of the kinetic region have been introduced by matching the mass fluxes of vapour leaving the kinetic region and entering into the surrounding hydrodynamic region, and the corresponding heat fluxes.

It has been pointed out that for the parameters typical for Diesel engine-like conditions, the heat flux in the kinetic region is a linear function of the vapour temperature at the outer boundary of this region, but practically does not depend on vapour density at this boundary for all models, including and not including the effects of inelastic collisions, and including and not including the effects of a non-unity evaporation coefficient. For any given temperature at the outer boundary of the kinetic region the
values of the heat flux have been shown to decrease with increasing numbers of internal degrees of freedom of the molecules. The rate of this decrease has been shown to be strong for small numbers of these degrees of freedom but becomes negligible when the number of degrees of freedom exceeds 20. This allows us to restrict our analysis to only the first 20 arbitrarily chosen degrees of freedom of n-dodecane molecules when considering the effects of inelastic collisions.

The mass flux at this boundary has been shown to decrease almost linearly with increasing vapour density at the same location for all above-mentioned models. For any given vapour density at the outer boundary of the kinetic region, the mass fluxes have been shown to be smaller for the model taking into account the contribution of internal degrees of freedom than the one ignoring these degrees of freedom (taking into account the contribution of only elastic collisions). Remembering these properties of heat and mass fluxes and using the matching conditions at the outer boundary of kinetic region, the temperature and fuel vapour density at this boundary have been found following the procedure earlier described by Sazhin and Shishkova [2009].

The model has been applied to the simulation of heating and evaporation of n-dodecane droplets in Diesel engine-like conditions. It has been shown that the effects of inelastic collisions lead to a stronger increase in the predicted droplet evaporation time relative to the hydrodynamic model, compared with the similar increase predicted by the kinetic model considering only elastic collisions. The effects of a non-unity evaporation coefficient have been shown to be weak at gas temperatures about or less than 1,000 K. These effects, however, have been shown to be noticeable for gas temperatures of 1,500 K. In all cases, the kinetic effects have been shown to be negligible at the initial stage of droplet heating and evaporation. At this stage the surface temperatures predicted by the ETC model have been shown to be larger than those predicted by the ITC model in agreement with the earlier results (e.g. Sazhin et al. [2006]).
The application of the rigorous kinetic model, taking into account the effects of inelastic collisions, a non-unity evaporation coefficient, and the ETC model, is recommended when accurate predictions of droplet surface temperature and evaporation time in Diesel engine-like conditions are essential.
Chapter 6

Conclusions and Future Work

6.1 Molecular Dynamics Simulations

Evaporation and condensation for n-dodecane (C\(_{12}\)H\(_{26}\)) at temperatures 400-600 K have been studied based on molecular dynamics simulations (Cao et al. [2011]; Xie et al. [2011c, 2012a]). The thickness of the liquid-vapour interface is predicted to be 2.3-3.5 nm. It is pointed out that the molecular chains lie preferentially parallel to the liquid-vapour interface in the immediate vicinity of this interface. It is shown that molecules at the liquid surface need to obtain relatively large translational energy to evaporate. The vapour molecules with large translational energy can easily penetrate deeply into the transition layer and condense in the liquid phase. Typical molecular behaviours in evaporation and condensation processes have been identified. It is pointed out that molecular exchange condensation, typical for simple molecules, has never been observed for n-dodecane molecular chains.

The evaporation/condensation coefficient at various liquid phase temperatures has been estimated. It is shown to decrease with increasing liquid temperature, in agreement with the prediction of the transition state theory. The velocity distribution functions of molecules in the liquid phase and interface have been shown to be close to isotropic Maxwellian with temperatures equal to that of the liquid phase. These
functions in the vapour phase, however, have been shown to deviate from the classical isotropic Maxwellian distributions. They can be approximated as bi-Maxwellian, with temperatures in the direction normal to the interface larger than those in the directions parallel to the interface. It is suggested that the traditional approach to the formulation of boundary conditions in kinetic modelling, when the distribution function of the evaporated molecules is assumed to be isotropic Maxwellian with the same temperatures for all velocity components, should be modified. Nobody, to the best of our knowledge, has considered MD simulation of molecules at this level of complexity.

6.2 Kinetic Modelling in the Presence of Inelastic Collisions

A new approach to the solution of the Boltzmann equation, taking into account the effect of inelastic collisions, is introduced. This approach is based on the presentation of collisions as the random movement along the surface of an $N$-dimensional sphere, the squared radius of which is equal to the total energy of colliding molecules in the reference system of the centre of mass. The projection of a point on the surface of this sphere in each of $N$ directions gives the root square of the kinetic energy in one of three directions in the physical space, or internal energy referring to one degree of freedom, of one of the colliding molecules. The kinetic energies of both colliding molecules in three directions are described by the first six dimensions of the system, and the remaining $(N-6)$ dimensions describe the internal energies. The new model has been applied to three test problems: shock wave structure in nitrogen, one-dimensional heat transfer through a mixture of n-dodecane and nitrogen and one-dimensional evaporation of n-dodecane into nitrogen. In the first problem, the predictions of the model, taking into account the contribution of the rotational degrees of freedom, are shown to be close to
experimental data and the predictions of an earlier developed model considering the
effects of inelastic collisions. This problem has been generalised to a hypothetical case
when the number of internal degrees of freedom of nitrogen (\(N_{int}\)) is assumed to be
in the range 0 to 10. It has been shown that the results visibly change when \(N_{int}\) is
increased from 0 to 2, but remain practically unchanged at \(N_{int} \geq 6\).

The predicted heat flux for the second problem has been shown not to depend
on the number of internal degrees of freedom of the mixture \(N_{int}\) when this number
exceeds about 15. In the third problem, the predicted mass flux of n-dodecane also
remains almost unchanged at \(N_{int} \geq 15\). These results open the way for considering
systems with arbitrarily large numbers of internal degrees of freedom by reducing the
analysis of these systems to the ones with relatively small numbers of internal degrees
of freedom.

\section*{6.3 Droplet Heating and Evaporation}

The previously developed kinetic model for droplet heating and evaporation into a high
pressure background gas (air), in which the effects of inelastic collisions in the kinetic
region, non-unity evaporation coefficient and temperature gradient inside droplets were
ignored, was generalised to take these effects into account. The Infinite Thermal Con-
ductivity (ITC) and Effective Thermal Conductivity (ETC) liquid phase models were
used in the analysis. The effects of inelastic collisions were investigated based on the
model introduced in Chapter 4. Both heat and mass transfer in the kinetic region were
taken into account. The boundary conditions at the outer boundary of the kinetic re-
gion were introduced by matching the mass fluxes of vapour leaving the kinetic region
and entering into the surrounding hydrodynamic region, and the corresponding heat
fluxes.
The model was applied to the simulation of heating and evaporation of n-dodecane droplets in Diesel engine-like conditions. It was shown that the effects of inelastic collisions lead to a stronger increase in the predicted droplet evaporation time relative to the hydrodynamic model, compared with the similar increase predicted by the kinetic model considering only elastic collisions. The effects of a non-unity evaporation coefficient were shown to be weak at gas temperatures of about or less than 1,000 K. These effects, however, were noticeable for gas temperatures of 1,500 K. In all cases, the kinetic effects were seen negligible at the initial stage of droplet heating and evaporation. At this stage the surface temperatures predicted by the ETC model were larger than those predicted by the ITC model in agreement with the earlier results. The application of the rigorous kinetic model, taking into account the effects of inelastic collisions, a non-unity evaporation coefficient and the ETC model, is recommended when accurate predictions of droplet surface temperature and evaporation time in Diesel engine-like conditions are essential.

6.4 Future Work

It is anticipated that the results of the kinetic calculations can be approximated by simple analytical functions as perturbations to the results of hydrodynamic calculations. This enables the kinetic effects to be directly incorporated into computational fluid dynamics codes (some preliminary results have been reported by Sazhin and Shishkova [2009]). Although the model was originally developed for stationary droplets, it can be easily generalised for the case of moving droplets via the adjustment of the convective heat transfer coefficient (the kinetic effects proper near the surface of the droplets will not be affected by droplet movement for the values of parameters typical for Diesel engines). Once the model is developed and validated, it could be incorporated into
KIVA 2 CFD code and its functionality testing can be performed.

Future work could also focus on the following three topics. Firstly, based on Eq.(1.3), a novel transition state theory (TST) for evaporation and condensation of chain-like molecules, such as n-dodecane (C_{12}H_{26}), could be introduced and the evaporation/condensation coefficient also recalculated in terms of the new TST. Secondly, work could focus on further study of the evaporation/condensation process using MD simulations. This includes the MD study of evaporation/condensation of n-dodecane in the presence of a background gas (air), investigation of transport properties of n-dodecane and the modification of the newly developed code to enable it to run on a supercomputer HECToR.

Thirdly, the kinetic model could be further developed in the following directions:

1) The improved kinetic boundary condition (KBC), as discussed in Chapter 3, could be implemented into the kinetic code.

2) The Wang-Chang-Uhlenbeck Master equation could be used to take into account the contributions of internal degrees of freedom.

3) The new kinetic model, taking into account the above new features, could be applied to the modelling of fuel droplet heating and evaporation.

4) A new GPU algorithm for kinetic modelling could be developed and used to run the code on HECToR.
Appendix A Calculations of Forces in Chain-like Molecules

The correct calculation of the forces resulting from a given potential model is essential in the construction of a properly functioning molecular dynamics programme. Following Allen and Tildesley [1987], we consider forces arising from the models discussed in Chapter 2: a polyatomic chain with constrained bond lengths, but realistic bond angle bending and torsional potentials.

**Dot and Cross Product**

We introduce four vectors, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{d}$. The dot product is defined, in terms of angle $\theta$ between vectors $\mathbf{a}$ and $\mathbf{b}$, as:

$$\mathbf{a} \cdot \mathbf{b} = |\mathbf{a}| |\mathbf{b}| \cos \theta$$

The relation between the cross product and the dot product is given by the following equations

$$|\mathbf{a} \times \mathbf{b}|^2 = |\mathbf{a}|^2 |\mathbf{b}|^2 - (\mathbf{a} \cdot \mathbf{b})^2$$

$$(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) = (\mathbf{a} \cdot \mathbf{c}) (\mathbf{b} \cdot \mathbf{d}) - (\mathbf{a} \cdot \mathbf{d}) (\mathbf{b} \cdot \mathbf{c})$$

The above relations will be used when the potentials between atoms are calculated in terms of the bond vectors.
Potential Energy

A chain-like molecule consists of $n_a$ ($n_a = 12$ for n-dodecane) atoms which are linked by rigid bonds. The angle between successive bonds, $\theta_a$, and the torsional angle $\phi_a$ defined by three successive bond vectors, are allowed to vary. Only bending and torsional potentials are taken into account. The bond vector between atoms $a - 1$ and $a$ can be presented as $d_a = r_a - r_{a-1}$, where $r_a$ and $r_{a-1}$ are the position vectors of atoms $a$ and $a - 1$, respectively. Thus

$$\cos \theta_a = \frac{d_a \cdot d_{a-1}}{|d_a||d_{a-1}|} \quad (A.1)$$

$$\cos \phi_a = \frac{(d_a \times d_{a-1}) \cdot (d_{a-1} \times d_{a-2})}{|d_a \times d_{a-1}| |d_{a-1} \times d_{a-2}|} \quad (A.2)$$

Note that the bond bending potential was taken in the form

$$u^\theta (\theta_a) = \frac{1}{2} k^\theta (\theta_a - \theta_a^0)^2$$

where $\theta_a^0$ is the equilibrium value. The potential associated with the torsional angles was presented as

$$u^\phi (\phi_a) = \sum_k c_k \cos^k \phi_a$$

where the summation is truncated at $k = 3$ in our MD simulations.

Atomic Force

Having specified the potential energy function $u(r_a)$, we were able to calculate the forces on the atoms and the atomic forces as

$$f_a = -\frac{\partial}{\partial r_a} u(r_a)$$

There will be contributions to the force acting on atom $a$ from both sources. These
Contributions are evaluated as

\[ f_a = \sum_{c=a}^{a+2} -\nabla_{r_a} u^\theta(\theta_c) + \sum_{c=a}^{a+3} -\nabla_{r_a} u^\phi(\phi_c) \]

\[ = \sum_{c=a}^{a+2} -\left( \frac{du^\theta(\theta_c)}{d\cos \theta_c} \right) \nabla_{r_a} \cos \theta_c + \sum_{c=a}^{a+3} -\left( \frac{du^\phi(\phi_c)}{d\cos \phi_c} \right) \nabla_{r_a} \cos \phi_c \]

To simplify these formulae, we introduce the following parameters

\[ C_{ab} = C_{ba} = d_a \cdot d_b = d_b \cdot d_a \]

\[ D_{ab} = D_{ba} = C_{aa}C_{bb} - C_{ab}^2 \]

\[ = (d_a \cdot d_a)(d_b \cdot d_b) - (d_a \cdot d_b)^2 \]

Note that

\[ \cos \theta_a = \frac{d_a \cdot d_{a-1}}{\sqrt{(d_a \cdot d_a)(d_{a-1} \cdot d_{a-1})}} \]

\[ \cos \phi_a = \frac{(d_a \cdot d_{a-1})(d_{a-1} \cdot d_{a-2}) - (d_a \cdot d_{a-2})(d_{a-1} \cdot d_{a-1})}{\sqrt{|d_a|^2|d_{a-1}|^2 - (d_a \cdot d_{a-1})^2 \sqrt{|d_{a-1}|^2|d_{a-2}|^2 - (d_{a-1} \cdot d_{a-2})^2}} \]

Remembering the definitions of \( C_{ab} \) and \( D_{ab} \), the above expressions can be simplified to

\[ \cos \theta_a = C_{a,a-1} \frac{1}{\sqrt{C_{aa}C_{a-1,a-1}}} \quad (A.3) \]

\[ \cos \phi_a = -\left( C_{a,a-1}C_{a-1,a-2} - C_{a,a-2}C_{a-1,a-1} \right) \frac{1}{\sqrt{D_{a,a-1}D_{a-1,a-2}}} \quad (A.4) \]

As for the bending potential, it includes the contributions to the forces on all three atoms, \( a-2 \), \( a-1 \) and \( a \). To calculate these, the chain rule is used to work out the
derivatives

\[ \frac{\partial}{\partial r_{a-2}} (d_a \cdot d_{a-1}) = d_a \cdot \frac{\partial}{\partial r_{a-2}} (d_{a-1}) + d_{a-1} \cdot \frac{\partial}{\partial r_{a-2}} (d_a) \]

\[ = d_a \cdot \frac{\partial}{\partial r_{a-2}} (r_{a-1} - r_{a-2}) + d_{a-1} \cdot \frac{\partial}{\partial r_{a-2}} (r_a - r_{a-1}) \]

\[ = -d_a \]

\[ \frac{\partial}{\partial r_{a-2}} (d_{a-1} \cdot d_{a-1}) = 2d_{a-1} \cdot \frac{\partial}{\partial r_{a-2}} (d_{a-1}) \]

\[ = 2d_{a-1} \cdot \frac{\partial}{\partial r_{a-2}} (r_{a-1} - r_{a-2}) \]

\[ = -2d_{a-1} \]

\[ \frac{\partial}{\partial r_{a-2}} (d_a \cdot d_a) = 2d_a \cdot \frac{\partial}{\partial r_{a-2}} (d_a) \]

\[ = 2d_a \cdot \frac{\partial}{\partial r_{a-2}} (r_a - r_{a-1}) \]

\[ = 0 \]

\[ \frac{\partial}{\partial r_{a-1}} (d_a \cdot d_{a-1}) = d_a \cdot \frac{\partial}{\partial r_{a-1}} (d_{a-1}) + d_{a-1} \cdot \frac{\partial}{\partial r_{a-1}} (d_a) \]

\[ = d_a \cdot \frac{\partial}{\partial r_{a-1}} (r_{a-1} - r_{a-2}) + d_{a-1} \cdot \frac{\partial}{\partial r_{a-1}} (r_a - r_{a-1}) \]

\[ = d_a - d_{a-1} \]

\[ \frac{\partial}{\partial r_{a-1}} (d_{a-1} \cdot d_{a-1}) = 2d_{a-1} \cdot \frac{\partial}{\partial r_{a-1}} (d_{a-1}) \]

\[ = 2d_{a-1} \cdot \frac{\partial}{\partial r_{a-1}} (r_{a-1} - r_{a-2}) \]

\[ = 2d_{a-1} \]

\[ \frac{\partial}{\partial r_{a-1}} (d_a \cdot d_a) = 2d_a \cdot \frac{\partial}{\partial r_{a-1}} (d_a) \]

\[ = 2d_a \cdot \frac{\partial}{\partial r_{a-1}} (r_a - r_{a-1}) \]

\[ = -2d_a \]

\[ \frac{\partial}{\partial r_a} (d_a \cdot d_{a-1}) = d_a \cdot \frac{\partial}{\partial r_a} (d_{a-1}) + d_{a-1} \cdot \frac{\partial}{\partial r_a} (d_a) \]

\[ = d_a \cdot \frac{\partial}{\partial r_a} (r_{a-1} - r_{a-2}) + d_{a-1} \cdot \frac{\partial}{\partial r_a} (r_a - r_{a-1}) \]

\[ = d_{a-1} \]
\[
\frac{\partial}{\partial r_a} (d_{a-1} \cdot d_{a-1}) = 2d_{a-1} \cdot \frac{\partial}{\partial r_a} (d_{a-1}) = 2d_{a-1} \cdot \frac{\partial}{\partial r_a} (r_{a-1} - r_{a-2}) = 0
\]

\[
\frac{\partial}{\partial r_a} (d_a \cdot d_a) = 2d_a \cdot \frac{\partial}{\partial r_a} (d_a) = 2d_a \cdot \frac{\partial}{\partial r_a} (r_a - r_{a-1}) = 2d_a
\]

To summarise, we obtained the following relations

\[
\begin{align*}
\frac{\partial}{\partial r_{a-2}} (d_a \cdot d_{a-1}) &= -d_a, \\
\frac{\partial}{\partial r_{a-1}} (d_a \cdot d_{a-1}) &= d_a - d_{a-1}, \\
\frac{\partial}{\partial r_a} (d_a \cdot d_{a-1}) &= d_{a-1} \\
\frac{\partial}{\partial r_{a-2}} (d_{a-1} \cdot d_{a-1}) &= -2d_{a-1}, \\
\frac{\partial}{\partial r_{a-1}} (d_{a-1} \cdot d_{a-1}) &= 2d_{a-1}, \\
\frac{\partial}{\partial r_a} (d_{a-1} \cdot d_{a-1}) &= 0 \\
\frac{\partial}{\partial r_{a-2}} (d_a \cdot d_a) &= 0, \\
\frac{\partial}{\partial r_{a-1}} (d_a \cdot d_a) &= -2d_a, \\
\frac{\partial}{\partial r_a} (d_a \cdot d_a) &= 2d_a
\end{align*}
\]

Note that there is a simple set of rules governing the vector differentiation of the \(C\) function with respect to the positions of atom \(a\):

\[
\nabla_{r_a} C_{aa} = 2d_a
\]
\[
\nabla_{r_a} C_{a,a+1} = d_{a+1} - d_a
\]
\[
\nabla_{r_a} C_{a+1,a+1} = -2d_{a+1}
\]
\[
\nabla_{r_a} C_{ab} = d_b (b \neq a, a + 1)
\]
\[
\nabla_{r_a} C_{a+1,b} = -d_b (b \neq a, a + 1)
\]
\[
\nabla_{r_a} C_{bc} = 0 (b, c \neq a, a + 1)
\]

Hence we have

\[
\nabla_{r_a} \cos \theta_a = -\frac{1}{\sqrt{C_{aa}C_{a-1,a-1}}} \left( \frac{C_{a,a-1}}{C_{aa}} d_a - d_{a-1} \right)
\]
\[
\nabla_{r_a} \cos \theta_{a+1} = \frac{1}{\sqrt{C_{a+1,a+1}C_{aa}}} \left( \frac{C_{a,a+1}}{C_{a+1,a+1}} d_{a+1} - \frac{C_{a,a+1}}{C_{aa}} d_a + d_{a+1} - d_a \right)
\]
\[
\nabla_{r_a} \cos \theta_{a+2} = \frac{1}{\sqrt{C_{a+2,a+2}C_{a+1,a+1}}} \left( \frac{C_{a+2,a+1}}{C_{a+1,a+1}} d_{a+1} - d_{a+2} \right)
\]

(A.5)
A similar approach applied to the torsional potential gives the expressions for the forces acting on all four atoms, $a - 3$, $a - 2$, $a - 1$ and $a$. To calculate these, the chain rule is used again and we have the following vector differentiation of the $D$ function with respect to the position of atom $a$

$$\frac{\partial}{\partial r_a} (D_{a,a-1}) = \frac{\partial}{\partial r_a} \left(C_{a,a-1} - C_{a,a-1}^2\right)$$

$$= C_{a,a-1} \frac{\partial}{\partial r_a} (C_{a-1,a-1}) + C_{a-1,a-1} \frac{\partial}{\partial r_a} (C_{a,a}) - 2C_{a,a-1} \frac{\partial}{\partial r_a} (C_{a,a-1})$$

$$= C_{a,a-1} \frac{\partial}{\partial r_a} (d_{a-1} \cdot d_{a-1}) + C_{a-1,a-1} \frac{\partial}{\partial r_a} (d_a \cdot d_a) - 2C_{a,a-1} \frac{\partial}{\partial r_a} (d_a \cdot d_{a-1})$$

$$= 2C_{a-1,a-1} d_a - 2C_{a,a-1} d_{a-1}$$

$$\frac{\partial}{\partial r_a} (D_{a-1,a-2}) = \frac{\partial}{\partial r_a} \left(C_{a-1,a-1} - C_{a-2,a-2} - C_{a-1,a-2}^2\right)$$

$$= C_{a-1,a-1} \frac{\partial}{\partial r_a} (C_{a-2,a-2}) + C_{a-2,a-2} \frac{\partial}{\partial r_a} (C_{a-1,a-1}) - 2C_{a-1,a-2} \frac{\partial}{\partial r_a} (C_{a-1,a-2})$$

$$= C_{a-1,a-1} \frac{\partial}{\partial r_a} (d_{a-2} \cdot d_{a-2}) + C_{a-2,a-2} \frac{\partial}{\partial r_a} (d_{a-1} \cdot d_{a-1}) - 2C_{a-1,a-2} \frac{\partial}{\partial r_a} (d_{a-1} \cdot d_{a-2})$$

$$= 0$$

$$\frac{\partial}{\partial r_a} (D_{a+1,a}) = \frac{\partial}{\partial r_a} \left(C_{a+1,a+1} C_{a,a} - C_{a+1,a}^2\right)$$

$$= C_{a+1,a+1} \frac{\partial}{\partial r_a} (C_{a,a}) + C_{a,a} \frac{\partial}{\partial r_a} (C_{a+1,a+1}) - 2C_{a+1,a} \frac{\partial}{\partial r_a} (C_{a+1,a})$$

$$= C_{a+1,a+1} \frac{\partial}{\partial r_a} (d_a \cdot d_a) + C_{a,a} \frac{\partial}{\partial r_a} (d_{a+1} \cdot d_{a+1}) - 2C_{a+1,a} \frac{\partial}{\partial r_a} (d_{a+1} \cdot d_a)$$

$$= 2C_{a+1,a+1} d_a - 2C_{a,a} d_{a+1} - 2C_{a+1,a} d_{a+1} + 2C_{a+1,a} d_a$$

$$\frac{\partial}{\partial r_a} (D_{a+2,a+1}) = \frac{\partial}{\partial r_a} \left(C_{a+2,a+2} C_{a+1,a+1} - C_{a+2,a+1}^2\right)$$

$$= C_{a+2,a+2} \frac{\partial}{\partial r_a} (C_{a+1,a+1}) + C_{a+1,a+1} \frac{\partial}{\partial r_a} (C_{a+2,a+2}) - 2C_{a+2,a+1} \frac{\partial}{\partial r_a} (C_{a+2,a+1})$$

$$= C_{a+2,a+2} \frac{\partial}{\partial r_a} (d_{a+1} \cdot d_{a+1}) + C_{a+1,a+1} \frac{\partial}{\partial r_a} (d_{a+2} \cdot d_{a+2}) - 2C_{a+2,a+1} \frac{\partial}{\partial r_a} (d_{a+2} \cdot d_{a+1})$$

$$= -2C_{a+2,a+2} d_{a+1} + 2C_{a+2,a+1} d_{a+2}$$

These relations are derived with the help of the vector differentiation of the $C$ function. Similarly, there is also a simple set of rules governing the vector differentiation of the
The expressions required for torsional potential are summarised below:

\[
\nabla_r \phi_a = \frac{1}{\sqrt{D_{a,a-1}D_{a-1,a-2}}} \left( C_{a-1,a-2}d_{a-1} - C_{a-1,a-1}d_{a-2} \right)
\]

\[
-\frac{1}{\sqrt{D_{a+1,a}D_{a,a-1}}} \left( C_{a,a-1}d_{a-1} - C_{a,a-2}d_{a} \right) + \frac{1}{\sqrt{D_{a+2,a+1}D_{a+1,a}}}
\]

\[
\times \left( C_{a+1,a+1}d_{a} - C_{a,a}d_{a+1} - C_{a,a+1}d_{a+1} + C_{a,a+1}d_{a} \right)
\]

\[
\nabla_r \phi_{a+1} = -\frac{1}{\sqrt{D_{a+1,a}D_{a,a-1}}} \left( C_{a,a+1}d_{a} - C_{a,a+1}d_{a} \right) + \frac{1}{\sqrt{D_{a+2,a+1}D_{a+1,a}}}
\]

\[
\times \left( C_{a+1,a+1}d_{a} - C_{a,a}d_{a+1} - C_{a,a+1}d_{a+1} + C_{a,a+1}d_{a} \right)
\]

\[
\nabla_r \phi_{a+2} = -\frac{1}{\sqrt{D_{a+2,a+1}D_{a+1,a}}}
\]

\[
\times \left( C_{a+1,a+1}d_{a} - C_{a,a}d_{a+1} - C_{a,a+1}d_{a+1} + C_{a,a+1}d_{a} \right)
\]

The forces acting on each atom \( a \) have been calculated. Note that some of the terms in these equations vanish if \( a \) is close to the end of the polyatomic molecule.
Appendix B Splitting the Finite-Difference Scheme for the Solution of the Boltzmann Equation

The collision integral $J_{\alpha\beta}$ in the Boltzmann equation can be written as

$$J_{\alpha\beta} = -\nu_{\alpha\beta} f_{\alpha} + N_{\alpha\beta}, \quad (B.1)$$

where

$$\nu_{\alpha\beta} = \frac{\sigma_{\alpha\beta}^2}{2} \int_{-\infty}^{+\infty} dv_1 \int_{0}^{\pi} \sin \theta d\theta \int_{0}^{2\pi} d\phi f_{\beta 1} |v_{\alpha} - v_{\beta 1}|$$

$$N_{\alpha\beta} = \frac{\sigma_{\alpha\beta}^2}{2} \int_{-\infty}^{+\infty} dv_1 \int_{0}^{\pi} \sin \theta d\theta \int_{0}^{2\pi} d\phi f'_{\alpha} f'_{\beta 1} |v_{\alpha} - v_{\beta 1}|$$

$\sigma_{\alpha\beta} = (\sigma_{\alpha} + \sigma_{\beta})/2$, $\sigma_{\alpha}$ and $\sigma_{\beta}$ are the corresponding diameters of molecules, $\theta$ and $\phi$ are angular coordinates of molecule $\beta$ relative to molecule $\alpha$, superscript $'$ indicates the velocities and distribution functions after collisions and subscript $\prime$ indicates that the function $f_{\alpha}$ is modified under the influence of collisions with molecules of the type $\beta$. 

124
The Boltzmann equation is solved by the splitting method with a time step $\tau = t^{j+1} - t^j$

$$\frac{\partial f'}{\partial t} + v\frac{\partial f'}{\partial r} = 0, \quad f^{j+1} = f^j$$

$$\frac{\partial f'}{\partial r} = J, \quad f^j = f^{j+1}$$

In this two step method, firstly, molecular displacements are calculated ignoring the collision effect ($J = 0$). Secondly, the collision integration is relaxed under the assumption of spatial homogeneity. This allows us to present the Boltzmann equation for each gas component in a discretised form (Shishkova and Sazhin [2006])

$$\begin{cases}
\frac{\Delta f_1^1}{\Delta t} + v_1^1 \frac{\Delta f_1^1}{\Delta r} = J_{\alpha\alpha}^1 + J_{\alpha\beta}^1 \\
\vdots \\
\frac{\Delta f_k^k}{\Delta t} + v_\alpha^k \frac{\Delta f_k^k}{\Delta r} = J_{\alpha\alpha}^k + J_{\alpha\beta}^k \\
\vdots \\
\frac{\Delta f_M^M}{\Delta t} + v_\alpha^M \frac{\Delta f_M^M}{\Delta r} = J_{\alpha\alpha}^M + J_{\alpha\beta}^M
\end{cases} \quad (B.2)$$

The discretisation of the velocity space is performed similarly to the physical space, by replacing the continuous velocity with a set of $v_k^M$, where $k$ indicates the position of a velocity cell and $M$ is the total number of cells. For each $v_k^M$, the corresponding $f_k^M$ is specified. Also, the boundary and initial conditions for the distributions are considered.

The numerical solution of System (B.2) in the first step is performed following the explicit approach, and the Courant condition

$$\Delta t \max(|v_x|, |v_y|, |v_z|) < \min(\Delta x, \Delta y, \Delta z)$$

is assumed to be valid. In the next step, the displacement of molecules stops and they start colliding. Again using the explicit approach, each equation in System (B.2) can
be written as
\[
\frac{f_{\alpha}^{k,n} - f_{\alpha}^{k,n-1}}{\Delta t} = J_{\alpha\alpha}^{k,n-1} + J_{\alpha\beta}^{k,n-1},
\]  
where $\sim$ indicates the value of the distribution function calculated in the first step, additional superscripts $n^{-1}$ and $n$ indicate consecutive time steps. Equations (B.2) are to be solved in each cell in the physical space. The distribution functions in the integrands are hereafter taken after the first step (the $\sim$ is omitted here).

Using the implicit approach the discretised version of Eq. (B.1) is presented as
\[
J_{\alpha\beta}^{k,n-1} = -\nu_{\alpha\beta}^{k,n-1} f_{\alpha}^{k,n} + N_{\alpha\beta}^{k,n-1},
\]  
where

\[
\begin{align*}
\nu_{\alpha\beta}^{k,n-1} &= \frac{\sigma_{\alpha\beta}^2}{2} \int_{-\infty}^{+\infty} dv_1 \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi f_{\beta_{\beta}1}^{k,n-1} \left| \mathbf{v}_{\alpha} - \mathbf{v}_{\beta_{\beta}1} \right| \\
N_{\alpha\beta}^{k,n-1} &= \frac{\sigma_{\alpha\beta}^2}{2} \int_{-\infty}^{+\infty} dv_1 \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi f_{\alpha_{\alpha}1}^{k',n-1} \left| \mathbf{v}_{\alpha} - \mathbf{v}_{\beta_{\beta}1} \right|
\end{align*}
\]

Remembering Eq. (B.4), the solution of Eq. (B.3) is presented as
\[
f_{\alpha}^{k,n} = \frac{\tilde{f}_{\alpha}^{k,n-1} + \Delta t \left[ N_{\alpha\alpha}^{k,n-1} + N_{\alpha\beta}^{k,n-1} \right]}{1 + \Delta t \left[ \nu_{\alpha\alpha}^{k,n-1} + \nu_{\alpha\beta}^{k,n-1} \right]}
\]  

The calculation of integrals $\nu_{\alpha\beta}^{k,n-1}$ and $N_{\alpha\beta}^{k,n-1}$ would be a big challenge for computing time. Instead, the conventional approach to the calculation of these integrals is replaced by integrations in terms of random cubature formulae and the expressions for $\nu_{\alpha\beta}^{k,n-1}$ and $N_{\alpha\beta}^{k,n-1}$ can be written as

\[
\begin{align*}
\nu_{\alpha\beta}^{k,n-1} &= \frac{\sigma_{\alpha\beta}^2}{2} V \sum_{l=1}^{K_0} f_{\alpha_{\alpha}1}^{k,n-1} \left| \mathbf{v}_{\alpha}^l - \mathbf{v}_{\beta_{\beta}1}^l \right| \sin \theta_l \\
N_{\alpha\beta}^{k,n-1} &= \frac{\sigma_{\alpha\beta}^2}{2} V \sum_{l=1}^{K_0} f_{\alpha_{\beta}1}^{k',n-1} \left| \mathbf{v}_{\alpha}^l - \mathbf{v}_{\beta_{\beta}1}^l \right| \sin \theta_l
\end{align*}
\]
where the $V$ is the volume of the five-dimensional space and $K_0$ is the total number of the points. The explicit expression for $V$ can be presented as

$$V = 2\pi^2 |v_{x,\text{max}} - v_{x,\text{min}}| |v_{y,\text{max}} - v_{y,\text{min}}| |v_{z,\text{max}} - v_{z,\text{min}}|.$$
Appendix C Properties of n-dodecane C$_{12}$H$_{26}$

The properties presented below are taken from Abramzon and Sazhin [2006]

Saturated vapour pressure $p_v = \exp[8.1948 - 7.8099(300/T_s) - 9.0098(300/T_s)^2]$ bar

Critical temperature $T_{cr} = 659$ K

Latent heat of vaporization $La(T_s) = 37.44(T_{cr} - T_s)^{0.38}$ kJ/kg

Vapour/Air binary diffusion coefficient $D = 5.27 \times 10^{-6}(T/300)^{1.583}p^{-1}$ m$^2$/s

Vapour thermal conductivity $\kappa_v = 0.02667(T/300) - 0.02087$ W/(m K)

Vapour dynamic viscosity $\mu_v = [0.5651 + 1.041 \times 10^{-3}(T - 300)] \times 10^{-5}$ (Pa s)

Vapour specific heat capacity $c_{pv} = 0.2979 + 1.4394(T/300) - 0.1351(T/300)^2$ kJ/(kg K)

Liquid density $\rho_l = 744.11 - 0.771(T - 300)$ kg/m$^3$

Liquid specific heat capacity $c_l = 2.18 + 0.0041(T - 300)$ kJ/(kg K)

Liquid dynamic viscosity $\mu_l = 10^{-3} \times \exp[2.0303(300/T)^2 + 1.1769(300/T) - 2.929]$ (Pa s)

Liquid thermal conductivity $\kappa_l = 0.1405 - 0.00022(T - 300)$ W/(m K)
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133


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