

Kinetic and Molecular Dynamic Modelling of n-dodecane Droplet Heating and Evaporation

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Abstract

A recently developed approach to taking into account the effects of inelastic collisions between two molecules on the solution of the Boltzmann equation is briefly described. This approach is based on presenting the change of state of molecules after collisions as a random movement along a surface of an N -dimensional sphere, the squared radius of which is equal to the total energy of the molecules before and after the collision 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 the internal energy of one of the degrees of freedom, of one of two molecules. The kinetic energies of two molecules are described by the first six dimensions of the system, and the remaining $(N - 6)$ -dimensions describe the internal energies. Recent results of molecular dynamics simulations to study the evaporation and condensation of n-dodecane ($C_{12}H_{26}$) at liquid-vapour phase equilibrium using the modified OPLS (Optimized Potential for Liquid Simulation) model are summarised. The predicted evaporation/condensation coefficient decreased from about 0.9 to about 0.3 when temperature increased from 400 K to 600 K.

Introduction

Although the hydrodynamic approximation is a widely used engineering approach to the modelling of evaporation and condensation processes, its limitations, even in the case of evaporation at high pressures, are well known. They have been discussed in a number of papers, including [1]-[5]. In these papers, the evaporation of liquid n-dodecane ($C_{12}H_{26}$) has been considered and the combination of the kinetic and hydrodynamic approaches has been developed for the analysis of droplet heating and evaporation. In the immediate vicinity of droplet surfaces (up to about one hundred molecular mean free paths), the vapour and ambient gas dynamics have been studied based on the Boltzmann equation (kinetic region), while at larger distances the analysis has been based on the hydrodynamic equations (hydrodynamic region). Mass, momentum and energy fluxes have been conserved at the interface between these regions.

These regions, alongside the liquid region, referring to the droplet interior, are schematically shown in Fig. 1. T_s and ρ_s are vapour temperature and density at the surface of the droplet, T_{Rd} and ρ_{Rd} are vapour temperature and density at the interface between the kinetic and hydrodynamic regions. Both heat (\mathbf{q}) and mass (\mathbf{j}) transfer processes in the kinetic region are taken into account. It has been assumed that gas consists of two components, fuel vapour and background air, both in the kinetic and hydrodynamic regions. It has also been assumed that the contribution of chemical reactions of fuel vapour and oxygen can be ignored.

The predictions of the model shown in Fig. 1 have been shown to be as accurate as those which follow from the solution to the Boltzmann equation in the whole domain, but both differed considerably (up to 10%) from the predictions of the hydrodynamic model under Diesel engine-like conditions. The practical applications of the combined approach for kinetic modelling, however, require the specification of the boundary conditions at the liquid surface [6]:

$$f^{\text{out}} = \alpha f^e + (1 - \alpha) f^r \quad (v_x > 0), \quad (1)$$

where f^{out} is the overall distribution function of molecules leaving the interface from the liquid phase, α is the evaporation coefficient, f^e is the distribution function of evaporated molecules, f^r is the distribution function of reflected molecules and v_x is the velocity component normal to the interface. In the equilibrium state the evaporation and condensation coefficients are equal to each other.

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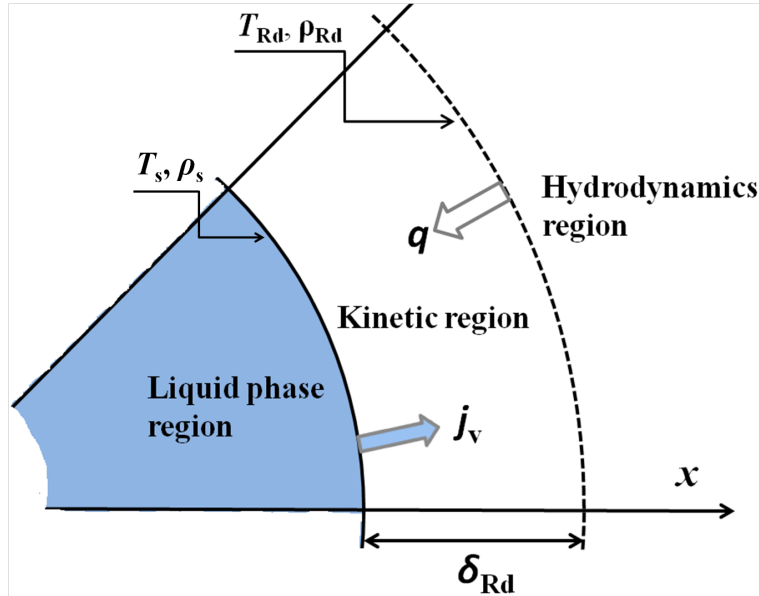


Figure 1. Liquid phase, kinetic and hydrodynamic regions in the vicinity of the surface of the droplet. T_s and ρ_s are the droplet surface temperature and vapour density in the immediate vicinity of the droplet surface, T_{Rd} and ρ_{Rd} are the temperature and density of vapour at the outer boundary of the kinetic region. δ_{Rd} indicates the thickness of the kinetic region, j_v and q show the directions of the vapour mass and heat fluxes respectively.

The kinetic models described in [1]-[5] are based on a number of assumptions, the most serious of which is that the contribution of inelastic collisions can be 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. Even if the analysis of the dynamics of these molecules is simplified by considering the united atom model [7], 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.

Also, it has been implicitly or explicitly assumed that the distribution function of molecules leaving the surface of the droplets is isotropic Maxwellian with the temperature equal to the liquid surface temperature. The values of the evaporation/condensation coefficients have been assumed equal to 0.04 and 0.5 [1] or 1 [2]-[5]. None of these assumptions have been rigorously justified. The only practical way to perform this justification would be to perform the molecular dynamics (MD) simulation in the vicinity of the liquid-vapour interface.

In our recent papers [7, 8], molecular dynamics simulations have been performed to study the evaporation and condensation of n-dodecane at liquid-vapour phase equilibria using the modified OPLS potential. The properties at the interface were studied and the evaporation/condensation coefficient was estimated. Typical molecular behaviours in the evaporation and condensation processes have also been presented and discussed.

The main objective of this paper is to summarise the recent (published and unpublished) developments in kinetic and molecular dynamics simulations of n-dodecane droplet heating and evaporation. In the next section, a new model of binary inelastic collisions is introduced, the solution of the Boltzmann equation, taking into account inelastic collisions, and some results of simulations are presented and discussed. The following section presents the molecular dynamics simulations of the evaporation and condensation of n-dodecane at the liquid-vapour interface, and some results of these simulations. Finally, the main conclusions of the present paper are drawn.

Kinetic Modelling

Our summary of recent results in kinetic modelling is focused on the description of the model for inelastic collisions, solution of the Boltzmann equation, and discussion of some recent results of this solution.

A model for inelastic collisions

As in our previous papers [2]-[5], it is assumed that the molecules can be approximated as hard spheres. 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 [9]). The details of our model for inelastic collisions

are described elsewhere. Here the focus will be on a brief summary of this model.

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 the reference system linked with this centre of mass. In this system, each of these molecules has three translational and a certain number of internal degrees of freedom, so that 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 the 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: $r = \sqrt{\sum_{i=1}^{i=N} E_i}$, 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_f , this equation 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.

The location of the points on the surface of this sphere can be described by an N -dimensional vector $\mathbf{X} = (x_1, x_2, \dots, x_N)$ with the basis $(\mathbf{e}_1, \mathbf{e}_2, \dots, \mathbf{e}_N)$ and the norm $\|\mathbf{X}\| = r = \sqrt{E_f}$. The redistribution of energy between the degrees of freedom during the collision process can be described in terms of the rotation of vector \mathbf{X} in the N -dimensional space. If none of the degrees of freedom has any preference over the others, then this rotation of the vector \mathbf{X} can be considered as random. In the most general form it can be described by the following equation:

$$\mathbf{X}' = \mathbf{A}\mathbf{X}, \quad (2)$$

where \mathbf{X}' is the new position of vector \mathbf{X} after rotation, \mathbf{A} is the rotation matrix:

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

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

$$\mathbf{A}^T \mathbf{A} = \mathbf{E}, \quad (3)$$

where \mathbf{A}^T is the transpose of the matrix \mathbf{A} , \mathbf{E} is the unit matrix.

Equation (3) can be presented in a more explicit form as the combination of the following systems of equations

$$\left. \begin{array}{l} a_{11}^2 + a_{21}^2 + \dots + a_{N1}^2 = 1 \\ a_{12}^2 + a_{22}^2 + \dots + a_{N2}^2 = 1 \\ \dots \quad \dots \quad \dots \quad \dots \\ a_{1N}^2 + a_{2N}^2 + \dots + a_{NN}^2 = 1 \end{array} \right\} \quad (4)$$

$$\left. \begin{aligned} a_{11}a_{12} + a_{21}a_{22} + \dots + a_{N1}a_{N2} &= 0 \\ a_{11}a_{13} + a_{21}a_{23} + \dots + a_{N1}a_{N3} &= 0 \\ \dots & \dots \dots \dots \\ a_{11}a_{1N} + a_{21}a_{2N} + \dots + a_{N1}a_{NN} &= 0 \end{aligned} \right\} \quad (5)$$

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$$a_{1(N-1)}a_{1N} + a_{2(N-1)}a_{2N} + \dots + a_{N(N-1)}a_{NN} = 0. \quad (6)$$

When writing Equations (5)-(6) identical equations have been excluded. The total number of Equations (5)-(6) is

$$(N-1) + (N-2) + (N-3) + \dots + 1 = \frac{N}{2}(N-1)$$

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 Equation (4) (normalization condition).

The following procedure for the construction of the components matrix \mathbf{A} is suggested.

1. The coefficients $a_{11}, a_{21}, \dots, a_{N1}$ are arbitrarily chosen but normalized based on the first equation in System (4).

2. The coefficients $a_{12}, a_{22}, \dots, a_{(N-1)2}$ are arbitrarily chosen, while the value of the coefficient a_{N2} is found from the first equation of System (5):

$$a_{N2} = -\frac{1}{a_{N1}} (a_{11}a_{12} + a_{21}a_{22} + \dots + a_{(N-1)1}a_{(N-1)2}). \quad (7)$$

Then all coefficients are normalized based on the second equation in System (4).

Following the same procedure all other components of the matrix \mathbf{A} are found, and this allows us to calculate \mathbf{X}' based on Equation (2).

Solution of the Boltzmann equation

Following [10], the numerical solution of the Boltzmann equations is performed in two steps. Firstly, molecular displacements are calculated ignoring the effect of collisions. Secondly, the collisional relaxation is calculated under the assumption of spatial homogeneity. A model for inelastic collisions, described in the previous section, allows us to obtain the energies of all degrees of freedom after individual collisions. However, we are interested only in the net change of the kinetic energy of each of two molecules 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, described in the previous section, on the three-dimensional space, describing the kinetic energies of both colliding molecules in three directions.

As mentioned by [2], 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 [2] 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. In the three dimensional case, the maximal number of possible combinations of momenta after collision is 24. This approach provides the consistency in discretisation processes used for the description of molecular dynamics and collision processes. It has been tested for numerous problems, some of which are discussed by [2]-[5].

If during the collision the net internal energy of molecules increases, this has to be compensated for by a decrease in their kinetic energies. In the opposite case, when the net internal energy of molecules decreases, this has to be compensated for by an increase in their kinetic energies.

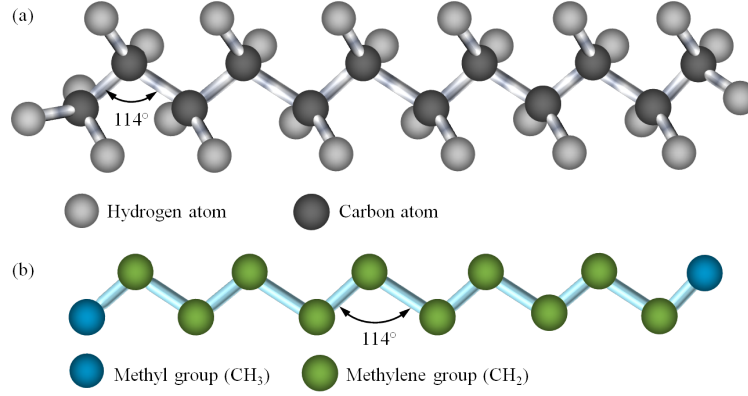


Figure 2. Molecular structure of n-dodecane ($C_{12}H_{26}$) (a) and the corresponding united atom model (b)

Applications

The new approach, described in the previous sections, 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 model, based on a different approach to taking into account the effects of inelastic collisions. This problem has been generalized to a hypothetical case when the number of internal degrees of freedom of nitrogen (N_{int}) has been 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 for $N_{\text{int}} \geq 6$.

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_{int} when this number exceeds about 15. In the third problem, the predicted mass flux of n-dodecane also remained almost unchanged for $N_{\text{int}} \geq 15$. 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.

Molecular Dynamics Modelling

The discussion of our recent results in molecular dynamics modelling is focused on the model for interatomic potentials, input parameters, simulation procedure, and some results of molecular dynamics simulations.

Interatomic potentials

The interactions between the molecules of n-dodecane are modelled using the Optimised Potential for Liquid Simulation (OPLS) [7, 8] and the chain-like molecules are modelled by the united atom model, including the methyl (CH_3) and methylene (CH_2) groups, as schematically illustrated in Fig. 2.

The non-bonded interactions between atoms are described by the truncated Lennard-Jones (L-J) 12-6 potential:

$$u^{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]. \quad (8)$$

The energy parameters of CH_2 and CH_3 groups (atoms) are $\varepsilon_{CH_2}/k_B = 47$ K and $\varepsilon_{CH_3}/k_B = 114$ K respectively, and the energy parameter between CH_2 and CH_3 groups is estimated as $\varepsilon_{CH_3-CH_3}/k_B = \sqrt{\varepsilon_{CH_2}\varepsilon_{CH_3}}/k_B = 73.2$ K (k_B is the Boltzmann constant). The diameters of the methylene and methyl groups are assumed to be equal and estimated as $\sigma = 3.93 \times 10^{-10}$ m. The L-J 12-6 interaction is truncated at 13.8×10^{-10} m.

The interactions within the chains include bond bending and torsion with the bond length constrained at 1.53×10^{-10} m. The bond bending potential between the three atoms is estimated as [11]:

$$u^{\text{bend}}(\theta) = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2, \quad (9)$$

where the bending coefficient is estimated as $k_{\theta}/k_B = 62,500$ K/rad², and the equilibrium angle is $\theta_0 = 114^\circ$ (see Fig. 2).

The torsion potential between the two atoms with two atoms between them is estimated as [12]:

$$u^{\text{tors}}(\varphi) = c_0 + 0.5 c_1 (1 + \cos \varphi) + 0.5 c_2 (1 - \cos 2\varphi) + 0.5 c_3 (1 + \cos 3\varphi), \quad (10)$$

where $c_0/k_B = 0$ K, $c_1/k_B = 355$ K, $c_2/k_B = -68.19$ K, $c_3/k_B = 791.3$ K and φ is the dihedral angle with 180° for the equilibrium state.

Input parameters and simulation procedure

A system of 720 n-dodecane molecules (8640 CH₂ and CH₃ groups) was considered in a three-dimensional rectangular simulation box of $L_x \times L_y \times L_z = 64.24\sigma \times 16.48\sigma \times 16.48\sigma$, where σ is the reduced length for liquid temperatures 400 K, 450 K, 500 K and 550 K [8]. This size of box corresponds to 25.25 nm \times 6.48 nm \times 6.48 nm. These molecules were initially oriented along the x axis and placed in the middle of the simulation box. They had zigzag configurations, and the number of molecules chosen was 5 in the x direction and 12 in both y and z directions.

The equations of motion of the atoms have been integrated using the Verlet leapfrog method [13]. The bond lengths are constrained by the SHAKE scheme [13]. The time step in all simulations has been taken equal to 5 fs. Periodic boundary conditions were applied in all directions.

The system was relaxed with a constraint of fixed homogeneous and isotropic temperature. The molecules started to relocate within the liquid phase and to evaporate gradually. Typically the system required 15,000 ps to reach an equilibrium state. Finally the liquid film was sandwiched between the layers of the vapour phases. Then data was sampled for another 5,000 ps. The positions of the two liquid-vapour interfaces were identified by the density profiles. The interface parameters, such as density and evaporation/condensation coefficient, were obtained by averaging them over these 5,000 ps.

Results of simulations

The evaporation and condensation of liquid n-dodecane (C₁₂H₂₆) were investigated, using the approach discussed in the previous sections [8]. The thickness of the transition layer between liquid and vapour phases at equilibrium was estimated to be 2.27-3.53 nm. It was pointed out that the molecules at the liquid surface need to have 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. The values of the evaporation/condensation coefficient at various liquid phase temperatures were estimated. It was demonstrated that this coefficient decreased from 0.93 at 400 K to 0.45 at 550 K, in agreement with the prediction of the transition state theory [14]. The molecular velocity distribution functions in the liquid phase and the interface were shown to be close to isotropic Maxwellian with temperatures equal to that of the liquid phase. These functions in the vapour phase, however, were 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 direction parallel to the interface.

Conclusions

Results of some recent developments in kinetic and molecular dynamics modelling and simulations of n-dodecane droplet heating and evaporation are summarised. A recently developed approach to the solution of the Boltzmann equation, taking into account the effect of inelastic collisions, is described. This approach is based on the presentation of the collisions as the random movement along a surface of an N -dimensional sphere, the squared radius of which is equal to the total energy of colliding molecules in the centre of mass reference system. 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 collision are assumed to be equal. If during the collision the net internal energy of molecules increases (decreases), this has to be compensated for by a decrease (increase) in the kinetic energies of molecules, and the radius of the corresponding sphere in the three-dimensional kinetic space decreases (increases). It is assumed that the momenta of molecules after the collisions belong to an *a priori* chosen set of momenta.

Recently reported results of investigation of the evaporation and condensation of liquid n-dodecane (C₁₂H₂₆), the closest approximation to Diesel fuel, using the MD simulation technique have been summarised. It has been pointed out that the molecules at the liquid surface need to gain relatively large translational energy to evaporate. Vapour molecules with high translational energy can easily penetrate deep into the transition layer and condense in the liquid phase. The values of the evaporation/condensation coefficient at various liquid phase temperatures

have been estimated and are shown to be in agreement with the prediction of the transition state theory. The properties of molecular velocity distribution functions in the liquid phase, the interface and vapour phases have been summarised. It is recommended that the results are taken into account when formulating boundary conditions in kinetic modelling.

Both kinetic and molecular dynamics models, described above, are recommended for use in the analysis of heating and evaporation of n-dodecane droplets in conditions relevant to Diesel engines.

Acknowledgements

The authors are grateful to EPSRC (Grant EP/H001603/1) of the UK for financial support of this project.

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