



# Quantum-chemical analysis of the processes at the surfaces of Diesel fuel droplets



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## ABSTRACT

The quantum-chemical methods used for describing the processes at the surface of Diesel fuel droplets are summarised. Some results relevant to practical engineering application in Diesel engines, obtained previously, are summarised. Assuming that the droplets are so small that their interaction with individual molecules can be described using the methods of the kinetic gas theory (they can be considered as clusters/nanodrops), it was shown that the evaporation rate depends on partial pressures, temperature, and the sizes and masses of molecules and clusters/nanodrops. The results of the analysis of the collision processes between n-dodecane (approximation of Diesel fuel) molecules and clusters/nanodrops, based on the Dynamic Reaction Coordinate (DRC) method, are described. It is concluded that the probability of the attacking molecule sticking to a droplet is maximal if the molecular plane is parallel or almost parallel to the droplet surface. If the kinetic energy of the attacking molecules is high (greater than that corresponding to the boiling temperature) then it is expected that it will scatter and be removed from the cluster/nanodrop surface. The mechanisms of evaporation of microdrops and nanodrops are shown to involve rather different processes. In the case of microdrops, individual C<sub>12</sub> molecules are evaporated from their surfaces, while in the case of nanodrops they can be disintegrated into clusters and individual molecules. The decrease in the likelihood of evaporation/condensation with temperature, predicted by the quantum-chemical (QC) approach, agrees with the prediction of the classical theory based on the MD simulations of n-dodecane molecules. The results of the estimation of the evaporation/condensation coefficient of n-dodecane molecules using the transition state theory (TST), based on the QC/DFT approach and taking into account the conformerisation of n-dodecane molecules, are summarised. It is shown that taking into account the QC effects leads to marginal modifications of the predicted evaporation/condensation coefficient, particularly at temperatures which are not close to the critical temperature.

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## 1. Introduction

The importance of the accurate modelling of the processes at the surfaces of Diesel fuel droplets is well recognised. These processes form integral parts of the processes of Diesel droplet heating and evaporation which precede the formation of the air/fuel vapour mixture and autoignition and combustion of this mixture in Diesel engines [1]. In almost all practical engineering approaches, the most basic models for these surface processes have been used. For example, it has been assumed that droplet convective heating can be adequately described by Newton's law of cooling, and Diesel fuel vapour in the vicinity of droplet surfaces has

been assumed to be always saturated. The latter assumption has allowed the modellers to reduce the problem of droplet evaporation to a much simpler problem of fuel vapour diffusion from droplet surfaces to the ambient gas (see [2] for a detailed review of this approach, commonly known as hydrodynamic approach).

The limitations of the above-mentioned approach, however, have been widely recognised since the pioneering studies of these phenomena more than a century ago (see [3] for a review of early studies). It has been shown that even in the case when the processes of droplet heating and evaporation take place at high pressures, the conventional hydrodynamic approach to their modelling is no longer valid in the immediate vicinity of droplet surfaces. It has been suggested that in this region the processes of heat and mass transfer should be modelled based on the Boltzmann equations for species (kinetic approach). In a number of studies,

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## Nomenclature

$b_{ij}$	coefficient defined by Eq. (5)
$E$	Hamiltonian eigenvalue
$G$	Gibbs free energy
$H$	Hamiltonian operator
$\hbar$	reduced Planck constant
$k_B$	Boltzmann constant
$m$	mass
$n$	number of molecules
$N$	number of conformers
$N_e$	number of electrons in the system
$p$	pressure
$r_i; r_j$	radii of droplets or clusters
$\mathbf{r}$	position
$R$	universal gas constant
$t$	time or the duration of the process
$T$	temperature

$V$  potential energy

### Greek symbols

$\beta$	evaporation coefficient
$\gamma$	evaporation rate
$\rho$	density
$\psi$	wave function

### Subscripts

$c$	critical
$e$	electron
$ev$	evaporation
$g$	gas
$l$	liquid
$0$	initial

including [4–9], the heating and evaporation of Diesel fuel (approximated by n-dodecane,  $C_{12}H_{26}$ ) droplets has been analysed based on a model using a combination of the kinetic and hydrodynamic approaches. In the immediate vicinity of droplet surfaces (up to about one hundred mean molecular free paths), the vapour and ambient gas dynamics have been studied based on the Boltzmann equation or equations (kinetic region), while at larger distances the analysis has been based on the hydrodynamic equations (hydrodynamic region). One of the important limitations of the approaches described in [4–9] is that they were based on the assumption that Diesel fuel can be approximated by n-dodecane. A more detailed analysis of the composition of Diesel fuel has shown that it includes in the region of a hundred or more hydrocarbon components of various kinds [2,10,11].

It is not feasible to take into account the contributions of all these components in the kinetic modelling. At the same time, one can see that these components can be subdivided into two main groups: alkanes and aromatics [2]. The assumption that n-dodecane can approximate alkanes is widely used (see [10,12,13]), while aromatics could be approximated by p-dipropylbenzene [12]. In this case it has been suggested that a more accurate approximation of Diesel fuel, compared with the one based on its approximation by n-dodecane, could be its approximation by a mixture of n-dodecane and p-dipropylbenzene. The investigation of the kinetic effects on heating and evaporation of two-component droplets (Diesel fuel was approximated as a mixture of n-dodecane and p-dipropylbenzene) has been described in [14].

The solution to the Boltzmann equations in the kinetic region is based on the boundary conditions at the surface of the droplet and at the interface between the kinetic and hydrodynamic regions. The boundary conditions at the interface between the kinetic and hydrodynamic regions are commonly formulated as the conservation of mass, momentum and energy fluxes at this interface. However, detailed knowledge of the processes at the surface of the droplets is required to formulate the boundary condition at this region. In most cases it has been assumed that the distribution function of the evaporating molecules is Maxwellian and the values of the evaporation coefficient have been specified.

The most common approaches to estimating the value of the evaporation coefficient have been based on molecular dynamic simulations. In [15,16] these simulations have been performed based on the assumption that Diesel fuel can be approximated by n-dodecane, and the structure of n-dodecane molecules has been simplified assuming that the bonds between carbon and hydrogen atoms are much stronger than those between carbon atoms,

leading to the so called United Atom Model. It has been shown that the evaporation coefficient of n-dodecane obtained using this approach increases with increasing temperatures and its values are reasonably close to those estimated by other methods and for other substances. These values have been used in the kinetic model for n-dodecane droplet evaporation described in [9]. Moreover, in [17] it has been shown that the distribution function of molecules in the vicinity of the droplet surface can deviate from the Maxwellian distribution, but this effect has not yet been taken into account in the kinetic modelling.

The main limitation of the model discussed in [15–17] is that in this model the interaction between individual molecules was described within the force field (FF) methods, which simplify both inter- and inner-molecular interactions by ignoring electrons *per se*. The applicability of this approach is far from obvious, as the dynamics of individual molecules in the vicinity of droplet surfaces are essentially a quantum mechanical process.

The quantum mechanical (quantum-chemical (QC)) models describing the processes at and in the vicinity of Diesel fuel droplet surfaces are described in [11,13,18,19]. These papers, however, primarily address the quantum chemistry community. The importance of the results presented in these papers might have been overlooked by a wider engineering audience. The main objective of the present paper is to summarise the main results reported in the above-mentioned four papers, but in a format that can be easily understood by the engineering community interested in modelling the heating and evaporation of Diesel fuel droplets.

The quantum-chemical methods used in the analysis and the compositions of Diesel fuel are discussed in Sections 2 and 3, respectively. The results of the analyses, using several approximations, are described in Section 4. The main results of the paper are summarised in Section 5.

## 2. Quantum-chemical methods of the analysis

Assuming that processes do not explicitly depend on time, the time independent Schrödinger equation for a single particle (electrons or nuclei) with potential energy  $V$  can be presented in the form

$$E\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V\psi(\mathbf{r}), \quad (1)$$

where  $E$  is the energy (Hamiltonian eigenvalue) including potential (electrons and nuclei) and kinetic (electrons) energy components,  $\psi$

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