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A molecular dynamics simulation investigation of fuel droplet in evolving ambient conditions

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ABSTRACT

Molecular dynamics simulations are applied to model fuel droplet surrounded by air in a spatially and temporally evolving environment. A numerical procedure is developed to include chemical reactions into molecular dynamics. The model reaction is chosen to allow investigation of the position of chemical reactions (gas phase, surface, liquid phase) and the behavior of typical products (alcohols and aldehydes). A liquid droplet at molecular scale is seen as a network of fuel molecules interacting with oxygen, nitrogen, and products of chemical fuel breakdown. A molecule is evaporating when it loosens from the network and diffuses into the air. Naturally, fuel molecules from the gas phase, oxygen and nitrogen molecules can also be adsorbed in the reverse process into the liquid phase. Thus, in the presented simulations the time and length scales of transport processes – oxygen adsorption, diffusion, and fuel evaporation are directly determined by molecular level processes and not by model constants. In addition, using *ab initio* calculations it is proven that the reaction barriers in liquid and gas phases are similar.

1. Introduction

Modeling of spray evaporation attracts much interest due to its significance for spray and combustion engineering applications. The theories of evaporation have been developed and improved over the last 100 years following the Maxwell paper [1]. Even today, the issue of primary interest in theoretical approaches is mass transfer of vapor quantized through evaporation and mass transport rates of the vapor molecules. There are two reasons for this. First, theory is relatively simple, and omits effects on the level of a single spray droplet, which are known to be important but hard to estimate. Second, experiments have mostly been restricted to observations of a spray as a whole, since it is hard to measure features important for the evaporation of a single droplet under realistic conditions. As a result, studies are usually focused on the evaluation of effects as an integral part of a wider problem of the spray dynamics [2–8]. A disadvantage of this approach is that complex interactions at the surface of an evaporating droplet that include heat transfer and chemical reactions are studied indirectly.

In contrast to the articles referenced above, evaporation was recently explored at level of a single droplet in a systematic way in several experimental and modeling studies. Fang and Ward, achieved a breakthrough in understanding heat transfer influence, with a series of very precise measurements of temperature distribution near an evaporating surface, see Ref. [9]. In Refs. [10–13] models for droplet heating and evaporation have been developed. These models include convective and radiative heating of single droplets, and effects of the recirculation inside droplets. Another line of research is dedicated to convective burning of droplets. Raghavan et al. [14] have made experimental and numerical investigations of a droplet burning in a convective environment. Wu and Sirignano [15] have analyzed transient behavior of an isolated convecting burning droplet. They have considered effects of droplet surface regression, deceleration due to the drag of the droplet, internal circulation inside the droplet, non-uniform surface temperature, and effect of surface tension. An initial envelope flame was found to persist in time, and an initial wake flame was always transitioned into the envelope flame at a later time, with the normalized transition delay controlled by the initial Reynolds number and the initial Damköhler number [15,16]. The moment of transition is postponed further into the lifetime for smaller initial droplet radius, greater initial Reynolds number, or smaller initial Damköhler number.

Localized ignition of droplet-laden flows is important for direct-injection internal combustion engines. An example of combustion concepts currently under development is homogeneous charged

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compression ignition (HCCI), expected to lead to low NO_x and smoke emissions without after treatment and with increased energy efficiency [7,17]. A great concern of HCCI engine design is how to control the start of combustion, evolution, and rate, once fuel is injected into the engine cylinder. For lean mixtures, HCCI has successfully controlled this process [17], but richer operation conditions remain a challenge (still lean but close to stoichiometry). A reason for this is that degree of pre-evaporation at ignition point, the number density of droplets, their chemical composition and droplet size are important parameters. A control of ignition delay is also important for control of combustion process. It is observed that it is easier to ignite droplet-laden mixtures than lean pre-vaporized mixtures. In droplet-laden mixtures, it is easier to control locally stoichiometric ratio as the droplets evaporate and obtain time resolved heat release [6,7]. Numerical simulations show that evaporative cooling in sprays can delay ignition, and that ignition delay is extended with decreasing droplet size [18]. Also, it is reasonable to assume that oxidation reactions take place in both liquid and gas phase. Current CFD simulations of droplet auto-ignition assume that most reactions in early stages of ignition take place close to the liquid surface where concentration of fuel molecule is the highest [19]. This could be a potential tackling point for the control of combustion. The first reaction of the fuel with oxygen produces peroxy radicals, cf. Ref. [20]. With the increase of temperature without presence of additional oxygen, peroxy radical will decompose to more stable chemical species [7,20]. A distinct acceleration of ignition process is expected, according to Warnatz et al. [20], as a result of the second oxygen reaction with peroxy radical. One can imagine combustion scheme, which utilizes molecular scale processes: If the injection point is selected at sufficiently high pressure and low temperature (e.g., by intake pressure boosting), evaporation rate would be moderate and oxygen would be spread by the diffusion throughout droplet and in that way come into the contact with fuel. The result would then be a kind of stable mixture of oxygen and fuel.

Although droplet evaporation has been a research topic for several decades, studies dealing with molecular aspects of the droplet interaction with the environment are rare and mainly intended to explore evaporation of noble gases and small molecules [21,22]. The first molecular dynamics study of argon droplet vaporization under subcritical conditions was done by Long et al. [23]. It was followed by a simulation of liquid oxygen vaporizing under super critical conditions [24] and water [25]. Consolini et al. [26] studied the evaporation of xenon droplets in a nitrogen environment under subcritical and supercritical conditions. Only recently in two separate studies, the simulations of n-heptane droplet vaporization were performed [27] and behavior of diffusion coefficient and clustering were investigated for *n*-alkanes in critical conditions [28].

We demonstrate in this work how molecular dynamics simulations can augment spray modeling and experiments at small length scales. Iso-octane is chosen as the liquid molecule interacting with gas (air) phase. Nevertheless processes and observed dynamical behavior should be generic to all liquid alkanes and their mixtures. We explore, if the first reaction of fuel molecules with oxygen could also take place in the liquid phase, and how the reaction products interact with the discrete molecular structure of the surface, i.e., their absorption, diffusion, and evaporation. Non-equilibrium molecular dynamics simulations use parameters obtained directly from *ab initio* considerations and do not require additional sub-models. However, a method of coarsening the scale and extracting conclusions from molecular simulation results to meso-scale or to continuum description is not obvious. At molecular level, one can observe molecules adsorbed onto the surface and fluxes of molecules penetrating from the surface into the liquid core (air molecules, surface reaction products). At scales under 0.1 μm, the fuel droplet surface is a network of fuel molecules, attached by intermolecular forces to their neighbors and in contact with air. A molecule is evaporating when it loosens from the network and diffuses into the air. Naturally, fuel molecules from the gas phase, oxygen and nitrogen molecules can also absorb into the liquid phase in a reverse process. *The strategy in this paper is based on calculating molecular fluxes and relating them to macroscopically observable quantities or processes, which determine the quality of combustion.* This allows us to introduce differentiation between molecular adsorption and absorption. Molecular adsorption is seen in simulations as adhesion from a gas to a surface and absorption is following process in which a molecule fluid permeates (diffuses) into a liquid core. *Since currently no single continuum model or simulation algorithm can encompass the range of length scales between molecular and meso-scales, the goal of the present work is set to study directly at molecular scale interaction of evaporation, diffusion, as well as, liquid and gas phase chemistry.*

The paper is organized as follows. Section 2 gives an overview of molecular dynamics approach used in this work. The formulation of model reaction is presented in Section 3. The results of all the simulations are presented in Section 4, followed by conclusions in final Section 5.

2. Approach to molecular evaporation

Non-equilibrium molecular dynamics (NEMD) simulations were developed as routine solutions of Newton's equations and in the meantime applied to simulate the motions of atoms and molecules in both solid, liquid, and gaseous materials [29–34]. The intermolecular and intramolecular forces are parameterized by incorporating quantum effects in the parameters of the potential function [35–38]. The classical equations of motion of Newton's mechanics are integrated with the force acting on each molecule obtained from the potential energy derivative. The position, velocity, and orientation of each molecule in the system is known at each instance of time. In this way, complex molecular phenomena can be studied and at the same time computationally expensive *ab initio* quantum mechanical calculations are avoided.

The NEMD simulations are performed using molecular dynamics code MDynamix [29]. The force field used in this work is TraPPE (Transferable Parameters for Phase Equilibria) which is shown to produce accurate results for the types of molecules of interest, i.e., branched alkanes, aldehydes and alcohols [35–38]. In the TraPPE force field, CH_x groups, e.g., methyl and methylene, are modeled as pseudoatoms located at the sites of the carbon atoms, whereas all other atoms (hydroxyl O and H) are introduced explicitly. The non-bonded interactions are described by pairwise-additive Lennard–Jones potential and Coulomb interactions of charges:

$$u(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \left[\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}\right] \tag{1}$$

where r_{ij} is the distance between atoms and CH_x group, and ϵ_{ij}, σ_{ij}, q_i, and q_j Lennard Jones potential well depth, size of the atom or CH_x group, and partial charges, respectively, for the pair of atoms and/or pseudo atoms i and j. A harmonic potential is used to control bond angle θ bending around equilibrium bending angle θ_0

$$u_{bend} = \frac{k_\theta}{2}(\theta - \theta_0)^2 \tag{2}$$

where k_θ is force constant. The parameters used in this work are listed in Table 1.

Having specified the potential energy function $V(r_N) = \sum_i u(r_{ij}) + \sum_{bonds} u_{bend}$, the next step is to calculate the atomic forces $F_i = -\partial V(r_N)/\partial r_i$ and use them to integrate the equation of motion. The output of such a simulation is the position and velocity of each molecule in the system. In order to reduce calculation time, we use