Transport of Sessile Droplet in Porous Medium with Evaporation and Chemical Reaction

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ABSTRACT

The dynamic of a sessile droplet spread of a wetting Newtonian fluid into a porous substrate in the presence of evaporation and chemical reaction is considered. The function for capillary pressure is found to be different from the classic Leverett-udell function. The evaporation and chemical reaction are fully coupled with the porous media flow with impact on the continuity, momentum, and energy equations. The multi-phase and multi-component Navier-Stokes equations for sessile droplets in a porous medium going through phase change and chemical reaction are solved explicitly on a finite difference mesh and the results are validated with laboratory and open air experimental data. The Runge-Kutta fourth order method is used to integrate the governing equations in time. In the model, chemical reactions are allowed among all phases; solid, liquid, and vapor. The local properties are functions of the species or phases that are present therefore, varying in time. Pesticides and any chemical that is released into the environment can evaporate and may also enter a chemical reaction with other pre-existing chemicals or simply moisture in the environmental substrates. The technique is proven to be very accurate and robust with widespread applications in defense, environmental safety, pharmaceuticals, and medical fields.

INTRODUCTION

Chemicals in the liquid phase are released into the environment are often in droplet form that are sprayed or atomized during the process. Pesticides are usually sprayed on crops and unfortunately sometimes malicious intentions are involved as in the release of chemical warfare agents. These chemical agents in droplet form may reside on porous or non-porous surfaces and depending on the type of surface, its chemical composition, and other pre-existing chemicals in the medium, their fate will vary. Surface evaporation, capillary transport, evaporation inside the pores, chemical reaction, and adsorption are physiochemical processes that take place simultaneously. The physical properties, volatility, and reactivity of the chemical/substrate combination will determine the form or extent of this process. A chemical in its vapor and liquid forms poses a respiratory or percutaneous threat, respectively. The challenge has been to develop a mathematical model based on first principles that can describe and quantify the outcome of these processes.

The spread of sessile droplets into a porous substrate, which can occur when a liquid is disseminated into the environment, has been addressed in the past [1-4]. However, most or all of the previous works have not either considered all the complex processes, or taken rigorous mathematical modelling approach. Surface evaporation of a sessile droplet has been addressed by Navaz *et al* [5] where a formula was developed that could scale the wind tunnel evaporation data to open air test data. The model was extensively validated with laboratory and open air experimental results. In the porous media, droplet spread in the model is momentum-driven by the capillary and hydrostatic pressures. If any liquid constituent (the droplet or products of any chemical reaction) is volatile, evaporation process inside the porous medium occurs during the liquid phase spreads [6].

Furthermore, additional transport properties needed to be modelled for this fully coupled problem. Permeability, capillary pressure, and gas diffusion coefficient need to be known. The relative permeability can be modelled using a power function, Brooks and Corey, or van Genuchten equations [7,8]. The capillary pressure is often modelled using the Leverett *J*-function [9,10]. This capillary pressure function was modified for a sessile droplet by Navaz, *et al* [6,11]. The local gas diffusion coefficient also needed to be derived as a function of porosity that is defined not only by the porous substrate, but also by any other solid product as a results of chemical reaction and any existing liquid phase [12].

To the best of our knowledge, there is no existing general-purpose computer model that couples all existing physiochemical processes that was discussed earlier by solving fully coupled conservation equations in 3-dimentional. The model described here was developed for use in assessing the spatial distribution and temporal behaviour of all species, in all phases, undergoing diffusion, evaporation and chemical reactions.

NOMENCLATURE

C	[-]	Mass Fraction
D	[m^2/sec]	Gas phase binary diffusion coefficient
K	[m^2]	Saturation permeability
k	[-]	Relative permeability
P	[Pa]	Pressure
R	[kJ/kg-K]	Gas constant
s	[-]	Saturation
t	[sec]	Time
$\vec{V}$	[m/sec]	Velocity vectors
T	[K]	Temperature
x	[m]	Cartesian axis direction
y	[m]	Cartesian axis direction
z	[m]	Cartesian axis direction

Special characters

ϕ	[-]	Porosity
μ	[Pa-sec]	Viscosity
ρ	[kg/m^3]	Density
$\dot{\omega}$	[mole/m^3-sec]	Rate of species production/destruction

Subscripts

g	Gaseous phase
i	Liquid phase constituent
j	Gas phase constituent
k	Solid phase constituent
ℓ	Liquid phase

The continuity and momentum equations for each phase ignoring the solidification and condensation processes can be written as:

Conservation of mass for each liquid species:

$$\frac{\partial(\phi\rho_{\ell i}s_{\ell i})}{\partial t}+\nabla\bullet\left(\phi\rho_{\ell i}s_{\ell i}\vec{V}_{\ell i}\right)=\begin{pmatrix}-\dot{\rho}_{\ell i}^{Secondary\,Evaporation}-\dot{\rho}_{\ell i}^{Surface\,Evaporation}\\-\dot{\omega}_{\ell i}^{Reaction}\end{pmatrix} \quad (1)$$

Conservation of mass for each gaseous species:

$$\frac{\partial(\phi\rho_{gj}s_g)}{\partial t}+\nabla\bullet\left(\phi\rho_{gj}s_g\vec{V}_{gj}\right)=\dot{\rho}_{\rho_{\ell i}}^{Secondary\,Evaporation}-\dot{\omega}_{gj}^{Reaction} \quad (2)$$

Conservation of mass for each solid species:

$$\frac{\partial\rho_{sk}}{\partial t}=\dot{\omega}_{sk}^{Reaction} \quad (3)$$

Momentum equation for liquid species

$$\vec{V}_{\ell i}=-\frac{Kk_{\ell i}}{\mu_\ell}\left(\nabla P_{\ell i}-\rho_{\ell i}gs_{\ell i}\right) \quad (4)$$

Momentum equation for gaseous species

$$\vec{V}_{gj}=-\frac{Kk_{gj}}{\mu_g}\left(\nabla P_{gj}-\rho_{gj}gs_g\right)-D_{j\to mixture}\nabla C_{gj}, \quad (5)$$

Where:

$$\rho_\ell=\sum_{i=1}^{N(Liquids)}\rho_{\ell i}C_{\ell i},\quad C_{\ell i}=Mass\ \ Fraction=\frac{s_{\ell i}}{s_\ell=\sum_{i=1}^{N}s_{\ell i}},$$

$$\mu_\ell=\sum_{i=1}^{N(Liquids)}\mu_{\ell i}C_{\ell i},\quad P_{\ell i}=P-P_{ci} \quad (6)$$

$$s_g=1-\sum_{i}^{N(Liquids)}s_{\ell i}\ ,\quad \rho_g=\sum_{j=1}^{M(Gases)}\rho_{gj}C_{gj},$$

$$C_{gj}=Mass\ \ Fraction=\frac{\rho_{gj}}{\rho_g},\quad \mu_g=\sum_{j=1}^{M(Gases)}\mu_{gj}C_{gj}$$

$\mu_{\ell i}, \rho_{\ell i}, s_{\ell_i}, P_{\ell i}=P-P_{ci}$ are respectively the viscosity, density, saturation, and pressure of liquid phase constituent "*i*". P_{ci} is the capillary pressure for liquid "*i*". *g* is the gravitational acceleration in the desired direction. μ_{gj} and ρ_{gj}, are the viscosity and density of each constituent in the gas phase. $\dot{\omega}$ is the rate of chemical species production/destruction in the related phase, *k* is the relative permeability, and $\phi=\phi(\rho_{sk})$ is the local porosity, and $D_{j\to mixture}(\phi,s_\ell)$ is the effective diffusion coefficient defined as molecular diffusivity of each gas constituent into the mixture attenuated by the local porosity and saturation. *K* is the saturation permeability. Note that the mixture properties for the liquid and gas phases are obtained by mass weighted constituents' properties. The Arrhenius form of reaction rate is assumed. Uni-directional, Forward, backward, and third body reaction rates can be considered for more complex systems like drug delivery process. The details are outlined by Navaz,*et al* [13].

NUMERICAL METHOD AND SUBMODELS

The above set of equations are transformed to the computational coordinates and are solved by finite-difference method using Runge-Kutta fourth order method on structured mesh. The droplet is assumed in the form of a spherical cap and the mesh is generated internally in the computer program. The mesh for a non-spherical droplet can be generated externally and read by the program. A sample mesh generated by the code is shown in Appendix A. For a non-porous substrate, the spread and morphology of the droplet at each instant of time differs from a porous substrate. For a porous substrate, the foot print of the droplet is constant and any transport including the lateral direction takes place by capillary forces. For a non-porous substrate, the foot print may initially be constant and after a certain time passed the evaporation, the droplet starts shrinking in height and radius of the foot print simultaneously. The non-dimensional groups for evaporation model was derived and it was found that if the Reynolds number in the evaporation model is based on friction velocity instead of the usual free stream velocity. Therefore, the calibration constants could be measured in a wind tunnel and be used for open air experiment indicating the universality of the model.

The Leverett-Udell equation for capillary pressure can be used for cases where an entire boundary is covered with the liquid phase. However, it needed to be modified for a sessile droplet. After extensive studies [11-13], a test must be conducted to find the proper scaling factor and multiply it by the Leverett-Udell equation. In this experiment, a droplet is placed on the porous substrate and the time that it takes for that droplet to disappear from the surface will be measured. A family of curves for different porosities are generated and this scaling factor will be determined from this graph [11]. Initial contact angle and volume of the droplet must be known for this procedure.

RESULTS AND DISCUSSION

The surface evaporation model was extensively validated with wind tunnel and open air data with time changing wind and temperature conditions for HD (known as mustard gas – nerve agent) evaporation on glass. Figure 1 shows one of the model/experiment comparisons at a temperature of *15°C* and *1.77 m/s* mean air velocity at turbulence intensity of *2.2%*. Numerous experiments were conducted changing these variables and the results are presented in Reference [11]. After numerous tests, basically no difference was found between model 1 and model 2 (different calibration constants based on either Prandtl or Schmidt numbers). Figure 2 shows an excellent agreement between the model prediction and open air test data under time dependent outdoor temperature and air velocity. The capillary pressure was determined as was mentioned earlier and model and experiment comparison for different droplets (wide range of viscosity and surface tension) are shown in Table 1. Comparison is made for the time that it takes for the droplet to disappear from the surface and the

spherical cap ceases to exist. VX is a very low volatile and potent nerve agent. The agreement is quite satisfactory. This method of specifying capillary pressure is used for all the future studies in this paper. An evaporation model for the liquid phase inside the pores were developed [11] using the capillary pressure function that was discussed earlier. Figure 3 shows the capillary transport and evaporation of *1 μL* HD droplet inside UK (United Kingdom) sand (there are different types of sand) at *15°C*.

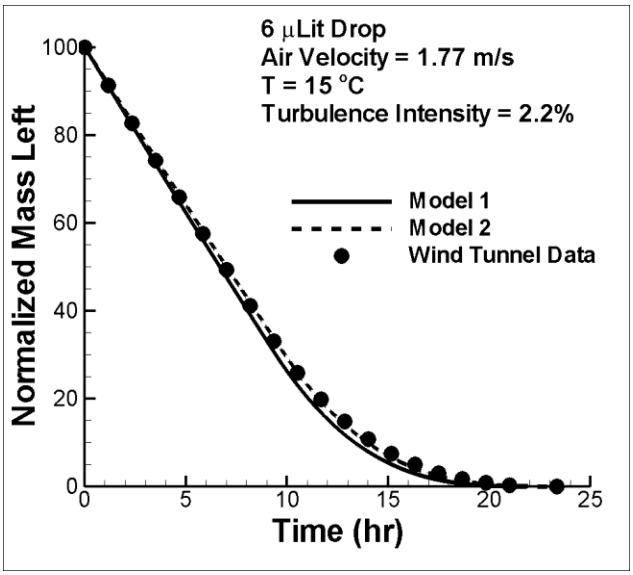

Figure 1 Normalized HD mass left during evaporation of *6 μL* HD droplet at *15°C* with mean wind tunnel air velocity of *1.77 m/s*.

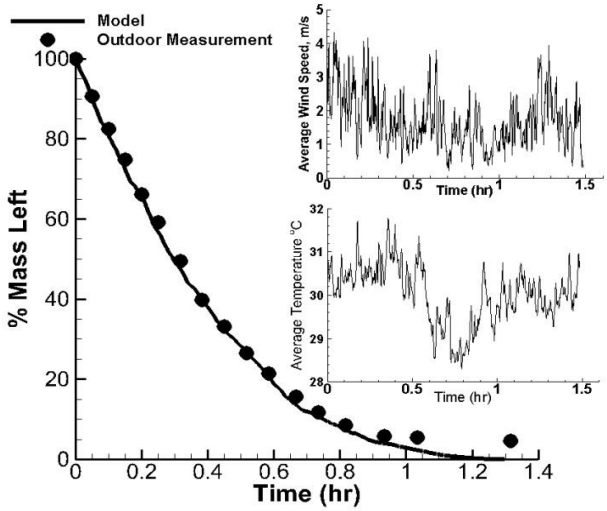

Figure 2 Normalized HD mass left during evaporation of *6 μL* HD droplet under open air transient velocity and temperature conditions

Further validation of the model was performed with Reis *et al* [14] and Mantle *et al* [15] data taken by MRI (Magnetic Resonance Imaging) method. They studied the evaporation of water inside porous media using advanced technology of MRI. Figure 4 shows an excellent comparison for the evaporation of water in sand and *180 μm*-diameter glass beads.

Table 1 Measured and calculated time for the disappearance of a droplet from the surface of a porous material. VX and HD are nerve agents.

Substance	Experiment (Time, sec)- Extracted from Video	Model (Time, sec.)
1-2 Propandiol	1.45	1.50
Castor Oil	27.50	28.30
Glycerin	12.30	11.95
VX	1.50	1.45
HD	0.90	0.87

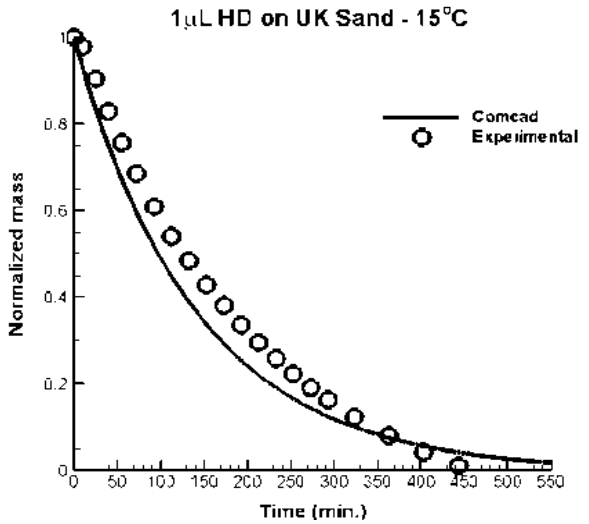

Figure 3 Capillary transport and evaporation of *1 μL* HD droplet inside UK sand at *15°C*.

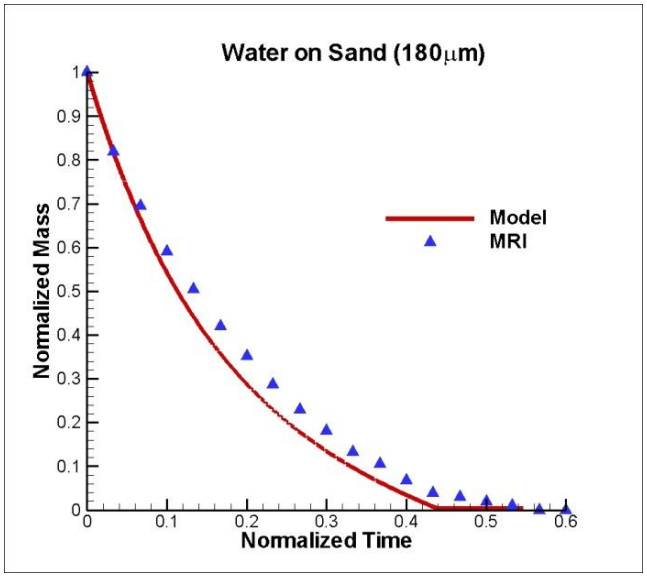

Figure 4 Evaporation of water in sand and *180 μm*-diameter glass beads. Model comparison with MRI results

Reaction of chemical agents or pesticides with water is of special interest because it describes a common degradation

pathway. It therefore presents a practical application due to the natural existence of moisture inside soil or environmental substrates. Malathion, an organophosphate widely used in agriculture as a pesticide, has physical properties similar to the nerve agent *VX*, especially their multiple reaction centres. Malathion degrades very slowly at low *pH*, but can undergo rapid hydrolysis in basic solutions. The model prediction for the remaining Malathion as it undergoes hydrolysis reaction in soil is compared with the experimental data while the *pH* of the substrate was maintained at constant value of 9 in Figure 5. The detail of the experimental procedure is outlined in references [11,13].

In another experiment involving a liquid and a solid phase, a *50 μL* droplet of Sulfuric acid (liquid phase) reacts with a brick of sodium sulfide (solid phase). The chemical reaction takes place according to:

$$Na_2S_{(s)} + H_2SO_{4\,(aq)} \rightarrow Na_2SO_{4\,(s)} + H_2S_{(g)}$$

The rate of loss for sulfuric acid was calculated. The results are shown in Figure 6, where quantitative as well as qualitative match to the experimental data is demonstrated.

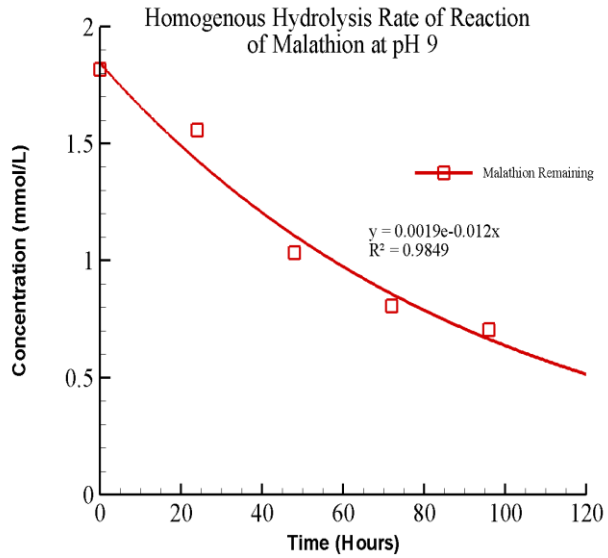

Figure 5 Concentration of remaining Malathion undergoing hydrolysis reaction in soil at a constant *pH* level of 9.

In a similar experiment, a *50 μL* liquid sulfuric acid was deposited on a porous substrate composed of 75% non-reacting sand and 25% reacting sodium sulfite. An excellent comparison for the remaining mole fraction of sulfuric acid between the model and experiment is shown in Figure 7.

In order to examine the model's response to multiple chemical reaction processes that are influenced by the spread of a droplet, a simulation of a *6μL* droplet of O-ethyl s-[2-N,N-(diisopropylamino)ethyl]methylphosphonothioate (*VX* nerve agent) was created. The droplet was allowed to spread into a media with porosity of *35%*. The rates of hydrolysis reaction were defined based on those reported in Brevett *et al* [16] for *VX* reacting on moist sand. Briefly, *VX* degrades into several

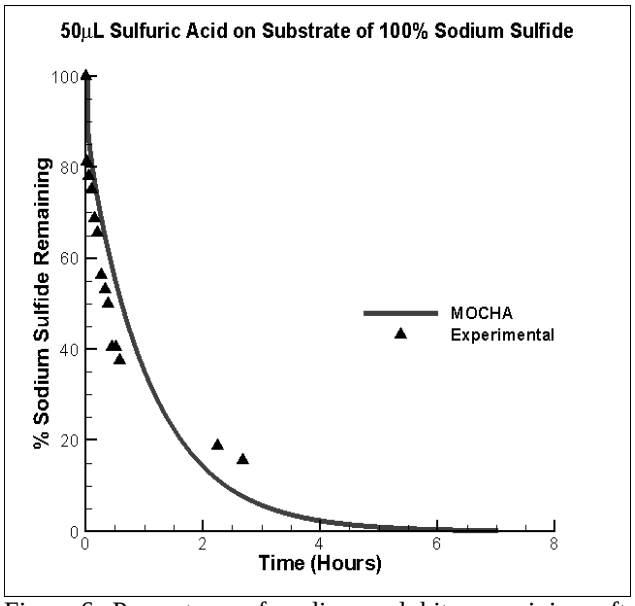

Figure 6 Percentage of sodium sulphite remaining after its reaction with Sulfuric acid. Model is the solid line and symbols represent the experimental result.

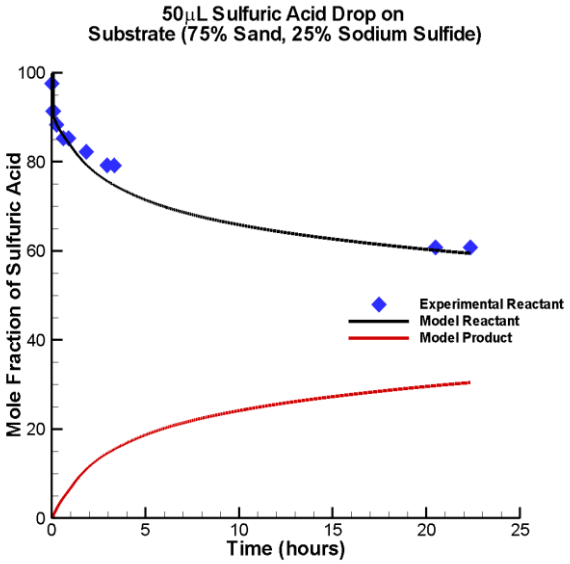

Figure 7 Mole fraction of *50 μL* sulfuric acid as it reacts with a solid substrate composed of 75% non-reacting sand and 25% of reacting sodium sulfite. The lower line is the model prediction for the products.

breakdown products shown in Table 2 in wet sand. All of the degradation reactions were approximated as first order in *VX*, due to the large excess of water (experiments reported a *25-32* fold molar excess). The degradation took place under sealed conditions and was therefore modeled without evaporation. The model indicated *VX* disappearance and appearance of breakdown products in quantities similar to those reported in the experimental study as shown in Figure 8.

Table 2 Breakdown species for VX hydrolysis reaction and their rate constants. EMPA [$CH_3P(O)(OC_2H_5)OH$], DESH [$HSCH_2CH_2N(isoPr)_2$]; EA 2192 [$CH_3P(O)(OH)SCH_2CH_2N(isoPr)_2$]; EMPT [$CH_3P(O)(OC_2H_5)SH$]

Reaction	Rate Constant [1/s]	Reaction Model
VX – EMPA+DESH	8.3e-6	K1[VX]
VX – VXH+	2.3e-5	K2[VX]
VXH+ - EMPA+DESH	1.06e-5	K3[VXH+]
VX – EMPT + DIAZ+	1.71e-6	K4[VX]
VX – EA-2192 + EtOH	2.75e-6	K5[VX]

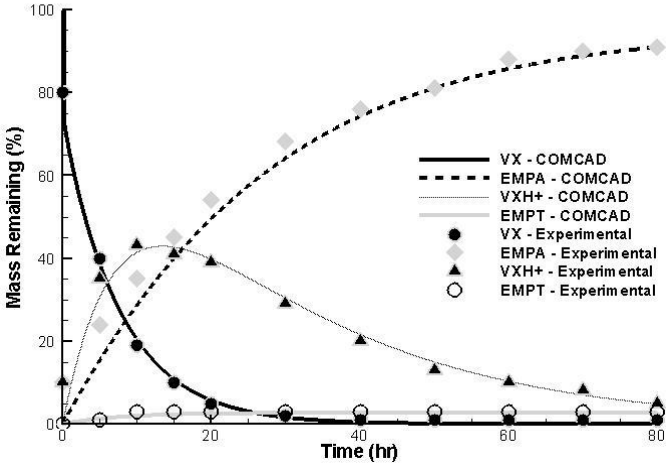

Figure 8 A *6μL VX* droplet undergoes hydrolysis in damp sand at *50°C* . Both agent and breakdown product amounts present in the sand, as measured in Brevett *et al* [16] experimental study, are characterized by the model

CONCLUSION

A comprehensive and general purpose model for the evaporation, transport, and chemical reaction of liquid droplets on and inside porous substrates is developed. All the sub-models such as evaporation rate, capillary pressure function, and effective diffusion coefficient needed to be developed to be compatible with the physics of the problem and the presence of different phases in the domain. The model demonstrated an ability to provide a time accounting of the total amounts of reactants present in a porous media. The simulated experiments exhibited the qualitative and quantitative trends observed in the experimental data. These responses indicate a robustness and accuracy in the model. The current model provides a tool for evaluating the local contamination levels in porous media exposed to a liquid which reacts in the environment.

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APPENDIX A

A sample mesh generated for two droplets of different size is generated internally by the developed computer program. This is shown in Figure A-1

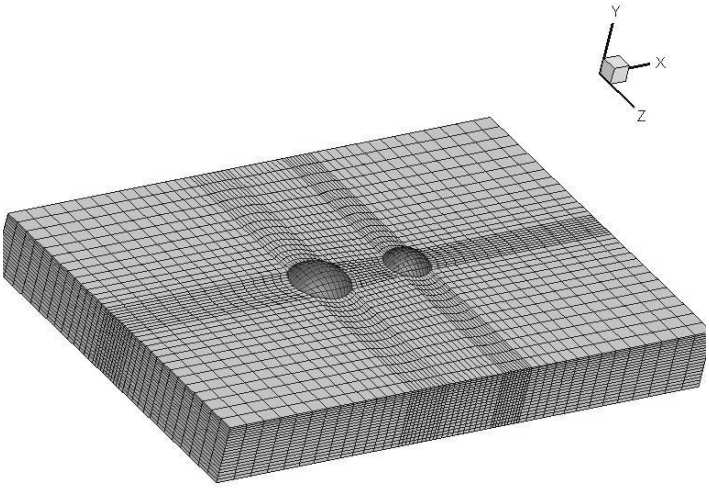

Figure A-1 Sample mesh internally generated by the developed computer program for two droplets of different size.