

A Molecular Kinetic Model of Reacting Gas Flows

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Abstract. This is an attempt to see the feasibility of molecular kinetic approach to complex flows with chemical reaction by the Boltzmann equation. We assume a simple reaction model in addition to the elastic collision term of the BGK model equation for reactive gas mixture. The computation is performed for one-dimensional flow with reacting hydrogen-oxygen mixture and two-dimensional turbulent flow with dissociating oxygen gas. We obtain reasonable solutions for diffusive mixing with reaction, flame front structure with exothermic chain reaction, and atomic evolution due to thermal dissipation of turbulence.

Keywords: Molecular kinetic model; Reacting gas flow; Numerical computation.

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INTRODUCTION

We consider the problem of computing chemically reacting gas flows. This problem is known to be not easy to cope with because of the fine structure of chemically reacting zone, where the reacting process is essentially molecular level. This situation makes it inevitably difficult for an approach based on continuum mechanics model. Here we introduce a kinetic model based on the Boltzmann equation to compute reacting complex flows. We construct a model by modifying the one originally proposed by Burgers [1], where the collision term is the sum of elastic collision given in BGK type expression and the one for the change by chemical reaction. We compute three cases, the first is for process of reactive mixing of hydrogen and air, the next is for a reacting uniform flow of hydrogen-oxygen mixture, and the last is for a flow of turbulent oxygen gas mixture accompanying the reaction process in a high temperature field.

BASIC EQUATIONS

The molecular kinetic model equation with chemical reaction is assumed here as

$$\frac{Df_j}{Dt} = \nu_j(f_{je} - f_j) + \left(\frac{dn_j}{dt} \right)_c f_{je}^*, \quad (1)$$

where f_j is the velocity distribution function of j -th chemical species, $f_{je} (= n_j f_{je}^*)$ is the Maxwellian distribution function based on the mean velocity \mathbf{u} and the mean temperature T for gas mixture, ν_j is the elastic collision frequency, and $(dn_j/dt)_c$ is the production rate of the number density n_j due to associated chemical reactions. We introduce a simplified model for reacting collision term by a product of the reaction rate with a Maxwellian distribution, assuming that reacting gas molecules are produced or lost with Maxwellian distributions. This approximation is based upon the assumption of a complete randomization of the velocities of the particles in the collisions [1], and can be considered to be adequate enough for reacting gases near thermal equilibrium. We assume that the reactive collision frequency is much smaller than the elastic collision frequency.

We use the reduced distribution functions G_j and H_j for j species [2], [3]. We extend its concept to include the rotational energy. Starting from the generalized Boltzmann equation including the rotational energy space [4], we can obtain the following reduced distribution functions for one or two dimensional flow.

$$\text{1-D flow:} \quad G_j = G_j(c_x, x, t) = \iiint f_j dc_y dc_z dE_r \quad (2)$$

$$H_j = H_j(c_x, x, t) = \iiint \left\{ \frac{1}{2} m_j (c_y^2 + c_z^2) + E_r \right\} f_j dc_y dc_z dE_r \quad (3)$$

$$\text{2-D flow:} \quad G_j = G_j(c_x, c_y, x, y, t) = \iint f_j dc_z dE_r \quad (4)$$

$$H_j = H_j(c_x, c_y, x, y, t) = \iint \left(\frac{1}{2} m_j c_z^2 + E_r \right) f_j dc_z dE_r \quad (5)$$

The distribution function $f_j = f_j(c_x, c_y, c_z, x, y, z, t, E_r)$ for j species is a function of the rotational energy E_r as well as the molecular velocity $\mathbf{c} (c_x, c_y, c_z)$, the spatial coordinate $\mathbf{x} (x, y, z)$, and the time t .

The normalized equations for G_j and H_j can be written for a flow of arbitrary dimension as

$$\frac{DG_j}{Dt} = \nu_j (G_{je} - G_j) + \left(\frac{dn_j}{dt} \right)_c G_{je}^*, \quad (6)$$

$$\frac{DH_j}{Dt} = \nu_j (H_{je} - H_j) + \left(\frac{dn_j}{dt} \right)_c H_{je}^* \quad (7)$$

where G_{je} and H_{je} are the reduced Maxwellian distribution functions of G_j and H_j as

$$G_{je} = n_j G_{je}^* = n_j (\pi T)^{-\alpha} \exp \left(-\frac{\mathbf{C}_j^2}{T} \right), \quad (8)$$

$$H_{je} = n_j H_{je}^* = \beta T G_{je}, \quad (9)$$

where for 1-D flow, $\alpha = 0.5$, $\beta = 1.0$ (monatomic) or 2.0 (diatomic); for 2-D flow, $\alpha = 1.0$, $\beta = 0.5$ (monatomic) or 1.5 (diatomic). We also use the coplanar gas model for some cases. It corresponds to a special case of the reduced distribution function under the assumption of $H_j = H_{je}$ for two dimensional velocity space.

We introduce the normalized properties as follows.

$$G_j (2kT_r / m_j)^\alpha / n_r \rightarrow G_j, \quad H_j (2kT_r / m_j)^\alpha / (kT_r n_r) \rightarrow H_j, \quad \mathbf{c} / (2kT_r / m_j)^{0.5} \rightarrow \mathbf{c}_j,$$

$$n_j / n_r \rightarrow n_j, \quad T / T_r \rightarrow T, \quad \mathbf{u} / (2kT_r / m_r)^{0.5} \rightarrow \mathbf{u}, \quad \mathbf{x} / L \rightarrow \mathbf{x}, \quad t (2kT_r / m_r)^{0.5} / L \rightarrow t,$$

where k is the Boltzmann constant, L is the reference length, n_r is the reference number density, m_r is the reference molecular mass, m_j is the molecular mass of j species, and T_r is the reference temperature. We use the molecular mass m_j of each species as a reference mass in the velocity space to minimize numerical errors due to mass difference between light and heavy molecules.

The macroscopic properties $n_j, n, \rho, \mathbf{u}_j, \mathbf{u}, T_j, T, p, p_{mn}, q$, and Φ_j are obtained in dimensionless forms as

$$n_j = \int G_j d\mathbf{c}_j, \quad n = \sum n_j, \quad \rho = \sum m_j n_j, \quad m_j n_j \mathbf{u}_j = m_j^{0.5} \int \mathbf{c}_j G_j d\mathbf{c}_j, \quad \rho \mathbf{u} = \sum m_j n_j \mathbf{u}_j, \quad \Phi_j = m_j n_j (\mathbf{u}_j - \mathbf{u}),$$

$$\lambda n_j T_j = \int (C_j^2 G_j + H_j) d\mathbf{c}_j \quad (\lambda = 1.5 \text{ for monatomic gas, } \lambda = 2.5 \text{ for diatomic gas}), \quad nT = \sum n_j T_j,$$

$$p = nT, \quad p_{mn} = \sum \int C_{mj} C_{nj} G_j d\mathbf{c}_j - p \delta_{mn}, \quad q = \sum m_j^{-0.5} \int (C_j^2 G_j + H_j) \mathbf{C}_j d\mathbf{c}_j,$$

where n is the total number density normalized by n_r , ρ is the total mass density normalized by $m_r n_r$, m_j is normalized by m_r , \mathbf{u}_j is the mean velocity of j species normalized by $(2kT_r / m_r)^{0.5}$, Φ_j is the diffusion mass flux

of j species normalized by $m_r n_r (2 k T_r / m_r)^{0.5}$, T_j is the temperature of j species normalized by T_r , p and p_{mn} are the pressure and the viscous stress tensor normalized by $k n_r T_r$, q is the total heat flux normalized by $k n_r T_r (2 k T_r / m_r)^{0.5}$, and $C_j = c_j - m_j^{0.5} u$. We use the common notations c_j and C_j for molecular velocities: for one dimensional flow, $c_j = c_{xj}$, $C_j^2 = C_{xj}^2$, and $d c_j = d c_{xj}$; for two dimensional flow, $c_j = (c_{xj}, c_{yj})$, $C_j^2 = C_{xj}^2 + C_{yj}^2$, and $d c_j = d c_{xj} d c_{yj}$.

ELASTIC COLLISION FREQUENCY AND CHEMICAL REACTION RATE

We assume the hard sphere collision model for elastic collisions. The elastic collision frequency ν_j for each species are given by the sum of the mutual collision frequency ν_{ji} between species j and i as $\nu_j = \nu_{j1} + \nu_{j2} + \dots$. We use a formula of mutual collision frequency for gas mixture in a dimensionless form as

$$\nu_{ji} = n_i \sigma_{ji}^2 \{ 2 T / (\pi m_{ji}^*) \}^{0.5} / K_n, \quad m_{ji}^* = m_j m_i / (m_j + m_i), \quad \sigma_{ij} = (d_j + d_i) / 2,$$

where m_{ji}^* is the reduced mass normalized by m_r , σ_{ij} and d_j are the collision diameter and the molecular diameter normalized by the reference molecular diameter d_r , and K_n is the Knudsen number defined by $K_n = \lambda_r / L$. The mean free path λ_r is given by $\lambda_r = (2^{0.5} \pi d_r^2 n_r)^{-1}$ for a reference gas molecule.

We consider here three types of chemical reaction A, B, and C. Each chemical reaction and its rate equation are described in the following. We use empiric parameters for the Arrhenius equation to evaluate the reaction rate.

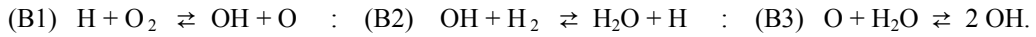
Reaction A: Forward reaction in hydrogen-air gas mixture: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$.

The gas components of the mixture are H_2 ($j=1$), H_2O ($j=2$), O_2 ($j=3$), and N_2 ($j=4$), where N_2 is assumed to be inert. The production rate of H_2O is given in a dimensionless form as

$$R_0 = (d n_2 / d t)_c = K_0 \rho \exp(-T_{f0} / T) (n_1 n_3)^{0.5} / K_n,$$

where $K_0 = 5.49 \times 10^{-4}$ and $T_{f0} = 9.85$ when we select the reference quantities as $T_r = 1,000 \text{ K}$, $n_r = n_{10}$ (initial number density of H_2), $d_r = d_1$, and $m_r = m_1$. We have the dimensionless molecular diameters $d_1 = 1.0$, $d_2 = 1.266$, $d_3 = 1.296$, $d_4 = 1.342$, and the dimensionless masses $m_1 = 1.0$, $m_2 = 9.0$, $m_3 = 16.0$, $m_4 = 14.0$. The reaction rates for other gases are given as $(d n_1 / d t)_c = -R_0$, $(d n_3 / d t)_c = -0.5 R_0$, and $(d n_4 / d t)_c = 0$. We use the reaction rate equation given in the usual Navier-Stokes analysis for the ignition process of turbulent hydrogen-air mixture [5].

Reaction B: Chain reactions in hydrogen-oxygen gas mixture:



The gas components of the mixture are H_2 ($j=1$), H_2O ($j=2$), O_2 ($j=3$), OH ($j=4$), H ($j=5$), and O ($j=6$). We denote the net production rates of right-side species for reactions (B1), (B2) and (B3), respectively, as R_1 , R_2 , and R_3 .

$$R_1 = k_{f1} (n_3 n_5 - n_4 n_6 / k_{c1}) / K_n, \quad k_{f1} = K_1 T^{-0.7} \exp(-T_{f1} / T), \quad k_{c1} = K_{a1} T^{-0.38} \exp(-T_{c1} / T),$$

$$R_2 = k_{f2} (n_1 n_4 - n_2 n_5 / k_{c2}) / K_n, \quad k_{f2} = K_2 T^{-1.3} \exp(-T_{f2} / T), \quad k_{c2} = K_{a2} \exp(T_{c2} / T),$$

$$R_3 = k_{f3} (n_2 n_6 - n_4^2 / k_{c3}) / K_n, \quad k_{f3} = K_3 T^{-0.384} \exp(-T_{f3} / T), \quad k_{c3} = K_{a2} T^{-0.13} \exp(-T_{c3} / T),$$

where $K_1 = 0.6104$, $K_2 = 0.0203$, $K_3 = 0.00549$, $T_{f1} = 8.588$, $T_{f2} = 1.828$, $T_{f3} = 6.435$, $K_{a1} = 127.6$, $K_{a2} = 0.174$, $K_{a3} = 22.98$, $T_{c1} = 8.672$, $T_{c2} = 8.347$, and $T_{c3} = 8.72$. The reaction rates for six species are given as $(d n_2 / d t)_c = R_2 - 0.5 R_3$, and so on. We use the reaction rates given in the detonation wave analysis of ethylene-air mixtures [6].

Reaction C: Dissociation-recombination reaction of oxygen gas: $\text{O}_2 + \text{M} \rightleftharpoons 2 \text{O} + \text{M}$ ($\text{M} : \text{O}_2 \text{ or } \text{O}$).

The gas components of the mixture are O ($j=1$) and O_2 ($j=2$). The production rate of O is given as

$$R_4 = (d n_1 / d t)_c = K_4 T^{-1.5} (n_1 + 0.1 n_2) \{ n_2 \exp(-T_d / T) - n_1^2 / \rho_d \},$$

where $K_4 = 6.26 \times 10^4$, $T_d = 11.9$, and $\rho_d = 4 \times 10^7$. We have also $(d n_2 / d t)_c = -0.5 R_4$. We use the reaction rate based on the Lighthill's ideal dissociating gas model [7].

COMPUTATIONAL RESULTS AND DISCUSSION

We transform the kinetic equation into an integrated form which is performed along the characteristics line for a computational scheme [8]. The computation is performed as an initial value problem of unsteady flow with chemical reaction, starting with the Maxwellian distribution for each species. The spatial and velocity spaces are discretized into grid points, and the computational procedure is divided into two steps in each time step. In the first translation step, we construct $G_j^{(1)}(\mathbf{c}, \mathbf{x}, t + \Delta t)$ from $G_j^{(0)}(\mathbf{c}, \mathbf{x} - \mathbf{c} \Delta t, t)$ without collision terms. The value of $f_j^{(0)}$ at $\mathbf{x} - \mathbf{c} \Delta t$ is estimated from a linear interpolation among grid-point values, since position $\mathbf{x} - \mathbf{c} \Delta t$ is not necessarily on a grid point. In the second collision step, we modify $G_j^{(1)}$ by taking into account the collision terms as

$$G_j^{(2)}(\mathbf{c}, \mathbf{x}, t + \Delta t) = G_j^{(1)} + \Delta t \{ \mathbf{v}_j^{(1)} (G_{je}^{(1)} - G_j^{(1)}) + (dn_j/dt)_c^{(1)} G_{je}^{*(1)} \}.$$

The macroscopic properties are evaluated after the first step calculation, and used for calculating the elastic collision frequency and the chemical reaction rate. We give a correction to the profile of G_{je}^* before performing the second step calculation at each time step, to avoid the numerical error which occurs due to the finiteness of the selected velocity space region. We must keep exactly the relation $\sum G_{je}^* \Delta \mathbf{c}_j = 1$ for numerical integration over the velocity space to preserve the mass conservation during the chemical reaction process.

Figure 1 shows number density distributions in a diffusive mixing process (left figure) and a one-dimensional premixed gas flow (right figure) accompanying forward reaction of hydrogen-air mixture (Reaction A). The molecules are assumed to be hard sphere molecules. We use the coplanar gas model with 2-D velocity space and 1-D physical space. The computational domain of the velocity space is fixed at $t = 0$ as $-6.0 < C_{xj} < 6.0$ and $-6.0 < C_{yj} < 6.0$ for peculiar velocity of each j species, and is discretized into 20x20 square cells. The x coordinate in the figure is expressed by the grid number. The mesh size Δx is equal to five times reference mean free path λ_r of initial hydrogen gas. The amplification factor of the reaction rate K_c is selected as 20.0. We assume the reaction occurs without chemical energy release. The initial temperature is assumed to be 1,500 K for both cases.

In the diffusive mixing case, the stationary hydrogen gas in a left chamber is initially separated from the stationary air in a right chamber by a thin diaphragm at $x = 100$. The initial number densities at $t = 0$ are given as $n_1 = 1.0$ for H_2 in the left and $n_3 = n_4 = 0.5$ for O_2 and N_2 in the right, including a small quantity of H_2O for stable computation. The figure shows the production of H_2O due to the diffusive mixing of hydrogen and oxygen at 60 time steps ($\Delta t = 0.08$). The H_2O number density n_2 is exhibited by 400 times amplification, since its amount is very small. The result suggests that the present kinetic model is applicable to diffusive mixing with reaction. In the premixed flow case, we consider a simple reacting flow in a half physical space of positive x to confirm the validity of the computational code for flowing gas mixture. The initial number densities at $t = 0$ are given as $n_1 = 1.0$ (H_2), $n_2 = 2 \times 10^{-5}$ (H_2O), and $n_3 = n_4 = 0.5$ (O_2 and N_2) for all grid points including $x = 0$, where the initial number densities are fixed as a boundary condition. The figure shows the premixed gas without reaction at $x = 0$ runs into the high temperature zone, and changes its components as time step proceeds from 1,000 to 2,000, exactly preserving the mass conservation law.

Figure 2 shows distributions of number density, diffusion flux, temperature, and heat flux in 1-D premixed gas flow accompanying hydrogen-oxygen exothermic chain reaction (Reaction B). We use the reduced distribution func-

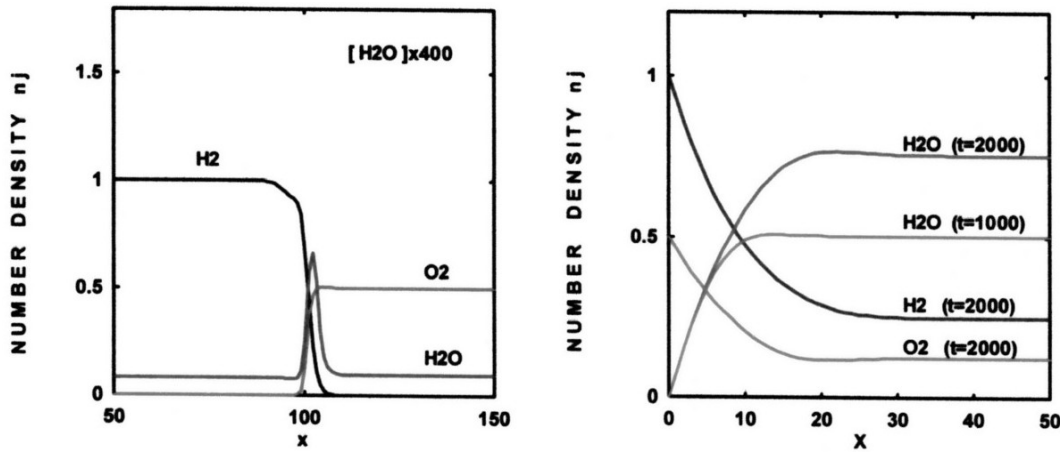


FIGURE 1. Reaction A: Number density distributions for diffusive mixing process (left figure) and 1-D premixed gas flow (right figure) in forward reaction of hydrogen-air mixture, $\Delta x = 1.0$, $\Delta t = 0.08$ and 0.04 , $K_n = 0.2$, $K_c = 20.0$, $T_0 = 1.5$ (1,500 K).

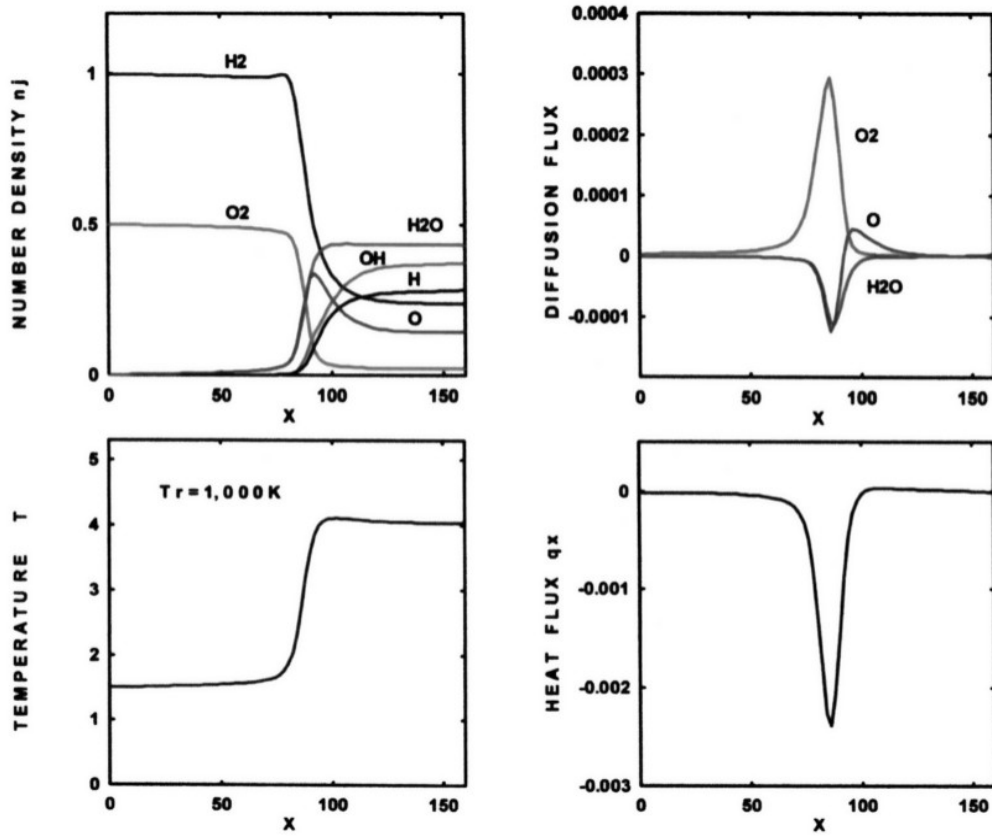


Figure 2. Reaction B: Flame front structure of hydrogen-oxygen exothermic chain reaction in 1-D premixed gas flow: Distributions of number density n_j , diffusion mass flux Φ_j , temperature T , and heat flux q_x at 20,000 time steps, $\Delta x = 2$, $\Delta t = 0.08$, $K_n = 0.2$, $K_c = 20.0$, $T_0 = 1.5$ (1,500 K), $u_0 = 0.125$.

tions with 1-D velocity space and 1-D physical space. The computational domain of the velocity space is fixed at $t = 0$ as $-6.0 < C_{xj} < 6.0$ for peculiar velocity of each j species, and is discretized into 30 meshes. We assume the energy transfer from released chemical energy to thermal energy of molecules and atoms occurs as volume heating in each collision step of computation. We use the energy conservation equation $\Delta E(T) = Q_c \Delta t$ to decide the temperature increase ΔT at each grid point, where $E(T)$ is the internal energy including the rotational energy and Q_c is the production rate of chemical energy. We assume here $Q_c = q_c n_2$ (n_2 : H_2O number density, $q_c = 20kT_r$; $T_r = 1,000$ K). We modify the reduced distribution functions to respond to the temperature increase by using the BGK equation as $\Delta G_j = \nu \{G_{jc}(T_a) - G_j\} \Delta t$, where T_a is the virtual equilibrium temperature. This computation process is repeated until the appropriate change for G_j is obtained for corresponding temperature increase. The initial number densities at $t = 0$ are given as $n_1 = 1.0$ (H_2), $n_2 = 2 \times 10^{-6}$ (H_2O), $n_3 = 0.5$ (O_2), $n_4 = n_5 = n_6 = 10^{-3}$ (OH , H , and O) in a similar manner to 1-D flow of Figure 1. The figure exhibits the detailed structure of a sharp flame front in 1-D flow. It should be noted from the viewpoint of the kinetic model validation that the diffusion and heat fluxes can be obtained directly from the distribution functions, and are nearly proportional to spatial gradients of number densities and temperature.

Figure 3 shows contours of temperature (upper figures) and mass fraction of oxygen atom (lower figures) at $t = 0.016$ and 0.04 in 2-D turbulence accompanying dissociation reaction of oxygen (Reaction C). We assume that the oxygen molecules and atoms are simple hard sphere particles without endothermic effect of dissociation reaction. We use the coplanar gas model with 2-D velocity space and 2-D physical space. The computational domain of the velocity space is given as $-6.0 < c_x < 6.0$ and $-6.0 < c_y < 6.0$ for molecular velocity, and is discretized into 20×20 square cells. We give a random initial velocity \mathbf{u}_0 (u_0, v_0) and an equilibrium mass fraction of atom $\rho_1 / \rho = 0.267$ for $T_0 = 3.0$ (3,000 K) at $t = 0$. We assume the diffuse reflection at a non-catalytic wall as a boundary condition for the surrounding square wall ($T_w = 3.0$). The upper figures of temperature contour indicate that various hot spots or hot islands appear due to the thermal dissipation of random initial velocity. The dissipation effect increases as the atom number density increases with dissociation reaction. The lower figures exhibit the 2-D complex structure of atom mass fraction generated by the complex structure of temperature field.

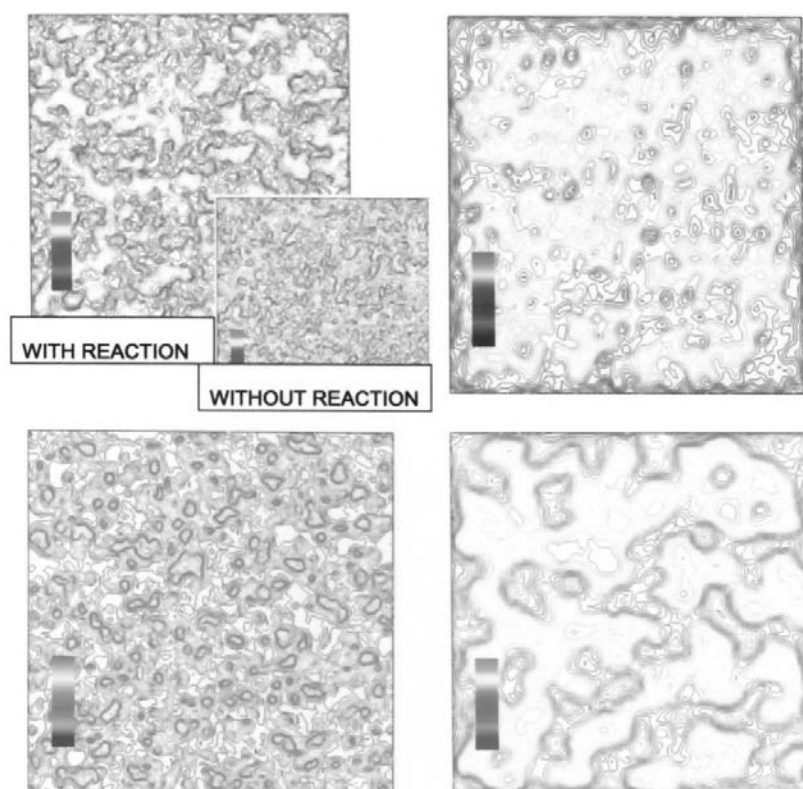


FIGURE 3. Reaction C: Two-dimensional turbulence in dissociating oxygen gas: Contours for temperature (upper figures) and mass fraction of oxygen atom (lower figures), time $t = 0.016$ (left figures) and $t = 0.04$ (right figures), $\Delta x = 0.01$, $K_n = 0.005$, $K_c = 1.0$, $T_0 = 3.0$ (3,000 K), $3.0 < T < 7.0$, $0.27 < \rho_1 / \rho < 0.99$.

CONCLUSION

The computation is performed for one-dimensional flow with reacting hydrogen-oxygen mixture and two-dimensional turbulent flow with dissociating oxygen gas. We obtain reasonable solutions for diffusive mixing with reaction, flame structure with exothermic chain reaction, and atomic evolution due to thermal dissipation of turbulence. The present molecular kinetic model including a simple reaction term seems to work for analyzing complex flows accompanying chemical reactions.

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