

Rarefaction Effect on Heterogeneous Reaction Rate. Temperature Jump on a Porous Surface

Alexander I. Erofeev, Oscar G. Friedlander, Mikhail N. Kogan

*Central Aerohydrodynamic Institute (TsAGI)
1, Zhukovsky str., 140180 Zhukovsky, Russia*

Abstract. Catalytic reaction inside a porous particle is studied. The value of Knudsen number (based on particle radius and mean free path of molecules far from particle) may be arbitrary one in aircraft environment applications. Direct DSMC research of flow inside pores and outside the particle is very laborious. Here it is assumed, that radii of pores are much less than molecule mean free path. Because of it flow inside pores is considered as free-molecular one. The results of joint DSMC – test particle method are analyzed. Approximate methods considerably simplifying the solution of the problem are developed. First method uses continuum idea. Second method is based on separate solutions of internal and external flows.

The general form of quasi-equilibrium boundary condition for temperature jump on porous surface is determined. The applicability of this generalized temperature jump boundary condition for arbitrary gas flows past porous particles is established.[†]

Catalytic processes are very extensively used in different technologies, (see, for example, [1]). In last years heterogeneous reactions of gas recombination and dissociation attract special attention, particularly in connection with aero-physical applications [2 – 5]. The catalytic aerosol particles are considered as impermeable or porous particles of various shapes and sizes [6 - 7]. In general case the analysis of catalytic process demands application the system of nonlinear kinetic Boltzmann equations with various boundary conditions on all surfaces of porous particles [8 – 11]. The research of the problem is cumbersome one. Because of that, below the simplified model of heterogeneous reaction is considered.

Direct and reverse reactions of recombination / dissociation are considered



It is assumed, that if j_A^\downarrow atoms impinge the surface then $j_M^\uparrow = (1/2)aj_A^\downarrow$ molecules arise and leave the surface. If j_M^\downarrow molecules strike the surface then $j_A^\uparrow = 2bj_M^\downarrow$ atoms arise (a and b is probability of heterogeneous recombination and dissociation). There are no homogeneous reactions in collisions of molecules and atoms.

Impermeable or porous particle with mentioned catalytic properties at the outer or inner surfaces is considered. This particle is placed in atom equilibrium gas with numerical density $n_{A,\infty}$ and temperature T_∞ . The value of Knudsen number, defined as the ratio of mean free path of atoms at infinity to particle characteristic radius R ($Kn_R = \lambda_{A,\infty} / R$), is believed to be arbitrary one. All collision cross-sections of atoms and molecules are constant (hard sphere model) and equal one another. The steady processes in the atom/molecule mixture are modeled by system of two nonlinear Boltzmann kinetic equations. Atoms and molecules reflected from surfaces or generated in reaction on its are distributed with Maxwell equilibrium function with temperature $T_w = T_\infty$.

Impermeable Catalytic Particle

At first let us consider the spherical particle of radius R with impermeable surface. The dissociation coefficient supposed to be zero. In free-molecule regime ($Kn_R \rightarrow \infty$) there is heat flux (in unit time on unit surface area)

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$$q = akT_{\infty} j_{A,\infty}^{\downarrow} = (1/2)akT_{\infty} n_{A,\infty} / \sqrt{\pi h_{A,\infty}} \quad (h_{A,\infty} = m_A / 2kT_{\infty})$$

into particle obeyed only kinetic energy of atoms and molecules. To stabilize particle temperature this flux as much as reaction heat flux must be compensated by some external heat, for example by radiation (it is easy to show also that temperature of a mixture is constant but number density is not constant in a gas mixture).

To find the number molecule flux j_M^{\uparrow} for arbitrary Knudsen number it is necessary to solve the system of two Boltzmann equations (for atoms and molecules) with boundary condition $j_M^{\uparrow} = (1/2)aj_A^{\downarrow}$ on the particle surface and Maxwell distribution function at particle surface and at infinity. System of nonlinear Boltzmann kinetic equations is solved by DSMC method [10]. Numerical grid, time step, molecules number in a mesh and total number of steps were taken so, that error was less than 1%. Range for Knudsen number was $0.05 \leq Kn_R \leq 3$, and range for recombination coefficient was $0.1 \leq a \leq 1$. The dissociation probability b supposed to be equal to zero in most cases.

The DSMC results for relative number flux for four values of recombination coefficients are presented in the Fig.1a. It is seen that influence of recombination coefficient on reaction rate decreases with decrease of Knudsen number (with increase of particle size or gas pressure) for large and moderate Knudsen number.

Above mentioned results were obtained on molecular level. Such consideration is most detail and valid for any Knudsen number. For small Knudsen numbers it is reasonable to exploit the continuum approach - Navier-Stokes equations. Concentration jump conditions at the outer surface particle are used for continuum statement. There is no correct derivation of such conditions for the problem under consideration up to now. But one may suppose that these conditions must be similar to that for evaporation problem with some new coefficient. The DSMC computations performed for $Kn_R \leq 0.2$ show that if the temperature of particle is equal to temperature at infinity, then temperature is practically constant in the whole flow around particle. That permits to neglect the thermo-diffusion effects. Therefore, it is possible to use Navier-Stokes equations (diffusion equation without thermodiffusion) and jump condition with one undetermined coefficient in this condition. The value of this coefficient was found for one value of Knudsen number and one value of recombination coefficient. Then solutions were performed for arbitrary values of Knudsen numbers and recombination coefficients with the same value of coefficient.

The continuum solution may be carried out in a simple algebraic form. The comparison of this continuum solution with results obtained using kinetic approach is presented in Fig.1b)-1c). It is seen that results, obtained by these different methods are in close agreement. The continuum results display the molecular flux for any values of Knudsen number and recombination coefficient. For small values of recombination coefficient ($a \leq 0.1$) this continuum results is applicable at any value of Knudsen number. At larger values of a continuum results is applicable for $Kn \leq 0.1$ only.

For applications at $j_{M,c} / j_{M,\infty} \geq 0.5$ the approximation of relative molecular number density flux j_{appr} may be used. It is determined by solution of quadratic algebraic equation (fluxes are normalized by absolute value of $j_{M,\infty}$)

$$((j_{M,c} - j_{appr}) / (j_{M,c,\infty} - 1) - 1)^2 + ((j_{appr} - 0.5) / 0.5)^2 = 1, \quad j_{M,c,\infty} = (1 - \alpha a)^{-1} \quad (2)$$

Eq.(2) give the possibility to determine molecular number flux from spherical particle surface at any particle size (at any value of Knudsen number) and at any value of recombination coefficient for atom at collisions with particle surface. This relation is based on continuum and free-molecular approximations only.

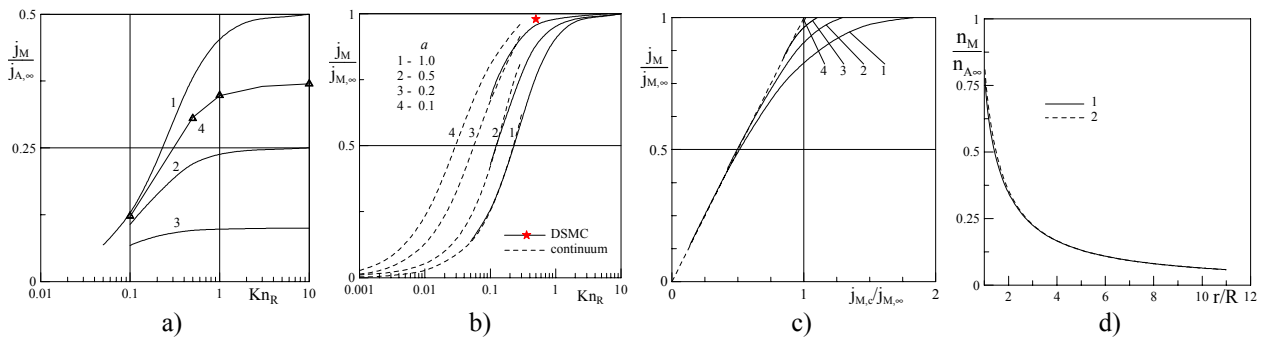


FIGURE 1. Molecular flux from catalytic spherical particle: a). output of molecules in recombination reaction on the impermeable surface of spherical particle; the numbers 1,2,3,4 correspond to $a=1.0, 0.5, 0.20, 0.74$; symbols – exact solution for porous particle; b)– c) comparison of kinetic and continuum computations, $j_{M,c}$ – continuum solution for number flux; d) number density distribution past porous particle: 1 – exact solution, 2 – approximate solution.

Porous Particle

Let us consider a porous particle. It is supposed that pore radius R_p is much less than radius of the particle. Therefore the flow inside pores may be considered as free molecular one. Boundary conditions on surface of the pore are the same as on impermeable surface. For the flow outside the porous body, nonlinear Boltzmann equations must be used. The assumption of pores radius to be much less than molecule mean free path makes characteristic lengths of flow outside and inside the particle incommensurable. Therefore, some method of boundary conditions conjugation for outside and inside solutions on outer surface of particle must be used [12]. Such joint solution will be named as exact solution. This approach is the most exact one.

The numerical model for atoms and molecules motion inside the porous particle is the following one. Atom or molecule flying inside the particle moves with mean free path λ_w , determined by porosity structure. The surface element under collision is assumed to be uniformly distributed with random attitude. Velocity distribution function of atoms and molecules, flying from this surface element, assumed to be Maxwell's one. Recombination probability in atom collisions with inner surface of pores was equal to a . Dissociation probability is supposed to be zero. It was assumed that recombination of atoms inside porous spherical particle take place with probability depending on distance to particle center in linear dependence (similar effects occur when degradation of catalyst exists) $a(r) = 0.5[(1 - (r/R))]$. Surface permeability was equal $P=1$ (this means that the surface of entrances of pores is much larger than impermeable part of sphere surface but the volume of pores may be less than volume of sphere). Mean free path inside particle was equal to $\lambda_w = 0.1R$. Wall temperature inside the particle was adopted to be equal to temperature far from particle, $T_w = T_\infty$.

In exact solution of problem in a whole test molecule method for internal flow and DSMC for external flow are simultaneously used. Besides exact solution it is possible to apply approximate solution, based on separation flow inside and outside the particle. If average probability of atom recombination inside particle is approximately independent from outside flow, it is possible to determine effective value of recombination coefficient on the outer surface of particle before kinetic research of outside flow. For testing of this possibility inner flow was solved by test particle method with Maxwell velocity distribution on outer surface of porous particle and the same distribution of recombination coefficient inside particle (as in exact solution). This solution leads to effective value of recombination coefficient $a_{eff} = j_M(Kn \rightarrow \infty)/(1/2)j_{A,\infty} = 0.74$. Then the problem of flow past impermeable particles with this effective value of recombination coefficient was solved. Comparison of exact solution (joint solution of inner and outer flows) and approximate solution (based on separation inner and outer flows) is shown on Fig.1a). It is seen that difference between exact and approximate solution is less 3%. The same difference exists in number density distribution near the particle, see Fig.1d).

Hence, for determination molecular flux from the porous particle at any Knudsen number there is possibility to solve at first the problem in free molecular regime (for determination of a_{eff}), then to use approximate solution for impermeable particle, based on continuum solution

These results were obtained using the crude model of pore structure (it was given by λ_w) and for spherical particle only. Let us estimate the influence of the particle shape and model of pore structure. Let us compare two different models of porosity for two different shapes of porous particles. We consider spherical particle, the pore structure of which is presented by one parameter λ_w , as it was done above with constant values of recombination / dissociation coefficients, and cylindrical pore with the same constant values of recombination / dissociation coefficients. We shall compare the probability for atom or molecule entering a pore to fly out after multiple collisions inside pores as atom or molecule:

$$P_A^A, P_M^A; P_A^M, P_M^M$$

here superscript designates flying inside component, subscript designates flying outside component. For example, P_M^A designates the probability of molecule outlet if atom flies into pore (into particle). The distribution function of atoms entering the pores of both shapes is Maxwellian one with prescribed zero average velocity.

As a criterion for comparison of processes in pores let us select the mean collision number with pores surfaces of atom when there are no reactions. In this case the distribution function inside pores is equilibrium one and is the same one as for entering atoms. Let us calculate mean collisions number in unit time with inner pore surface of cylindrical shape with length L , radius R_p , and specular end-wall. Total number of collisions of all atoms with inner pore surface in time unit is equal to: $N_w^c = 0.25nc(2\pi RL)$. The number of atoms, flying inside cylindrical pore in

time unit is equal to $N_{in}^c = 0.25nc(\pi R^2)$. Therefore mean collision number of one atom, flying inside pore, with inner side-surface is equal to $\langle N^c \rangle = N_w^c / N_{in}^c = S_w / S_{in} = 2L / R$.

Let us determine mean number of atom collisions inside porous sphere with above mentioned collision model and with the same assumptions on distribution functions and temperatures of atom gas and particle. Atom distribution inside particles becomes equilibrium in this case also. Collisions rate of one atom inside the sphere is equal to $(\lambda - \text{mean free atom path inside sphere}) \nu = c / \lambda$. In these conditions the total collision number (with pores walls inside the spherical particle) of atoms in time unit is equal to $N_w^{sph} = \nu n (\frac{4}{3} \pi R^3)$. The total number of atoms flying into the porous spherical particle in time unit is equal to $N_{in}^{sph} = (0.25nc)(4\pi R^2) = nc\pi R^2$. Therefore mean collision number of one atom with pores sidewalls in the sphere is equal to $\langle N^{sph} \rangle = N_w^{sph} / N_{in}^{sph} = (4/3)(R / \lambda)$.

Consider now porous catalytic bodies with heterogeneous recombination and dissociation. For the simplest case $a \ll 1$, $b=0$ the probability $p_A^M = a \langle N \rangle$. Let us compare the values of outlet probabilities for cases of cylindrical pore and spherical particle under the equal values of parameter $\langle N \rangle$, (in these conditions $2(L^c/R) = (4/3)(R^{sph} / \lambda)$).

Let values of recombination and dissociation probabilities in collisions with inner surfaces be uniform and equal to $a=0.2$, $b=0.8$ respectively. In the case of sphere, molecules fly with unique free path length λ_w . In the cylindrical case the path length is determined by test molecule method. In Table 1 the outlet probabilities values calculated by proposed above methods are shown for two cases (for two ratio of cylindrical pore length to radius and two ratio of spherical particle to mean free path inside the particle).

TABLE 1. Outlet Probabilities.

Cylinder, Sphere	$\langle N \rangle$	p_A^A	p_M^A	p_A^M	p_A^A
$L^c / R = 5$	10.0000	0.80192	0.09904	1.58443	0.20779
$R^{sph} / \lambda_w = 7.5$	9.9954	0.80174	0.09913	1.58576	0.20712
$L^c / R = 2$	4.0000	0.81110	0.09445	1.51101	0.24450
$R^{sph} / \lambda_w = 3$	3.9988	0.81081	0.09460	1.51264	0.24368

The results show that presented approximate similarity parameter $\langle N \rangle$ gives the possibility of comparison the numerical results for atoms and molecules outlet probabilities at essentially different models of porosity. Moreover, the outlet probabilities p_i^j depend substantially on value of parameter $\langle N \rangle$ and weakly depend on porosity model and body shape.

Temperature Jumps on the Porous Surface

If flows of weakly rarefied gas are described by the continuum equation then boundary conditions must be conditions of slip velocity, temperature jump, generalized Hertz-Knudsen condition for normal gas velocity component in the case of evaporation. The existence of these boundary conditions is connected with the existence non-equilibrium thin boundary layers (Knudsen layers) with thickness of the order of mean free molecular path near the particle surface. Non-equilibrium feature of these layers is determined by gradients of gas velocity and gas temperature near to impermeable boundary and by existence of normal gas velocity component to surface in the case of evaporation/condensation. However the flows past porous particles demand separate research. As an example the heterogeneous chemical processes on porous aerosol particles in aircraft near trail may be specified [5]. In the case of nonuniform temperature inside the particles various boundary layers arise. If pores diameters of porous particles are less than molecular mean free path, then these layers are Knudsen layers. Here the influence of non-equilibrium process of heat flux inside the porous body on temperature jump across Knudsen layer near the surface is researched.

Up to now the existence of Knudsen layers was neglected in gas flows research through porous membrane. In the case of simplest porous membrane model, - perforated membrane, - the flow through membrane was considered as simple sum of individual flows through separated capillaries. This consideration is correct only for thick membrane, in which capillaries length is much more its diameter. The review of numerous investigations of flow through

infinitely long capillary with various values of diameter or flow through separate capillary, which connect two vessels, is posed in [13].

Gas flow or gas states past plane perforated non-isothermal membrane are considered. This membrane is bounded by gas half-spaces (or by plane gas layer, with some boundary condition on outer boundary of this layer). In first case gas is in equilibrium apart of membrane. Just this feature the layers are named quasi-equilibrium ones.

Here the mathematical model for porous membrane, elaborated in [14], was used. Membrane is the plane layer of parallel cylindrical capillaries with conventionally adopted porosity value P equal to unity $P=1$ (in one calculated case $P=0.5$). Temperature distribution inside membrane is adopted linear one in distance along normal to porous surface (parallel to symmetry axes of capillaries) $T_w(x) = T_{w1}[1 + (x/L)]$, $0 \leq x \leq L$, L - membrane thickness, T_{w1} - temperature of colder porous membrane surface. For the consideration of quasi-equilibrium Knudsen layers it is supposed that temperature distribution is created not by the heat transfer through the gas (in this case temperature gradient arises outside the membrane). The flow outside the membrane was modeled by DSMC method. The variable hard sphere (VHS) model was used: $\varphi \propto r^{-s}$. Potential parameter was equal to $s=10$.

Free-molecular flow inside capillaries (inside membrane pores) was modeled by test molecule method. Specular reflection was adopted as boundary condition far from membrane. This statement of boundary conditions implies kinetic problem solution with equilibrium state of a gas far from membrane.

The examples of temperature fields near the porous membrane are shown on Fig.2a.

Gas extents in equilibrium states are separated from membrane by kinetic quasi-equilibrium Knudsen layers. The values of gas temperatures in equilibrium states differ from temperatures of membrane surfaces. That is temperature jump there exist across Knudsen layer. Of course, the existence of this layer is possible only in consequence of existing the non-equilibrium process inside porous membrane (heat flux from hot to cold part of membrane). The value of temperature jump depends on temperature gradient near the surfaces.

Note that transformation of equilibrium molecular distribution function of incident molecules into non-equilibrium one of reflected molecules is impossible at usually adopted reciprocity relation (in another words: if principle of detailed balance is applied) for molecular reflection kernel from rigid body surface. This means that at the surface of temperature-non-uniform porous medium (with open pores) there exists "Maxwell's demon" for molecules sorting and transforming equilibrium molecule distribution function into non-equilibrium one.

The values of temperature jumps across quasi-equilibrium Knudsen layer, arising owing to heat transfer inside porous medium (see Fig.2a), don't depend upon mean free molecule path (if it much more than pores diameter) and is determined only by extent of deviation of distribution function (of molecules flowing out) from equilibrium one.

The value of quasi-equilibrium temperature jump may be included in usual temperature jump boundary condition

$$T_g(0) - T_w = \Delta T_u + \Delta T_{\nabla T, g} + \Delta T_{\nabla T, w} = -a_u u h T + a_{gT} \frac{hT}{p} k \frac{\partial T}{\partial y} \Big|_{0+} - a_{wT} PR \frac{\partial T_w}{\partial y} \Big|_{0-} \quad (3)$$

$$h = (2 \frac{k}{m} T)^{-1/2}, \quad a_{wT} = 1.432 + 0.256 \left(\frac{PR}{T_w} \frac{\partial T_w}{\partial y} \Big|_{0-} - 8.916 \left(\frac{PR}{T_w} \frac{\partial T_w}{\partial y} \Big|_{0-} \right)^2 \right)$$

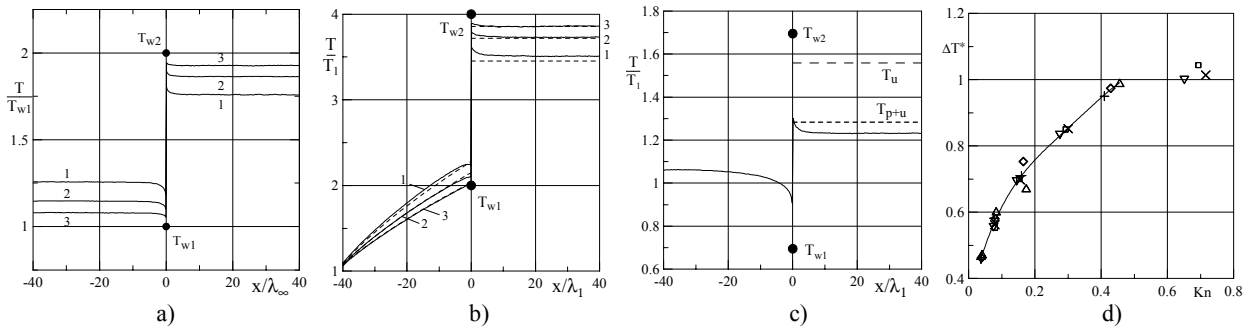


FIGURE 2. a) Temperature distributions at zero gas flux through porous membrane; temperature drop across membrane: $T_{w2}/T_{w1}=2$; relative value of membrane thickness: $L/R=5, 10, 20$ designated by the figures 1, 2, 3; symbols show temperature values of porous membrane surfaces; b, c) testing of generalized temperature jump boundary condition (3); b) zero gas mass flow rate through membrane, $T_g(0) - T_w = \Delta T_{\nabla T, g} + \Delta T_{\nabla T, p}$ ($1, 2, 3 - L/R = 5, 10, 20$); c) zero temperature gradient far from membrane, $T_g(0) - T_w = \Delta T_u + \Delta T_{\nabla T, p}$ ($L/R = 5$); solid lines – Boltzmann equation solution, dashed lines – solution of Navier-Stokes equation with generalized temperature jump boundary conditions; d) reduced porous temperature jump (see text) upon small Knudsen number; symbols – DSMC results, solid line – fitting curve.

Here P – permeability of porous membrane. Approximate values of coefficients a_u and a_{gT} [8, 9, 11] are equal to $a_u \approx 0.448$, $a_{gT} \approx 1.032$. In linear approximation upon gradients (usual for theory of Knudsen layers) the value of third coefficient is equal to constant ($a_{wT} \approx 1.432$).

Because of absence the strong theory of such jumps (the necessity to consider various types of porosity does it difficult) the possibility of proposed generalization must be verified for various flows. Below there are examples of flows in which simultaneously exist two jump types. At first, jumps owing to temperature gradients in a gas and in a porous membrane are exist (see Fig.2b) and, secondly, jumps owing to gas velocity and temperature gradients in a porous membrane are exist (see Fig. 2c). In the case of non-isothermal gas state on one side of membrane diffusive boundary condition with the value of T_1 was prescribed at a conventional boundary plane on some distance from membrane. On the other side of membrane, as in above considered case, specular reflection was used far from the membrane. Temperature inside the membrane varied in the manner: $T_w = 2T_1(1+x/L)$. Out of membrane there is temperature gradient in a gas at this statement of boundary condition.

On the Fig.2b, 2c the results of numerical solution of Boltzmann equation by DSMC method are compared with the solutions of Navier-Stokes equation with generalized temperature jump boundary condition (3) for two mentioned above testing cases. The role of temperature jump on nonisothermal porous medium is well seen at Fig. 2c. Here on right side of membrane the values of temperature, calculated by the Navier-Stokes equation, are shown for the case, at which the jump only owing to normal velocity component was taken into account, and for case, at which both, velocity and porosity jumps are taken into account (in these cases relative value of normal component of gas velocity was equal to $u_\infty / c_1 = u_\infty / \sqrt{2kT_1 / m} = 0.09575$).

For control of correctness the introduction permeability parameter in boundary condition (3), the kinetic calculation were made for quasi-equilibrium layers on porous membrane with permeability value $P=0.5$. Difference between the jumps, estimated by (3), and numerical jumps values is less than 3%.

Besides the case with free-molecular flow inside the pores the problem of two-dimensional flow with moderate Knudsen number, based on pore radius, was investigated. As Knudsen number decreases, the boundary layers on both sides of porous membrane tend from kinetic one to continuum one. The last is determined only by solution of $\Delta T = 0$ equation. On Fig. 2d the dependence of reduced temperature jump $\Delta T^* = -\Delta T_{\nabla T, p} / (R \partial T_w / \partial x)$ upon Knudsen number based on pore radius is shown for various calculated cases. It is seen that for $Kn_R < 0.5$ there exist unique dependence ΔT^* (Kn).

From these results may be made following conclusion. Generalization (3) of temperature jump boundary condition may be used for calculation complex flows with possible mass flux on surface and with nonuniform temperature field, particularly past condensing aerosol porous particles. For example, under investigation the transport and heterogeneous chemical problems inside porous non-isothermal particles, the neglecting temperature jump on particle surface may lead to error of the order 20% in temperature values and to more essential errors in chemical rates.

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