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Technical Note

One dimensional heat transfer on the thermal diffusion and piston effect of supercritical water

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1. Introduction

In order to utilize supercritical fluids as chemical reaction processes, it is absolutely necessary to understand transport phenomena in the supercritical fluids. As the temperature and pressure approaches its critical point, heat capacity becomes very large, whereas thermal diffusivity becomes very small. It had been believed that thermal energy could not be transferred near the critical point due to this small thermal diffusivity. However, very fast heat transfer phenomena have been observed in several experiments under microgravity conditions in which natural convection due to buoyancy effect was suppressed. These phenomena are called "piston effect". Onuki et al. [1], Zappoli et al. [2] and Straub et al. [3] solved the piston effect analytically and numerically, but they did not consider supercritical water as fluid.

Ikushima et al. [4,5] reported some kinds of noncatalytic organic syntheses in supercritical water. From a chemical engineering point of view, industrial importance of supercritical water has been recognized recently. However, transport phenomena with the piston effect in supercritical water has not been studied so far analytically and experimentally. It is impossible to solve the problem analytically because the changes in fluid properties with temperature and pressure are huge in supercritical fluids. We thus wish to clarify the heat transfer in supercritical water by using numerical calculation. For the first step, we calculate the piston effect and thermal diffusion in supercritical water; we emphasize that this paper's results limit completely no convection case.

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2. Theory and problem statement

The mechanism of piston effect runs as follows: when a near-critical fluid is heated (cooled) at a boundary, a thin thermal boundary layer forms near the heated (cooled) point; due to the small thermal diffusivity of the supercritical fluid, this layer expands and behaves like a piston by compressing the rest of the fluid; this compression, being adiabatic, results in a homogeneous temperature rise throughout the fluid [6].

Straub et al. [3] show a model that can deal with pressure changes. The basic equation is shown as

$$\frac{\partial T}{\partial t} = \frac{1}{\rho c_p}\nabla(\lambda \cdot \nabla T) + \left[1 - \frac{c_V}{c_p}\right]\left[\frac{\partial T}{\partial p}\right]_\rho \frac{\partial P}{\partial t}. \tag{1}$$

The second term on the right-hand side is the heat generation rate and is responsible for an isentropic temperature change in the bulk fluid. For an incompressible fluid $c_V/c_p = 1$, the pressure term equals zero, and Eq. (1) corresponds to the thermal diffusion equation. To determine the pressure change, we write

$$\frac{\partial P}{\partial t} = \frac{\int_V \rho\alpha_p(\partial T/\partial t)\,dV}{\int_V \rho\chi_T\,dV}, \tag{2}$$

where α_p is the isobaric expansion coefficient and χ_T is the isothermal compressibility. The pressure is assumed to be constant in the whole volume. From Eq. (2), $\rho\alpha_p(\partial T/\partial t)$ and $\rho\chi_T$ are integrated numerically over the whole volume and then the pressure is obtained.

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To calculate physical properties by the changes in temperature and pressure, the program from IAPWS-IF97 (IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam) is used.

In order to understand the influence of the piston effect, a simple (no flow) model is employed for this calculation. The geometry used in a physical model is given in Fig. 1. We consider a one-dimensional segment whose length is 0.01 m and left-hand-side wall is temperature constant and right-hand-side wall is adiabatic. When $t = 0$, the temperature of the left-hand-side wall is suddenly increased from T_{init} to T_h. At the steady state, the temperature comes to equilibrium with T_h throughout the area.

Fig. 2 shows thermal diffusivity, defined by $\lambda/\rho c_p$, versus temperature at pressures from 25 to 50 MPa using IAPWS-IF97. The minimum thermal diffusivity when $P = 25$ MPa is about 1.6×10^{-8} m^2/s at $T = 648$ K and it becomes 0 theoretically at the critical point. Thermal boundary layer is very thin near the left-hand side because the thermal diffusivity is very small. In order to estimate the influence of the piston effect, we have to calculate the temperature field in the thermal boundary layer accurately. In general, an accurate solution shall be obtained when the grid in the very thin boundary layer is sufficiently fine. Therefore we employ a large number of grid points even if one solves such a simple problem. The properties of supercritical water are also considered in this calculation after each time step. For these reasons, this calculation needs very long CPU time. In this paper we focus on the result of considering the fluid property changes of supercritical water and the small length case.

3. Results and discussion

Fig. 3 shows the time-dependence on the temperature distribution when the initial temperature T_{init} is 650 K, initial pressure P_{init} is 22.1 MPa and the temperature of the left-hand-side wall rises to 651 K at $t = 0$ s. Even when $t = 0.1$ s, the slight rise in temperature can be found in the whole volume. As the time progresses, one can clearly recognize the temperature rising and the constant temperature field. This is due to the influence of piston effect; the rate of heat transfer is quite high compared to heat conduction and the temperature is constant except for the near boundary region. From IAPWS-IF97, thermal diffusivity is 4.41×10^{-8} m^2/s when $T = 651$ K and $P = 22.1$ MPa. If only thermal diffusion is considered, it takes about 550 s to reach 650.3 K at the

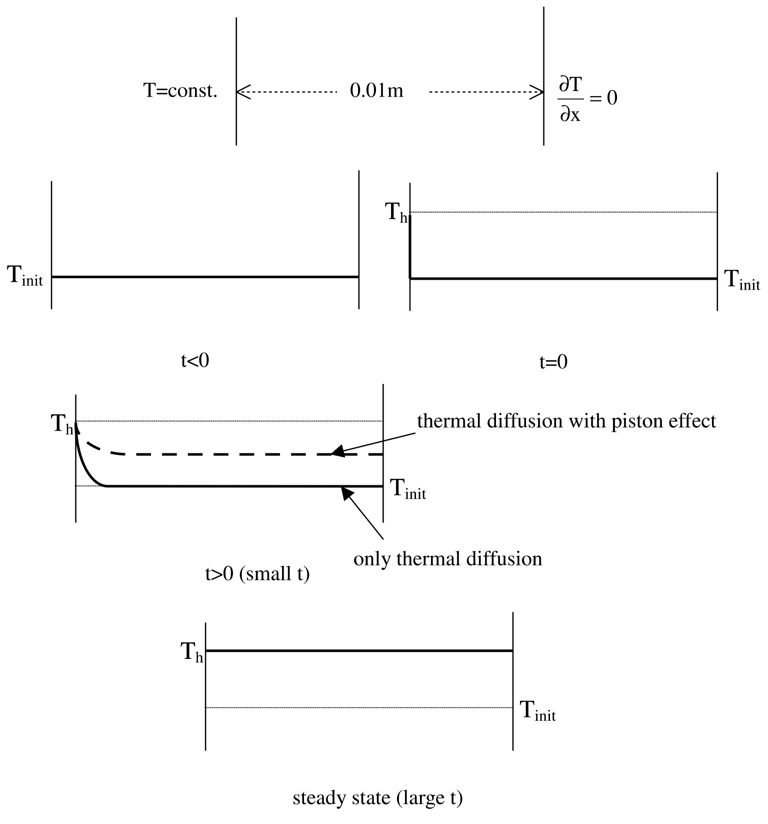

Fig. 1. Physical model and time-dependent temperature profiles between two plates.

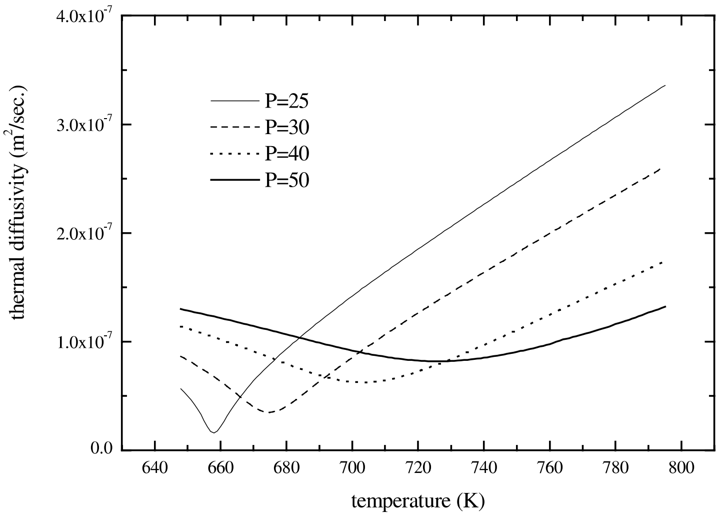

Fig. 2. Thermal diffusivity of water as a function of temperature and pressure.

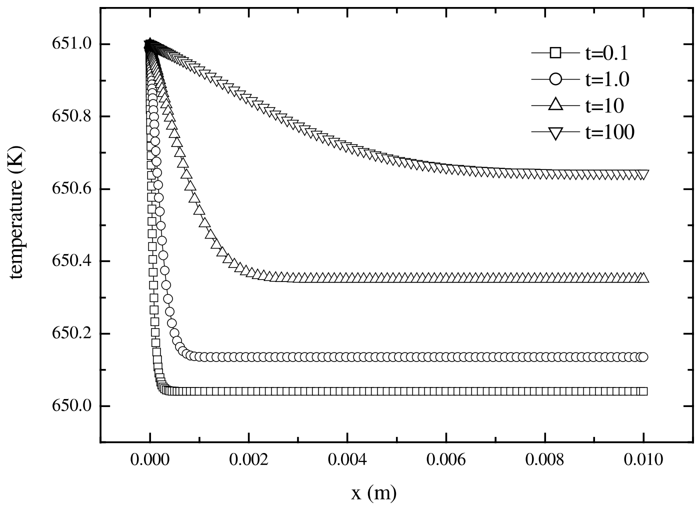

Fig. 3. Temperature distributions when initial temperature is 650 K and initial pressure is 22.1 MPa.

right-hand-side. On the other hand, it takes only about 6.6 s if the piston effect is also added. These calculation results agree with previous ones that the piston effect is characterized by very fast heat transfer as well as the constant bulk temperature. The influence of the changes in the fluid properties is further investigated. Fig. 4 shows changes in temperature at the right-hand-side wall. A solid line means the result when the fluid property changes are considered and symbols mean that the fluid properties are assumed to be constant when $T = 651$ K and $P = 22.1$ MPa. In Fig. 4, the difference between the solid line and symbols can be seen. At the beginning, the temperature difference becomes larger and as the time becomes longer, a nearly constant difference is observed. The calculation results lead to the two distinct cases even if the temperature difference is only 1 K. It is important to introduce the change of fluid properties when the piston effect is calculated.

Critical temperature T_c and pressure P_c of water from IAPWS-IF97 are 647.096 K and 22.064 MPa, respectively. Can one observe the piston effect far from the critical point of water? Fig. 5 shows the differences in temperature profiles after 10 s when the initial temperatures T_{init} are 650 K ($T - T_c = 2.904$) and/or 700 K ($T - T_c = 52.904$) and the initial pressures P_{init} are 22.1 MPa ($P - P_c = 0.036$) and/or 30.0 MPa ($P - P_c = 7.936$). Temperature distributions in Fig. 4 are based on the influence of piston effect. In the previous study [2,3], the

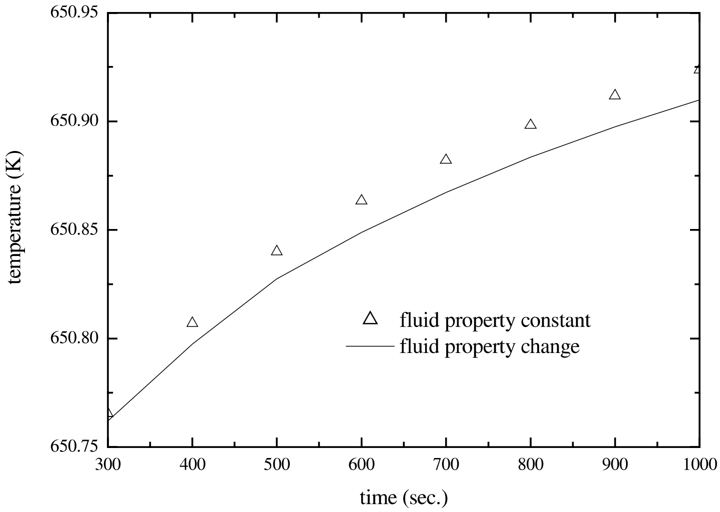

Fig. 4. Temperature at the right-hand-side wall when initial temperature is 650 K and initial pressure is 22.1 MPa. A solid line means the result when the fluid property changes are considered and plots mean that the fluid properties assumed to be constant value of $T = 651$ K and $P = 22.1$ MPa.

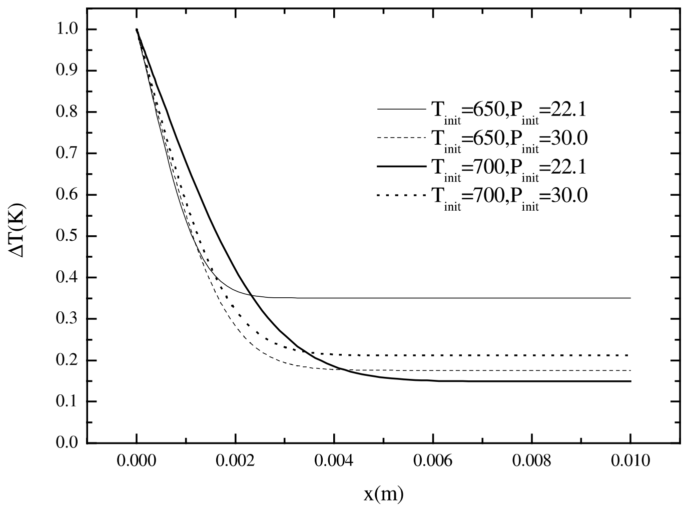

Fig. 5. Temperature distributions after 10 s when initial temperature is 650 and 700 K, initial pressure is 22.1 and 30 MPa.

piston effect was observed only in the region of very near-critical point. However, in the region not very close to the critical point, for example, $T_{init} = 700$ K and $P_{init} = 30.0$ MPa ($T - T_c = 52.904$ and $P - P_c = 7.936$), the piston effect can be seen from the rise in temperature at $x = 0.01$ m.

Eq. (1) and the Figs. 3 and 5 lead to the relation between piston effect and the heat capacity ratio c_p/c_V. For example, c_p/c_V is about 8.76 when $T = 650$ K and $P = 22.1$ MPa and c_p/c_V is about 3.01 when $T = 650$ K and $P = 30.0$ MPa. The influence of the piston effect is stronger as the heat capacity ratio is larger while the thermal diffusivity is smaller from Fig. 2. Even though the temperature and pressure are far from the critical point, the influence of the piston effect is stronger than when $T_{init} = 700$ K and $P_{init} = 22.1$ MPa. Fig. 6 shows the heat capacity ratio versus temperature at pressures from 25 to 50 MPa using IAPWS-IF97. When the pressure is 25 MPa, a peak temperature of c_p/c_V appears around 660 K. The peak shifts to higher temperature of 675 K as the pressure is increased to 30 MPa.

In conclusion, the piston effect plays an important role in heat transfer in microgravity environment not only near critical point, but also in wide temperature

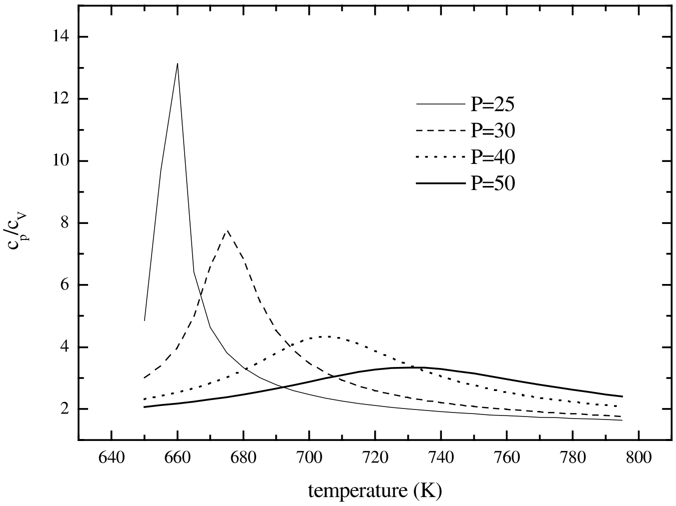

Fig. 6. Heat capacity ratio of water as a function of temperature and pressure.

and pressure range when $c_p/c_V > 1$ of fluid and even remarkable for ideal gas $c_p/c_V = 1.4$ [3]. Under earth condition, however, we never neglect natural convection heat transfer. Especially in supercritical fluids, very strong convection appears because coefficient of volumetric thermal expansion becomes infinite at the critical point. As explained in Section 2, we have found that CPU time was quit long in this simple-model calculation. If one calculates two-dimensional fluid flow and heat transfer with the piston effect by a simple extension of this paper's method, CPU time will be too long to get results. We estimate that the calculation in this paper is accurate but its method is far from practical. To calculate two or three dimensional piston effect and the flow, a construction of new model and new method will be needed.

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