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Studies on piston and soret effects in a binary mixture supercritical fluid

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Abstract

Heat and mass transport phenomena in a binary mixture compressible supercritical fluid around the pseudo-critical line were investigated theoretically and numerically. In this study, we focused on supercritical artificial air with a composition of 79% nitrogen and 21% oxygen, and investigated the piston effect, the soret effect, and the interactions between these effects. We derived thermo-fluid dynamic equations, in which the compressibility of the fluid, the temperature, the pressure, and the concentration dependences of the entropy were taken into account. The governing equations were solved numerically by using the finite difference method. We could verify that the thermal energy was propagated by the piston effect in a binary mixture supercritical fluid, and the concentration change certainly occurred due to the soret effect. Moreover, we could also estimate the thermal diffusion ratio, which made a direct correlation between the temperature gradient and the concentration gradient.

Keywords: Piston effect; Soret effect; Artificial air

1. Introduction

The combination of very high thermal compressibility and small thermal diffusion around the pseudo-critical lines of fluids affects thermal energy propagation, leading to the formation of weak acoustic wave as carriers of thermal energy. Nowadays, this heat transport phenomenon is known as the piston effect. This effect was first detected in the microgravity experiment for measuring the specific heat of SF_6 near the critical point [1]. In the experiment, unexpected fast dynamic temperature propagation was observed. Straub et al. [2] verified the fast dynamic temperature propagation in a Spacelab Mission. Onuki et al. [3] provided an explanation about the fast heat transfer with adiabatic temperature propagation. Around the same time, Boukari et al. [4] analyzed this phenomenon from a thermodynamic point of view. Behringer et al. [5] investigated the adiabatic heating process in a pure fluid and a binary mixture. Zappoli et al. [6] accounted for the temperature propagation by solving the hydrodynamic equations and named the phenomenon "piston effect". Ferrel and Hao [7] and Zappoli et al. [8,9] investigated the effect, theoretically and numerically. In terms of past numerical endeavors, Zappoli et al. [10] successfully achieved the first direct numerical simulation of the piston effect in a single fluid. Frohlich et al. [11], Zhong et al. [12], Wilkinson et al. [13], and Garrabos et al. [14] carried out experiments on the piston effect and compared them with their theoretical predictions. Maekawa and Ishii [15] analyzed the piston effect from both macroscopic and microscopic points of view. Maekawa et al. [16], Shiroishi et al. [17], Furukawa and Onuki [18], and EL-Khouri and Carles [19] investigated the convective instabilities and discussed the interactions between the piston effect and convection. We also successfully observed the piston effect in supercritical nitrogen by using a laser holography interferometer [20,21] and confirmed the piston effect experimentally and numerically [22] around the pseudo-critical line. Recently, the piston

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Nomenclature

C_p	specific heat at constant pressure, J/(mol K)
C_v	specific heat at constant volume, J/(mol K)
c	concentration
D	diffusion coefficient, m^2/s
D_T	thermal diffusion coefficient, m^2/s
k_T	thermal diffusion ratio (D_T/D)
M	molecular weight
P	pressure, Pa
Q	thermal energy flow per unit volume, J/m^3
s	entropy per unit mol, J/(mol K)
T	temperature, K
T_{MC}	Max–Condentherm temperature, K
t	time, s
u	velocity (x-direction), m/s
V	velocity, m/s
x	distance from the heat wall, m
$x^*(i)$	dimensionless computation domain ($i = 1, 2, \ldots, \max - 1, \max$), where $x^*(1) = 0$ and $x^*(\max) = 1$

Greek symbols

ρ	density, mol/m^3
α	thermal diffusion factor
α_T	isothermal compressibility, 1/Pa
β	volume expansion coefficient, 1/K
γ	ratio of the specific heats, C_p/C_v
κ	thermal conductivity, W/(m K)
η	dynamic viscosity, Pa s
δ_{ik}	unit tensor
σ'_{ij}	viscous stress tensor
μ	chemical potential, J/mol

effect was successfully observed on acoustic time scales [23]. The piston effect has been mainly observed in a single-component fluid; however, the effect in a multi-component fluid has not been investigated thoroughly.

In our previous experiment, a critical opalescence phenomenon was observed near the critical point of air [24]. It meant that the molecules composing the air had coalesced into clusters. This implies that air possesses high compressibility and the piston effect can be observed in supercritical air. To confirm the validity of the supposition that the piston effect does occur, a laser holography interferometer was applied to visualize the piston effect in supercritical air [25]. However, its corroboration was insufficient, since air is composed of many substances. Then, we carried out a visualization experiment using artificial air composed of 79% nitrogen and 21% oxygen [26]. The spatial distribution of the density change due to heating was investigated and we successfully obtained typical density profiles due to the piston effect. Additionally, we also observed the density gradient in the bulk of fluid. It is formed by the soret effect. The soret effect is a phenomenon in which the temperature gradient induces a concentration flux. However, we have little evidence to support this effect. Then, we studied heat and mass transport mechanism in a supercritical binary mixture, theoretically and numerically. In this paper, we describe the theoretical consideration and the results of the numerical simulation for the supercritical artificial air around the pseudo-critical line.

2. Theoretical consideration

The following thermo-fluid equations were used to investigate the heat and mass transport mechanism in a binary mixture supercritical fluid [27]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho V_i)}{\partial x_i} = 0, \tag{1}$$

$$\frac{\partial(\rho c)}{\partial t} + \frac{\partial(\rho c V_i)}{\partial x_i} = \frac{\partial}{\partial x_i}\left[\rho D\left(\frac{\partial c}{\partial x_i} + \frac{k_T}{T}\frac{\partial T}{\partial x_i}\right)\right], \tag{2}$$

$$\rho\frac{\partial V_i}{\partial t} + \rho V_j\frac{\partial V_i}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j}\left[\eta\left(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial V_k}{\partial x_k}\right)\right], \tag{3}$$

$$\frac{dQ}{dt} = \sigma'_{ij}\frac{\partial V_i}{\partial x_j} - \frac{\partial}{\partial x_i}(q - \mu i), \tag{4}$$

where

$$q = \left[k_T\left(\frac{\partial \mu}{\partial c}\right)_{P,T} - T\left(\frac{\partial \mu}{\partial T}\right)_{P,c} + \mu\right] i - \kappa\frac{\partial T}{\partial x_i} \tag{5}$$

and

$$i = -\rho D\left[\frac{\partial c}{\partial x_i} + \frac{k_T}{T}\frac{\partial T}{\partial x_i}\right]. \tag{6}$$

Eqs. (1), (2), (3) and (4) represent the equation of continuity, the equation of concentration, the momentum equation of viscous fluid, and the energy balance equation, respectively. The suffixes i, j, k take the values 1, 2, 3 corresponding to the components of vectors and tensors along the axes x, y, z. In this study, the following assumptions were adopted that no significant pressure gradient was formed in the system due to heating, that there was no macroscopic motion in fluids, and that the second order small terms were ignored. The effect of gravity was not taken into account, here.

The pressure, P, in Eq. (3) was calculated from the following pressure derivative that

$$\frac{dP}{dt} = \frac{1}{\rho\alpha_T}\left[\frac{d\rho}{dt} - \left(\frac{\partial \rho}{\partial c}\right)_{P,T}\frac{dc}{dt}\right] + \frac{\beta}{\alpha_T}\frac{dT}{dt}. \tag{7}$$

For details, refer to the appendix.