Numerical simulations of the piston effect for near-critical fluids in spherical cells under small thermal disturbance

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Abstract

Near the liquid-vapor critical point, strong anomalies in thermodynamic and transport properties induce the piston effect. In the present study, the piston effect is investigated in spherical cells filled with near-critical fluids under zero gravity and small thermal disturbance conditions by numerically solving the thermodynamic model. The results show typical fast-responding bulk temperature, together with high and stable temperature efficiency, which is determined by the particular nature of near-critical fluids. Particularly, a nondimensionalization method is developed to study the influences of the specific heat ratio on the piston effect by simulations for eight near-critical fluids. Results show the specific heat ratio is an efficient indicator, which is negatively correlated with the nondimensional bulk temperature change. The influences of the characteristic length and the boundary conditions on the piston effect are also studied for near-critical carbon dioxide.

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In addition, some rules concerning the boundary heat flux and the overall heat transfer are also discussed and concluded.

Keywords: Near-critical fluids; Piston effect; Numerical simulations.

1. Introduction

The liquid-vapor critical point is the end point of the pressure-temperature curve under which a liquid and its vapor can coexist. At the liquid-vapor critical point, defined by a critical pressure P_c and a critical density ρ_c , phase boundaries vanish. A supercritical fluid is any substance at a temperature and pressure above its critical point. In this study, near-critical fluid refers to a supercritical fluid whose state slightly above critical state. Approaching the liquid-vapor critical point, strong anomalies can be found in thermal and transport coefficients. For example, both of the isothermal compressibility and thermal expansion grow dramatically while the thermal diffusivity tends to zero [1]. The peculiar thermophysical properties of fluids induce a new mode of heat transfer in fixed-volume cells filled with near-critical fluids, which is called the piston effect (PE) [2, 3, 4].

In microgravity environment, the thermal relaxation of a near-critical fluid was long thought to be infinitely slow without convection, which was termed as the critical slowing down. However, in 1985, Nitsche and Straub [5] carried out a space experiment and found the temperature at the center of the fluid following the rising wall temperature closely, which meant they actually observed a critical speeding up. Early theoretical studies mainly focused on the physical process of the PE. In 1990, three independent teams [2, 3, 4] put forward their explanations using different approaches. Afterwards, Zappoli and Carlès [6] applied matched asymptotic expansions and multiple-time-scale techniques to solve

the one-dimensional compressible Navier-Stokes equations for a van der Waals gas and revealed the leading role of the acoustic waves in the PE. Then they [7] used matched asymptotic descriptions techniques and noted that ignoring the influence of bulk viscosity, energy should be transported by acoustic process very close to the critical point. And in this regime, the reflection rules of acoustic waves on thermostatted boundaries are inverted [8]. The amplitude of the reflected wave changes of sign, which is different from normal compressible gases. Moreover, Carlès [9] discovered the existence of viscous regime, during which going closer to the critical point, the heat transfer then slows down. As for density relaxation, Bailly and Zappoli [10] presented a complete hydrodynamic theory of density relaxation. They used matched asymptotic expansion technique to solve one-dimensional Navier Stokes equations and noted that the density relaxation is governed by the PE and heat diffusion. The whole process can be summarized as an expansion-compression zone traveling at the diffusion velocity and ultimately disappearing before reaching the other end of the sample cell. Early experimental studies [11, 12, 13, 14] mainly focused on the verification of the PE.

In 2006, Miura et al. [15] made the first experimental observation of the thermally induced acoustic waves. Then part of their experimental data was verified analytically by Carlès [16] using asymptotic methods. Onuki [17] presented a general theory of thermoacoustic waves involving the heat conduction in the boundary walls and bulk viscosity. Afterwards, the nature of thermoacoustic waves attracted increasing attention. Shen and Zhang studied the thermoacoustic waves emission, propagation and reflection under different temperature boundary conditions by solving the governing hydrodynamic equations [18]. Besides, they studied the thermoacoustic waves emission under internal and boundary thermal disturbance

[19]. Hasan and Farouk also studied the thermoacoustic waves generation under different boundary heating rate using a real-fluid CFD model [20]. The results provided details regarding the thermal transport mechanisms at near-critical and pseudo-critical state fluids, and showed that the heating rate and the initial reduced temperature (i.e. $\varepsilon = (T_0 - T_c)/T_c$, where T_0 and T_c are initial and critical temperature) are key factors in the generation of acoustic waves.

The interplay between buoyant convection and PE has also been an active research topic. Zappoli et al. conducted a series of two-dimensional [21, 22, 23] and three-dimensional [24] numerical simulations for near-critical van der Waals fluid by a finite volume method together with an acoustic filtering procedure. A similar problem was further studied by Shen and Zhang [25, 26]. Notably, an unexpected temperature oscillations at the convection onset in terms of the PE were found by Amiroudine and Zappoli [27]. The Rayleigh-Taylor-like gravitational instability and thermovibrational instability in near-critical fluids were also studied by Amiroudine et al. [28, 29]. A monograph by Zappoli et al. [30] and a review by Shen and Zhang [31] give a detailed summary of previous researches on this topic.

In this paper, the PE in spherical cells filled with near-critical fluids under zero gravity condition is studied numerically to identify how some key factors influence the PE. The thermodynamic model presented by Boukari et al. [3] is used, and an explicit finite difference method using a central difference scheme for the spatial discretization is developed to solve the model iteratively. The NIST database [32] is used to obtain the $\rho - P - T$ relations for near-critical fluids.

The important factors we study in this paper are the specific heat ratio, the characteristic length and the boundary condition. As for the specific heat ratio,

72 some previous studies [33, 34] have revealed the relationship between it and the
73 bulk temperature increase. However, their conclusions are drawn from the PE for
74 one near-critical fluid. In the present study, the PE for different near-critical fluids
75 is further studied to show how the specific heat ratio influences the PE. In order
76 to make different fluids be able to be compared with each other, a nondimension-
77 alization method is particularly developed. Regarding the characteristic length, it
78 is an important geometrical factor that changes the physical model. The PE under
79 different characteristic lengths must differ greatly. With regard to the boundary
80 condition, previous studies only focused on the influences of boundary condition
81 on the thermoacoustic process. Thus, it is also significant to study the problem
82 on a longer timescale and deepen our understandings from a macroscopic view.
83 The last two factors are studied for near-critical CO₂, so it is not necessary to
84 nondimensionalize variables.

85 Besides, it should be mentioned here that small thermal disturbance is con-
86 sidered only in the present study, because under strong thermal disturbance, the
87 initial reduced temperature (i.e. ε , which can be seen as the distance to critical
88 point) will be altered during the PE. As a result, the nature of a near-critical fluid
89 will change dramatically and the controlled variable is altered. For example, when
90 we study the influences of the characteristic length on the PE, the strong thermal
91 disturbance will change the specific heat ratio considerably too. As a result, it is
92 difficult to distinguish the dominant factor.

93 In Section 2, we introduce the problem formulation and the numerical method
94 used in simulations. An explicit finite difference method using a central difference
95 scheme for the spatial discretization is relied on solving the governing equations,
96 whose validity is also discussed. In Section 3, related definitions of physical quan-

97 titles are presented. In Section 4, how the specific heat ratio, the characteristic
 98 length and the boundary condition, influence the PE is shown and discussed. The
 99 paper is finally concluded in Section 5.

100 **2. Physical and numerical model**

101 *2.1. Physical model*

102 As shown in Fig.1, the physical model is a spherical cell filled with near-
 103 critical fluid under zero gravity condition. R is the radius of the cell and the origin
 104 O is placed at the surface of the sphere. Being highly symmetrical, the spherical
 105 cell was adapted by Straub et al. [12, 35, 36] in their space experiments, which
 106 certified the presence of the PE both in one-phase and two-phase region, and eval-
 107 uated the isochoric heat capacity measurements at the critical isochore of SF_6 .
 108 On the other hand, the critical pressure for most fluids are much higher than stan-
 109 dard atmospheric pressure. Owing to good pressure bearing ability, many pressure
 110 vessels are designed as spherical geometry. Thus a spherical cell filled with one
 111 near-critical fluid is a reasonable configuration in experiments and applications.

Initially, the fluid is in thermodynamic equilibrium. The density and tempera-
 ture are uniform throughout the whole cell. The initial conditions are

$$\rho_0 = \rho_c, \quad (1)$$

$$T_0 = (1 + \varepsilon)T_c, \quad (2)$$

112 with T_c the critical temperature, ρ_c the critical density, ε the initial reduced tem-
 113 perature and $\varepsilon = (T_0 - T_c)/T_c$. At $x = 0$, the boundary conditions used in this
 114 study are of the Dirichlet type:

$$T_{wall} = T_0 + \Delta T_{wall}, \quad (3)$$

Figure 1: Physical model. R is the radius of the cell and the origin O is placed at the surface of the sphere.

namely that the boundary temperature suddenly rises by ΔT_{wall} at $t = 0$ s. With clear physical meaning, this type of boundary condition is also used in some previous studies [33, 34, 37]. But it is not directly realizable in experiments [12, 14] under the influence of heat capacity of a container. In particular, Garrabos et al. [14] pointed out the relevance of applying identical total energy to make comparable simulations and experiments. A symmetry boundary condition is applied for $x = R$ in this study, which is equivalent to a Neumann boundary condition with the value of heat flux set to zero.

2.2. Mathematical model and numerical method

There are two main methods that can be used to simulate the PE. One is to solve the complete hydrodynamic description of an isotropic, Newtonian, compressible, and dissipative (viscous and heat-conducting) fluid. The equations were first solved by Zappoli et al. [4] and the essence of the PE can be captured by this model [31]. Afterwards this model was mainly used to investigate the nature of thermoacoustic waves [18, 19, 38]. This model can give an accurate description

130 of the PE but involves complicated and heavy computations.

131 Boukari et al. [3] presented a thermodynamic model to describe the PE under
 132 zero gravity condition. They assumed that there is no velocity field and the pres-
 133 sure in the cell is only the function of time, since pressure equilibrium is achieved
 134 by sound propagation during a very short time period. This non-flow model has
 135 a relatively simple form and has been widely used by researchers to validate the
 136 experimental data [37] and explore the nature of PE [12, 33, 34].

137 In the present study, this thermodynamic model is chosen and the spherical
 138 coordinate is applied to describe and solve physical quantities. Because there is no
 139 velocity, and the pressure is space-independent, and the temperature and density
 140 change along the radius of the cell spatially, this problem can be simplified into
 141 one-dimensional form. The thermodynamic model in one-dimensional spherical
 142 coordinate system can be derived as following:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho C_P} \frac{1}{(R-x)^2} \frac{\partial}{\partial x} \left(\lambda (R-x)^2 \frac{\partial T}{\partial x} \right) + \left(1 - \frac{1}{\gamma} \right) \left(\frac{\partial T}{\partial P} \right)_\rho \frac{\partial P}{\partial t}, \quad (4)$$

$$\frac{\partial P}{\partial t} = \frac{\int_0^R (R-x)^2 \rho \alpha_P (\partial T / \partial t) dx}{\int_0^R (R-x)^2 \rho \kappa_T dx}, \quad (5)$$

144 with T the temperature, ρ the density, P the pressure, t the time, λ the thermal
 145 conductivity, C_P the isobaric specific heat, $\gamma = C_P/C_V$ the specific heat ratio, α_P
 146 the isobaric expansion coefficient and κ_T the isothermal compressibility. This one-
 147 dimensional thermodynamic model was also derived and used in Straub's study
 148 [12]. The spatial coordinate x is along the radial direction with $x = 0$ at the
 149 sample wall and $x = R$ at the center of the cell (shown in Fig.1) [12]. Eq.(4) is
 150 derived based on the energy conservation equation. The second term on the right-
 151 hand side of Eq.(4) is the heat generation rate and is responsible for an isentropic

152 temperature change in the bulk fluid. For an incompressible fluid $\gamma = 1$, this term
 153 equals zero and Eq.(4) becomes the Fourier equation. Eq.(5) is derived based on
 154 both the equation of state and mass conservation and can be used to calculate the
 155 pressure derivative in Eq.(4).

156 Eq.(4) and Eq.(5) are solved by an explicit finite difference method using a
 157 central difference scheme for the spatial discretization. An iteration procedure is
 158 used to determine the pressure for each time step, in which the temperature in the
 159 whole fluid volume is calculated for some trial values of P . The $\rho = f(P, T)$ re-
 160 lations and thermodynamic properties of near-critical fluids are obtained from the
 161 NIST standard database [32]. Every parameter is the function of both temperature
 162 and pressure. The convergence criterion for P is

$$\frac{|P^{i+1} - P^i|}{P^i} \leq 10^{-5}. \quad (6)$$

163 Masuda et al. [33] pointed out that an accurate solution to a near-critical fluid
 164 PE problem shall be obtained when the grid in the very thin boundary layer is
 165 sufficiently fine. But a large number of grid nodes means a heavy calculation
 166 and long computing time. Taking into consideration both the computing time and
 167 accuracy, nonuniform grids are carefully generated in the calculation domain of
 168 the present study. The minimum grid spacing Δx is 0.005 mm at the boundary ($x =$
 169 0), which is half of Shen's [18] and Hasan's [38] grid spacing in their studies, and
 170 the spacing ratio for adjacent grid nodes is 1.001 along the direction of increasing
 171 x (with around 1000 mesh grids for the $R = 10$ mm case).

172 For explicit finite difference method, the time step should be small enough
 173 to have numerical stability. So we test a selection of time steps, ranging from
 174 0.0001 s to 0.01 s. At last, a time step 0.001 s is adopted in most cases. In
 175 addition, a numerical algorithm based on implicit finite difference method is also

176 established and operates under the same condition. The resulting temperature
177 responses from two methods are almost identical. Notably, the approximation of
178 space-independent pressure is only supported when the timescales of interest are
179 much larger than L/v_a [3], where v_a is the speed of sound and L is characteristic
180 length, and all cases throughout this study satisfy this constraint ($L/v_a \sim 10^{-5}$ s).

181 2.3. Verification of the numerical scheme

182 In this section, the numerical prediction of the PE in near-critical SF_6 based on
183 the present numerical method is compared with an experimental measurement. In
184 the Ref.[12], Straub et al. measured dynamic temperature propagation in a spher-
185 ical cell filled with near-critical SF_6 using four thermistors monitored at three
186 different radial positions in the fluid and the cell wall. They pasted the heater (a
187 wound wire) on the outer surface of the cell along a great circle and the surface can
188 be treated as an almost isothermal heating area. Thirty nine cases of different ini-
189 tial conditions were measured and the existences of PE were confirmed. Besides,
190 numerical simulations were performed by iteratively solving the energy equation
191 to test and verify their measurements and good agreements were obtained.

192 In order to verify the numerical scheme presented in the present study, we
193 carried out a simulation based on the same initial ($T_0 = T_c + 0.1$ K, $\rho_0 = \rho_c$)
194 and boundary conditions with the measurements. Figure 2 shows the comparison
195 between the computation in the present study and the measurements. It can be
196 seen that the calculated bulk temperature change agrees well with experimental
197 result. The average deviation is only 0.24 mK and average relative deviation is
198 4.81 %. Thus the numerical scheme developed in this paper is acceptable and
199 proved being effective to simulate the PE problem.

Figure 2: Comparison between the calculated bulk temperature change (ΔT) and measurements in the time region $0 < t < 20$ s at $x = 8.4$ mm of a spherical cell ($R = 9.6$ mm) filled with near-critical SF_6 . Solid line, calculated result; ■, experimental data from [12].

200 3. Definitions of physical quantities

201 In this section, some important physical quantities are introduced, which are
 202 used in the present study to describe the PE problem.

203 Firstly, the timescale of the PE for a spherical enclosure is derived following a
 204 thermodynamic approach proposed by Onuki et al. [2]. It is convenient to assume
 205 that a small quantity of heat, ΔQ , is added uniformly to a spherical enclosure.
 206 Then there forms a thin thermal boundary layer with a thickness δ near the wall.
 207 The whole volume can be divided into two parts, namely the thermal boundary
 208 layer and the bulk fluid, whose volumes are

$$V_1 \approx 4\pi R^2 \delta, \quad V_2 \approx \frac{4}{3}\pi R^3, \quad (7)$$

209 respectively. Under the influence of ΔQ , the temperature and volume in V_1 will
 210 change by

$$\Delta T_1 = \frac{\Delta Q}{V_1 C_p}, \quad \Delta V_1 = \alpha_p V_1 \Delta T_1, \quad (8)$$

211 respectively, in which the approximation of a constant pressure process is ap-
 212 plied. Because the total volume is constant, the expansion causes an adiabatic
 213 contraction of the bulk fluid V_2 by ΔV_1 . According to the adiabatic coefficient,
 214 $V(\partial T/\partial V)_S = -(\gamma - 1)/\alpha_P$, the temperature of the bulk fluid will increase by

$$\Delta T_2 = \left(\frac{\partial T}{\partial V} \right)_S (-\Delta V_1) = \frac{\gamma - 1}{\alpha_P} \Delta V_1. \quad (9)$$

215 The thermal equilibrium is reached when $\Delta T_1 = \Delta T_2$. Along with Eq.(7-9), it
 216 leads to

$$\delta = \frac{R/3}{\gamma - 1}. \quad (10)$$

217 Since $\delta = L/(\gamma - 1)$, the characteristic length for a spherical cell is $L = R/3$. Since
 218 diffusion dominates the formation of a thermal boundary layer, the timescale of
 219 the PE is

$$t_{PE} = \frac{\delta^2}{D_T} = \frac{(R/3)^2}{D_T(\gamma - 1)^2}, \quad (11)$$

220 where D_T is thermal diffusivity.

221 In order to measure temperature equilibrium capability of the PE, the temper-
 222 ature efficiency ξ_T is defined as

$$\xi_T = \frac{\Delta T_{bulk}}{\Delta T_{bulk,ideal}}, \quad (12)$$

223 where ΔT_{bulk} is the real bulk temperature increase and $\Delta T_{bulk,ideal}$ is the temperature
 224 which would be reached if the energy uniformly distributes in the fluid by heat
 225 diffusion. Physically, it implies the temperature improving ability ratio of the PE
 226 to pure heat diffusion. $\Delta T_{bulk,ideal}$ can be expressed as

$$\Delta T_{bulk,ideal} = \frac{E_{total}}{mC_V}, \quad (13)$$

where m is the mass of the fluid in the cell and C_V is the specific heat capacity at constant volume. E_{total} is calculated by

$$E_{total} = \int A Q dt = \int A \lambda \left. \frac{dT}{dx} \right|_{x=0} dt, \quad (14)$$

where $A = 4\pi R^2$ is surface area of the cell.

4. Results and discussion

4.1. Effects of the specific heat ratio on the PE

Numerical simulations were carried out for eight near-critical fluids to find out the influences of the specific heat ratio on the PE. The cell radius R is 0.01 m. Initially, the fluids are at their critical isochore ($\rho_0 = \rho_c$) and at the same initial reduced temperature ($\varepsilon = 0.0005$). The reduced temperature is a nondimensional parameter which is nondimensionalized by critical temperature. Inspired by the reduced temperature, we define a nondimensional boundary temperature rise as $\Delta T_{wall}/T_c$ and set it equals 0.00001 for all fluids. The initial and boundary conditions in this section are summarized in Eq.(1-3) and $R = 0.01$ m. The chosen fluids and their detailed critical parameters, initial and boundary conditions are shown in Table 1.

The chosen fluids are representative since their critical parameters cover a large scope (the critical temperature varies from about 5.2 K to 647.1 K and the critical pressure varies from 0.23 MPa to 22.06 MPa). As a result, it can be seen from Table 1 that the dimensional boundary temperature change ΔT_{wall} varies widely. The nondimensional boundary temperature rise change $\Delta T_{wall}/T_c = 0.00001$ is negligible compared with $\varepsilon = 0.0005$. The main purpose is to ensure the physical properties do not change dramatically during the PE process.

Table 1: Critical parameters, initial and boundary conditions for eight fluids.

Fluid	T_c (K)	P_c (MPa)	T_0 (K)	ρ_0 (m ³ /kg)	ΔT_{wall} (mK)
He	5.1953	0.228	5.1979	72.567	0.052
H ₂	33.145	1.296	33.162	31.262	0.331
Xe	289.73	5.842	289.88	1102.9	2.897
O ₂	145.58	5.043	145.66	436.14	1.546
N ₂	126.19	3.396	126.25	313.30	1.262
H ₂ O	647.10	22.06	647.42	322.00	6.471
CO ₂	304.13	7.377	304.28	467.60	3.041
SF ₆	318.72	3.755	318.88	742.30	3.187

Table 2 presents the PE timescale and thermophysical properties of these near-critical fluids under initial conditions. The fluids are listed in the order of descending γ . As we can see, the data in each column of Table 2 differs greatly. For example, the γ of He is about four times that of SF₆, and the t_{PE} of CO₂ is about three times that of H₂O.

In this section, the temperature, time and length are nondimensionalized by the critical temperature T_c , the PE timescale t_{PE} and the cell radius R respectively to make different fluids be able to be compared with each other, which leads

$$T' = \frac{T}{T_c}, t' = \frac{t}{t_{PE}}, x' = \frac{x}{R}. \quad (15)$$

As will be seen later, after nondimensionalization, results show general rules between the specific heat ratio and the PE. In the studies of the effects of characteristic length and boundary conditions on the PE, only one near-critical fluid is involved, so it is not necessary to nondimensionalize variables.

Table 2: The PE timescale and thermophysical properties under initial conditions.

Fluid	γ	t_{PE} (s)	D_T (m ² /s)	λ (W/m · K)
He	1398.8	0.0523	1.0868×10^{-10}	0.0374
H ₂	1257.4	0.0361	1.9546×10^{-10}	0.0641
Xe	969.80	0.0262	4.5225×10^{-10}	0.1077
O ₂	909.30	0.0491	2.7441×10^{-10}	0.1464
N ₂	793.92	0.0464	3.8049×10^{-10}	0.1766
H ₂ O	687.18	0.0228	1.0348×10^{-09}	1.3992
CO ₂	555.09	0.0677	5.3469×10^{-10}	0.3021
SF ₆	361.03	0.0604	1.4187×10^{-09}	0.4000

261 4.1.1. Bulk temperature evolutions

262 Displayed in Fig.3 (a) are the nondimensional temperature evolutions at the
 263 cell center for the near-critical fluids. Under the influence of PE, the nondimen-
 264 sional bulk temperature increases rapidly for $t' = 0 \sim 5$. Besides, its increase rate
 265 reduces gradually with the nondimensional time. This is a sign of the weakening
 266 PE and this trend is identical for all fluids.

267 In order to show the differences more clearly, Fig.3 (b) presents spatial profiles
 268 of $\Delta T'$ for the different fluids at $t' = 15$. It is clear that the nondimensional bulk
 269 temperature increase for these fluids are markedly different and can be ranked as
 270 follows:

$$\text{He} < \text{H}_2 < \text{Xe} < \text{O}_2 < \text{N}_2 < \text{H}_2\text{O} < \text{CO}_2 < \text{SF}_6, \quad (16)$$

271 which coincides with the descending order of γ (see the second column in Table
 272 2). That is, the larger the γ is, the slower the nondimensional bulk temperature
 273 increases with the nondimensional time. This will be clarified later in this section.

Figure 3: (a) Nondimensional temperature rise versus nondimensional time for fluids at $x = R$. (b) Spatial profiles of $\Delta T'$ for fluids at $t' = 15$, where $\Delta T' = \Delta T/T_c = (T - T_0)/T_c$ and $t' = t/t_{PE}$. ●, He; ■, H₂; ◆, Xe; ▲, O₂, ▼, N₂; ◀, H₂O; ▶, CO₂; +, SF₆.

274 Under small thermal disturbance, the physical properties of a fluid can be as-
 275 sumed as constant, which means they are time-independent and space-independent.
 276 Note that this approximation is justified under small thermal disturbance. Then
 277 Eq.(4) and Eq.(5) can be simplified into the following form

$$\begin{aligned} \frac{\partial T}{\partial t} = & \frac{D_T}{(R-x)^2} \frac{\partial}{\partial x} \left((R-x)^2 \frac{\partial T}{\partial x} \right) + \\ & \left(1 - \frac{1}{\gamma} \right) \frac{3}{R^3} \int_0^R (R-x)^2 \frac{\partial T}{\partial t} dx. \end{aligned} \quad (17)$$

278 Define nondimensional variables as Eq.(15), and Eq.(17) is transformed into nondi-
 279 mensional form

$$\begin{aligned} \frac{\partial T'}{\partial t'} = & \frac{1}{9(\gamma-1)^2} \frac{1}{(1-x')^2} \frac{\partial}{\partial x'} \left((1-x')^2 \frac{\partial T'}{\partial x'} \right) + \\ & 3 \left(1 - \frac{1}{\gamma} \right) \int_0^1 (1-x')^2 \frac{\partial T'}{\partial t'} dx' \end{aligned} \quad (18)$$

280 It is shown that the specific heat ratio is the unique physical property in Eq.(18),
 281 which means all the others being equal, the specific heat ratio is the only factor
 282 that influence the nondimensional bulk temperature increase for the different near-
 283 critical fluids under small thermal disturbance. As shown in Eq.(18), $1/(\gamma-1)^2$
 284 and $(1-1/\gamma)$ are coefficients in the right-hand side of Eq.(18). The effects of γ on
 285 the coefficients can be illustrated by the following equations:

$$\frac{1/(\gamma_{\text{He}}-1)^2}{1/(\gamma_{\text{SF}_6}-1)^2} = 0.0663, \quad \frac{1-1/\gamma_{\text{He}}}{1-1/\gamma_{\text{SF}_6}} = 1.0021, \quad (19)$$

286 where $\gamma_{\text{He}} = 1398.8$, $\gamma_{\text{SF}_6} = 361.03$. It can be seen from Eq.(19) that the first
 287 coefficient $1/(\gamma-1)^2$ is more sensitive to the variation of γ , and it is appropriate
 288 to suppose γ has no effect on the second coefficient $(1-1/\gamma)$. So the increase of γ
 289 will reduce the first term in the right-hand side of Eq.(18) considerably, and cause
 290 the decrease of the left-hand term $\partial T'/\partial t'$ further. However, the second term in

291 the right-hand side of Eq.(18) is responsible for the bulk temperature change and
292 is strongly coupled with $\partial T'/\partial t'$. Thus the increase of γ will further diminish the
293 nondimensional bulk temperature change.

294 Note that Masuda et al. [33] and Mao et al. [34] simulated the PE in near-
295 critical H₂O. They compared the bulk temperature change at the same time and
296 concluded that the influence of the PE is stronger as the γ is larger. However, it
297 seemingly contradict with the conclusion presented here based on simulations of
298 eight near-critical fluids. In fact, there is no contradiction and the type of time
299 chosen to compare (t' or t) is the key reason to this observed phenomenon. For
300 a single near-critical fluid, a larger γ means a smaller t_{PE} [34] and consequently
301 means a larger nondimensional time t' at the same normal time t . As a result, when
302 nondimensional bulk temperature increase at the same nondimensional time t' is
303 compared, it is found that a larger γ means a slower nondimensional bulk tempera-
304 ture increase; but when the comparison is made for dimensional bulk temperature
305 increase at the same normal time t , it is found that a larger γ means a faster bulk
306 temperature increase. Besides, Masuda et al. [33] pointed out for a single near-
307 critical fluid, a larger γ means a smaller thermal diffusivity D_T . But it can be
308 concluded from Table 2 that if more than one near-critical fluids are involved, the
309 relationship among γ and D_T can't be simply established. For example, the γ of
310 H₂O is larger than that of CO₂, but the D_T of H₂O is also larger than that of CO₂.

311 In order to verify above analysis, numerical simulations are preformed for
312 near-critical CO₂ under two typical reduced temperature. The PE timescale and
313 thermophysical properties are shown in Table 3, and the calculated dimensional
314 and nondimensional bulk temperature responses are shown in Fig.4. It is shown in
315 Table 3 and Fig.4(a) that near the critical point, the specific heat ratio of CO₂ in-

creases and bulk temperature change accelerates, which is consistent with Masuda et al. [33]. But as shown in Fig.4(b), nondimensional variables show opposite trend, which is consistent with the conclusions in the present study.

Table 3: The PE timescale and thermophysical properties for near-critical CO₂ under different reduced temperature.

ε	γ	t_{PE} (s)	D_T (m ² /s)	λ (W/m · K)
0.00100	286.56	0.1643	8.2935×10^{-10}	0.2247
0.00329	90.993	0.7128	1.9246×10^{-09}	0.1388

4.1.2. Temperature efficiency evolutions

Figure 5 presents variations of the temperature efficiency with the nondimensional time for the different near-critical fluids. It is seen that there are three obvious trends related to this temperature efficiency.

Firstly, the observed temperature efficiencies are all higher than 0.995, which indicates the PE is extremely efficient in terms of temperature equilibrium. This has also been reported by Garrabos et al. [14] and was attributed to the fact that the internal energy of near-critical fluid is very sensitive to density variations. The small mass flux getting into the bulk at the hot boundary layer border causes the density change precisely [14].

Secondly, the temperature efficiencies for the different fluids are unequal, but the observed maximum difference is only 0.002. This maybe because the temperature efficiency is related to the particular nature of near-critical fluids. The initial reduced temperature for the eight fluids are identical, so the nature of near-critical fluids are nearly the same. Moreover, the temperature efficiencies almost do not

Figure 4: (a) Dimensional and (b) nondimensional bulk temperature responses for near-critical CO₂ and different reduced temperature, where $\Delta T' = \Delta T/T_c = (T - T_0)/T_c$ and $t' = t/t_{PE}$; $\bullet$, $\epsilon = 0.001$, $\blacksquare$, $\epsilon = 0.00329$.

Figure 5: Temperature efficiency ξ_T versus nondimensional time $t' = t/t_{PE}$ for different near-critical fluids. The definitions of ξ_T see Eq.(12). ●, He; ■, H₂; ◆, Xe; ▲, O₂; ▼, N₂; ◄, H₂O; ►, CO₂; +, SF₆.

334 change with the nondimensional time. This maybe because the imposed thermal
 335 disturbance is too small to change the initial reduced temperature during the PE
 336 process.

337 Thirdly, the specific heat ratio simply reflects the temperature efficiency, which
 338 shows the larger the specific heat ratio, the higher the temperature efficiency. The
 339 relative temperature efficiency of the eight near-critical fluids are as follows:

$$\text{He} > \text{H}_2 > \text{Xe} > \text{O}_2 > \text{N}_2 > \text{H}_2\text{O} > \text{CO}_2 > \text{SF}_6, \quad (20)$$

340 which coincides with the ascending order of γ (see Table 2). Thus in terms of
 341 temperature equilibrium, the PE is strong and capable as the specific heat ratio
 342 becomes larger. This maybe because the underlying mechanisms of the density-
 343 sensitive internal energy and the enlarged specific heat ratio are closely related.

344 In this section, a nondimensionalization method (T_c , t_{PE} , and R for temper-
 345 ature, time, and length respectively) is developed and numerical simulations of
 346 the PE for eight near-critical fluids are preformed. Results show the specific heat

ratio is an efficient indicator of the PE, which is negatively corrected with the increase rate of nondimensional bulk temperature and positively correlated with the temperature efficiency.

4.2. Effects of the characteristic length on the PE

As mentioned in Section 3, the characteristic length, denoted as L , equals $R/3$ for a spherical cell. Moreover, the heating-surface-area-to-volume ratio for the physical model shown in Fig.1 is

$$\frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{R}, \quad (21)$$

which is exactly the reciprocal of the characteristic length. So physically, the characteristic length is the ratio of the cell volume to the heating surface area and is negatively correlated with the thermal disturbance obtained by per unit volume.

According to the analytical solution given by Onuki et al. [39], Straub et al. [12] noted that with an decreasing characteristic length, the bulk temperature increase accelerates, which is in agreement with its physical meaning. In this section, a series of numerical simulations are carried out to elaborate how the L influences the PE. Three spherical cells ($R = 0.1, 0.01$ and 0.001 m, $L = 3.33 \times 10^{-2}, 3.33 \times 10^{-3}$ and 3.33×10^{-4} m respectively) filled with near-critical CO_2 ($T_c = 304.13$ K, $\rho_c = 467.6$ kg/m³) are used in the present study. The initial and boundary conditions are shown in Eq.(1-3), with $\varepsilon = 0.00033$, $\Delta T_{wall} = 10$ mK.

4.2.1. Bulk temperature evolutions

Figure 6 shows bulk temperature evolutions for the characteristic lengths. It is shown that the bulk temperature increases rapidly at initial stage, and the increase

rate reduces gradually. They are typical bulk temperature responses and have been observed and explained in Section 4.1.1.

Figure 6: Temperature changes at $x = R$ versus t for the different characteristic lengths. ●, $L = 3.33 \times 10^{-2}$ m; ■, $L = 3.33 \times 10^{-3}$ m; ◆, $L = 3.33 \times 10^{-4}$ m.

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Moreover, it is observed that the shorter the characteristic length is, the faster the bulk temperature increases. For example, the L changing from 3.33×10^{-2} m to 3.33×10^{-4} m, the time for the bulk temperature increasing by 8.5 mK reduces from 10 s to 0.2 s. This can be explained by the fact that for a shorter L , the propagating period of thermoacoustic waves is shorter, which will help to enhance the bulk temperature increase. This law has also been pointed out by Straub et al. [12], based on the analytical solution given by Onuki et al. [39].

377 4.2.2. Boundary heat flux evolutions

Shown in Fig.7 are time variations of the boundary heat flux for the characteristic lengths. Three obvious characteristics concerning the boundary heat flux can be seen from the computed curves.

Firstly, the heat flux approaches zero rapidly. It is because the temperature of the hot boundary layer increases and reaches boundary temperature.

Figure 7: Temporal variations of the heat flux at the boundary for the different characteristic lengths. Inset: the enlarged portion for $t = 0.1 \sim 0.5$ s. ●, $L = 3.33 \times 10^{-2}$ m; ■, $L = 3.33 \times 10^{-3}$ m; ◆, $L = 3.33 \times 10^{-4}$ m.

Secondly, the shorter the L is, the faster the heat flux falls. This is because for a shorter L , the bulk temperature is higher and the PE is weaker at the same time.

Thirdly, the shorter the L is, the less heat is sent into the fluid. This is because a decreasing L leads to a decreasing surface area and boundary heat flux, both of which will reduce the total heat sent into the fluid. Calculated results show, the L changing from 3.33×10^{-2} m to 3.33×10^{-4} m, the total heat sent into the fluid decreases by six order of magnitude.

4.2.3. Temperature efficiency evolutions

Figure 8 shows time variations of the temperature efficiency for the characteristic lengths. One can see the high and barely changing temperature efficiency, which has been reported and explained in Section 4.1.2. Besides, it is seen that the temperature efficiency is higher for a larger L . This maybe because for a shorter L , less heat is transferred into the bulk fluid owing to the smaller bulk fluid volume. That is to say, a larger part of energy is stored in the hot boundary layer and the

temperature efficiency is low.

Figure 8: Temperature efficiency evolutions for the different characteristic lengths. ●, $L = 3.33 \times 10^{-2}$ m; ■, $L = 3.33 \times 10^{-3}$ m; ◆, $L = 3.33 \times 10^{-4}$ m.

397

398 4.3. Effects of the boundary condition on the PE

399 The boundary condition is an important factor influencing the PE. Shen and
 400 Zhang studied the thermoacoustic waves emission, propagation and reflection un-
 401 der different temperature boundary conditions by solving the governing hydrody-
 402 namic equations [18]. Besides, they studied the thermoacoustic waves emission
 403 under internal and boundary heat flux conditions [19]. Hasan and Farouk also
 404 studied the thermoacoustic waves generation under different boundary heating
 405 rates using a real-fluid CFD model [20]. The thermodynamic model can reveal
 406 problems from a macroscopic view but it is not be adopted before to investigate
 407 effects of the boundary condition on the PE.

408 In this section, several Dirichlet boundary conditions are designed to study the
 409 effects of boundary conditions on the PE, in which the boundary temperature is
 410 known. A spherical cell ($R = 0.01$ m) filled with near-critical CO_2 ($T_c = 304.13$ K,

411 $\rho_c = 467.6 \text{ kg/m}^3$) is considered in the presented analysis. The initial conditions
 412 are shown in Eq.(1) and Eq.(2), with $\varepsilon = 0.00033$.

413 The boundary condition is the independent variable in this section. Taking
 414 into account the increase rate (the slope of the curve), four representative bound-
 415 ary conditions are designed, which have the same starting and end point (see Fig.9
 416 and Table 4). The boundary conditions are named taking more of their geometry
 417 information into consideration. The variation laws for the increase rates are sum-
 418 marized as follows:

- 419 a. IR: the increase rate equals infinity when $t = 0 \text{ s}$ and equals zero when $t > 0 \text{ s}$;
- 420 b. LUQR: the increase rate reduces gradually from infinity to zero;
- 421 c. LR: the increase rate is constant and equals 1 mK/s ;
- 422 d. RLQR: the increase rate increases gradually from zero to infinity.

Figure 9: Temporal variations of change in boundary temperature. Implications of the abbreviations are listed in Table 4. ●, IR; ■, LUQR; ◆, LR; ▲, RLQR.

Table 4: Detailed information of the boundary conditions.

Abbreviation	Full name	Mathematical expression
IR	Impulsive Rise.	$\Delta T_{wall} = 10 \text{ (mK)}$
LUQR	Left Upper Qurant Rise.	$\Delta T_{wall} = \sqrt{20t - t^2} \text{ (mK)}$
LR	Linear Rise.	$\Delta T_{wall} = t \text{ (mK)}$
RLQR	Right Lower Qurant Rise.	$\Delta T_{wall} = 10 - \sqrt{100 - t^2} \text{ (mK)}$

They are representative because the increase rates cover the range from zero to infinity and all the possibility of variations. Note that we do not discuss the situation that the boundary temperature rise curve has negative slope, which may cause alternate hot piston effect and cool piston effect (CPE) [6] depending on the particular behaviors of the boundary temperature.

4.3.1. Bulk temperature and pressure evolutions

Shown in Fig.10 is the calculated responses of bulk temperature and pressure. Comparing the two figures, we can draw a conclusion that the bulk temperature and the pressure change synchronously. It is because the bulk temperature change is calculated from the pressure change. As illustrated in Fig.10 (a), the curves of the bulk temperature increase under the different boundary conditions are entirely different from each other. Thus the boundary condition is crucial in determining the bulk temperature response. Under IR, the boundary temperature suddenly increases by 10 mK at $t = 0$ s, and most of the bulk temperature change is accomplished during $0 \sim 2$ s. Compared with IR, under the other boundary conditions, the bulk temperature closely follows the boundary temperature.

Figure 10: (a) Temporal variations of change in bulk temperature. (b) Temporal variations of change in pressure. ●, IR; ■, LUQR; ◆, LR; ▲, RLQR.

439 In order to evaluate boundary conditions, we define thermal impulse I_T as

$$I_T = \int \Delta T_{wall} dt, \quad (22)$$

440 which indicates the thermal disturbance imposed to the fluid during a period of
 441 time, and equals the area enclosed by the curves, the line $\Delta T_{wall} = 0$ mK and the
 442 vertical line $t = 10$ s (see Fig.9). The thermal impulse, bulk temperature increase,
 443 and total heat sent into the fluid at $t = 10$ s for the different boundary conditions
 444 are given in Table 5. It is shown that the higher the thermal impulse, the larger
 445 the bulk temperature increase. Thus the thermal impulse can be considered as an
 446 efficient parameter to evaluate boundary conditions, which is positively correlated
 with the bulk temperature increase.

Table 5: Thermal impulse, bulk temperature increase and total heat sent into the fluid at $t = 10$ s.

Boundary Condition	I_T (mK·s)	ΔT_{bulk} (mK)	E_{total} (J)
IR	100	9.4564	0.0380
LUQR	79	9.1742	0.0369
LR	50	8.6394	0.0349
RLQR	21	7.0578	0.0291

447

448 The relationship between the thermal impulse and bulk temperature increase
 449 is explained below. As mentioned before, the temperature difference between the
 450 boundary and bulk temperature is the driving force of PE. However, the thermal
 451 impulse is just the accumulation of the driving force during some time and conse-
 452 quently, should be positively correlated with the bulk temperature increase.

453 The relationship can also be explained by analogy with the *impulse-momentum*
 454 *theorem* in classical mechanics. A force can cause an object with mass to change

its velocity; the impulse in classical mechanics is the integral of a force over the time interval during which it acts; the *impulse-momentum theorem* states that the impulse causes a change in momentum, which is to say the impulse is proportionate to the change in velocity. Analogously, a thermal disturbance can cause the bulk temperature change with the help of the PE; the thermal impulse is the integral of a thermal disturbance over the time interval during which it is imposed; therefore, the thermal impulse is positively correlated with the bulk temperature change. Thus, it is reasonable to call this kind of relationship as the *impulse-momentum theorem* in the PE. To be more specific, analogously, the *force* in PE is thermal disturbance, the *impulse* in PE is thermal impulse I_T , and the *momentum* in PE is the bulk temperature change.

Garrabos et al. [14] studied the PE under three heat pulses with identical total energy, and pointed out the bulk temperature responses eventually become identical over a period of time. Note as well in the present study, the thermal impulse is also positively correlated with the total heat sent into the fluid (see Table 5). So the differences in amount of heat sent into the fluid may be a reasonable explanation of the *impulse-momentum theorem* analogy.

4.3.2. Boundary heat flux evolutions

Figure 11 shows time variations of the boundary heat flux and the increase rate of boundary temperature for the different boundary conditions. There are obvious differences in the boundary heat flux curves, so the boundary condition has a strong influence on the boundary heat flux.

To be specific, the boundary heat flux is almost positively correlated with the increase rate of boundary temperature. This discipline can be concluded from comparing the curves in (a) and (b) respectively. According to Fourier's heat con-

Figure 11: Temporal variations of (a) the boundary heat flux and (b) the increase rate of boundary temperature for the different boundary conditions. ●, IR; ■, LUQR; ◆, LR; ▲, RLQR.

duction equation, the heat flux is proportionate to the spatial temperature gradient. Because it takes some time for heat transfer process to improve the near-boundary fluid temperature, the higher the increase rate, the larger the temperature difference between the boundary and the near-boundary fluid. Thus the increase rate is positively correlated with the spatial temperature gradient and the boundary heat flux.

4.3.3. Temperature efficiency evolutions

Shown in Fig.12 are temperature efficiency evolutions for the different boundary conditions. As previously mentioned, the temperature efficiency is related to the particular nature of near-critical fluids. However, the thermal disturbances imposed here are too weak to change the initial reduced temperature. As a result, the largest difference in temperature efficiency is only 0.0012, which is negligible taking the calculation error into consideration. Hence, boundary conditions slightly influence the temperature efficiency under small thermal disturbance.

Figure 12: Temperature efficiency evolutions for the different boundary conditions. ●, IR; ■, LUQR; ◆, LR; ▲, RLQR.

494 5. Conclusion

495 In this paper, a series of numerical explorations have been conducted into the
496 piston effect in a spherical cell filled with near-critical fluid under zero gravity and
497 small thermal disturbance conditions. Various factors that influence the piston ef-
498 fect (PE), such as the specific heat ratio, the characteristic length and the boundary
499 condition, are investigated by numerically solving the thermodynamic model.

500 The results exhibit the fast-responding bulk temperature, which is a sign of
501 the PE, along with high and stable temperature efficiency, which is determined
502 by the particular nature of near-critical fluids. A nondimensionalization method is
503 developed to study the influences of the specific heat ratio on the PE based on sim-
504 ulations for eight near-critical fluids. Results show that the specific heat ratio is an
505 efficient indicator of the PE, which is negatively correlated with the increase rate
506 of nondimensional bulk temperature, but positively correlated with the tempera-
507 ture efficiency. The characteristic length weighs heavily upon the PE. Similarly, it
508 is negatively correlated with the increase rate of bulk temperature, but positively
509 correlated with the temperature efficiency. In addition, the newly defined thermal
510 impulse can be considered as an efficient parameter to evaluate boundary condi-
511 tions, which is positively correlated with the bulk temperature increase, but has
512 slight influence on the temperature efficiency under small thermal disturbance. It
513 is reasonable to call this kind of relationship as the *impulse-momentum theorem*
514 in the PE.

515 In the present study, small thermal disturbance is only considered. Under
516 strong thermal disturbance, the critical distance will be altered during the PE. As
517 a result, the nature of near-critical fluids will change dramatically and the rules
518 mentioned above may not well-established. Besides, the boundary temperature

519 curve with negative slope is not studied, which may cause alternate hot and cool
520 piston effect depending on the particular behaviors of the boundary temperature.
521 Both of the two topics are interesting and need to be studied furthermore.

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