Piston effect induced by cross-boundary mass diffusion in a binary fluid mixture near its liquid-vapor critical point

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Abstract

In this paper, we study the thermalization process of an enclosed fluid mixture near its liquid-vapor critical point subjected to cross-boundary mass diffusion. We reveal that the mass piston effect, a fast and efficient thermalization phenomenon can take place, as a result of three cooperative or competing mechanisms: the boundary velocity, the Dufour effect, and the concentration variation. We propose a theory to formulate the mass piston effect on the acoustic timescale, including the amplitudes of the acoustic wave, the wave's propagation, and the energy and temperature efficiencies measuring the performance of the mass piston effect in terms of energy transfer and thermalization. We apply our theory to the representative C2H6 – CO2 mixture, and present the behavior of various thermodynamic indicators in the critical region over the whole concentration range. We identify that the boundary velocity is the main factor that restricts the efficiency of the thermalization. By comparing with numerical simulations of different initial states and boundary conditions, the theoretical predictions are quite satisfactory. The current work adds a new member to the family of piston effect and gives new insights into the thermalization process in the critical region.

1. Introduction

For a single-component fluid near the liquid-vapor critical point (CP), the large compressibility and the diminishing thermal diffusivity are responsible for a rapid thermalization process known as the piston effect (PE) [1–4]. Due to buoyant convection on the earth, the PE had long been ignored and was first observed in a microgravity experiment [5]. Indeed, the heating of a confined near-critical fluid provokes a thin thermal boundary layer (BL), which expands strongly, acting as a piston, and drives an acoustic wave in the fluid. This acoustic wave travels back and forth at the speed of sound, causing adiabatic compression of the bulk fluid and rapid relaxation of temperature [6]. Similarly, the cooling of such a system can also induce the so-called cooling PE. Asymptotic expansions were employed to study the relaxations of temperature and density fields [7,8]. Meanwhile, several experimental studies were carried out to evidence the PE [9–12], observe thermoacoustic waves [13], and investigate whether the PE can be used to perform long-distance heat transfer [14]. The generation and reflection of thermoacoustic waves were discussed thoroughly by Shen and Zhang [15,16]. A recent study of Long et al. [17] discussed the PE in binary fluid mixtures. Related research progresses have been widely described in a recent book written by Zappoli et al. [18].

The core concept of the PE is a rapid and efficient thermalization induced by the input (output) of energy to (from) a confined near-critical fluid system. In previous studies, the PE is triggered by boundary heating or cooling, so the energy flux always takes the form of heat. However, what will happen if the energy flux is given in different forms? Inspired by this idea and the chemical extraction process (one of the most important engineering applications of near-critical and supercritical fluids), we chose a near-critical binary fluid mixture as the research object, and studied its response to a boundary concentration perturbation. In this situation, the boundary concentration perturbation mimics the variation in solubility, which is responsible for a cross-boundary diffusion flux of the solute. The question that naturally arises is whether the PE can occur in the current configuration to induce a fast and efficient thermalization.

This work is also motivated by some indirect experimental observations. It is well-known that the thermodynamic and transport properties of fluid mixtures also exhibit singularities at the CP,
which is believed to be responsible for the previously reported fact that large density gradient and natural convection are often encountered when a solute dissolves into a near-critical fluid \[19,20\]. In this process, the effects of concentration are very similar to those of temperature in the phenomenon reported before the PE was discovered. Therefore, we conjecture that the PE also exists but has been hidden in natural convection.

After systematically theoretical and numerical explorations, we have confirmed that the PE can take place in the current configuration. This paper is dedicated to reporting our interesting findings. For the sake of clarity, we call the PE induced by cross-boundary diffusion flux \textit{mass piston effect} (MPE), differentiating from the thermal PE.

This paper is organized as follows. In Section 2, we present details about the physical and mathematical descriptions of the problem. In Section 3, the thermodynamic theory is proposed to describe the MPE on the acoustic timescale. In Section 4, we apply the theory to the representative \(\text{C}_2\text{H}_6 - \text{CO}_2\) system to report the behavior of various thermodynamic quantities, and to test the accuracy of the theory. The paper is concluded in Section 5.
is measured by the reduced temperature $c = (T_1 - T_C)/T_C$, where $T_1$ is the initial temperature. We denote the concentration (mass fraction) of $A$ as $c$ and the initial concentration as $c_i$.

The fluid system is subjected to a concentration perturbation at the left side resulting in a cross-boundary diffusion flux of $A$, while $B$ is rejected by the left boundary. The other side is impermeable. There is no temperature gradient at the two boundaries. The boundary condition (BC) employed in this study mimics chemical extraction processes, where a solute $(A)$ dissolves into a near-critical/supercritical solvent $(B)$ from the solid substrate (the left boundary).

The energy flux $q$ and diffusion flux $i$ are given by [21] (along the x-direction)

$$q = k_i T \frac{\partial i}{\partial x}$$

$$i = -\rho D \frac{\partial}{\partial x} \left( \rho k_i T \frac{\partial T}{\partial x} \right)$$

respectively, where $k_i$ is the thermal conductivity, $\rho$ is the density, $D$ is the diffusion coefficient, and $k_i$ is the thermal diffusion ratio. The partial enthalpy $H$ is related to the partial molar enthalpies of the two components $H_A$ and $H_B$ by $H = H_A/M_A - H_B/M_B$, where $M$ is the molar mass, and the subscripts $A, B$ indicate the components.

The quantity $c_i = (\partial c/\partial p)_{T, p}$ is the concentration susceptibility (the chemical potential $\mu$ is related to the partial molar enthalpies of the two components $\mu_A$ and $\mu_B$ by $\mu = \mu_A/M_A - \mu_B/M_B$). The first and second terms on the right-hand side of Eq. (1) are energy fluxes due to Dufour effect (DE) and interdiffusion of components, respectively. The second term on the right-hand side of Eq. (2) is the diffusion flux due to Soret effect.

Employing the above expressions for $q$ and $i$, the conservation equations [22] are given by

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho \mathbf{u}}{\partial x} = 0,$$

$$\frac{\partial \rho u}{\partial t} + \frac{\partial \rho u \mathbf{u}}{\partial x} = \frac{\partial p}{\partial x} + \frac{4}{3} \frac{\partial ^2 u}{\partial x^2},$$

$$\eta \left( \frac{\partial}{\partial t} + \frac{\partial \mathbf{u}}{\partial x} \right) \left( \frac{\partial T}{\partial x} + T \frac{\partial}{\partial x} \left( \frac{\partial u}{\partial x} + \mathbf{u} \frac{\partial \mathbf{u}}{\partial x} \right) \right) = \frac{k_i}{c_i} \frac{\partial i}{\partial T} + \frac{4}{3} \left( \frac{\partial u}{\partial x} \right)^2,$$

$$\frac{\partial p}{\partial t} + \frac{\partial \rho u \mathbf{u}}{\partial x} = -\frac{\partial i}{\partial x},$$

$$\frac{\partial p}{\partial \rho} = \frac{u}{\rho} \frac{\partial p}{\partial \rho} + \frac{\rho}{\rho} \frac{\partial T}{\partial \rho} + \kappa_e \frac{\partial c}{\partial x},$$

where $u$ is the velocity, $p$ is the pressure, $\eta$ is the viscosity, $c_p$ is the specific heat at constant pressure, $\alpha = 1/\rho \times (\partial p/\partial \rho)_{T, \rho}$ is the isothermal compressibility, $\beta_p = -1/\rho \times (\partial p/\partial T)_{\rho, \rho}$ is the thermal expansion coefficient, and $\kappa_e = 1/\rho \times (\partial \rho/\partial \rho)_{c, \rho}$ is the concentration contraction coefficient. Note that in order to get concise equations, $\eta$ has been fully substituted, while $i$ is retained.

In writing the governing equations in the above form, we have linearized the equation of state (EOS) around the initial state ($\delta$ represents the deviation from the initial value) and assumed constant physical properties. These approximations require small concentration perturbations at the left boundary. They are involved in the present work to keep the grace of the physical mechanisms and facilitate theoretical analyses in Section 3.

Mathematically, the BCs are given by

$$x = 0, \quad \frac{\partial T}{\partial x} = 0, \quad c = c_i + \Delta c, \quad \text{or} \quad \frac{\partial c}{\partial x} = -g_0, \quad u_0 = \frac{D g_0}{1-c_i},$$

$$x = L, \quad \frac{\partial T}{\partial x} = \frac{\partial c}{\partial x} = u = 0,$$

where we use the subscript 0 to denote a quantity at $x = 0$, and consider the BC for $c$ to be Dirichlet or Neumann type with the adjustable quantity of $\Delta c$ or $g_0$, respectively.

Note that the non-zero $u_0$ is caused by the partial permeability of the left boundary (only the component $A$ is permeable) [23]:

$$u_0 = \frac{1}{\rho (1 - c_i)} \frac{D}{1 - c_i} \frac{\partial c}{\partial x} \big|_{x=0} \approx \frac{D g_0}{1 - c_i},$$

where the approximation is justified since the concentration perturbations considered in this study are small.

3. Theory

In this section, we present a theory to account for and analytically model the PPE. We plot in Fig. 2 a heuristic explanation for the behavior of the BL, where $u_0$ is the boundary velocity caused by the partial permeability of the left wall (see Eq. (10)), and $u'$ is the velocity amplitude of the acoustic wave. Without loss of generality, we consider the case of $u_0 > 0$ (a result of a positive $g_0$ or $\Delta c$), $k_T > 0$ and $\kappa_e < 0$. In this situation, the cross-boundary diffusion flux of $A$ induces $u_0$. Then there forms a concentration BL, expanding in the velocity $u_0$ owing to $\kappa_e < 0$. Also, an accompanying heat flux due to the DE enters the fluid ($k_T > 0$), leading to a thermal BL expanding in the speed of $u_0$. We define the thickness of the BL, denoted by $L_{BL}$, as the very first location measured from $x = 0$ where both $T$ and $c$ remain unperturbed in terms of pure diffusion. We define the acoustic timescale as $t_a = L/u_0$, where $u_0$ is the speed of sound. Because on the acoustic timescale, $L_{BL}$ is very small and $t_a$ is usually a large value, we assume the perturbations reach $x = L_{BL}$ at the same time, leading to

$$u' = u_0 + u_d + u_c.$$
3.1. The emission of the acoustic wave

We assume the expansion of the BL is isobaric [1] and neglect the viscous heating and the velocity in the BL (since their effects are second-order). Eqs. (5) and (6) are simplified into

\[
\frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} - \frac{k_i}{\rho_i \epsilon_{\text{BS}}} \frac{\partial \tilde{u}}{\partial x}
\]

(12)

\[
\frac{\partial \tilde{u}}{\partial t} = \frac{1}{\rho_i} \frac{\partial \tilde{u}}{\partial x}
\]

(13)

respectively, where \( \rho_i = \rho_i^0 \) is the initial density. Integrating the two equations over the whole BL we obtain

\[
\int \frac{\partial \tilde{u}^2}{\partial t} \, dx = \frac{k_i}{\rho_i \epsilon_{\text{BS}}} \int \frac{\partial \tilde{u}}{\partial x} \, dx = \frac{1}{\rho_i^0} \tilde{u}_0.
\]

According to the linearized EOS and the relationship between \( \tilde{u}_0 \) and \( u_0 \) given in Eq. (10), Eq. (11) can be transformed into

\[
u' = \beta_p \frac{\partial \tilde{u}^2}{\partial t} - \kappa \frac{\partial \tilde{u}^2}{\partial t} \, dx + u_0 = \varphi_u u_0,
\]

(14)

where

\[
\varphi_u \equiv \frac{u'}{u_0} = 1 + (1 - c_i) \left( \frac{k_i \beta_p}{c_i \epsilon_{\text{BS}}} - \kappa \right)
\]

(15)

dis is a dimensionless ratio of the total perturbation velocity to the boundary one.

\( \varphi_u \) is an important thermodynamic indicator of the MPE. On the one hand, the absolute value of \( \varphi_u \) reflects the amplification effect of the BL to \( u_0 \). On the other hand, the sign of \( \varphi_u \) reflects the nature of the acoustic wave. If the initial propagation direction of the perturbation (before reflection) is taken as the positive direction, \( u' = \varphi_u u_0 > 0 \) corresponds to a compression wave (CW) or heating MPE, while \( u' = \varphi_u u_0 < 0 \) results in an expansion wave (EW) or cooling MPE. In a limiting case of \( c_i = 1 \), the problem degenerates into an injection (or extraction) of pure fluid \( A \), so \( \varphi_u = 1 \). The MPE is thus solely driven by the mechanical perturbation of \( u_0 \).

Given \( u' \), the amplitude of density \( \rho' \), pressure \( p' \) and temperature \( T' \) can be obtained directly from mass conservation and the isentropic nature of the acoustic wave [13]. The expressions for the amplitudes \( u', \rho', p' \) and \( T' \) can be summarized and written in a compact form:

\[
\begin{bmatrix}
u' \\ \rho' \\ p' \\ T'
\end{bmatrix} = \begin{bmatrix}
\varphi_u \\ \varphi_p \\ \varphi_p \\ \varphi_T
\end{bmatrix} u_0,
\]

(16)

where

\[
\varphi_p = \frac{\rho_i}{u_0} \varphi_u, \quad \varphi_p = \rho_i u_0 \varphi_u, \quad \varphi_T = \frac{T \beta_p v_p}{c_p} \varphi_u.
\]

(17)

are thermodynamic indicators, standing for the amplitudes of the denoted properties (see their subscripts) under the perturbation of unit \( u_0 \). Note that \( \rho', p', T' \) are evaluated in the direction of \( u' \). So if the initial propagation direction of the perturbation (before reflection) is taken as the positive direction, \( \rho', p', T' > 0 \) means a CW (namely the heating MPE), while they are negative for an EW (namely the cooling MPE).

3.2. The propagation of the acoustic wave

Based on the description presented at the beginning of this section, we develop the following equations to describe the propagation of the acoustic wave in the bulk fluid:

\[
f(x, t) = \begin{cases}
\sum_{n=1}^{\infty} \int f(t - \tau(x, n)) H(t - \tau(x, n)), & f \in \{u\}, \\
\sum_{n=1}^{\infty} \int f(t - \tau(x, n)) H(t - \tau(x, n)), & f \in \{p, p, T\},
\end{cases}
\]

(18)

where

\[
f'(s) = \varphi_u u_0(s),
\]

(namely Eq. (16)), \( H[s] \) is the Heaviside step function satisfying

\[
H[s] = \begin{cases}
1, & s \geq 0, \\
0, & s < 0.
\end{cases}
\]

and

\[
\tau(x, n) = |n - \text{mod}(n, 2)| t_0 + (1)^{n-1} x / u_0,
\]

(19)

with \( n \) being an integer obeying \( 1 \leq n < t / t_0 + 1 \).

The physics behind the above equations is straightforward. The integer \( n \) indicates the minimum upper bound for how many times the perturbations are being superposed in the whole domain (the upper bound of how many acoustic times have been consumed). For a specific \( x \) and \( t \), the array \( \tau \) gives the time taken by these perturbations to reach the location \( x \), and the array \( (t - \tau) \) calculates the moments when they were created. The transient amplitude is a superposition of all the perturbations that are reaching \( x \), which is accomplished by Eq. (18). For \( u' \), the reflection results in a change in its sign, so its expression is different from those of \( \rho', p' \) and \( T' \) since the reflection does not alter the nature of the acoustic wave (CW or EW). We will test this theoretical representation by comparing with numerical simulations in Section 4.5.

3.3. Energy balance analysis

Neglecting the viscous heating, the equivalent form of Eq. (5) written for \( c_v \) is given by

\[
\frac{\partial \rho c_v T}{\partial t} = - \frac{\partial \rho c_v u T}{\partial x} + \lambda \frac{\partial^2 T}{\partial x^2} + \left( \frac{T \beta_p \kappa}{\rho \alpha T} - \frac{\kappa_i}{\alpha_i} \right) \frac{\partial u}{\partial x} - \frac{T \beta_p}{\alpha} \frac{\partial u}{\partial x}.
\]

(20)

To facilitate theoretical analysis, we linearize this equation as

\[
\frac{\partial \rho c_v T}{\partial t} = - \frac{\partial \rho c_v T u}{\partial x} + \frac{\lambda}{\kappa} \frac{\partial^2 T}{\partial x^2} + \left( \frac{T \beta_p \kappa_c}{\rho \alpha T} - \frac{\kappa_i}{\alpha_i} \right) \frac{\partial u}{\partial x} - \frac{T \beta_p}{\alpha} \frac{\partial u}{\partial x},
\]

(21)

since the perturbations are small. Integrating the above equation over the whole domain and applying the BCs yield

\[
E_{in}(t) = \frac{\partial}{\partial t} \int_0^x \rho c_v T \, dx = \left( \rho c_v T + \frac{T \beta_p}{\alpha} u_0 \right) + \rho_i (1 - c_i) \frac{k_i}{c_i} u_0 - \rho_i (1 - c_i) \frac{T \beta_p}{\rho \alpha T} u_0,
\]

(22)

where \( E_{in} \) is energy injection rate. We divide the right-hand side of Eq. (22) into three parts: The term I stands for the energy carried by the boundary velocity, where the second quantity in the bracket is a correction for this non-isochoric process. The term II represents in the thermal effect of diffusion, namely the DE. The term III comes from \( T \beta_p (p / \alpha T) \epsilon_{\text{BS}} (\text{D}c / \text{D}t) \), representing the concentration-related pressure work rate, which vanishes for an isobaric process. The energy reception rate of the bulk fluid is actually the rate of the BL’s mechanical work, which can be expressed as (neglecting small pressure variations)

\[
E_{bulk}(t) = \rho_i u'.
\]

(23)
In previous studies about thermal PE, the energy efficiency is defined as \( \xi \equiv \frac{E_{\text{bulk}}}{E_{\text{mod}}} \) [12], reflecting the energy transfer capability of the PE. After a calculation, this traditional definition leads to

\[
\xi = r_{\text{mod}}^{\rho_{\text{mod}}^0} + r_{\text{mod}}^{\rho_{\text{mod}}^0} + r_{\text{mod}}^{c_{\text{mod}}^0},
\]

where

\[
r_{\text{mod}}^{\rho_{\text{mod}}^0} = \frac{1}{1 + \frac{I}{I_{\text{mod}}}}, \quad r_{\text{mod}}^{\rho_{\text{mod}}^0} = \frac{I}{1 + \frac{I}{I_{\text{mod}}}}, \quad r_{\text{mod}}^{c_{\text{mod}}^0} = \frac{I}{1 + \frac{I}{I_{\text{mod}}}},
\]

are the ratios of the individual terms to their arithmetic sum, and

\[
E_{\text{mod}}^{\rho_{\text{mod}}^0} + E_{\text{mod}}^{\rho_{\text{mod}}^0} + E_{\text{mod}}^{c_{\text{mod}}^0} = \rho_{\text{mod}}^0 + \rho_{\text{mod}}^0 + \rho_{\text{mod}}^{c_{\text{mod}}^0},
\]

are the energy efficiencies of boundary velocity, DE and concentration variation, respectively. These efficiencies are pure thermodynamic properties. Note that because the expansion due to DE is essentially a thermal effect, \( \xi_{\text{mod}}^0 \) is the same as the energy efficiency of the thermal PE [13].

In Eq. (24), we have expressed \( \xi_{\text{mod}}^0 \) as a weighted average of the three sub-efficiencies in Eq. (26). We notice that when both \( k_t \) and \( -k_e \) are positive (i.e., \( I > 0 \), Eq. (24) is physically clear and correct. However, in other situations, Eq. (24) no longer reflects the average effect of three aspects and one may get puzzling results such as \( \xi_{\text{mod}}^0 < 0 \). Hence, to fix this issue by virtue of a truly weighted average, we define the modified \( \xi_{\text{mod}}^0 \) as

\[
\xi_{\text{mod}}^0 = r_{\text{mod}}^{\rho_{\text{mod}}^0} + r_{\text{mod}}^{\rho_{\text{mod}}^0} + r_{\text{mod}}^{c_{\text{mod}}^0}.
\]

The other important aspect of the MPE is the efficiency of thermalization, which is measured by the temperature efficiency \( \xi_T \), defined as the ratio of the bulk temperature change rate \( T_{\text{bulk}} \) induced by the acoustic wave, to the ideal one \( T_{\text{ideal}}^{\text{bulk}} \) the expected bulk temperature change rate if the energy is uniformly distributed in the fluid. According to the feature of the acoustic wave and Eq. (22), they are given by

\[
T_{\text{bulk}}(t) = T_{\text{mod}}^{\text{ideal}}(t), \quad T_{\text{ideal}}^{\text{bulk}}(t) = \frac{E_{\text{ideal}}(t)}{\rho_{\text{ideal}}C_L}.
\]

The traditional definition of \( \xi_T \) contains the same issue as in \( \xi_{\text{mod}}^0 \). Therefore, we focus on the modified temperature efficiency \( \xi_{\text{mod}}^T \), and obtain its expression after a calculation

\[
\xi_{\text{mod}}^T = r_{\text{mod}}^{\rho T_{\text{mod}}^0} + r_{\text{mod}}^{\rho T_{\text{mod}}^0} + r_{\text{mod}}^{c T_{\text{mod}}^0},
\]

where

\[
E_{\text{mod}}^{\rho T_{\text{mod}}^0} + E_{\text{mod}}^{\rho T_{\text{mod}}^0} + E_{\text{mod}}^{c T_{\text{mod}}^0} = \rho_{\text{mod}}^T + \rho_{\text{mod}}^T + \rho_{\text{mod}}^{c T_{\text{mod}}^0},
\]

are the temperature efficiencies of boundary velocity, DE and concentration variation, respectively. In fact, the calculation gives \( \xi_{\text{mod}}^T = 1 \), which is somehow unphysical since \( \xi_{\text{mod}}^0 < 1 \). We attribute this puzzling value to the linearization we applied throughout the analysis, which results in the disregard of high-order terms. Hence in real situations, we conjecture \( \xi_{\text{mod}}^T \) should tend to but smaller than 1. So we write \( \xi_{\text{mod}}^T \rightarrow 1 \) in Eq. (31). Besides, \( \xi_{\text{mod}}^T \rightarrow 1 \) also conforms to the previous conclusion that the temperature efficiency of thermal PE (exactly \( \xi_{\text{mod}}^0 \) due to the thermal nature of the DE) is close to 1 [4,12].

In this section, we propose a theoretical model for the MPE, including the expressions of various amplitudes, the theoretical representation of the propagating wave, and the modified energy and temperature efficiencies. In the next section, we apply our theory to C₂H₆ – CO₂ binary fluid, which is an extensively used model system to study the critical behavior of binary mixtures [24]. On the other hand, by applying to a real fluid system, we can understand the behavior of the involved thermodynamic quantities in the critical region over a whole concentration range. Essentially, the critical universality guarantees the generality of our conclusions. On the other hand, we can test the theory by comparing with numerical simulations of the full equations.

4. Application to C₂H₆ – CO₂ system

4.1. Modeling of physical properties

The phase diagram and the critical behavior of the physical properties of a binary fluid mixture are more complicated than a pure fluid, which has been studied extensively since the 1970 s. In short, the complexity can be understood from the following three aspects:

(1) Phase behavior. For binary fluid mixtures, according to the classification of van Konynenburg and Scott [25], there are six basic types of phase behavior. In actual applications such as chemical extractions, the phase behavior is further complicated by the presence of solid phases [26]. Except for conventional liquid-vapor critical phenomena, the binary mixtures can also exhibit liquid-liquid critical phenomena, where the CPs are referred to consolute points (the liquid-vapor CPs considered in this study are also known as plait points) [27]. Given the complexity, the theoretical modeling of the critical behavior of physical properties has been mainly focused on some reference mixtures [27], such as \(^4\text{He} – ^4\text{He}, \text{C}_2\text{H}_6 – \text{CO}_2, \text{CH}_4 – \text{C}_2\text{H}_6\). These reference mixtures exhibit the type I phase behavior, where the locus of the liquid-vapor critical points is a continuous function of c.

(2) Thermodynamic properties. It has been acknowledged that asymptotic close to a liquid-vapor CP, the universal scaling laws of pure fluids can be generalized to binary fluids as long as a hidden field, usually taken as \( \mu \), is kept constant instead of the convenient field \( c \) [27]. However, the EOS developed on this idea is not practical for the current work since the asymptotic region is substantially small. Along the critical isochore, the asymptotic region usually lies in \( c < 10^{-3} \) [28]. We do not intend to get so close to the CP because the Navier-Stokes equations may become invalid [29]. In order to model the properties in a wider region around the CP, the crossover EOS must be implemented [30], which bridges the asymptotic behavior and the regular behavior far away from the CP. Such a kind of EOS has mainly been developed for the above-mentioned reference mixtures.

(3) Transport properties. Asymptotic close to a CP, the scaling laws predict D vanishes while Kₜ diverges for a binary mixture [31]. However, similar to thermodynamic properties, the validity of the asymptotic scaling laws for transport properties are also restricted to a small vicinity around the CP. In order to describe the transport properties in a wider range, one must include the crossover to the classical behavior far away from the CP. Crossover models for transport properties have been successfully proposed for some reference mixtures.
Accurate predictions of the physical properties are prerequisite for the present work. It requests us to implement a complete crossover model to calculate all the involved physical properties. After a survey on the available models, we chose \( \text{C}_2\text{H}_6 - \text{CO}_2 \) as a reference fluid system. It has drawn substantial attention because it exhibits critical azeotropy at a particular composition, under which some properties would show pure-fluid-like behavior [32]. Moreover, Kiselev and his coworkers had [30,33,34] published a series of practical and effective approaches for the predictions of physical properties in a wide critical region for \( \text{C}_2\text{H}_6 - \text{CO}_2 \) and other simple reference mixtures. In this paper, the thermodynamic properties are predicted by the parametric crossover EOS developed by Kiselev and Rainwater [33]. Different from normal cubic EOS, it is written for the isomorphic Helmholtz free energy. The expressions for thermodynamic derivatives have been summarized in [30]. The critical locus of \( \text{C}_2\text{H}_6 - \text{CO}_2 \) is calculated by the equations proposed by Abbaci et al. [32]. The transport properties are calculated by the practical representation proposed by Kiselev and Huber [34], which incorporates the crossover from universal scaling laws to regular background parts.

4.2. Critical behavior of the physical properties

We present in Fig. 3 the contours of eight representative properties as functions of \( \varepsilon \) (from \( 10^{-6} \) to \( 10^{-1} \)) and \( c \) for \( \text{C}_2\text{H}_6 - \text{CO}_2 \) mixture along the critical isochore. The horizontal axes are in log-

![Fig. 3. Contour plots for some representative physical properties of \( \text{C}_2\text{H}_6 - \text{CO}_2 \) mixture along the critical isochore for \( 10^{-6} \leq \varepsilon \leq 10^{-1} \) over the whole concentration range. (a) The specific heat at constant pressure \( c_p \), (b) the specific heat at constant volume \( c_v \), (c) the concentration contraction coefficient \( \kappa_c \), (d) the partial molar enthalpy \( \bar{H} \), (e) the thermal diffusion ratio \( k_T \), (f) the concentration susceptibility \( c_s \), (g) the diffusion coefficient \( D \), and (h) the thermal conductivity \( \lambda \). Solid curves: positive levels, dotted curves: negative and zero levels, and dashed lines: azeotropic concentration. The horizontal axes are in logarithmic scale.](image-url)
arithmetic scale, while the vertical axes vary linearly. The levels of the contour lines are chosen to clearly exhibit the critical behavior. We use solid curves for positive levels and dotted curves for negative and zero levels. The dashed lines are plotted to denote the azotropic concentration, which is predicted to be \( c = 0.218 \). We note that there is a small difference between the previously reported value of 0.21 in [32]. At the azotropic concentration and along the liquid-vapor coexistence curve, liquid and vapor phases are identical in compositions. The mixture hence behaves like a pure fluid.

At the pure-fluid conditions \((c = 0.1)\), the classical critical behavior is observed, such as the strong divergence of \( \rho_p \) (see Fig. 3a), the critical enhancement of \( \lambda \) (see Fig. 3h) and the weak divergence of \( c_p \) (see Fig. 3b). For other physical properties of mixtures, we note that \( k_T = c_s = 0 \) (see Fig. 3e and f). \( \kappa_c \) and \( H \) diverge strongly (see Fig. 3c and d), and \( D \) remains finite (see Fig. 3g). The existence of critical azeotropy complicates the critical behavior. At the azotropic state, as manifested by Fig. 3, the pure-fluid behavior shows up again, except that \( c_s \) remains finite instead of being zero, and \( k_T \) and \( H \) being zero instead of the strong divergence. In the two regions sandwiched by these three special concentrations, there are continuous transitions from pure-fluid behavior to mixture’s ones. As a result, the divergences of \( \rho_p, \kappa_c \) and \( H \), and the critical enhancement of \( \lambda \) are weakened, while the strong divergences of \( k_T \) and \( c_s \), and the vanishing of \( D \) appear.

Overall, the critical behavior of most properties is featured by a two-layer structure, bounded by the pure-fluid limits from top and bottom and separated by the critical azeotropy in the middle. Besides, in the present range of \( \varepsilon, k_T, \kappa_c \) and \( H \) alter their signs. The negative values of \( k_T \) and \( \kappa_c \), together with the positive values of \( H \), only appear when \( c \) is lower than the azotropic concentration. For later reference, we summarize the critical behavior for all the involved properties in Table 1.

### 4.3. The emission of the acoustic wave

Now we study the emission of the acoustic wave on the parametric space of \( \varepsilon \) and \( c \). In this section, we let all initial states in the parametric space subjected to an identical \( u_0 \) (\( u_0 \) is taken as the external factor). As a result, according to Eq. (16), the differences in various initial states in terms of wave emission can be understood directly from \( \varphi_{\varepsilon}, \varphi_c, \varphi_D \) and \( \varphi_{\kappa_c} \).

Fig. 4 presents the contour plots of \( \varphi_{\varepsilon}, \varphi_c, \varphi_D \) and \( \varphi_{\kappa_c} \) on the parametric space. It is striking to note that their distributions are very similar. According to Eq. (17), it suggests that the additional multipliers in \( \varphi_c, \varphi_D \) and \( \varphi_{\kappa_c} \) compared to \( \varphi_\varepsilon \) mainly influence the magnitudes, while the trends and relative sizes are almost unaffected. Therefore, without loss of generality, our discussions are centered on \( \varphi_\varepsilon \) (see Eq. (15) and Fig. 4a). First consider the behavior at the three special concentrations. At \( c = 0 \), we infer from Table 1 that \( \varphi_{\varepsilon} \) diverges strongly to the positive infinity, since \( k_T = 0 \) and \( \kappa_c \) diverges strongly to the negative infinity. At the azeotropic concentration \((c = 0.218)\), as the CP is approached, \( \varphi_{\varepsilon} = 1 \) due to \( k_T = \kappa_c = 0 \). At \( c = 1 \), Eq. (15) also yields \( \varphi_{\varepsilon} = 1 \). Second, consider the behavior in the two sandwiched regions. For a concentration between \( c = 0 \) and \( c = 0.218 \), \( \varphi_{\varepsilon} \) is always positive.

As the CP is approached, it first varies gently until a weak divergence appears. The intensity of the divergence and the \( \varepsilon \) where the divergence starts to occur decrease with \( c \). For a concentration between \( c = 0.218 \) and \( c = 1 \), the behavior is more complicated. If the mixture is not dilute, as the CP is approached, \( \varphi_{\varepsilon} \) undergoes a transition from a positive value to a negative one. The transition points are indicated by the solid curve in Fig. 4. The weak divergence only appears in the negative region, whose intensity and range increase at first, and then decline as \( c \) tends to 1. However, if the mixture is dilute, \( \varphi_{\varepsilon} \) is mainly governed by the first term in Eq. (15), thus being a value close to 1. We summarize the above behavior in Table 2.

Physically speaking, Fig. 4 is very informative to understand the emission of the acoustic wave. Consider the model shown in Fig. 1, where the positive direction has been set as the initial traveling direction of the acoustic wave (from left to right). If we further assume \( u_0 > 0 \), then the positive zones in Fig. 4 correspond to the CW (heating MPE, where the bulk temperature is increased), while the negative zones indicate the EW (cooling MPE, where the bulk temperature is decreased). As shown in Fig. 4(a), for \( 5 \times 10^{-4} \leq \varepsilon \leq 0.1 \), and if \( c \) is not extremely close to 0, \( \varphi_{\varepsilon} \) falls into the range of \([0.7, 4.6]\) (obtained for \( 0.007 \leq \varepsilon \leq 1 \)), so \( \varphi_{\varepsilon} \) is not sensitive to the variations of \( \varepsilon \) and \( c \). However, for \( \varepsilon < 5 \times 10^{-4} \), the strong or weak divergences occur and produce two singular cores. The first core is positive and centered at \( c = 0 \). Due to the strong divergence of \( \kappa_c, \varphi_\varepsilon \) develops a high peak on the order of \( 10^6 \) at \( \varepsilon = 10^{-6} \). However, the singularity is so sensitive to \( c \) that for \( c = 0.007 \) at the same \( \varepsilon, \varphi_{\varepsilon} = 58.25 \). The second one is negative and centered at \( c = 0.331 \), which equals \(-9.46 \) at \( \varepsilon = 10^{-6} \).

To understand the mechanism that governs the sign of \( \varphi_{\varepsilon} \), Fig. 5 plots the isolines of \( k_T = 0, \kappa_c = 0 \) and \( \varphi_{\varepsilon} = 0 \), where the three isolines divide the whole parametric space into four regions labeled as I to IV. The roles of the boundary velocity, DE, and concentration variation are listed in Table 3. It is interesting to note that only in region III that all of the three aspects are cooperating. In regions I and III, the negative factor is always offset by the two positive ones, until in region IV, where the negative factor, i.e., concentration variation, dominates and results in the negative zone.

### 4.4. The energy and temperature efficiencies

Fig. 6 presents the contour plots of individual energy efficiencies defined in Eq. (26) and the modified total energy efficiency defined in Eq. (27). As the CP is approached, \( \eta_{\text{T, e}} \) and \( \eta_{\text{T, f}} \) tend to a finite value around 0.14. On the contrary, \( \eta_{\text{T, e}} \), mainly influenced by \( c_s \), tends to zero slowly. For the three individual efficiencies,

<table>
<thead>
<tr>
<th>Properties</th>
<th>( \text{CO}_2 ) (c = 0)</th>
<th>( \text{C}_2\text{H}_6 ) (c = 1)</th>
<th>Azeotropy (c = 0.218)</th>
<th>0 \leq c \leq 0.218</th>
<th>0.218 \leq c \leq 1</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Fig. 3(a)</td>
</tr>
<tr>
<td>( H )</td>
<td>+</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(d)</td>
</tr>
<tr>
<td>( \kappa_c )</td>
<td>-</td>
<td>+</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(c)</td>
</tr>
<tr>
<td>( D )</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(g)</td>
</tr>
<tr>
<td>( k_T )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(e)</td>
</tr>
<tr>
<td>( c_s )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(f)</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(h)</td>
</tr>
<tr>
<td>( c_s, \lambda )</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>Fig. 3(b)</td>
</tr>
</tbody>
</table>
obvious variations are commonly observed in the high concentration regions far away from the CP (see the top right corners). Hence, in the other part of the parametric space, the three individual energy efficiencies change mildly with $c$ and $\varepsilon$.

As for the modified total energy efficiency shown in Fig. 6(d), by surveying the distributions of $f_{D\text{mod}}^r$ and $f_{C\text{mod}}^r$, we conclude that in a large portion of the parametric space, the total energy is mainly contributed by terms II and III. Therefore, $\varepsilon_{\text{mod}}^t$ is mainly confined between 0.1 and 0.15. Exceptions occur first in the high concentration region, where the term I dominates according to Eq. (22), leading to relatively low efficiencies. The second exceptional region where the term I dominates is the area confined by the two isolines of $k_T = 0$ (or $r_{D\text{mod}}^r$) and $j_c = 0$ (or $r_{C\text{mod}}^r$), where the low efficiency shows up again.

In Fig. 7, we plot the temperature efficiencies of the boundary velocity and DE defined in Eq. (31), and the modified total temperature efficiency defined in Eq. (30). According to Eq. (31), the critical behavior of $\varphi_{u\text{mod}}^t$ is also controlled by $c_v$, tending to 0 gradually as the CP is approached, as shown in Fig. 7(a). However, consistent with the previous conclusion of the temperature efficiency for
thermal PE, \( \dot{c}_E \) remains finite and being a high value close to 1, consistent with \( \xi_T \rightarrow 1 \). Similar to \( \dot{c}_E \) and \( \xi_T \), except for the region close to \( c = 1 \) and that confined by the isolines of \( k_l = 0 \) and \( k_r = 0 \) (see Fig. 7c). Therefore, in the majority area of the parametric space, \( \dot{c}_E \) is very high (close to 1). Moreover, \( \dot{c}_E \) is always larger than \( \xi_T \).

From the above discussions, we conclude that the MPE is more efficient in terms of thermalization than energy transfer. This conclusion is valid for each specific mechanism and their superpositions. Besides, compared to the boundary velocity, the DE and concentration variation are so alike that if the CP is close enough, we have \( \dot{c}_E \approx \xi_T \approx 0.14 \) and \( \dot{c}_E \approx \xi_T \approx 1 \). To some extent, it reflects the thermodynamic consistency between the two aspects, since they can be regarded as the mechanical response of a near-critical fluid to perturbations in a thermodynamic variable. However, because the boundary velocity is a purely mechanical effect, it owns different features, such as a relatively low \( \dot{c}_E \). As a result, the MPE is no longer an efficient thermalization process (but still fast) in the regions where the contribution of boundary velocity dominates.

### 4.5. Comparisons with numerical simulations

In this section, we test our theory by comparing with numerical simulations of the full governing equations. We choose the five reference states denoted by 1 to 5 in Fig. 5 (points 3 and 5 coincide). They are situated in different regions partitioned according to the interactions among different mechanisms. The physical properties at these states are summarized in Table 4. For cases 1 to 4, we apply Neumann BCs. For the sake of comparison, \( g_0 \) is given to generate a constant \( u_0 = 10^{-5} \) m/s for different cases. In case 5, we consider Dirichlet BC, namely a sudden concentration increase of \( 5 \times 10^{-5} \) occurs at the left boundary to understand the MPE under different BC and further test the theory.

### 4.5.1. Numerical method and validation

To simulate the MPE on acoustic time scale, Eqs. (2)–(7) with initial and BCs were solved by SIMPLE algorithm after finite volume discretization implemented based on OpenFOAM [35], an open source C++ library for computational fluid dynamics. Convective terms are discretized using a TVD (total variation diminishing) scheme with OpenFOAM’s limited linear limiter. Transient terms are discretized with a first-order Euler scheme. The mesh, including 1080 points, was refined near the boundaries so as to accurately represent thin BLs. A time step \( \Delta t = 0.01 \) s was chosen to assure proper numerical convergence of the solutions.

In 2006, Miura et al. [13] observed the acoustic waves experimentally using an ultra-sensitive interferometer. Continuous heating of 1.83 kW/m² is applied during 0.2 ms to a cell filled with near-critical \( \text{CO}_2 \). They measured density changes on a timescale of 1 ms. To validate our code, a simulation has been conducted in a 1D configuration and with the same initial and BCs as in the experiments. The comparisons are presented in Fig. 8, where generally fair agreements are noticed, with overestimation in the late stage of propagation. Such an overestimation is also observed in the calculation of Amiroudine et al. [36], where the same model but a totally different method was used. It thus suggests that the overestimation is a universal issue of the 1D model, where the lateral walls in the experimental apparatus are omitted. However, the no-slip nature of the lateral walls imposes damping effects on the acoustic waves. The neglecting of these effects is believed to result in the overestimation of the 1D calculation in the late stage of propagation.

### 4.5.2. Results and discussions

Let us first focus on cases 1 to 4. Case 5 will be discussed in the next section to elaborate the influences of the BC. Presented in Fig. 9 is the temperature profiles at different acoustic times for various cases, which are obtained from our theory (see Section 3.2) and numerical simulations. The corresponding velocity profiles

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Fig. 6. Contour plots for the energy efficiencies of individual mechanisms: (a) \( \xi_T \), (b) \( \xi_E \), and (c) \( \dot{c}_E \), along with that for \( \xi_T \) in (d). The solid curve in (d) represents the zero level of \( k_L \) (or \( \xi_T \)), and the dashed curve indicates the zero level of \( k_R \). The horizontal axes are in logarithmic scale.
are shown in Fig. 10. In each figure, a step-like CW (cases 1, 2 and 3) or EW (case 4) traveling in the fluid is observed, which reflects back at the right boundary with its nature (i.e. CW or EW) remains unchanged. As a result, the velocity changes its sign after reflection and offsets its later part. A traveling increase or decrease in the bulk temperature is identified. The profiles of $\delta \rho$ and $\phi$ are not shown here, because their shapes are identical to those of $\delta T$ with different magnitudes.

Comparing between the left and right columns of Figs. 9 and 10, our theoretical predications are in excellent agreements with the results from numerical simulations, except for the shapes of the wavefronts. In our theory, the wavefront is described by the Heaviside function. Hence, the gradient of the wavefront is infinite. However, in real situations, the gradient is finite and decreases with time due to diffusion. This is the main imperfection of the current theoretical representation. However, since the diffusion is usually very slow and its influence is relatively local, our theory is acceptable especially when the spatial resolution is not the main concern.

To further show the accuracy of the theory quantitatively, we list in Table 5 the amplitudes of the acoustic waves obtained from both methods. For simulations, we measure the amplitudes in the first acoustic time. The accuracies of our theory are satisfactory in all the four cases since the maximum absolute relative deviation (ARD) of theoretical predictions, defined by

$$\text{ARD} \% = \left| \frac{\text{theoretical prediction} - \text{simulation}}{\text{simulation}} \right|,$$

is only 1.36 % (in $T$ of case 1).

Fig. 7. Contour plots for the temperature efficiencies of individual mechanisms: (a) $\xi_T$ and (b) $\xi_P$, along with that for $\xi_{\text{mod}}$ in (c). The solid curve in (c) represents the zero level of $k_t$ (or $r'_t$), and the dashed curve indicates the zero level of $k_c$ (or $r'_c$). Note that $\xi_{\text{mod}}$ is not shown here since $\xi_{\text{mod}} = 1$ (see Eq. (31)). The horizontal axes are in logarithmic scale.

Fig. 8. The normalized density change at the cell center versus time. The set-up of the numerical model mimics the experiment of Miura et al. [13], serving as the numerical code.

Table 4
Details of the five simulated cases.

<table>
<thead>
<tr>
<th>No.</th>
<th>$c$</th>
<th>$\varepsilon$</th>
<th>$T_c$/(K)</th>
<th>$\rho_c$/(kg/m$^3$)</th>
<th>$c_p$/(J/kg/K)</th>
<th>$\sigma_r$/(1/Pa)</th>
<th>$\beta_p$/(1/K)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.18</td>
<td>$3 \times 10^{-5}$</td>
<td>293.39</td>
<td>372.10</td>
<td>$2.02 \times 10^5$</td>
<td>$1.14 \times 10^{-5}$</td>
<td>1.70</td>
<td>$-11.11$</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>$3 \times 10^{-2}$</td>
<td>298.12</td>
<td>419.94</td>
<td>$1.36 \times 10^4$</td>
<td>$6.65 \times 10^{-7}$</td>
<td>0.11</td>
<td>$-0.94$</td>
</tr>
<tr>
<td>3</td>
<td>0.60</td>
<td>$1 \times 10^{-5}$</td>
<td>294.52</td>
<td>248.81</td>
<td>$6.17 \times 10^4$</td>
<td>$3.69 \times 10^{-6}$</td>
<td>0.43</td>
<td>14.97</td>
</tr>
<tr>
<td>4</td>
<td>0.60</td>
<td>$1 \times 10^{-5}$</td>
<td>294.52</td>
<td>248.81</td>
<td>$6.77 \times 10^4$</td>
<td>$3.93 \times 10^{-6}$</td>
<td>0.46</td>
<td>15.95</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>$1 \times 10^{-3}$</td>
<td>294.52</td>
<td>248.81</td>
<td>$6.17 \times 10^4$</td>
<td>$3.69 \times 10^{-6}$</td>
<td>0.43</td>
<td>14.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>$c_t$/(J/kg)</th>
<th>$\eta$/(Pa s)</th>
<th>$\varepsilon$/(W/m$^2$/K)</th>
<th>$D_r$/(m$^2$/s)</th>
<th>$k_t$</th>
<th>$v_d$/(m/s)</th>
<th>$g_{\theta}$/(1/m)</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.53 \times 10^{-6}$</td>
<td>$3.59 \times 10^{-5}$</td>
<td>0.100</td>
<td>$1.74 \times 10^{-7}$</td>
<td>$-2.72 \times 10^0$</td>
<td>177.23</td>
<td>$4.713 \times 10^1$</td>
<td>$-$</td>
</tr>
<tr>
<td>2</td>
<td>$1.20 \times 10^{-6}$</td>
<td>$3.75 \times 10^{-5}$</td>
<td>0.052</td>
<td>$1.56 \times 10^{-7}$</td>
<td>$2.13 \times 10^{-1}$</td>
<td>406.09</td>
<td>$5.886 \times 10^1$</td>
<td>$-$</td>
</tr>
<tr>
<td>3</td>
<td>$5.45 \times 10^{-3}$</td>
<td>$2.49 \times 10^{-3}$</td>
<td>0.152</td>
<td>$1.39 \times 10^{-8}$</td>
<td>$1.15 \times 10^0$</td>
<td>169.95</td>
<td>$2.882 \times 10^2$</td>
<td>$-$</td>
</tr>
<tr>
<td>4</td>
<td>$1.54 \times 10^{-2}$</td>
<td>$2.49 \times 10^{-3}$</td>
<td>1.686</td>
<td>$8.58 \times 10^{-11}$</td>
<td>$1.99 \times 10^4$</td>
<td>132.13</td>
<td>$4.662 \times 10^4$</td>
<td>$-$</td>
</tr>
<tr>
<td>5</td>
<td>$5.45 \times 10^{-3}$</td>
<td>$2.49 \times 10^{-3}$</td>
<td>0.152</td>
<td>$1.39 \times 10^{-8}$</td>
<td>$1.15 \times 10^2$</td>
<td>169.95</td>
<td>$-$</td>
<td>$5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Because the increase rate of average bulk temperature is usually the main concern for a PE, we calculate the spatially average bulk temperature, denoted by $d_T^{\text{avg}}_{\text{bulk}}$, for each time step, and measure the ARDs of our theoretical predictions. The results are plotted in Fig. 11. All the curves suggest fast growths in ARDs after the initial emissions of the acoustic waves, followed by stable stages with slight oscillations. Our theory is satisfactory since the maximum ARD among the four cases is less than 5%.

### 4.5.3. Influences of boundary condition

Now we turn to discuss case 5. Fig. 12 presents the temperature and velocity profiles at several acoustic times obtained from both the numerical simulation (solid curves) and the theoretical representation in Section 3.2 (dash-dotted curves). In the theoretical representation, $u_0$, the external factor, is imported from the results of numerical simulation. Different from the MPE under the Neumann BC, the Dirichlet BC yields a pulse-like wavefront. In each period, $p$, $q$ and $T$ at a fixed point in the fluid first experience a sudden increase and then decrease gradually, differing from the behavior under Neumann BC (a sudden increase then remaining constant). Note that since it is a CW, the long-term average effect is to increase $p$, $q$ and $T$.

The shape of the acoustic wave is controlled by the temporal variation of $u_0$. According to Eq. (10), the behavior of $u_0$ is domi-
nated by $g_c$. Initially, the sudden increase of $c$ at left boundary induces a large gradient in a very short time, leading to a large cross-boundary diffusion flux. Then the gradient decreases gradually due to the establishment of the BL, resulting in a deceleration in expansion. In other words, if we consider the BL as a piston, it first moves rightward suddenly (causing a strong compression

**Fig. 10.** Velocity profiles at several acoustic times for cases 1 to 4 in Table 4 subjected to a constant $u_0 = 10^{-5}$ m/s. See the caption of Fig. 9 for more details.

**Table 5**

Amplitudes of the acoustic waves obtained from numerical simulations within the first acoustic time (denoted by Sim.) and those calculated from our theory.

<table>
<thead>
<tr>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho^\ast (kg/m^3)$</td>
<td>0.057</td>
<td>0.056</td>
<td>0.033</td>
</tr>
<tr>
<td>$P^\ast (Pa)$</td>
<td>1.775</td>
<td>1.775</td>
<td>5.422</td>
</tr>
<tr>
<td>$T^\ast (\mu K)$</td>
<td>11.811</td>
<td>11.652</td>
<td>32.067</td>
</tr>
</tbody>
</table>
head in the wave) and then decelerates gradually (causing the gentle expansion tail). While in the Neumann BC, the piston moves in a constant speed, resulting in a step-like wavefront.

As shown in Fig. 12, the differences between the numerical and theoretical results lie in the steepnesses of wavefronts. Since the diffusion has been omitted in the theory, the wavefront is strongly pulse-like and does not vary with time. However, in simulations, the diffusion smooths the gradient of the wavefront, so it is gradually flattened over time. In the Dirichlet case, the size of the wavefront is substantially larger than that in the Neumann case, so the spatial resolution is more important. Fig. 13 presents $\delta T_{\text{avg}}^\text{bulk}$ calculated from the two methods as functions of $t$, together with the ARDs of our theoretical predictions. The two curves almost coincide, and the ARDs in the stable stage are less than 1.5%. Therefore, as far as the average effect of MPE is concerned, our theory is successful and reliable, which is consistent with the conclusions drawn under the Neumann BC.

So far, we have applied our theory to the typical $C_2H_6 – CO_2$ binary fluid. We have reported the distributions of various thermodynamic indicators of MPE on the parametric space of $\varepsilon$ and $\sigma$, in which the most informative ones are $\varphi_{\text{MPE}}$ (the relative intensity of the MPE and its nature, i.e., heating or cooling, see Fig. 4a), $\varphi_{\text{MPE}}^{\text{mod}}$ (efficiency of energy transfer, see Fig. 6d) and $\varphi_{\text{MPE}}^{\text{mod}}$ (efficiency of thermalization, see Fig. 7c). We have compared our theoretical representation with numerical simulations and excellent agreements have been shown under both Neumann and Dirichlet BCs. The main drawback of the current theoretical representation lies in the omitting of diffusion, so its flattening effect on the wavefront is not included. We have identified that it does not influence the increase rate of average bulk temperature, which is usually the main concern for a PE.
5. Conclusions

This paper is devoted to presenting the thermodynamic theory of the MPE induced by the cross-boundary partial diffusion flux in a binary fluid mixture near the liquid–vapor critical point. We discovered that the MPE is driven by three cooperative or competing mechanisms: $\omega_0$, the DE, and the concentration variation. We developed a full thermodynamic theory to formulate the amplitudes of the acoustic wave and the wave's propagation, along with the modified energy and temperature efficiencies measuring the capabilities of the MPE in terms of energy transfer and thermalization, respectively.

We then applied our theory to the representative binary mixture of $\text{C}_2\text{H}_6 - \text{CO}_2$ to understand the behavior of various thermodynamic indicators in a broad parametric space of $c$ and $e$, and to test the validity of the theory. As the CP is approached, the intensity of the MPE, measured by the thermodynamic ratio $\phi$, varies slowly first and then diverges weakly. Before the weak divergence appears, $\phi$ may alter its sign, which also changes the nature of the MPE (heating or cooling). Regarding the efficiencies, we identified that the DE and the concentration variation are featured by high efficiencies in thermalization (close to 1) and relatively low efficiencies in energy transfer (about 0.14), and their efficiencies tend to constant as the CP is approached. On the contrary, the efficiencies of $\omega_0$ are much lower and tend to zero as the CP is approached, which substantially reduce the total efficiencies in the regions where the energy carried by $\omega_0$ dominates. Through comparing with numerical simulations of different initial states and BCs, the predictions from the theory are quite satisfactory.

This work enriches the concept of the PE by introducing the energy flux carried by a cross-boundary mass diffusion, which is a common occurrence in chemical extraction processes. In the future, a promising direction is to explore other forms of cross-boundary energy flux to discover more new members of the PE's family.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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[2] B. Zappoli, D. Bailly, Y. Gharabos, B. Le Neindre, B. Zappoli, Thermal cycle around the critical point of $\text{C}_2\text{H}_6 - \text{CO}_2$ to understand the behavior of various thermodynamic indicators in a broad parametric space of $c$ and $e$, and to test the validity of the theory, as the CP is approached, the intensity of the MPE, measured by the thermodynamic ratio $\phi$, varies slowly first and then diverges weakly. Before the weak divergence appears, $\phi$ may alter its sign, which also changes the nature of the MPE (heating or cooling).