

Calculation Methodology for the Degree of Non-equilibrium after Two-Phase Expansion of Air through a Nozzle in a PWR-Integrated Liquid Air Energy Storage System

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1. Introduction

The increasing penetration of intermittent renewable energy has intensified the imbalance between electricity supply and demand, motivating the load-following operation of pressurized water reactors (PWRs) in combination with energy storage systems (ESS) [1]. Among various ESS technologies, Liquid Air Energy Storage (LAES) has emerged as a promising solution owing to its high round-trip efficiency (RTE), large energy density, and grid-scale power output using air as a natural working fluid [2].

In LAES, the liquid yield produced during the liquefaction process determines the discharge mass flow rate and therefore strongly governs the overall performance [3]. The liquid yield is fixed at the two-phase expansion stage, where the pressurized air is expanded into the two-phase region. In a previous study, the authors compared representative two-phase expansion configurations and showed that a single-phase expander (SPE) combined with a nozzle provides the best performance, in which the expansion is treated as isentropic [4]. The nozzle efficiency was further found to strongly affect not only the RTE and liquid yield but also the composition of the liquefied air, particularly the oxygen concentration that governs the long-term storage safety [5].

These analyses, however, were all conducted under the assumption of thermodynamic equilibrium after the ideal expansion. A preliminary survey of models for the rapid expansion of a fluid through a nozzle shows that non-equilibrium phenomena are unavoidable and that models accounting for this non-equilibrium describe the process more faithfully than an equilibrium assumption; among these, the Delayed Equilibrium Model (DEM) has been reported as the most suitable [6]. In the DEM, the rapid expansion is represented by carrying a metastable liquid — a liquid that does not vaporize even at temperatures higher than the saturation temperature because nucleation has not yet occurred — as a distinct phase alongside the saturated vapor and the saturated liquid, and the departure from equilibrium is quantified by a single scalar, the equilibrium degree γ . The DEM is only briefly introduced here and is described in detail in Section 2.1.

Existing DEM-based studies of non-equilibrium two-phase nozzle flow, however, have been developed for

pure fluids and employ the degree of non-equilibrium mainly to predict the critical mass flow rate and pressure [6,7]. For air, which is a multi-component mixture, the degree of non-equilibrium determines not only the liquid yield but also the composition of each phase, and thus the oxygen concentration of the stored liquid air. The degree of non-equilibrium is therefore critical for both performance and storage safety, yet no value nor model exists for a multi-component air mixture.

The present study therefore proposes a methodology to calculate the equilibrium degree, γ , at the nozzle outlet for a two-phase expansion of air. Building upon an existing pure-fluid DEM, the pure-fluid γ calculation and its limitation for a mixture are first examined, and the methodology is then extended to a multi-component air mixture for a single-phase-to-two-phase expansion. Finally, an experimental method and concept to determine γ for air are proposed.

2. Delayed Equilibrium Model for a Two-Phase Nozzle

2.1 Overview and assumptions of the DEM

Two-phase flow models can be classified by whether mechanical, kinetic, and thermal/chemical equilibrium are assumed between the phases. The Homogeneous Equilibrium Model (HEM) assumes equilibrium in all three, whereas the DEM assumes mechanical (equal pressure) and kinetic (equal velocity) equilibrium while retaining the thermal and chemical non-equilibrium [6]. For the rapid expansion of cryogenic air, the pressure and velocity differences between the phases are negligible while the thermal and chemical departure from equilibrium is dominant, so the DEM is adopted as the two-phase model in this work.

The assumptions of the DEM are summarized in Fig. 1. The model carries three phases at each station — saturated vapor (SV), saturated liquid (SL), and metastable liquid (ML) — with equal pressure and velocity for all phases. The metastable liquid is a liquid that has not yet nucleated, so its temperature is higher and its pressure lower than the saturation values; its properties are evaluated as compressible and isentropic from an equation of state (EOS) extrapolated from the single-phase liquid region. Temperature equilibrium is imposed between the saturated vapor and the saturated liquid, whereas the metastable liquid remains in thermal

non-equilibrium with the others. The extent of this departure is quantified by the equilibrium degree γ , defined as the mass fraction of the mixture that has reached saturated equilibrium, so that $(1 - \gamma)$ is the metastable-liquid fraction and $\gamma = 1$ recovers the fully equilibrated HEM limit; γ develops along the nozzle through a relaxation driven by the superheat of the metastable liquid.

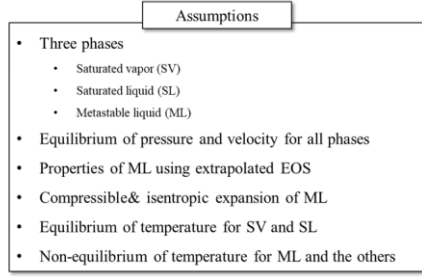


Fig. 1. Assumptions of the DEM

2.2 γ calculation for a pure fluid and its limitation

The measurable variables are listed in Table I. For a pure fluid, only the pressure, temperature, and cross-sectional area at the nozzle inlet and outlet, together with the total mass flow rate, are measured, and none of the metastable-liquid properties is measured directly. The procedure that converts these measurements into the equilibrium degree γ , shown in Fig. 2, proceeds in three steps.

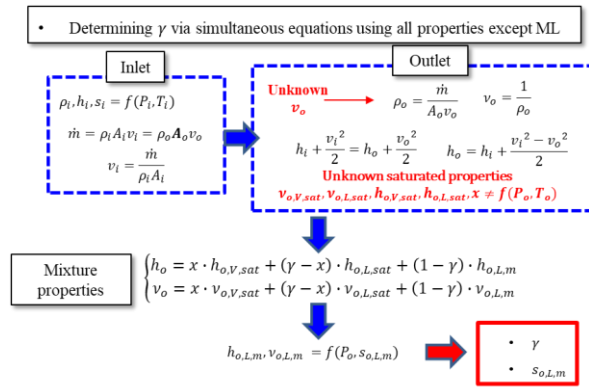


Fig. 2. Procedure of γ calculation based on DEM for pure fluid

Table I: Measurable variables of γ calculation at the nozzle exit for a pure fluid.

Measurable variables	Inlet			Outlet			Total
	P	T	A	P	T	A	Mass flow rate
Symbol	P_i	T_i	A_i	P_o	T_o	A_o	$\dot{m}$

First, the inlet state is fixed: from the measured inlet pressure and temperature the density, enthalpy, and entropy are obtained from the equation of state, and the inlet velocity is calculated from continuity as the mass flow rate divided by the inlet density and area. Second, the outlet is expressed in terms of a single unknown, the outlet velocity: the outlet density follows from continuity, and the outlet enthalpy from the energy balance between inlet and outlet, so that both depend only on the outlet velocity.

Third, the outlet mixture is decomposed into the three phases. Because a single pressure fixes the saturation state of a pure fluid, the saturated-vapor and saturated-liquid properties are known at the outlet pressure, whereas the vapor mass fraction and the metastable-liquid state are not fixed by pressure and temperature alone; the metastable-liquid properties come from the extrapolated equation of state as a function of the outlet pressure and the metastable-liquid entropy. Equating the mixture enthalpy and specific volume, written as the mass-weighted sum of the three phases (Fig. 2), to the outlet enthalpy and specific volume found above gives a closed set of equations whose only unknowns are the equilibrium degree γ , the vapor mass fraction, and the metastable-liquid entropy; solving them simultaneously yields γ at the nozzle exit.

This closure relies on the saturation state being fixed by pressure alone, which no longer holds for a multi-component mixture. For air, the saturated properties depend on the composition, so the phase compositions become additional unknowns and γ cannot be obtained from pressure and temperature alone. The following section extends the procedure accordingly.

3. Proposed γ Calculation Methodology for Multi-Component Air

Air is a binary mixture of nitrogen and oxygen, so at a given pressure the saturated vapor and the saturated liquid have different compositions, related through the bubble- and dew-point curves. The assumptions are revised as summarized in Fig. 3: the three-phase structure and the equilibrium of pressure and velocity are retained and the metastable liquid is still treated as compressible and isentropic, but the saturated vapor and the saturated liquid now take individually varying compositions whose equilibrated mixture equals the bulk composition (Z_i), while the metastable liquid keeps a constant composition equal to the inlet composition ($Z_o = Z_i$).

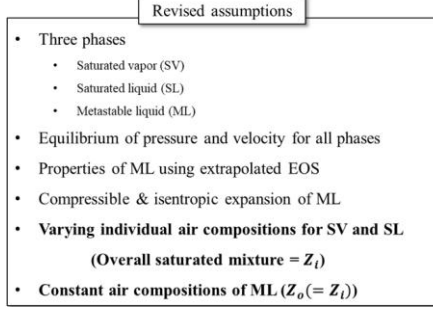


Fig. 3. Revised assumptions of the DEM for a two-component fluid.

The measurable variables are listed in Table II. Two composition measurements are added relative to the pure fluid — the overall oxygen concentration at the inlet and the vapor oxygen concentration at the nozzle outlet — in addition to the pressure, temperature, and area at the inlet and outlet and the total mass flow rate. These compositions are indispensable because, for a binary mixture, the outlet pressure no longer fixes the saturation state: the saturated vapor and the saturated liquid lie on a tie-line of the bubble- and dew-point curves, and the measured outlet vapor composition pins this tie-line so that the saturated-vapor and saturated-liquid properties and the vapor mass fraction can be evaluated.

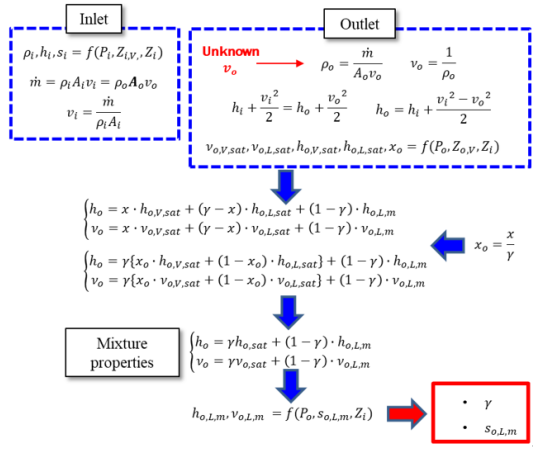


Fig. 4. Procedure of γ calculation based on the DEM for a two-component fluid

Table II: Measurable variables of γ calculation at the nozzle exit for a two-component fluid.

Measurable variables	Inlet				Outlet				Total
	P	T	A	Z	P	T	A	Z	Mass flow rate
Symbol	P_i	T_i	A_i	Z_i	P_o	T_o	A_o	$Z_{o,V,sat}$	$\dot{m}$

The calculation procedure, shown in Fig. 4, follows the same three steps as the pure fluid. The inlet state is

obtained from the inlet pressure and the measured inlet and overall compositions, and the inlet velocity from continuity; the outlet density and enthalpy are again written in terms of the unknown outlet velocity. The saturated-vapor and saturated-liquid properties and the vapor mass fraction are then evaluated from the outlet pressure together with the measured outlet vapor composition, which sets the saturated-liquid composition through the tie-line, while the metastable liquid keeps the inlet liquid composition and its properties come from the extrapolated equation of state.

Two additional relations then close the system, beyond the mixture enthalpy and specific-volume relations of Fig. 4: an overall oxygen mass balance that distributes the oxygen among the saturated vapor, the saturated liquid, and the metastable liquid, and the isentropic condition of the metastable liquid. The remaining unknowns — the equilibrium degree γ , the metastable-liquid entropy, and the outlet saturated composition — are then obtained by solving these relations simultaneously. The result yields γ together with the composition of every phase, from which the liquid yield and the oxygen concentration of the stored liquid air follow directly.

4. Summary and Future Works

This study proposes a methodology to calculate the degree of non-equilibrium — the equilibrium degree γ — after a two-phase expansion of air through a nozzle in a PWR-integrated LAES, for which no γ framework for multi-component air had existed. The pure-fluid DEM procedure, which closes because the saturation state is fixed by pressure alone, is extended to a two-component air mixture by allowing the saturated-phase compositions to vary while keeping the metastable-liquid composition equal to the inlet composition, so that γ is obtained from commonly measurable variables together with the inlet and outlet compositions.

To supply these inputs, an experimental method and concept are proposed. A cryogenic two-phase air nozzle facility measures the pressure, temperature, and mass flow rate, and the phase-resolved oxygen concentration through a three-way sampling of the overall stream and of the vapor at the nozzle inlet and outlet. A converging nozzle of simple geometry is used to validate the framework, and the test matrix spans oxygen groups of 15, 18, and 21 vol% at nozzle-inlet saturation pressures of 4–6 bar.

Future work will broaden the dataset and add a test matrix that decouples the saturation pressure from the inlet quality, adopt a converging–diverging nozzle or a larger pressure ratio to access a wider γ range, develop a multi-component DEM for air using the measured γ dataset, and examine the generality of the framework for other multi-component mixtures beyond cryogenic air.

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REFERENCES

- [1] J.Y. Heo, J.H. Park, Y.J. Chae, S.H. Oh et al., Evaluation of various large-scale energy storage technologies for flexible operation of existing pressurized water reactors, *Nuclear Engineering and Technology*, 2021.
- [2] A. Vecchi, Y. Li, Y. Ding, P. Mancarella and A. Sciacovelli, Liquid air energy storage (LAES): A review on technology state-of-the-art, integration pathways and future perspectives, *Advances in Applied Energy*, 100047, 2021.
- [3] Yong Jae Chae et al., Preliminary Analysis of Two-Phase Expansion on Liquid Air Energy Storage System Integrated to a Conventional Pressurized Water Reactor, *ICAPP*, 2023.
- [4] Yong Jae Chae et al., Thermodynamic analysis of a PWR-integrated LAES considering composition change of liquefied air after cryogenic expansion, *Transactions of the Korean Nuclear Society Spring Meeting*, 2025.
- [5] Yong Jae Chae, Jeong Ik Lee, Performance and oxygen concentration assessment of two-phase expansion in a PWR-integrated LAES using a single-phase expander with nozzle, *Transactions of the Korean Nuclear Society Autumn Meeting*, 2025.
- [6] G. De Lorenzo et al., Benchmark of Delayed Equilibrium Model (DEM) and classic two-phase critical flow models against experimental data, *International Journal of Multiphase Flow*, 92, 112–130, 2017.
- [7] C. Tammone et al., Extension of the delayed equilibrium model to flashing flows of organic fluids in converging-diverging nozzles, *International Journal of Multiphase Flow*, 171, 104661, 2024.