

Numerical investigation of hydrogen bubble growth enhancement using variable-frequency ultrasonic waves

Jaesung Park^{ID}, Gihun Son^{ID} *

Research Institute for Smart Design & Manufacturing Technology, Department of Mechanical Engineering, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 04107, South Korea

ARTICLE INFO

Keywords:

Hydrogen production
Variable frequency
Phase change
Mass transfer
Rectified diffusion

ABSTRACT

The enhancement of hydrogen bubble growth induced by ultrasonic waves is investigated using a numerical model that incorporates both vapor phase change and dissolved hydrogen mass transfer. The model couples the Keller–Miksis equation with energy and hydrogen mass fraction equations, directly computing vapor phase change rates and hydrogen mass flux based on temperature and mass fraction fields. A bubble growing under ultrasonic excitation experiences a sudden increase in hydrogen mass under resonance conditions. The timing and magnitude of this rapid bubble growth are highly sensitive to ultrasonic frequency, emphasizing the need for precise frequency modulation to effectively induce bubble resonance and enhance hydrogen mass growth. The resonance frequency-bubble radius correlation for hydrogen bubbles in a supersaturated solution is provided, incorporating both vapor phase change and hydrogen mass transfer effects. Ultrasonic waves with a variable resonance frequency, adapting to the continuously growing bubble, significantly enhance hydrogen accumulation within the bubble compared to both silent conditions and conventional single-frequency excitation. The influence of operating parameters, including the initial bubble radius, electrolyte concentration, and temperature, on the hydrogen mass enhancement achieved by variable-frequency excitation is also examined.

1. Introduction

Hydrogen, with its high energy density, is recognized as a sustainable and eco-friendly energy source, particularly when integrated with renewable energy. Among various methods for obtaining hydrogen, the alkaline electrolysis process (AWE) is a widely utilized eco-friendly approach that produces hydrogen without emitting carbon byproducts such as carbon monoxide and carbon dioxide. In AWE, bubbles help alleviate dissolved hydrogen gas accumulation around the electrode [1], but their undesirable coverage of active sites and ion transport blockage increase cell resistance, leading to excessive energy consumption and reduced production efficiency [2,3]. Various strategies, including ultrasound, electrolyte flow, and magnetic force, have been explored to control hydrogen bubble dynamics in AWE [2,4].

Ultrasound is a promising tool for removing bubbles from the electrode, driving extensive experimental research on ultrasound-assisted alkaline water electrolysis [5–7]. Li et al. [5] defined hydrogen production efficiency as the ratio of the experimentally collected hydrogen volume to the estimated volume from the ideal gas law and reported a 5–18% increase under ultrasonic excitation. Araujo et al. [6] defined the efficiency as the ratio of the measured hydrogen volume to the

electrical power supplied to the cell and also reported improved efficiency in the presence of ultrasound. However, these definitions do not account for the electrical power required to generate the ultrasound field and therefore do not represent the net electrolysis efficiency. More recently, Kwon et al. [7] explicitly included the electrical power consumed by the ultrasonic transducer when evaluating the net power gain of ultrasonic-assisted electrolysis. They demonstrated that optimized ultrasound on/off timing can reduce the overall energy consumption even when the power input for ultrasound generation is taken into account. While most studies have focused on bubble removal, bubbles in AWE also act as hydrogen sinks by reducing dissolved gas concentration, thereby mitigating the concentration overpotential [1,8], and serve as carriers transporting hydrogen gas to collection surfaces, as in ultrasonic degassing [9]. Despite the critical role of bubbles in water electrolysis, research on increasing hydrogen production rates by promoting bubble growth using ultrasound remains limited.

Numerous studies [10–13] have investigated ultrasound-driven bubble growth to enhance various applications such as particle separation, cleaning, and emulsification. Chen et al. [10] effectively controlled the stable growth of carrier bubbles using high-frequency ultrasound

* Corresponding author.

E-mail address: gihun@sogang.ac.kr (G. Son).

<https://doi.org/10.1016/j.ijhydene.2026.154929>

Received 5 June 2025; Received in revised form 17 December 2025; Accepted 6 April 2026

0360-3199/© 2026 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

Nomenclature

Variables

$\bar{R}_b$	radius averaged over a single pulse cycle
$\dot{R}$	differentiation of radius
C	sound speed
c	specific heat at constant volume
C_H	Henry's constant
D_l	diffusivity
f_u	frequency of ultrasonic pulse
G	mass flux
h_{fg}	latent heat
M	Molar mass
m	mass
p	pressure
P_u	pressure amplitude of ultrasonic pulse
R	radius
r	radial coordinate
R_g	gas constant
T	temperature
t	time
u	flow velocity
Y	mass fraction

Greek Symbols

α	accommodation coefficient
Δ	increment
γ	parameter in equations of state
λ	thermal conductivity
μ	viscosity
ρ	density
σ	surface tension coefficient

Subscripts

∞	ambient
b, l	bubble, liquid
g, h, v	gas, hydrogen, vapor
o	initial
s	surface
sat	saturation
u	ultrasonic

to enhance coal particle transport while preventing cavitation collapse. Sahoo et al. [11] suppressed the transition of bubble nuclei into large resonance radii matching the excitation frequency by surfactant adsorption onto bubble surfaces, mitigating excessive damage from cavitation collapse. Udepurkar et al. [12] regulated the upper limit of bubble growth, typically the resonant size where cavitation collapse occurs and tiny gas bubbles begin to be ejected, using high-frequency ultrasound to reduce oil emulsion size. The above studies focus on controlling bubble growth to induce or suppress acoustic cavitation, but research on utilizing frequency control or resonance effects to enhance ultrasound-driven bubble growth itself is still lacking.

Several experimental and numerical studies [14–16] have investigated bubble growth enhancement through dissolved gas mass transfer under resonance conditions. Soto et al. [14] experimentally visualized the sudden jump growth of CO₂ bubbles in a supersaturated liquid subjected to ultrasonic excitation. More recently, Smith and Wang [15,16] numerically examined the resonance-induced jump growth of spherical air bubbles with varying surfactant concentrations, emphasizing

the role of surfactant-modulated surface tension in rectified diffusion dynamics. While these studies provide important insights into resonance-driven bubble growth enhancement via frequency control, resonance-induced jump growth of hydrogen bubbles in the context of water electrolysis has remained largely unexplored.

In addition, several recent studies [17–19] have explored bubble growth enhancement by controlling the excitation frequency using dual- and multi-frequency ultrasonic excitation based on the Keller–Miksis equation. Zhang et al. [17,18] demonstrated that dual-frequency excitation can accelerate rectified diffusion-driven bubble growth and reported that the lower-frequency component, corresponding to a larger resonance radius, plays a dominant role. Wang et al. [19] showed that multi-frequency ultrasonic excitation can reduce the effective pressure threshold required for rectified diffusion-driven bubble growth; however, it did not increase the final bubble size compared to dual-frequency excitation. These findings suggest that combinations of fixed frequencies have inherent limitations in sustaining resonance during continuous bubble growth, thereby motivating the need for variable-frequency strategies.

Despite these advances, systematic numerical investigations of hydrogen bubble growth enhancement in water electrolysis using variable-frequency control remain scarce. To the best of our knowledge, no such systematic investigation has been reported. The present study addresses this gap by systematically examining resonance-induced hydrogen bubble growth under variable-frequency ultrasonic excitation.

In this study, a comprehensive numerical model for the diffusive growth of hydrogen (H₂) bubbles in supersaturated liquid, incorporating H₂ mass transfer and vapor phase change effects, is developed by coupling the Keller–Miksis (KM) equation with energy and H₂ mass fraction equations. The model directly calculates the vapor phase change rate and diffusive mass flux from local temperature and H₂ mass fraction distributions without additional assumptions. A resonant frequency-bubble radius relationship that considers both gas phase change and mass transfer effects is presented. Based on this formulation, a novel idea is proposed to promote hydrogen bubble growth by varying the resonant frequency depending on the bubble radius.

2. Numerical analysis

The numerical model simulates the evolution of a hydrogen-vapor mixture bubble in a 1M potassium hydroxide (KOH) solution with dissolved H₂ gas. The mixture spherical bubble is assumed to contain a uniform H₂ mass fraction Y_b , while the surrounding liquid contains dissolved H₂ with a spatially varying mass fraction Y_l . The bubble is initially in thermal and mechanical equilibrium, immersed in an ambient solution at $T_\infty = 50^\circ\text{C}$ and $p_\infty = 1\text{ atm}$, and undergoes periodic growth and contracts under applied acoustic waves. The Van der Waals (VDW) gas law is applied to accurately capture rapid bubble contraction and collapse [20–22]. Although this is not a primary consideration in the present study, the formulation incorporating the VDW gas law remains applicable under high-intensity ultrasonic excitation, where it provides a more reliable prediction of the internal pressure during intense bubble collapse than the ideal gas law. The VDW equation of state (EOS) for the ideal mixture bubble is written as

$$p = \frac{\rho R_g T}{1 - b\rho} - a\rho^2 \quad (1)$$

where

$$a_b = a_h Y_b^2 + 2\sqrt{a_h a_v} Y_b(1 - Y_b) + a_v(1 - Y_b)^2 \quad (2)$$

$$b_b = b_h \frac{M_b}{M_h} Y_b^2 + \frac{1}{4} \left[\left(b_h \frac{M_b}{M_v} \right)^{1/3} + \left(b_v \frac{M_b}{M_h} \right)^{1/3} \right]^3 Y_b(1 - Y_b) + b_v \frac{M_b}{M_v} (1 - Y_b)^2 \quad (3)$$

Here, R_g is the gas constant, a_b and b_b are the VDW coefficients for the mixture bubble expressed in terms of Y_b [21,23], and the subscripts h , v , and b refer to hydrogen, vapor and bubble, respectively. The molar mass M_b and gas constant $R_{g,b}$ inside the bubble are evaluated as $M_b^{-1} = M_h^{-1}Y_b + M_v^{-1}(1 - Y_b)$ and $R_{g,b} = R_{g,h}Y_b + R_{g,v}(1 - Y_b)$.

2.1. Governing equations

The acoustic cavitation model, incorporating vapor phase change and non-condensable gas effects from our previous study [21], is extended to account for the growth of hydrogen-vapor mixture bubble in supersaturated KOH solution. Assuming a homogeneous distribution of vapor and H_2 gas inside the bubble, the governing equations for the bubble, with uniform mass fraction Y_b and density ρ_b , are expressed as

$$\frac{\partial r^2 \rho_b u_b}{\partial t} + \frac{\partial}{\partial r}(r^2 u_b \rho_b u_b) = -r^2 \frac{\partial p_b}{\partial r} + \frac{4}{3} \left[\frac{\partial}{\partial r} r^2 \mu_b \left(\frac{\partial u_b}{\partial r} - \frac{u_b}{r} \right) + r \mu_b \left(\frac{\partial u_b}{\partial r} - \frac{u_b}{r} \right) \right] \quad (4)$$

$$\frac{\partial r^2 \rho_b e_b}{\partial t} + \frac{\partial}{\partial r}(r^2 u_b \rho_b e_b) = -p_b \frac{\partial}{\partial r}(r^2 u_b) + \frac{\partial}{\partial r} r^2 \lambda_b \frac{\partial T_b}{\partial r} + \frac{4}{3} r^2 \mu_b \left(\frac{\partial u_b}{\partial r} - \frac{u_b}{r} \right)^2 \quad (5)$$

Here, the bubble viscosity μ_b , the specific heat c_b , and the thermal conductivity λ_b , are evaluated as $\mu_b = \mu_h Y_b + \mu_v(1 - Y_b)$, $\lambda_b = \lambda_h Y_b + \lambda_v(1 - Y_b)$ and $c_b = c_h Y_b + c_v(1 - Y_b)$, respectively. The temperature is calculated from $T_b = (e_b + a_b \rho_b)/c_b$ and the pressure p_b is obtained from the VDW Eq. (1). It is noted that ρ_b and Y_b are explicitly obtained from the mass flux across the interface, which will be described later.

In the region of incompressible liquid KOH solution with dissolved H_2 gas, the conservation equations are expressed as

$$\frac{1}{r^2} \frac{\partial}{\partial r}(r^2 u_l) = 0 \quad (6)$$

$$\rho_l \left(\frac{\partial u_l}{\partial t} + u_l \frac{\partial u_l}{\partial r} \right) = -\frac{\partial p_l}{\partial r} + \mu_l \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u_l}{\partial r} \right) - \frac{2u_l}{r^2} \right] \quad (7)$$

$$\rho_l c_l \left(\frac{\partial T_l}{\partial t} + u_l \frac{\partial T_l}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \lambda_l \frac{\partial T_l}{\partial r} \right) + 2\mu_l \left[\left(\frac{\partial u_l}{\partial r} \right)^2 + 2 \left(\frac{u_l}{r} \right)^2 \right] \quad (8)$$

$$\rho_l \left(\frac{\partial Y_l}{\partial t} + u_l \frac{\partial Y_l}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho_l D_l \frac{\partial Y_l}{\partial r} \right) \quad (9)$$

The conservation Eqs. (4)–(9) are coupled through the following matching conditions, accounting for mass flux due to vapor phase change and H_2 mass transfer at $r = R_b$:

$$\rho_l (\dot{R}_b - u_{ls}) = \rho_{bs} (\dot{R}_b - u_{bs}) = G_b \quad (10)$$

$$Y_{ls} = C_H \frac{\rho_{bs}}{\rho_l} Y_{bs} \quad (11)$$

$$p_{ls} = p_{bs} - \frac{2\sigma}{R_b} + G_b^2 \left(\frac{1}{\rho_{bs}} - \frac{1}{\rho_l} \right) + 2\mu_l \left. \frac{\partial u_l}{\partial r} \right|_{r=R_b} - \frac{4}{3} \mu_b \left(\frac{\partial u_b}{\partial r} - \frac{u_b}{r} \right)_{r=R_b} \quad (12)$$

$$T_{ls} = T_{bs} = T_s \quad (13)$$

and the boundary conditions at $r = \infty$ are written as follows:

$$u_l = 0 \quad (14)$$

$$p_l = p_\infty + p_u \quad (15)$$

$$T_l = T_\infty \quad (16)$$

Here, p_u denotes an ultrasonic pressure condition and C_H is Henry's constant. Note that the bubble surface velocity $\dot{R}_b = dR_b/dt$ in Eq. (10) differs from u_{ls} and u_{bs} used in the conservation Eqs. (4), (6) and

(7) due to the total mass flux G_b from both vapor phase-change flux and H_2 mass transfer. Eq. (12) describes the force balance, accounting for pressure difference, surface tension, total mass flux, and viscous stress at the liquid-bubble interface. Eq. (11) is derived using Henry law, based on the densities and mass fractions inside and outside the bubble. The mass fraction interface condition allows discontinuity at the interface, while the temperature continuity is maintained in Eq. (13).

2.2. Mass fluxes from vapor phase change and hydrogen mass transfer

Considering the energy balance at the bubble-liquid boundary, the vapor transport rate G_v from evaporative phase change is obtained based on the heat flux at $r = R_b$ [24,25] as

$$G_v = \frac{1}{h_{fg}} \left(\lambda_l \left. \frac{\partial T_l}{\partial r} \right|_{r=R_b} - \lambda_b \left. \frac{\partial T_b}{\partial r} \right|_{r=R_b} \right) \quad (17)$$

To determine the bubble surface temperature T_s used in Eq. (17), the gas kinetic theory is applied as [21,23,26]

$$G_v = \frac{2\alpha}{2 - \alpha} \frac{p_{v,sat} - p_{vs}}{\sqrt{2\pi R_{g,v} T_s}} \quad (18)$$

Here, the accommodation coefficient α , which varies between 0 and 1 [26,27], governs the extent of vapor phase change at the bubble interface. In the present analysis, noticeable deviation appears only for $\alpha \leq 0.1$, whereas the results for $\alpha = 0.3$ – 0.7 show minimal difference. Accordingly, an intermediate value of $\alpha = 0.5$ is adopted in this study. The vapor partial pressure p_{vs} at the bubble surface and the saturation pressure $p_{v,sat}$ are obtained using the VDW Eq. (1) and the following relations for water vapor:

$$\rho_{vs} = \rho_b(1 - Y_b) \quad (19)$$

$$p_{v,sat} = \exp \left(c_1 - \frac{c_2}{T_s - c_3} \right) \quad (20)$$

Here, $c_1 = 23.3025$, $c_2 = 3893$ and $c_3 = 42.68$ for water vapor, and T_s is solved iteratively by coupling Eqs. (17) and (18). This indicates that evaporation and condensation during hydrogen bubble growth and contraction are driven by the imbalance between p_{vs} at the bubble surface and $p_{v,sat}$ in the surrounding liquid [26].

The H_2 mass flux G_h at the interface is expressed as

$$G_h = G_b Y_{ls} + \rho_l D_l \left. \frac{\partial Y_l}{\partial r} \right|_{r=R_b} \quad (21)$$

Using the total mass flux relation $G_b = G_h + G_v$, G_b can be expressed in terms of G_v from Eq. (21) as

$$G_b = \frac{G_v}{1 - Y_{ls}} + \frac{\rho_l D_l}{1 - Y_{ls}} \left. \frac{\partial Y_l}{\partial r} \right|_{r=R_b} \quad (22)$$

2.3. Modified KM equation with phase change and mass transfer effects

To precisely compute the effects of liquid compressibility, during rapid bubble contraction in resonance regions, we use the KM equation [21,28], extended to include mass flux across the bubble surface in the matching conditions for u_{ls} and p_{ls} from Eqs. (10) and (12), expressed as

$$\begin{aligned} & \rho_l \left[1 - \frac{1}{C_{l,\infty}} \left(\dot{R}_b - \frac{G_b}{\rho_l} \right) \right] R_b \frac{d\dot{R}_b}{dt} \\ &= -\frac{3}{2} \left[1 - \frac{1}{3C_{l,\infty}} \left(\dot{R}_b - \frac{2G_b}{\rho_l} \right) \right] \rho_l \dot{R}_b^2 + \left(1 + \frac{\dot{R}_b}{C_{l,\infty}} + \frac{R_b}{C_{l,\infty}} \frac{d}{dt} \right) (p_{ls} - p_\infty) \\ & \quad + G_b \left(\dot{R}_b + \frac{G_b}{2\rho_l} + \frac{G_b \dot{R}_b}{2C_{l,\infty}\rho_l} \right) + \rho_l \left[1 - \frac{1}{C_{l,\infty}} \left(\dot{R}_b - \frac{G_b}{\rho_l} \right) \right] R_b \frac{d}{dt} \left(\frac{G_b}{\rho_l} \right) \end{aligned} \quad (23)$$

where

$$p_{ls} = p_{bs} - \frac{2\sigma}{R_b} - \frac{4\mu_l}{R_b} \left(\dot{R}_b - \frac{G_b}{\rho_l} \right) + G_b^2 \left(\frac{1}{\rho_{bs}} - \frac{1}{\rho_l} \right) \quad (24)$$

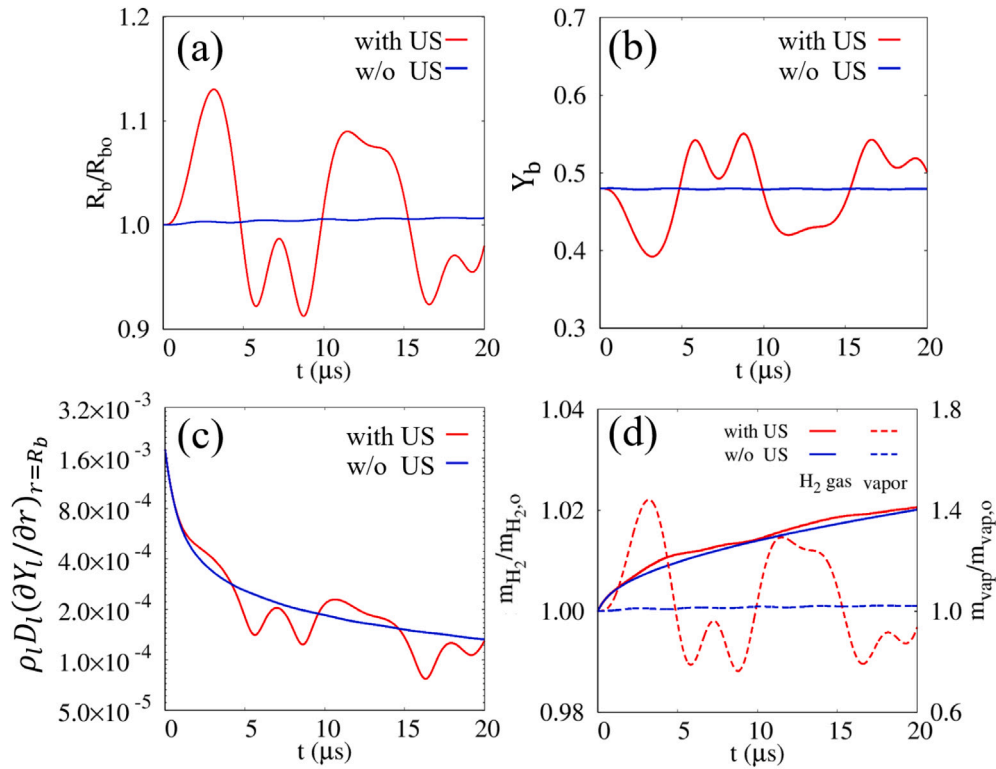


Fig. 1. Ultrasound-driven bubble motion in a supersaturated KOH solution at $Y_{l,\infty} = 10Y_{l,sat}$, $R_{bo} = 10\mu\text{m}$, $P_u = 0.02\text{ MPa}$ and $f_u = 0.1\text{ MHz}$ during first two ultrasound pulse periods ($0 \leq t \leq 20\mu\text{s}$): (a) Bubble radius, (b) H_2 mass fraction inside the bubble, (c) diffusive mass flux at the bubble interface, and (d) H_2 mass and vapor mass inside the bubble. The solid and dotted lines in the Figure (d) represent the H_2 gas mass and vapor mass, respectively.

Here, it is noted that when $\dot{R}_b$ is much smaller than the sound speed $C_{l,\infty}$ ($\dot{R}_b/C_{l,\infty} \approx 0$), the KM Eq. (23) simplifies to a modified RP equation, incorporating phase-change mass flux as in our previous studies [21]. During bubble collapse, if T_b surpasses the vapor critical temperature $T_{v,cr}$ and the thermodynamic distinction between liquid and gas phases vanishes [29], no vapor phase change occurs ($G_v = 0$) [21, 22] and T_s is determined from the balance of heat flux $\lambda_b(\partial T_b/\partial r) = \lambda_l(\partial T_l/\partial r)$ from the Eq. (17), with $G_v = 0$.

2.4. Numerical methods

To track the oscillating bubble wall, the moving coordinate system is defined as $\xi_b = r/R_b$ for the bubble domain, and $\xi_l = r - R_b$ for the liquid domain, in accordance with our previous studies [21,22]. The bubble region ($r \leq R_b$) is discretized with a grid spacing of $R_{bo}/15 \leq \Delta r \leq R_{bo}/50$, while the liquid region ($R_b < r \leq L$), extending sufficiently far to avoid boundary effects ($L > 1\text{ m}$), is discretized using a uniform grid with Δr near the bubble surface and a non-uniform grid with a size ratio of 1.09 for the rest ($R_{bo} < r \leq R_{bo} + 80R_{bo}$).

Detailed numerical formulations for the governing equations based on the moving coordinates have been described in our previous numerical studies [21,22,25,30]. An adaptive time-stepping algorithm is utilized to precisely capture rapid bubble contraction during resonance while keeping numerical errors under control [21]. The governing Eqs. (4)–(6), (8) and (9) are solved for U_b , e_b , u_l , T_l , and Y_l using the boundary conditions u_{ls} , u_{bs} , T_s , and Y_{ls} provided by the Eqs. (10), (11), and (13). Here, G_b and R_b in the Eq. (10) are determined from the mass flux Eq. (22) and the modified KM Eq. (23).

Our earlier numerical frameworks for acoustic cavitation [21] and acoustic droplet vaporization [22], although not specifically developed for hydrogen bubble growth under ultrasonic excitation, were

previously validated against available numerical solutions [31] and experimental data [32], as reported in Ref. [21]. In addition, grid- and time step convergence tests were independently performed by systematically varying Δr_l and Δt . The evolution of the bubble radius showed negligible sensitivity to further grid refinement or time-step reduction. These results indicate that the spatial and temporal resolutions adopted in the present simulations ($\Delta r_l = 1 \times 10^{-7}\text{ m}$ and $\Delta t = 1 \times 10^{-9}\text{ s}$) satisfy numerical convergence requirements without compromising computational accuracy.

3. Results and discussion

A spherical hydrogen-vapor mixture bubble, initially having a radius of R_{bo} , is immersed in liquid solution containing dissolved hydrogen gas at $Y_{l,\infty} = 10Y_{l,sat}$, considering the supersaturation ratio reported in previous Refs. [33,34]. We use the following physical properties of liquid solution [35], hydrogen and vapor [21]: $\rho_l = 1070\text{ kg/m}^3$, $\mu_l = 1.1 \times 10^{-3}\text{ Pa s}$, $c_l = 4.2 \times 10^3\text{ J/kgK}$, $\lambda_l = 0.6\text{ W/mK}$, $\mu_h = 9.4 \times 10^{-6}\text{ Pa s}$, $\mu_v = 1.5 \times 10^{-5}\text{ Pa s}$, $c_h = 1.02 \times 10^4\text{ J/kgK}$, $c_v = 1.4 \times 10^3\text{ J/kgK}$, $\lambda_h = 1.9 \times 10^{-2}\text{ W/mK}$, $\lambda_v = 1.9 \times 10^{-2}\text{ W/mK}$, $R_{g,h} = 4124\text{ J/kgK}$, $R_{g,v} = 461.5\text{ J/kgK}$, $a_h = 6083.5\text{ m}^6\text{Pa/kg}^2$, $a_v = 1727.2\text{ m}^6\text{Pa/kg}^2$, $b_h = 1.32 \times 10^{-2}\text{ m}^3/\text{kg}$, $b_v = 1.7 \times 10^{-3}\text{ m}^3/\text{kg}$, $\sigma = 7.0 \times 10^{-2}\text{ N/m}$, $h_{fg} = 2.45 \times 10^6\text{ J/kg}$, $T_{v,cr} = 652\text{ K}$, $D_l = 8.5 \times 10^{-9}\text{ m}^2/\text{s}$, $C_H = 1.9 \times 10^{-2}$. As initial conditions, the internal bubble pressure is estimated using $p_{bo} = 2\sigma/R_{bo} + p_\infty$, and ρ_{bo} is assumed to follow the VDW Eq. (1).

The following ultrasonic pressure wave p_u , used in the Eq. (15), is imposed at the domain boundary ($r = L$):

$$p_u = -P_u \sin(2\pi f_u t) \quad (25)$$

Here, P_u and f_u represent the ultrasonic pressure amplitude and frequency, respectively.

3.1. Hydrogen-vapor bubble growth in an ultrasonic field

Fig. 1 illustrates the temporal evolution of bubble dynamics during the first two ultrasound oscillation periods under ultrasonic excitation (with US) and under silent conditions (w/o US) at $R_{b0} = 10 \mu\text{m}$, $P_u = 0.02 \text{ MPa}$ and $f_u = 0.1 \text{ MHz}$. Under ultrasound, the bubble radius R_b exhibits oscillations in response to ultrasonic forcing, whereas in the silent condition, the bubble remains nearly unchanged, as shown in Fig. 1(a). The hydrogen mass fraction Y_b inside the ultrasonically excited bubble fluctuates with bubble expansion and contraction due to bubble internal pressure variations, decreasing during expansion ($\dot{R}_b > 0$) and increasing during contraction ($\dot{R}_b \leq 0$), as depicted in Fig. 1(b). In contrast, under silent conditions, Y_b remains nearly constant as hydrogen gas and water vapor are transferred while maintaining thermodynamic equilibrium. The hydrogen mass fraction inside the bubble in Fig. 1(b) serves as a boundary condition for dissolved H_2 gas distribution Y_l in the KOH solution, influencing the diffusive flux $j'' = \rho_l D_l (\partial Y / \partial r)_{r=R_b}$ at the bubble surface, as seen in Fig. 1(c). For the silent condition, the initially high and uniform hydrogen mass fraction, $Y_l(r, t=0) = 10Y_{l,\text{sat}}$, induces a high diffusive flux at the bubble surface, and gradually decreases from 1.8×10^{-3} to 1.8×10^{-4} as $t \rightarrow 10 \mu\text{s}$. For the ultrasonic condition, the hydrogen influx is larger than in the silent case during $R_b/R_{b0} > 1$ due to the reduced bubble pressure and the associated lower hydrogen mass fraction inside the bubble ($Y_b < Y_{b0}$). During $R_b/R_{b0} < 1$, the influx becomes smaller. Overall, the hydrogen mass transferred into the bubble is governed by the combined effects of the internal bubble pressure, gas density, and internal gas composition, as described by the boundary condition for the dissolved hydrogen mass fraction based on Henry's law (Eq. (11)). A similar bubble-growth mechanism is observed during the second oscillation cycle. The hydrogen mass m_{H_2} continues to increase slightly when $R_b/R_{b0} > 1$, owing to the reduced internal pressure and the corresponding decrease in the interfacial concentration Y_{ls} , as shown in Fig. 1(d). In contrast, the vapor inflow and outflow closely follow the radial oscillation of the bubble. Over the first two oscillation cycles, the hydrogen mass inside the bubble increases more significantly under ultrasonic excitation than under the silent condition, with the increment ($m_{\text{H}_2} - m_{\text{H}_2,0}$) at $t = 20 \mu\text{s}$ being approximately 44.1% larger than that at $t = 10 \mu\text{s}$. This progressively increasing increment over successive oscillation cycles contributes to bubble growth enhancement through cumulative hydrogen mass accumulation under prolonged acoustic excitation.

When the bubble grows over an extended duration ($t \leq 0.15 \text{ s}$), the bubble radius $\bar{R}_b$ averaged over one acoustic pulse cycle and the hydrogen mass inside the bubble under silent conditions and ultrasonic excitation are compared in Fig. 2. Under silent conditions, the bubble exhibits smooth diffusion-dominated growth following a $t^{0.70}$ scaling, as plotted in Fig. 2(a), which is greater than the classical $t^{0.5}$ scaling for diffusion-driven growth in saturated liquid [8]. This difference in the exponent is qualitatively explained by previous numerical findings [36], which reported that bubble growth in a 300% supersaturated solution followed a $t^{0.64}$ scaling, implying that the time exponent may increase as the supersaturation ratio of the liquid solution rises. Under ultrasonic excitation, the bubble initially grows more rapidly than under silent conditions, and a slight bump in $\bar{R}_b$ appears around $t = 0.01 \text{ s}$. This feature arises when a weak rebound during the contraction phase momentarily reaches or slightly exceeds the cycle-averaged radius, temporarily altering the oscillation dynamics. Subsequently, $\bar{R}_b$ exhibits an abrupt increase near $t = 84 \text{ ms}$, marking the onset of the resonance regime. In this region, $\bar{R}_b$ exhibits a sharp peak, followed by a temporary decrease before stabilizing and gradually increasing again. It should be noted that $\bar{R}_b$ represents the time-averaged bubble radius over one acoustic pulse cycle, expressed as $\bar{R}_b = \int_t^{t+T} R_b dt / T$, where T denotes the period of ultrasonic pulse. Considering the abrupt increase in $\bar{R}_b$, within the bubble resonance region, the hydrogen mass m_{H_2} also exhibits a rapid growth at this moment ($t = 84 \text{ ms}$), as

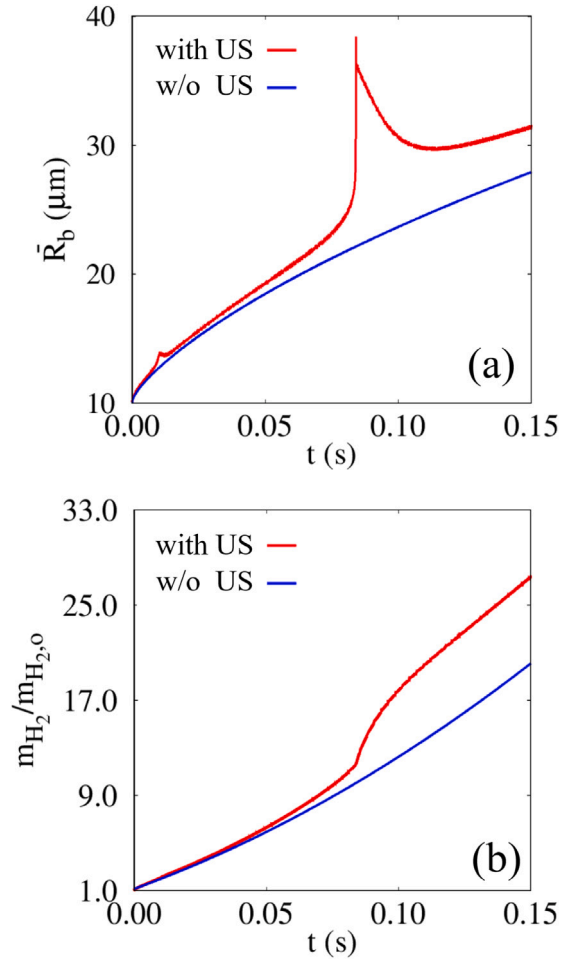


Fig. 2. Bubble growth and hydrogen mass increase until $t \leq 0.15 \text{ s}$ at $R_{b0} = 10 \mu\text{m}$, $P_u = 0.02 \text{ MPa}$ and $f_u = 0.1 \text{ MHz}$: (a) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (b) H_2 mass inside the bubble.

observed in Fig. 2(b). This is consistent with previous numerical studies [15,16], which reported rectified diffusion-driven bubble growth and jump growth due to bubble resonance. Overall, the hydrogen mass m_{H_2} inside the ultrasound-driven bubble increases more rapidly than that of the diffusion-dominated bubble under silent conditions. After the sharp increase associated with resonance-induced jump growth, the mass growth rate gradually decreases, although the bubble mass continues to increase monotonically even for $t > 0.15 \text{ s}$.

Fig. 3 compares the spatial distribution of the hydrogen mass fraction Y_l in the liquid surrounding the bubble interface at $t = 30 \text{ ms}$ (left) and $t = 84 \text{ ms}$ (right), shown relative to the ambient hydrogen mass fraction $Y_{l,\infty}$ in the electrolyte. The time $t = 30 \text{ ms}$ corresponds to a stage at which the bubble motion under ultrasonic excitation has evolved beyond the initial transient perturbation and remain in a non-resonant regime, whereas $t = 84 \text{ ms}$ represents a stage where the bubble exhibits resonance-induced jump behavior. For $30 \text{ ms} < t < 30 \text{ ms} + 10 \mu\text{s}$ (non-resonant regime), the cycle-averaged bubble radius is $\bar{R}_b = 16.2 \mu\text{m}$, whereas for $84 \text{ ms} < t < 84 \text{ ms} + 10 \mu\text{s}$ (resonant regime), within the resonance region, $\bar{R}_b = 31.3 \mu\text{m}$. Through the bubble growth period, the bubble surface pushes the surrounding liquid, affecting the H_2 mass fraction distribution, as seen in Fig. 3(a). Near $t = 30 \text{ ms}$, the temporal variation of the H_2 mass fraction around the bubble surface remains nearly unchanged during $R_b > \bar{R}_b$. However, in the resonance

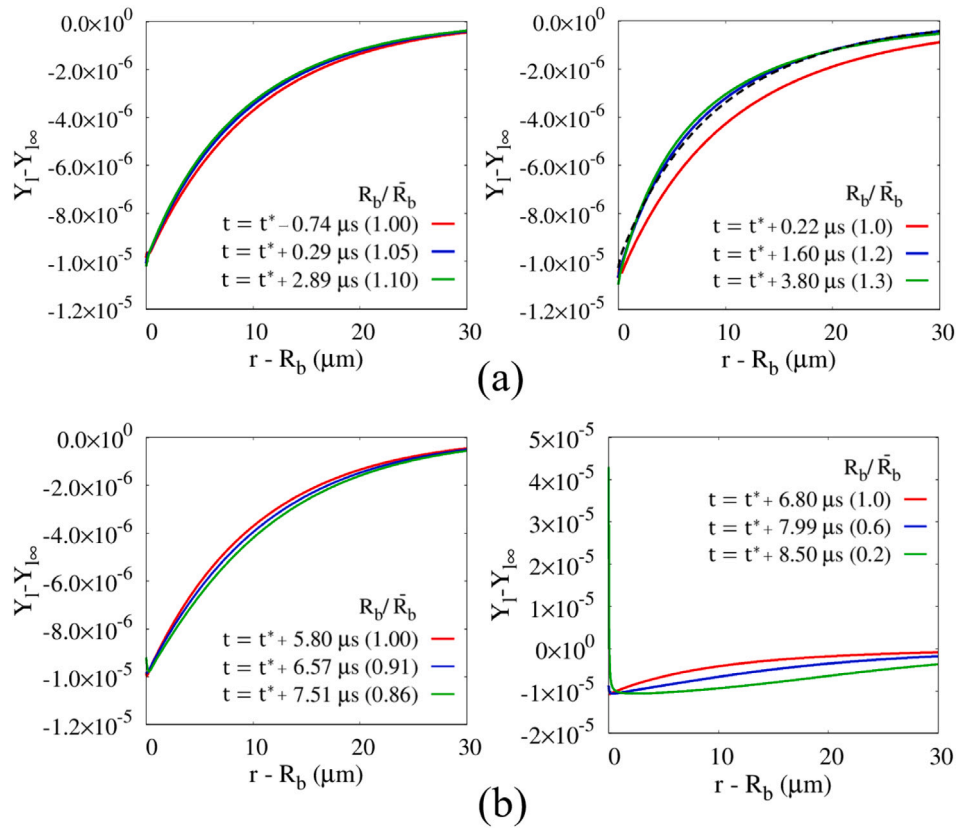


Fig. 3. Detailed H_2 mass fraction distribution in the liquid solution surrounding the bubble surface at two different moments of diffusive growth around $t^* = 30$ ms (left) and resonant oscillation around $t^* = 84$ ms (right), during (a) bubble growth ($R_b \geq \bar{R}_b$) and (b) contraction ($R_b \leq \bar{R}_b$), respectively.

region near $t = 84$ ms, a noticeable variation in H_2 mass fraction profile occurs. Considering the dashed black line near $t = 84$ ms (right) which corresponds to the steepest gradient profile for $t = 30$ ms (left), the large bubble expansion during resonance steepens the local concentration gradient near the bubble surface, accelerating hydrogen influx. During the bubble contraction phase, the H_2 mass fraction profile near $t = 30$ ms remains almost unchanged, as shown in Fig. 3(b), closely resembling the profile observed during the growth phase. However, in the resonance region near $t = 84$ ms (right), the H_2 mass fraction exhibits significant perturbations. As $R_b/\bar{R}_b$ decreases, the internal bubble pressure increases, which in turn raises the interfacial hydrogen mass fraction Y_{ls} according to Henry's law (Eq. (11)). This pressure-induced increase in Y_{ls} generates a negative concentration gradient of Y_l near the bubble surface. Over a very short time interval, the resulting inverted concentration profile induces a transient hydrogen outflux. However, during the relatively longer expansion phase, hydrogen influx over the enlarged bubble surface area dominates, leading to a marginal net increase in the hydrogen mass inside the bubble. This behavior is qualitatively consistent with previous interpretations of bubble growth driven by rectified diffusion in cavitation bubbles [37].

3.2. Effects of ultrasonic amplitude and frequency on bubble resonance

The influence of acoustic excitation amplitude P_u on bubble evolution and hydrogen mass increase, while keeping other variables constant, is presented in Fig. 4. As P_u increases by 1.5 and 2 times from 0.02 MPa, $\bar{R}_b$ not only grows more rapidly but also exhibits a more pronounced sharp peak within the resonance region, as shown in Fig. 4(a). Beyond the generation of a sharp peak, an increase in P_u reduces the bubble resonance radius for jump growth and shifts the onset of bubble resonance to an earlier time. This trend qualitatively agrees with previous experimental and numerical findings [38,39] that

observed nonlinear deformation of the resonance curve with increasing pressure amplitude. Given the earlier onset of bubble resonance a similar shift in the jump growth of $m_{H_2}/m_{H_{2,o}}$ can also be observed in Fig. 4(b). The rapid increase in $m_{H_2}/m_{H_{2,o}}$ with rising P_u indicates that stronger ultrasonic forcing enhances bubble expansion and contraction, thereby promoting the influx of dissolved hydrogen. While a higher P_u intensifies bubble resonance and growth, $P_u = 0.02$ MPa is chosen for the subsequent calculations, considering the quadratic relationship between P_u and acoustic intensity $I = P_u^2/2\rho c_{l,\infty}$ [40]. The results are plotted only for $t < 0.1$ s, corresponding to the time interval dominated by resonance oscillations; once the bubble leaves the resonance region, both the radius and the bubble mass increase monotonically without further jump growth.

Fig. 5 plots the influence of ultrasonic frequency f_u on bubble resonance and hydrogen mass increase. Increasing f_u by 1.5 and 2 times from 0.2 MHz reduces negative pressure period while increasing the number of oscillation cycles. These opposing effects balance each other, resulting in a lower sensitivity of bubble growth rate to f_u before its resonance, as shown in Fig. 5(a). However, within the resonance region, the sharp peak of $\bar{R}_b$ exhibits high sensitivity, not only shifting significantly earlier from $t = 84.1$ ms to $t = 24.2$ and 4.4 ms due to the reduction in resonance radius but also undergoing a substantial decrease in magnitude as f_u increases from 0.1 to 0.2 MHz. Similarly, as shown in Fig. 5(b), the onset time of $m_{H_2}/m_{H_{2,o}}$ growth at the resonance point shifts earlier with increasing f_u , which aligns with the previous numerical investigations [15] that compares the temporal evolution of equilibrium radius for five different applied acoustic frequencies. The most pronounced jump growth in $m_{H_2}/m_{H_{2,o}}$ occurs at $f_u = 0.1$ MHz, indicating that lower frequencies induce stronger nonlinear oscillations despite the reduced number of oscillation cycles during bubble resonance. These findings indicate the potential to maximize hydrogen bubble growth by appropriately controlling the resonance frequency

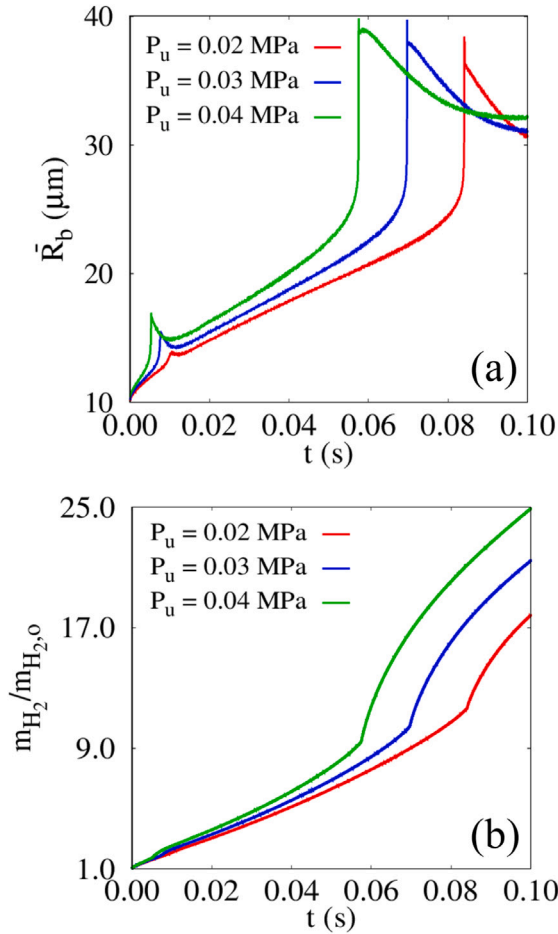


Fig. 4. Influence of ultrasonic pressure amplitude on bubble growth and hydrogen mass increase until $t \leq 0.1$ s at $R_{b0} = 10 \mu\text{m}$ and $f_u = 0.1$ MHz: (a) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (b) H_2 mass inside the bubble.

based on $\bar{R}_b$ enabling more frequent jump growth in synchronization with continuous bubble growth.

3.3. Resonance frequency including mass transfer and phase change effects

Fig. 6 presents the numerical results up to $t \leq 500 \mu\text{s}$ to determine the resonance frequency for an initially stationary bubble with R_{b0} at $P_u = 0.02$ MPa and $Y_{l,\infty} = 10Y_{l,\text{sat}}$. The theoretical resonance frequency $f_{res,0}$ for a gas bubble, neglecting phase change and mass transfer, is given in previous literature [16] as:

$$f_{res,0} = \frac{1}{2\pi R_{b0}} \sqrt{\frac{1}{\rho_{l,\infty}} (3\gamma p_\infty + 2(3\gamma - 1) \frac{\sigma}{R_{b0}})} \quad (26)$$

where γ is the specific heat ratio, we set $\gamma = 1$ in this study considering phase change. For $R_{b0} = 10 \mu\text{m}$, the theoretical prediction yields $f_{res,0} = 0.28$ MHz, but as shown in Fig. 6(a), the most significant bubble growth occurs near $f_u = 0.24$ MHz, indicating that the actual resonance frequency f_{res} is lower than $f_{res,0}$. Similarly, bubbles with $R_{b0} = 20 \mu\text{m}$ and $30 \mu\text{m}$ exhibit maximum growth near $f_u = 0.12$ MHz and 0.08 MHz, respectively, which are lower than the theoretical values $f_{res,0} = 0.14$ MHz and 0.09 MHz, as plotted in Figs. 6(b)–(c). Numerical results for f_{res} demonstrate an overall reduction of more than 11% compared to $f_{res,0}$. It is numerically found that neglecting vapor phase change and gas diffusion leads to an overestimation of the resonance

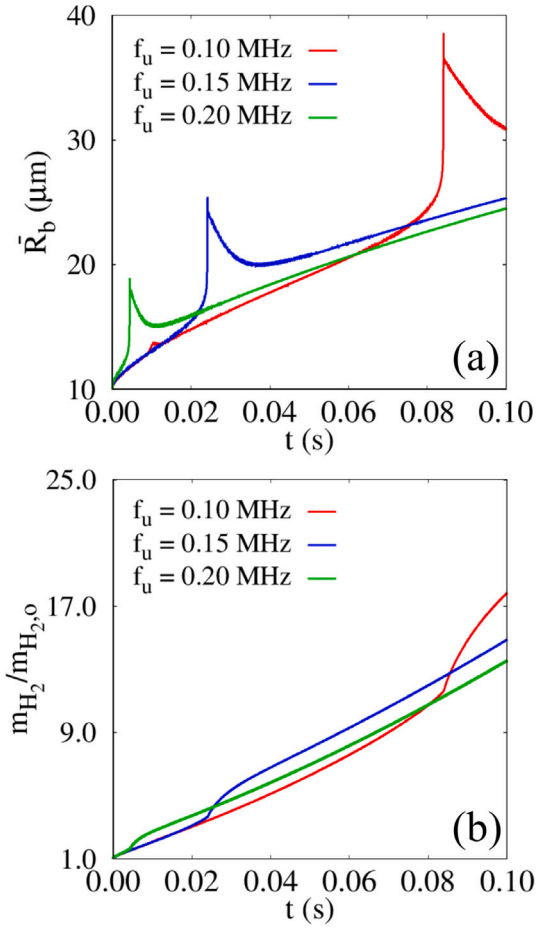


Fig. 5. Influence of ultrasonic frequency on bubble growth and hydrogen mass increase until $t \leq 0.1$ s at $R_{b0} = 10 \mu\text{m}$ and $P_u = 0.02$ MPa: (a) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (b) H_2 mass inside the bubble.

frequency or resonance radius in our case. This is due to the damping effect of phase change and dissolved gas transport in relieving the bubble internal pressure fluctuation, analogous to bubble stiffness [41]. This phenomenon can be qualitatively explained by the theoretical formulation in Refs. [41,42] which incorporates phase change and mass transfer effects into the bubble resonance frequency. Therefore, enhancing hydrogen bubble growth through variable resonance frequency must account for vapor phase change and hydrogen mass transfer in the resonance formulation.

Fig. 7(a) compares the resonance frequency-initial bubble radius relationship obtained from numerical simulations and theoretical predictions at $P_u = 0.02$ MPa and $Y_{l,\infty} = 10Y_{l,\text{sat}}$. The square markers represent the numerically computed resonance frequency f_{res} , which decreases inversely with increasing R_{b0} . The numerical data are fitted with a power-law relation, yielding $f_{res}(R_{b0}) = 2.40R_{b0}^{-1.0076}$. Overall, $f_{res}(R_{b0})$ is lower than theoretical predictions from Eq. (26), with deviations increasing as R_{b0} decreases. These deviations arise from the more pronounced effects of vapor phase change flux and hydrogen mass transfer in smaller bubbles due to their higher surface-to-volume ratio. Note that $f_{res}(R_{b0})$ is formulated for initially stationary bubble. The bubble response at its resonance radius corresponding to the driving frequency f_u for continuously growing bubble is presented in Fig. 7(b). Bubbles growing under ultrasound exhibit sharp resonance peaks near $\bar{R}_b = 14.7 \mu\text{m}$, $19.6 \mu\text{m}$, and $29.2 \mu\text{m}$ for $f_u = 0.16$ MHz, 0.12 MHz, and 0.08 MHz, respectively, based on the fitted relation in Fig. 7(a).

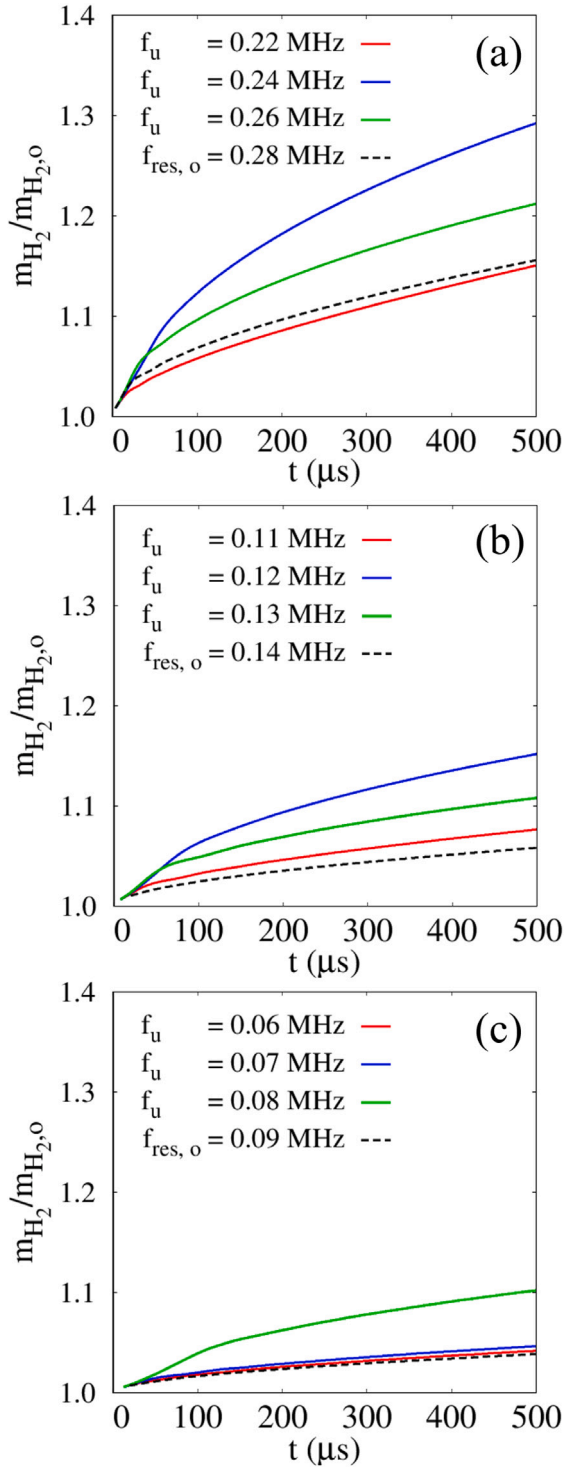


Fig. 6. Effect of resonance frequency on H₂ mass inside the bubble until $t \leq 500 \mu s$ at $P_u = 0.02$ MPa: (a) $R_{bo} = 10 \mu m$, (b) $R_{bo} = 20 \mu m$, and (c) $R_{bo} = 30 \mu m$.

However, the actual jump growth timing may not only deviate from the predicted resonance size due to the ambiguity in defining the exact resonance moment, but also appear to initiate gradually at a slightly lower value than the predicted one. This suggests that effective hydrogen bubble growth enhancement via variable resonance frequency control may require substituting a slightly smaller value than $\bar{R}_b$ in our fitted correlation.

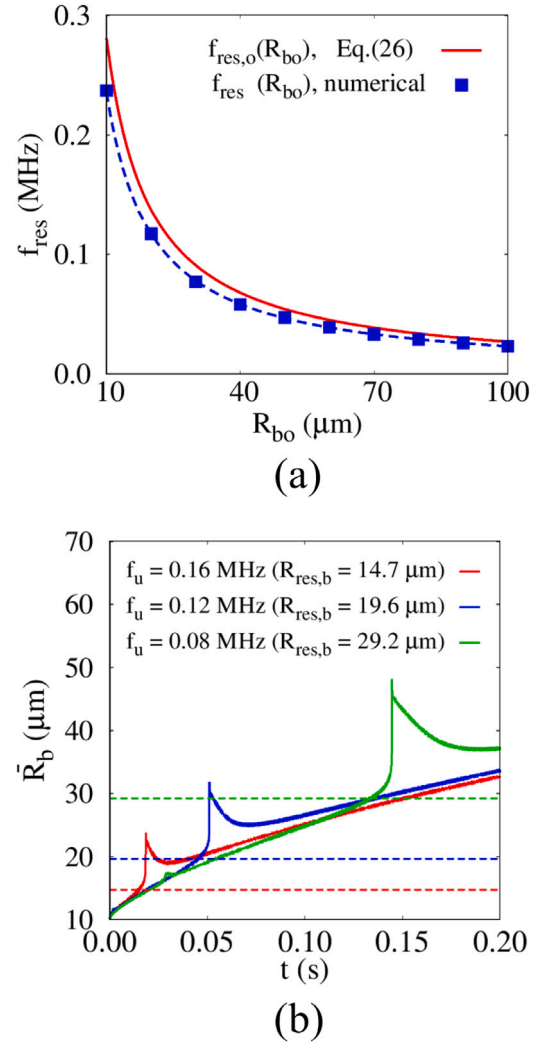


Fig. 7. Correlation between ultrasonic frequency and the corresponding bubble resonance radius at $P_u = 0.02$ MPa and $Y_{l,\infty} = 10Y_{l,sat}$ for: (a) initial stationary bubble ($10 \leq R_{bo} \leq 100 \mu m$) and (b) continuously growing bubble ($R_{bo} = 10 \mu m$).

3.4. Hydrogen bubble growth enhancement using variable resonance frequency

The results of applying a variable resonance frequency, adjusted to the evolving bubble resonance radius $\bar{R}_{b,var}$ with each growth increment $\Delta \bar{R}_{b,var} = 5 \mu m$, are plotted in Fig. 8. As $\bar{R}_{b,var}$ increases by $\Delta \bar{R}_{b,var} = 5 \mu m$, the corresponding resonance frequency f_{res} gradually decreases from 0.25 MHz, continuously inducing resonance at larger radii, as plotted in Fig. 8(a). Notably, $0.9\bar{R}_{b,var}$ is applied in the fitted correlation $f_{res}(\bar{R}_{b,var}) = 2.40\bar{R}_{b,var}^{-1.0076}$, as numerical results suggest that greater jump growth occurs at $0.9\bar{R}_{b,var}$ instead of $\bar{R}_{b,var}$, likely due to differences in assumptions between the initial stationary bubble and continuously growing bubble. Fig. 8(b) compares bubble growth under variable-frequency conditions with single-frequency cases for $t \leq 0.2$ s. Here, $f_u = 0.08$ MHz and $f_{res}(R_{bo}) = 0.24$ MHz are chosen as single frequencies, and the dashed black line represents diffusive growth under silent conditions. The time range is extended to $t = 0.2$ s, to demonstrate that, for the fixed-frequency excitation ($f_u = 0.08$ MHz), no additional sudden growth occurs beyond the sharp peak observed at $t = 0.14$ s, whereas continuous resonance under variable-frequency excitation, $f_{res}(\bar{R}_b)$, is further confirmed by the sequential sharp peaks

in $\bar{R}_b$. Continuous resonance under variable frequency $f_{res}(0.9\bar{R}_{b,var})$ is further confirmed by the sequential sharp peaks in $\bar{R}_b$. After $\bar{R}_b$ reaches its sharp peak in each resonance event, it decreases and eventually stabilizes ($\dot{\bar{R}}_b \approx 0$), with $\bar{R}_b$ increasing by approximately $5 \mu\text{m}$ compared to its pre-resonance state. This may justify the choice of $\Delta\bar{R}_{b,var} = 5 \mu\text{m}$ for maximizing bubble growth. It is noted that although the peak $\bar{R}_b$ surpasses $\Delta\bar{R}_{b,var} = 5 \mu\text{m}$, frequency variation occurs only when the resonance is stabilized ($\dot{\bar{R}}_b \approx 0$). Such continuous induction of bubble resonance by variable-frequency ultrasonic waves significantly enhances the hydrogen mass inside the bubble, as observed in Fig. 8(c). Under variable-frequency control with $f_u = f_{res}(0.9\bar{R}_{b,var})$, m_{H_2} reaches approximately 73.7 times its initial hydrogen mass. Compared to the cases of silent condition and $f_u = 0.08 \text{ MHz}$, m_{H_2} is about 2.5 and 1.8 times larger, respectively. For $f_u = f_{res}(R_{bo})$, m_{H_2} does not exhibit abrupt jump growth, as observed in single-frequency case as $f_u = 0.08 \text{ MHz}$, but instead shows minimal deviation from the silent case.

Fig. 9 shows the effect of different increment sizes $\Delta\bar{R}_{b,var}$. Compared to $\Delta\bar{R}_{b,var} = 5 \mu\text{m}$, the step size of $\Delta\bar{R}_{b,var} = 10 \mu\text{m}$ causes longer intervals before each resonance event, reducing the number of resonance-induced frequency variations, as observed in Fig. 9(a). While the case of $\Delta\bar{R}_{b,var} = 5 \mu\text{m}$ exhibits six resonance peak before $t = 0.2 \text{ s}$, the $\Delta\bar{R}_{b,var} = 10 \mu\text{m}$ case presents only two resonant events, as depicted in Fig. 9(b). For $\Delta\bar{R}_{b,var} = 10 \mu\text{m}$, after each resonance and subsequent stabilization ($\dot{\bar{R}}_b \approx 0$), $\bar{R}_b$ continues growing for a relatively longer duration compared to the $5 \mu\text{m}$ case before reaching its next resonance condition. However, for $\Delta\bar{R}_{b,var} = 5 \mu\text{m}$, $\bar{R}_b$ increases by approximately $5 \mu\text{m}$ immediately after resonance and following stabilization, enabling more frequent frequency variation. This leads to a significant increase in the m_{H_2} growth rate, as seen in Fig. 9(c). At $t = 0.2 \text{ s}$, m_{H_2} for $\Delta\bar{R}_{b,var} = 5 \mu\text{m}$ is 1.8 times greater than that for $\Delta\bar{R}_{b,var} = 10 \mu\text{m}$. This suggests that selecting a $5 \mu\text{m}$ step size effectively enhances hydrogen bubble growth.

3.5. Influence of initial bubble radius, electrolyte concentration, and temperature

Fig. 10 compares the growth behavior of bubbles with initial radii of $R_{bo} = 10 \mu\text{m}$ and $20 \mu\text{m}$. Since it is practically impossible to selectively irradiate bubbles of different initial sizes with individually tailored variable-frequency ultrasound, the same variable-frequency waveform used in Fig. 9(a), which was designed based on $R_{bo} = 10 \mu\text{m}$, is applied in both cases. For the bubble with $R_{bo} = 20 \mu\text{m}$, the bubble radius increases monotonically and does not enter resonance as early as the $R_{bo} = 10 \mu\text{m}$ case, as shown in Fig. 10(a). Once the bubble radius approaches the resonance radius corresponding to the applied variable frequency, resonance-induced jump growth begins to occur. As the resonance timing becomes synchronized with that of the $R_{bo} = 10 \mu\text{m}$ bubble, the subsequent growth behavior of the two bubbles becomes similar.

A comparable trend is observed for hydrogen mass growth in Fig. 10(b). In both cases, the hydrogen mass exhibits a sudden increase at nearly the same moment when the resonance condition is satisfied, followed by successive jump-growth events. Under the variable-frequency excitation, the bubble with $R_{bo} = 20 \mu\text{m}$ attains a hydrogen mass approximately 1.6 times larger than that under the silent condition, which is slightly smaller than the enhancement observed for the $R_{bo} = 10 \mu\text{m}$ case. It should be noted that the initial hydrogen mass for the $R_{bo} = 20 \mu\text{m}$ case is about 7.4 times larger than that of the $R_{bo} = 10 \mu\text{m}$. However, when the $R_{bo} = 10 \mu\text{m}$ bubble grows to $20 \mu\text{m}$ at $t = 0.048 \text{ s}$, its internal hydrogen mass differs by only about 4% from that of the initial mass of $R_{bo} = 20 \mu\text{m}$ bubble.

These results indicate that the resonance-induced growth enhancement is essentially similar for bubbles with different initial sizes once they enter the resonance regime. This finding highlights that bubbles

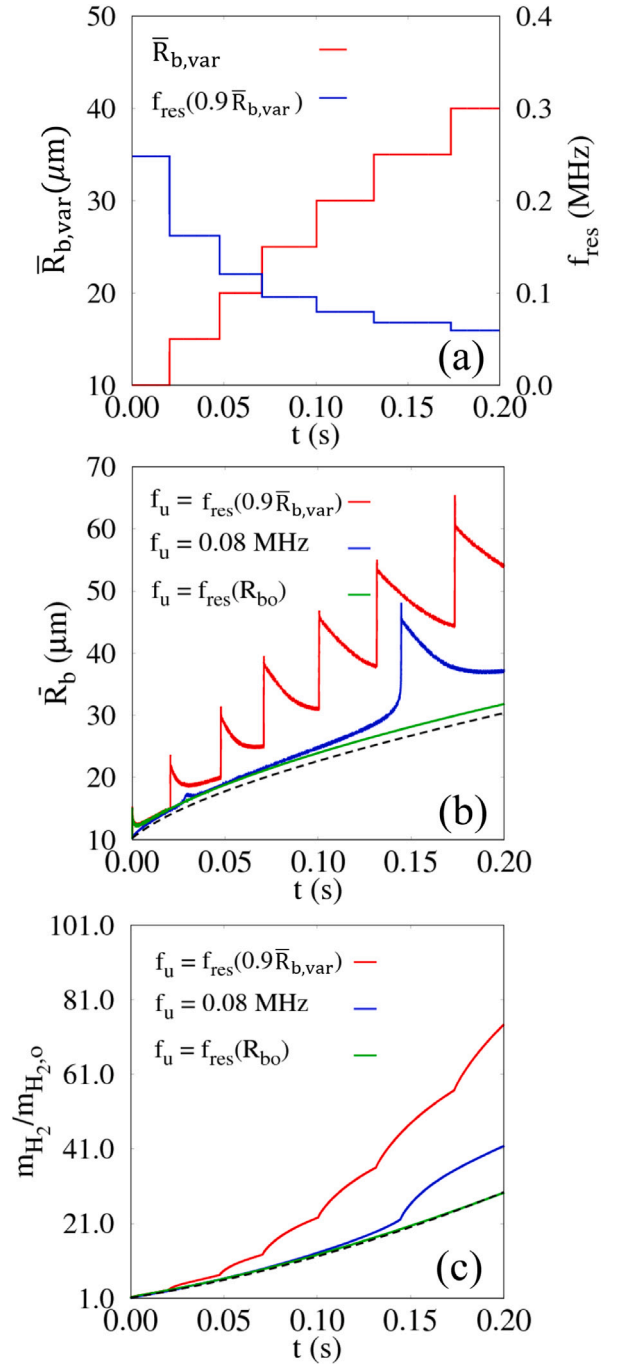


Fig. 8. Comparison of the influence of single-frequency and variable-frequency ultrasonic waves on bubble growth and hydrogen mass increase until $t \leq 0.2 \text{ s}$ at $R_{bo} = 10 \mu\text{m}$ and $P_u = 0.02 \text{ MPa}$: (a) variation in bubble resonance radius $\bar{R}_{b,var}$ and the resulting resonance frequency f_{res} , (b) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (c) H_2 mass inside the bubble.

$R_{bo} > 10 \mu\text{m}$ present in the electrolyte can still undergo accelerated growth through repeated resonance-induced jump events when subjected to the proposed variable-frequency ultrasound, even though individual real-time frequency tuning for each bubble is not feasible.

Fig. 11 plots the bubble growth patterns for initial dissolved hydrogen concentrations $Y_{l,\infty} = 10Y_{l,sat}$ and $20Y_{l,sat}$. At higher supersaturation, the bubble undergoes resonance-induced sudden growth, followed by rapid stabilization, which subsequently leads to more frequent jump

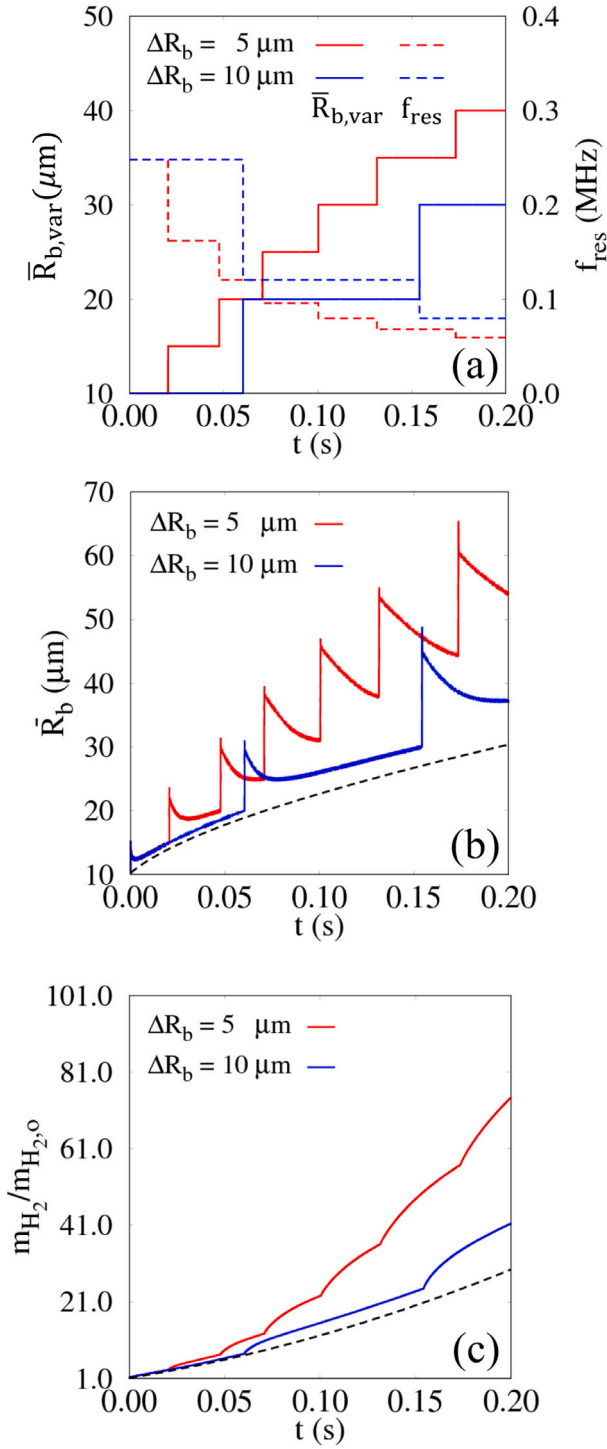


Fig. 9. Influence of frequency variation criteria (ΔR_b) on bubble growth and hydrogen mass increase until $t \leq 0.2 \text{ s}$ at $R_{bo} = 10 \mu\text{m}$ and $P_u = 0.02 \text{ MPa}$: (a) variation in bubble resonance radius $\bar{R}_{b,var}$ and the resulting resonance frequency f_{res} , (b) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (c) H_2 mass inside the bubble.

events. This behavior is attributed to the accelerated diffusive growth rate after resonance and the bubble's faster escape from the resonance condition. It is noted that the hydrogen mass increase driven by gas influx directly alters the bubble size, unlike vapor exchange, and is therefore strongly coupled to the resonance dynamics. Overall, the

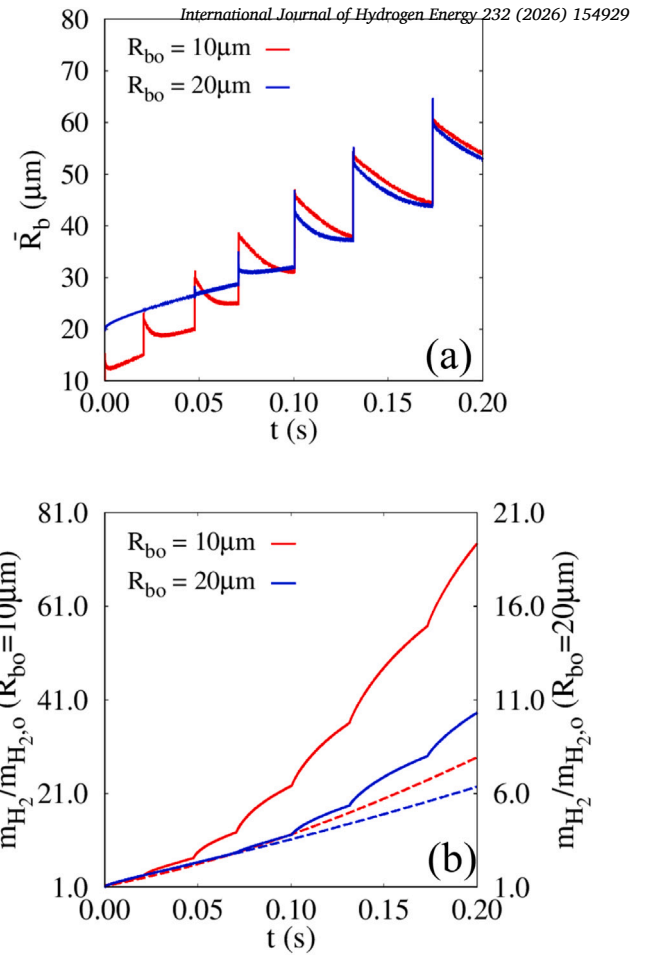


Fig. 10. Effect of the initial bubble radius R_{bo} using the time-dependent waveform derived from the pulse in Fig. 8 at $P_u = 0.02 \text{ MPa}$: (a) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (b) H_2 mass inside the bubble. The dashed line represents the hydrogen mass under the silent condition.

rapid growth of bubbles in highly supersaturated electrolytes leads to a faster increase in hydrogen mass, as shown in Fig. 11(b). In the higher-concentration electrolyte, the hydrogen mass inside the bubble increases more rapidly under the variable-frequency excitation and reaches a value 1.65 times larger than that for $Y_{l,\infty} = 10Y_{l,sat}$ at $t = 0.2 \text{ s}$. However, the enhancement ratio relative to the silent condition is only 1.10 because the faster diffusive growth in the absence of ultrasonic pulsing already yields substantial hydrogen accumulation. This suggests that the effect of ultrasonic forcing becomes more pronounced when the concentration of dissolved hydrogen near the electrode is not excessively high.

Fig. 12 presents the bubble growth behavior for different electrolyte temperatures. At $T_{l,\infty} = 70^\circ\text{C}$, the amplitude of the jump-growth events is smaller than observed that at $T_{l,\infty} = 50^\circ\text{C}$, as plotted in Fig. 12(a). This behavior arises from the strong temperature sensitivity of the resonance-frequency relation $f_{res}(R_b)$, which weakened the resonance-induced growth and consequently reduces the hydrogen mass increase, as shown in Fig. 12(b). As the electrolyte temperature increases, the hydrogen mass under the silent condition increases more significantly due to the higher hydrogen influx required to maintain thermodynamic equilibrium with the enhanced vapor influx. When this accelerated mass increase under the silent condition is taken into account, the hydrogen mass enhancement achieved by variable-frequency excitation becomes less pronounced than that at lower temperatures, leading to a reduced enhancement ratio of 1.79 at $T_\infty = 70^\circ\text{C}$. These results indicate

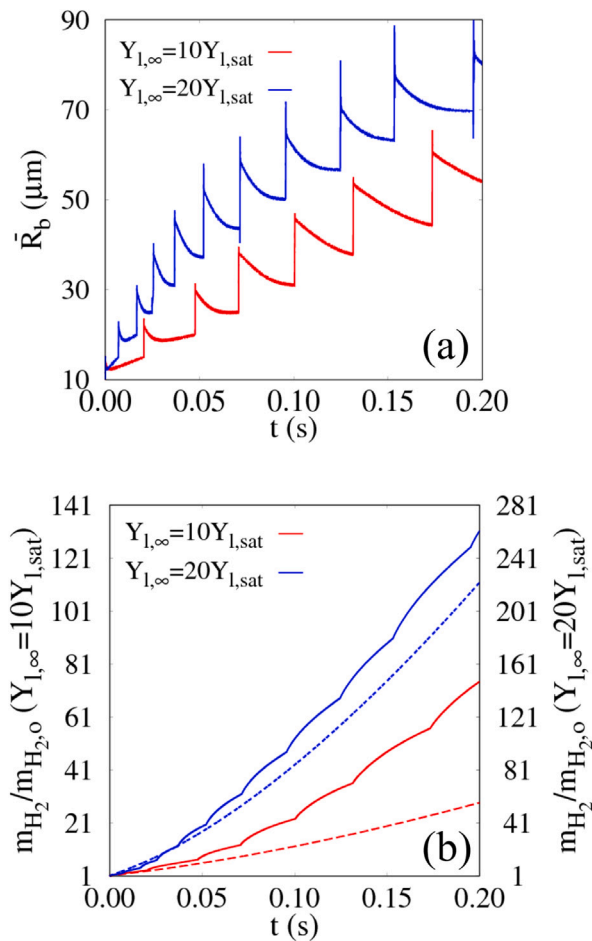


Fig. 11. Effect of initial dissolved hydrogen concentrations on bubble growth at $P_u = 0.02$ MPa, $f_u = f_{res}$ (fitted from Fig. 7(a)), and $R_{b0} = 10$ μm : (a) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (b) H_2 mass inside the bubble. The dashed line represents the hydrogen mass under the silent condition.

that maximizing hydrogen mass enhancement requires appropriate adjustment of the resonance-frequency correlation $f_{res}(R_b)$ in accordance with the operating temperature of the electrolysis cell.

4. Conclusions

We developed a numerical model for ultrasound-induced hydrogen bubble growth, incorporating vapor phase change and dissolved gas mass transfer by combining the Keller–Miksis equation with energy and hydrogen mass fraction equations in a supersaturated solution. This model directly evaluated vapor phase-change rates and hydrogen gas mass transfer from local temperature and hydrogen mass fraction distributions. The hydrogen mass inside the bubble increased abruptly as the bubble in a supersaturated solution continuously grows to approach its resonance size. This abrupt jump growth was attributed to the perturbed and convected dissolved hydrogen distribution near the interface during resonance, leading to a significantly higher mass influx than before resonance. The timing and amplitude of mass jump growth at resonance were highly sensitive to ultrasonic frequency, highlighting the potential of resonance frequency modulation to maximize continuous jump growth. The resonance frequency in a supersaturated solution, incorporating vapor phase change and gas mass transfer, was numerically computed and fitted to provide a resonance frequency–bubble radius correlation. Variable resonance frequency control significantly increased hydrogen mass compared to silent conditions and

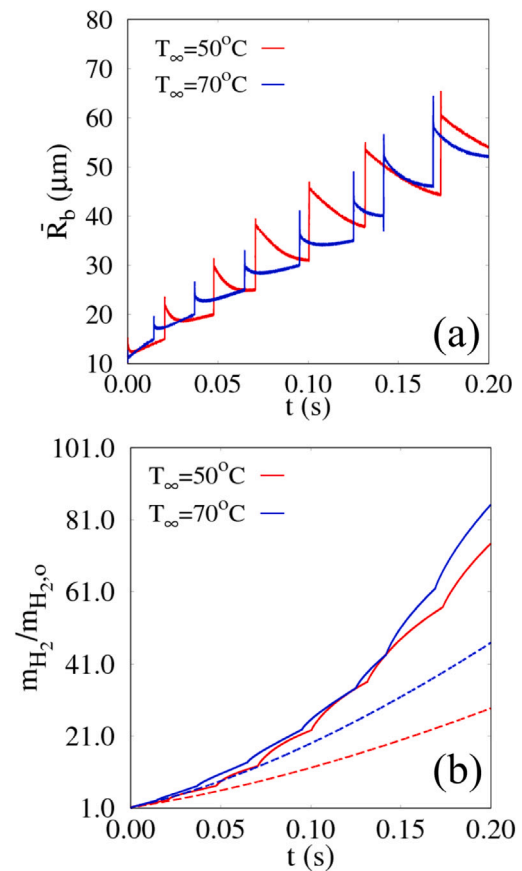


Fig. 12. Effect of electrolyte temperature on bubble growth at $P_u = 0.02$ MPa, $f_u = f_{res}$ (fitted from Fig. 7(a)), and $R_{b0} = 10$ μm : (a) bubble radius $\bar{R}_b$ averaged over one pulse cycle and (b) H_2 mass inside the bubble. The dashed line represents the hydrogen mass under the silent condition.

also outperformed conventional single low-frequency excitation. In this study, an incremental step of 5 μm for resonance frequency variation was found to be the most effective in promoting hydrogen bubble growth. The enhancement ratio achieved by variable-frequency excitation decreases with increasing initial bubble radius, due to the larger initial hydrogen mass within the bubble and the reduced number of resonance-induced jump events during growth. Furthermore, increases in electrolyte concentration and temperature also result in a reduced enhancement ratio. These results indicate that the effectiveness of resonance-radius-based variable-frequency excitation is strongly dependent on electrolysis operating conditions, and that robust operating frequencies exist as a function of temperature and electrolyte concentration.

CRediT authorship contribution statement

Jaesung Park: Writing – original draft, Software, Investigation, Conceptualization. **Gihun Son:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gihun Son has patent pending to Sogang university. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT)(RS-2024-00350110).

References

- [1] Zhao X, Ren H, Luo L. Gas bubbles in electrochemical gas evolution reactions. *Langmuir* 2019;35(16):5392–408. <http://dx.doi.org/10.1021/acs.langmuir.9b00119>.
- [2] He Y, Cui Y, Zhao Z, Chen Y, Shang W, Tan P. Strategies for bubble removal in electrochemical systems. *Energy Rev* 2023;2(1):100015. <http://dx.doi.org/10.1016/j.enrev.2023.100015>.
- [3] Duan X, Xiao J, Lin W, Wang S, Wen J. Experimental and numerical investigation of the impact of operating conditions on water electrolysis with ultrasonic. *Int J Hydrog Energy* 2024;49:404–16. <http://dx.doi.org/10.1016/j.ijhydene.2023.08.066>.
- [4] Angulo A, van der Linde P, Gardeniers H, Modestino M, Rivas DF. Influence of bubbles on the energy conversion efficiency of electrochemical reactors. *Joule* 2020;4(3):555–79. <http://dx.doi.org/10.1016/j.joule.2020.01.005>.
- [5] Li S-D, Wang C-C, Chen C-Y. Water electrolysis in the presence of an ultrasonic field. *Electrochim Acta* 2009;54(15):3877–83. <http://dx.doi.org/10.1016/j.electacta.2009.01.087>.
- [6] Araújo F, Neto RC, Moita AS. Alkaline water electrolysis: Ultrasonic field and hydrogen bubble formation. *Int J Hydrog Energy* 2024;78:594–603. <http://dx.doi.org/10.1016/j.ijhydene.2024.06.263>.
- [7] Kwon S, Bae S, Son G. Experimental study of ultrasound-assisted alkaline water electrolysis for hydrogen production. *J Mech Sci Technol* 2025;39(2):663–669. <http://dx.doi.org/10.1007/s12206-025-0113-9>.
- [8] Higuera F. A model of the growth of hydrogen bubbles in the electrolysis of water. *J Fluid Mech* 2021;927:A33. <http://dx.doi.org/10.1017/jfm.2021.778>.
- [9] Puga H, Barbosa J, Teixeira JC, Prokic M. A new approach to ultrasonic degassing to improve the mechanical properties of aluminum alloys. *J Mater Eng Perform* 2014;23:3736–44. <http://dx.doi.org/10.1007/s11665-014-1133-2>.
- [10] Chen Y, Chelgani SC, Bu X, Xie G. Effect of the ultrasonic standing wave frequency on the attractive mineralization for fine coal particle flotation. *Ultrason Sonochem* 2021;77:105682. <http://dx.doi.org/10.1016/j.ultsonch.2021.105682>.
- [11] Sahoo BN, Han SY, Kim H-T, Ando K, Kim T-G, Kang B-K, Klipp A, Yerriboina NP, Park J-G. Chemically controlled megasonic cleaning of patterned structures using solutions with dissolved gas and surfactant. *Ultrason Sonochem* 2022;82:105859. <http://dx.doi.org/10.1016/j.ultsonch.2021.105859>.
- [12] Udepurkar AP, Clasen C, Kuhn S. Emulsification mechanism in an ultrasonic microreactor: Influence of surface roughness and ultrasound frequency. *Ultrason Sonochem* 2023;94:106323. <http://dx.doi.org/10.1016/j.ultsonch.2023.106323>.
- [13] Hao X, Suo H, Peng H, Xu P, Gao X, Du S. Simulation and exploration of cavitation process during microalgae oil extracting with ultrasonic-assisted for hydrogen production. *Int J Hydrog Energy* 2021;46(3):2890–8. <http://dx.doi.org/10.1016/j.ijhydene.2020.06.045>.
- [14] Moreno Soto Á, Peñas P, Lajoinie G, Lohse D, Van Der Meer D. Ultrasound-enhanced mass transfer during single-bubble diffusive growth. *Phys Rev Fluids* 2020;5(6):063605. <http://dx.doi.org/10.1103/PhysRevFluids.5.063605>.
- [15] Smith WR, Wang Q. A tractable mathematical model for rectified diffusion. *J Fluid Mech* 2022;951:A12. <http://dx.doi.org/10.1017/jfm.2022.849>.
- [16] Smith W, Wang Q. The role of surface tension on the growth of bubbles by rectified diffusion. *Ultrason Sonochem* 2023;98:106473. <http://dx.doi.org/10.1016/j.ultsonch.2023.106473>.
- [17] Zhang Y. Rectified mass diffusion of gas bubbles in liquids under acoustic field with dual frequencies. *Int Commun Heat Mass Transf* 2012;39(10):1496–9. <http://dx.doi.org/10.1016/j.icheatmasstransfer.2012.10.017>.
- [18] Zhang Y, Billson D, Li S. Influences of pressure amplitudes and frequencies of dual-frequency acoustic excitation on the mass transfer across interfaces of gas bubbles. *Int Commun Heat Mass Transf* 2015;66:167–71. <http://dx.doi.org/10.1016/j.icheatmasstransfer.2015.05.026>.
- [19] Wang X, Yan X, Min Q. Mass transfer of microbubble in liquid under multifrequency acoustic excitation—a theoretical study. *Ultrason Sonochem* 2024;102:106760. <http://dx.doi.org/10.1016/j.ultsonch.2024.106760>.
- [20] Dehane A, Merouani S, Hamdaoui O, Alghyamah A. A complete analysis of the effects of transfer phenomena and reaction heats on sono-hydrogen production from reacting bubbles: Impact of ambient bubble size. *Int J Hydrog Energy* 2021;46(36):18767–79. <http://dx.doi.org/10.1016/j.ijhydene.2021.03.069>.
- [21] Hong S, Son G. Numerical modelling of acoustic cavitation threshold in water with non-condensable bubble nuclei. *Ultrason Sonochem* 2022;83:105932. <http://dx.doi.org/10.1016/j.ultsonch.2022.105932>.
- [22] Park S, Son G. Numerical investigation of acoustic vaporization threshold of microdroplets. *Ultrason Sonochem* 2021;71:105361. <http://dx.doi.org/10.1016/j.ultsonch.2020.105361>.
- [23] Yasui K. Effects of thermal conduction on bubble dynamics near the sonoluminescence threshold. *J Acoust Soc Am* 1995;98(5):2772–82. <http://dx.doi.org/10.1121/1.413242>.
- [24] Lai T, Yan S, Zhao Q, Zhang Z, Ding W, Liu Y, Hou Y. Numerical study on thermodynamic growth of single hydrogen bubble in an infinite space. *Int J Hydrog Energy* 2022;47(58):24406–20. <http://dx.doi.org/10.1016/j.ijhydene.2022.05.209>.
- [25] Park J, Son G. Numerical investigation of acoustic droplet vaporization and tissue deformation. *Math Comput Simulation* 2024;225:412–29. <http://dx.doi.org/10.1016/j.matcom.2024.05.030>.
- [26] Qin D, Lei S, Chen B, Li Z, Wang W, Ji X. Numerical investigation on acoustic cavitation characteristics of an air-vapor bubble: Effect of equation of state for interior gases. *Ultrason Sonochem* 2023;97:106456. <http://dx.doi.org/10.1016/j.ultsonch.2023.106456>.
- [27] Peng K, Qin FG, Jiang R, Kang S. Interpreting the influence of liquid temperature on cavitation collapse intensity through bubble dynamic analysis. *Ultrason Sonochem* 2020;69:105253. <http://dx.doi.org/10.1016/j.ultsonch.2020.105253>.
- [28] Wong CC, Preso DB, Qin Y, Sinhmar PS, Zong Z, Kwan J. Ultrasound-driven seawater splitting catalysed by TiO₂ for hydrogen production. *Int J Hydrog Energy* 2025;111:723–34. <http://dx.doi.org/10.1016/j.ijhydene.2025.02.327>.
- [29] Akhatov I, Lindau O, Topolnikov A, Mettin R, Vakhitova N, Lauterborn W. Collapse and rebound of a laser-induced cavitation bubble. *Phys Fluids* 2001;13(10):2805–19.
- [30] Park J, Son G. A level-set method for ultrasound-driven bubble motion and tissue deformation. *Commun Nonlinear Sci Numer Simul* 2023;128:107619. <http://dx.doi.org/10.1016/j.cnsns.2023.107619>.
- [31] Man YAG, Trujillo FJ. A new pressure formulation for gas-compressibility dampening in bubble dynamics models. *Ultrason Sonochem* 2016;32:247–57. <http://dx.doi.org/10.1016/j.ultsonch.2016.03.013>.
- [32] Löfstedt R, Barber BP, Putterman SJ. Toward a hydrodynamic theory of sonoluminescence. *Phys Fluids* 1993;5(11):2911–28. <http://dx.doi.org/10.1063/1.858700>.
- [33] Westerheide DE, Westwater J. Isothermal growth of hydrogen bubbles during electrolysis. *AIChE J* 1961;7(3):357–62. <http://dx.doi.org/10.1002/aic.690070303>.
- [34] Dapkus KV, Sides PJ. Nucleation of electrolytically evolved hydrogen at an ideally smooth electrode. *J Colloid Interface Sci* 1986;111(1):133–51. [http://dx.doi.org/10.1016/0021-9797\(86\)90014-7](http://dx.doi.org/10.1016/0021-9797(86)90014-7).
- [35] Riegel H, Mitrovic J, Stephan K. Role of mass transfer on hydrogen evolution in aqueous media. *Russ J Appl Chem* 1998;28:10–7. <http://dx.doi.org/10.1023/A:1003285415420>.
- [36] Ilinskii YA, Wilson PS, Hamilton MF. Bubble growth by rectified diffusion at high gas supersaturation levels. *J Acoust Soc Am* 2008;124(4):1950–5. <http://dx.doi.org/10.1121/1.2973235>.
- [37] Manickam S, Boffito DC, Flores EM, Leveque J-M, Pflieger R, Pollet BG, Ashokkumar M. Ultrasonics and sonochemistry: Editors' perspective. *Ultrason Sonochem* 2023;99:106540. <http://dx.doi.org/10.1016/j.ultsonch.2023.106540>.
- [38] Lauterborn W. Numerical investigation of nonlinear oscillations of gas bubbles in liquids. *J Acoust Soc Am* 1976;59(2):283–93. <http://dx.doi.org/10.1121/1.380884>.
- [39] Murakami K, Yamakawa Y, Zhao J, Johnsen E, Ando K. Ultrasound-induced nonlinear oscillations of a spherical bubble in a gelatin gel. *J Fluid Mech* 2021;924:A38. <http://dx.doi.org/10.1017/jfm.2021.644>.
- [40] Zhao Y, Feng Y, Wu L. Nonlinear effects of dual-frequency focused ultrasound on the on-demand regulation of acoustic droplet vaporization. *Ultrason Sonochem* 2024;104:106848. <http://dx.doi.org/10.1016/j.ultsonch.2024.106848>.
- [41] Prosperetti A. Vapor bubbles. *Annu Rev Fluid Mech* 2017;49(1):221–48. <http://dx.doi.org/10.1146/annurev-fluid-010816-060221>.
- [42] Hao Y, Prosperetti A. The dynamics of vapor bubbles in acoustic pressure fields. *Phys Fluids* 1999;11(8):2008–19. <http://dx.doi.org/10.1063/1.870064>.