Radical production inside an acoustically driven microbubble

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ABSTRACT

The chemical production of radicals inside acoustically driven bubbles is determined by the local temperature inside the bubbles and by their composition at collapse. By means of a previously validated ordinary differential equations (ODE) model [L. Stricker, A. Prosperetti, D. Lohse, Validation of an approximate model for the thermal behavior in acoustically driven bubbles, J. Acoust. Soc. Am. 130 (5) (2011) 3243–3251], based on boundary layer assumption for mass and heat transport, we study the influence of different parameters on the radical production. We perform different simulations by changing the driving frequency and pressure, the temperature of the surrounding liquid and the composition of the gas inside the bubbles. In agreement with the experimental conditions of new generation sonochemical reactors, where the bubbles undergo transient cavitation oscillations [D. F. Rivas, L. Stricker, A. Zijlstra, H. Gardeniers, D. Lohse, A. Prosperetti, Ultrasound artificially nucleated bubbles and their sonochemical radical production, Ultrason. Sonochem. 20 (1) (2013) 510–524], we mainly concentrate on the initial chemical transient and we suggest optimal working ranges for technological applications. The importance of the chemical composition at collapse is reflected in the model, including the role of entrapped water vapor. We in particular study the exothermal reactions taking place in H_2 and O_2 mixtures. At the exact stoichiometric mixture 2:1 the highest internal bubble temperatures are achieved.

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1. Introduction

An acoustically driven microbubble can produce extreme conditions of temperature and pressure, thus giving rise to emission of light ("*sonoluminescence*", SL) [1–5] and chemical conversions, involving the gas inside the bubble and the surrounding liquid ("*sonochemistry*") [6–11]. Chemical reactions also play the main role in stabilizing single sonoluminescent air bubbles [12,13].

The chemical output, as well as the light emission, is highly influenced by the experimental parameters such as the driving pressure and frequency, the initial saturation concentration, the liquid temperature and pressure and the kind and amount of dissolved gas. For technological applications, a deep understanding of these dependencies is crucial in order to optimize the radical production.

A number of studies of the frequency effect have been published, some with conflicting results. Experiments on multi-bubble systems (MBSL) reported an increase in OH radical production with increasing frequency [14,15] up to an optimal value around 300–400 kHz [16,17]. On the other side, experiments on single sonoluminescent bubbles (SBSL) revealed that the radical production decreased as the frequency increased [18]. These two results may

seem contradictory but can be explained considering that, at low frequency, the bubbles grow bigger and their collapses are more violent, often leading to transient cavitation. Therefore each bubble undergoes only few oscillations before fragmentation at these low frequencies and it is mainly filled with water vapor [19,20]. Conversely, at high frequency stable cavitation is generally the main form of cavitation: bubbles exist for a long period of time and they contain mainly the gas originally dissolved in water [19,21]. Moreover, the different sizes of the nucleated bubbles have to be considered: the bubbles are smaller at higher frequency and therefore possibly more chemically active [22]. Bubble–bubble interaction and its induced flow could also play a role on the chemical activity, which is however not yet understood.

Other relevant parameters to the radical production are the conditions of the liquid. It has been calculated that there is an optimal bulk temperature for radical production both with air [23] and argon bubbles [24]. This trend is related to the competing effects of the entrapped water vapor, that decreases the temperature of the gas inside the bubble at collapse [25] but also increases the amount of reactants. This trend was retrieved in experiments both with water [26,14,16] and organic solvents, such as methanol/water mixtures [27].

The dependence of the radical production on the ambient pressure has been studied both experimentally [28,29], and theoretically [30], showing that decreasing the ambient pressure has the same effects than increasing the driving amplitude, as a higher

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radical production follows [16,18]. Some authors reported an asymptotic behavior of the oxidants production with increasing driving pressures and ascribed it to the entrapped vapor [31].

Many authors examined the effect of the kind and composition of the dissolved gas, both experimentally [32–34,16,17] and numerically [24]. Studies of different kinds of noble gases [32,33] have established a correlation between the light emission, and therefore the temperature at collapse, and the thermal conductivity of the gas: as the latter increases, more heat can escape from the bubble at collapse, thus reducing the peak temperature. Investigations over different mixtures of a noble and a diatomic gas reported higher reaction rates for large percentages of the noble gas, both from experiments [16,17] and numerics [24]. This behavior was ascribed to the larger adiabatic exponent γ of the mixture: as γ rises, so does the temperature at collapse. However, these studies should be considered with care, when the focus is the sonochemical outcome from MBSL, as not all of the chemically active bubbles emit light [35]. In a strict sense, talking about "the temperature" inside the bubble at collapse may also be misleading, since thermal equilibrium is not reached and a non-thermal plasma is formed, where the electron temperature is different from the vibrational temperature (e.g. of OH) and from the gas temperature [36–38].

Direct quantitative comparisons between the mentioned theoretical studies on single bubble sonochemistry and experiments have always been problematic. Few experimental data are available on the radical production of a single air bubble in water [39,40]. Such experiments are difficult to perform in controlled conditions, because of the low amount of radicals produced per cycle and the long operating time required to detect any chemical output (some hours). In order to compare calculations with experiments, theoretical studies mainly concentrate on steady cavitation [41]. Some numerical papers include data on the early transient phase [42,43] but, to our knowledge, no systematic parametric study has been published on that yet.

Nevertheless, we believe that such a study can be crucial for technological applications, as in new generation efficient sonochemical multibubble reactors the bubbles are nucleated from oscillating menisci and present a lifetime of few acoustic cycles [22]. In our previous work [22], we considered each bubble as an independent sonochemical reactor and we used the bubbles themselves to measure the effective driving pressure. In the present work we concentrate on the transient state and we carry on an extensive scan of the parametric range. We also examine the temperatures inside the bubbles and we try to correlate it to the radical production for different gases. Yasui et al. [31,43] calculated that, for air bubbles, there is an optimal range of bubble temperature at collapse (between 4000 K and 6500 K) where oxidants production is maximum. If the temperature raises too much (above 7000 K) the sonochemical rate decreases due to oxidizing nitrogen reactions. Our results confirm this observation. Moreover, we found that under that threshold, the relevant element to chemical conversion is the temperature, as its increase always corresponds to an increase in the chemical output. Over that threshold, the dependence is not so clear anymore and other elements, such as the reactants concentration, become more relevant.

In our study, we use the simplified ODE model based on boundary layer approximation, previously developed in Refs. [25,44,45] and validated in Ref. [46], which was also found to be in good agreement with results by Storey and Szeri [47]. This model includes the Rayleigh–Plesset equation for the radial dynamics of the bubble, van der Waals law for the inner pressure, the energy equation for the temperature, heat and mass fluxes, water evaporation/condensation, changes of transport parameters according to changes of the mixture composition and a complete set of non-equilibrium chemical reactions for gas and water.

Despite the high level of simplification, this model manages to reproduce various features of chemical reactions, such as the explosive nature of stoichiometric mixtures of oxygen and hydrogen. Therefore we are confident that this approach could lead to realistic estimates of the radical production rate of single spherical collapsing bubbles and considerable increased efficiencies.

2. Model

We use an ODE model, based on the boundary layer approximation, previously developed in [20,44,45] and validated in [46]. We give here a summarizing description and we refer the reader to those papers for additional details.

We assume that the bubble contains a perfect gas with a spatially uniform temperature and pressure, i.e. low Mach numbers, and we neglect the formation of a non-thermal plasma inside the bubble at collapse [36–38]. We also assume spherical symmetry and shape stability, thus restricting our study to a range of parameters where these assumptions are reasonable [48,49].

We use the Rayleigh–Plesset equation to describe the radial dynamics of the bubble:

$$\left(1 - \frac{\dot{R}}{c}\right)R\ddot{R} + \frac{3}{2}\left(1 - \frac{\dot{R}}{3c}\right)\dot{R}^2 = \frac{1}{\rho}\left(1 + \frac{\dot{R}}{c}\right)(p - p_\infty - P(t)) + \frac{R\dot{p}}{\rho c}$$
$$- \frac{4v\dot{R}}{R} - \frac{2\sigma}{\rho R}. \tag{1}$$

The dot denotes time derivatives, R is the bubble radius, c is the speed of sound, ρ and v are the density and the kinematic viscosity of the liquid respectively, σ is the surface tension, p_∞ is the static pressure and $P(t) = P_a \cos \omega t$, with P_a the acoustic driving amplitude and $f = \omega/2\pi$ the frequency.

The gas pressure inside the bubble p is calculated from a modified van der Waals equation of state taking into account the gas inertia [45]:

$$p = \frac{N_{tot}k_B T}{V - N_{tot}B} - \frac{1}{2}\rho_B R\ddot{R}, \tag{2}$$

in which N_{tot} is the total number of gas molecules, ρ_B is the gas density, k_B the Boltzmann constant, and B the molecular co-volume.

The temperature T is determined by means of an energy balance over the bubble volume:

$$\dot{E} = \dot{Q} - p\dot{V} + \sum_i (h_{w,i} + e_{form,i})\dot{N}_i^d, \tag{3}$$

where E is the total energy of the bubble, V is the bubble volume, $\dot{N}_i^d$ the number of particles of component i diffusing inside the bubble per unit time, $h_{w,i}$ the molecular enthalpy of component i at the cold bubble wall and $e_{form,i}$ its enthalpy of formation. The net heat absorbed by the bubble per unit time $\dot{Q}$ is provided by

$$\dot{Q} = 4\pi R^2 \lambda_{mix} \frac{T_0 - T}{l_{th}}, \tag{4}$$

$$l_{th} = \min\left(\sqrt{\frac{R\chi}{|\dot{R}|}}, \frac{R}{\pi}\right), \tag{5}$$

with λ_{mix} the thermal conductivity of the gas mixture, l_{th} an estimate of the thickness of the thermal boundary layer inside the bubble [44,45] and T_0 the temperature of the liquid. Similarly the diffusive flux of component i is expressed by

$$\dot{N}_i^d = 4\pi R^2 D_i \frac{n_{i,0} - n_i}{l_{i,d}}, \tag{6}$$