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# The thermocapillary effect on gas bubbles growing on electrodes of different sizes

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## Abstract

Recently, the strongly inhomogeneous current density occurring near a microelectrode was identified as driving a thermocapillary electrolyte flow near gas bubbles growing during electrolysis [1]. The present paper is investigating this effect in more detail under various operating conditions. Furthermore, by simplified modeling, the question is answered of whether this effect is also of importance at large planar electrodes. The direction of the thermocapillary force on the bubble is found to change from retarding to advancing the bubble release when the size of the electrode is increased. Conclusions are drawn on how the thermocapillary effect at planar electrodes depends on the electrode coverage and the bubble departure size, also considering industrially relevant values of the current density.

*Keywords:* hydrogen evolution, electrolysis, thermocapillarity, Marangoni force, microelectrode, macroelectrode

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## 1. Introduction

Interfaces between media of different phases are ubiquitous in nature and play an important role in many physico-chemical systems. If liquids are involved, capillary effects often influence the system behavior [2]. The surface tension for a given liquid-gas pair is known to depend on physical properties of the interface, namely the temperature, chemical composition and electric potential in the presence of interfacial charge [3]. Thus, interfacial gradients of these physical properties cause the surface tension to vary along the interface. As a result, due to unbalanced forces at the interface, fluid elements there experience a net shear stress and move towards interface regions of higher interfacial tension. The resulting capillary flow is commonly called Marangoni flow [4]. This Marangoni effect is known to occur in many systems of scientific and technological importance. For example, thermo-capillarity is the mechanism which drives the well-known Bénard cells ([5–7] and references therein), a phenomenon occurring in many engineering heat transfer applications. In liquid-liquid extraction processes, soluto-capillary flows may significantly change the mass transfer rate

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21 [8]. Furthermore, Marangoni flow exists at sessile evaporating droplets due to the interfacial temperature  
22 gradient caused by a nonuniform rate of evaporation [9]. This influences the well-known coffee-ring-like  
23 structures [10], and may thus affect patterned deposition [11] and particle self-assembly [12].

24 In 1959, Young et al. [13] demonstrated the profound effect which Marangoni flow can have on air bubbles  
25 in liquids by applying a positive temperature gradient in the direction of gravity to suspend them against  
26 buoyancy. The temperature gradient induced a surface tension gradient along the bubble interface and  
27 thus exerted a thermocapillary stress on the interface, which caused the bubble to experience a force against  
28 buoyancy. At a sufficiently steep temperature gradient, the thermocapillary force can be as large as buoyancy.  
29 Later, with the advent of space research, bubble actuation in micro-gravity by means of thermocapillarity  
30 attracted much interest [14, 15]. Experiments conducted in the space shuttle in orbit showed that by applying  
31 a temperature gradient of the order of 1 K/mm, a bubble migration speed of  $\sim 1$ mm/s could be achieved  
32 for a bubble of millimeter size [16]. McGrew et al. [17] speculated that Marangoni convection might have a  
33 significant contribution to heat transfer in nucleate boiling, as the observed flow structure around a pendant  
34 air bubble heated from above was found to be similar to that of a vapor bubble during boiling. Later, in  
35 nucleate boiling experiments conducted under microgravity conditions, the heat transfer rate obtained by  
36 Straub was similar to that obtained under normal gravity conditions [18], which lent further credence to the  
37 importance of Marangoni flow around the bubbles. Further experiments and numerical simulations [19–21]  
38 established the significant importance of thermocapillarity-driven flow in the subcooled boiling regime and  
39 showed that the resulting Marangoni force acting on the bubble slowed down their detachment from the  
40 boiling surface [22].

41 It has long been hypothesised that the Marangoni effect also influences the dynamics of bubbles grown  
42 electrochemically on electrodes [23, 24]. Definitive experimental evidence of the Marangoni effect was first  
43 provided by Yang et al. [25], who performed a detailed investigation of the interfacial flow around hydrogen  
44 bubbles grown on a Platinum microelectrode. Then, by simultaneously measuring the electrolyte velocity  
45 and temperature and correlating the results with the numerical solution obtained when considering only ther-  
46 mocapillarity, Massing et al. [1] were able to show that the Marangoni flow observed is primarily attributed  
47 to the thermocapillary effect caused by the temperature gradient along the bubble interface. Interestingly,  
48 for strong local boiling at microheaters, the thermocapillary flow found near the gas bubble qualitatively  
49 matches the flow structure near the electrogenerated gas bubble at a microelectrode [1], though due to strong  
50 laser heating the maximum flow velocity is about 10 times higher [26].

51 As gas bubbles are generated in many electrochemical processes such as plating, refining of metal or  
52 the chloralkali process [27–29], a better understanding of the dynamics of electrogenerated bubbles and  
53 associated thermo-fluidic phenomena is of great technological and scientific interest. This is particularly  
54 relevant for  $H_2$  production through water electrolysis, as the bubble evolution rate directly influences both  
55 the system throughput and the process efficiency [30], which may be of increasing importance for next-

56 generation green energy storage and mobility applications [31–33].

57 As bubbles attached to the electrode surface disturb a homogeneous surface reaction rate, reduce the  
58 active reaction area and increase the electrical resistance of the cell, the speedy removal of generated bubbles  
59 from the electrode surface is highly desirable with respect to both deposit quality and electrical efficiency.  
60 The instant of bubble departure and the departing diameter is determined by the equilibrium of forces acting  
61 on the bubble [34]. However, the often-used Fritz equation [35] does not provide an accurate prediction of  
62 the departure diameter [36]. For the special case of oxygen bubbles grown photocatalytically on TiO<sub>2</sub>  
63 nanorods where a temperature gradient is caused by light irradiation, Chen et al. have recently shown that  
64 the inclusion of both thermocapillary and solutal Marangoni forces in the force balance of the bubble could  
65 considerably improve the estimate of the bubble departure [37]. However, beside the aforementioned study  
66 by Massing et al. [1], where a retarding influence of the thermocapillary effect on the bubble departure was  
67 found, no systematic study has been carried out for electrogenerated bubbles.

68 For studying bubble evolution during electrolysis, microscale electrodes have been widely used, as the  
69 nucleation area is limited, and single bubble growth can be more easily observed compared to the spatially  
70 random nucleation occurring at large planar electrodes [38–41]. The recent work which was the first to  
71 confirm the existence of thermocapillary flow around electrogenerated bubbles [1] was also carried out at  
72 microelectrodes. However, there remains a need for more detailed investigations of this phenomenon. In  
73 particular, the question has not yet been addressed of whether this effect is also of importance at the larger  
74 electrodes, which are more relevant to industrial applications. Therefore, in this study we perform detailed  
75 numerical simulations and analyses of the thermocapillary effect at electrogenerated bubbles on electrodes  
76 of varying size. Different operating conditions are investigated, and the important qualitative differences  
77 found between microelectrodes and macroelectrodes will be emphasized.

## 78 2. Simulation setup

79 *Microelectrode.* To study the thermocapillary effect around a hydrogen bubble at a microelectrode of vary-  
80 ing size, our simulation setup closely follows the methodology used by Massing et al. [1]. A cylindrical  
81 electrochemical cell with a radius  $R_c = 5$  mm and a height  $R_h = 5$  mm is considered. It is filled with an  
82 aqueous solution of 1 M H<sub>2</sub>SO<sub>4</sub>. The computational domain is sketched in Figure 1a. At the bottom of  
83 the cell, a bubble with a radius  $R_b = 560$   $\mu$ m sits on a Pt microelectrode (radius  $R_e$ ), which works as the  
84 cathode. The contact angle between the bubble and electrode is  $\theta_c = 4.2^\circ$  [1]. It should be noted here that  
85 the bubble radius is much smaller than the size of the cell. The Pt microelectrode is embedded in a glass  
86 bottom. The top of the cell is completely covered by a counter-electrode made of platinum. The electrodes  
87 and the glass bottom have a height of 5 mm each. The inclusion of the glass bottom and both electrode  
88 domains is important for an accurate calculation of the temperature field in the electrolyte due to non-zero

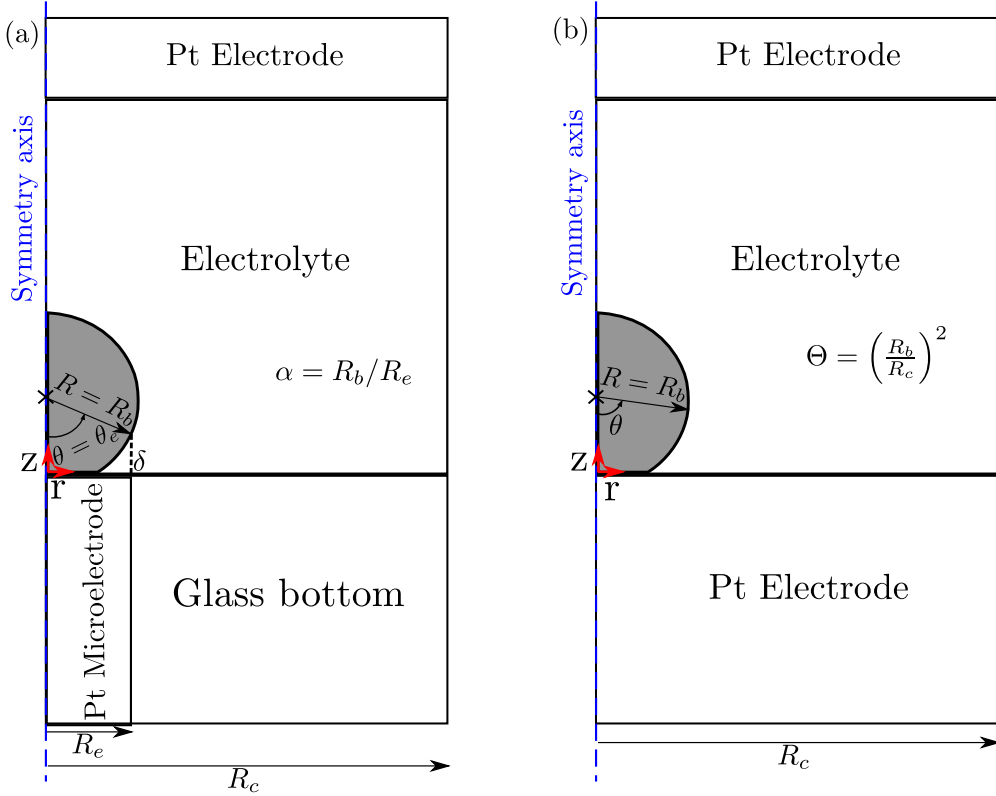


Figure 1: Computational domain (not to scale). a) microelectrode, b) macroelectrode.

89 and non-uniform heat flux through these domains.

90 We follow Massing et al. [1] and consider a bubble of fixed size to resemble a late stage of the bubble  
 91 growth cycle. As shown in Figure 1, we utilize the rotational symmetry of the cell and hence perform  
 92 axisymmetrical simulations. The leftmost edge in Figure 1 is the axis of symmetry. The following equations  
 93 to be solved describe the spatial and temporal distribution of the electric potential ( $\phi$ ), velocity ( $\mathbf{u}$ ) and  
 94 temperature ( $T$ ) in the electrolyte:

$$\nabla^2 \phi = 0 \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

$$\rho \left( \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (3)$$

$$\rho C_p \left( \frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T \right) = k \nabla^2 T + \frac{|\mathbf{j}|^2}{\sigma} \quad (4)$$

98 Here, the primary current density  $\mathbf{j} = -\sigma \nabla \phi$  is obtained by solving Eq. (1), where  $\sigma$  denotes the electrical  
 99 conductivity of the electrolyte, which is assumed to be constant. The electrolyte velocity is obtained by  
 100 solving the incompressible Navier-Stokes equation (3) complemented by the incompressibility constraint (2),

101 where  $p$ ,  $\rho$  and  $\mu$  denote the pressure field and the material properties of density and viscosity. Thermal  
 102 and solutal buoyancy effects may safely be neglected, as discussed in [1]. The electrolyte temperature is  
 103 obtained by solving Equation (4), where  $C_p$  and  $k$  denote the material properties of the specific heat capacity  
 104 and thermal conductivity. The latter term denotes Joule heating due to electric current passing through the  
 105 electrolyte. It should be noted here that this term may be neglected in the electrodes, where the electrical  
 106 conductivity  $\sigma$  is several orders of magnitude larger than in the electrolyte. Therefore, in all other domains  
 107 (both electrodes, glass bottom and gas bubble), only heat diffusion is solved:

$$\rho C_p \frac{\partial T}{\partial t} = k \nabla^2 T \quad (5)$$

108 Here, convective heat transport in the gas bubble may safely be neglected, as discussed in [1].

109 The boundary conditions applied to these equations are as follows: for Equation (1), the electrode  
 110 surfaces exposed to electrolyte are kept at a fixed potential, i.e.  $\phi = 0$  for the working electrode and  $\phi = \phi_0$   
 111 for the counter electrode. The outer boundary at  $R_c$  is electrically insulating, i.e.  $\frac{\partial \phi}{\partial \mathbf{n}} = 0$ , where  $\mathbf{n}$  is the  
 112 normal unit vector. For Equation (3), a shear stress balance is applied at the electrolyte–bubble interface,  
 113 i.e.  $\tau_H = \tau_M$ , where the hydrodynamic shear stress is given by  $\tau_H = \mu \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) \cdot \mathbf{n}$ , and the thermal  
 114 Marangoni stress is given by

$$\tau_M = \frac{\partial \gamma}{\partial T} \cdot \nabla_s T \quad (6)$$

115 Here,  $\gamma$  denotes the interfacial tension, which is assumed to depend on the temperature only, and  
 116  $\nabla_s \equiv \nabla - (\nabla \cdot \mathbf{n}) \mathbf{n}$  denotes the gradient along the surface of the interface. As the temperature field is  
 117 solved in all domains by Eqns. (4) and (5), boundary conditions are required only at the outermost surfaces.  
 118 The top and the bottom of the computational domain are kept at an ambient temperature  $T_{amb} = 20^\circ \text{C}$ ,  
 119 while at the outer surface at  $R_c$  far from the bubble an adiabatic condition  $\frac{\partial T}{\partial \mathbf{n}} = 0$  is applied. Finally, at the  
 120 symmetry axis at  $r = 0$ , a zero radial gradient condition is applied on all variables, i.e.  $\frac{\partial}{\partial r}(\phi, \mathbf{u}, T) = 0$ . The  
 121 temperature coefficient of the surface tension at the gas-liquid interface is taken to be  $\partial \gamma / \partial T = -1.6 \cdot 10^{-4}$   
 122 N/m·K [1]. The value of the surface tension  $\gamma$  does not appear directly in our model as the bubble is  
 123 assumed to be of fixed shape and size. All other material properties are assumed to be constant over the  
 124 electric potential and temperature range solved for and are shown in Tables 1 and 2.

125 All equations are solved using the FEM-based simulation software COMSOL 5.4. The initial conditions  
 126 applied are zero potential, electrolyte at rest and ambient temperature. As discussed extensively in [1],  
 127 a time integration period of one second was chosen at which nearly stationary and realistic values of the  
 128 temperature and velocity distribution and the resulting Marangoni force may be expected. To study the  
 129 effect of the size of the working microelectrode,  $R_e$  is varied while  $R_b$  is kept constant. We introduce a

Electrolyte	$\mu = 10^{-3} \text{ Pa}\cdot\text{s}$
	$\sigma = 40 \text{ S/m}$
	$\rho = 10^3 \text{ kg/m}^3$
	$C_p = 4.182 \text{ kJ/kg}\cdot\text{K}$
	$k = 0.58 \text{ W/m}\cdot\text{K}$

Table 1: Material properties of the electrolyte for Equations 3 and 4

Material	$\rho(\text{kg/m}^3)$	$C_p(\text{kJ/kg}\cdot\text{K})$	$k(\text{W/m}\cdot\text{K})$
Platinum	21450	0.13	72
Glass	2201	1.052	1.38
Hydrogen	0.09	14.32	0.186

Table 2: Material properties for Equation 5

130 non-dimensional length parameter as the ratio of the bubble radius and the microelectrode radius,

$$\alpha = \frac{R_b}{R_e} \quad (7)$$

131 As we are here primarily interested in studying how the increasing size of the microelectrode affects the  
 132 behavior in the vicinity of the gas bubble, unless otherwise mentioned, the radius of the microelectrode is  
 133 varied from  $50 \mu\text{m}$  to  $400 \mu\text{m}$  such that  $R_e < R_b$ , i.e.  $\alpha > 1$ .

134 *Macroelectrode.* To study the thermocapillary effect on a large, flat electrode where multiple gas bubbles  
 135 are growing simultaneously, we take a simplified approach as follows: we first zoom into a small part of the  
 136 electrode in order to focus only on a single bubble. A cylindrical domain around this bubble is considered,  
 137 where the radial extension  $R_c$  of the domain is half the distance to the next neighboring bubble. We  
 138 assume that the cell with large electrodes is essentially composed of this periodically repeating domain.  
 139 Though there are time shifts between the evolution cycles of neighboring bubbles, our simplified approach  
 140 therefore assumes that all bubbles develop synchronously and also ignores possible coalescence phenomena  
 141 of neighboring bubbles during growth. A further approximation consists in neglecting azimuthal variations  
 142 of potential, temperature and velocity which might arise from the finite number of neighboring bubbles  
 143 sitting at unknown azimuthal positions. This approach treats neighboring effects in an approximate manner  
 144 averaged over the azimuthal direction and allows the problem to be simulated axisymmetrically. We can  
 145 therefore make use of the axisymmetric computational domain shown in Figure 1b, which is similar to the  
 146 one used previously for the microelectrode shown in Figure 1a, and which only needs minor modifications:  
 147 at the bottom of the cell, the outer glass part is removed, and the electrode is now enlarged over the full  
 148 radial extent of the cell  $R_c$ . At the outer radial boundary, the conditions of electrical insulation for the

149 potential and an adiabatic condition for the temperature remain unchanged, but in the case of the velocity,  
 150 vertical slip is applied. The governing equations to be solved for remain as before. In order to quantify the  
 151 ratio between the bubble size and the size of the cell, we introduce

$$\Theta = \left( \frac{R_b}{R_c} \right)^2 \quad (8)$$

152 In the framework of our approach, this ratio describes the bubble coverage of the electrode which is defined  
 153 as the ratio of the bubble area projected on the electrode and the electrode surface area. We can later simply  
 154 change the bubble coverage of the electrode (which is known to depend on e.g. the mean current density),  
 155 for example by varying the radial extension of the cell while retaining a fixed bubble size.

### 156 3. Results and Discussion

#### 157 3.1. Microelectrode

##### 158 3.1.1. General overview

159 It is evident from Equation 4 that the electrolyte is heated because of the electric current passing through  
 160 the cell. This causes a temperature gradient along the bubble interface which gives rise to Marangoni  
 161 flow. Therefore, the current distribution near the interface strongly influences the temperature and flow  
 162 distribution in the electrolyte. Figure 2(a) shows numerically obtained current lines near the interface for  
 163  $\alpha = 11.2$ . As the gas bubble is electrically insulating, current must pass around it to converge at the  
 164 microelectrode. Therefore, as the entire cell current must squeeze through a narrow wedge-like region at  
 165 the bubble foot, the local current density there is very high. In addition, the presence of the bubble makes  
 166 the outer region of the electrode more accessible to the electric current. This causes an inhomogeneous  
 167 distribution of the current density over the electrode surface wetted by the electrolyte, as shown in Figure 2(b)  
 168 for different microelectrode sizes. Here, the cell voltage was kept constant at  $\phi_0 = 4.5$  V, and the radial  
 169 position on the microelectrode is presented normalized by the electrode radius, i.e.  $r^* = r/R_e$ . As the  
 170 current density is shown on a logarithmic scale, it clearly can be seen that it varies quite strongly over the  
 171 radial electrode position and is largest at the electrode periphery. The smaller the microelectrode becomes,  
 172 the stronger the radial variation of the current density and also its maximum value at the electrode periphery.

173 As the rate of heat generation scales with the current density squared ( $|\mathbf{j}|^2$ ), the electrolyte experiences  
 174 strong heating near the periphery of the electrode. Figure 3 shows a zoomed view of the distribution of the  
 175 temperature rise ( $\Delta T = T - T_{amb}$ ) in the vicinity of the outer electrode edge for  $R_e = 200 \mu\text{m}$  ( $\alpha = 2.8$ ). It  
 176 can be seen that the temperature maximum occurs just above the microelectrode periphery at  $r^* = 1$ . As  
 177 the surface tension of the bubble interface decreases with increasing temperature, the electrolyte is pulled  
 178 towards colder parts of the interface, thus establishing an interfacial flow away from the point of maximum  
 179 temperature. As this bidirectional interfacial flow must be replenished from the bulk, a double-vortex



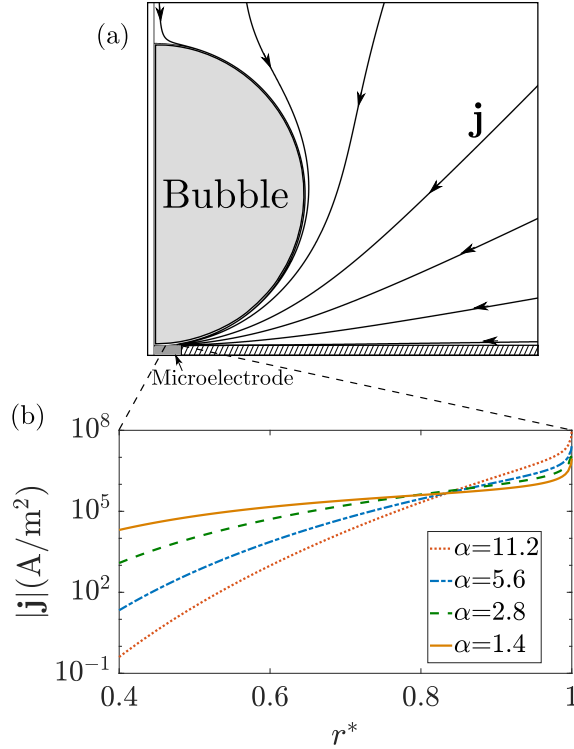


Figure 2: (a) Current lines near the bubble interface as obtained from a simulation for  $\phi_0 = 4.5$  V and  $\alpha = 11.2$ . (b) Distribution of the magnitude of the current density ( $|j|$ ) on microelectrodes of different size versus the radial position on the wetted part of the electrode normalized with the electrode radius ( $r^* = r/R_e$ ).  $\phi_0 = 4.5$  V.  $|j|$  is shown in log scale.

180 structure is created, as shown for the first time in Figure 3. As will be elaborated in the following, this  
 181 double-vortex structure is a characteristic feature of the thermocapillary flow driven at the interface of an  
 182 electrogenerated bubble. In the case of microelectrodes, for geometric reasons, the temperature hotspot  
 183 appears above the electrode periphery, thus confining the left vortex, and the thermocapillary effect is  
 184 dominated by the large right vortex. The small size of the left vortex explains, why it was not observed  
 185 during earlier work at microelectrodes [1].

### 186 3.1.2. Interfacial temperature and velocity profile

187 We now discuss the interfacial temperature and velocity profiles at electrodes of different sizes  $R_e$  while  
 188 the cell voltage is kept constant at  $\phi_0 = 4.5$  V. It is to be noted here that, at constant voltage, the electrical  
 189 resistance of the cell decreases and hence the cell current increases when the microelectrode is enlarged. The  
 190 obtained profiles of the temperature increment  $\Delta T$  and tangential velocity ( $u_t = \mathbf{u} \cdot \mathbf{t}$ ) along the bubble  
 191 interface are shown in Figure 4, with the definition of the angular position  $\theta$  based on Figure 1. Starting  
 192 from the point of contact between the bubble and electrode ( $\theta_c = 4.2^\circ$ ), an initial temperature increment  
 193 is seen in all cases. The smaller the microelectrode is, i.e. the larger  $\alpha$  is, the steeper the increase in

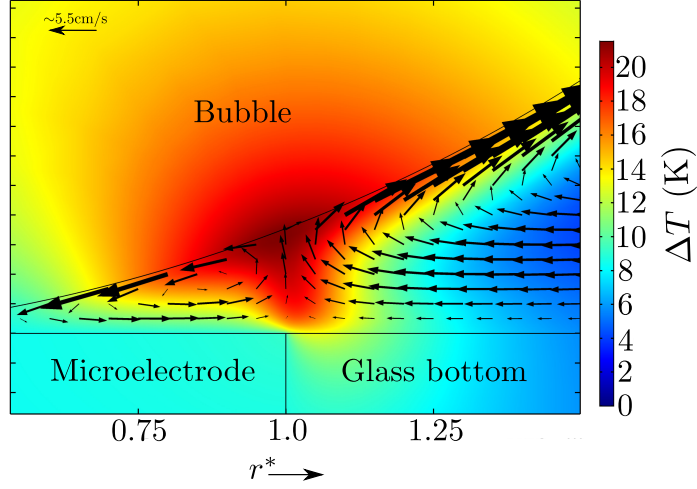


Figure 3: Color contours of the temperature distribution ( $\Delta T = T - T_{amb}$ ) and related electrolyte flow pattern (black: velocity vectors) near the temperature hotspot for a microelectrode of  $R_e = 200 \mu\text{m}$  ( $\alpha = 2.8$ ) at potential  $\phi_0 = 4.5 \text{ V}$ . The radial coordinate is  $r^* = r/R_e$ .

194 temperature becomes. At the same time, the angle  $\theta_m$  at which the maximum temperature increase  $\Delta T_m$   
 195 is observed reduces. This behavior can qualitatively be understood from the discussion on the temperature  
 196 hotspot in the section above: this was found to be located approximately above  $r^* = 1$ . Therefore, when the  
 197 microelectrode grows in size,  $\theta_m$  also increases. A more detailed discussion on  $\theta_m$  is given in Section 3.1.3.  
 198 Moving further along the interface away from  $\theta_m$ ,  $\Delta T$  gradually decreases towards the bubble north pole at  
 199  $\theta = 180^\circ$ . This general trend in the interfacial temperature profile is seen for all cathode sizes investigated.

200 It is also to be noted here that the variation of  $\Delta T_m$  with  $\alpha$  is not monotonic. This is because increasing  
 201  $R_e$  while keeping  $\phi_0$  constant increases the cell current. Thus the total heat generation in the cell increases,  
 202 which tends to increase the peak interfacial temperature. As the electrode gets bigger, more heat is carried  
 203 away by the Pt microelectrode. Greater heat advection from the hotspot by the electrolyte (cf. Figure 4(b))  
 204 also contributes similarly. These effects tend to reduce  $\Delta T_m$ . As a result of the combined action of greater  
 205 heat generation and higher heat transfer,  $\Delta T_m$  varies non-monotonically with  $R_e$  and thus  $\alpha$ . Hence we can  
 206 see from Figure 4(a) that  $\Delta T_m$  first increases and then decreases to an almost constant value with a larger  
 207 electrode i.e. smaller  $\alpha$ .

208 The non-uniform interfacial temperature profile causes thermocapillary stress as shown in Equation 6.  
 209 Because of the stress balance at the interface,  $\tau_M = \tau_H \sim \frac{\partial u_t}{\partial \theta}$ , where  $u_t$  denotes the tangential velocity  
 210 at the interface, a Marangoni flow is driven, as already mentioned in Section 3.1.1. The interfacial flow  
 211 profiles for different microelectrode sizes are shown in Figure 4(b) and can be understood by applying the  
 212 following sequence of reasoning: According to Equation 6, when the negative temperature coefficient of the  
 213 surface tension of the electrolyte mentioned in Section 2 is taken into account, positive or negative slopes

214 of the temperature profile cause negative or positive thermocapillary stress, respectively. Hence, because of  
 215 the stress balance, the tangential velocity of the Marangoni flow becomes negative or positive, respectively.  
 216 Consequently, as the flow is purely driven by thermocapillarity, the temperature hotspot separates a region  
 217 of negative tangential velocity at small angles from a region of positive tangential velocity at larger angles.  
 218 At the temperature hotspot  $\theta_m$  itself, the tangential velocity must vanish, i.e.  $u_t = 0$ . In Figure 4 and later  
 219 also in Figure 5, an example of this is emphasized for the case  $\alpha = 5.6$  by a vertical black line. The two  
 220 regions of velocity of opposite sign are the interfacial parts of the two counter-rotating vortices already seen  
 221 in Figure 3. As the microelectrode increases in size, the region of negative velocity also increases, yielding  
 222 a larger vortex above the microelectrode. At the same time, the extremum positions of maximum negative  
 223 and positive interfacial velocity are both shifted towards larger angles. During this process, the maximum  
 224 negative velocity decreases monotonically in amplitude, with the initially growing maximum velocity later  
 225 seeming to level out near a value of about 15 cm/s for  $\alpha \sim 1$ . However, the total kinetic energy at the  
 226 interface reaches a maximum at the largest microelectrode size, a straightforward example of the above  
 227 argument of maximum heat generation at smallest  $\alpha$ .

228 The interfacial temperature distribution at the bubble is determined by the interplay between the gener-  
 229 ation of heat and the diffusion and advection of heat. For the case of a constant cell voltage ( $\phi_0$ ) considered  
 230 above, all these quantities vary with varying electrode size ( $\alpha$ ). In order to partly decouple these effects, in  
 231 the following we study the case of a constant electric cell power which mainly (apart from kinetic losses)  
 232 determines the generation of heat by Joule dissipation. The total electric power of the cell is given by  
 233  $P = \phi_0 I_c$ , where  $I_c$  is the cell current, which in the simulations was determined by integrating the normal  
 234 current density over the counter-electrode surface ( $I_c = \int j_n dA$ ). In the following, the electrical power is  
 235 kept constant at  $P = 13.4$  mW and  $\alpha$  is varied. This power value chosen is the same as the constant cell  
 236 voltage case at  $\alpha = 11.2$ , i.e. for the smallest electrode. Hence, the constant cell potential and constant  
 237 cell power cases are identical for  $\alpha = 11.2$ . This way, a major remaining factor determining  $\Delta T(\theta)$  along  
 238 the bubble interface is the heat carried by the Pt microelectrode, which increases with decreasing  $\alpha$ . The  
 239 simulation results are shown in Figure 5. The interfacial temperature profile still maintains the character-  
 240 istics seen in Figure 4(a). However, because the heat generation is kept constant and the heat carried away  
 241 from the electrolyte increases along with the electrode size,  $\Delta T_m$  decreases monotonically with decreasing  
 242  $\alpha$ , as seen in Figure 5(a). Accordingly, the extrema of maximum negative and positive interfacial velocity  
 243 eventually decrease monotonically with decreasing  $\alpha$ , as seen in Figure 5(b). The same holds for the total  
 244 kinetic energy at the interface.

### 245 3.1.3. Position of the temperature hotspot

246 As mentioned in Section 3.1.2, the reversal of the direction of interfacial flow coincides with the location  
 247 of the temperature maximum  $\Delta T_m$  at the angular position  $\theta_m$ . It can be further seen in Figure 3 that

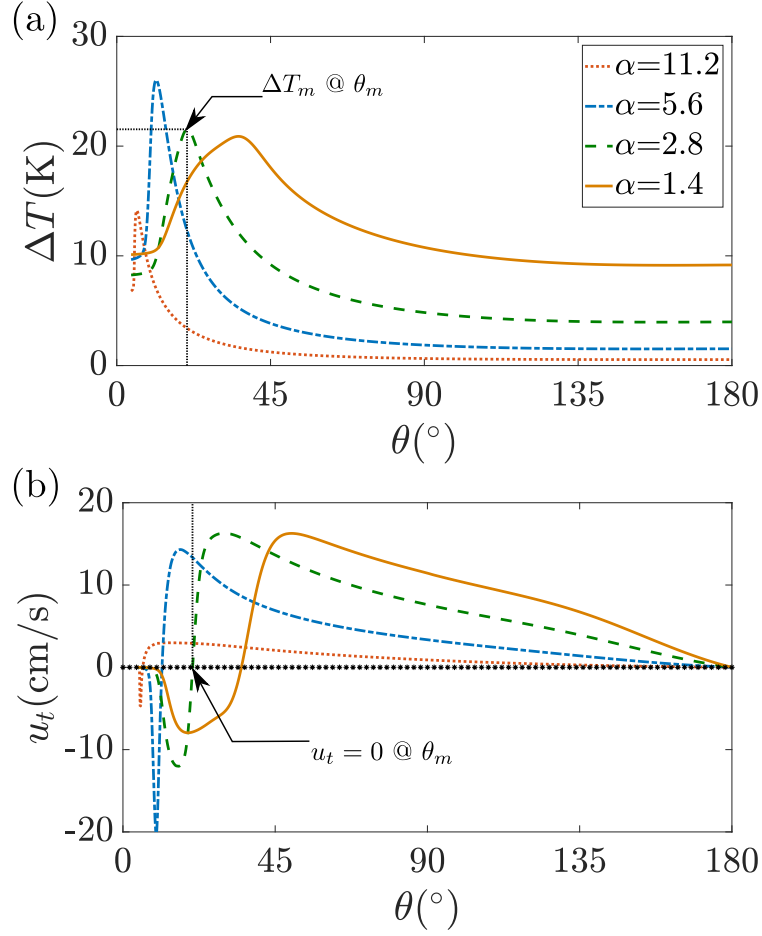


Figure 4: Constant cell voltage case: interfacial temperature (a) and tangential velocity (b) profile as a function of angular position for different electrode sizes expressed by  $\alpha = R_b/R_e$

248 for  $\alpha = 2.8$  the position of  $\Delta T_m$  coincides with the upward projection of the microelectrode's outer edge  
 249 ( $r^* = 1$ ) onto the bubble interface, as shown in Figure 1. Therefore, we intend to study  $\Delta T_m$  closer to see  
 250 whether this geometrical interpretation also holds true for other microelectrode sizes. The angular position  
 251 of the projection of the microelectrode's outer edge ( $r^* = 1$ ) on the bubble interface is given as

$$\theta_e = \sin^{-1}(R_e/R_b) = \sin^{-1}(1/\alpha). \quad (9)$$

252 Figure 6 displays the angular position of the interfacial temperature maximum  $\theta_m$  versus the inverse relative  
 253 electrode size  $\alpha = R_b/R_e$  as obtained from simulations for the cases of constant cell voltage (Figure 4a) and  
 254 of constant cell power (Figure 5a) in comparison with the values  $\theta_e$  obtained from the geometrical approach  
 255 by Equation 9. At small relative electrode size, i.e. at large  $\alpha$ , the simulation results for both cases perfectly  
 256 match with the geometrical relation from Equation 9, which provides a very accurate estimate of the location  
 257 of the temperature maximum at the interface. As the microelectrode increases in size, only small differences

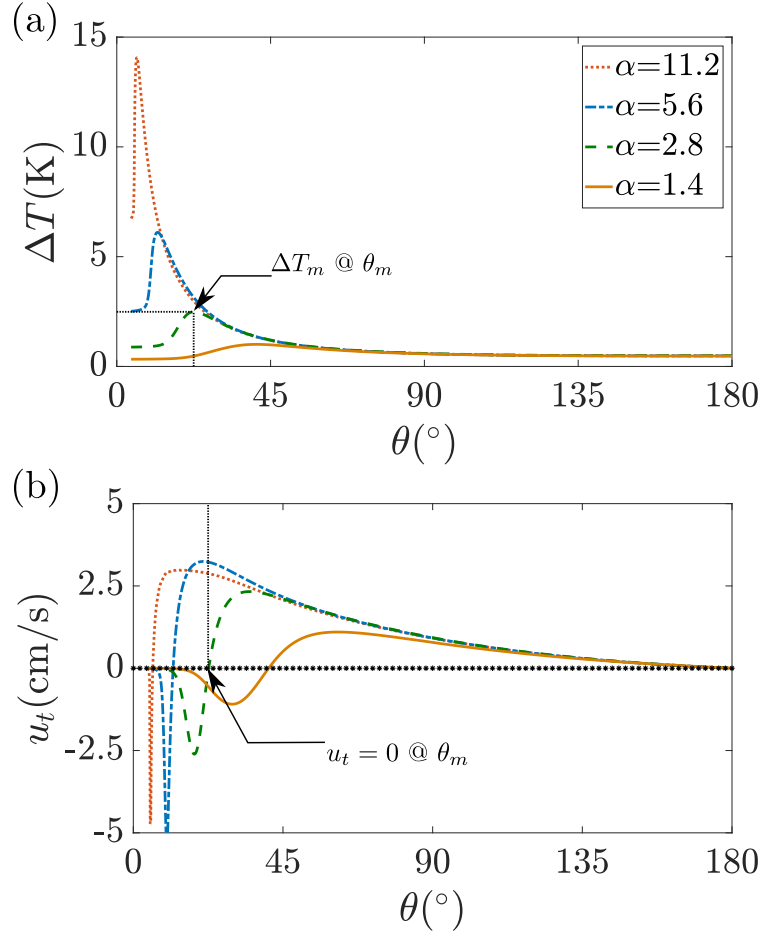


Figure 5: Constant cell electric power ( $P = 13.4$  mW) case: interfacial temperature (a) and velocity (b) profile as a function of the angular position for different electrode sizes expressed by  $\alpha = R_b/R_e$

258 are seen between the two simulation cases, besides an overall good match being maintained with Equation 9.  
 259 Eventually, at  $\alpha = 1.2$ , both cases seem to deviate from the analytical curve and deliver smaller angular  
 260 positions of the temperature hotspot than Equation 9. This is caused by the fact that as the microelectrode  
 261 increases in size, as seen from Figure 2, the non-uniformity of the current density, i.e. the ratio of the peak  
 262 value at the electrode edge in comparison to the mean value, decreases. Therefore, as  $\alpha$  approaches unity,  
 263 inner parts of the electrode surface also contribute to the generation of the temperature hotspot, which leads  
 264 to the observed slight shift in the position of the temperature maximum towards smaller angular positions.  
 265 In summary, the geometrically estimated angular position  $\theta_e$  of the temperature maximum  $\theta_m$  based on the  
 266 inhomogeneous distribution of the current density at the microelectrode provides a useful estimation of the  
 267 position of the temperature maximum  $\theta_m$  and the resulting interfacial flow characteristics at the bubble  
 268 interface at the microelectrode without the need to perform detailed simulations or experimentation. We  
 269 would also like to point out here that Equation 9 is only valid for  $R_e \leq R_b$ , which coincides with the range

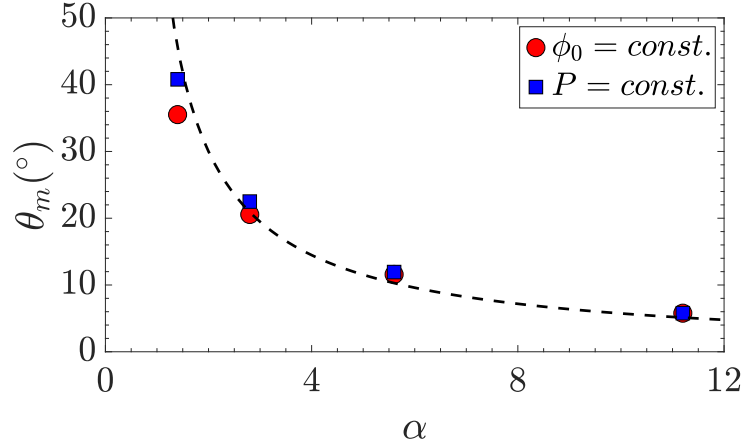


Figure 6: Angular position of the interfacial temperature maximum ( $\theta_m$ ) versus  $\alpha = R_b/R_e$  at fixed  $R_b = 560 \mu\text{m}$  for the cases of constant cell voltage (red circles) and of constant cell power (blue squares). The dashed curve denotes the geometrical relation from Equation 9.

of studies for the microelectrode case presented here.

#### 3.1.4. Marangoni force

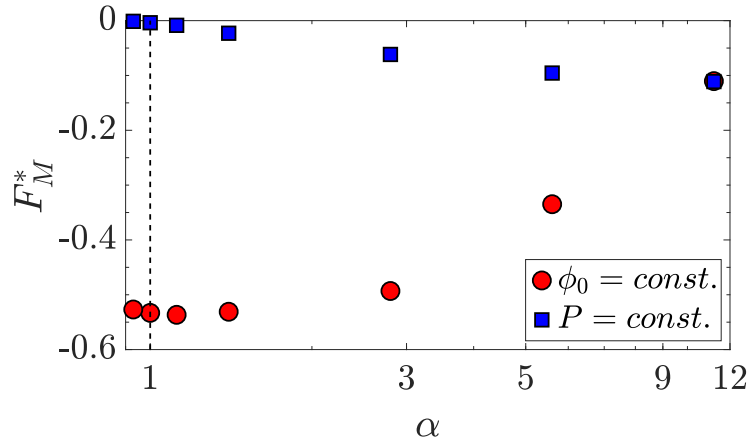


Figure 7: Marangoni force acting on the bubble, shown as normalized by the buoyancy force ( $F_M^* = F_M/F_B$ ), at different values of  $\alpha = R_b/R_e$ . The  $x$ -axis is shown in logarithmic scale to emphasize the behavior at low  $\alpha$ . In the case of constant cell voltage,  $\phi_0 = 4.5 \text{ V}$ . In the case of constant cell power,  $P = 13.4 \text{ mW}$ .

We now focus on investigating the resulting thermocapillary force on the bubble at different microelectrode sizes. As already mentioned in the introduction, the moment of bubble detachment is determined by the equilibrium of forces acting on the bubble. Therefore, a comprehensive treatment of all the forces acting on a bubble is of importance. A number of different forces may act on the bubble depending on

276 the predominant physical conditions i.e. growth rate, imposed flow condition, orientation relative to gravity,  
 277 etc. [34] The relevant static forces acting on an electrogenerated bubble are in general the buoyancy force,  
 278 surface tension force, contact pressure force and hydrodynamic force originating from the flow of the elec-  
 279 trolyte [42, 43]. Recently it was shown that beside the thermocapillary force [1], an electrostatic force may  
 280 also play an important role [44].

281 The thermocapillary force on the bubble is a hydrodynamical force by nature and results from the  
 282 interfacial flow around the bubble driven by temperature gradients. In the following, we will denote the  
 283 force as the Marangoni force, which can be calculated by integrating the Marangoni shear stress over the  
 284 bubble interface ( $\Sigma$ ),

$$F_M = - \int_{\Sigma} \tau_M dA. \quad (10)$$

285 Here,  $dA$  denotes the related surface differential. Because of the axial symmetry around the bubble, the above  
 286 integration results in a force which is acting parallel to the  $z$ -axis, i.e. vertically upwards or downwards,  
 287 thus influencing the moment of detachment. In the following, we consider the Marangoni force  $F_M$  in relation  
 288 to the buoyancy force  $F_B = gV\Delta\rho$  where  $g$ ,  $V$  and  $\Delta\rho$  denote the gravitational acceleration, the bubble  
 289 volume and the density difference between the electrolyte and gas, respectively. Thus, we introduce

$$F_M^* = \frac{F_M}{F_B} \quad (11)$$

290 where positive values of  $F_M^*$  imply a Marangoni force acting in the direction of buoyancy.

291 Figure 7 shows the dependence of  $F_M^*$  on the inverse relative electrode size ( $\alpha$ ) at a constant cell voltage  
 292 and constant cell electric power. Note that the differential local Marangoni force experienced by any part  
 293 of the interface is opposite to the direction of local interfacial velocity. According to the velocity profiles  
 294 shown in Figure 4(b) and 5(b), the lower part of the bubble ( $\theta < \theta_m$ ) experiences a net Marangoni force in  
 295 the upward direction and the upper part of the bubble experiences a net Marangoni force in the downward  
 296 direction. As for the microelectrode, the extent of the flow vortex to the left of temperature hotspot is  
 297 smaller than that to the right of the temperature hotspot. The integration of Equation 10 gives a net  $F_M$   
 298 in the downward direction, hence  $F_M^*$  is negative at large  $\alpha$ . For the potentiostatic case, as with decreasing  
 299  $\alpha$ , the mean current density and thus the heat generation in the electrolyte grows,  $F_M^*$  also increases in  
 300 magnitude. When decreasing  $\alpha$  further, the growing contribution from the left vortex becomes more and  
 301 more important, and  $F_M^*$  starts to decrease in magnitude near  $\alpha \sim 1$ . We further see that at  $\alpha \sim 1$ , due  
 302 to very strong heating, the Marangoni force has reached a magnitude of roughly 55% of buoyancy, which  
 303 corresponds to a very large mean current density value of 34.8 A/cm<sup>2</sup>.

304 As the electrode size is increased while keeping the total heat generation constant, the temperature  
 305 nonuniformity along the interface reduces and the contribution from the two vortices becomes comparable.  
 306 Thus,  $F_M^*$  decreases with decreasing  $\alpha$ , becoming approximately zero at  $\alpha \sim 1$ .

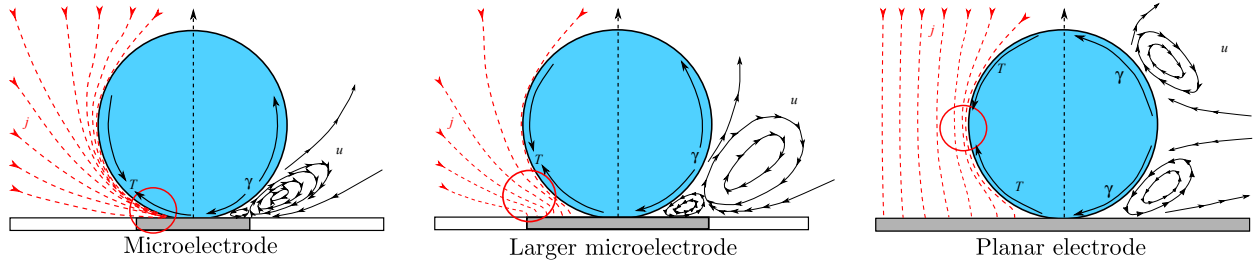


Figure 8: Sketch depicting the qualitative differences in current distribution, position of temperature hotspot (red circle) and resulting thermocapillary flow pattern when the size of the electrode is increased from micro (left) to macro (right). The flow inside the gas bubble and the movement of the interface are not shown.

308 So far we have presented a detailed characterization of the thermocapillary effect on gas bubbles growing  
 309 at microelectrodes of different sizes. As larger electrodes are prevalent in industrial processes, an in-depth  
 310 understanding of similar phenomena at macroelectrodes is of technological importance. An attempt is made  
 311 here to gain an understanding of this kind for the first time. With respect to the modeling, we follow  
 312 the simple approach described in detail in Section 2, based on considering single bubble phenomena, and  
 313 originating from the previous study of microelectrodes after accounting for differences in length scales and  
 314 boundary conditions.

315 Figure 8 schematically displays important qualitative differences of the thermocapillary effect when the size  
 316 of the electrode is increased from micro (left) to macro (right) with respect to the bubble size. For the  
 317 sake of simplicity, at the macroelectrode only a small part of the electrode is shown, above which a single  
 318 bubble evolves. Looking at the distribution of the current density, shown by red dotted lines, important  
 319 differences become obvious. At the microelectrode, as discussed before, the current has to squeeze through  
 320 a narrow region at the bubble foot, and large current densities occur above the electrode, with a maximum  
 321 near its outer edge. In the center of the figure, the intermediate case of a large microelectrode is shown,  
 322 where, as discussed before, the temperature hotspot has already moved upward slightly towards a larger  
 323 value of  $\theta$ . At the macroelectrode, however, the situation is changed, as the main geometrical obstacle for  
 324 a uniform current flow is now the bubble itself and not the electrode. Here, the current has to pass the  
 325 narrower equatorial space between neighboring bubbles. Hence, the maximum of the current density appears  
 326 at the bubble's equator. As the position of the temperature hotspot correlates directly with the location of  
 327 the maximum current density, the temperature maximum moves from the bubble foot towards the bubble  
 328 equator when the size of the electrode is increased from micro to macro.

329 The thermocapillary flow patterns driven at the bubble interface from hot towards cold regions are sketched  
 330 in the right half of the subfigures for all three cases. In line with the changing position of the temperature  
 331 hotspot, the size and the position of the two counter-rotating vortices driven by thermocapillary stress



332 change accordingly. At the microelectrode, a dominating large vortex brings electrolyte upward along the  
 333 interface, and the small vortex above the electrode does not contribute much to the thermocapillary effect.  
 334 This small vortex grows in size when the size of the microelectrode is increased and starts contributing to  
 335 the Marangoni force on the bubble, as already discussed in the previous section. At the macroelectrode,  
 336 eventually, two counter-rotating vortices of almost equal size are therefore expected which advect electrolyte  
 337 away from the temperature hotspot at the equator. The ramifications of these qualitative changes are  
 338 investigated quantitatively in the following.

### 339 3.2.1. Temperature and velocity distribution

340 We now study in detail the temperature and velocity distribution near a gas bubble of constant size  
 341 ( $R_b = 560 \mu\text{m}$ ) at different values of the bubble coverage  $\Theta$  of the macroelectrode. In the following, a  
 342 potential difference of  $\phi_0 = 1 \text{ V}$  is applied between the electrodes. We note that, e.g. for a bubble coverage  
 343 of  $\Theta = 0.87$ , an average current density of  $4.9 \text{ kA/m}^2$  is obtained, which is close to typical values of 1–3  
 $\text{kA/m}^2$  in related industrial applications [30]. Figure 9(a) shows the temperature distribution in and around

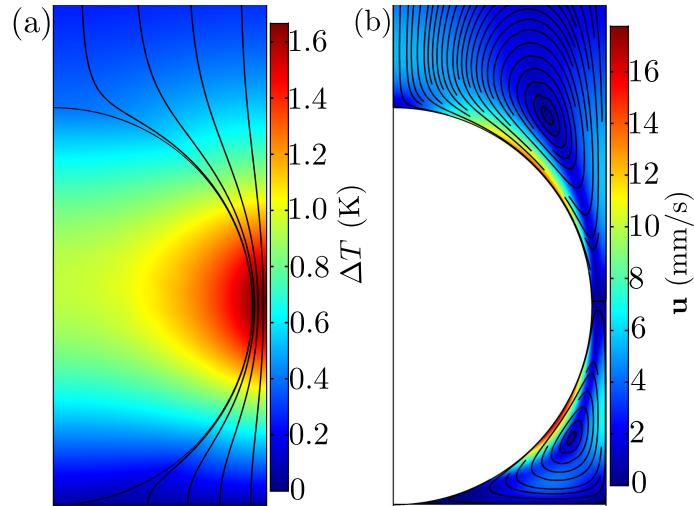


Figure 9: ( $\phi_0 = 1 \text{ V}$  and  $\Theta = 0.87$ ) (a) Temperature contours and field lines of the electrical current density. Temperature is maximum at the location of maximum current density near bubble equator. (b) Contours of the electrolyte flow velocity distribution along with velocity streamlines. The electrolyte at the bubble interface flows away from the equator towards both poles.

344  
 345 the gas bubble at a bubble coverage of  $\Theta = 0.87$ . As can be seen from the current lines in the electrolyte, the  
 346 electric current must pass around the gas bubble and hence is highly concentrated in the narrow inter-bubble  
 347 region near the bubble equator, where the largest current density occurs, in agreement with the expectations  
 348 formulated in the previous section. The temperature maximum also occurs at the same spot, as can be seen  
 349 from the temperature distribution.

350 Figure 9(b) shows the velocity distribution and the streamlines in the electrolyte. The thermocapillary  
 351 flow is driven away from the temperature hotspot, and the electrolyte flows away from the equator towards  
 352 either pole. This gives rise to two vortices in the northern and southern hemisphere of the bubble and causes  
 353 two interfacial velocity maxima, visible as the red regions in Figure 9(b). It is also to be noted here that the  
 354 vortices are not fully symmetric with respect to the equatorial plane. The lower vortex is constrained by  
 355 the electrode surface, the bubble interface and the outer boundary of the domain, whereas the upper vortex  
 extends upward above the top of the bubble.

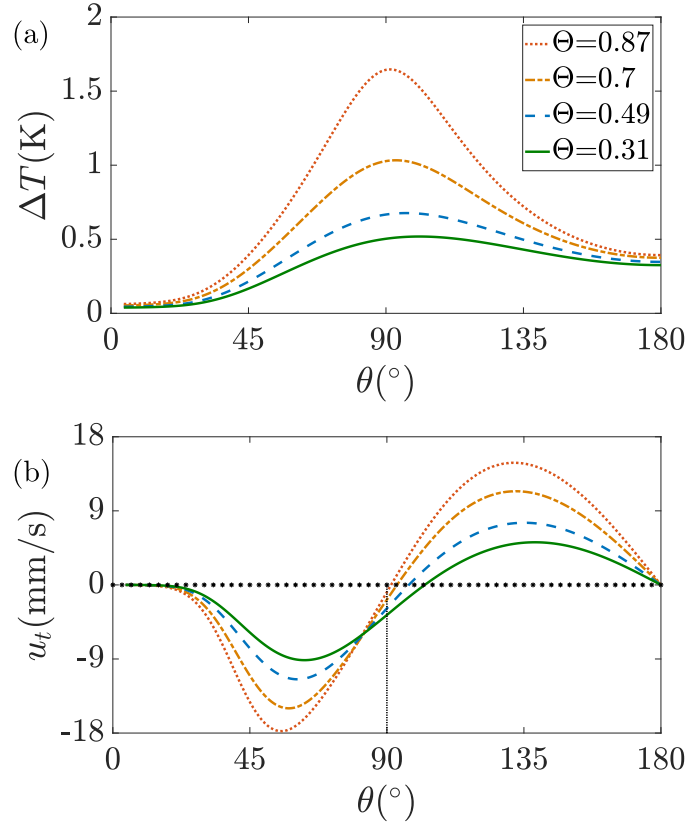


Figure 10: Interfacial (a) temperature and (b) velocity distribution as a function of  $\theta$  as defined in Figure 1 for different electrode coverage  $\Theta$  at  $\phi_0 = 1$  V. The vertical dashed line marks  $\theta = 90^\circ$ .

356  
 357 Next we study in detail the influence of the bubble coverage on the interfacial temperature and flow  
 358 profiles.  $R_c$  is varied from 0.6 mm to 1 mm, yielding a range of  $\Theta$  from 0.87 to 0.31, which, according  
 359 to earlier work, provides a realistic range of gas coverage values [45]. Figure 10(a) shows the interfacial  
 360 temperature profile as a function of the angular position  $\theta$ . The occurrence of a temperature maximum  
 361 close to the bubble equator ( $\theta_m \sim 90^\circ$ ) is clearly visible in all cases. The temperature maximum also  
 362 increases with increasing bubble coverage, as the electric current lines are more densely placed in the inter-  
 363 bubble space, causing larger local Joule heating. Figure 10(b) shows the related interfacial velocity profile.

364 Similarly to the microelectrode case discussed in Section 3.1.2, the tangential velocity  $u_t$  vanishes at the  
365 position of the temperature maximum at  $\theta_m$ . According to the slopes of opposite sign in the temperature  
366 profile left and right of  $\theta_m$ , interfacial flow in the southern or northern hemisphere is directed downward  
367 and upward, respectively, as also shown in Figure 10(b). In this figure, the value of zero tangential velocity  
368  $u_t = 0$  and the angular position of the equator  $\theta = 90^\circ$  are additionally marked by lines to allow the more  
369 accurate identification of the location of the flow reversal ( $\theta_m$ ) in relation to the bubble equator. As can  
370 be seen, the temperature hotspot is slightly shifted above the equator at smaller bubble coverage values.  
371 Furthermore, it is to be noted that the magnitude of the velocity minimum in the southern hemisphere  
372 is larger than the magnitude of the velocity maximum in the northern hemisphere in general. The latter  
373 can easily be explained. As the metal electrode at the bottom is a good conductor of heat compared to  
374 the electrolyte, the related downward heat flux tends to increase the temperature gradient in the southern  
375 hemisphere, leading to a larger velocity magnitude. This larger velocity magnitude also causes enhanced  
376 advection of heat at the interface, which leads to a shift in the temperature hotspot above the equator.  
377 As increasing the bubble coverage narrows the gap between the bubble equator and domain boundary, the  
378 temperature hotspot at the equator increases, and the relative influence of cooling and advection reduces.  
379 This is also seen in the two extrema of the velocity profiles, which grow closer to each other in terms of  
380 magnitude.

### 381 3.2.2. Marangoni force on the bubble

382 It is well known from measurements on large planar electrodes that the bubble evolution characteristics  
383 depend on the operating current density [45, 46]. At a higher current density, more nucleation sites are  
384 activated at the electrode, and thus the bubble coverage increases. Increasing the average current density  
385 also reduces the departure diameter and causes early detachment from the electrode surface [47]. In order  
386 to discuss the possible influence of thermocapillary effects on these phenomena, we carried out parametric  
387 studies to elaborate the influence of varying bubble coverage and bubble size on the Marangoni force under  
388 different operating conditions. The results are shown in Figure 11.

389 *Constant bubble radius.* In Figure 11(a) the Marangoni force normalized with the buoyancy force  $F_M^*$  (as  
390 defined in Section 3.1.4) is shown versus the bubble coverage of the electrode  $\Theta$  for a gas bubble of fixed  
391 size ( $R_b = 560 \mu\text{m}$ ) at a constant cell voltage of  $\phi_0 = 1 \text{ V}$ . It should be noted first that unlike the case of  
392 the microelectrode considered earlier, the Marangoni force is directed upwards, thus advancing the bubble  
393 departure. The Marangoni force  $F_M^*$  is found to amount to about 2% of the buoyancy force in the range of  
394 parameters considered and increases almost linearly with the bubble coverage  $\Theta$ .

395 As the Marangoni force ( $F_M$ ) results from the integration of the interfacial temperature gradient along  
396 the interface (see Equation 10), the slight asymmetry of the interfacial temperature profile with respect to  
397 the equator seen in Figure 10(a) gives rise to a remaining nonzero force  $F_M$ . As the temperature gradient

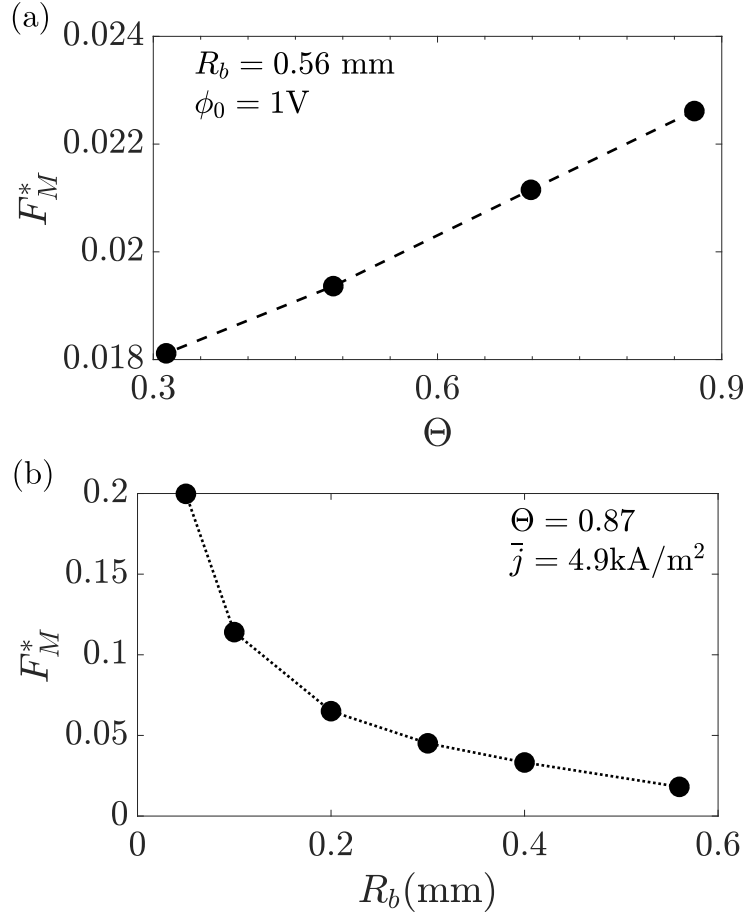


Figure 11: Marangoni force normalized with buoyancy force  $F_M^*$  versus (a) bubble coverage  $\Theta$  at a constant bubble radius  $R_b = 560 \mu\text{m}$  and cell voltage  $\phi_0 = 1 \text{ V}$  and versus (b) bubble radius  $R_b$  at a constant bubble coverage  $\Theta = 0.87$  and mean cell current density  $\bar{j} = 4.9 \text{ kA/m}^2$ .

398 is negative in the region below the equator and larger in magnitude than the positive gradient above the  
 399 equator, eventually an upward Marangoni force appears. The almost linear increase in the Marangoni force  
 400 as the bubble coverage increases is related to the strong temperature increase of the hotspot near the equator  
 401 in conjunction with the heatflux through the electrode, thus retaining a steep temperature profile below the  
 402 equator.

403 *Constant bubble coverage.* In order to extend our study to include smaller gas bubble departure sizes,  
 404 Figure 11(b) summarizes the Marangoni force  $F_M^*$  obtained for different bubble radii  $R_b$  at a constant  
 405 bubble coverage of  $\Theta = 0.87$  and at mean cell current density of  $\bar{j} = 4.9 \text{ kA/m}^2$ . We would like to point out  
 406 here that smaller bubbles have shorter residence times [47]. This was taken into account by adapting the  
 407 integration time in the simulations accordingly. The simulation details are summarized in Table 3. Starting

408 out from an integration time of 1 s at  $R_b = 560 \mu\text{m}$  in accordance with the constant bubble radius case  
 409 considered earlier, the integration time is then linearly decreased along with the bubble size such that for a  
 410 bubble of  $200 \mu\text{m}$  radius it matches the bubble lifetime of about 0.4 s reported in [48]. Please also note that  
 411 for smaller bubbles the contact angle between the bubble and electrode was slightly increased. As can be  
 412 seen in Figure 11(b), the Marangoni force  $F_M^*$  strongly increases when the size of the bubble reduces. This  
 413 behavior is mainly caused by the corresponding variation in the buoyancy force, which scales with the cube  
 414 of the bubble size. For a small bubble of  $R_b = 50 \mu\text{m}$ , the Marangoni force is found to amount to about 20%  
 of the buoyancy force.

$R_b$ ( $\mu\text{m}$ )	$\theta_c$	Integration Time (s)
50	14.1°	0.15
100	9.9°	0.23
200	7.0°	0.4
300	5.7°	0.57
400	5.0°	0.73
560	4.2°	1.0

Table 3: Bubble radius, contact angle and integration time in the simulation

415

#### 416 4. Conclusions

417 In this study we characterized in detail the thermocapillary flow around electrogenerated bubbles at  
 418 electrodes of different sizes, ranging from microelectrodes to large planar electrodes. At microelectrodes, a  
 419 detailed analysis of the current density and temperature profiles revealed a clear correlation between the  
 420 position of the temperature hotspot at the bubble interface and the upward projection of the outer edge  
 421 of the microelectrode. As a result, a double vortex structure of the thermocapillary flow was unveiled  
 422 which was overlooked previously [1] because the lower vortex is small at the microelectrodes. This double  
 423 vortex structure is also found at larger electrodes. Increasing the electrode size changes the position of the  
 424 temperature hotspot, thus increasing the size of the lower vortex and affecting the amplitude and also the  
 425 direction of the Marangoni force.

426 At large planar electrodes, multiple bubbles grow simultaneously at random nucleation sites where the  
 427 electrical current must pass through the inter-bubble space. The simplified approach we take in order to  
 428 gather initial results assumes that the bubbles grow synchronously at a given uniform nucleation density,  
 429 meaning that a single bubble can only be considered in the simulations. As a result, the maximum current  
 430 density and thus the temperature hotspot are located close to the equatorial inter-bubble region, and a  
 431 nearly symmetric double vortex structure is generated near the bubble interface. However, mainly because

432 of the cooling effect of the metal electrode, the interfacial flow of the lower vortex is stronger than that of  
433 the upper vortex. Consequently, an upward Marangoni force acts on the bubble, assisting its release, which  
434 is the opposite of what is found at the microelectrodes. This clearly helps explain why larger bubbles can  
435 be grown on macroelectrodes compared to microelectrodes. At a constant cell voltage, the Marangoni force  
436 is found to grow as the bubble coverage of the electrode increases due to higher temperatures occurring in  
437 the smaller inter-bubble gaps. For a fixed current density and related large bubble coverage, the force on  
438 the bubble is found to get larger when the bubble size is reduced, reaching about 20% of the buoyancy force  
439 at  $\Theta = 0.87$ ,  $\bar{j} = 4.9$  kA/m<sup>2</sup>.

440 We note here that the quantitative results obtained for the macroelectrode are based on the assumption of  
441 uniform bubble distribution, i.e. simultaneous in-phase bubble evolution, and that azimuthal dependencies  
442 of quantities originating from neighboring bubbles growing at certain angular positions have so far been  
443 neglected. The Marangoni force values obtained for reasonable integration times in our model may further  
444 depend on the specific value of the contact angle and neglect more complex aspects such as microbubbles  
445 partly covering the cathode. It should also be noted that our results for all electrode sizes naturally depend  
446 in quantity on the details of the thermal boundary conditions of the cell. This especially holds true for  
447 the metal electrode where the bubble grows, which takes heat out of the electrolyte and thereby shapes the  
448 thermocapillary effect. Nevertheless, as this is a common feature, we believe the qualitative findings of the  
449 thermocapillary effect are valid in general.

450 In summary, the thermocapillary effect is found to be important for the dynamics of bubbles generated  
451 at electrodes under various conditions. A proper inclusion of this effect in future studies may lead to  
452 an improved understanding of the instant of the bubble departure and the departure diameter. Finally,  
453 appropriate temperature management of the electrodes may be a useful means of improving the efficiency  
454 of electrolyzers.

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459 GAS).

## 460 References

## 461 References

- 462 [1] J. Massing, G. Mutschke, D. Baczyzmalski, S. S. Hossain, X. Yang, K. Eckert, C. Cierpka, Thermocapillary convection dur-  
463 ing hydrogen evolution at microelectrodes, *Electrochimica Acta* 297 (2019) 929–940. doi:10.1016/j.electacta.2018.11.187.

- 464 [2] V. Levich, V. Krylov, Surface-tension-driven phenomena, *Annual Review of Fluid Mechanics* 1 (1) (1969) 293–316.  
465 doi:10.1146/annurev.fl.01.010169.001453.
- 466 [3] A. W. Adamson, *Gast, Physical Chemistry of Surfaces*, Wiley-Interscience, 1967.
- 467 [4] L. G. Leal, *Advanced Transport Phenomena: Fluid Mechanics and Convective Transport Processes*, Vol. 7, Cambridge  
468 University Press, 2007.
- 469 [5] J. Pearson, On convection cells induced by surface tension, *Journal of fluid mechanics* 4 (5) (1958) 489–500.
- 470 [6] D. Nield, Surface tension and buoyancy effects in cellular convection, *Journal of Fluid Mechanics* 19 (3) (1964) 341–352.
- 471 [7] K. Eckert, M. Bestehorn, A. Thess, Square cells in surface-tension-driven Bénard convection: experiment and theory,  
472 *Journal of Fluid Mechanics* 356 (1998) 155–197.
- 473 [8] K. Schwarzenberger, T. Köllner, H. Linde, T. Boeck, S. Odenbach, K. Eckert, Pattern formation and mass transfer under  
474 stationary solutal marangoni instability, *Advances in colloid and interface science* 206 (2014) 344–371.
- 475 [9] H. Hu, R. G. Larson, Analysis of the microfluid flow in an evaporating sessile droplet, *Langmuir* 21 (9) (2005) 3963–3971.
- 476 [10] H. Hu, R. G. Larson, Marangoni effect reverses coffee-ring depositions, *The Journal of Physical Chemistry B* 110 (14)  
477 (2006) 7090–7094. doi:10.1021/jp0609232.
- 478 [11] B. J. Fischer, Particle convection in an evaporating colloidal droplet, *Langmuir* 18 (1) (2002) 60–67.
- 479 [12] Á. G. Marín, H. Gelderblom, A. Susarrey-Arce, A. Van Houselt, L. Lefferts, J. G. Gardeniers, D. Lohse, J. H. Snoeijer,  
480 Building microscopic soccer balls with evaporating colloidal fakir drops, *Proceedings of the National Academy of Sciences*  
481 109 (41) (2012) 16455–16458.
- 482 [13] N. Young, J. Goldstein, M. J. Block, The motion of bubbles in a vertical temperature gradient, *Journal of Fluid Mechanics*  
483 6 (3) (1959) 350–356. doi:10.1017/S0022112059000684.
- 484 [14] R. Balasubramaniam, R. S. Subramanian, The migration of a drop in a uniform temperature gradient at large marangoni  
485 numbers, *Physics of Fluids* 12 (4) (2000) 733–743.
- 486 [15] R. Balasubramaniam, R. Subramanian, Thermocapillary bubble migration—thermal boundary layers for large marangoni  
487 numbers, *International journal of multiphase flow* 22 (3) (1996) 593–612.
- 488 [16] R. Balasubramaniam, C. E. Lacy, G. Woniak, R. S. Subramanian, Thermocapillary migration of bubbles and drops at  
489 moderate values of the marangoni number in reduced gravity, *Physics of Fluids* 8 (4) (1996) 872–880.
- 490 [17] J. L. McGrew, F. L. Bamford, T. R. Rehm, Marangoni flow: an additional mechanism in boiling heat transfer, *Science*  
491 153 (3740) (1966) 1106–1107.
- 492 [18] J. Straub, The role of surface tension for two-phase heat and mass transfer in the absence of gravity, *Experimental Thermal*  
493 *and Fluid Science* 9 (3) (1994) 253–273.
- 494 [19] S. Petrovic, T. Robinson, R. L. Judd, Marangoni heat transfer in subcooled nucleate pool boiling, *International Journal*  
495 *of Heat and Mass Transfer* 47 (23) (2004) 5115–5128.
- 496 [20] V. K. Dhir, G. R. Warrier, E. Aktinol, D. Chao, J. Eggers, W. Sheredy, W. Booth, Nucleate pool boiling experiments  
497 (npbx) on the international space station, *Microgravity Science and Technology* 24 (5) (2012) 307–325.
- 498 [21] J. Straub, J. Betz, R. Marek, Enhancement of heat transfer by thermocapillary convection around bubbles—a numerical  
499 study, *Numerical Heat Transfer* 25 (5) (1994) 501–518.
- 500 [22] R. Marek, J. Straub, The origin of thermocapillary convection in subcooled nucleate pool boiling, *International Journal*  
501 *of Heat and Mass Transfer* 44 (3) (2001) 619–632.
- 502 [23] S. Lubetkin, The fundamentals of bubble evolution, *Chemical Society Reviews* 24 (4) (1995) 243–250.
- 503 [24] S. Lubetkin, The motion of electrolytic gas bubbles near electrodes, *Electrochimica Acta* 48 (4) (2002) 357–375.  
504 doi:10.1016/S0013-4686(02)00682-5.
- 505 [25] X. Yang, D. Baczynski, C. Cierpka, G. Mutschke, K. Eckert, Marangoni convection at electrogenerated hydrogen  
506 bubbles, *Physical Chemistry Chemical Physics* 20 (2018) 11542–11548. doi:10.1039/C8CP01050A.

- 507 [26] F. Li, R. Gonzalez-Avila, D. Nguyen, C.-D. Ohl, Oscillate boiling from microheaters, *Phys. Rev. Fluids* 2 (2017) 014007.
- 508 [27] W. Tsai, P. Hsu, Y. Hwu, C. Chen, L. Chang, J. Je, H. Lin, A. Groso, G. Margaritondo, Electrochemistry: building on  
509 bubbles in metal electrodeposition, *Nature* 417 (6885) (2002) 139.
- 510 [28] J. Jorne, J. F. Louvar, Gas-diverting electrodes in the chlor-alkali membrane cell, *Journal of The Electrochemical Society*  
511 127 (2) (1980) 298–303.
- 512 [29] J. C. Puippe, R. Acosta, R. Von Gutfeld, Investigation of laser-enhanced electroplating mechanisms, *Journal of the*  
513 *Electrochemical Society* 128 (12) (1981) 2539–2545.
- 514 [30] K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, *Progress in*  
515 *energy and combustion science* 36 (3) (2010) 307–326.
- 516 [31] A. Körner, C. Tam, S. Bennett, J. Gagné, Technology roadmap – hydrogen and fuel cells, Tech. rep., International Energy  
517 Agency (IEA): Paris, France (2015).
- 518 [32] I. Staffell, D. Scamman, A. V. Abad, P. Balcombe, P. E. Dodds, P. Ekins, N. Shah, K. R. Ward, The role of hydrogen  
519 and fuel cells in the global energy system, *Energy & Environmental Science* 12 (2) (2019) 463–491.
- 520 [33] N. Brandon, Z. Kurban, Clean energy and the hydrogen economy, *Philosophical Transactions of the Royal Society A:*  
521 *Mathematical, Physical and Engineering Sciences* 375 (2017) 20160400.
- 522 [34] G. Thorncroft, J. F. Klausner, Bubble forces and detachment models, *Multiphase Science and Technology* 13 (3&4) (2001).  
523 doi:10.1615/MultScienTechn.v13.i3-4.20.
- 524 [35] W. Fritz, Berechnung des maximalvolumes von dampfblasen, *Physik. Zeitschr* 36 (1935) 379–384.
- 525 [36] D. Fernandez, P. Maurer, M. Martine, J. Coey, M. E. Möbius, Bubble formation at a gas-evolving microelectrode, *Langmuir*  
526 30 (43) (2014) 13065–13074.
- 527 [37] J. Chen, L. Guo, X. Hu, Z. Cao, Y. Wang, Dynamics of single bubble departure from tio2 nanorod-array photoelectrode,  
528 *Electrochimica Acta* 274 (2018) 57–66.
- 529 [38] D. E. Westerheide, J. Westwater, Isothermal growth of hydrogen bubbles during electrolysis, *AIChE Journal* 7 (3) (1961)  
530 357–362.
- 531 [39] N. P. Brandon, The growth kinetics and interfacial properties of electrogenerated bubbles, Ph.D. thesis, Imperial College  
532 London (1985).
- 533 [40] H. Matsushima, D. Kiuchi, Y. Fukunaka, K. Kuribayashi, Single bubble growth during water electrolysis under micro-  
534 gravity, *Electrochemistry Communications* 11 (8) (2009) 1721–1723.
- 535 [41] X. Yang, F. Karnbach, M. Uhlemann, S. Odenbach, K. Eckert, Dynamics of single hydrogen bubbles at a platinum  
536 microelectrode, *Langmuir* 31 (29) (2015) 8184–8193. doi:10.1021/acs.langmuir.5b01825.
- 537 [42] A. Taqieddin, M. R. Allhouse, A. N. Alshawabkeh, Editors’ choice - critical review - mathematical formula-  
538 tions of electrochemically gas-evolving systems, *Journal of The Electrochemical Society* 165 (13) (2018) E694–E711.  
539 doi:10.1149/2.0791813jes.
- 540 [43] D. Baczyzmaliski, F. Karnbach, G. Mutschke, X. Yang, K. Eckert, M. Uhlemann, C. Cierpka, Growth and detachment of  
541 single hydrogen bubbles in a magnetohydrodynamic shear flow, *Physical Review Fluids* 2 (9) (2017) 093701.
- 542 [44] A. Bashkatov, S. S. Hossain, X. Yang, G. Mutschke, K. Eckert, Oscillating hydrogen bubbles at pt microelectrodes,  
543 *Physical Review Letters* 123 (2019) 214503. doi:https://doi.org/10.1103/PhysRevLett.123.214503.
- 544 [45] H. Vogt, On the supersaturation of gas in the concentration boundary layer of gas evolving electrodes, *Electrochimica*  
545 *Acta* 25 (5) (1980) 527–531.
- 546 [46] H. Vogt, R. Balzer, The bubble coverage of gas-evolving electrodes in stagnant electrolytes, *Electrochimica Acta* 50 (10)  
547 (2005) 2073–2079.
- 548 [47] H. Vogt, The actual current density of gas-evolving electrodes—notes on the bubble coverage, *Electrochimica Acta* 78  
549 (2012) 183–187.



550 [48] H. Matsushima, T. Iida, Y. Fukunaka, Gas bubble evolution on transparent electrode during water electrolysis in a  
551 magnetic field, *Electrochimica Acta* 100 (2013) 261–264.