Short Communication

Electric field induced deformation of hemispherical sessile droplets of ionic liquid.

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Abstract

Sessile droplets of an ionic liquid with contact angles close to 90° were subjected to an electric field $E = V/w$ inside a capacitor with plate separation w and potential difference V. For small field induced deformations of the droplet shape the change in maximum droplet height, $\Delta h = h(E) - h(0)$, was found to be virtually independent of the plate separation provided that $w > 3h(0)$. In this regime a scaling law obtains $\Delta h \propto E^2 r^2$, where r is the constant droplet radius, in agreement with the asymptotic predictions Basaran and Scriven (*J. Coll. Int. Sci. 140*, 10, 1990).

Keywords

Wetting; Contact angle; Ionic liquid; Electrostatic field; Parallel plate capacitor

1. Introduction

The study of the stability of charged water droplets was first reported by Lord Rayleigh [1]. This seminal paper in the established the field of electrohydrodynamics, which continues to be an area of intense interest and investigation including for understanding the behaviour of raindrops in rainclouds as well as for diverse technological applications based on electrospraying and in printing and coating processes [2] [3] [4] [5]. When a conducting liquid drop is subjected to an electric field it tends to elongate along the direction of the electric field, and this was reported in relation to the stability of water droplets in an electric field [6]. Now consider the case where the liquid forms an axisymmetric sessile drop supported on the inside face of a parallel plate capacitor. The presence of the electric field distorts the shape of droplet away from the equilibrium spherical cap profile (assuming the droplet is smaller than the capillary length) and the droplet apex rises towards the opposite plate. The ability to control the shape via an externally applied electric field provided by this geometry has been exploited for applications including surface tension measurement [7], an optical display mode [8], and optimising the optical properties of polymer microlenses [9] [10]. Further potential applications of this geometry are reviewed in references [11] and [12]. Previous quantitative experimental and theoretical work on the distortions produced in conducting liquids in this geometry includes on soap bubbles [13] [14] [15], water droplets [16], and water droplets immersed in dielectric oil [17]. In the current work we consider small distortions, in which the voltage-induced height increase is less than 5% of the initial height, for droplets with contact angles close to 90°.

2. Materials and Methods

Figures 1(a) and 1(b) show the experimental geometry. A sessile droplet of liquid of maximum height $h(0)$ and radius r rests on the lower plate inside a parallel plate capacitor with variable gap w between the electrodes. The electrodes were formed from a continuous layer of transparent conductor, indium tin oxide (100 Ohm/square, 25 nm thickness, Praezisions Glas and Optik GmbH, Iserlohn, Germany) on borosilicate glass slides. The lower plate was coated with a commercial hydrophobic coating (Grangers International Ltd, Derbys., UK) which gave contact angles close to 90° with sessile droplets of the conducting ionic liquid butyl methyl imidazolium tetrafluoroborate. Applying either a D.C. voltage, $V = V_{d.c.}$, or an A.C. voltage, $V = V_{r.m.s.}$, between the capacitor plates deformed the shape of a sessile drop of the liquid within the capacitor and increased the maximum height by an amount $\Delta h = h(E) - h(0)$, where $E = V/w$. Figures 1(c) and 1(d) show images of a sessile droplet for which $h(0) = 1.20$ mm and $w = 2.55$ mm with both capacitor plates grounded and with an D.C. voltage of 2300 V applied across the capacitor plates respectively. The ratio $w/h(0)$ for figure 1 is much smaller than the values actually used in the study.

The ionic liquid butyl methyl imidazolium tetrafluoroborate is an excellent conductor and has a low vapour pressure so shows negligible evaporation during the experiments [18] [19] [20]. The surface tension of the liquid was found from pendant drop measurements [21] (Drop shape analysis, A. Krüss Optronic GmbH, Hamburg, Germany) to be 40.9 ± 0.5 mN/m and taking a literature value of the density of 1120 kg/m^3 [22] this gives a capillary length of 1.9 mm. Since this capillary length is greater than the diameters of any of the drops used in the study, gravity can be neglected and the sessile droplets form a spherical cap in the absence of the electric field. In the study A.C. voltages (applied using a Trek model 609E-6 4 kV amplifier) at 1 kHz were used to avoid continuous charging effects. The D.C. conductivity of dry butyl methyl imidazolium tetrafluoroborate is reported to be 0.295 S/m at 303.2 K [23], and this increases significantly when the material is hydrated [24], which is expected as the droplet is used here in an ambient atmosphere. The estimated charge density of the liquid, at 10^{26} to 10^{27} m^{-3} [25] is sufficient to screen and exclude electric fields many orders of magnitude higher than used in the experiment from the inside of the liquid droplet. The charge is also sufficiently mobile; the conductivity of the dry liquid increases with frequency and a relaxation which has been observed in the ionic motions is in the range 10^4 to 10^5 Hz [25] (at 280 K) is well above the value of 1 kHz used in our experiments at 293 K.

The height change values, $\Delta h = h(E) - h(0)$, in response to D.C. and A.C. voltages were found to agree to within ±1% over the full range of voltage, cell gap and drop heights used in the studies. Using transparent electrodes enabled the drops to be viewed both from above and from the side during the experiments. Accurate values for the small height changes in the range 1 to 40 μm were obtained using a 20× microscope objective which imaged an area at the top of the droplets. The recorded images were contrast enhanced, thresholded, and the position of the top of the droplet was accurately obtained using a quadratic fit to the shape near to the apex.

3. Results and discussion

Figure 2 shows data for the voltage induced change in maximum droplet height, $\Delta h = h(E) - h(0)$, plotted against the square of the electric field E^2, where $E = V_{r.m.s.}/w$. Data are shown for a droplet with a zero-field height of $h(0) = 0.71$ mm and contact angle 88.4° for 4 different cell gaps w: 1.15, 1.67, 2.33 and 2.90 mm. Data for the largest cell gaps, 2.33 and 2.90 mm, fall on the same straight line. When $w = 1.67$ mm there is still a linear relationship between Δh and E^2, but the gradient has increased. When the cell gap is reduced again to $w = 1.15$ mm the gradient is further increased and the plot becomes super linear for the higher electric fields shown. In order to elucidate the cell gap dependence the deformation of a droplet of zero-field height $h(0) = 0.74$ mm was measured for different values of w with the voltage adjusted at each gap to maintain a constant value for the electric field of $E = V_{r.m.s.}/w = (6.6 \pm 0.2) \times 10^5$ V m^{-1}. The voltage induced change in droplet height, Δh, is plotted as a function of $w/h(0)$ in the inset graph in figure 2. This shows that the variation in Δh with plate separation w is small and lies within the experimental accuracy of setting the electric field when $w > 3h(0)$.

Figure 3 shows Δh plotted against E^2 for a number of droplets with zero-field heights ranging from $h(0) = 0.476$ mm (indicated by cross symbols) up to $h(0) = 0.985$ mm (indicated by open diamond symbols). For each of the droplets the cell gap was fixed at

$w = 2.67 \pm 0.05$ mm, so that the condition $w > 3h(0)$ was maintained across the whole range of droplet sizes except for the largest droplet for which $w > 2.7h(0)$. Droplets were selected for study for which the contact angle was in a narrow range of ±1.6° around the average value of 91.8°. For each droplet height a linear fit is shown to the data. The gradients from these fits are plotted against the square of the droplet radius r in the inset graph in figure 4, which also shows a linear dependence. In figure 4 the data from figure 3 for the voltage induced change in maximum droplet height, $\Delta h = h(E) - h(0)$, is plotted against $(Er)^2$, which is the same as $r^2 V_{r.m.s.}^2/w^2$. All the data for the different droplet sizes falls close to a single straight line, including for the largest droplet used in the study.

The observed scaling relationship, $\Delta h \sim r^2 V_{r.m.s.}^2/w^2$ can be intuitively understood as arising from the applied Maxwell stress producing a change in the droplet curvature associated with a balancing increase in the Laplace pressure. The Maxwell stress, $\frac{1}{2}\varepsilon_o E^2$, [26] is given under the assumptions that E is the normal electric field in air at the apex of the droplet, and that the permittivity of a conducting droplet is infinite and tangential electric fields at its surface are zero. The additional Laplace pressure at the droplet apex due to an increase Δh in height can be approximated by [21]: $\Delta\left(-\gamma_{LV}\frac{\partial^2 y}{\partial x^2}\right) \sim 2\gamma_{LV}\frac{\Delta h}{r^2}$, where γ_{LV} is the surface tension of the liquid. Equating these two contributions accounts for the observed scaling with a predicted coefficient given by $0.25\gamma_{LV}$. A quantitative asymptotic analysis of this system is reported by Basaran and Scriven in reference [15] for an initially hemispherical droplet on the inside of a capacitor plate for small values of the electrical Bond number, $N_e = (\varepsilon_o r V^2)/(2\gamma_{LV} w^2) \ll 1$ (here including an extra factor of “2” in the denominator as used in reference [15]). They predicted a scaling relationship of the form shown in equation 1, with $\alpha = 9/8$ in the case of a fixed 90° contact angle, and with $\alpha = 3/8$ in the case of a fixed contact line (i.e. a fixed radius).

(equation 1) $$\Delta h = (r - h(0)) + \alpha\frac{\varepsilon_o r^2 V^2}{\gamma_{LV} w^2}$$

The gradient of figure 4 gives $(w^2\Delta h)/(r^2V^2)$ = (1.03 ± 0.05) × 10^{-10} m V^{-2}, compared to the theoretical gradient 0.81 × 10^{-10} m V^{-2} for a fixed contact line if α = 0.375. Along with our measured value for the surface tension this gives an experimental value for the coefficient in equation 1 of α = 0.47 ± 0.02. The experimental coefficient lies between the two theoretical values predicted for a fixed 90° contact angle (α = 1.125) and for a fixed contact line (α = 0.375), being closer to, but 25% higher than the fixed contact line value. This is consistent with our observations of the top view of the droplets showing that, for the small deformations considered in the study, i.e. $\Delta h/h(0) < 5\%$, the contact lines remained circular and a change in the value of radius *r* could not be detected during the application of voltages.

4. Summary

For a plate separation that satisfies $w > 2.7h(0)$ we find very good agreement with a scaling relationship of the form $\Delta h \propto r^2V^2/w^2$ (c.f. equation 1), as predicted from the asymptotic analysis for a contact angle of 90° in reference [15]. Our experimental value of the coefficient of proportionality falls between the values predicted in the fixed contact line and in the fixed contact angle limits. There are two physical phenomena that are not taken into account in the theory and the analysis. Firstly, small changes in surface tension have been reported for liquids subject to large electric fields applied in related experimental geometries. For example, in reference [27] it was found that the electric field distorted profiles of droplets of water, propylene carbonate and formamide fit to numerically calculated theoretical profiles if their surface tensions increased by 6.6%, 2.1% and 3.1% respectively when subject to an electric field of 5.6 × 10^5 V/m provided by a voltage of 7 kV applied across a gap of 12.5mm. The highest electric fields used in our study ranged from 6.3 × 10^5 V/m to 7.7 × 10^5 V/m, somewhat higher than the value in the study reported in [27]. Secondly, we report a liquid and surface treatment combination which provides contact angles values which are reproducibly close to 90°. As stated above, the contact angles of different droplets used in our scaling investigation were all within ±1.6° of the average value of 91.8°. A full numerical analysis of the system with a fixed contact line indicates that the coefficient α would be increased by 10% for an increase in the contact angle of just 1.42° above 90°. An investigation of this strong contact angle dependence will be the subject of a future study.

Acknowledgements

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http://dx.doi.org/10.1016/j.colsurfa.2006.04.016

Figure captions

Figure 1 (a) and (b) show the experimental geometry. A sessile drop with a contact angle close to 90° rests on the lower plate inside a parallel plate capacitor structure. A voltage applied across the capacitor plates deforms the drop which increases in height, (b). Images of a sessile droplet of the ionic liquid butyl methyl imidazolium tetrafluoroborate for which $h(0) = 1.20$ mm and $w = 2.55$ mm are shown (c) with both capacitor plates grounded and (d) with a D.C. voltage of 2300 V applied across the capacitor plates.

Figure 2 The voltage induced change in height of the drop, $\Delta h = h(E) - h(0)$, plotted against the square of the electric field, E^2. Data are shown for a droplet of zero-field height of $h(0) = 0.71$ mm and contact angle 88.4° for 4 different cell gaps w. Inset: deformation Δh plotted against $w/h(0)$ for a droplet of zero-field height $h(0) = 0.74$ mm and contact angle 89.2° subject to a constant electric field of $(6.6 \pm 0.2) \times 10^5$ V m^{-1}.

Figure 3 Change in height of the drop, $\Delta h = h(E) - h(0)$, plotted as a function of the square of the electric field, E^2, for a range of zero-field droplet heights between $h(0) = 0.476$ mm (indicated by cross symbols) and $h(0) = 0.985$ mm (indicated by open diamond symbols). The cell gap was fixed in the range $w = 2.67 \pm 0.05$ mm.

Figure 4 Inset: The linear relationship between the gradients of Δh versus E^2, from figure 3, is plotted against the square of the radius of the droplet, r^2. The uncertainties on the gradient values, found using linear regression, ranged from ±0.9% to ±1.2% Main panel: When the Δh data from figure 3 for different zero-field droplet heights is re-plotted as a function of E^2r^2 it collapses onto a single straight line.

Figure 1

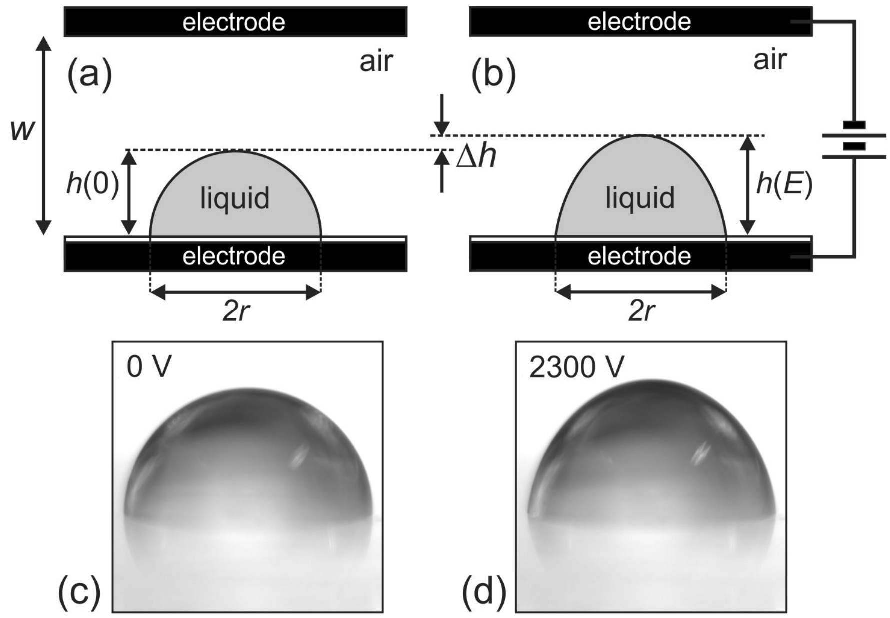
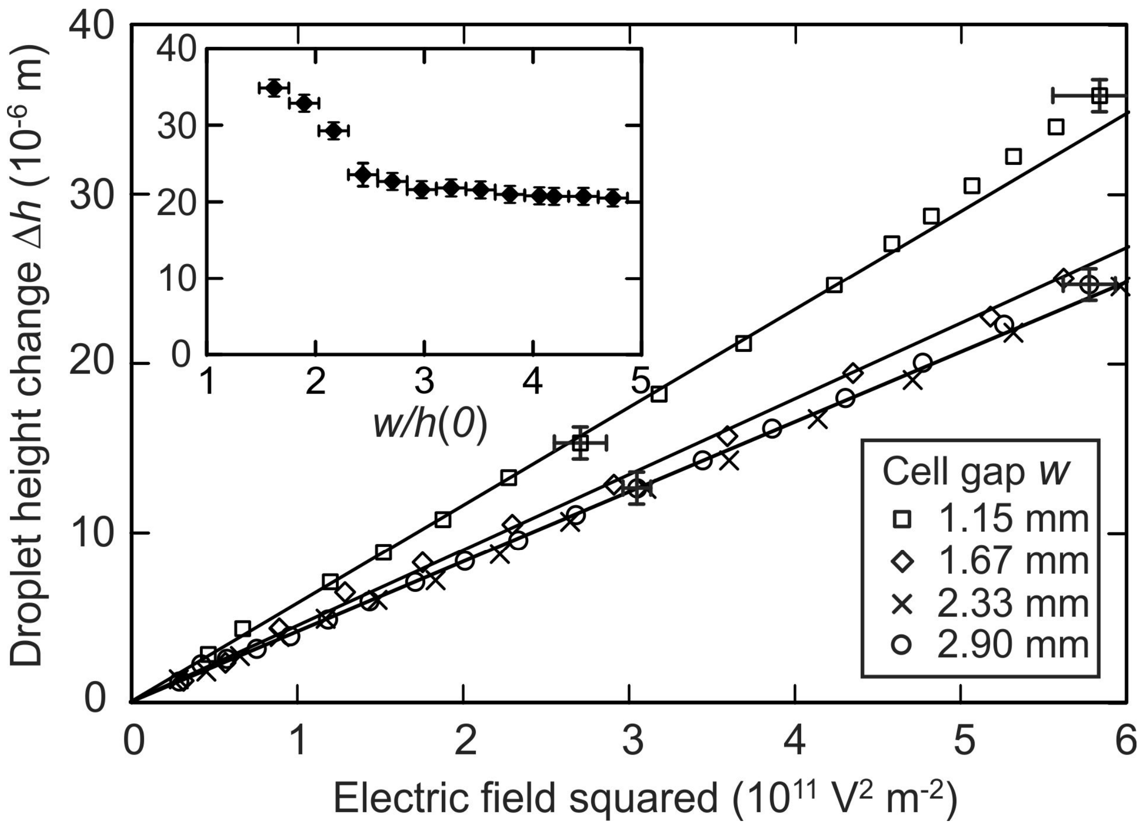

electrode
air
(a)
w
h(0)
liquid
electrode
2r
electrode
air
(b)
Δh
liquid
h(E)
electrode
2r
0 V
(c)
2300 V
(d)

Figure 2



Droplet height change Δh (10-6 m)
Electric field squared (1011 V2 m-2)
w/h(0)
Cell gap w
1.15 mm
1.67 mm
2.33 mm
2.90 mm

Figure 3

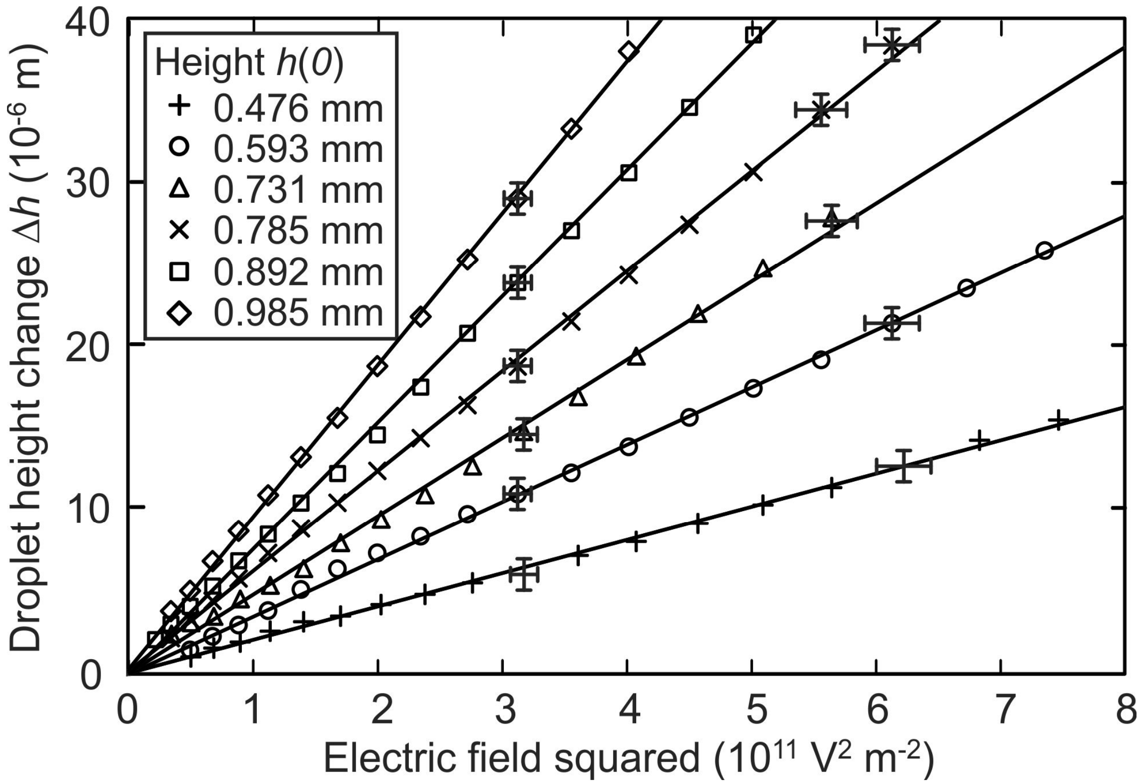
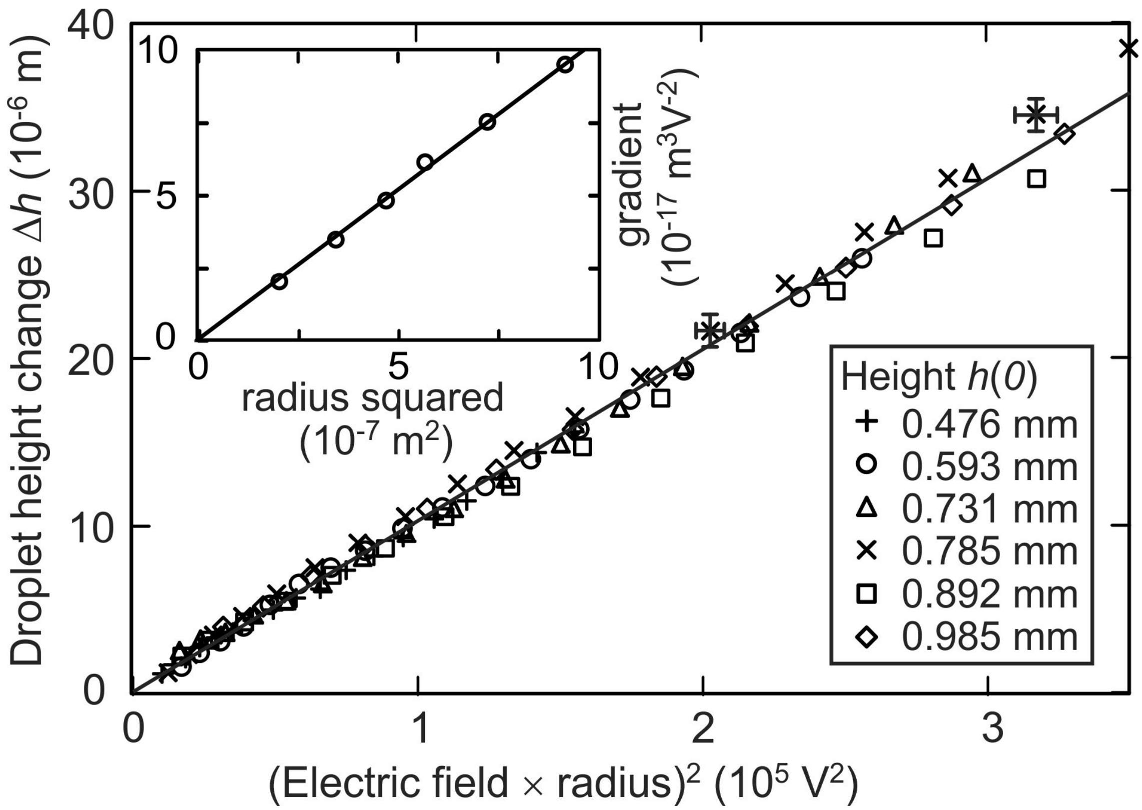

Height *h*(*0*)
0.476 mm
0.593 mm
0.731 mm
0.785 mm
0.892 mm
0.985 mm
Droplet height change Δ*h* (10⁻⁶ m)
Electric field squared (10¹¹ V² m⁻²)
0
10
20
30
40
0
1
2
3
4
5
6
7
8

Figure 4



Droplet height change Δh (10-6 m)
(Electric field × radius)2 (105 V2)
gradient
(10-17 m3V-2)
radius squared
(10-7 m2)
Height h(0)
0.476 mm
0.593 mm
0.731 mm
0.785 mm
0.892 mm
0.985 mm

Figure 1
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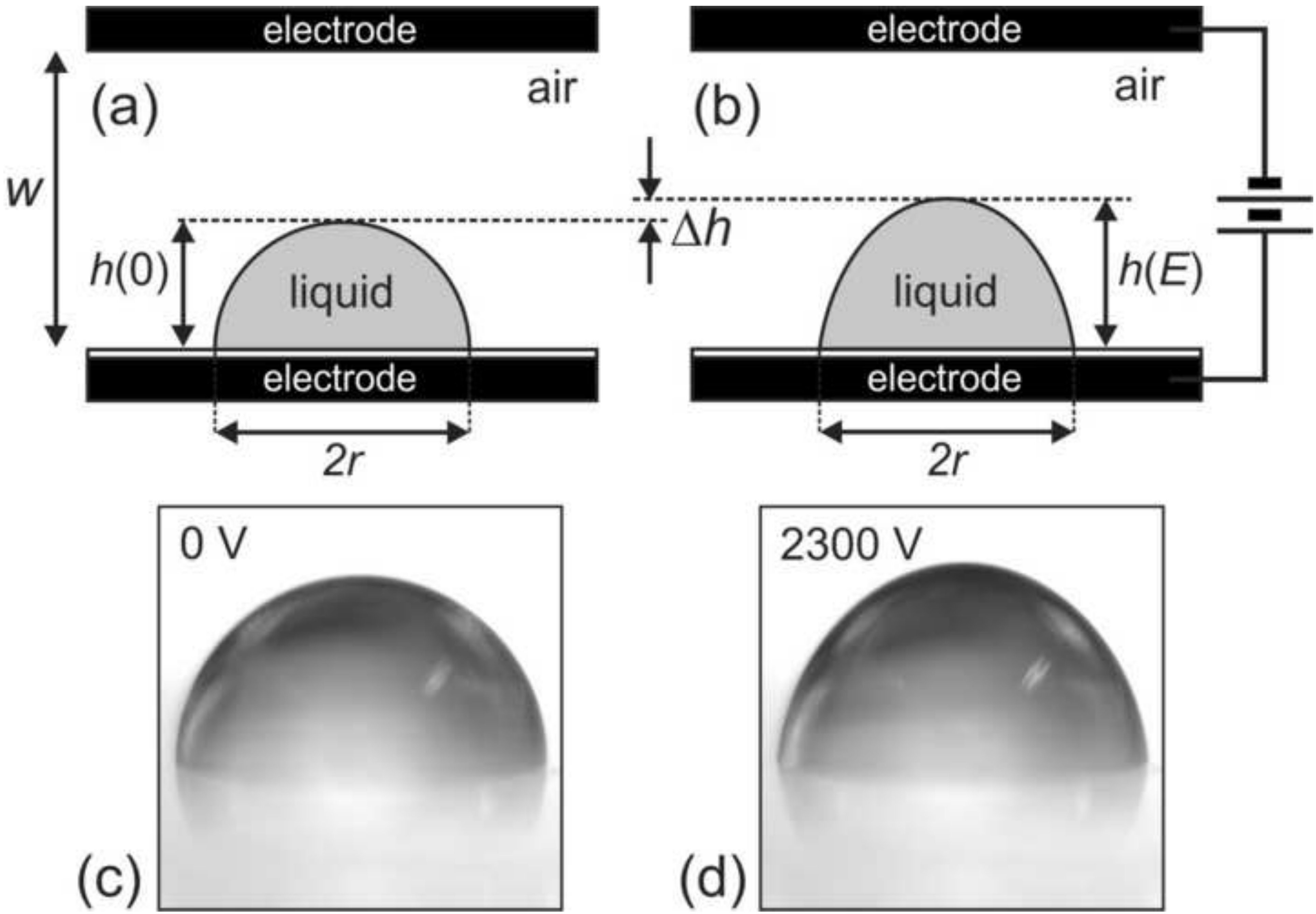

Figure 2
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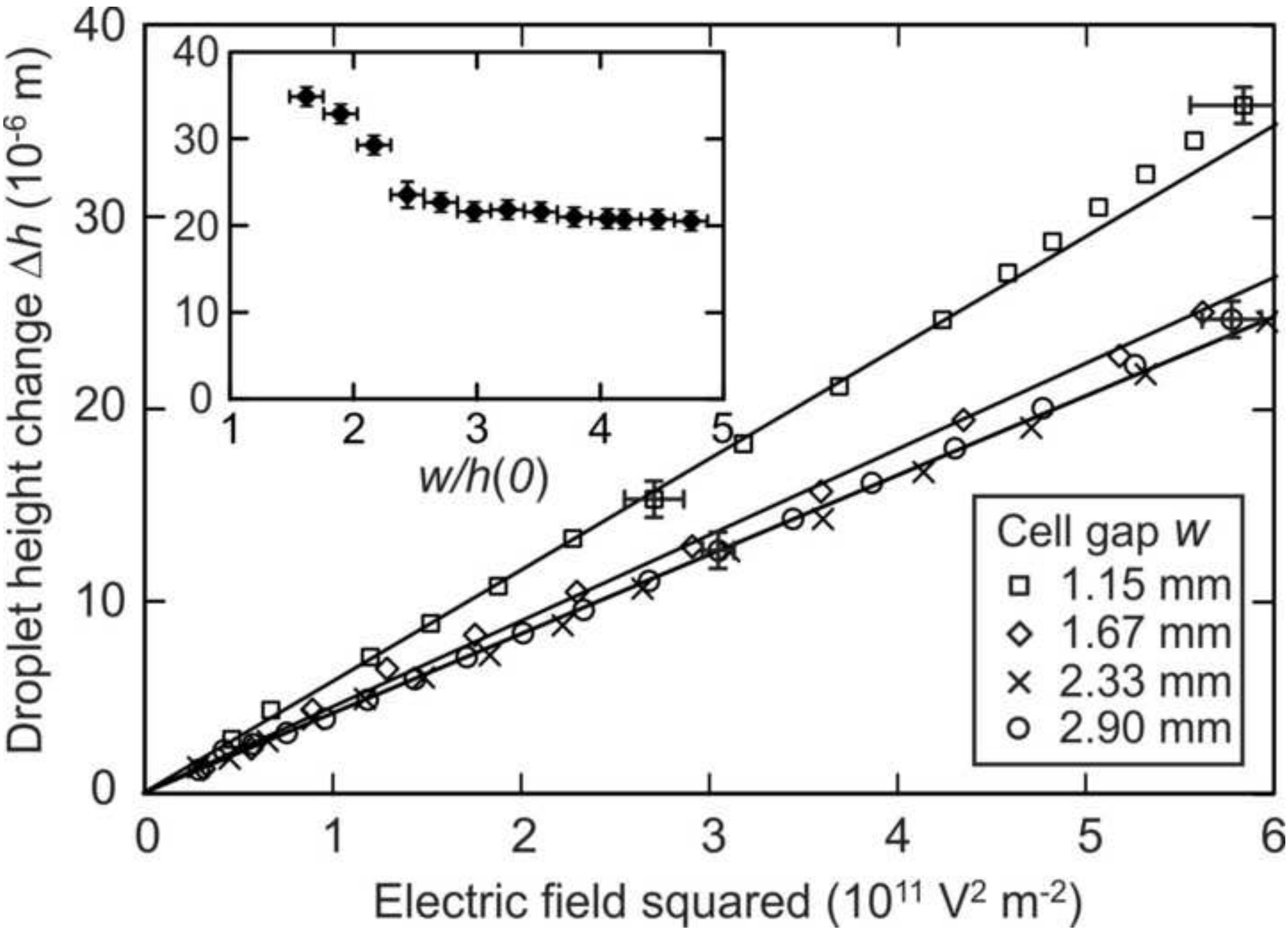

Figure 3
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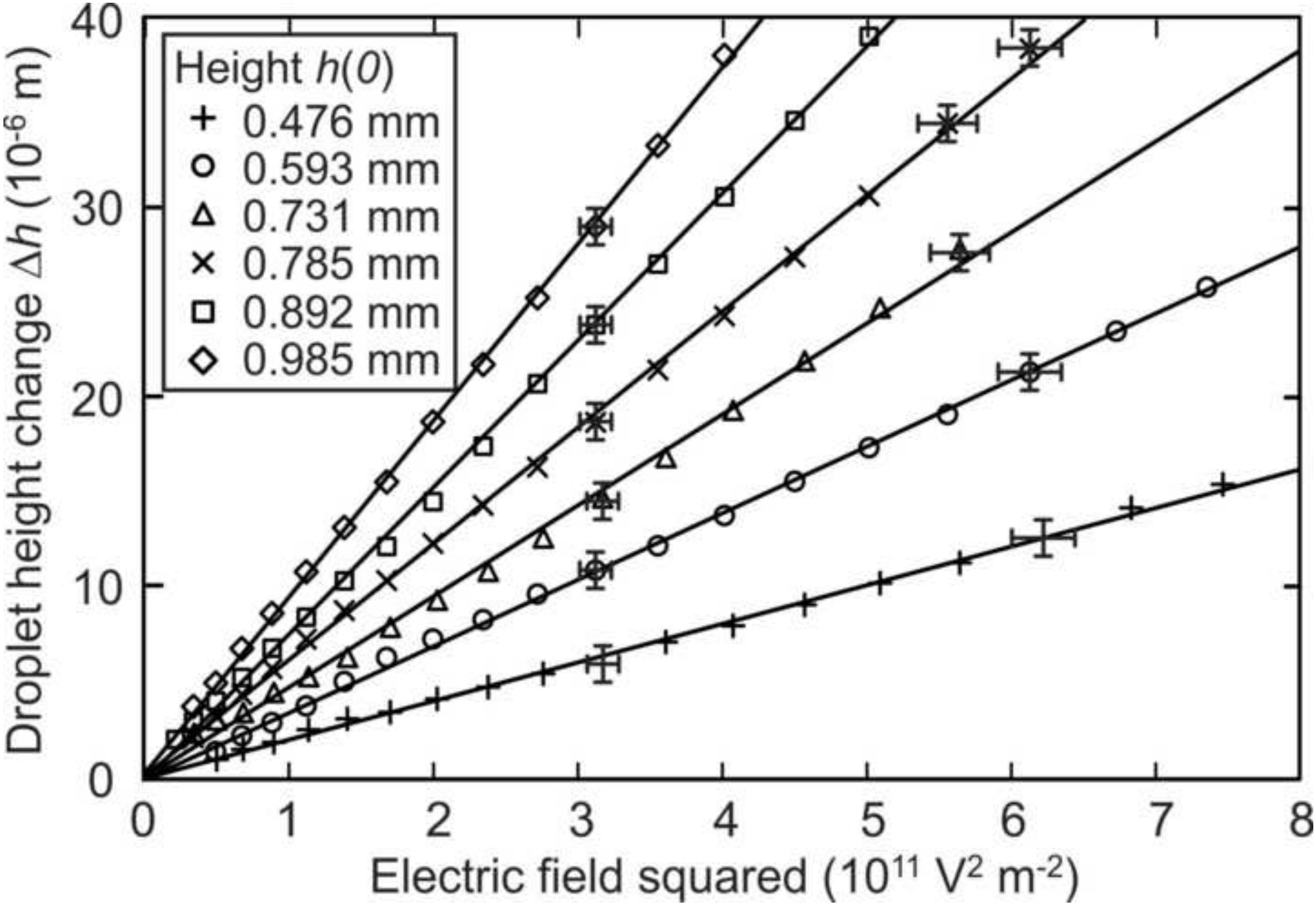

Figure 4
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