

## Plasmas in Liquids and their Applications

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The production of plasmas in liquids is discussed, with a focus on conducting liquids such as saline solution. The initiation of the plasma production event is the creation of a vapour layer around the powered electrode. Once this has grown completely over the electrode surface, so isolating it from the liquid, an electric field is present which leads to the plasma production. The plasma then generates reactive and charged species and em radiation which in turn interact with the liquid at its interface with the vapour layer. The subsequent soup of reactive species can then be exploited in a growing number of applications e.g. in the environment, nano-science, bioprotection, biomedicine and medical procedures.

Plasmas produced by electrical discharges in liquids have been received much attention over the years. The last decade or so has seen a pronounced increase in attempts to gain an understanding of this complex and multidisciplinary environment [1-7 and references therein]. This has been motivated by advances in experimental and computational techniques and also in increased applications for such systems.

The thermodynamic, fluid-dynamic, and electrical properties of liquids all contribute to a system with interesting physical phenomena, often including phase-changing vapour formation. This vapour formation is considered to be the precursor to most electrical breakdown in liquids. The combination of high density and strongly non-equilibrium plasma conditions can also produce many interesting and useful chemically-active environments.

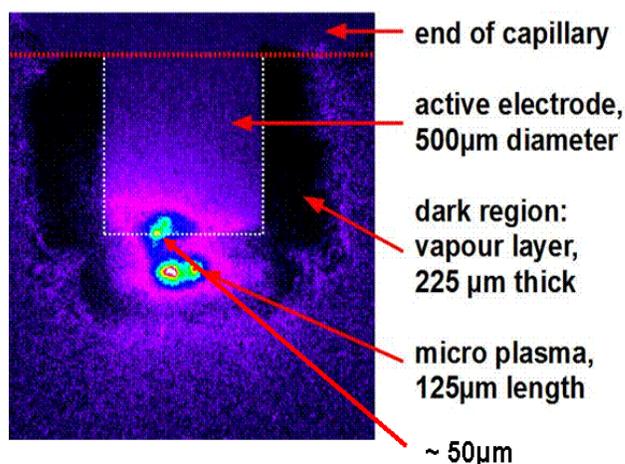
Most studies have focused on plasma production with a pin to a plane electrode geometry in a low conductivity liquid, usually water using voltage pulses with durations from tens of nanoseconds to dc. These have revealed that electrical fields of  $\sim 1\text{MVcm}^{-1}$  are needed and that plasmas are created in vapour filaments growing out through the liquid from the pin electrode, see for example [7]. As yet there is no single comprehensive theory describing these phenomena but prevalent opinion is that pre-existing bubbles, photo-ionization and field enhancement effects in the near electrode region are involved. It is worth noting here that this specifically excludes the recent work with ultra-short, intense voltage pulses, which intriguingly suggests direct ionization in the liquid phase [8].

Here the focus will be on an important subset of this work relating to plasmas formed in conducting liquids, specifically saline solution. Conducting liquids contain free ions in solution, and can therefore respond to electric and magnetic fields much more strongly than non-conducting liquids. Therefore, while non-conducting liquids require very large voltages, in conducting liquids voltages of a few hundred volts are adequate which considerably extends their application potential.

Experimental and finite element modelling methods have been used to study the formation of vapour layers in plasma discharges in saline solution [9,10]. The experiments use shadowgraphic and fast imaging techniques to observe the time dependence of thin vapour layers evolution and the subsequent plasma formation around small, e.g. 0.5 mm, diameter tungsten electrode immersed in a conducting saline solution. The applied voltages are generally less than 500 volts with pulse lengths of up to a few ms. The vapour layer growth rate is very reproducible from pulse to pulse but varies with liquids parameters such as the conductivity and ambient temperature of the liquid. A typical image is shown in figure 1. Finite element multiphysics software, coupling thermal and electrical effects, is employed to model the vapour layer formation. All relevant electrical and thermal properties of the saline are incorporated into the model. The shadowgraph and modelling images are in very good agreement. The comparison of experiment and modelling gives insight into both vapour layer production and subsequent plasma production. For example, it became clear that superheating of the saline above its normal vaporization temperature played a significant role in the formation of the vapour layer. The simulation also shows that electric fields of approaching  $10^7\text{Vm}^{-1}$  can be achieved within the vapour layer. Surface analysis of a used electrode indicated the presence of sodium and

chlorine on the electrode surface and spectroscopy showed sodium in the vapour layer. These observations could also be pertinent to plasma production mechanisms.

The timing, numbers and characteristics of the plasmas produced are not reproducible for identical voltage pulses. There are generally multiple plasmas, often of different characters in each voltage pulses of more than a few ms. An example is shown in Figure 1. The plasmas can be broadly classified as short (few  $\mu\text{s}$ ) or long (up to 500  $\mu\text{s}$ ) lived. Vapour layer and plasma production is faster and occurs at lower voltages with negative polarity pulses.



The highly non-equilibrated plasma drives the production of new species in the water vapour on rapid time scales and initially through electron collision reactions and there is direct spectroscopic evidence of production of reactive OH, O and H. Then neutral molecule reactions are predicted, by kinetic modelling [11], to form stable, chemically active species e.g.  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , plus metastable  $\text{O}_2(^1\Delta_g)$ , superoxide ions  $\text{O}_2^-$ , and protonated water cluster ions such as  $\text{H}^+\cdot\text{H}_2\text{O}$ . These chemically-active species can diffuse to the vapour-liquid interface and enter the liquid; and vice-versa. The charged particles will also reach the

Fig. 1: An image from a 300 $\mu\text{s}$ , 275V pulse taken 250 $\mu\text{s}$  after pulse initiation with an exposure time of 10 $\mu\text{s}$ .

interface. Free electrons will be rapidly thermalised in the liquid and hydrated on sub-nanosecond timescales to form aqueous electrons. Aqueous electrons can also react with solute particles. There may also be a small yield of positive and negative ions ( $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ), which may account for measured changes in pH. There is also a flux of radiation, with a wavelength range extending from VUV to Infra-red, from the plasma. Its role is currently less clear at present.

The resultant reactive soup can then be exploited in a growing number of applications. Examples from the environment, nano-science, bioprotection biomedicine and medical procedures will be presented.

The author acknowledges the major contributions of Colin Kelsey, Lucas Schaper and Kenneth Stalder to the QUB work reported here.

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