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*Reprinted from AIAA JOURNAL, Vol. 15, No. 5, May 1977, pp. 734-736*  
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## **Onset of Boiling in Electrohydrodynamic Spraying**

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### **I. Introduction**

**W**HEN a high voltage is applied to a liquid surface, the liquid is often observed to form conical protuberances that emit a spray consisting of ions and charged droplets. This phenomenon, called electrohydrodynamic spraying, has been used commercially in such applications as painting and printing and has been suggested as a source of particles for colloid and ion thrusters for space propulsion. Taylor<sup>1</sup> has pointed out that the liquid cone can exist in mechanical equilibrium, since the increasing electric pressure at the tip is balanced by the increasing surface tension there.

This high electric field implies some sort of electric discharge, supplied by a current flow that heats the cone to a temperature that depends on the thermal and electrical conductivity of the liquid. An earlier paper<sup>2</sup> suggested that this temperature might be high enough to cause the liquid to boil, thus ejecting large particles of liquid, which could ac-

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Received Nov. 8, 1976; presented as Paper 76-1057 at the AIAA International Electric Propulsion Conference, Key Biscayne, Fla., Nov. 14-17, 1976; revision received Feb. 4, 1977.

Index categories: Electric and Advanced Space Propulsion; Thermochemistry and Chemical Kinetics.

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count for the numerous charged droplets observed in electrohydrodynamic spraying. This suggestion is explored further in this paper by comparing the temperature rise produced by Joule heating to that needed to boil a small volume of liquid in a vacuum. This temperature will differ from the usual boiling point, for reasons discussed below.

## II. Rate of Formation of Vapor Nuclei

Ordinary concepts of boiling must be discarded when dealing with the effects of heat in a small liquid cone. In any liquid placed in a vacuum, for instance, the boiling point of the liquid will be close to 0 K, and yet many liquids can sit quietly without boiling under these nonequilibrium conditions, although they may eventually evaporate. Boiling can occur only if vapor bubbles can form in the liquid and then grow to macroscopic size. In macroscopic containers, these bubble nuclei form at the walls from gas trapped in minute crevices. In a liquid Taylor cone, however, highest temperatures are reached near the tip, far from any solid surface, so that boiling cannot be initiated in the usual manner.

Boiling that occurs inside a liquid mass requires some other source of vapor nuclei. These may consist of solid impurities, ionizing radiation, or, if all else fails, vapor nuclei formed by the random thermal motion of the molecules, which will occasionally leave some small region of the liquid, forming a small bubble. The rate at which bubble nuclei of a given radius form can be estimated from absolute reaction rate theory as<sup>3</sup>

$$R = n_T \left( \frac{kT}{h} \right) \exp \left( - \frac{4\pi\sigma r^2}{3kT} \right) \quad (1)$$

where  $n_T$  is the total number of participating atoms,  $\sigma$  is the surface tension of the liquid,  $r$  is the radius of the bubble,  $k$  is Boltzman's constant,  $h$  is Planck's constant, and  $T$  is the absolute temperature.

It is apparent from this equation that small nuclei are formed more often than large ones, since the energy of the new surface is smaller. The number of participating atoms can vary from one experiment to another, but in most work with bulk liquids the exact number is not critical, since the exponential term dominates the calculation. A typical value is the number of atoms in 1 cc of the liquid.

In electrohydrodynamic spraying, on the other hand, the volume in which bubble nuclei may form is considerably smaller than the standard of 1 cc, and this will reduce the rate of occurrence of these nuclei. For vapor nuclei that form within a distance  $r$  from the apex, the volume available for

bubble information is approximately  $r^3$ . Using this value gives the number of participating atoms as approximately

$$n_T = \frac{\rho A_v}{(\text{MW})} r^3 \quad (2)$$

where  $\rho$  is the density,  $A_v$  is Avogadro's number, and MW is the molecular weight.

## III. The Stability of Vapor Nuclei

Once the vapor nucleus is created, however, its continued existence is not guaranteed. The surface tension of the interface between the bubble and the liquid acts to compress the bubble, and return the liquid molecules to the empty space. This effect is strongest when the area/volume ratio is largest, i.e., for small bubbles. Once the bubble exceeds a critical radius  $r_c$  (in the range 10-200 Å),<sup>3</sup> it will continue to grow to macroscopic size, leading to homogenous boiling. This type of boiling, unlike ordinary boiling, tends to be explosive, since vapor nuclei simultaneously form and grow throughout the entire liquid, not just at the solid surface.

Far from the tip ( $r \gg r_c$ ), the rate of formation of critical nuclei is given by

$$R = \frac{\rho A_v}{(\text{MW})} \left( \frac{kT}{h} \right) r^3 \exp \left( - \frac{4\pi\sigma r_c^2}{3kT} \right) \quad (3)$$

in which the critical radius  $r_c$  determines the activation energy in the exponential term.

Near the tip of the cone, however, a bubble smaller than the critical size for homogenous boiling may still be large enough to sever the tip from the remainder of the cone, producing chunks of charged liquids as part of the spray. Thus the critical size for nuclei produced in the tip is smaller than that for homogenous boiling. On the other hand, the volume of the liquid near the tip is very small, and since the number of vapor nuclei produced depends on the volume available, vapor nuclei will be produced more infrequently in this region, compared to the bulk of the cone behind the tip. The rate at which bubbles large enough to sever the tip are generated can be estimated as before, if the critical radius  $r_c$  is replaced by the smaller distance  $r$  which is approximately equal to the width of the cone at a distance  $r$  from the origin. Using this substitution, the rate is given by

$$R = \frac{\rho A_v}{(\text{MW})} \left( \frac{kT}{h} \right) r^3 \exp \left( - \frac{4\pi\sigma r^2}{3kT} \right) \quad (4)$$

## IV. Calculation of the Boiling Temperature

Once an expression for the rate of formation of critical nuclei is available, the temperature needed to produce explosive boiling can be calculated by requiring this rate to be rapid. In this context, rapid has been defined differently by different authors,<sup>3,4</sup> with typical values ranging  $1 \text{ sec}^{-1}$  to  $10^{12} \text{ sec}^{-1}$ . Setting Eq. (3) equal to an average rate of  $10^6$  gives the temperature needed to produce homogenous boiling at a distance  $r$  from the origin, while using Eq. (4) gives the temperature needed to sever the tip at the distance  $r$ . The critical boiling temperatures for two common liquids, water and mercury, are given in Fig. 1 as a function of distance from the origin. Close to the origin, the boiling temperature is low because the cone is very thin, and even small nuclei, which are frequently formed, can sever the tip. Farther from the origin, larger nuclei must be formed, corresponding to higher temperatures. Eventually, however, the cone becomes wide enough to accommodate the nuclei larger than the critical size for homogenous boiling, and the required temperature then drops as the available volume increases. Although the nuclei are unstable, the volume available for their formation is still much smaller than usual macroscopic amounts ( $1 \text{ mm}^3$ - $1 \text{ cm}^3$ ) so that the explosive boiling in this small volume occurs at a

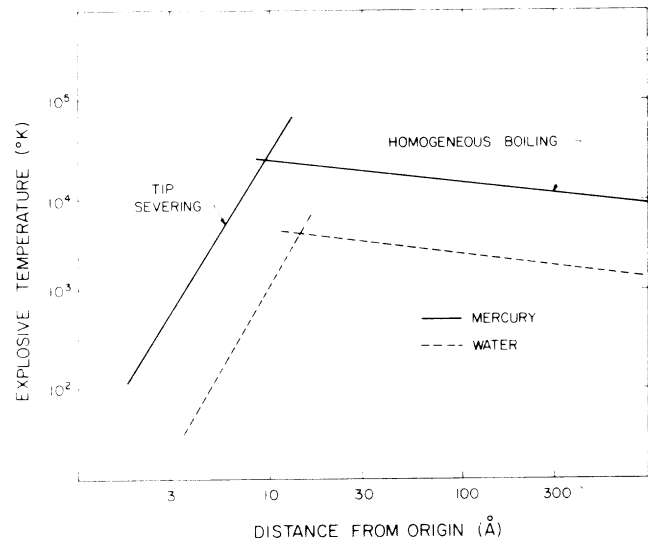


Fig. 1 The temperature needed for explosive boiling as a function of distance from the tip of the spraying cone.

**Table 1 The current expected to produce explosive boiling in a spraying liquid cone**

	$r_A$ (Å)	$\rho$ ( $\frac{\text{gm}}{\text{cc}}$ )	$\sigma$ ( $\frac{\text{dyne}}{\text{cm}}$ )	$K$ $\frac{\text{watts}}{\text{cm K}}$	$R \times 10^6$ ( $\Omega\text{-cm}$ )	$i_{\text{crit}}$ ( $\mu\text{A}$ )
Salt water	1.45	1.0	70	0.006	1000	-
Hg	1.55	13.6	467	0.075	98.5	46.7
Na	1.86	0.92	200	0.8	10.2	403
Cs	2.62	1.87	70	0.19	36.6	112
K	2.31	0.87	411	0.48	13	757
Cu	1.28	8.9	1100	1.75	22	549

much higher temperature than in a large bulk. Farther back from the tip, as the volume increases, the boiling temperature drops to the bulk value of approximately  $0.9 T_c$ ,<sup>3</sup> where  $T_c$  is the absolute critical temperature of the liquid. From the figure, it is clear that the lowest temperature for boiling will occur near the tip of the cone. Also, the temperature in a spraying cone tends to be highest at the tip, as pointed out in a previous paper. For both of these reasons we would expect the discharge to begin with the smallest particles, namely ions. As the temperature is raised, large pieces of the tip can be severed by the formation of vapor nuclei, and the discharge will then contain dimers and trimers in addition to the ions. The sequence is often observed in practice, as monomers and then dimers and large particles are emitted as the current increases. The transition from monomers to dimers would be expected when the temperature reached the explosive boiling point several atomic radii from the tip. From the geometry of the cone it is clear that this distance will be approximately  $2r_A$ – $3r_A$ , where  $r_A$  is the atomic radius.

The discharge current at which the transition to dimer spraying occurs can be estimated by calculating the current needed to produce the boiling temperature at the critical distance from the tip, using the results of Ref. 2. The required currents, shown in Table 1, were calculated for several of the liquids of interest in electrohydrodynamic spraying, using an assumed radius of  $2.5 r_A$ . The values for thermal conductivity  $K$  and electrical resistivity  $R$  were taken from Ref. 2.

## V. Implications for the Selection of Spraying Liquids

Explosive boiling sets a limit on the maximum current and

hence power that can developed in electric spraying without the formation of larger fluid particles than ions. If this limit is to be extended, liquids must be selected to lower the rate of formation of critical vapor nuclei. This rate depends chiefly on the exponential term,

$$\exp - (4\pi\sigma r_c^2 / 3kT) \quad (5)$$

To keep this term low, the surface tension should be high, since this increases the energy threshold for the formation of vapor nuclei. The atomic radius should be large, since this requires the formation of a larger bubble to split off the tip of the cone, and this too increases the activation energy for the transition.

The temperature of the cone should be kept as low as possible to keep the thermal energy low. From the results of Ref. 2, the temperature depends most strongly on the ratio of material properties  $R/K$ , where  $R$  is the electrical resistivity and  $K$  is the thermal conductivity. To keep the temperature low, the liquid chosen should be a good conductor of both heat and electricity.

Liquid metals obviously are good candidates for this application, with large surface tensions, thermal conductivities, and electrical conductivities. In fact, all the successful ion beams produced so far have employed liquid metals or alloys such as NaK, Cs, and GaIn. There are still many liquid metals that have not been tried, however, and the search for superior spray liquids may well begin with liquid metals with higher conductivities and surface tension than those used so far. Copper, for example, has a critical current higher than most of the other liquids listed in the table, but has not yet been tried, to the author's knowledge. Other, more exotic metals and alloys may occur to the interested reader.

## References

- <sup>1</sup>Taylor, G. I., "Disintegration of Water Drops in an Electric Field," *Proceedings of the Royal Society (London)*, Vol. A280, 1964, p. 383.
- <sup>2</sup>Crowley, J. M., "Role of Joule Heating in the Electrostatic Spraying of Liquids," *Journal of Applied Physics*, Vol. 48, 1977, p. 145.
- <sup>3</sup>Cole, R., "Boiling Nucleation," *Advances in Heat Transfer*, Vol. 10, 1974, p. 85.
- <sup>4</sup>Reid, R. C., "Superheated Liquids," *American Scientist*, Vol. 64, 1976, p. 146.